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Presented by

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Functional and Adaptive Covalent Dynamic Polymers

Professor Jean-Marie LEHN	Director of Thesis
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par

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Polymères Covalents Dynamiques Fonctionnels et Adaptatifs

Professeur Jean-Marie LEHN	Directeur de thèse
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Abbreviations

A	acceptor
Å	Ångstrom
Ac	acetyl
aq.	aqueous
amor.	amorphous
arom.	aromatic
Bn	benzyl
Boc	tert-Butoxycarbonyl
b.p.	boiling point
br.	broad
cat.	catalyst, catalyzed
calcd.	calculated
ca.	about, approximately
CDC	Constitutional Dynamic Chemistry
CDCl3	deuterated chloroform
CDPL	Constitutional Dynamic Polymers Library
conc.	concentrated
cryst.	crystalline, crystals
CSD	cambridge structural data base
d	doublet
D	donor
DCM	dichloromethane
dec.	decomposition, decompose
δ	chemical shift
dist.	distilled
DSC	differential scanning calorimetry
DME	1,2-dimethoxyethane
DMF	N, N- dimethyl folmamide
DMSO	dimethyl sulfoxide
ESI	electrospray ionisation
Et	ethyl

et al	and others
Et2O	diethyl ether
EtOAc	ethyl acetate
EtOH	ethanol
eq.	equivalent, equation
Fig.	figure
g	gram
GC	gas chromatography
h	hour
HPLC	high performance liquid chromatography
HR	high resolution
Hz	hertz
J	coupling countant
L	litre
λ	wave length
LUMO	lowest unoccupied molecular orbital
m	milli (10-3), multiplet (NMR)
M	molar (mol L-1)
μ	micro (10-6)
MALDI	matrix assisted laser desorption/ionization
Me	methyl
MeOH	methanol
MS	mass spectroscopy
MW	molecular weight
n	nano (10-9)
NDI	naphthalene diimide
n.d.	not determined
NMR	nuclear magnetic resonance
NOE	nuclear overhauser effect
ppm	parts per million
q	quartet
quant.	quantitative

quint	quintet
ref.	reference
Rf	retention factor
s	singlet
sat.	saturated
sext	sextet
sept	septet
t	triplet
TBDMS	tert-butyl dimethyl silyl
temp.	temperature
TFA	trifluoroacetic acid
TG	thermogravimetry
THF	tetrahydrofuran
TLC	thin layer chromatography
Tosyl	toluene sulfonyl
Triflate(Tf)	trifluoromethane sulfonate
UV	ultraviolet
Vis	visible

Abstract

The development of supramolecular chemistry over the past 3 decades has shown that chemistry is a science of information and that control of molecular information through dynamic non-covalent interactions can lead to the formation of well-defined, self-organized entities exhibiting specific functions. Understanding the relationship between molecular information and the production of self-organized supramolecular architectures has consequences ranging from the development of materials chemistry to the comprehension of biological processes, and eventually to the study of the origin and evolution of life.

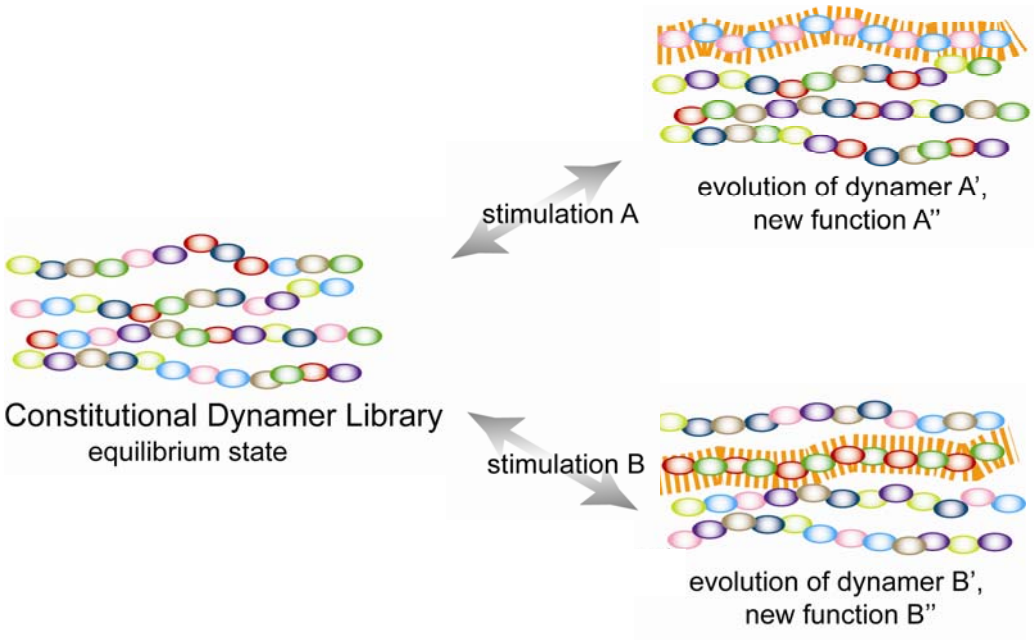
Supramolecular chemistry is intrinsically a *dynamic chemistry* as a result of the lability of the non-covalent interactions connecting the molecular components of a supramolecular entity, which results in the ability of supramolecular species to exchange their components. In systems where covalent bond formation is also reversible and labile, what is observed may be termed *Constitutionally Dynamic Chemistry* (CDC), where lability is observed on both the molecular level by formation of reversible covalent bonds and the supramolecular level through non-covalent interactions. This lability ensures the thermodynamic control of constituents represented by all possible combinations of the components present, and ensures also the rapid response to changes in imposed conditions.

Dynamic polymers (*dynamers*) are constitutionally dynamic polymeric entities based on monomers linked through reversible connections at both the molecular and supramolecular levels and having the capacity to undergo spontaneous and continuous changes in their constitution by exchange, reshuffling, incorporation and decorporation of various monomeric components.

In the first part of the present thesis, it is demonstrated that useful modification of the mechanical strength, hydrophobicity/hydrophilicity, optical characteristics and other properties of polymeric entities, dynamers, can be achieved via incorporation, decorporation or exchange of their monomeric components. The dynamers were generated by polycondensation via poly(acyl)hydrazone formation from dihydrazide and dialdehyde monomer units. Dynamers involving oligodimethylsiloxane entities have been developed and named *DYNASILs*. These *DYNASILs* present a distinctive feature, the ability to exchange

monomeric components through reversible covalent bond formation, as well as showing the properties of conventional polydimethylsiloxane polymers such as flexibility (low Tg), heat stability, and hydrophobicity. It was demonstrated that the properties of the *DYNASILs* could be converted from mechanically soft to hard and from hydrophobic to hydrophilic by incorporation of different components into the original polymer. *Optodynamers* based on a polyhydrazone backbone were also studied. Their color and fluorescence changes were expressed at the interface between two different polyhydrazone dynamer films as induced by hydrazone bond exchange and component recombination through the interface, resulting in an extension of conjugation.

In the second part, this thesis illustrates the possibility of development of new forms of materials behaviour such as healing, adaptation, response to a variety of external factors (heat, light, chemical additives, etc.). This work was based on exploitation of the concept of a *constitutional dynamic polymer library (CDPL)*, based upon the combination of dynamers with dynamic combinatorial chemistry.



Scheme 1. Symbolic representation of a constitutional dynamic polymers (*dynamers*) library (CDPL) as an adaptive smart material responding to different external stimuli, such as medium (solvent), interacting species (proton, metal ions, substrate molecule, etc.), and physical factors (temp., pressure, electric or magnetic fields, light, etc.).

Dynamic combinatorial chemistry is defined as combinatorial chemistry under thermodynamic control and is based on libraries of species connected by reversible supramolecular and molecular bonds. In a dynamic combinatorial library, all constituents are in equilibrium resulting from the interconversion of library members into others through reversible connections. A *Constitutional Dynamic Polymer library (CDPL)* is thus expected to have the ability to respond to interacting species or to environmental conditions by shifts in equilibria towards the preferred, or "the fittest" dynamers. The properties that are displayed may evolve in response to a variety of external factors (Scheme 1).

A specific CDPL, involving *Folded Dynamers*, was generated by poly-condensation through reversible imine bonds. These dynamic libraries were found to undergo driven evolution under the double effect of donor-acceptor stacking and metal cation binding. In the presence of alkali metal ions, the polymers undergo binding of these metals, thereby undergoing specific constitutional changes resulting in different optical effects reflecting the presence and the positioning of donor and acceptor units within the folded dynamer.

Another CDPL study was based upon the induction of changes in crystallization behaviour as a result of the presence or absence of solvents. *Dynamers* based on reversible imine formation reactions were found to respond to changes in their neat or solution environment, thus displaying adaptive behavior through modification of their constitution in order to maximize the stability of their mesoscopic state as a function of conditions.

This work has demonstrated that dynamic polymers (*Dynamers*) introduce into the chemistry of materials a paradigm shift with respect to constitutionally static chemistry and open new perspectives in materials science. A rich variety of novel architectures, processes and properties could be expected to result from the blending of molecular and supramolecular dynamic chemistry with materials chemistry.

Résumé

Depuis plusieurs décennies, la chimie supramoléculaire s'est révélée une science de l'information moléculaire, qui permet, par le biais d'intéractions non covalentes, la génération d'entités structurellement auto-organisées, possédant des fonctions spécifiques. La compréhension de la relation entre l'information moléculaire et la production d'architectures auto-assemblées peut donner suite à des développements dans la chimie des matériaux, l'élucidation des processus biologiques, voire même à l'étude des origines et de l'évolution de la vie !

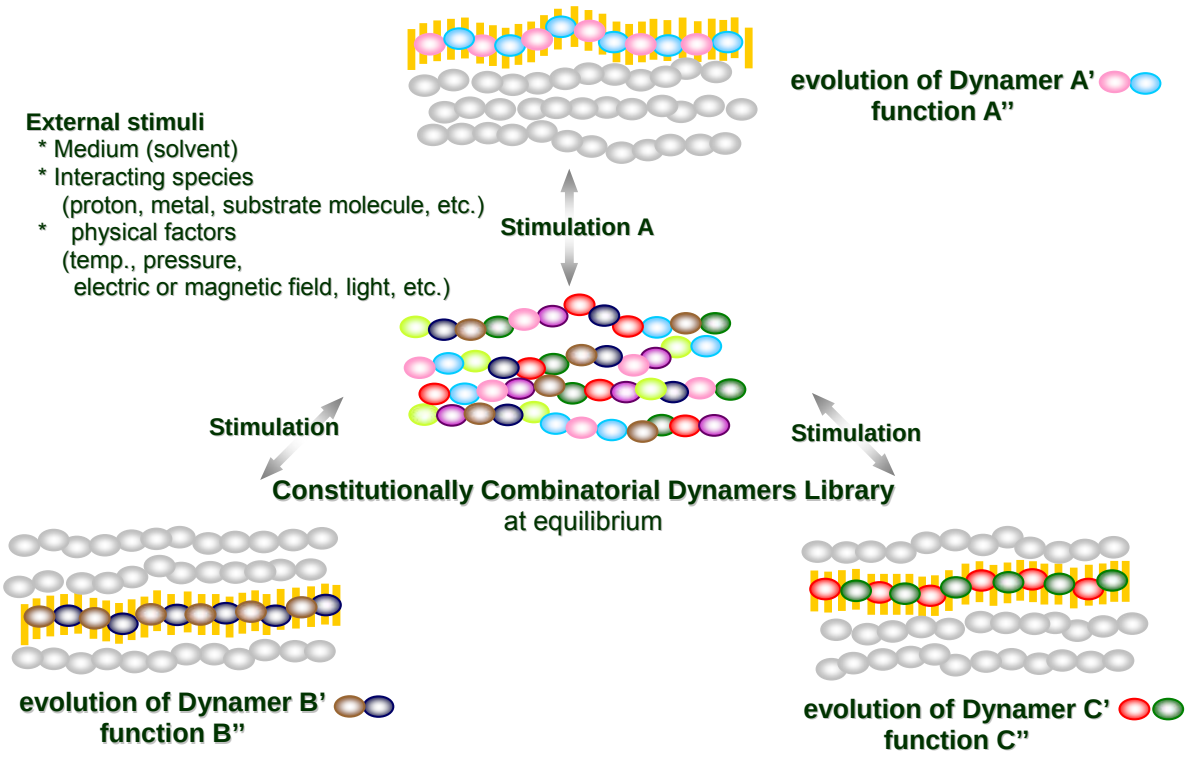
La labilité des liaisons non-covalentes confère à la chimie supramoléculaire un caractère *dynamique* intrinsèque qui se manifeste par la capacité des espèces supramoléculaires à s'adapter à différentes conditions par l'échange de leurs composants moléculaires. La Chimie Dynamique Constitutionnelle (CDC) étudie la dynamique de systèmes chimiques qui s'opère à l'échelle supramoléculaire, mais également à l'échelle moléculaire par l'utilisation de liaisons covalentes réversibles. Ces labilités permettent le contrôle thermodynamique des constituants, représentés par toutes les combinaisons possibles de composants moléculaires. Une réversibilité rapide des interactions moléculaires et supramoléculaires mises en jeu assure une réponse rapide aux changements extérieurs imposés.

Les polymères dynamiques sont constitués de monomères liés par des liaisons réversibles, au niveau moléculaire comme supramoléculaire. Ces *dynamers* peuvent changer leur constitution spontanément et continûment, par échange, remaniement, incorporation et expulsion de leurs composants monomériques.

Dans la première partie de cette thèse, nous démontrerons que par incorporation et expulsion de monomères, des modifications importantes peuvent être apportées, que ce soit au niveau des propriétés mécaniques des polymères obtenus (dynamères), hydrophobes ou hydrophiles, ainsi que du point de vue de leurs caractéristiques optiques. Les dynamères polyhydrazone ont été préparés par polycondensation entre des unités monomériques dihydrazide et dialdéhyde. Certains dynamères incluant des unités oligodiméthylsiloxane ont été développé, et nommés *DYNASILs*. Ces *DYNASIL* présentent la particularité d'échanger leurs composants monomériques par l'utilisation de réactions covalentes réversibles, et

possèdent les propriétés intrinsèques des polydiméthylsiloxane : flexibilité (faible Tg), résistance à la chaleur, et hydrophobicité. Il a été démontré que par incorporation d'unités monomériques différentes dans le polymère original, les propriétés mécaniques des DYNASILs peuvent varier de «flexible » à «rigide », et d'hydrophobiques à hydrophiliques.

Des *optodynamères* basés sur un squelette polyhydrazone ont été également étudiés. Des changements de couleur et de fluorescence à l'interface de deux films dynamère-polyhydrazone, induits par l'échange et la recombinaison de composants à l'interface, ont été observés.



Scheme 1. Symbolic representation of a constitutionally dynamic polymers (*dynamers*) library (CDPL) as an adaptive smart material responding to different external stimuli, such as medium (solvent), interacting species (proton, metal ions, substrate molecule, etc.), and physical factors (temp., pressure, electric or magnetic fields, light, etc.)

La seconde partie de cette thèse dépeint les possibilités de développement de nouveaux matériaux capables de s'auto-réparer, de s'adapter et de répondre à des facteurs extérieurs

(chaleur, lumière, addition de produits chimiques, etc). Ce travail est basé sur l'exploitation du concept de « Constitutionally Dynamic Polymer Library (CDPL) », défini par la combinaison de dynamères avec la chimie combinatoire dynamique (CCD). La CCD est définie comme une chimie combinatoire sous contrôle thermodynamique basée sur une bibliothèque d'espèces connectées par des liaisons réversibles moléculaires et supramoléculaires. Dans une bibliothèque combinatoire dynamique, tous les éléments sont dans un équilibre résultant des échanges des membres de la bibliothèque entre eux, à travers des liaisons réversibles. Une CPDL doit donc avoir la capacité de répondre à la présence de facteurs physico-chimiques internes ou externes par des déplacements d'équilibre qui favorisent le polymère le plus adapté à la contrainte. Les propriétés de ces systèmes dynamiques peuvent donc s'adapter à divers stimuli (Schéma 1).

Une classe de CDPL, incluant les « dynamères repliés », a été générée par polycondensation de liaisons imines. Ces bibliothèques dynamiques présentent la faculté d'adapter leur constitution sous le double effet d'interactions d'empilement donneur-accepteur et de coordination. En présence d'ions du métaux alcalins, les polymères présentent des changements constitutionnels spécifiques qui résultent en des effets optiques qui reflètent la présence et le positionnement des unités donneur et accepteur dans le dynamer replié. Une autre étude CDPL a été basée sur l'énumération de changements dans le behaviour de la cristallisation par suite de la présence ou absence de dissolvants. Des dynamers basés sur la réversibilité des liaisons imine s'adaptent à des changements dans leur environnement, à l'état solide et en solution. Ceci démontre un comportement adaptatif qui se manifeste à travers la modification de leur constitution afin de maximiser l'espèce possédant l'état mésoscopique le plus adapté.

Ce travail a démontré que l'introduction des polymères dynamiques en chimie des matériaux conduit à un changement de paradigme par rapport à la chimie constitutionnellement statique, et ouvre ainsi nouvelles perspectives dans science des matériaux. Une variété riche de nouvelles architectures, processus et propriétés pourrait résulter de la combinaison de la chimie dynamique supramoléculaire avec la chimie des matériaux.

Publications

In the thesis,

• **Fujii, S.**; Lehn, J.-M. "Structural and Functional Evolution of a Library of Constitutional Dynamic Polymers driven by Recognition of Alkali Metal Ions" *Angew. Chem., Int. Ed.,* **2009,** 48, 7635-7638. (hot paper)

• Chow, C. F.; **Fujii, S.**; Lehn, J.-M. "Crystallization-driven constitutional changes of dynamic polymers in response to neat/solution conditions " *Chem. Commun*., **2007**, 4363-4365.

• **Fujii, S.**; Ono, T.; Nobori, T.; Lehn, J.-M. "Dynamers (Dynmic Polymers): Silicon Polymeric Materials Exhibiting Reversible Formation and Component Exchange.(Dynasil) " *US provisional Patent,* **2006** (August).

• Ono, T.; **Fujii, S.**; Nobori, T.; Lehn, J.-M. "Soft to Hard Transformation of the Mechanical Properties of Dynamic Covalent Polymers through Component Incorporation" *Chem.Commun.,* **2007**, 46-48. (Top 10 paper)

• Ono, T.; **Fujii, S.**; Nobori, T.; Lehn, J.-M. "Optodynamers: Expression of color and fluorescence at the interface between two films of different dynamic polymers" *Chem. Commun.*, **2007,** 4360-4362.

• **Fujii, S.**; Nobori, T.; Lehn, J.-M. "Hydrophobic-Hydrophilic Transition on a Surface through the Exchange Reaction" *Manuscript in Preparation*, **2010.**

Collaborative works during the thesis period (not in the thesis),

• Nasr, J.; Barboiu, M.; Ono, T.; **Fujii, S.**; Lehn, J.-M. "Dynamic polymer membranes diplaying tunable transport properties on constitutional exchange" *J. Memb. Sci.,* **2008,** *321*, 8-14.

• Chow, C. F.; **Fujii, S**.; Lehn, J.-M. "Metallo-Dynamers: Neutral Dynamic Metallosupramolecular Polymers" *Angew. Chem., Int. Ed.,* **2007,** *46*, 5007-5010.

• Chow, C. F.; **Fujii, S**.; Lehn, J.-M. "Metallo-Dynamers: Neutral Double-Dynamic Metallosupramolecular Polymers" *Chem. Asian J.,* **2008**, *3*, 1324 – 1335.

CHAPTER I : Introduction

1. 1 Supramolecular Chemistry " *Chemistry is a science of information* "

1. 1. 1 Prologue

In recent times, the development of supramolecular chemistry has shown that chemistry is a science of information[1.1-1.3] and that control of molecular information through dynamic non-covalent interactions can lead to the formation of well-defined, self-organized entities exhibiting specific functions. Understanding the relationship between molecular information and the production of self-organized supramolecular architectures has consequences ranging from the development of materials chemistry to the comprehension of biological processes, and eventually to the study of the origin and evolution of life.[1.4, 1.5]

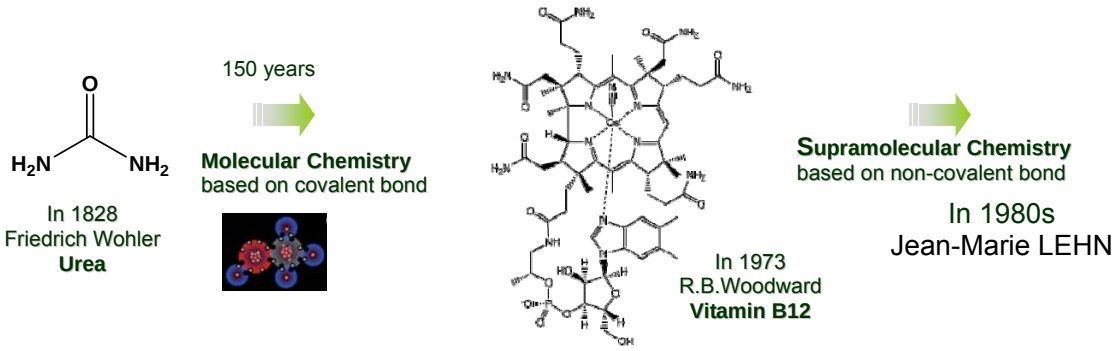


Figure 1-1. From molecular to supramolecular chemistry.

As background, we must understand the history of the development from molecular chemistry to supramolecular chemistry (Figure 1-1). Since the synthesis of urea by Friedrich Wöhler in 1828,[1.3] molecular chemistry has developed a vast array of highly sophisticated and powerful methods for the construction of ever more complex molecular structures by the making and breaking of covalent bonds between atoms through synthesis. Such a strategy, combined with a focus on efficiency and selectivity in the area of organic synthesis, in particular, led to a whole series of brilliant achievements in the last century. An impressive example was the synthesis of Vitamin B_{12} by Robert B. Woodward and Albert Eschenmoser achieved in 1973,[1.3] showing just how great the progress had been in the 150 years since Wöhlers' work.[1.3] Molecular chemistry based on the covalent bond, thus, was

well-established.

Supramolecular chemistry, defined by Lehn in 1980s,[1.1-1.5] is the chemistry of intermolecular bonds such as hydrogen bonds**,** π-π stacking, dipolar interactions, van der Waals forces and hydrophobic interactions (Figure 1-2), covering the structures and functions of the entities formed by association of two or more chemical species.[1.1-1.5] In other words, it is "chemistry beyond the molecule". Its development requires the use of all resources of molecular chemistry combined with the designed manipulation of non-covalent interactions so as to form supramolecular entities, supermolecules possessing features as well defined as those of molecules themselves. One may say that supermolecules are to molecules and the intermolecular bond what molecules are to atoms and the covalent bond.

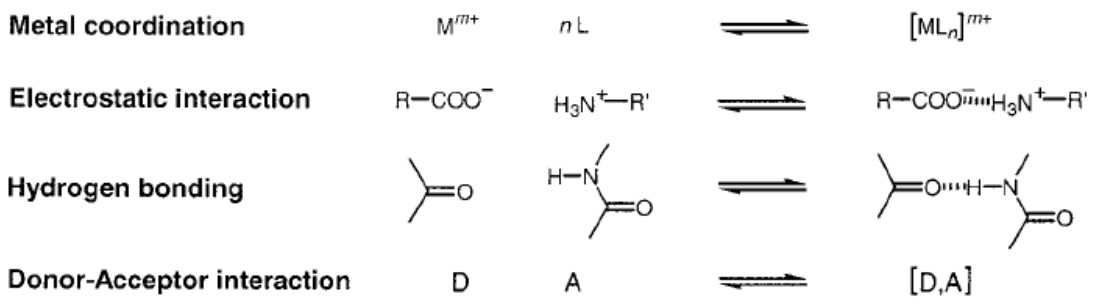


Figure 1-2. Reversible interactions for supramolecular chemitry.

Much of the work in supramolecular chemistry has focused on molecular design for achieving complementarity between single-molecule hosts and guests.[1.6-1.8] Besides complementarity, recognition, self-organization, preorganisation and even self-replication represent important 'key words' in supramolecular chemistry.[1.1-1.5] As a consequence, the practice of supramolecular chemistry tends to be a somewhat interdisciplinary activity, often requiring knowledge of a range of appropriate chemical, physical and biochemical procedures and techniques. Indeed, aspects of supramolecular chemistry have affected all the scientific worlds (Figure 1-3).[1.9, 1.10]

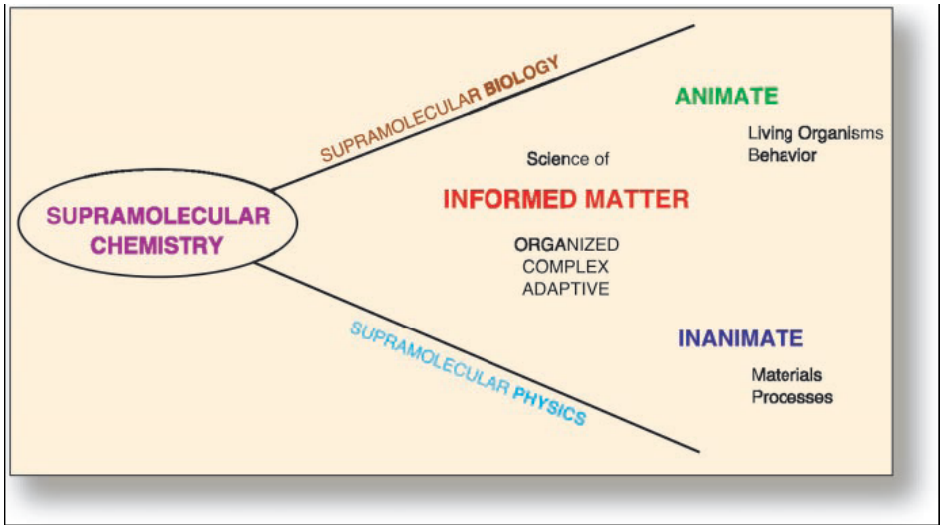


Figure 1-3. Supramolecular science as the science of informed matter at the interfaces of chemistry with biology and physics.[1.10]

Three main themes outline the development of supramolecular chemistry.[1.1-1.5] (i) Molecular recognition between artificial receptors and their substrates relies on design and preorganization and implements information storage and processing. (ii) The investigation of self-organization relies on design for inducing the spontaneous but controlled assembly of sophisticated supramolecular architectures. It implements programming and programmed systems. (iii) The third, emerging, phase introduces adaptation and evolution. It relies on self-organization through selection in addition to design, and implements chemical diversity and "informed" dynamics, toward constitutional dynamic chemistry (CDC),[1.11] which are mentioned later, in 1. 2 Constitutional Dynamic Chemistry, in Chapter 1.

1. 1. 2 Molecular Recognition

Molecular recognition basically rests on the principles of both molecular energetic and geometrical complementarity. The latter is the celebrated "lock and key", steric fit concept enunciated by *Emil Fischer* in 1894.[1.3] In biological systems, molecular recognition is of central importance such as in substrate binding to a receptor protein,[1.12, 1.13] enzymatic reactions,[1.14, 1.15] assembling of protein-protein complexes,[1.16, 1.17] immunological antigen-antibody association,[1.18, 1.19] intermolecular reading, translation and transcription of the genetic code,[1.20-1.22] signal induction by neurotransmitters,[1.23-1.27] cellular recognition, [1.28-1.31] etc (Figure 1-4).[1.32]

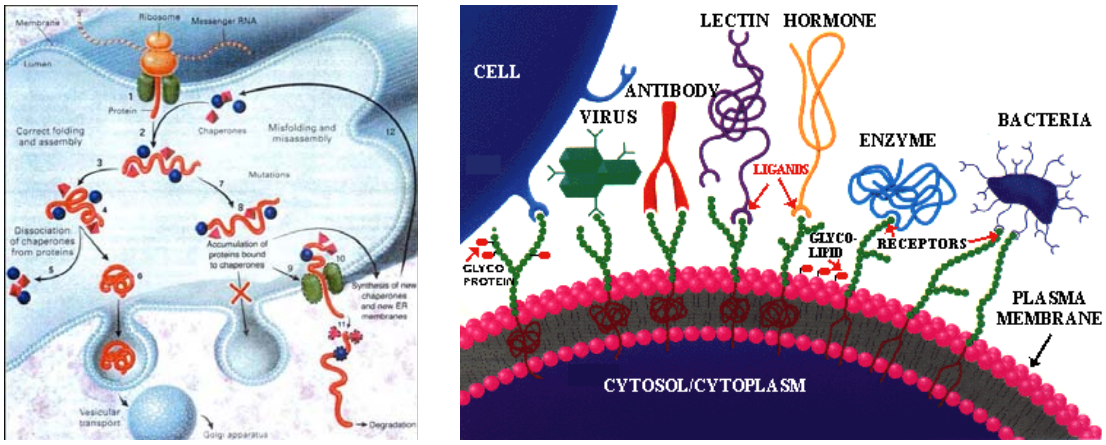


Figure 1-4. Representations of the processes of the association of proteins with their molecular chaperones[1.22] and of a variety of molecular recognition events occurring on a cell surface.

Likewise, it is clearly of fundamental importance in the functioning of, for example, sensors and other analytical devices, in separation science and in aspects of catalysis. The best-known examples of synthetic molecular receptors for substrate recognition are macrocyclic species such as crown ethers, cryptands, spherands and calixarenes.[1.1-1.8] The development of their chemistry has led to many applications in, for example, both biological and medical areas. The essence of artificial receptor design is that they should contain cavities of appropriate size and shape for recognition and binding of a substrate into the cavity to yield an inclusion complex, as in the case of the cryptates (Figure 1-5).[1.33-1.35]

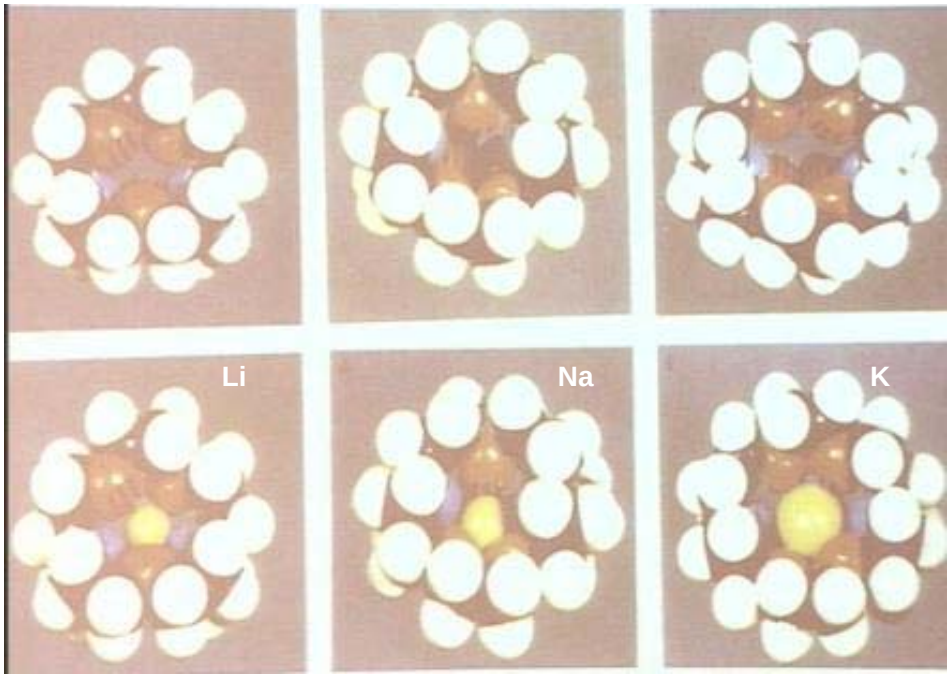


Figure 1-5. Molecular models of cryptants and cryptates for a series of alkali metal ions.

Molecular recognition thus is defined as a process involving both binding and selection by a given molecule and/or ions, as well as possibly a specific function,[1.36] and implies a structurally well-defined pattern of intermolecular interactions. Molecular recognition thus is a question of *information storage* at molecular level and *readout* at the supramolecular level. Information may be stored in the architecture of molecule based on its covalent framework, and it is read out at the supramolecular level through formation/dissociation and interactions/recognition of the supermolecular entities, which define processing algorithms.[1.2, 1.3]

1. 1. 3 Self-Organization

Self-organization may be defined as the process by which a supramolecular species forms spontaneously (meaning it is thermodynamically favoured or just that it is kinetically rapid) from its components.[1.3] For the majority of synthetic systems it appears to be a beautifully simple convergent process, giving rise to the assembled target in a straightforward manner.[1.37, 1.38] Self-organization processes are also the origin of the properties/functions expressed in all matter, ranging from synthetic chemistry, e.g., the nano architecture of materials, to biological activity such as DNA double helix (Figure 1-6),[1.39, 1.40] protein folding,[1.41, 1.42] protein, oligopeptide assembly (Figure 1-7),[1.43-1.45] lipid bilayer[1.46, 1.47] and ultimately to the study of origin and evolution of life.[1.48-1.50]

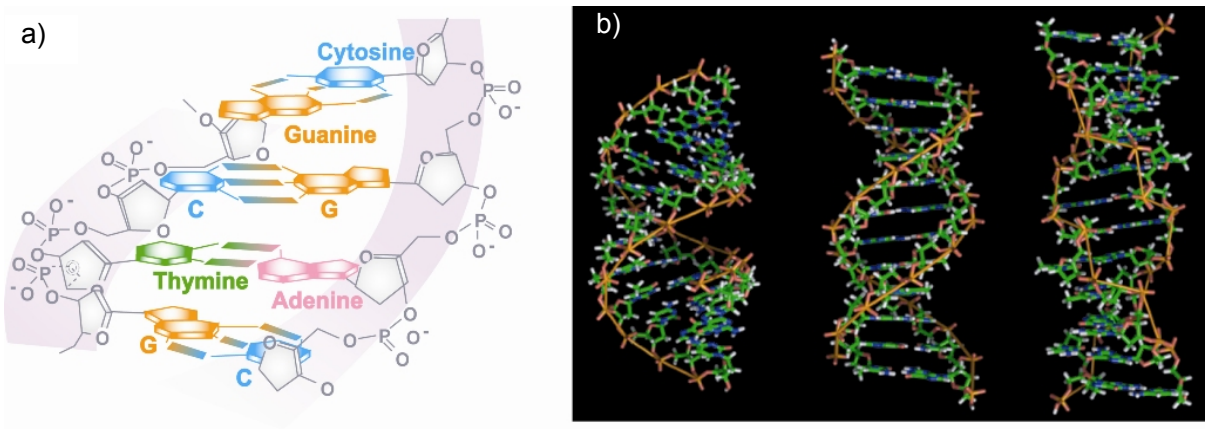


Figure 1-6. Schematic representation of the double-helix structure of DNA. Left: schematic representation of the complementary pairs of nucleic bases, Right: representation of the skeleton composed of nucleic bases and sugars of DNA.

Self-organization is the driving force that led to the evolution of the biological world from inanimate matter[1.1-1.5] The inclusion of dissipative nonequilibrium processes,[1.51] like those present in the living world, constitutes a major goal and challenge for supramolecular chemistry.

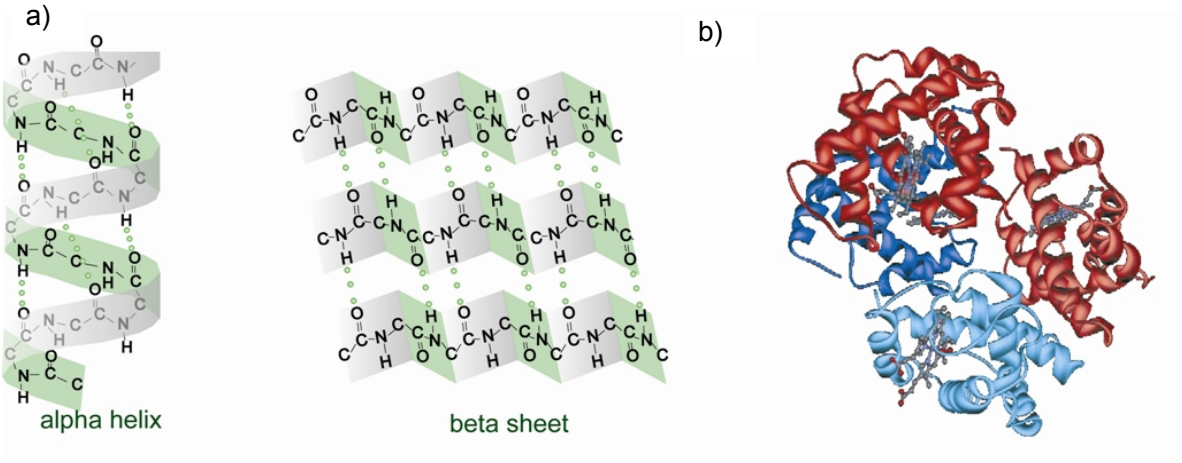


Figure 1-7. Schematic representation of the structure in proteins. Left: a) schematic representation of the supramolecular structure of alpha helix and beta sheet in proteins b) representation of the supramolecular organization of proteins to form a highly complex protein assembly.

They may be directed via the molecular information stored in the covalent framework of components and read out at the supramolecular level through specific interaction/recognition patterns, which define processing algorithms,[1.2, 1.3] and the precise design of molecular information can lead to well-defined supramolecular self-organized entities/architecture.[1.52]

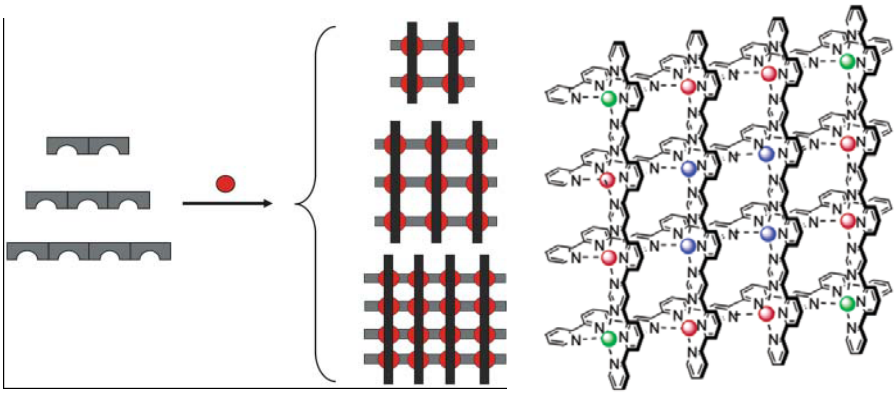


Figure 1-8. Schematic representation of the self assembly of metallosupramolecular [2 6 2], [3 6 3] and [4 6 4] grid-type architectures from ligand strands possessing respectively 2, 3 and 4 complexation subunits. Subunits containing either 2 or 3 binding sites (e.g. N sites) correspond respectively to metal ions of tetrahedral and octahedral coordination.[1.61]

Realizing such a correlation between molecular information and the resulting self-organized supramolecular entities has led to the design of many different molecular

components capable of transforming the molecular information into the formation of well defined architectures such as grid arrays (Figure 1-8),[1.53, 1.61] multistrand helices,[1.54, 1.55] circular helicates(Figure 1-9),[1.56] folding entities,[1.57-1.60] metal coordination complexes (Figure 1-10),[1.62, 1.63] synthetic lipid bilayers,[1.64] liquid crystals,[1.65-1.67] hydrogen-bonded multicomponent entities,[1.68-1.75] interlocked mechanically linked compounds,[1.76, 1.77] and many others.[1.78-1.82]

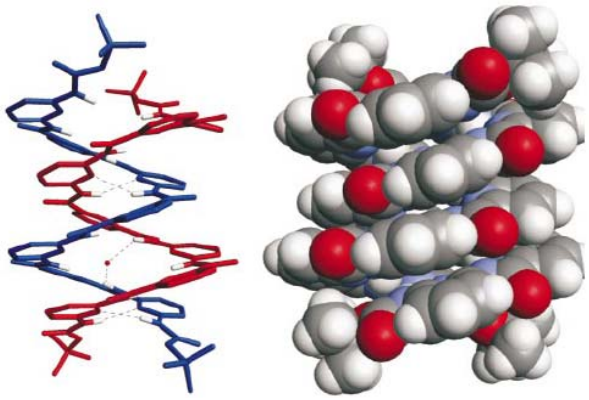


Figure 1-9. Solid state structure of a self-assembled metallohelicate.[1.55]

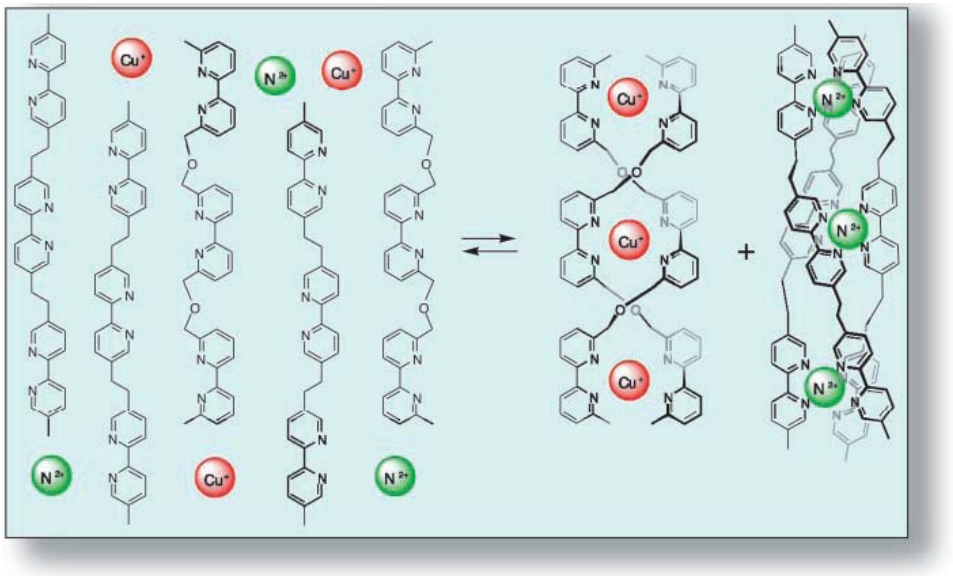


Figure 1-10. Parallel formation of a double helicate and a triple helicate with self-recognition from a mixture of two different suitably instructed ligands and two different types of metal ions that present specific processing/coordination algorithms. CuI (red) and NiII (green) have tetrahedral and octahedral coordination, respectively.[1.63]

A distinctive feature of using weak, non-covalent forces in molecular assemblies is that such interactions are normally readily reversible so that the final product is in thermodynamic equilibrium with its components. It is a factor that will assume increasing importance for the construction of the new (larger) synthetic systems as both the number of intermolecular contacts present and overall structural complexity are increased. Note that supramolecular systems may also form under kinetic rather than thermodynamic control.[1.124, 1.125]

This situation will tend to be more likely for larger supramolecular assemblies incorporating many intermolecular contacts, especially when moderately rigid components are involved. It may also tend to occur when metal ions, and especially kinetically inert metal ions, are incorporated in the framework of the resulting supramolecular entity or when, for example, an intermediate product in the assembly process precipitates out of solution because of its low solubility.[1.5] Understanding, inducing, and directing such self processes are key to unraveling the progressive emergence of complex matter.

1. 1. 4. Supramolecular Polymer Science

Supramolecular polymers[1.83, 1.84] are defined as the entities generated by the polyassociation of molecular monomers based on complementary directional and reversible binding groups connecting through non-covalent interactions such as electrostatic, hydrogen bonding, donor-acceptor and Van der Waals interactions as well as metal ion coordination.

The first instance of a designed supramolecular main-chain polymer was produced in the Lehn laboratory. By triple hydrogen bonding between difunctional diaminopyridines and difunctional uracil derivatives (Figure 1-11), supramolecular polymer chains were formed.[1.85, 1.86]

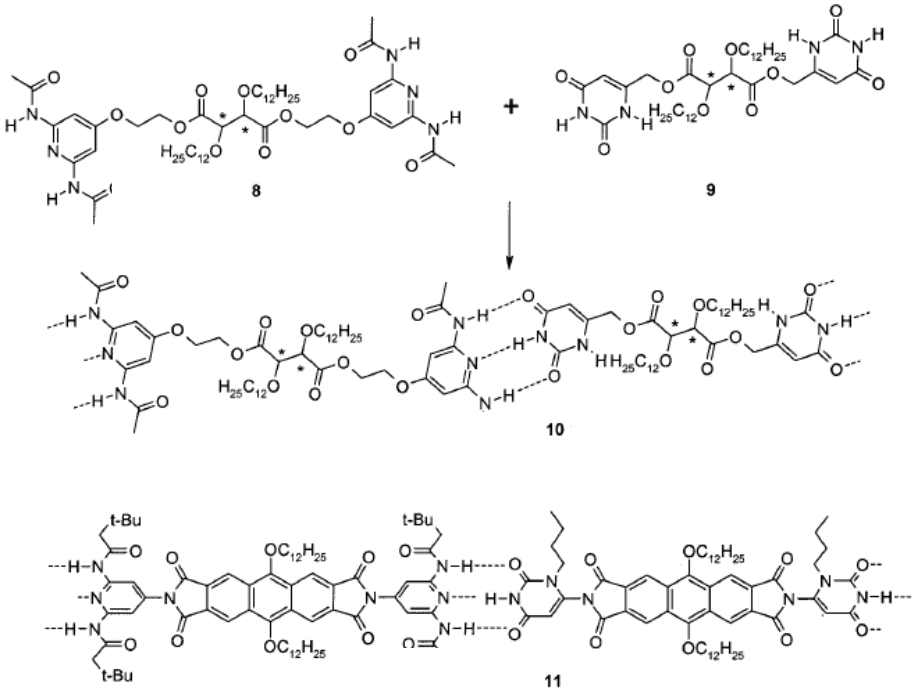


Figure 1-11. Liquid crystalline supramolecular polymers developed in the Lehn laboratory based on triple hydrogen bonds between both chiral, tartaric acid based monomers and rigid monomers. [1.85-1.89]

The 1:1 mixture of difunctional diaminopyridines and difunctional uracil exhibits liquid crystallinity over a broad temperature window, whereas, in contrast, the pure compounds are solids which melt into an isotropic liquid without displaying a liquid crystalline phase. Because of the chirality of the tartaric acid spacer used, the fibers observed by electron microscopy showed biased helicity.[1.87] Lehn and co-workers expanded the scope of

supramolecular polymers by the development of rigid rod polymers (Figure 1-11).[1.88, 1.89] In these polymers, a rigid 9,10-dialkoxyanthracene core connects the hydrogen-bonded groups via an imide group. Because of the increased molecular rigidity, the system is not thermotropic liquid crystalline, but a lyotropic liquid crystalline phase is observed in apolar solvents that is birefringent and highly viscous. The high directionality of the hydrogen bonding interactions results in an inherent one – dimensional nature, either in melts or in solution.

Hydrogen bonding type

Other supramolecular polymers based on hydrogen bonding have been developed and well-characterized by the E. W. Meijer group (Figure 1-12).[1.90-1.92]

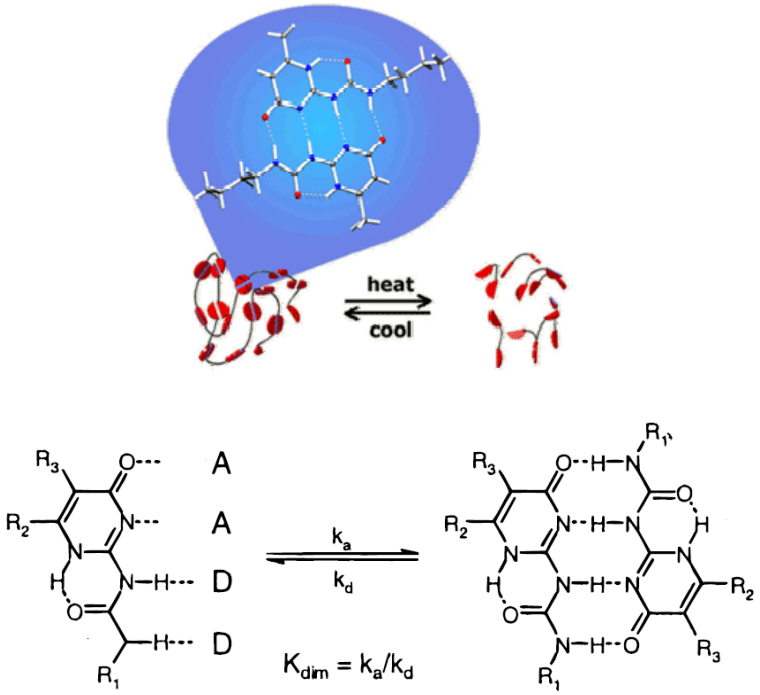


Figure 1-12. Supramolecular polymeric materials based on 2-ureido-4[1H]-pyrimidinones. The hydrogen bonding unit dimerizes through quadruple hydrogen bonding.[1. 93, 1.94]

Derivatives of 2-ureido-4-pyrimidone (Figure 1-12) strongly dimerize with a binding constant K_{dim} of 10^7 M^{-1} in $CHCl_3$, by means of a self-complementary DDAA (donor-

donor-acceptor-acceptor) array of four hydrogen bonds. Polymers based on this unit have found applications similar to conventional thermoplastic elastmers as flexible films (Figure 1-13). Their most important property, one not observed in conventional polymers, is the strong dependence of their melt viscosities on temperature because of their unique mechanism of stress relaxation.

Motion in supramolecular polymers occurs not only through reptation like a conventional polymer but also through breaking and reforming of the molecular chain, so that the main chain rapidly becomes shorter with an increase of temperature, showing liquid-like character. These novel properties may bring many applications such as adhesive reagents, coatings and heat-sensitive materials.

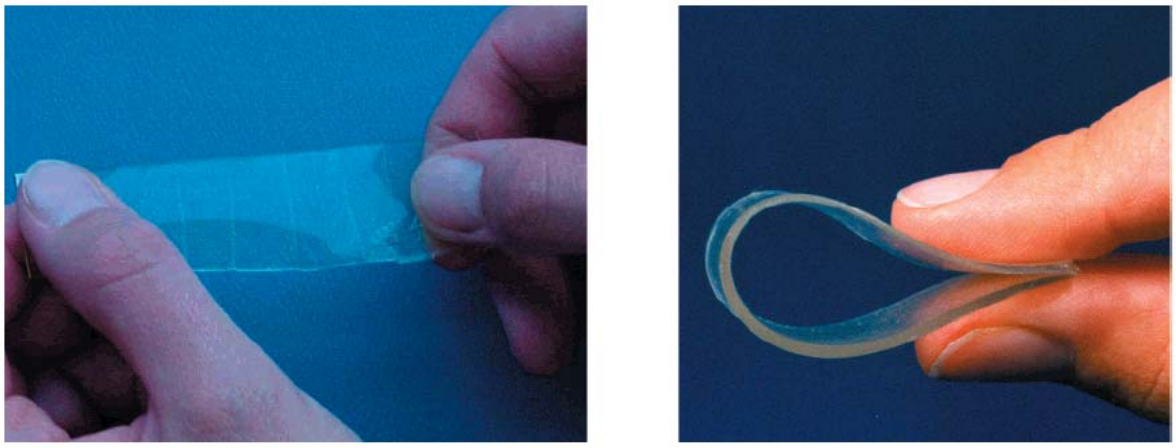


Figure 1-13. Supramolecular materials rest on the ureidopyrimidone unit.[1.95]

Although hydrogen bonds between neutral organic molecules are not the strongest noncovalent interactions, its cooperativity, directionality and versatility in a supramolecular polymer results in significant degrees of polymerization. The use of aromatic compounds as multiple hydrogen-bonding units for self-assembly has been developed. There is opportunity for developing new multiple hydrogen-bonding units for stronger association by using arrays of 6 bonds (Figure 1-14)[1.96] or 8 hydrogen bonds (Figure 1-15).[1.97]

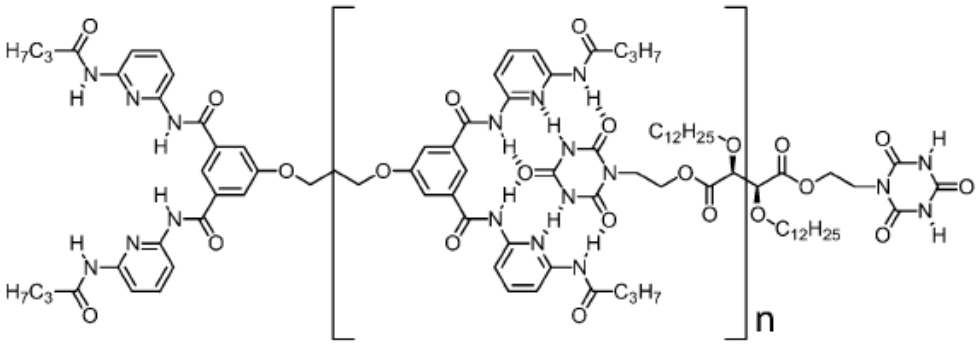


Figure 1-14. Main-chain supramolecular polymer generated via sextuple hydrogen bonding.[1.96]

Ghadiri[1.97] has studied nanotubes that self-assemble from cyclic peptides. These tubes, which can be considered reversible polymers because of their multiple-hydrogen bonding, assemble into extended linear stacks through hydrogen bonding.

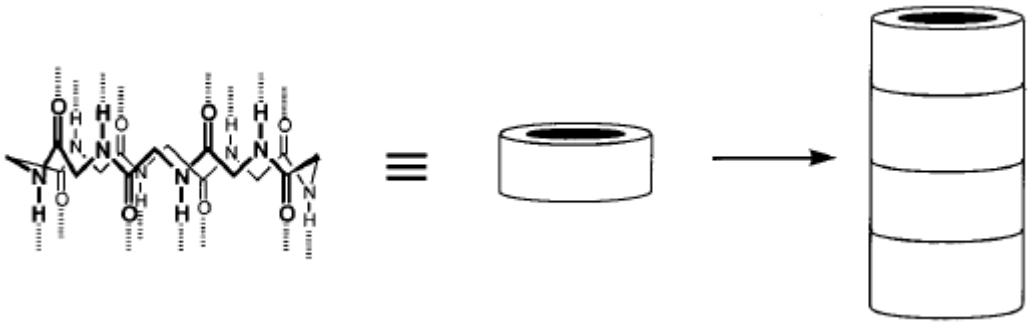


Figure 1-15. Formation of nanotubes based on hydrogen bonding between cyclic peptides.[1.97]

Metal - ligand coordinative type

Metal ion coordination has been used to prepare a wide range of supramolecular complexes with various geometries and recently has drawn much attention in polymer science because properties such as charge, color, luminescence, magnetism, macroscopic morphology and kinetic lability can be in principle tuned with the appropriate combination of ligands and metal ions (Figure 1-16).[1.98-1.105]

Author[1.104] demonstrated that in coordination complexes of Co(II), Zn(II), La(III) and Eu(III) ions with the tridentate ligand, bis(2,6-bis(methylbenzimidazolyl)- 4-hydroxypyridine) ligand exchange takes place in solution, resulting in a response to thermo-, chemo-, and mechano-stimuli, as well as changes in light-emitting properties (Figure 1-17).

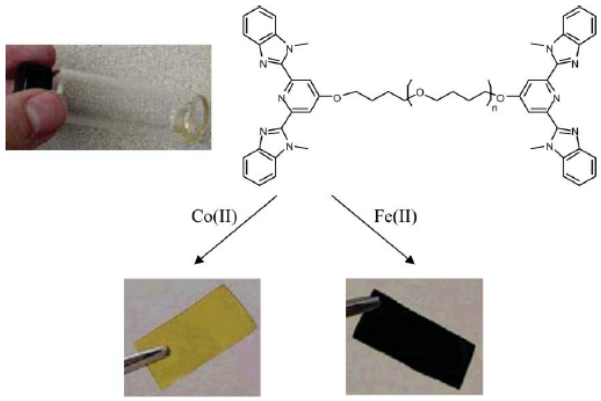


Figure 1-16. Formation of metallo-supramolecular polymer films by complexation of the 2,6-bis(19-methylbenzimidazolyl)pyridine-terminated oligomers with Fe(II) and Co(II).[1.100]

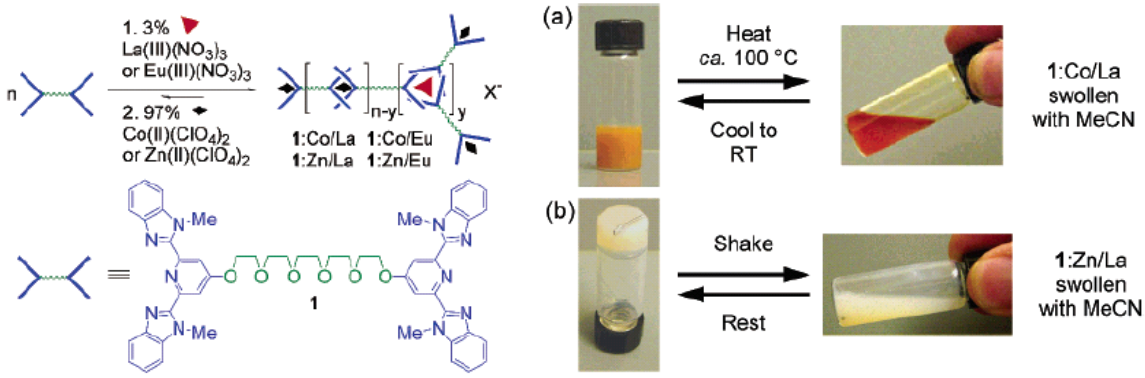


Figure 1-17. Schematic representation of the formation of a metallo-supramolecular gel-like material using a combination of lanthanide and transition metal ions mixed with monomer **1** (a) The thermoresponsive nature of **1**:Co/La and (b) the mechanoresponsive nature of the thixotropic **1**:Zn/La system. Both materials are swollen in acetonitrile (800% by wt.).[1.104]

While most known coordination polymers are either cationic or anionic,[1.98- 1.105] novel, neutral coordination polymers (Figure 1-18)[1.106, 1.107] have been obtained by the use of well-designed monomeric ligands and metal ions, and these can ultimately be used to blend

into conventional neutral polymers. Such coordination polymers displayed remarkable functional changes in both their mechanical and optical properties through ligand exchange.

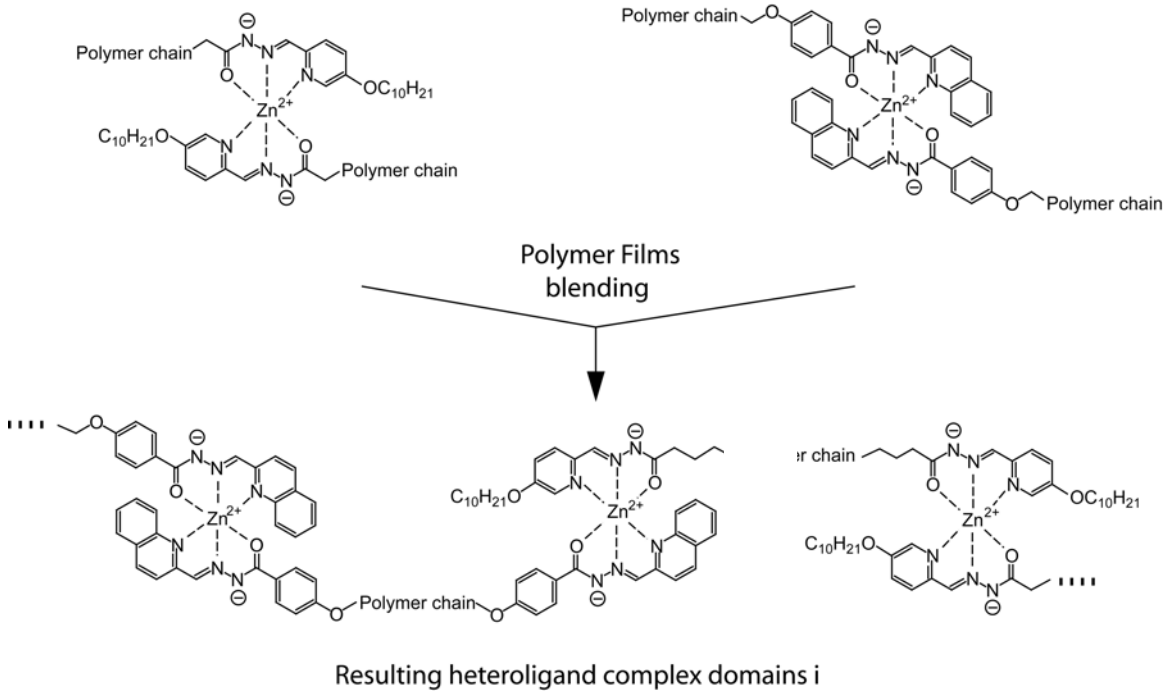


Figure 1-18. Metal-ligand exchange reaction between metallodynamers – evolution of the metallodynamers containing only homoligand domains towards the polymer blend containing heteroligand domains.[1.106, 1.107]

Host–guest Type (Donor-Acceptor, Electro static, hydrophobic interaction)

Other types of supramolecular polymers based on donor-acceptor, electrostatic and solvophobic interactions have also been reported.[1.108-1.111] Martin *et al.*[1.109] described the building of organized donor–acceptor arrays based on a host–guest system, by use of recognition between [60] fullerene as acceptor and a TTF derivative as a donor, in which the large and concave aromatic surface of the TTF units serves as a recognition motif for the convex surface of C_{60}.

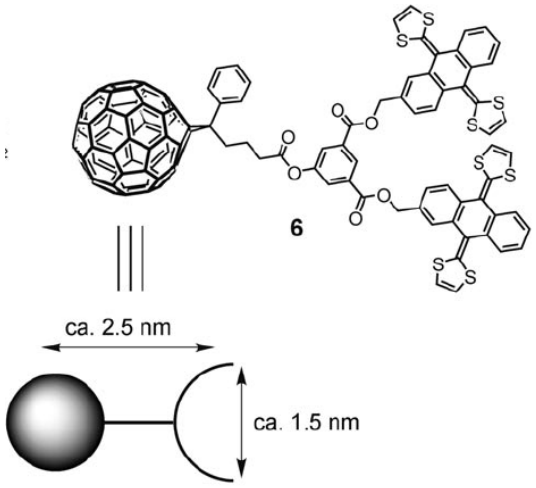


Figure 1-19. Molecular structure of monomer of donor-acceptor supramolecular polymer formed through recognition between C_{60} and TTF.[1.109]

The Dalcanale group has reported[1.110] a new class of supramolecular polymers whose self-assembly is driven by the complexation properties of tetraphosphonate cavitands toward methylpyridinium guests through electrostatic interactions. Tetraphosphonate cavitands are resorcinarene-based molecular receptors having a negative charge and therefore cavitands in their all-inward configuration are able to complex positively charged species, such as ammonium salts or inorganic cations, with very high association constants (K_{ass} = 10^7–$10^9 M^{-1}$).

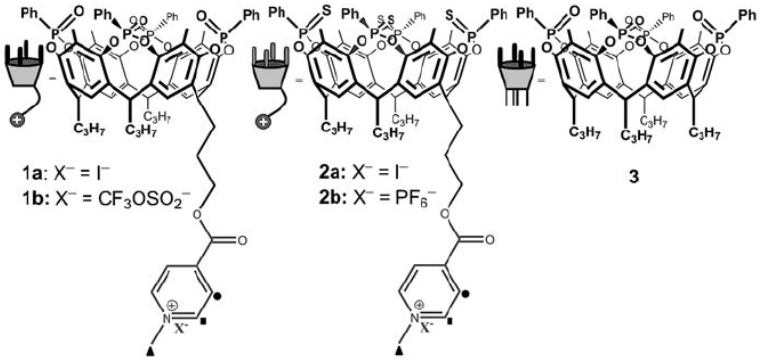


Figure 1-20. Molecular structure of monomers 1a,b, of chain stoppers 2a,b, and of model cavitand 3.[1.110]

The Harada group has published work concerning supramolecular polymers based on cyclodextrins and using solvophobic effects (Figure 1-21).[1.111] Taking advantage of

host–guest phenomena, a guest covalently attached to a cyclodextrin brought about the formation of supramolecular oligomers and polymers.

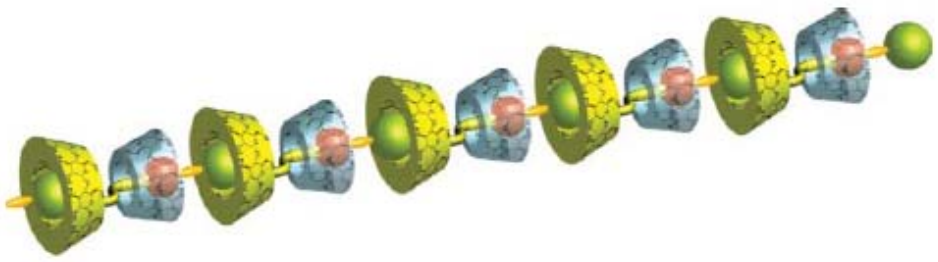


Figure 1-21. Structure of a supramolecular [2]rotaxane polymer based on host–guest complexation of cyclodextrins. [1.111]

Supramolecular self-organization of block copolymer

Supramolecular chemistry also plays an important role in the self-organization processes of conventional synthetic polymers. The field in which supramolecular chemistry and polymer science meet has developed into a vast area of research, ranging from the study of interacting biomacromolecules, such as DNA and proteins, to the self-assembly of large synthetic molecules into well-defined architectures. Examples of the latter include the formation of stereocomplexes,[1.112] highly organized blockcopolymer architectures.[1.113] Noncovalent interactions have also been employed to fold macromolecules.[1.114] The weak, noncovalent interactions of monomer units along a polymer chain tend to act cooperatively, amplifying with either/both intermolecular or/and intramolecular interactions through supramolecular effects. Thus, polymers are self organized, displaying specific functions dependent on their nanoscale structure (Figure 1-22). The understanding and manipulation of such self-organization has potential application in variety of fields from solar cells to drug delivery.

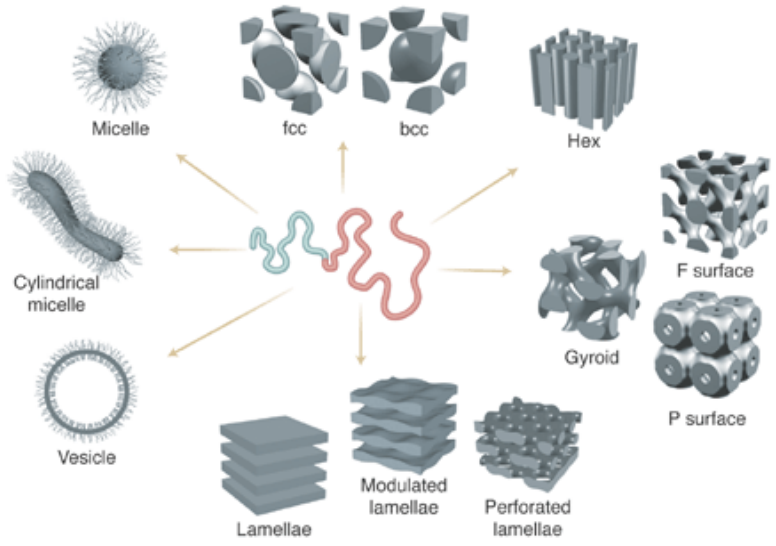
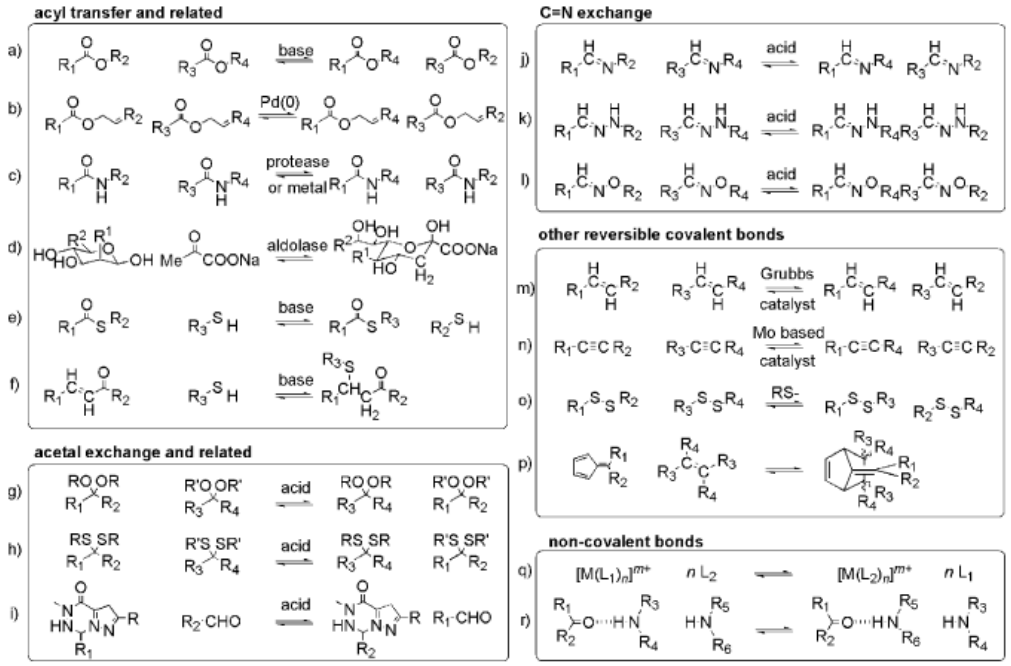


Figure 1-22. Self-organization of block copolymer. Block copolymers can form spherical and cylindrical micelles, vesicles, spheres with face-centered cubic and body-centered cubic packing, hexagonally packed cylinders, minimal surface arrays, simple lamellae and modulated and perforated lamellae. [1.113]

1. 2 Constitutional Dynamic Chemistry

1. 2. 1 Dynamic Chemistry

As non-covalent interactions, which include hydrogen bonds, π-π stacking, coordinative, electrostatic or Van der Waals interactions, are usually labile (As coordinate bonds, in particular, are frequently not labile. Noted that H.Taube mentioned that "labile" complexes arbitrarily defined as those whose reactions appear to be complete on mixing and "inert" as those for which continuing reaction can be observed.),[1.142] the self-assembled supramolecular entities formed through their action are inherently dynamic in regard to their constitution. This ability of supramolecular species to reversibly dissociate and associate, to deconstruct and reconstruct allows them to incorporate, decorporate and rearrange their molecular components.



[a] (a) Transesterification; (b) transallylesterification; (c) transamidation; (d) aldol exchange; (e) transthioesterification; (f) Michael/retro-Michael reactions; (g) acetal exchange; (h) thioacetal exchange; (i) pyrazolotriazone metathesis; (j) transimination; (k) hydrazone exchange; (l) oxime exchange; (m) alkene metathesis; (n) alkyne metathesis; (o) disulfide exchange; (p) Diels−Alder/retro-Diels−Alder reactions; (q) metal−ligand exchange; (r) hydrogen-bond exchange.

Figure 1-23. Reversible reactions used for Constitutional Dynamic Chemistry to Date. [1.115, 1.116]

Such dynamic character opens up the unique possibility of self-repair if faults occur in their synthesis or self-assembly. Molecular chemistry may, however, also show dynamic behavior,

provided substructures are linked through reversible covalent bonds (Figure 1-23).[1.115-1.117] Supramolecular chemistry has thus evolved toward a *constitutional dynamic chemistry* (CDC)[1.11] which can lead to the generation and implementation of dynamic aspects in a variety of systems on both the molecular and supramolecular levels. Prior to discussing CDC in detail, dynamic chemistry in a general sense should be explained, since the word "dynamic" has been used in many different areas.

The term "dynamic", as used in chemistry, can be conveniently assessed in terms of three different forms of molecular motion. Thus, we consider *reactional dynamics*, *motional dynamics* and *constitutional dymamics.*

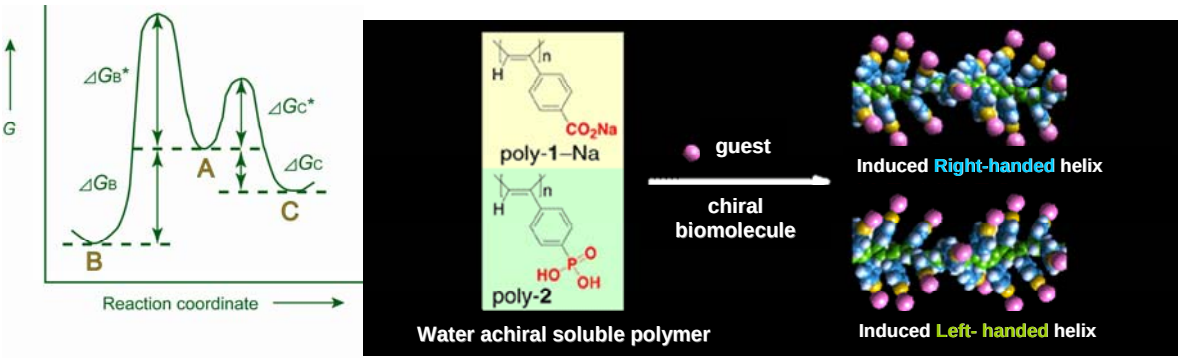


Figure 1-24. Schematic explanation of *reactional dynamics* and *motional dynamics*.[1.122, 1.123]

Reactional dynamics concern the kinetics and mechanisms of chemical reactions. Motional dynamics involve whole-molecule movements as in molecular motions in liquids, and dynamics in soft matter such as polymer chains, colloids, etc as well as internal motions such as rotations around bonds or site inversions. Morphological dynamics involving changes in molecular shape, such as in molecular machines and oriented motion are also covered.[1.118-1.121] An example of motional dynamics is provided in the work of Yashima, *et al.*[1.122, 1.123] where external chiral stimuli, in the form of optically-active guests such as an amino-acid or an oligopeptide, were found to control the chirality of the helical form adopted by an achiral polymer in its complexes. Switching from one helicity to the other was readily achieved on changing the guest. A third type of dynamic processes has been defined by Lehn.[1.11] It is *constitutional dynamics*, whereby a chemical entity which is both molecular and supramolecular, can undergo continuous change in its constitution through dissociation

into various components and reconstitution into the same entity or into different ones (Figure 1-25).

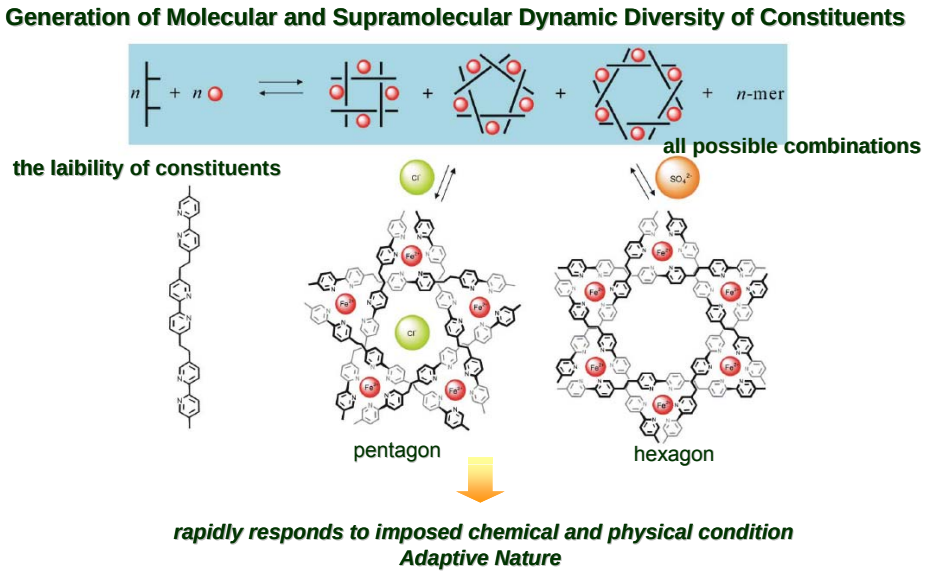


Figure 1-25. Dynamic (virtual) library of circular helicates generated from a tritopic ligand strand and octahedrally-coordinating metal ions, expressing different constituents depending on the counter ion (chloride or sulfate).[1.124, 1.125]

Constitutional dynamic chemistry (CDC) relies on the generation of both molecular and supramolecular dynamic diversity of constituents by reversible connection between a set of basic building blocks. The lability of constituents ensure thermodynamic control, in which all possible combinations of component may be present (although they may also just remain virtual depending on conditions). Such a system rapidly responds to imposed chemical and physical conditions and, as a result, any equilibrium may be shifted to the expression of selected constituent products through dissociation into various components and reconstitution into the same entity or into different entities. In others words, the change in expression of different constituents as a function of external parameters represents an *adaptation* of the system.

Dynamic combinatorial chemistry (DCC) (Figure 1-26) is included under the concept of CDC.[1.116] It is defined as combinatorial chemistry under thermodynamic control and based on libraries of species connected by reversible interactions. In a dynamic combinatorial library, all constituents are equilibrium and this requires the interconversion of library members into

another through reversible connections. As a consequence, the additional presence of molecular targets can lead to the *in situ* screening of the "best-fitted" constituents. CDC also covers kinetic selection based on the "fastest-fitted" constituents within a library (Figure 1-27).

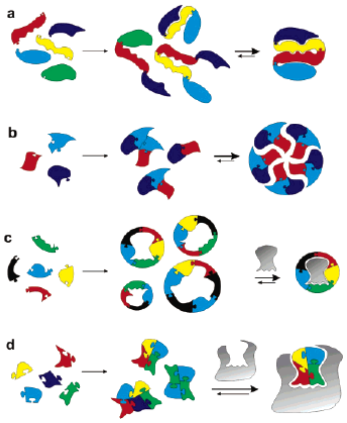


Figure 1-26. Different ways of selecting specific members of a dynamic combinatorial library on the basis of noncovalent interactions: (a) selection of foldamers driven by internal noncovalent interactions; (b) selection of self-assembling molecules on the basis of noncovalent interactions between different library members; (c) selection of a host by a separately introduced guest; (d) selection of a guest by a separately introduced host.[1.116]

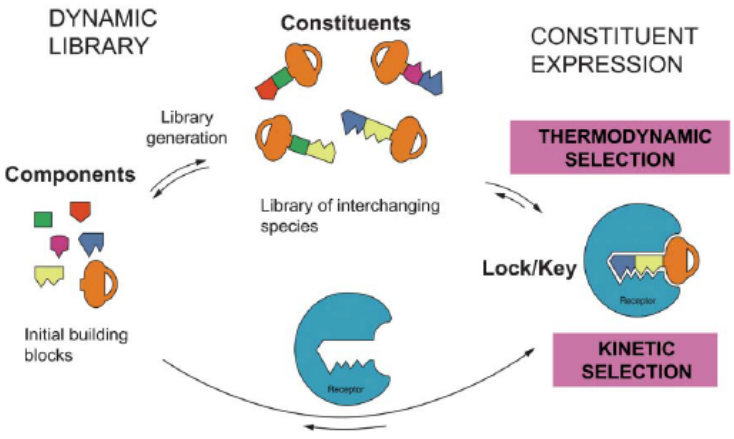


Figure 1-27. Schematic representation of the principle of dynamic combinatorial/covalent chemistry(DCC) A dynamic library of constituent keys is generated from reversibly connecting fragments of the keys. The receptor/lock amplifies/favours the expression of the constituent/key that binds best to it (thermodynamic selection) or that forms fastest within it (kinetic selection).[1.115]

Thus, the concept of constitutional dynamic chemistry (CDC) can be applied broadly and is

very powerful. The following three fields can be considered as important targets for CDC: (1) exploration of synthetic systems, (2) searching for bioactive substances and (3) development of dynamic materials.

J. K. M. Sanders'group reported the dynamic combinatorial library based on the pseudo-dipeptide building block pPFm, incorporating phenyl alanine and proline residues. In this system, addition of LiI or NaI induces the amplification of the cyclic trimer, whereas an addition of acetylcholine chloride leads to an unexpected catenane receptor.[1.126, 1.127]

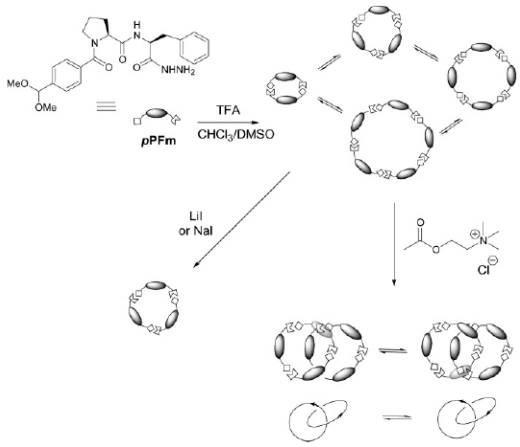


Figure 1-28. A Dynamic Combinatorial Library Based on the Pseudo-Dipeptide Building Block *p*PFm.[1.126, 1.127]

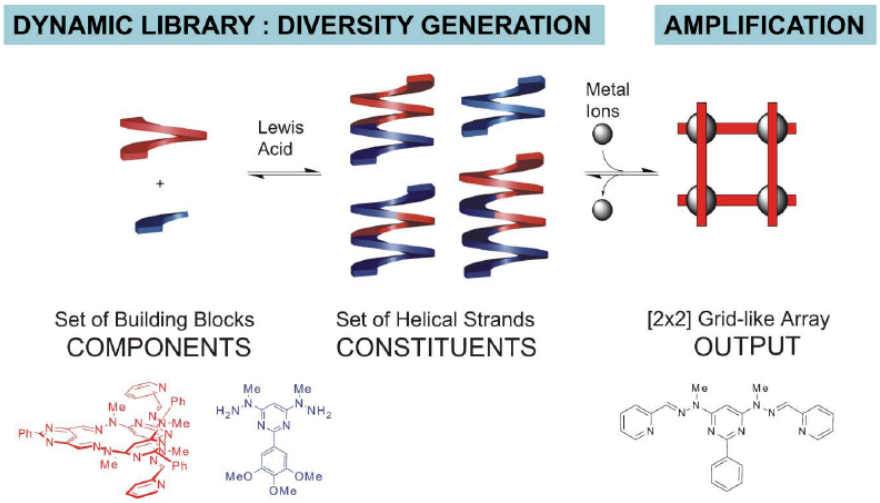


Figure 1-29. Driven evolution of a constitutional dynamic library of helical strands under the pressure of metal ion coordination towards the generation of the ligand strand (bottom right) that forms a [2 : 2] grid-type complex.[1.141]

Another example of dynamic constitutional chemistry is that the addition of Zn cations to a combinatorial library of helical ligands drives the system towards the expression of a grid –type complex (Figure 1-29). A further example is found in collaborative work between the Lehn group and the Firmenich company in Switzerland.[1-126] Fragrances have to be efficiently delivered to their target site (and usually released at well defined rate) but normally they are very volatile and their effectiveness is therefore limited in time. Constitutional dynamic chemistry was applied to the controlled delivery of fragrances. The dynamic system based on reversible hydrazone formation by the odorants responds to pH change as an external stimulus so that the consituents reform and thus release the fragrance at the desired time and place (Figure 1-30).

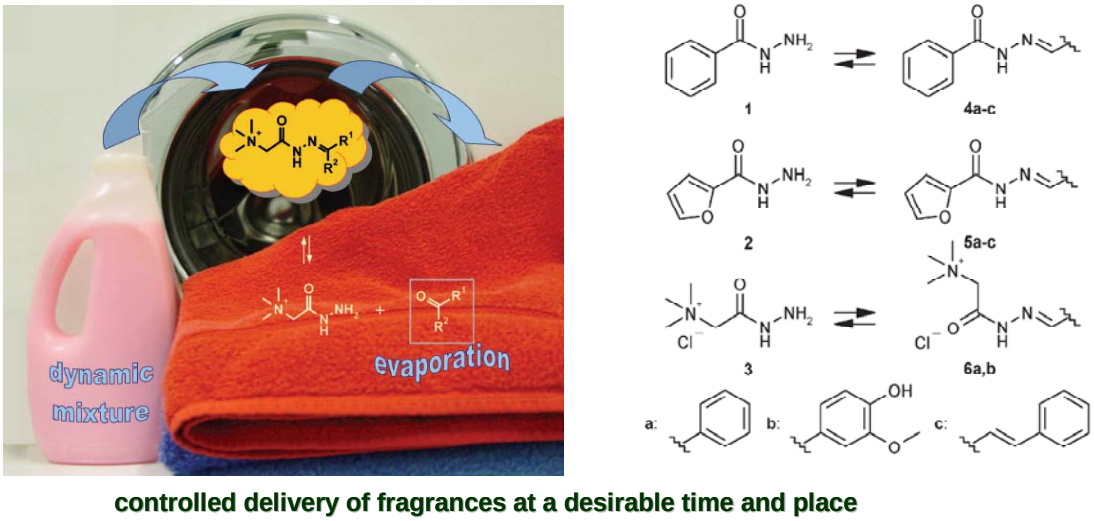


Figure 1-30. Controlled release of volatile aldehydes and ketones by reversible hydrazone formation – ‘‘classical’’ profragrances are getting dynamic.[1.128]

1. 2. 2 Dynamic Materials, - Dynamers (Dynamic Polymers) -

Dynamic adaptive materials,[1.129] capable of responding to physical triggers or to chemical effectors by modification of their very constitution, represent an intriguing class of "smart" materials of both basic and applied interest. One may define dynamic materials as those whose components are linked through reversible covalent or non-covalent connections and which undergo spontaneous and continuous change in constitution by assembly/disassembly processes in a given set of conditions. Because of their intrinsic ability to exchange their components, they may in principle select them in response to external stimuli or environmental factors and therefore behave as adaptive materials of either molecular or supramolecular nature.

Applying such considerations to polymer chemistry leads to the definition of *constitutional dynamic polymers*, *DYNAMERs*,[1.129, 1.130] of both molecular and supramolecular types. The dynamic and combinatorial features of dynamic polymers give access to higher levels of behavior such as healing, adaptation and response to external stimulants (heat, light, chemical additives, etc.).[1.108]

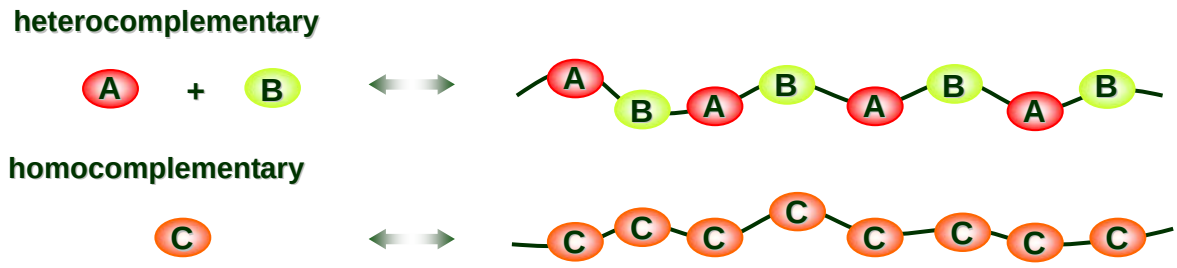


Figure 1-31. Schematic cartoons of dynamers. They may be of the supramolecular type involving polyassociation with interactional recognition or of the reversible covalent type formed by polymerization/polycondensation with functional recognition between the connecting subunits.

Description has already been given in Chapter 1.1 of supramolecular polymers generated by the polyassociation of monomers through non-covalent interactions between complementary recognition groups. In addition, dynamic covalent polymers may be generated by polycondensation via reversible chemical reactions (Figure 1-23).

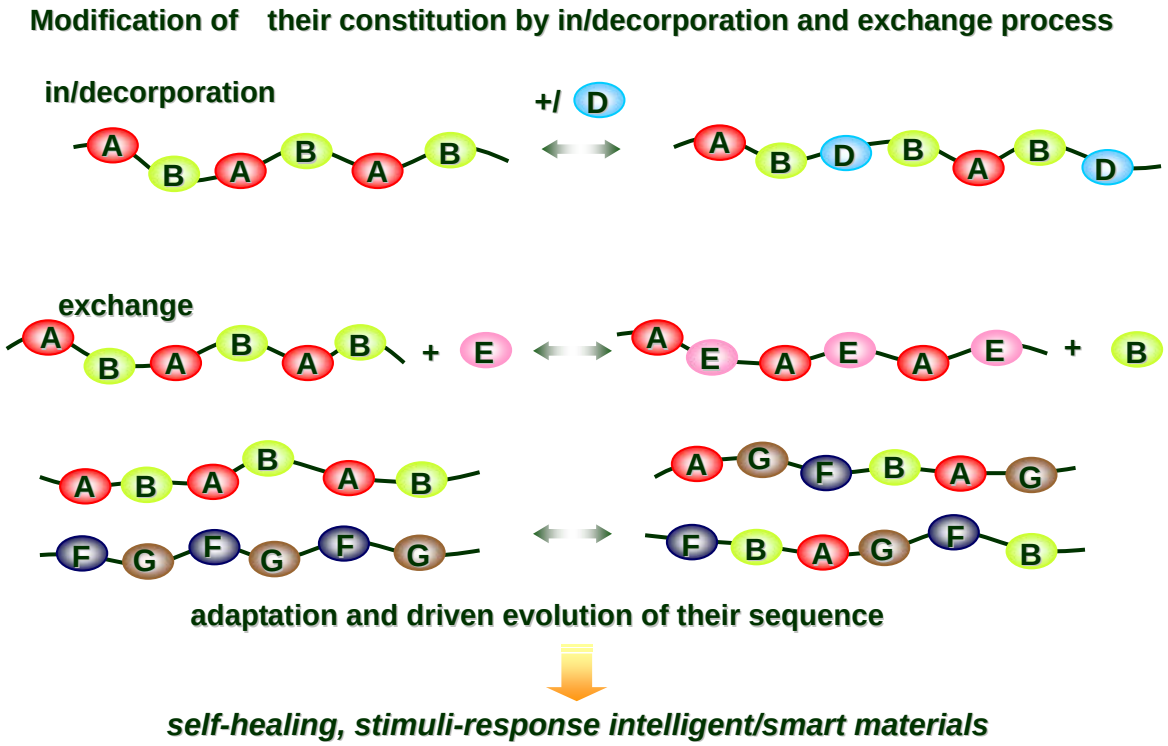


Figure 1-32. Schematic cartoons of dynamic processes in dynamers.

The dynamic properties confer to dynamers the ability to undergo spontaneous and continuous change in the constitution by in/decorporation and exchange process through assembly/disasssembly of components in a given set of conditions, so that dynamers possess the capacity of adaptation and driven evolution of their sequence and behave as high level materials showing properties such as self-healing and selective responses to different stimuli (Figure 1-32).

Dynamic polymers are also seen in a nature, for example in the behaviour of RNA (Figure 1-33).[1.131, 1.132] By a process called splicing, pre-mRNA formed by transcription from DNA changes its constitution and becomes mRNA by linking the exons and ejecting the portion of pre-mRNA which is not essential for the synthesis of the proteins called introns. This process is just the behavior of a constitutionally dynamic polymer, which is one of the key properties that nature uses to adapt and evolve when the environment is changing.

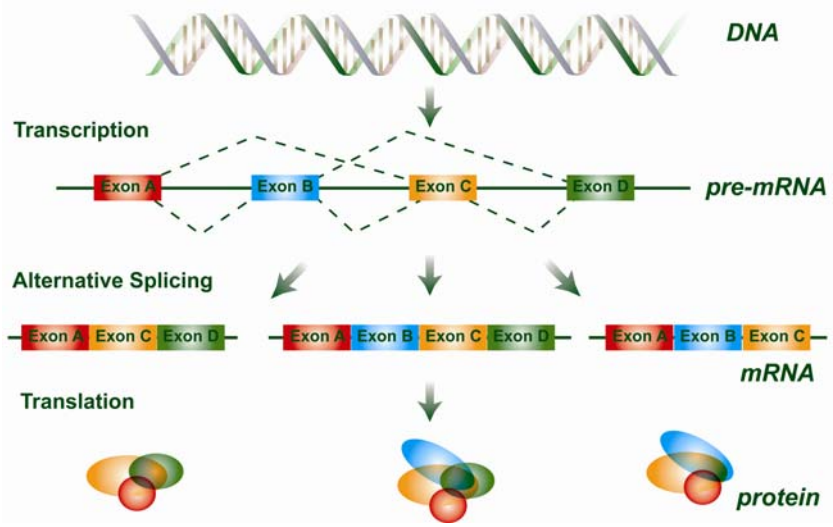


Figure 1-33 Constitutionally Dynamic Polymers in nature. Schematic cartoon of the processing of RNA.

A number of dynamic polymers have been recently synthesized and developed.[1.129] The library of dynamic polymers synthesized in Lehn group is shown in Figure 1-34.[1.83, 1.84, 1..96, 1.133-1.140] As for the supramolecular type, dynamic polymers with both hydrogen bond and metal coordinative bonds have been successfully synthesized while Diels-Alder, imine, hydrazone/hydrazide and oxime reversible covalent bonds have been employed to synthesize covalent type dynamers.

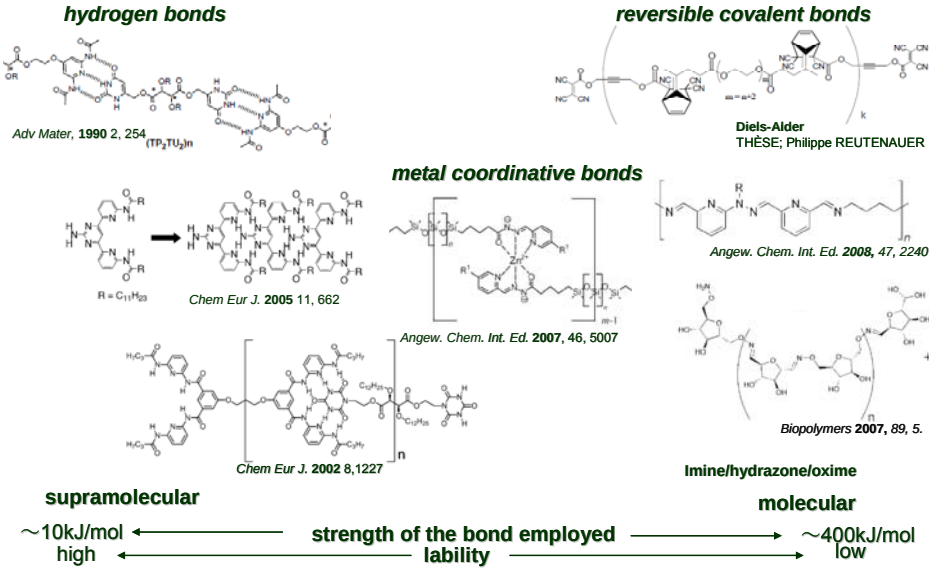


Figure 1-34. The library of dynamic polymers synthesized in the Lehn laboratory, the relative lability of their bonds being indicated.[1.83, 1.84, 1..96, 1.133-1.140]

The Lehn group has focused on the acylhydrazone bond among many reversible connections, since this bond has three specific features suitable for dynamic materials science. The first is that the binding constant for acylhydrazone formation is around 10^{5-7} M^{-1}, even in water, so that they have thermodynamic stability and are inert under the normal atmosphere including normal humidity. The second is the facile control of the reversibility of the reaction, which requires only mild (acid) conditions. The last is the capacity of the amide group to form hydrogen bonds, resulting in high modulus, fracture strength and solvent resistance (Figure 1-35).

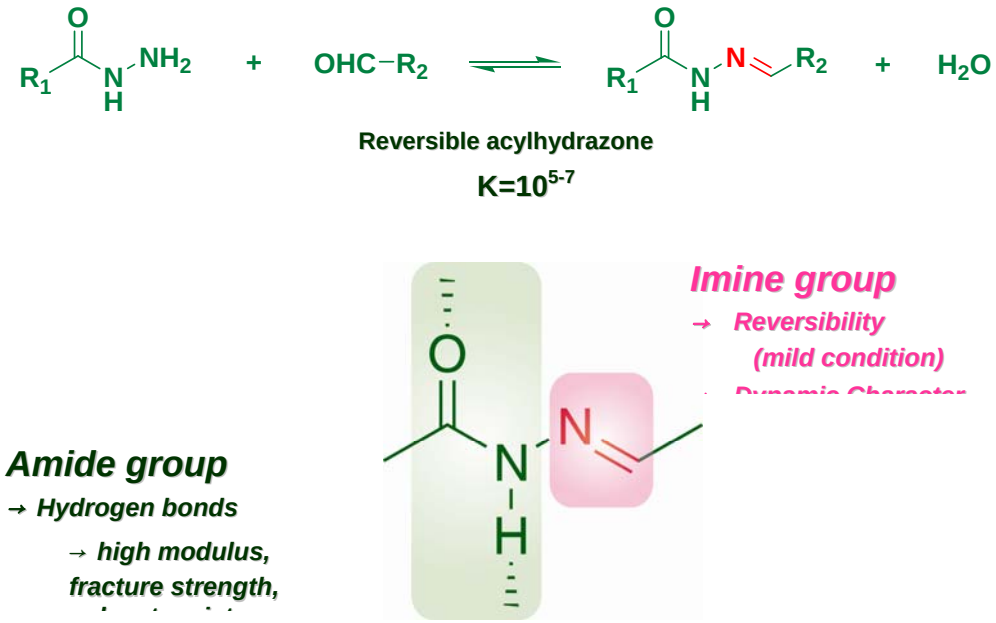


Figure 1-35. Representation of the specific features of the acylhydrazone functionality displaying both a hydrogen-bonding amide group and a reversible imine bond.

Dynamic polymers based on acylhydrazone bonds[1.139] in the linear main chains were found to show bond exchange leading to crossover component recombination as neat polymers under acid catalysis, thus generating randomized copolymers (Figure 1-36). CDC introduces into the chemistry of materials a paradigm shift with respect to constitutionally static chemistry and opens new perspectives in materials science. A rich variety of novel architectures, processes and properties may be expected to result from the blending of molecular and supramolecular dynamic chemistry with materials science.

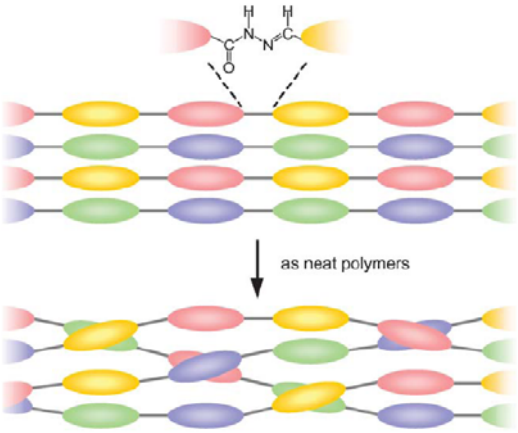


Figure 1-36. Dynamic polymer blends: Schematic representation of crossover component recombination between neat films of dynamic covalent polyacylhydrazone copolymers. The coloured units represent different monomers.[1.139]

CHAPTER 2 : Dynamic Polymeric Silicones, *DYNASILs*

2. 1 Design of *DYNASILs*, Dynamic Polymeric Silicones

2. 1. 1 Prologue

2. 1. 2 Materials Design

2. 1. 3 Results and Discussion

2. 2 Modification of Mechanical Properties

- Soft to Hard Transformation of the Mechanical Properties of Dynamic Covalent Polymers through Component Incorporation. -

2. 2. 1 Prologue

2. 2. 2 Materials Design and Synthesis

2. 2. 3 Results and Discussion

2. 2. 4 Conclusions

2. 3 Applications based on Surface Chemistry

- Hydrophobic-Hydrophilic Transition on a Surface through the Exchange Reaction.-

2. 1 Design of *DYNASILs,* Dynamic Polymeric Silicones

2. 1. 1 Prologue

At the outset of polymer science, reversible systems were avoided, both because of the difficulties encountered in controlling depolymerisation and because of the desire to produce stable and chemically well-defined materials. In the present thesis, the opposite standpoint is taken of deliberately pursuing constitutional diversity rather than emphasizing stability. We envisage that dynamers science will open a range of novel perspectives in polymer chemistry. In beginning the present work, we anticipated in particular that useful modification of the mechanical strength, hydrophobicity/hydrophilicity and other familiar properties of polymers might be achieved via rapid incorporation, decorporation or exchange of their monomeric components.

Dynamers involving oligodimethylsiloxane entities have been developed and named *DYNASILs*. These *DYNASILs* present a distinctive feature, the ability to exchange monomeric components through reversible covalent bond formation, as well as showing the properties of conventional polydimethylsiloxane polymers such as flexibility (low Tg), heat stability, and hydrophobicity. It has been demonstrated that the properties of the *DYNASILs* could be changed from mechanically soft to hard and from hydrophobic to hydrophilic by incorporation of different components into the original polymer.

2. 1. 2 Materials Design

Polydimethylsiloxane (PDMS) (Figure 2-1) is a familiar member of a group of polymeric organosilicon compounds and has found many applications ranging from contact lenses and medical devices to shampoos, caulking products, lubricating oils and heat resistant films. PDMS is an optically clear, viscous liquid and an elastic solid, and it is generally considered to be inert and non-flammable, with high heat resistance and external hydrophobicity.

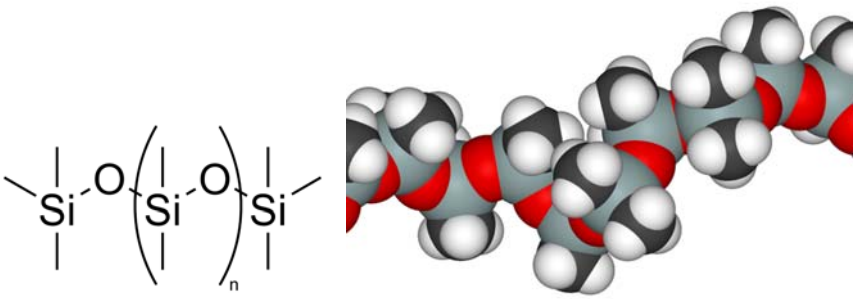


Figure 2-1. Chemical structure of PDMS and its space filling model.

Among the known reversible covalent reactions (Figure 1-23 in Chapter 1),[2.1-2.3] amino-carbonyl condensations to give C=N products,[2.4] such as imines, hydrazones, acylhydrazones and oximes, are particularly attractive in view of the very wide range of structural variations available, their easy synthetic accessibility, the control through conditions of yields, rates, and reversibility, and their role and potential for application in materials sciences (Figure 2-2).

There are two main reasons that acylhydrazone formation in particular was chosen as reversible reaction for this project. One is that the reaction displays reversibility under mild conditions,[2.5-2.7] promoted by acid catalysis and or heat. Another is that the acylhydrazone functionality provides hydrogen bonding sites through the amide group as in a conventional amide polymer (Figure 1-35 in Chapter 1).

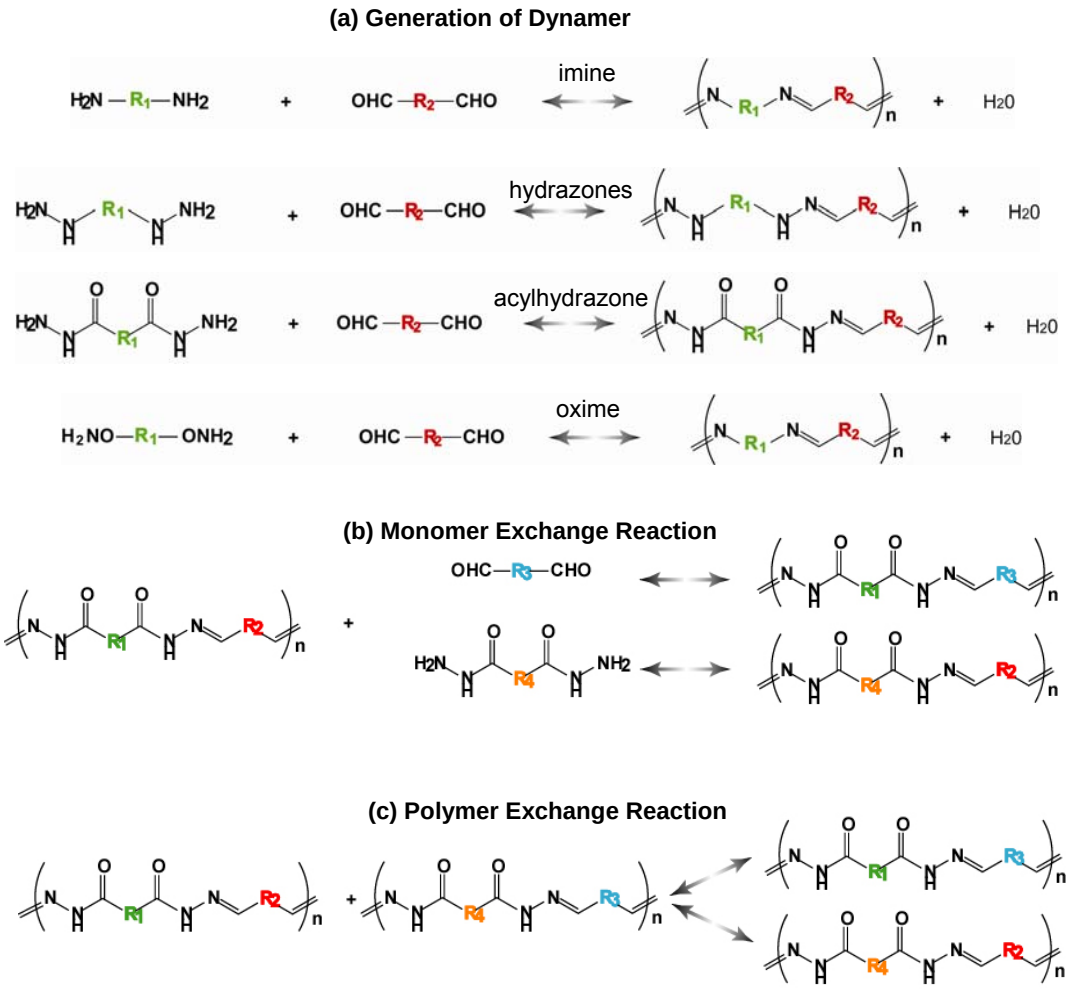


Figure 2-2. Reversible C=N bond formation and exchange process involving condensation of an amine derivative and an aldehyde.

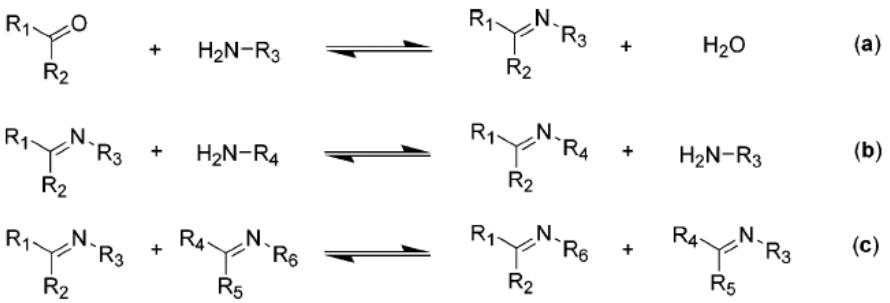


Figure 2-3. Types of Amine Exchange Processes Involving the Imine Bond: (a) Condensation and Hydrolysis; (b) Transimination; (c) Imine Metathesis.[2.8]

When dihydrazides are reacted with dicarbonyl compounds, polycondensation to give

polyacylhydrazone polymers may occur (Figure 2-2). Thus, materials may be produced which possess the attractive features of monomer exchange and polymer-polymer exchange through the mechanism shown in Figure 2-3.[2.8]

As described below, the formation of polyhydrazones by reaction between bisacylhydrazine (dihydrazide) and dialdehyde species where the two functional groups in each are bridged by an oligodimethylsiloxane unit has indeed proved to be successful. These polydimethylsiloxane polymers are dynamic, as seen in their capacity to exchange their dialdehyde or diacylhydrazine components, while they also retain the properties of a conventional polydimethylsiloxane polymer such as flexibility, hydrophobicity and heat stability. By virtue of the special properties of the acylhydrazone unit, polyacylhydrazones can be considered as *reversible, dynamic polymeric silicones,* for which reason we have termed them *DYNASILs*. Through monomer exchange, they allow the generation of novel, constitutionally modified alternating copolymers, exhibiting physical properties different from those of the original unexchanged polymer. They also offer the possibility of obtaining new crossover entities by mixing different dynamers.

2. 1. 3 Results and Discussion

In initial, screening experiments, the condensations between diamines as well as dihydrazides involving silicone backbones of different length and aromatic or aliphatic terminal groups with dialdehydes also having silicone backbones of different length and aromatic/aliphatic terminal groups, were investigated. The objective was to obtain a soft stretchy film suitable for materials design (Figure 2-4).

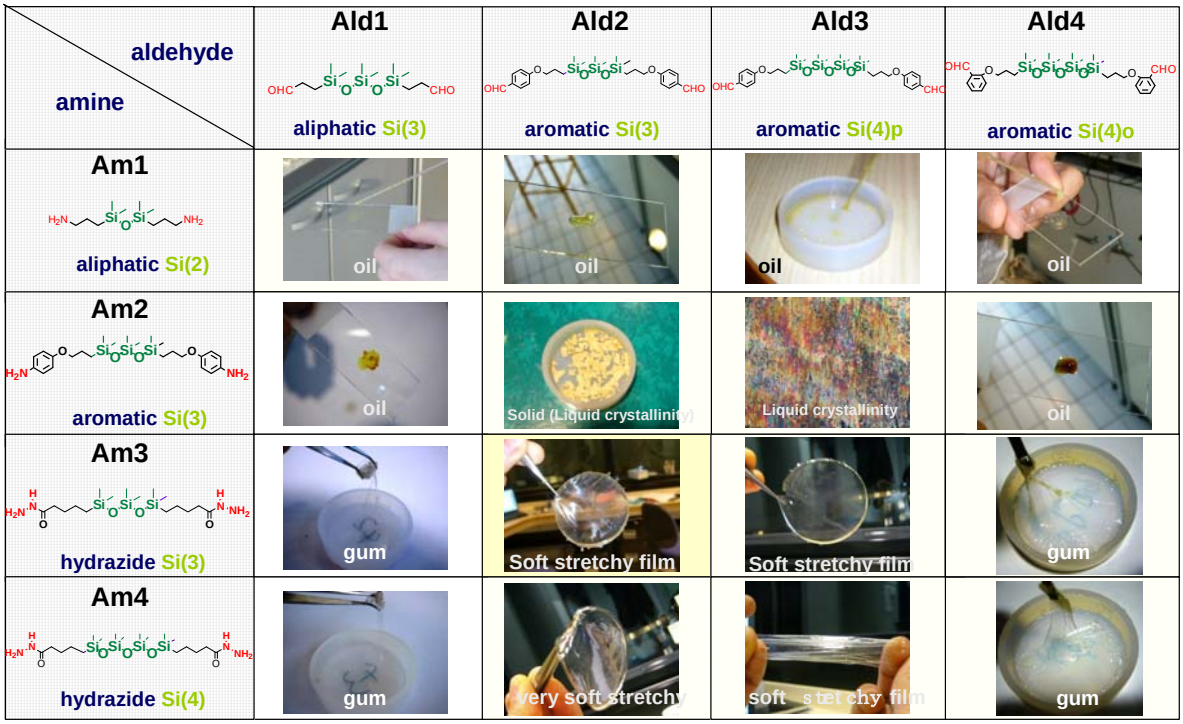


Figure 2-4. *DYNASILs* library from polycondensation between silicone diamine or dihydrazide and dialdehyde.

The synthesis of the dynamic silicones shown in Figure 2-4 was performed by direct condensation of the corresponding diamine or dihydrazide and the corresponding dialdehydes in 1:1 molar ratio in the presence of anhydrous Na_2SO_4 in chloroform. Figure 2-4 shows the line drawings of the library of *DYNASILs*. The condensation reactions between **Am1** or **Am2** and any dialdehydes formed opaque oils similar to those found with conventional silicones. The product of reaction between **Am2** and **Ald2** or **Ald3** was a brittle solid, displaying liquid crystalline properties when heated and examined under a polarising microscope, presumably a reflection of the presence of aromatic mesogenic moieties. In contrast, the condensation products formed between dihydrazide **Am3** and **Am4**, were obtained as sticky gums or soft

stretchy films suitable for use as dynamic materials (later demonstrated). Their stickiness and stretchability indicated an enhanced viscosity due to the presence of hydrogen-bonds formed by the amide unit of the acylhydrazone bond.

Unlike the relatively stable polymers obtained from the acylhydrazines **Am3** and **Am4**, the polymers derived from **Am1** and **Am2** and involving a simple imine bond could not be readily characterized by standard techniques such as GPC for molecular weight determination because of the low binding constant of imine bond,[2.9] which resulted in its dissociation during the GPC measurements. Proton NMR, however, was suitable for determining the average DP (degree of polymerisation) and the polymer molecular weight *M*n by integration of the terminal aldehyde proton signal at around 10 ppm with respect to the C=N bond proton at around 8 ppm (Eq. 2-1). Such calculations led to the determination of average DP, with values in the 50-70 range being obtained for the polymers derived from **Am1** and **Am2**.

$$[DPn] = 1/2\ [\ \sum \text{Imine } {}^{1}H\ /\ \sum \text{Aldehyde } {}^{1}H + 1\ ] \qquad (2\text{-}1)$$

Polycondensation in $CHCl_3$ between the monomeric dihydrazide **Am4** and dialdehyde **Ald2**, both containing a highly flexible siloxane-derived spacer unit, yielded the polysilicone acylhydrazone polymer **P1** as a very soft and quite stretchy film after solvent evaporation (Figure 2-5).

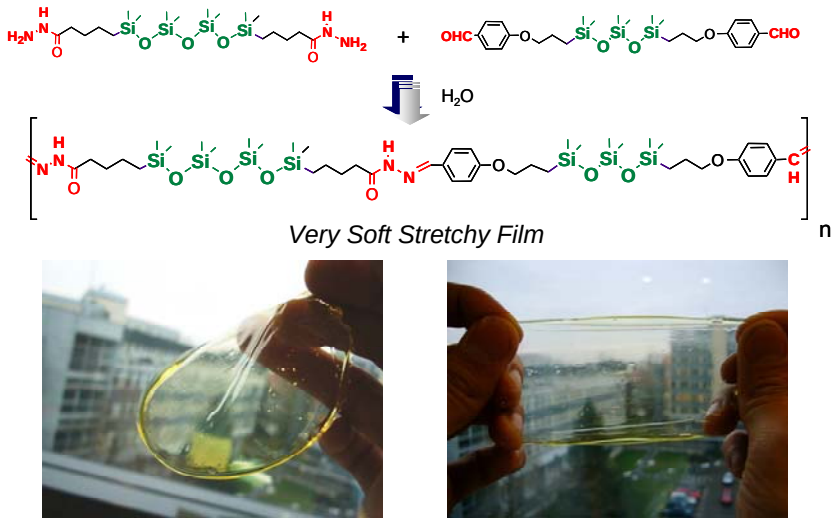


Figure 2-5. Chemical structure of *DYNASIL* formed between **Am4** and **Al2** and illustration of its physical properties as a soft, stretchy film.

Due to the stability of acylhydrazone bond rather than imine bond mentioned before, it was possible to perform gel permeation chromatography (GPC), giving a mean molecular weight Mn = 42,000, Mw = 66,000 and a distribution Mw/Mn = 1.58 (with polystyrene calibration). Differential scanning calorimetry (DSC) yielded a glass transition temperature Tg = 5.0 °C. Viscoelasticity measurement revealed that the storage elastic modulus E' of the film was 0.032 GPa at 25 °C, indicating that it possessed rubber-like elasticity at room temperature and the loss elastic modulus E'' gave Tg = 15.1 °C. These results are in accordance with the soft and stretchy behavior of the dynasil as shown in Figure 2-5.

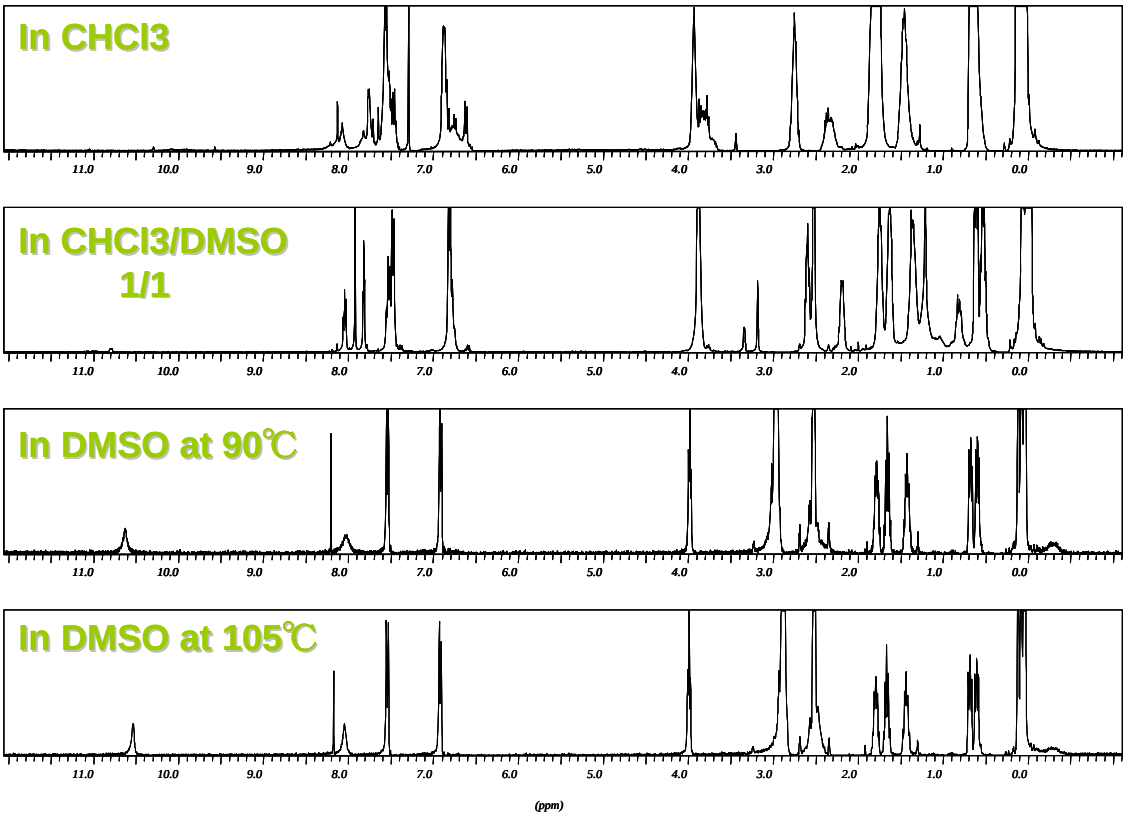


Figure 2-6. ^{1}H NMR spectra of the *DYNASILs* derived from **Am4** and **Al2** under various conditions, showing the different patterns of amide protons and of H-C=N protons of the acylhydrazone bond affected by the strength of hydrogen bonding of amide group.

Typically H-C=N proton of imine and acylhydrazone bonds exhibits the chemical shifts in the region of 7.5-9.0 ppm, moreover in the case of acylhydrazone bonds, the NH amide proton appears at 10-12 ppm. These fingerprint regions allow easy determination of the dialdehyde or the diamine and bis acylhydrazide from the polymer backbone concomitant with the

inclusion of a different one leading to a new polyimine or acylhydrazone dynamers. The ^{1}H NMR spectrum of the film (at a concentration of ca. 7 mg/ml) was measured under various conditions, both in different solvents (nonpolar $CDCl_3$ or polar DMSO) and at different temperatures, to elucidate the influence of hydrogen bonding of the amide unit.

The spectra (Figure 2-6) showed that the H-C=N protons of the acylhydrazone links between **Am4** and **Al2** gave peaks between 7.5-8.5 ppm, while the N-H protons of amide functions were identified at 10-11 ppm.

In non-polar $CDCl_3$, the interactions through hydrogen bonding being enhanced, the H–C=N protons of acylhydrazone connections showed broad, multiple peaks due to the aggregation through hydrogen-bonding including isomerisation of the hydrazone unit, and the peaks due to the protons of the functionalised benzene rings at 6.5-7.5 ppm were also complex. On increasing the polarity of the solvent by using a 1:1 mixture of DMSO and $CDCl_3$, those peaks became rather sharp, although the H-N=C protons of the acylhydrazone units still showed inequivalences (total integrated ratio of the separated peaks that corresponds to the peak of H-N=C proton is accordance with the calculation value) presumably due to weaker interactions between polymer chains. On increasing the temperature to 105°C in DMSO, those signals became clearly assigned by the break of interactions of polymer. Thus, the hydrogen bonding interactions of dynamic acylhydrazone polymers have a strong influence on the interactions between polymer chains, as macroscopically displayed in the stretchability of the bulk polymer.

2. 2 Modification of Mechanical Properties

- Soft to Hard Transformation of the Mechanical Properties of Dynamic Covalent Polymers through Component Incorporation. -

2. 2. 1 Prologue

The mechanical properties of acylhydrazone dynamic polymers may be changed from soft to hard by incorporation of rigid monomeric components into the original soft polymer backbone, taking advantage of acylhydrazone bond exchange.

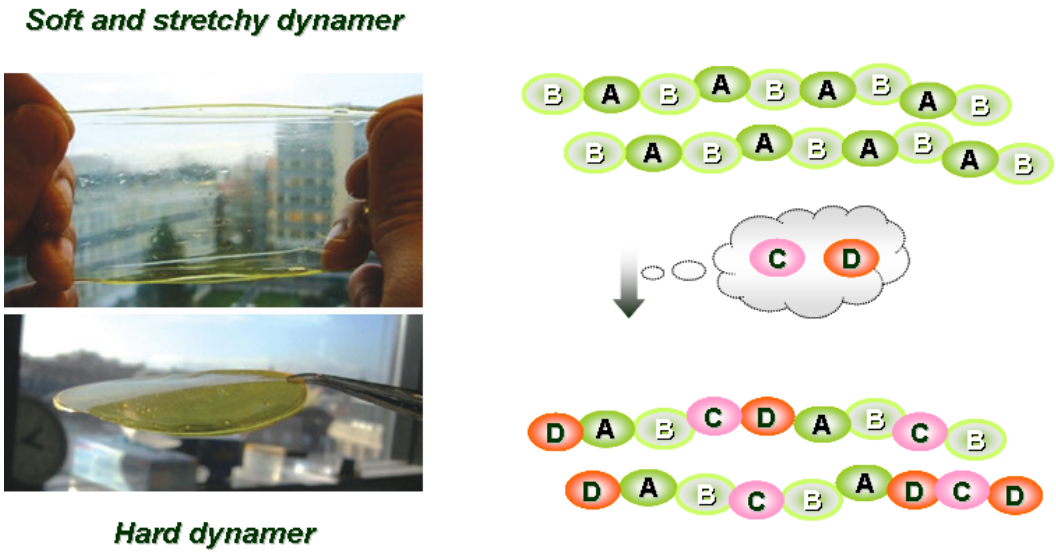


Figure 2-7. Schematic drawing of dynamic exchange process and the photographs illustrating the properties of hard and soft dynamers.

Dynamic feature offers to polymer science perspectives towards a functional plasticity involving modification and control of the intrinsic properties of polymeric entities from within.[2.10-2.18] Since the mechanical behavior of polymers plays an important role in materials science, the ability to mutate the mechanical properties of polymers would be of much interest by giving access to a new class of functional polymeric materials.

We now demonstrate here that dynamic covalent polymers, *DYNASILs*, based on an acylhydrazone bond involving siloxane backbone can undergo a progressive change in their mechanical properties through introduction of other monomeric components into their main

chain, showing the difference between chemical blend through the exchange reaction and physical blend like a conventional polymer blend.

2. 2. 2 Materials Design and Synthesis

The dialdehyde monomer **Ald2** was obtained from a hydrosilylation reaction between 4-(but-3-enyloxy)benzaldehyde and hexamethyltrisiloxane in the presence of Karstedt catalyst,[2.19,2.20] and **Ald5** and **Al6** were synthesized by treatment of 4-hydroxy-2-methoxybenzaldehyde with 1,10-dibromodecane or di(2-chloroethyl)ether in the presence of K_2CO_3. The bis-hydrazide monomers **Am4** were obtained in a synthesis analogous to that of **Ald2** by coupling methyl pent-4-enoate with octamethyltetrasiloxane using Karstedt catalyst,[2.19, 2.20] followed by the reaction of the dimethyl ester derivative with hydrazine monohydrate. In the same manner, **Am5** was obtained from 2-tert-butylbenzene-1,4 dimethyl ester by treatment with hydrazine monohydrate. Figure 2-8 shows the structures of bis-hydrazides **Am4** and **Am5**, and dialdehydes **Ald2, Ald5** and **Ald6** (which was not used here but has been previously reported).[2.21]

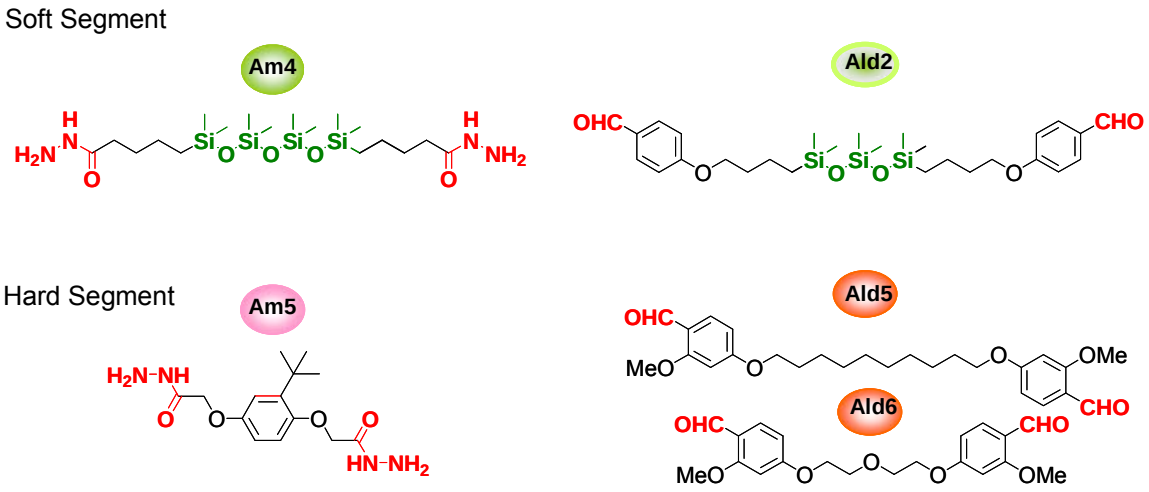


Figure 2-8 Chemical structures of the bis-hydrazides **Am4** and **Am5**, and of the dialdehydes **Ald2**, **Ald5** and **Ald6**.

To achieve polycondensation, the bis-hydrazide(s) and the dialdehyde(s) were dissolved in 1 : 1 stoichiometry in $CHCl_3$ and heated to 60 °C for 3 h. The solution was poured into a Petri dish, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared and then kept at 60 °C in vacuo for 24 h, affording the films which were used for the study of their mechanical properties. Polycondensation in $CHCl_3$ between the monomers **Am4** and **Ald2**, containing both a highly flexible siloxane-derived spacer unit, as *soft*

components, yielded the alternating polymer **P1** as a very soft and quite stretchy film (being, in the usual experiment, of about 0.060 mm thickness) after solvent evaporation (Figure 2-9). **P1** possessed rubber-like elasticity at room temperature (Figure 2-10) and the small decrease of E" between –80 °C and –40 °C must arise from the siloxane units of the polymer **P1**. The detailed phsycal properties are shown in Table 2-1.

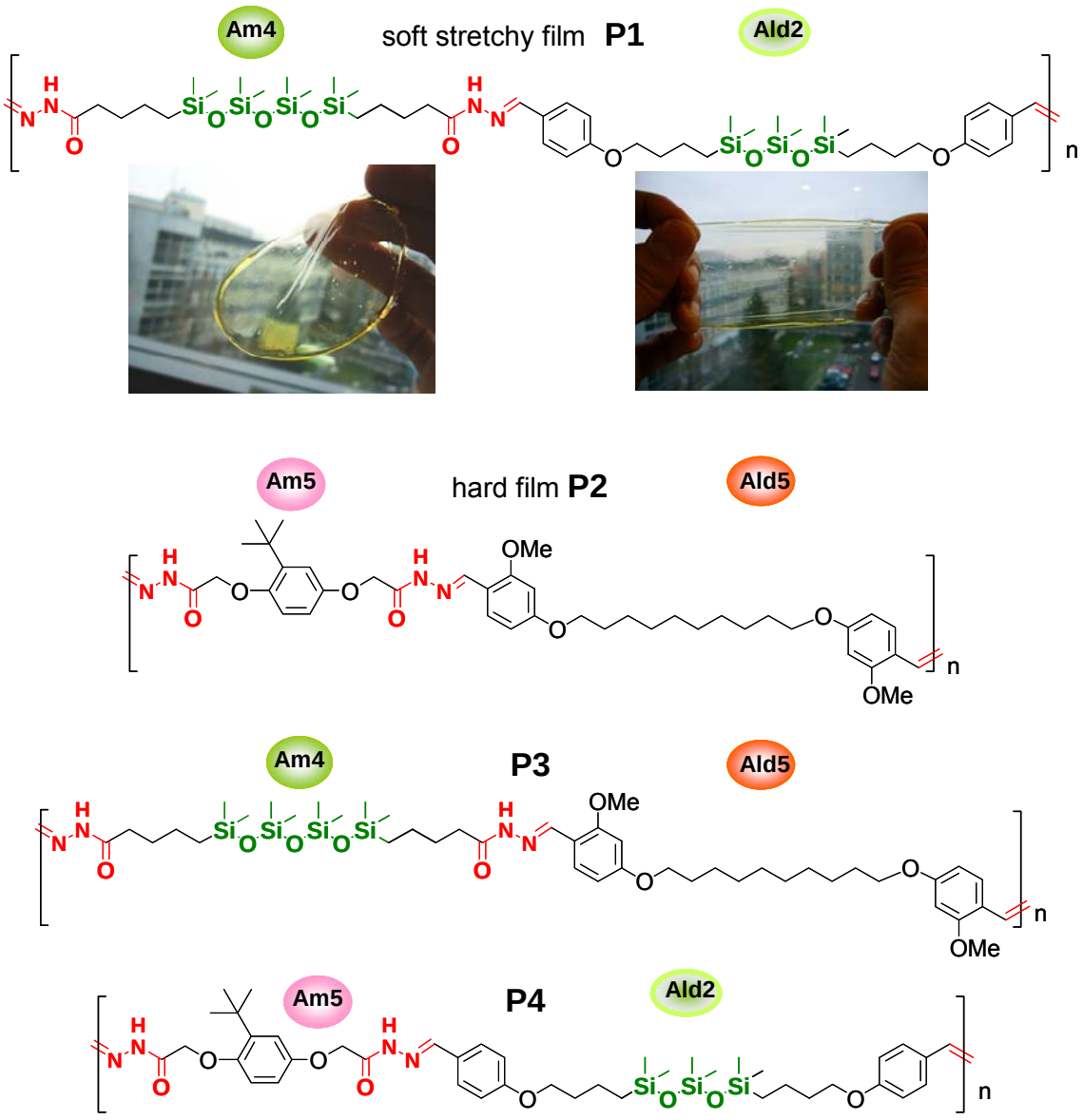


Figure 2-9 Structures of the polymers, **P1**-**P4**, used in the experimental set and photographs showing the properties of **P1** as soft and stretchy film.

In contrast, the polyacylhydrazone derived from the monomers **Am5** and **Ald5**, containing

rather rigid spacer groups than a siloxane chain, as *hard* components, afforded the alternating polymer **P2** as a hard film, with Mn = 90,000, Mw = 137,000, Mw/Mn = 1.52 determined by GPC, while DSC measurements showed Tg = 119.6 °C (an almost negligible transition was also observed at -7.1 °C). Viscoelasticity measurements showed that the storage elastic modulus E' of **P2** was 2.232 GPa at 25 °C, indicating that it possessed harder nature than **P1** film at room temperature (Figure 2-10). The profile of the loss elastic modulus E'' gave Tg = 106.6 °C. These results are in accordance with the hard (high elastic modulus) behavior of **P2** as shown in Figure 2-9, which indicates that **P2** could be used as a provider of hardening units via a chemical constitutional exchange reaction rather than by simple physical admixture as in conventional polymer processing.

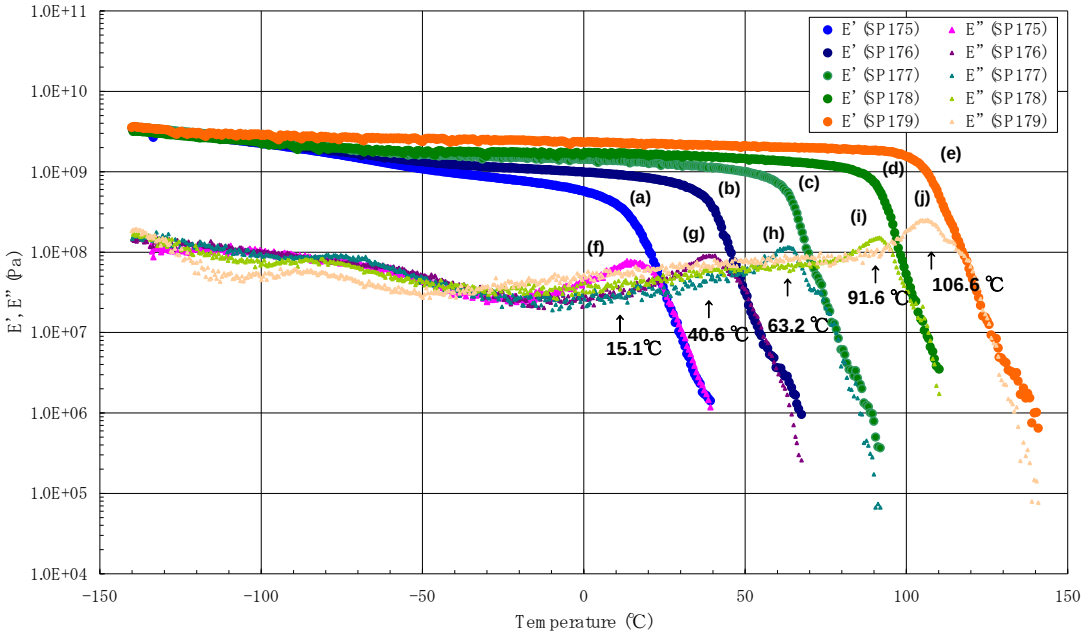


Figure 2-10. Temperature dependence of the storage elastic modulus E' of the films (a)**P1**, (b)**P6**, (c)**P7**, (d)**P8**, and (e)**P2**, and the loss elastic modulus E' of the films (f)**P1**, (g)**P6**, (h)**P7**, (i)**P8**, and (j)**P2**.

The dynamers **P3** and **P4**, and the random copolymer **P5** were also prepared as reference materials, respectively from the monomers **Am4** and **Ald5**, **Am5** and **Ald4**, and all four monomers in equal molar ratio, in the same manner. ^{1}H NMR analyses in 1:1 DMSO–d_6/CD_2Cl_2 solution (*ca.* 7 mg/ml) allowed identification of separate signals of the H-C=N protons for the four different acylhydrazone links between 7.8–8.7 ppm (Figure 2-11).

Although the H-C=N signals are inequivalences due to the aggregation through hydrogen-bonding including isomerisation of the hydrazone unit, showing separately two or three signals (indicated by arrows), the separated signals could be assigned since the total integrated ratio of the separated peaks corresponding to the H-C=N protons agrees with the calculated value in comparison with other protons of polymer backbone.

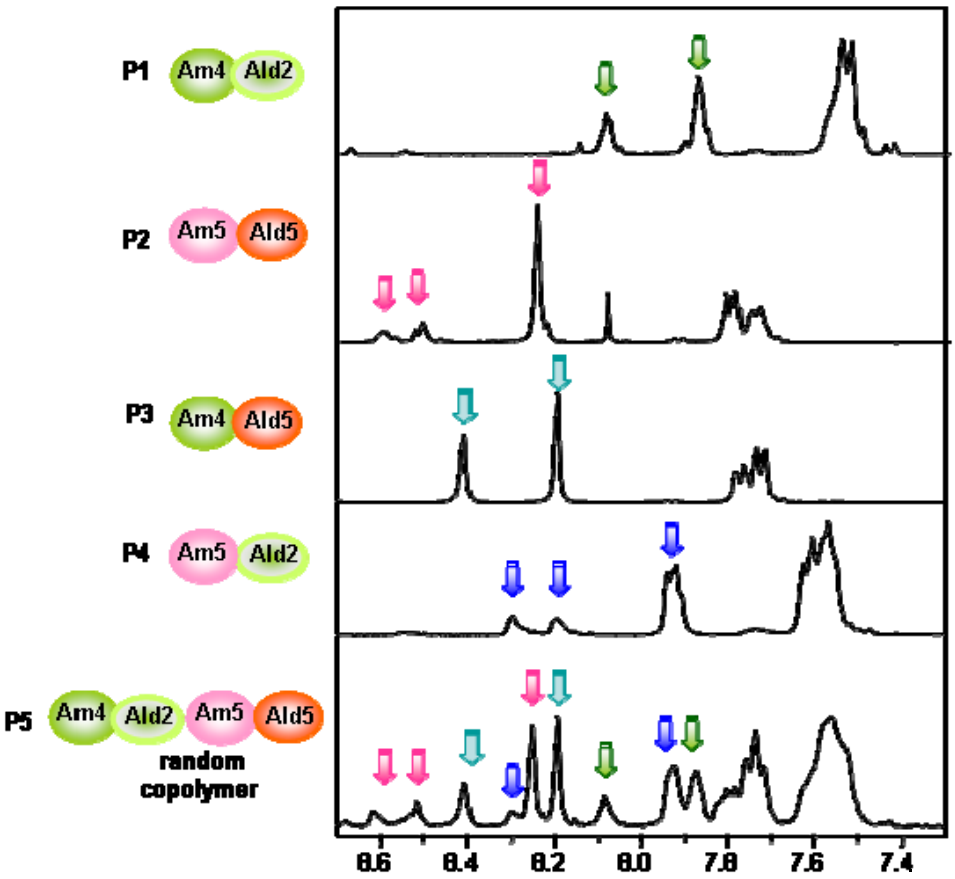


Figure 2-11. ^{1}H NMR spectra of the polymers (a) **P1**, (b) **P2**, (c) **P3** and (d) **P4**, and (e) the random copolymers **P5** in a 1:1 mixture of DMSO-d_6/CD_2Cl_2 (ca. 7 mg/ml) showing the H-C=N proton signals of the acylhydrazone functions.

2. 2. 3 Results and Discussion

Changes of mechanical properties of acylhydrazone polymers induced by bond interchange and component incorporation were demonstrated by introducing hard components, that is **Am5** and **Ald5,** into the soft polymer structure **P1**. Equimolar amounts of polymer **P1** on the basis of its repeating unit, the bis-hydrazide **Am5** and the dialdehyde **Ald5** were dissolved in $CHCl_3$, followed by addition of pentadecafluorooctanoic acid as a catalyst which to accelerate the exchange reaction and to reach to the equilibrium.

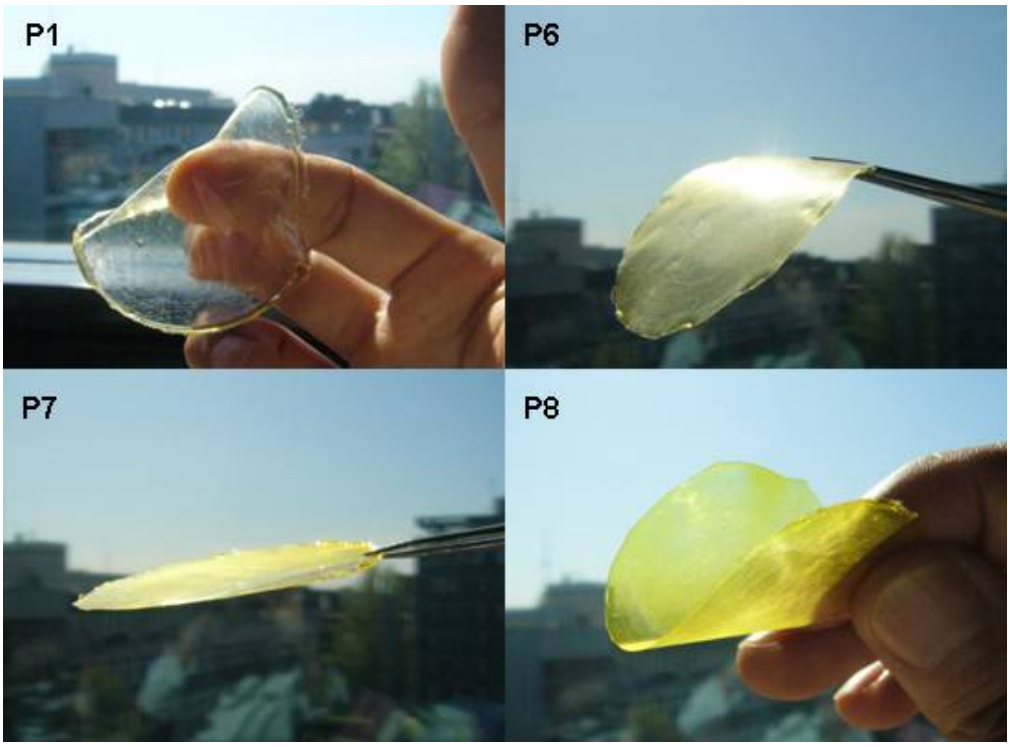


Figure 2-12. Evolution in appearance and mechanical properties of the polymer films **P1, P6**, **P7** and **P8**.

The acid was used in 0.025 molar ratio with respect to the total acylhydrazone bonds. The solution was heated to 60 °C for 24 h and then poured into a Petri dish to allow solvent evaporation at 60 °C at normal pressure. The residue was then heated *in vacuo* for 24 h at the same temperature, giving a transparent film **P7**. The film **P7** was distinctly harder than the parent film **P1,** quite enough to stand by itself (Figure 2-12).

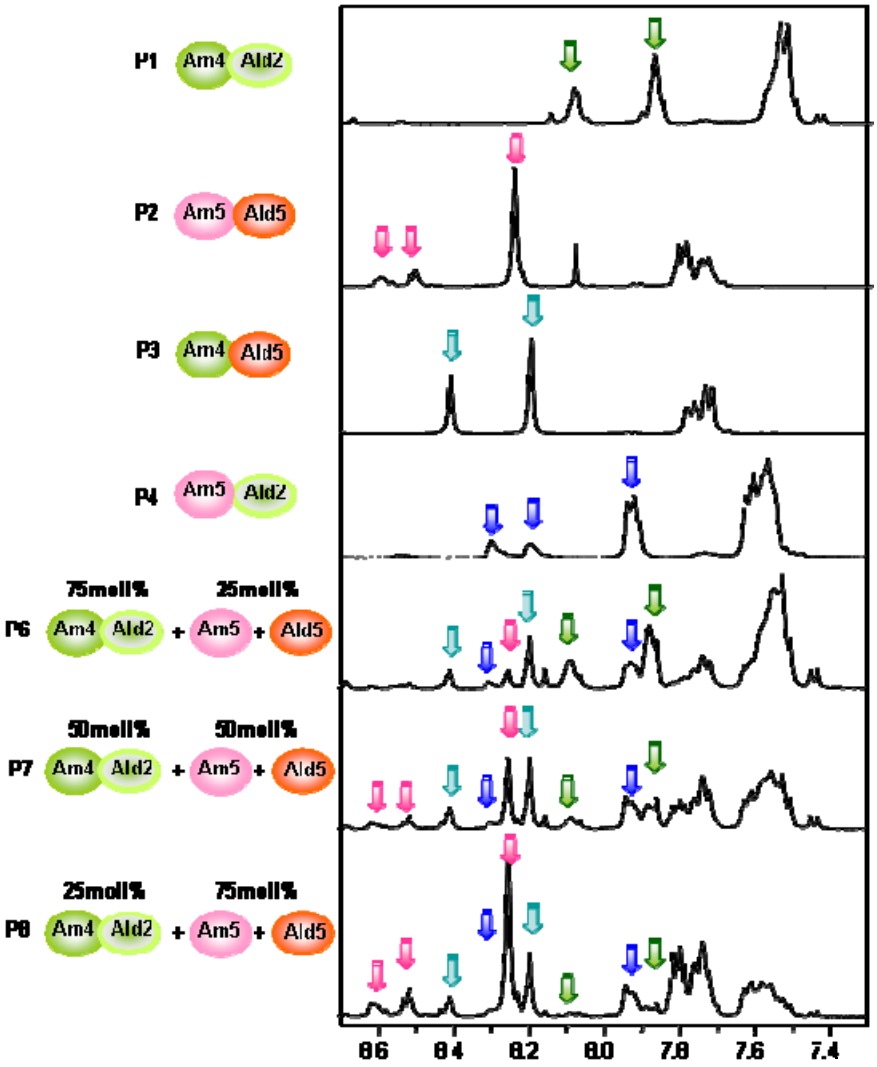


Figure 2-13. ^{1}H NMR spectra of **P1**, **P2**, **P3** and **P4** and of the exchanged polymers **P6**, **P7** and **P8** in a 1:1 mixture of DMSO-d_6/CD_2Cl_2 (ca. 8mg/ml) showing the H-C=N proton signals of the acylhydrazone functions.

The ^{1}H NMR spectrum of the film **P7** (in 1:1 DMSO–d_6/CD_2Cl_2) showed that there were four kinds of signals of nearly equal area, which were assigned to the H-C=N protons of the acylhydrazone connections between **Am4** and **Ald2**, **Am5** and **Ald5**, **Am4** and **Ald5**, and **Am5** and **Ald2** (Figure 2-13). This observation indicated that monomers **Am5** and **Ald5** were introduced into the main chain of the polymer **P1**, generating the random copolymer **P7** obtained as a film**,** and which was expected to be similar to the random copolymer **P5** obtained from the mixture of the four components **Am4**, **Ald2**, **Am5** and **Ald5**. GPC gave Mn = 69,000 and Mw/Mn = 1.49 for **P7**, of the same order as the parent polymer **P1**.

Introduction of **Am5** and **Ald5** into the polymer **P1** led to a striking evolution of its mechanical properties. The glass transition temperature Tg of **P7** increased to 59.3 °C, beyond room temperature, compared to that of 5.0 °C of **P1** based on the DSC measurement. This increment nicely reflected the difference in film hardness at room temperature between **P1** and **P7** illustrated in Figure 2-12. The E' profile of **P7** indicated that it had a typical glass state up to around 60 °C and its hardness increased to 1.270 GPa at 25 °C from 0.032 GPa at 25 °C of parent polymer **P1**.

Table 2-1. Evolution in mechanical properties of the polymer films **P1**, **P2** and **P6-P8** as a function of incorporation of monomers **Am5** and **Ald5** into the polymer **P1** through exchange reaction.[a] Mechanical properties of physical blend films **P9-P11** between **P1** and **P2** in absence of acid catalyst. [h]

	Ratio of **Am5** and **Ald5** into **P1**	Mn [c]	Mw [c]	Mw/Mn [c]	Tg (DSC)[d]	Tg (E")[e]	E'[f]
P1	0 mol%	42,000	66,000	1.58	5.0 °C	15.1 °C	0.032 GPa
P2	100 mol%	90,000	137,000	1.52	(-7.1 °C) 119.6 °C	106.6 °C	2.232 Gpa
P6	25 mol%[b]	52,000	81,000	1.56	35.6 °C	40.6 °C	0.773 GPa
P7	50 mol%[b]	70,000	104,000	1.49	59.3 °C	63.2 °C	1.270 GPa
P8	75 mol%[b]	70,000	108,000	1.53	84.0 °C	91.6 °C	1.579 GPa
P9	25 mol%[h]	67,000	100,000	1.49	23.9 °C	27.1°C	0.353 GPa
P10	50 mol%[h]	79,000	121,000	1.53	17.4 °C 122.9 °C	28.6 °C 110.6 °C	0.581 GPa
P11	75 mol%[h]	92,000	144,000	1.57	17.3 °C 125.2 °C	26.9 °C 116.3 °C	1.176 GPa

[a]In presence of 2.5 mol% acid per acylhydrazone unit for **P6**–**P8**; no acid added for **P9-P11**. [b]Total molar ratio of **Am5** and **Ald5** in the resulting polymers on the basis of monomer units. [c]Molecular weight Mn and distribution Mw/Mn determined by GPC with polystyrene calibration. [d]Glass transition temperature determined by DSC. [e]Glass transition temperature determined by the profile of the loss elastic modulus E''. [f]Storage elastic modulus E' at 25 °C. [g] Not determined. [h]Total mol ratio of **P2** in the resulting polymers blend.

The degree of evolution in mechanical properties was correlated with the ratio of **Am5** and **Ald5** incorporated in the resulting polymers (Table 2-1). **Am5** and **Ald5** of 75 mol % on the basis of **P1** units led to a film **P8** harder than **P7**, whereas **Am5** and **Ald5** of 25 mol% gave a film **P6** softer than **P7** (Figure 2-12). The ^{1}H NMR spectra of **P8** and **P6** showed that both were also random copolymers, consisting of **Am4**, **Am5**, **Ald2** and **Ald5** in about the expected ratios. In the case of **P8**, for instance, the ratio of the peak areas assigned to the connections between **Am4** and **Ald2**, **Am4** and **Ald5**, **Am5** and **Ald2**, and **Am5** and **Ald5** was about 1 : 3 : 3 : 9, whereas **P6** was a random copolymer made of **Am4**, **Am5**, **Al2** and

Ald5 in about 1 : 3 : 1: 3 molar ratio as calculated from the quantities of added mononers (Figure 2-13). Tg and viscoelasticity were in accordance with the proportion of **Am5** and **Ald5** in the polymers (Figure 2-10).

The mechanical properties of these resulting polymers were thus markedly different from those of the parent polymer **P1** (Figure 2-12), implying that the mechanical properties of the acylhydrazone polymers are adjustable via the nature and/or the proportion of the different components incorporated.

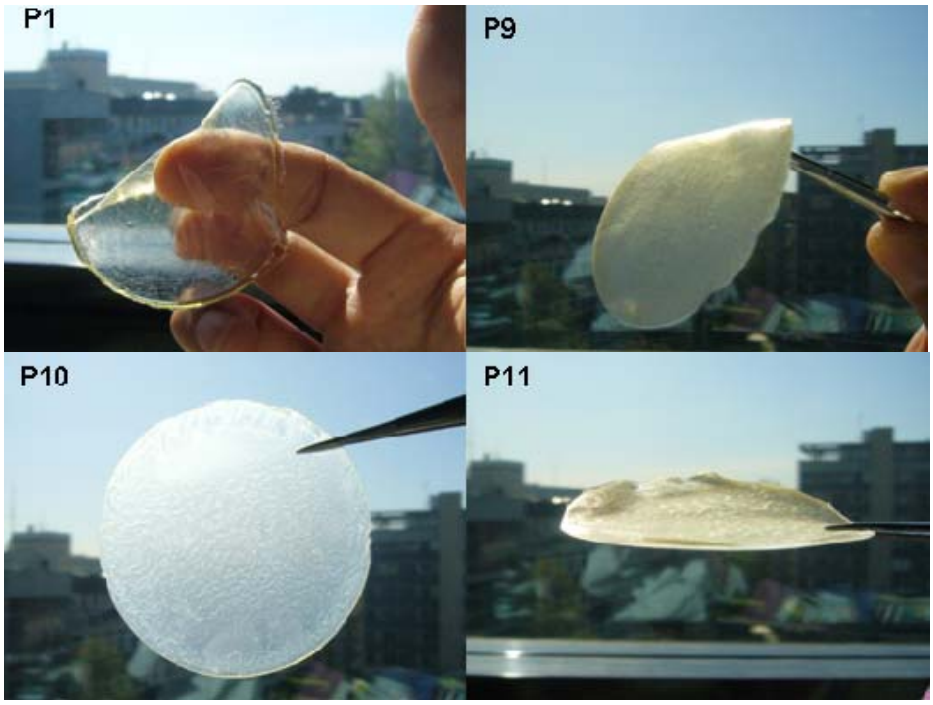


Figure 2-14. The appearance and mechanical properties of physical blend films **P1** as parent polymer, **P9**, **P10** and **P11**.

In contrast, lack of incorporation did not bring evolution in mechanical properties, just leading to the behavior expected for a blend of the parent polymers **P1** and **P2**. Thus, cloudy films **P9, P10** and **P11** caused by phase segregation were obtained from the mixture of **P1** and **P2** of 25 mol%, 50mol% and 75 mol%, respectively (Figure 2-14). These were obtained in $CHCl_3$ solution at 60 °C for 24h in the *absence* of acid catalyst, followed by solvent evaporation in the same condition as the sample preparation of **P6-P8**. The ^{1}H NMR spectra (Figure 2-15) of the polymer **P9**, **P10** and **P11** showed that they were just a blend of **P1** and

P2 with only a very small amount of exchange (<5% for **P10** and **P11**, 8% for **P9**). The observations on films **P9**, **P10** and **P11** implied that **P2** was microdisperesed in a **P1** matrix in the polymer blend, giving rise to the white cloudy appearance caused by phase segregation between **P1** and **P2**, which are mutually repellent. Two peaks for transition temperatures of (**P9**), **P10** and **P11** based on loss elastic modulus E'' (Figure 2-16), were observed at around 30 °C and at around 110 °C, corresponding to the glass transition temperature of **P1** at 15.1 °C and that of **P2** at 106.6 °C, respectively.

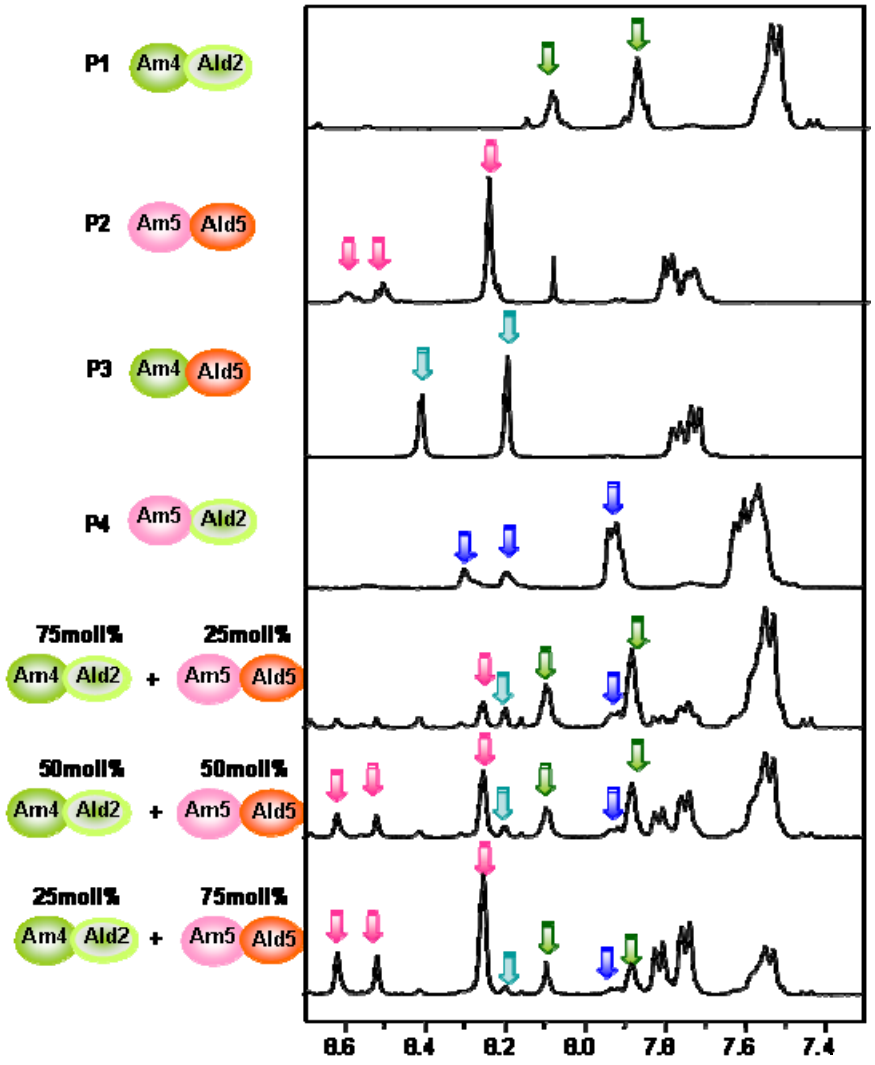


Figure 2-15. ^{1}H NMR spectra of **P1**, **P2**, **P3** and **P4** and of the exchanged polymers **P9**, **P10** and **P11** in a 1:1 mixture of DMSO-d_6/CD_2Cl_2 (ca. 8mg/ml) showing the H-C=N proton signals of the acylhydrazone functions.

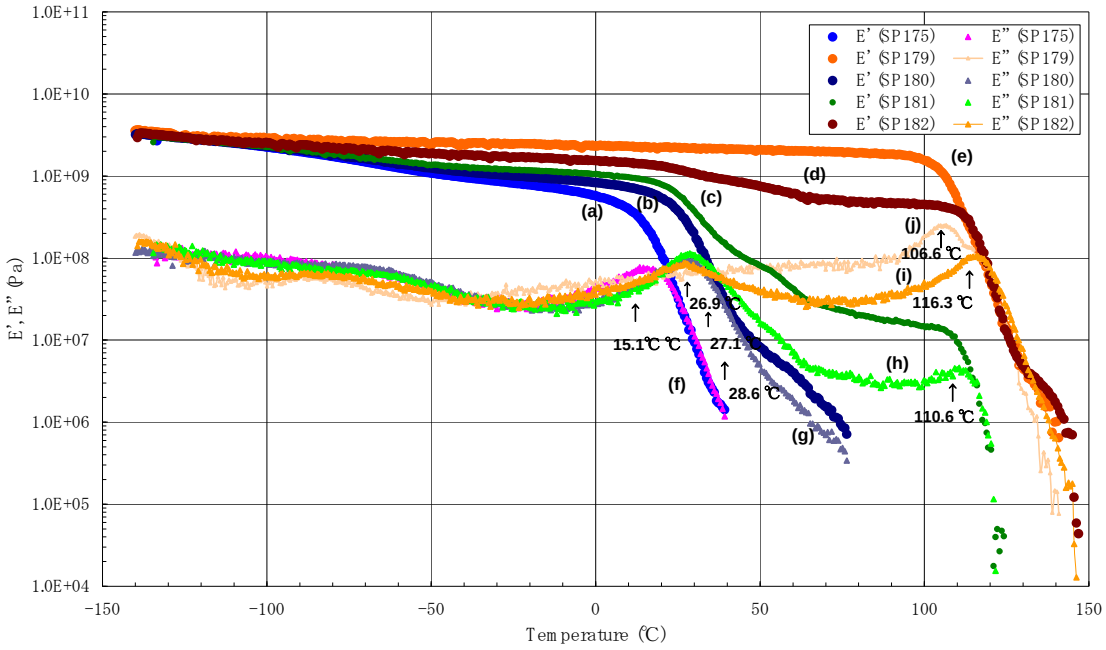


Figure 2-16. Temperature dependence of the storage elastic modulus E' of the films (a)**P1**, (b)**P9**, (c)**P10**, (d)**P11**, and (e)**P2**, and the loss elastic modulus E'' of the films (f)**P1**, (g)**P9**, (h)**P10**, (i)**P11**, and (j)**P2**.

All three physically blended polymers **P9**, **P10** and **P11** gave two peaks in their viscoelastic modulus measurements, and the peaks are equivalent to the glass transition temperature of each phase segregated parent polymer **P1** and **P2**. Although both chemically exchanged polymers **P6**, **P7** and **P8** and physically blended polymers **P9**, **P10** and **P11** were composed originally of the same components, their sequence difference and the degree of exchange produced completely different mechanical characteristics.

In relation to their potential use as thermostable materials able to resist distortion at relatively high temperatures, an important industrial use, chemically exchanged polymer **P7** (equimolar amount of soft and hard component, 50 mol% : 50 mol%) and physically blended polymer **P10** (equimolar amount of soft and hard component, 50 mol% : 50 mol%) display significant differences (Figure 2-17). The profile of the storage elastic modulus E' showed that **P7** possessed a glass state up to 63.2 °C, corresponding to a normal heat deflection temperature, and E' itself decreased relatively moderately above Tg as the temperature increased. In contrast, for **P10** the storage elastic modulus E' decreased from 28.6 °C and the

P10 film lost heat resistance at that temperature.

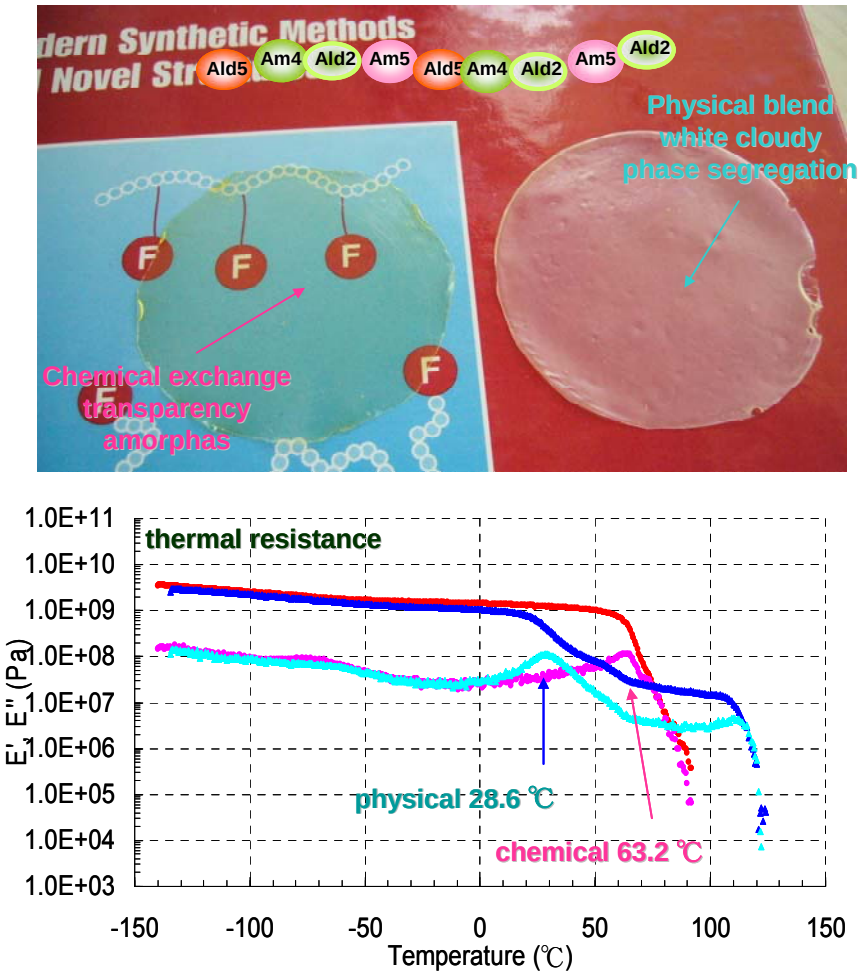


Figure 2-17. (top) The appearance of polymer films **P7** and **P10**. (bottom) The temperature dependence of the storage elastic modulus E' and the loss elastic modulus E'' of **P7** and **P10**.

Thus the observation showed the heat deflection temperature of chemical exchanged polymer **P7** at 63.2 °C is around 35 °C higher than that of physical blended polymer **P10**, although the components of both polymers are exactly the same. The difference of constituents in materials derived from the same components brings entirely different phenomena.

2. 2. 4 Conclusions

In conclusion, the present results show that the mechanical properties of polyacylhydrazone dynamers can be varied through incorporation of other components into the main chain of the original polymer, making use of the reversible nature of acylhydrazone bond, displaying the large diference between chemical exchanged blend and physical conventional blend. This feature provides a very useful methodology for modification of the mechanical properties of polymers, giving access to smart and adaptive dynamic materials, such as self-strengthening polymeric materials controlled by and responding to external stimuli. Such a behavior, presented by dynamers, is thus a result of the application of the principles of constitutional dynamic chemistry to polymer science.

2. 3 Applications of *DYNASILs* based on Surface Chemistry

- Hydrophobic-Hydrophilic Transition on a Surface through the Exchange Reaction.-

DYNASILs show the ability to undergo component exchange as well as the properties of conventional polydimethylsiloxane polymers such as flexibility and hydrophobicity. A project has been initiated to see if the characteristic hydrophobicity of a siloxane could be converted into hydrophilicity by component exchange within a hydrophobic *DYNASILs* coated onto a surface. Since it is as yet unfinished and reproducibility in a quantitative sense remains a problem, the project and its results so far are described below in outline only.

The control of wettability on a surface has aroused great interest because of its wide variety of practical applications,[2.22-2.25] especially those concerning coatings, adhesive materials, cosmetics and biomaterials. A water droplet on surface will either remain as droplet if the surface is hydrophobic or spread if the surface is hydrophilic, and the control of such characteristics for specific applications would allow the design of advanced "intelligent" surface materials. The static wettability of a simple surface is determined by its chemical composition, although recently some examples of surfaces susceptible to dynamic control of their wettability have been reported.[2.26-2.29] In principle, any switchable feature of chemical structure can be used for the production of smart surfaces, changes between hydrophilicity and hydrophobicity being the consequences of the action of stimuli such as light, heat, changes in pH or introduction of guest molecules.

Here we have shown that a hydrophobic to hydrophilic transition on a surface may be achieved through the interfacial contact of two different polyacylhydrazone polymer films (*DYNASILs* and hydrophilic dynamers). These changes are driven by the bond exchange and the component migration through the interface, resulting in the change of macroscopic surface properties.

Figure 2-18 shows the designed hydrophobic dynamic polymers **P12, P13** involving both siloxane and poly-tetrafluoroethylene backbones and the hydrophilic dynamic polymers **P14-P17** based on malic acid, tartaric acid and polyethyleneglycol spacers.

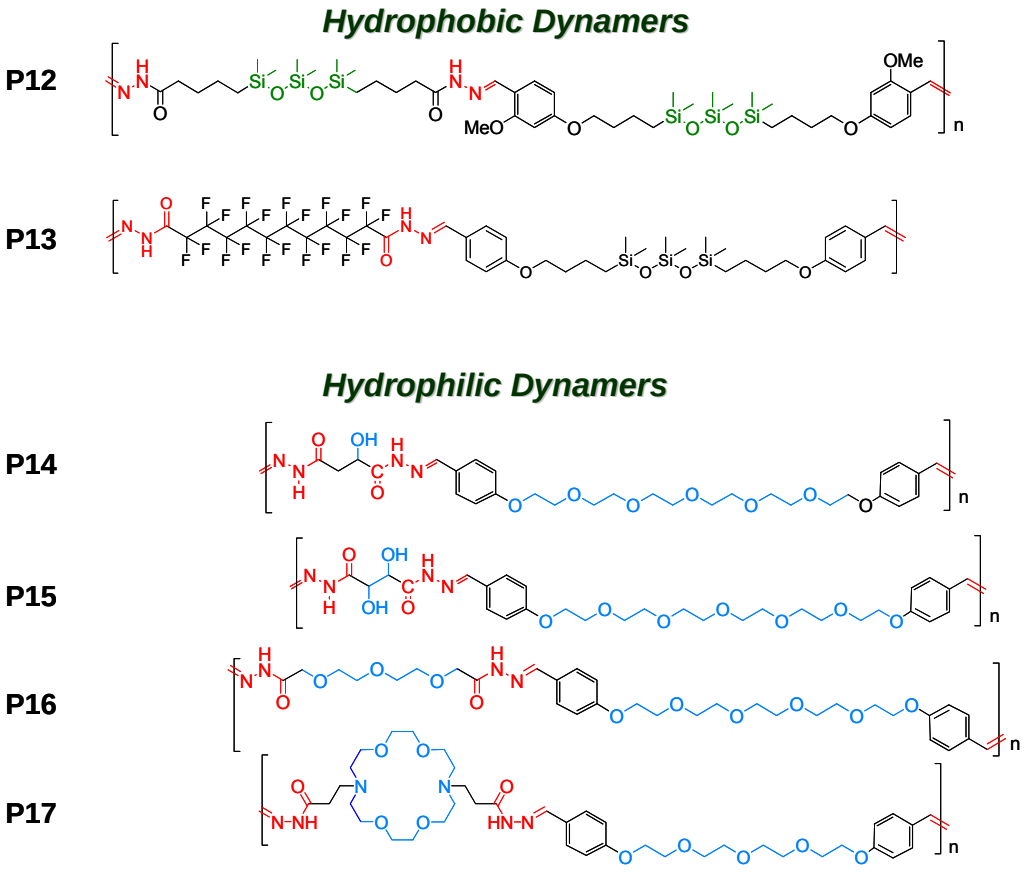


Figure 2-18. Structures of the hydrophobic dynamic polymers **P12**, **P13** and of hydrophilic dynamic polymers **P14-P17**.

These were synthesized in the same way (polycondensation) as the polymers of the previous project. Key features of the design of these structures are the presence of hydrophobic and hydrophilic units providing the means to modify the macroscopic wettability of a water droplet on the surface. Polycondensation yielded the polysilicone acylhydrazone polymer **P12** as a hydrophobic film, gel permeation chromatography (GPC) giving a mean molecular weight Mn = 7,4000, Mw = 150,000 and a distribution Mw/Mn = 2.02. The contact angle for a water droplet was 90 º. In comparison, the hydrophilic dynamer **P16** selected for present study showed Mn = 100,000, Mw = 232,000 and Mw/Mn = 2.31, and gave a water contact angle of 38 º.

The acid-catalysed bond exchange and crossover component recombination reactions between two films of equimolar amounts of **P12** and **P16** were monitored by ^{1}H-NMR spectroscopy as in the preceding study (soft to hard). The ^{1}H NMR spectra (Figure 2-19) of

the blend film between **P12** and **P16** after the exchange reaction with acid catalyst induced by heat treatment at 60 ºC for 12 hours showed that there were four sorts of signals between 7.5–8.6 ppm of nearly equal area which were assigned to the H-C=N protons (in 1:1 DMSO–d_6/CD_2Cl_2) of the acylhydrazone links (Figure 2-19). The new peaks generated were assigned to the H-C=N protons of the acylhydrazone connections of two evolved polymers shown as reference polymers in Figure 2-19, which were produced by the bond exchange of monomeric components of **P12** and **P16** in the same manner as shown in Figure 2-11 and 2-13. This observation indicated that parent polymers **P12** and **P16** underwent a bond exchange reaction in the blend, generating new connections characteristic of two evolved polymers, the spectra showing that the proportion based on the integration of H-C=N signals of parent polymer : resulting polymer was about 1 : 1 after 12 h heat treatment.

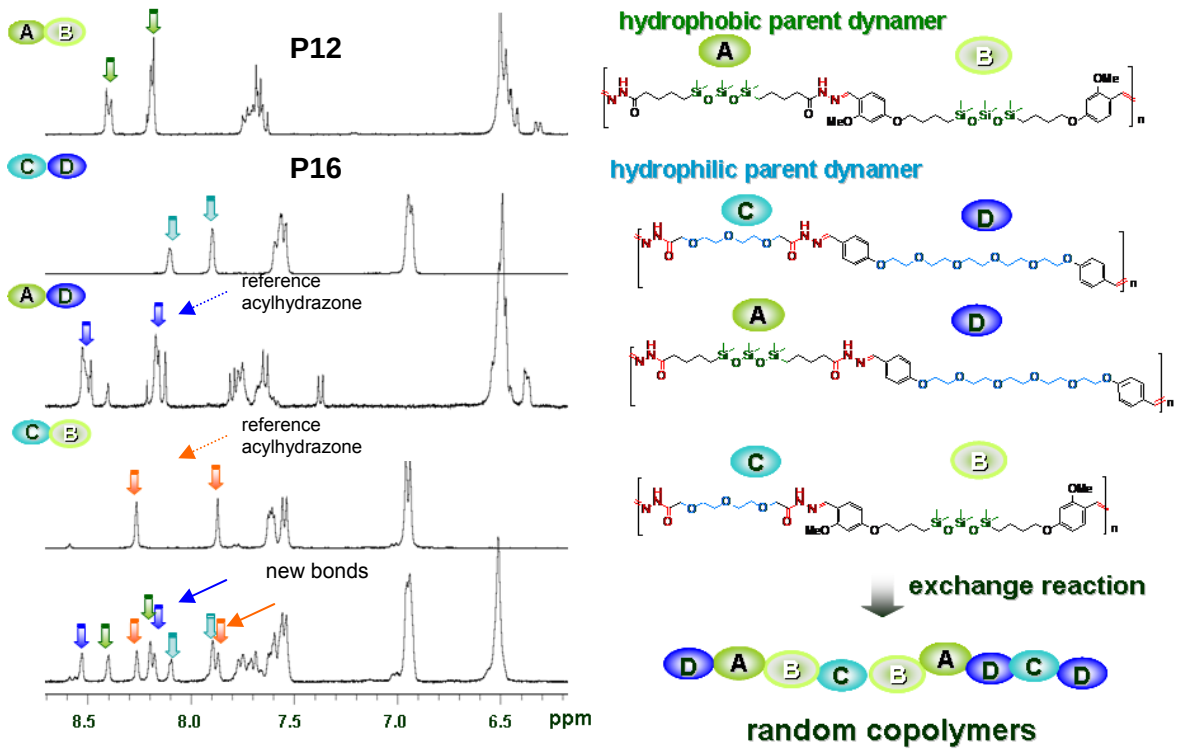


Figure 2-19. ^{1}H NMR spectra of **P12**, **P16**, the two reference dynamers (the bond exchanges between monomers of **P12** and **P16** generates new connections characteristic of two reference polymers) and the exchanged polymers in a 1:1 mixture of DMSO-d_6/CD_2Cl_2 showing the H-C=N proton signals of the acylhydrazone functions.

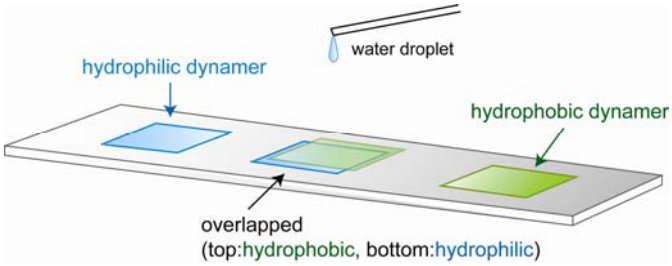


Figure 2-20. Schematic representation of experimental set. The superimposition of two hydrazone polymer layers located in middle part on a rectangle glass plate. One side of the original double film is hydrophobic and the other hydrophilic as a control set.

A simple demonstration of the surface change of wettability was performed with two thin layers of dynamers **P12** with an average thickness of aroud less than 0.1 μm as a hydrophobic upper layer deposited by spin-coating on a 20 - 60 micron thick hydrophilic lower layer of **P16** previously spin-coated onto a glass plate (Figure 2-20). This multilayer deposit was subsequently heated to 60 °C for 6 h, and then to 80 °C for 6 h in an oven under a nitrogen stream. The contact angle of a water droplet was measured at 25 °C as a function of heating time to observe the hydrophobicity/philicity of the film surfaces, as shown in Figure 2-21.

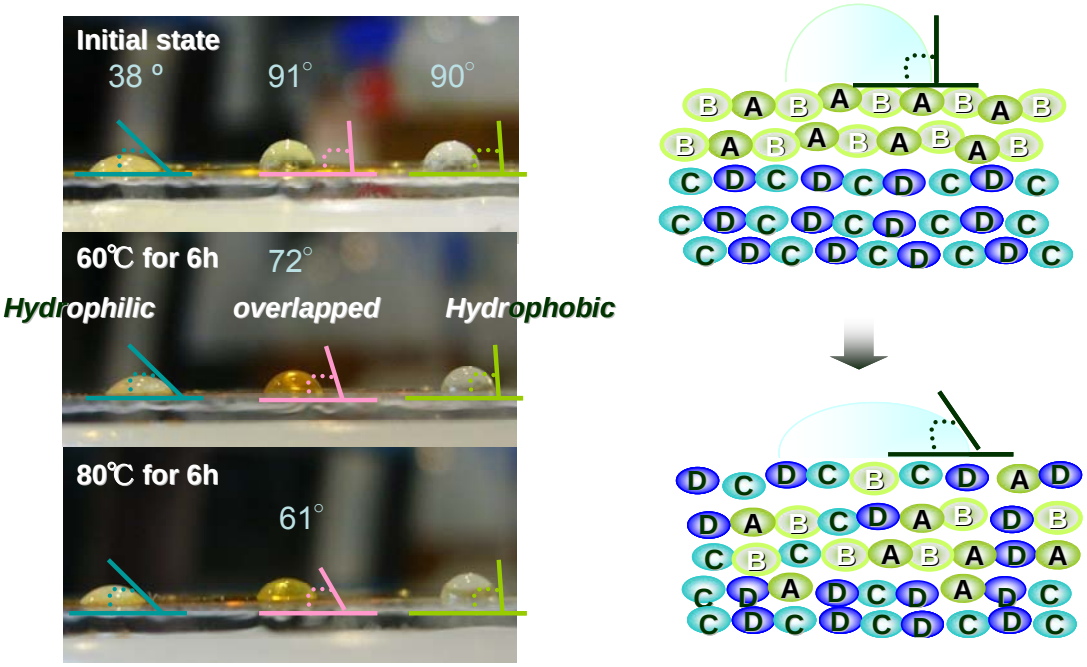


Figure 2-21. Water droplet profiles of the surface generated by **P16** (right), **P13** deposited on **P16** (middle), and **P13** (left). Schematic cartoon of the bond exchange and component migration of the dynamic surface in the overlap region.

Only the domain where the two films layer were superimposed changed to a rather hydrophilic surface, the water contact angle dropping from 91° initially to 72° after 6 h, and further heating at 80 °C for 6 hrs made the overlap region even more hydrophilic, with a contact angle of 61°, thus macroscopically generating a hydrophilic surface from a hydrophobic one through the exchange reaction and component migration between two thin layers (Figure 2-21). The control experiment with the individual films showed that no contact angle transition occurred in the absence of any overlap.

In conclusion, the present results show that the modification of surface wettability can be induced by acylhydrazone bond exchange and component recombination in dynamers. They also demonstrate that such processes can occur at the interface of two different polymer films, resulting in a change in macroscopic properties. The macroscopic hydro-phobic to -philic transition of a water droplet on a surface was created by the application of dynamer science.

CHAPTER 3: Optodynamers.

- Expression of color and fluorescence at the interface between two films of different dynamic polymers -

3. 1 Prologue

3. 2 Materials Design and Synthesis

3. 3 Results and Discussion

3. 4 Conclusions

It has been found in the present work that color and fluorescence changes may be expressed at the interface between two different polyhydrazone polymer films. These changes are induced by hydrazone bond exchange and component recombination through the interface, resulting in an extension of conjugation.

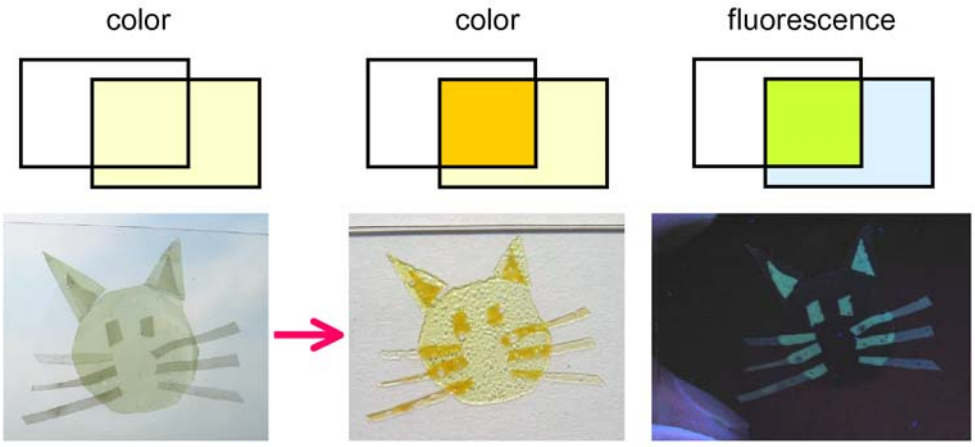


Figure 3-1. Visual color change and fluorescence emergence by constitutionally exchange reaction of superimposed dynamers

3. 1 Prologue

The induction of variable optical properties in dynamers [3.1-3.7] would be of special interest, as it could both demonstrate the occurrence of constitutional dynamics[3.8- 3.10] in a system and implement dynamics to confer novel physical features (Figure 3-1).

We herewith describe some results of our studies on the modulation of optical properties in a system of two films of hydrazone-based dynamic polymers, demonstrating the following three aspects.

i) the expression of novel optical features,

ii) the occurrence of bond reorganization and component diffusion through the interface of the two films,

iii) the generation of optical patterns.

The process relies on the modification of conjugation on bond recombination, leading to changes in absorption and emission properties due to the generation of moieties presenting a more extended conjugation pathway. Polymeric or supramolecularly assembled materials possessing conjugated moieties have attracted considerable attention for implementation in systems such as sensors or molecular electronic devices, because they have an inherent potential to change their conjugation and optical properties by recombination or reconfiguration in response to external stimuli.[3.11, 3.12]

3. 2 Materials Design and Synthesis

In order to obtain information on the color and fluorescence of bishydrazone containing moieties presenting different extents of conjugation, UV-visible and emission spectroscopic measurement were first performed on the model compounds **1**–**3** (Figure 3-2), obtained by condensation of the corresponding hydrazine and aldehyde molecules.

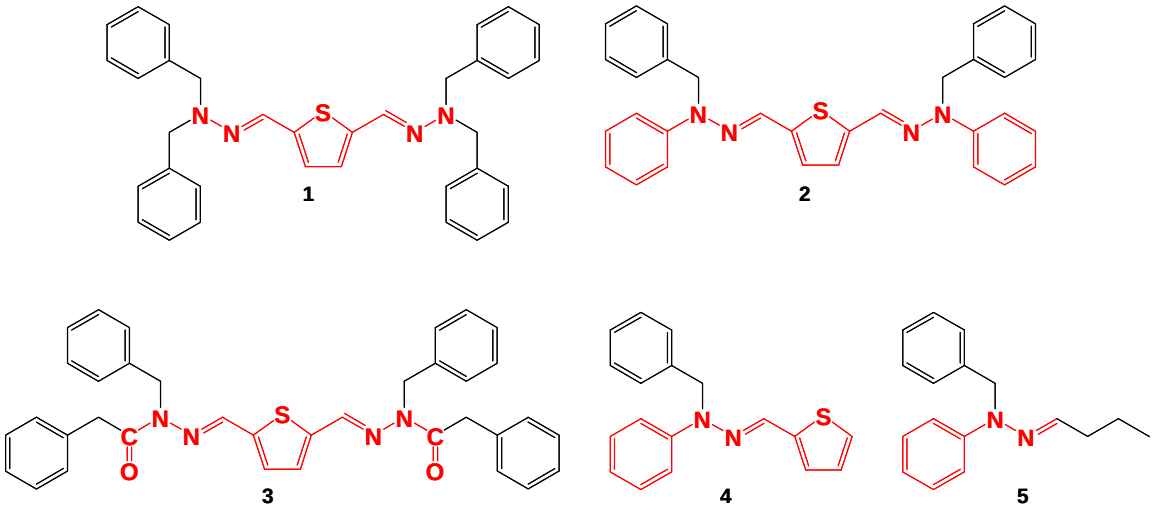


Figure 3-2 Structures of hydrazone compounds. The conjugation domain is represented in red color.

The absorption spectrum of the bis-hydrazone compound **1** showed λ_{max} = 384 nm and extended to around 430 nm, conferring a light yellow color in $CHCl_3$ solution (Figure 3-3). Compound **1** is expected to possess a certain degree of conjugation through the two hydrazone bonds and a thiophene moiety (Figure 3-2). Introduction of a phenyl group instead of benzyl on the hydrazone moieties was effective to expand the degree of conjugation in **2** with respect to **1**. Indeed the absorption band of the bis-hydrazone compound **2** shifted to λ_{max} = 421 nm and extended to around 480 nm, yielding a vivid yellow color in $CHCl_3$ solution. Compound **2** exhibited strong fluorescence around 450–550 nm under excitation at 421 nm. This distinct yellow-green fluorescence was also observed visually for the neat powder under 365 nm excitation. When a carbonyl group was introduced directly into the conjugation system, the λ_{max} of the bis-hydrazone compound **3** was shifted to 368 nm and the absorption in the visible region was extremely weak, so that the compound appeared colorless in $CHCl_3$ solution. Furthermore, compound **4** containing a single phenyl hydrazone unit on one thiophene moiety

displayed much less effective conjugation and compound **5** derived from an aliphatic aldehyde gave a much more blue-shifted absorption (Figure 3-3).

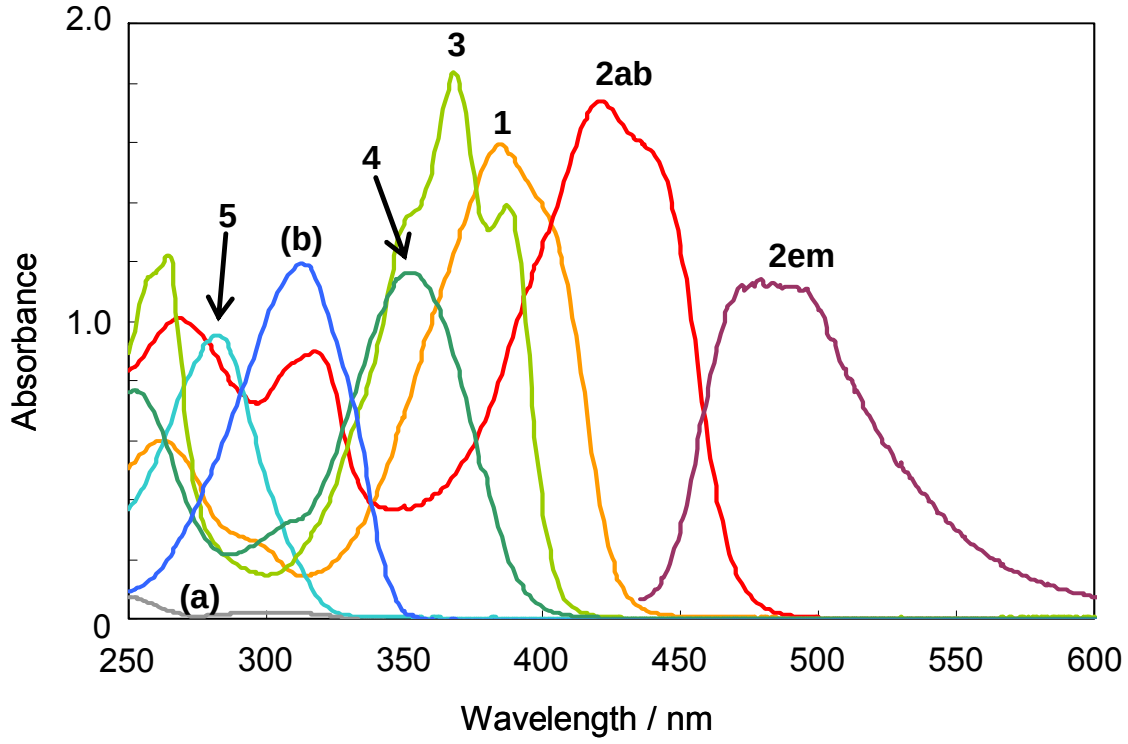


Figure 3-3 UV-visible absorption spectra of the hydrazone compounds **1**–**5**, (a)N,N-dibenzyl hydrazine and (b)thiophene-2,5-dicarboxaldehyde in $CHCl_3$ (0.05mM on the basis of hydrazone, hydrazine or aldehyde) and fluorescence emission spectrum of bis-hydrazone compound **2** in $CHCl_3$ (0.02mM) under excitation at 412 nm.

In views of these results, polyhydrazone polymers **P1** and polyacylhydrazone **P2** (Figure 3-4) were designed and synthesized as initial materials to demonstrate color and fluorescence changes induced by bond exchanges and component migration through the interface of these two polymer films. Figure 3-4 shows the monomer units used, the bis-hydrazine **M1** and **M2**, the commercially available glutaraldehyde and 2,5-thiophenedicarbaldehyde, the four different hydrazone bonds, that may form during the polycondensation reaction, and the four possible dynamers **P1**-**P4** generated. In this study, **P3** and **P4** were obtained as referenced polymers to demonstrate the bond exchange reaction between the parent polymers **P1** and **P2**. Key features of the design of these structures are the presence of bis-hydrazone functions suitable for the exchange reaction and of units enabling the extent of conjugation within the

chromophore to be controlled. A tert-butyl group was introduced in the polymer **P2** to increase solubility and facilitate the polycondensation reaction. Only the dynamer **P3** involves both conjugated bis-phenyl hydrazine **M1** and conjugated 2,5-thiophenedicarbaldehyde components capable of engendering sufficiently extended conjugation to allow the emergence of color and fluorecence in the visible region.

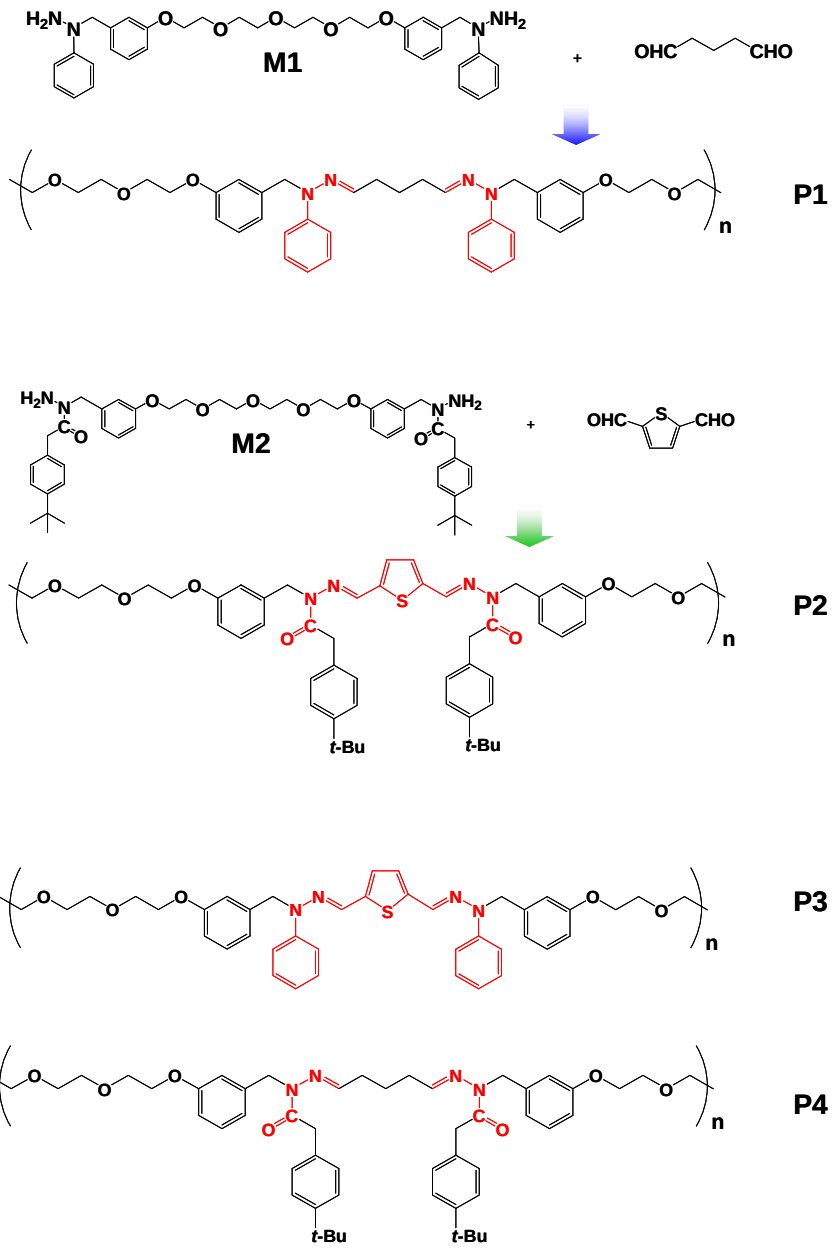


Figure 3-4. Structures of monomers **M1** and **M2** and of polyhydrazone dynamers **P1**–**P4** (whose conjugation pathway is shoun in red color).

Equimolar amounts of the corresponding bis-hydrazine and the dialdehyde monomers were dissolved in the mixture of $CHCl_3$ and THF (8 : 2 in volume ratio; for the polymer **P1**) or $CHCl_3$ (for the polymer **P2**, **P3** and **P4**), followed by addition of pentadecafluorooctanoic acid as a catalyst in 0.1 molar ratio. The solution was heated to 60 °C for 12 h, then poured into a Petri dish, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared. The residue was then kept at 60 °C in vacuo for 12 h, affording respectively an almost colorless, slightly turbid film for the polymer **P1** and a light yellow film for the polymer **P2**. The polymers **P3** and **P4** were prepared as a reference materials in the same manner, giving a dark orange film for **P3** and a transparent film for **P4**. These films were soft, slightly stretchy and easily cut with scissors. Gel permeation chromatography afforded a molecular weight Mn = 38400, Mw = 111,400 and a distribution Mw/Mn = 2.9 for the polymer **P1**, Mn = 13900, Mw = 43,100 and Mw/Mn = 3.1 for the polymer **P2**, Mn = 34,500, Mw = 93,200 and Mw/Mn = 2.7 for the polymer **P3**, and Mn = 32000, Mw = 80,000 and Mw/Mn = 2.5 for the polymer **P4** (with polystyrene calibration).

3. 3 Results and Discussion

Changes in UV-visible absorption and fluorescence induced by bond exchange and crossover component recombination were demonstrated firstly by means of a polymer blend film, prepared by just mixing solution of the two homopolymers **P1** and **P2** in presence of added acid. The visual color of the blend polymer film obtained, initially light yellow, changed progressively to vivid yellow on heating at 120 °C.

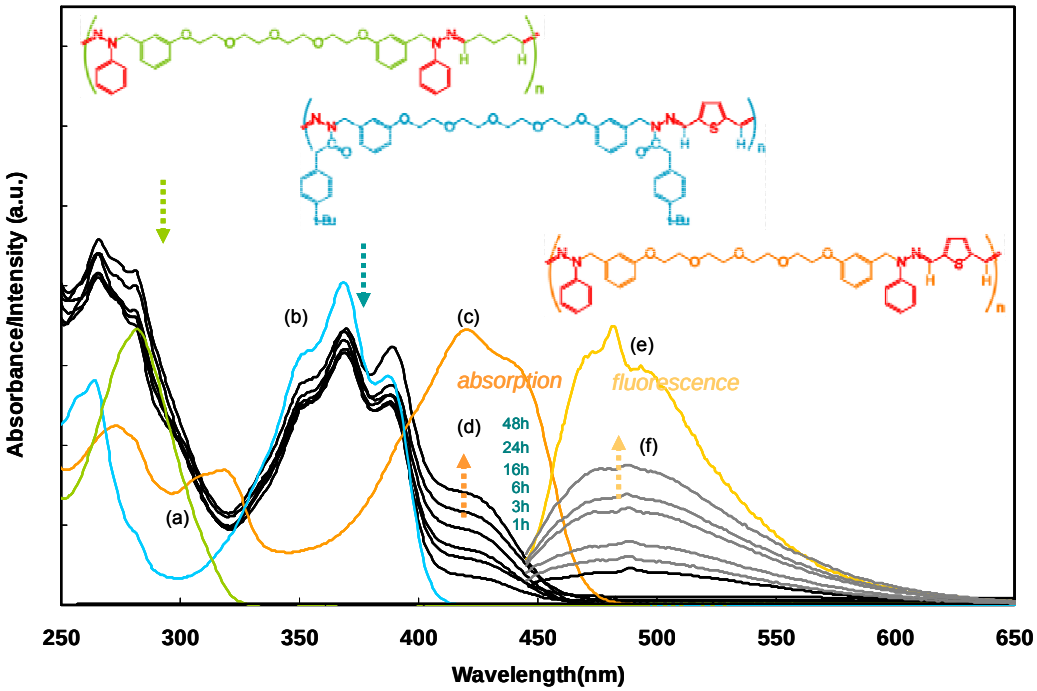


Figure 3-5. UV-visible absorption spectra in $CHCl_3$ of the hydrazone polymers (a)**P1**, (b)**P2** and (c)**P3**, and (d) heating time dependence of polymer blend **P1** and **P2**; fluorescence emission spectra in $CHCl_3$ of (e)the hydrazone polymer **P3** and (f)heating time dependence of the fluorescence of polymer blend **P1** and **P2** under excitation at 425 nm.

The UV-visible absorption around 400–450 nm in $CHCl_3$ evolved toward that of a new polymer **P3** as a function of heating time (Figure 3-5, Figure 3-6). In a similar way, a fluorescence band appeared around 450–600 nm and its intensity increased toward that of polymer **P3**.

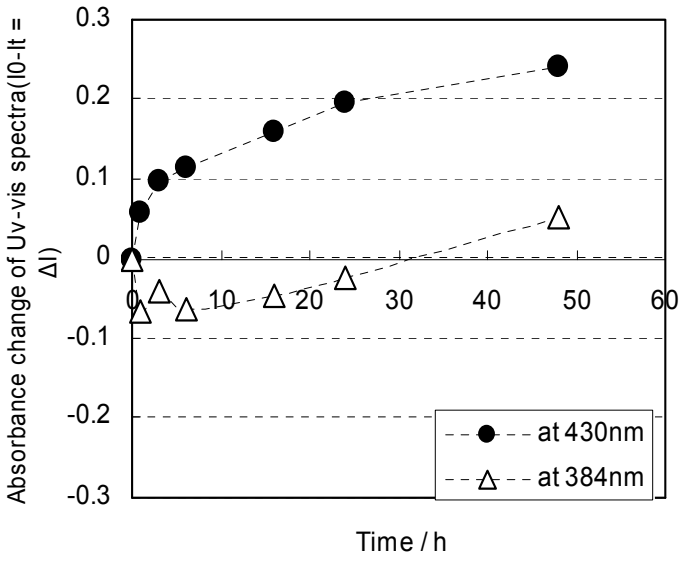


Figure 3-6. Exchange reaction as a function of heating time between **P1** and **P2** plotted for (a)the absorbance change($\Delta I = I_0 - I_t$) at the indicated wavelengths of UV-vis spectra in Figure 3-5.

These results indicate that the change of color and the emergence of fluorescence resulted from bond exchange and crossover component recombination between the dynamic polymers **P1** and **P2**, generating the functional fragment characteristic of polymer **P3**. ^{1}H NMR analyses in DMSO–d_6 solution (10 mM) allowed identification of the connections between bishydrazine and dialdehyde by the signals of the H-C=N protons of the hydrazone functions of the four different connections, between 7.2–8.2 ppm (Figure 3-7). The ^{1}H NMR spectra of the blend of **P1** and **P2** as a function of heating time showed that there were new peaks generated, assigned to the H-C=N protons of the hydrazone connections between **M1** and 2,5-thiophenedicarbaldehyde of evolved polymer **P3**, and **M2** and glutaraldehyde of evolved **P4** (Figure 3-7).

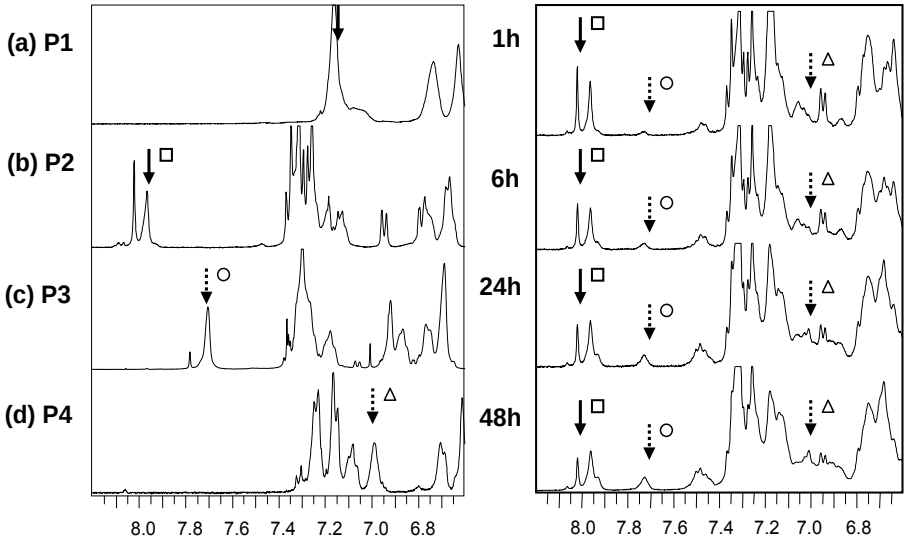


Figure 3-7. (left) ^{1}H NMR spectra of the dynamic polymers (a) **P1**, (b) **P2**, (c) **P3** and (d) **P4**. (right) ^{1}H NMR spectra of the polymer blend between **P1** and **P2** as a function of heating time in a DMSO-d_6(10mM) showing the H-C=N proton signals.

This observation indicated that parent polymer **P1** and **P2** underwent a bond exchange reaction in the blend, generating new connections characteristic of **P3** and **P4**, the spectra showing that the proportion based on the integration of H-C=N signals of parent polymer **P2** : resulting polymer **P3** was about 3 : 1 after 48 h heat treatment. The fourth combination that results from reaction of all the monomer units in **P1** and **P2** is that of the bis-hydrazone moieties found in polymer **P4**. This link would not be expected to show notable absorption or emission features in view of the presence of the isolating trimethylene chain between the two hydrazone groups. In addition to the four "symmetrical" domains present in **P1-P4**, the blend may also contain "unsymmetrical" domains having different components on each side.

Color and fluorescence changes may be expected to emerge even at the interface of two different dynamer films. Indeed, superposing films of the dynamers **P1** and **P2** and applying bond exchange conditions should lead to the appearance of the absorption and emission features characteristic of dynamer **P3** in the overlapping region of the two films (Figure 3-8, top). A simple demonstration was performed (Figure 3-8, bottom) with two polymer films **P1** and **P2**, of 54 μm and 64 μm thickness, respectively. Two films cut by scissors were superimposed on a glass plate and heated around at 160–170 °C with a heat gun for 5 min.

Only the domain where the two films were superimposed changed to vivid yellow and produced a yellow-green fluorescence observable visually under 365 nm excitation, thus generating a distinctive pattern. On the other hand, the colors of the rest of the films remained the same as the original ones and no fluorescence was observed.

A detailed study on the emergence of fluorescence at the intereface was performed with two thin layers (with an average thickness of about 0.15–0.2 μm, determined by a stylus method) of dynamers **P1** and **P2** coated on quartz plate. Thin polymer layers were prepared using a 2 wt% THF solution of the polymer **P1** or **P2** by spin-coating onto 5 cm square quartz plates, which were rinsed with acetone prior to use. The spin-speed and the period were 500 rpm and 60 sec, respectively. These layers were subsequently dried *in vacuo* at 60 °C for 12 hr. The spin-coated quartz plates were superimposed face-to face (Figure 3-9) and heated to 120 °C in a oven under a stream of argon.

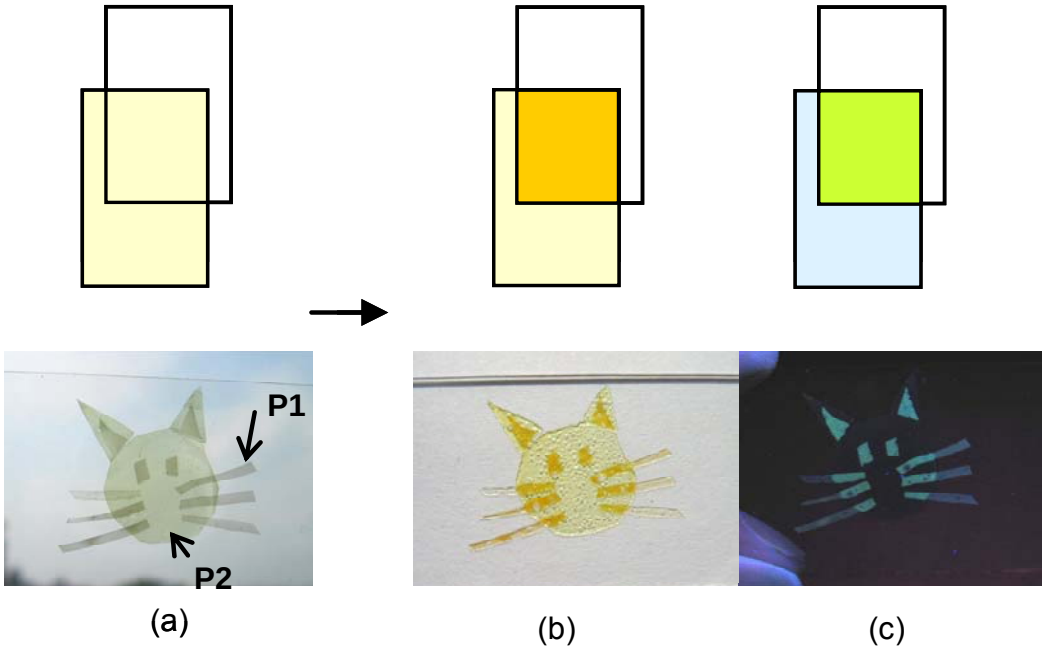


Figure 3-8. Visual color change and fluorescence emergence by heating of superimposed polymer films **P1** and **P2**. (top) Schematic representation; (bottom) an illustrative example; (a) color before heating under sunlight, Noted that the cats eyes and ears initially contained **P1** on **P2**. (b) color after heating, (c) fluorescence after heating, under excitation at 365 nm.

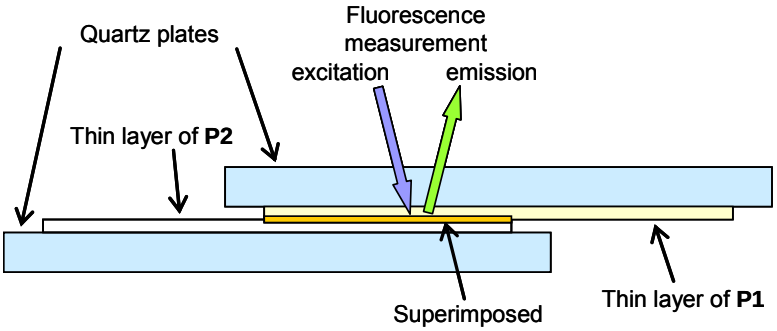


Figure 3-9. Cross-sectional schematic representation of the superimposition of two hydrazone polymer layers.

The fluorescence intensity of the overlapping part increased with heating time in a manner similar to the case of the polymer blend (Figure 3-10). The broad emission peak was centered about 480 nm.

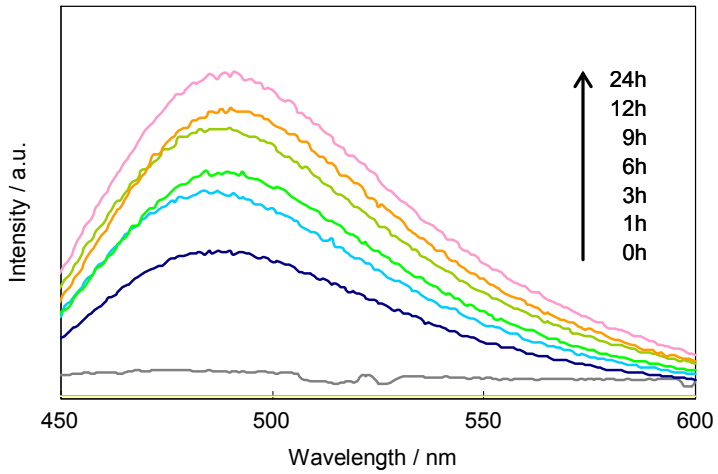


Figure 3-10. Fluorescence emission spectra of the overlapping domain of neat hydrazone polymer films **P1** and **P2** under excitation at 425nm as a function of heating time.

Figure 3-11 shows the rate plots of the exchange reaction of blended and interfaced condition between parent polymer **P1** and **P2** based on the fluorescence intensity of **P3**. Although the exchange reaction rate in homogeneously blended conditions between **P1** and **P2** was observed to be two to three times as fast as that of contacted films, the result indicates that hydrazone bond exchange and component migration occurred by heating through the interface between the polymer layers **P1** and **P2**, leading to generation of fluorescence as a

result of the conjugation extension between the hydrazone moieties.

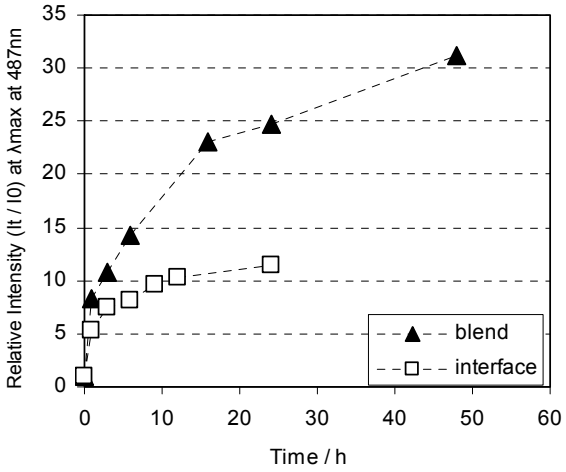


Figure 3-11. the relative intensity at λ max 487 nm(I_t / I_t) of the fluorescence spectra in Figure 3-5 and Figure 3-9.

3. 4 Conclusions

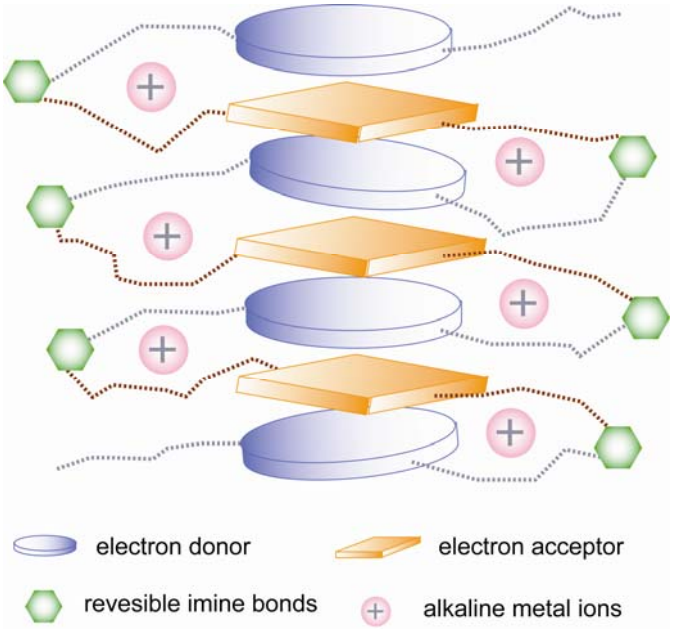
In conclusion, the present results show that color and fluorescence of polyhydrazone dynamers can be modified by hydrazone bond exchange and component recombination. They also demonstrate that such processes can occur even at the interface of two different polymer films, resulting in chemical interconnection of the films. This feature has promising potential for implementation in optical materials for systems such as molecular sensing or photoactive devices. It gives access to smart and adaptive dynamic materials[3.1, 3.8-3.10, 3.13] controlled by and responding to external stimuli, and may extend over the modulation of other properties such as electronic (redox modifications, conductivity), magnetic, mechanical. The dynamic polymers are illustrative of the potential offered by the application of the principles of constitutional dynamic chemistry[3.1, 3.2, 3.8-3.10] to materials science.

CHAPTER 4 : Folded Dynamers,

The Constitutional Dynamic Polymer Library (CDPL), *Concept*

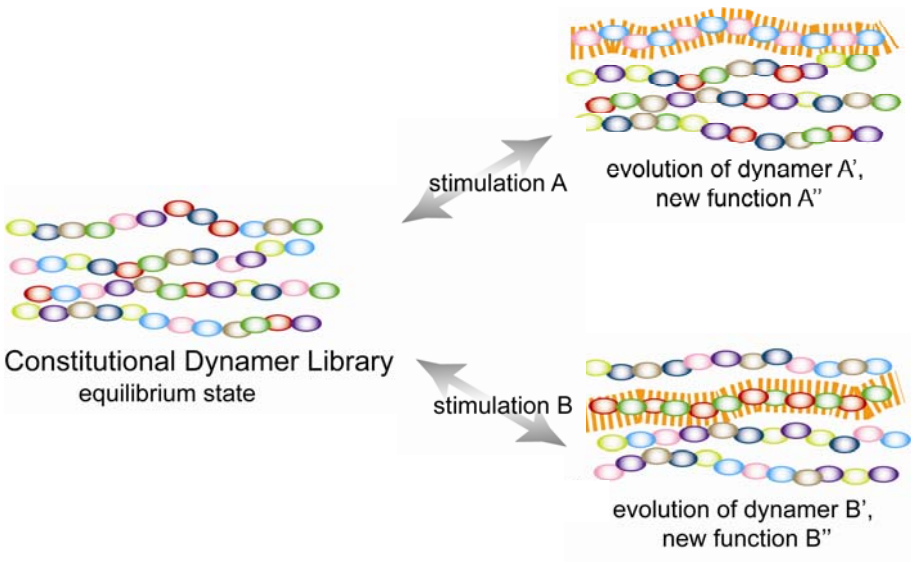
- Structural and Functional Evolution of a Library of Constitutional Dynamic Polymers driven by Alkali Metal Ion Recognition -

Dynamic polymer libraries were generated by polycondensation through reversible imine bonds and have been shown to undergo driven evolution under the stimuli of donor–acceptor stacking and metal-ion binding (see picture). The specific binding modes of alkali-metal ions are associated with specific constitutional changes and with different optical natures that reflect the presence and the positions of donor and acceptor units within the folded dynamer.



4. 1 Prologue

Adaptive materials, capable of responding to physical triggers or to chemical effectors by modification of their very constitution, represent an intriguing class of "smart" materials of both basic and applied interest. Their development rests on the implementation of Constitutional Dynamic Chemistry (CDC),[4.1, 4.2] based upon the lability of entities. This lability ensures the thermodynamic control of the dynamic libraries of constituents, represented by all possible combinations of the components present, as well as the rapid response of such libraries to changes in imposed conditions.[4.3, 4.4]



Scheme 4-1. Symbolic representation of a constitutionally dynamic polymer (*dynamer*) library (CDPL) as an adaptive smart material responding to different external stimuli, such as medium (solvent), interacting species (proton, metal ions, substrate molecule, etc.), and physical factors (temp., pressure, electric or magnetic fields, light, etc.).

A constitutional dynamic polymer library (CDPL) is expected to have the ability to respond to interacting species or to environmental conditions by shifts in equilibria towards the preferred, the fittest dynamer(s). Thus, the properties that are displayed may evolve in response to a variety of external factors, so that constitutional variation by component exchange in a CDPL offers a basis for a new class of adaptive, "intelligent" materials (Scheme 4-1).

The understanding, the design and the control of the folding of molecular strands has attracted great interest in both chemistry and biology.[4.14-4.34] In biopolymers, such as double-stranded DNA and proteins, folding is a crucial aspect of the development and expression of their specific functions. In materials science, especially polymer science, an understanding of folded forms and of folding processes should enable the design of foldamers on the nano-scale and thus allow for control of macroscopic properties such as electrical and optical features.[4.21-4.25, 4.29-4.33]

In this chapter, we describe the combined adaptation and folding behavior of a CDPL[4.3, 4.4, 4.5-4.13, 417, 4.26-27] generated by condensation polymerization through reversible formation of imine bonds between α,ω- diamines and dialdehydes functionalised by various groups potentially giving rise to supramolecular interactions expected to induce or favor particular folded forms. The imine bond was here employed as a reversible covalent interaction in order to demonstrate the concept of CDPL, since the imine exchange reaction responds more rapidly and reaches equiliblium faster than the exchange reactions involving hydrazone or acylhydrazone bonds.[4.28] We show that these dynamic libraries can undergo driven evolution under the double effect of donor-acceptor stacking[4.29-4.33] and metal cation binding.[4.34] In the presence of alkali metal ions, the specific binding modes of these metal ions induce an adaptation behavior, associated with specific constitutional changes and with different optical characteristics reflecting the presence and the positioning of donor and acceptor units within the folded dynamer.[4.29-4.33, 4.34]

4. 2 Materials Design and Synthesis

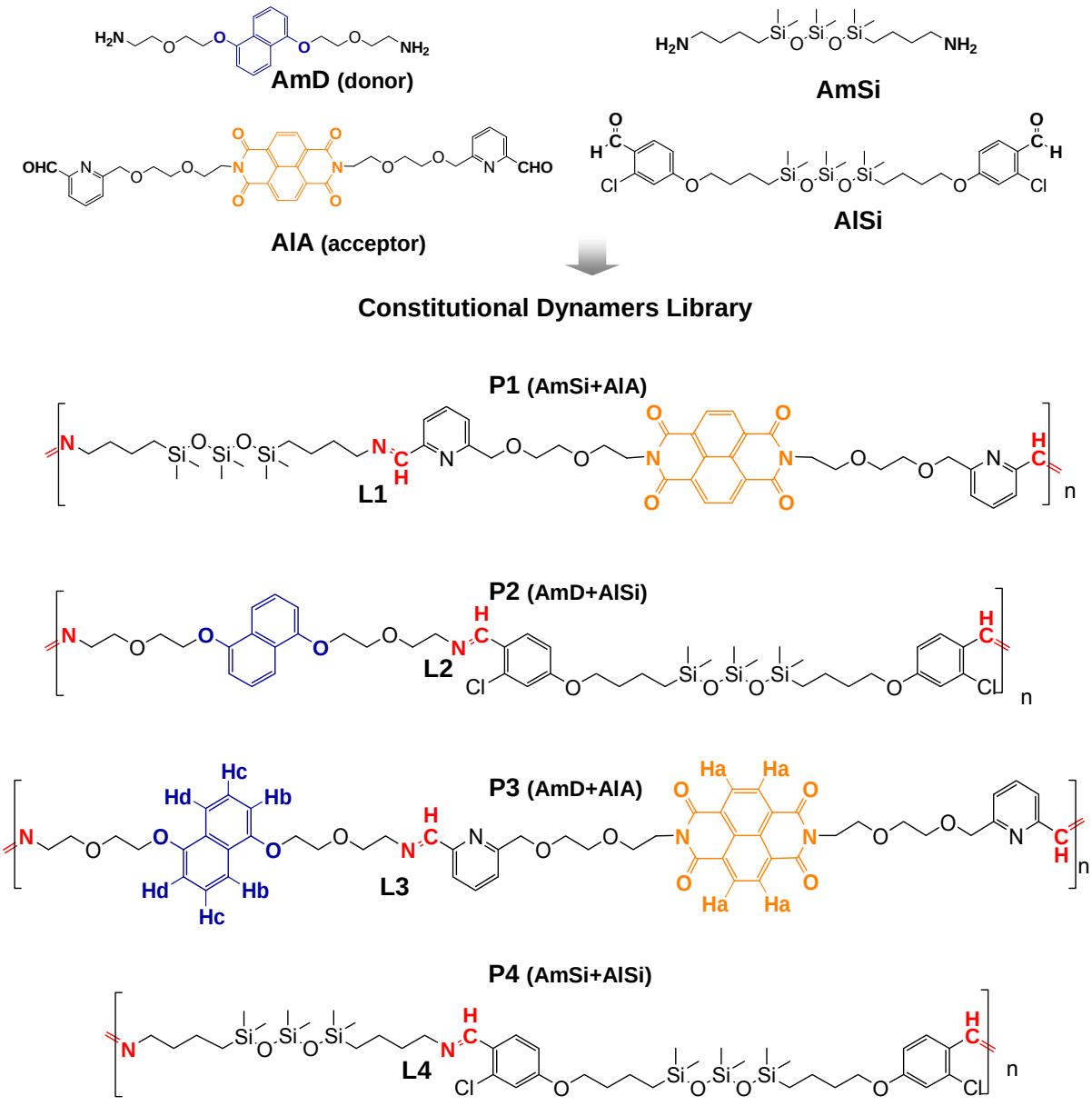


Figure 4-1. Molecular structures of the donor diamines **AmD** and **AmSi**, of the acceptor dialdehydes **AlA** and **AlSi** and of the constitutional dynamic polymers (dynamers) obtained by polycondensation: **P1 (AmSi+AlA), P2 (AmD+AlSi), P3 (AmD + AlA)** and **P4 (AmSi + AlSi)** containing the different imine links **L1**-**L4**. "**L**" stands for the imine links in the resulting polymer.

Figure 4-1 shows the monomer units used, the diamines **AmD** and **AmSi**, the dialdehydes **AlA** and **AlSi**, the four different imine links **L1**-**L4**, that may form during the polycondensation reaction, and the four possible dynamers **P1**-**P4** generated. Key features of

the design of these structures are the presence of C=N, N and ether-O sites suitable for the binding of alkali metal ions, and the presence, respectively in the diamines and the dialdehydes, of electron-rich 1,5-dialkoxy-naphthalene and electron-deficient 1,4,5,8-naphthalene- tetracarboxylic diimide units for charge-transfer interactions. These groups were chosen in view of the fact that their features are well documented.[4.18, 4.29, 4.30] Only the dynamer **P3** involves both the donor and acceptor components, connected by a heteroatom containing chain, capable of binding metal cations and sufficiently flexible to allow folding to result in stacking and thus in CT interactions. The dynamers **P1**-**P4**, which are formed through reversible imine bonds of one type only, were obtained separately by polycondensation of equimolar amounts of the relevant diamine and dialdehyde monomers in $CHCl_3$ in the presence of anhydrous $MgSO_4$.

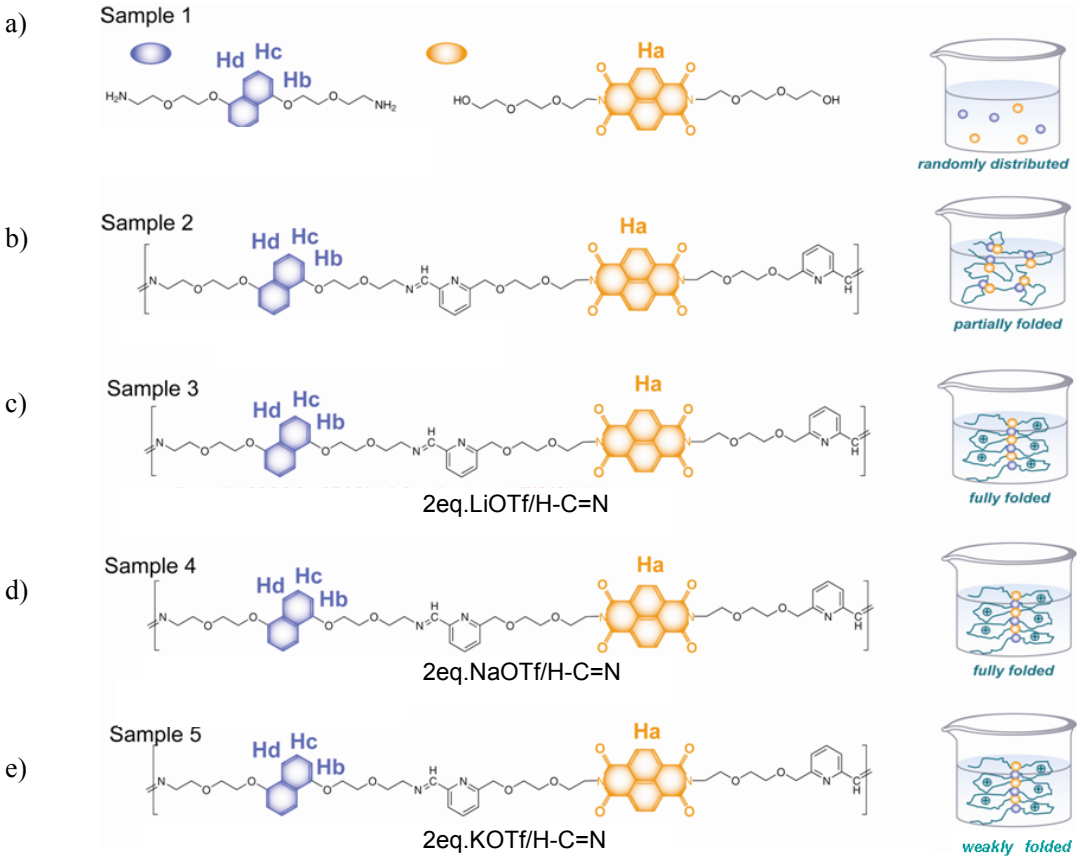


Figure 4-2. Chemical structure and schematic cartoons of dynamer **P3** (C = 3 mM in 8:2 CD_2Cl_2: CD_3CN) in absence and presence of different alkali metal ions. a) **P3**-sample 1 referenced monomers, b) **P3**-sample 2 in absence of any metal, c) **P3**-sample 3 in presence of Li^+, d) **P3**-sample 4 in presence of Na^+, e) **P3**-sample 5 in presence of K^+.

As a prelude to the study of the full CDPL, the folding behaviour of dynamer **P3**, derived from **AmD** and **AlA**, was examined in organic solution (the essential results being summarised in Figure 4-2). In comparison with **AmD** and referenced monomers designed for the prohibition of polymer growth or **P3** in absence of metal, peaks in the ^{1}H NMR spectra for Hb, Hc and Hd of the donor and Ha of the acceptor units (Figure 4-2) of **P3** were shifted downfield by the addition of 2 molar equivalent / H-C=N bond of LiOTf, NaOTf and KOTf in an 8:2 mixture of CD_2Cl_2 and CD_3CN at 3 mM. The shifts due to the larger K^+ ion were relatively small.

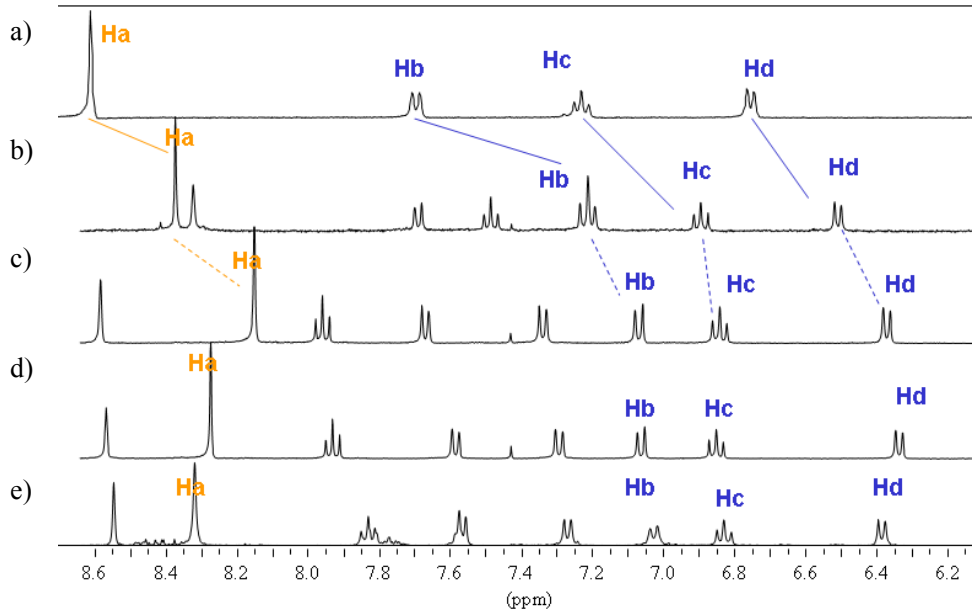


Figure 4-3. Part of ^{1}H NMR spectra (aromatic proton region) of dynamer **P3** (C = 3 mM in 8:2 CD_2Cl_2: CD_3CN) in absence and presence of different alkali metal ions. a) **P3**-sample 1 monomers, b) **P3**-sample 2 in absence of any metal, c) **P3**-sample 3 in presence of Li^+, d) **P3**-sample 4 in presence of Na^+, e) **P3**-sample 5 in presence of K^+. (Ha, Hb, Hc and Hd identified in Figure 4-1 and 4-2 are indicated.)

2D NOESY ^{1}H NMR spectroscopy showed that addition of the alkali metal salts LiOTf, NaOTf and KOTf to **P3** led, in the first two cases, to folding which brings the donor and acceptor units into proximity, as indicated in the spectra (Figure 4-4, top) by the correlation of Hb, Hc and Hd of the donor with Ha of the acceptor, as well as by colour changes. Binding of the larger K^+ ion to the polymer seems to be less compatible with close approach of the donor and acceptor units. An absorption band indicative of the charge-transfer (CT) interaction occurring in the Na^+ complex appears at 517 nm (Figure 4-4, bottom).[4.29, 4.43] In our

experimental range of concentration from 0.3 mM to 3.0 mM, adherence to Beer's Law was observed, indicating that a single species was present over this range and that the interaction must be intra- and not inter-molecular, implying that the complex must be of high stability for Beer's Law to be obeyed.

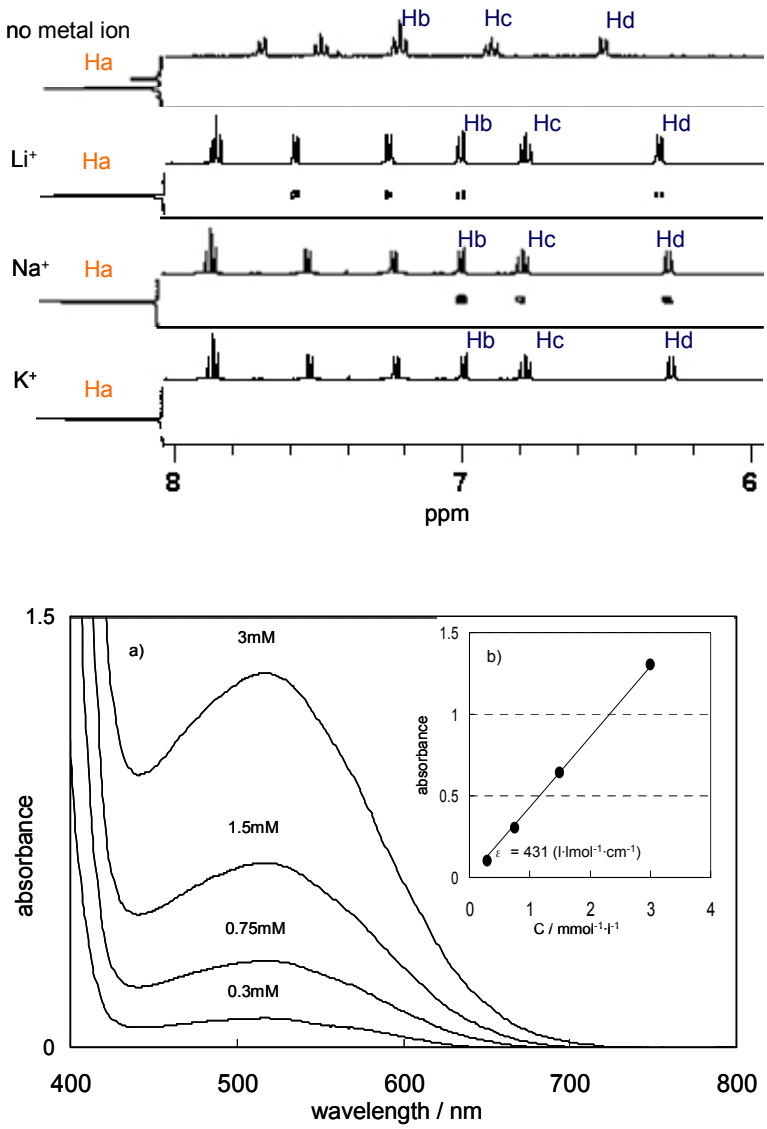


Figure 4-4. Top: 2D NOESY ^{1}H NMR spectra (aromatic proton region) of dynamer **P3** (C = 3 mM in 8:2 CD_2Cl_2: CD_3CN) in presence of different alkali metal ions. Bottom: a) absorption spectra and b) Lambert-Beer plot at λ_{max} 517 nm for the CT band of **P3** in presence of Na^+ (in 8:2 CD_2Cl_2:CD_3CN); λmax 517 nm, **ε** = 431 l·mol^{-1} cm^{-1} at 3mM.

The solid-state molecular structure of the NaOTf and KOTf complex of a model oligomer for **P3**, formed by reaction of a mono-amine analogue of **AmD**[4.35] with **AlA** in a 2:1 molar ratio, was determined by X-ray crystallography (Figure 4-5). Both cases present indeed a folded structure. In the Na complex, two donor and one acceptor units form a stack and two equivalent Na^+ ions are bound to the connecting chains. Each Na^+ ion is hexacoordinated to pyridine-N, imine-N, two ether-O and one carbonyl-O sites of the oligomer (Figure 4-5), as well as to one triflate-O (not shown in Figure 4-5). K complex behaved as similar structure.

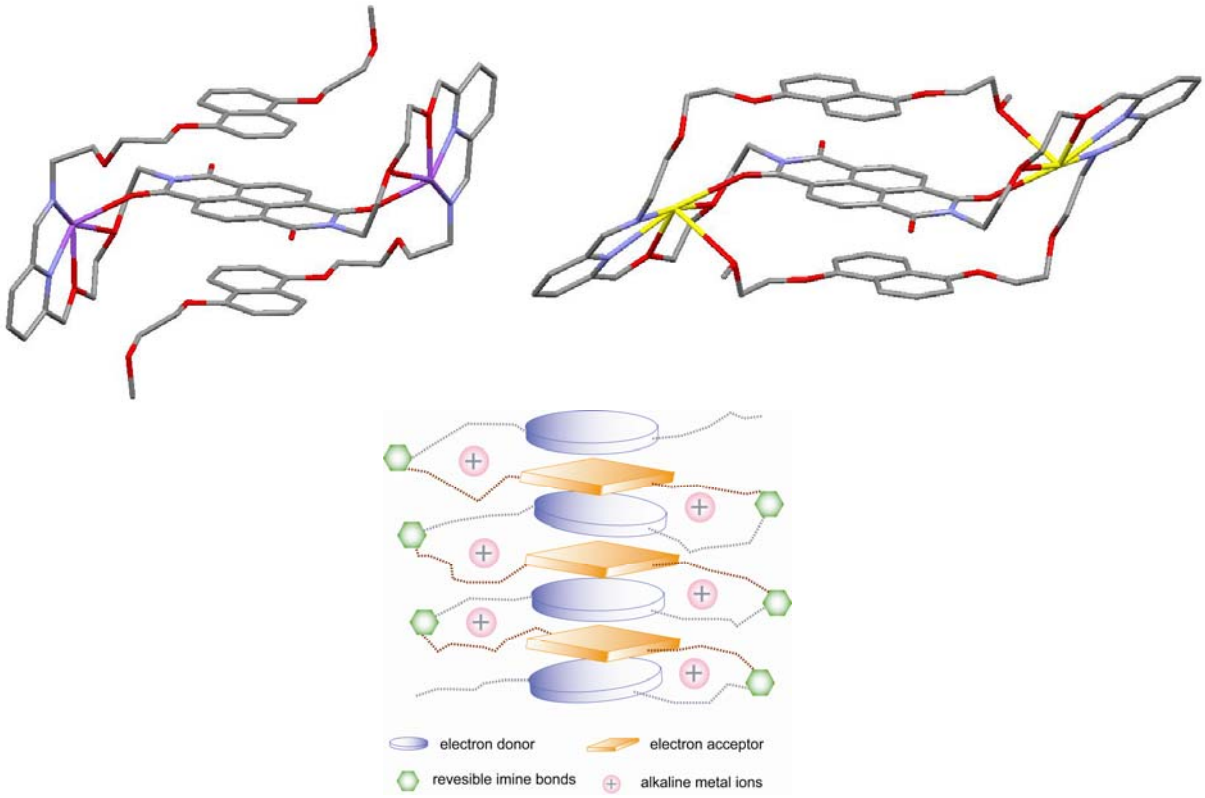


Figure 4-5. Left: Solid state structure of the NaOTf complex of the model compound generated from two molecules of a monoamine analogue of **AmD** with one molecule of **AIA**. It shows the stacking of the donor and acceptor units, resulting from the folding of the chains and the binding of two Na^+ ions (triflate counteranions not shown). Right: of KOTf complex. Bottom: cartoon representation of the folded dynamer **P3** as its alkali ions complex based on the crystal structure of the model compound.

The preference for Na^+ (and Li^+) complexation with respect to K^+ may be related to the size as well as to the adaptability of the binding cavity defined by the strands of the stacked folded form of the ligand, in analogy to the selectivity shown by macrocyclic polyethers of different sizes. The Na^+ -O and K^+-O distances in the complex average respectively 2.6 Å and 2.75 Å

as compared to 2.44 Å in 15-crown-5 [4.34] and 2.80 Å [4.38] in 18-crown-6 respectively and the distances between donor and acceptor aromatic ring indicates 3.60 Å of Na complex and 3.82 Å of K complex respectively, implying that **P3** with KOTf was not observed the close approach of the donor and acceptor units in 2D NOESY spectroscopy (Figure 4-4). Addition of NaOTf to the dynamer **P3**, obtained from **AmD** and **AlA**, resulted also in the formation of Na^+ complexes, as indicated by gel permeation chromatography, the species detected showing a mean molecular weight Mn = 45,000 and dispersivity Mw/Mn = 1.2. These data indicate that addition of NaOTf to the dynamer **P3** does not result in a small oligomer such as a macrocycle, but that a polymeric chain is formed as shown in Figure 4-1.

4. 3 Results and Discussion

A CDPL was generated from a mixture of equimolar amounts of preformed **P1** and **P2** (each 3 mM in 8:2 CD_2Cl_2:CD_3CN) in the presence of 2 mol % CF_3COOD as acid catalyst for the imine equilibration. ^1H NMR studies are useful for obtaining structural information about both static and dynamic entities, for it is possible to follow the polymer length, the degree of polymerization DP, by integration of the imine and remaining aldehyde proton signals. Such data allow a detailed analysis of the molecular constitution during the exchange processes The degree of polymerization DP and polymer weight Mn were estimated by integration of the imine and the residual terminal aldehyde proton signals using Eq. (4-1). The values obtained are given in Table 4-1.

$$[DPn] = 1/2\ [\ \sum \text{Imine}\ ^1H\ /\ \sum \text{Aldehyde}\ ^1H + 1\ ] \qquad (4\text{-}1)$$

Table 4-1. Degree of polymerization and molecular weight obtained from ^1H NMR and GPC measurements for starting dynamic polymer **P1**, **P2** and dynamic polymers in the dynamic library with and without each alkali metal ion

	DP*n* [a]	Mn [b]	Mn [c]	Mw/Mn [c]
Parent dynamer **P1**	65	64,700	--- [d]	--- [d]
Parent dynamer **P2**	67	62,300	--- [d]	--- [d]
Initial equilibrium [e]	58	55,900	--- [d]	--- [d]
LiOTf [e]	47	45,200	--- [d]	--- [d]
NaOTf [e]	49	47,000	59,600	2.85
KOTf [e]	51	48,800	--- [d]	--- [d]
RbOTf [e]	45	43,200	--- [d]	--- [d]
CsOTf [e]	50	47,600	--- [d]	--- [d]

[a] The mean DP was determined from equation (1). [b] Calculated from the mean DP. [c] Molecular weight Mn and distribution Mw/Mn determined by GPC with polystyrene calibration. [d] Not determined. [e] Initial equilibrium was established in the presence of acid only, then the various alkali metal salts (2 eq./imine unit) were added.

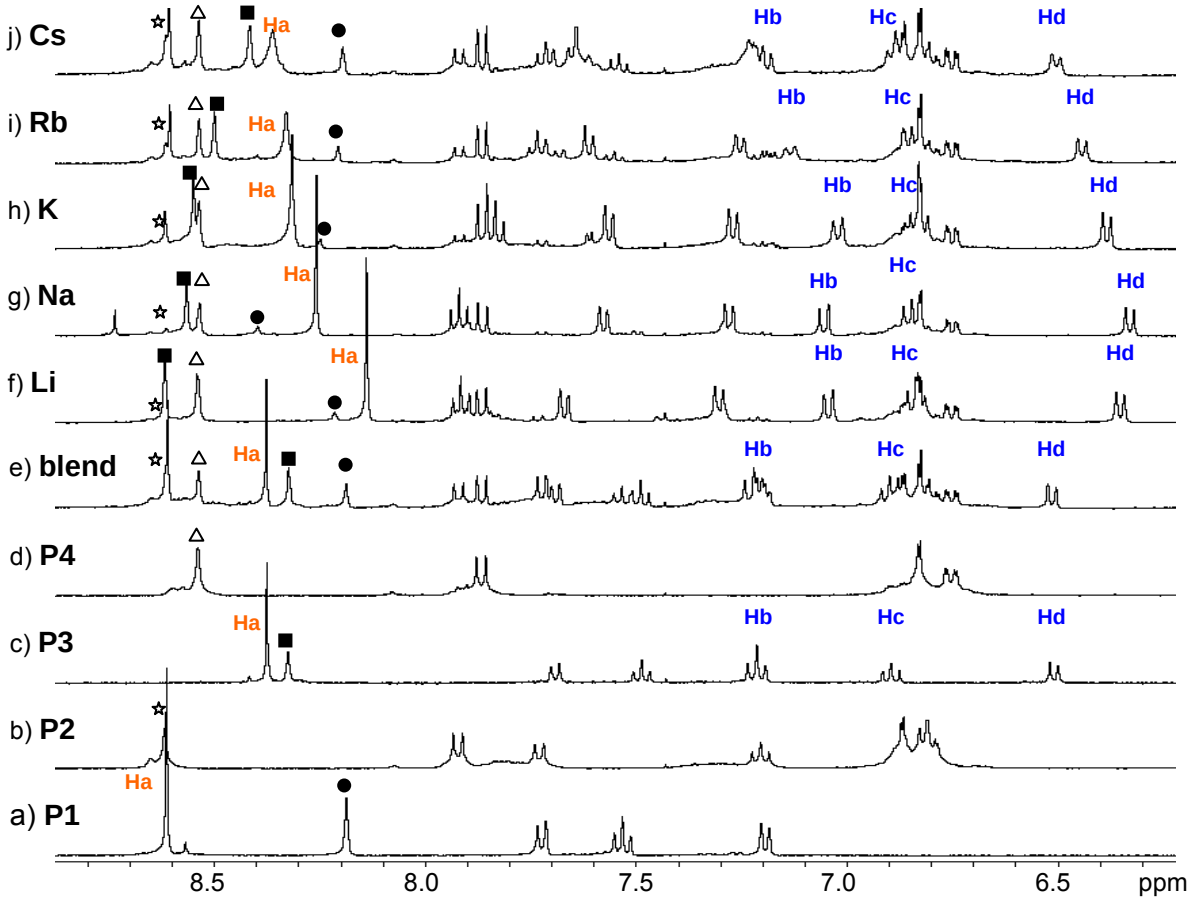


Figure 4-6. ^{1}H NMR spectra of the C–H proton signals of the imine and aromatic groups for (a) **P1**; (b) **P2**; (c) **P3**; (d) **P4**; (e) equilibrium state of a mixture of **P1** and **P2** in solution in the absence of metal ions after 12 hours' stirring; (f) dynamer equilibrium state in the presence of LiOTf, (g) NaOTf, (h) KOTf, (i) RbOTf, (j) CsOTf. The symbols identify the characteristic proton signals of the imine C–H proton of the reference polymers (● = **P1**, ☆ = **P2**, ■ = **P3**, Δ = **P4**). The proton signals of the donor and acceptor units derived from **L3**, Ha, Hb, Hc and Hd (identified in Figure 4-1) are also indicated.

The mean molecular weight of the dynamers estimated from the equation (4-1) did not show a significant change throughout the CDPL study. Thus, the addition of the different metal triflate salts caused only a minor effect in the overall degree of polymerization of the dynamic library. To ensure equilibration, the dynamer mixture was stirred for 12 h at room temperature, after which time its ^{1}H-NMR spectrum showed the four sets of characteristic imine proton signals of the link units **L1**-**L4** in the **P1**-**P4** dynamers resulting from exchange and recombination of the monomer constituents of **P1** and **P2** (Figure 4-6e).

From peak integration, the ratio **L1**: **L2**: **L3**: **L4** was determined to be 22: 22: 28: 28. The nearly statistical distribution of links at equilibrium shows their essentially isoenergetic nature under the given conditions. Subsequent addition of alkali metal triflates (2 mol/mol of imine) led to shifts in the initial equilibrium distribution, dependent upon the nature of the cation and reflected not only in the NMR spectra but also in colour changes due to modification of CT interactions. Consistent with expectations based on the structural characterisation of the NaOTf complex of the model bis(imine) (Figure 4-5) and with the observation of color development due to CT interaction, addition of NaOTf (as well as LiOTf) resulted in a strong increase in the fraction of link **L3** and therefore in the **P3** constituent (or **P3** blocks) of the polymer mixture. The **L1**: **L2**: **L3**: **L4** ratios in presence of LiOTf and NaOTf were about 8: 8: 42: 42 and 7: 7: 43: 43, respectively (Figure 4-7).

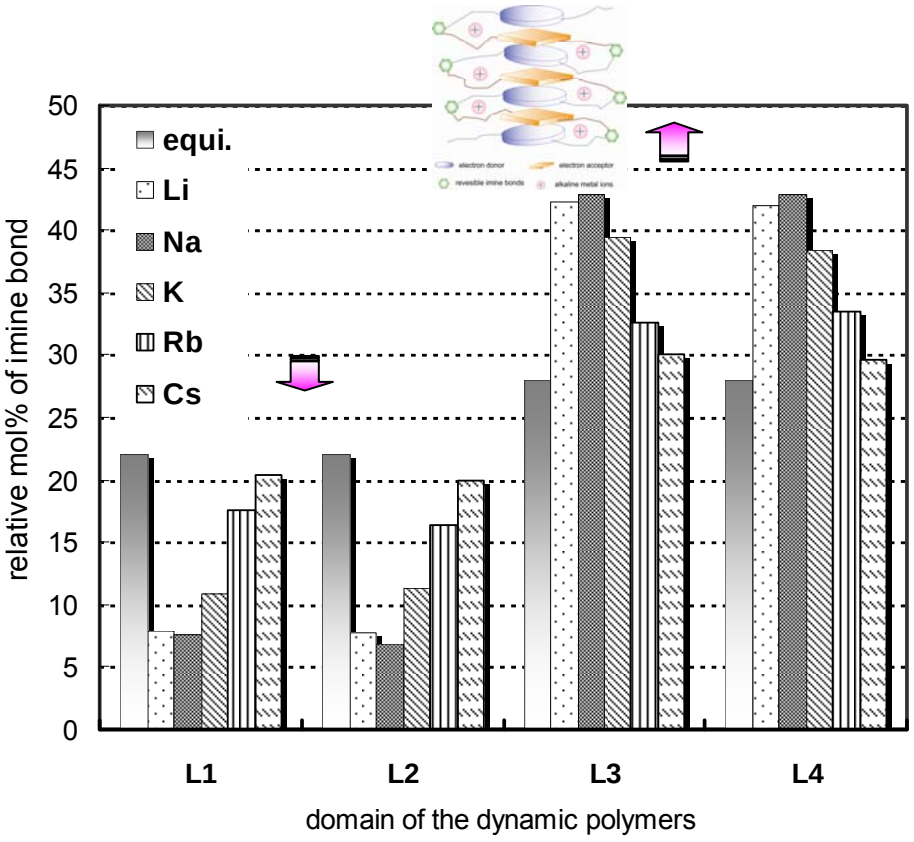
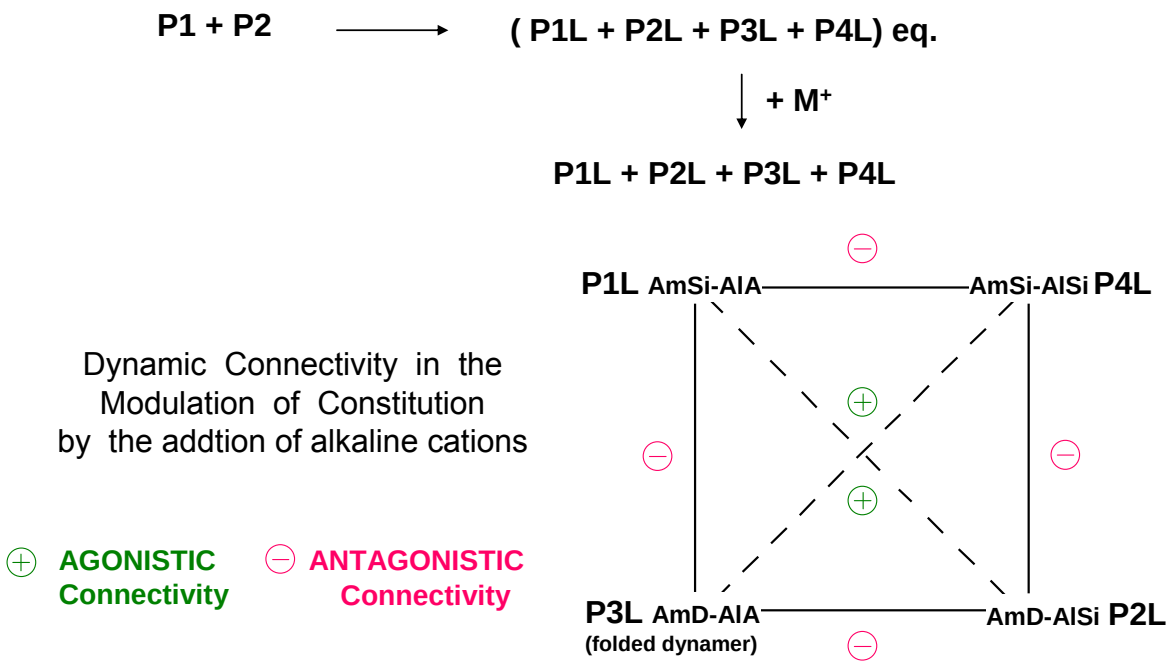


Figure 4-7. Representation of the distribution of the imine link domains **L1**-**L4** generated from the library of **P1, P2, P3** and **P4** dynamers, induced by the addition of different alkali metal cations, after reaching equilibrium, as determined by integration of the imine proton signals in the ^{1}H NMR spectra in Figure 4-6.

Note that the enhanced formation of **L3** must necessarily result in the release of the components of **L4**, so that the increase of **L4** and therefore of **P4** (blocks) can be regarded as an agonistic[4.36] consequence of the formation of **L3**. ^{1}H NMR measurements and GPC analyses are in good agreement in indicating that the overall degree of polymerisation in the dynamic library is little affected by the addition of the different metal triflates.



Scheme 4-2. Networks of dynamically interconverting constituents connected either structurally (molecular and supramolecular arrays) or reactionally (sets of connected reactions or interactions).

As noted previously, the constitutional evolution of the CDPL gives rise to changing optical characteristics as well as changes in the NMR spectra, and the differing abilities of the metal ions to bring donor and acceptor units into proximity through folding are nicely illustrated by the colors of the library mixture (as in Figure 4-8) in the presence of the various metal triflates. A marked color change, from the light brown of the initial equilibrium state to a much deeper purple tint, was observed for Li^+ and Na^+, while K^+ produced a weaker effect and the color decreased further for Rb^+ and Cs^+. The color observed for the Li^+ and Na^+ ions corresponds to the same absorption spectrum as that observed for pure **P3** in presence of Na^+ (Figure 4-4).

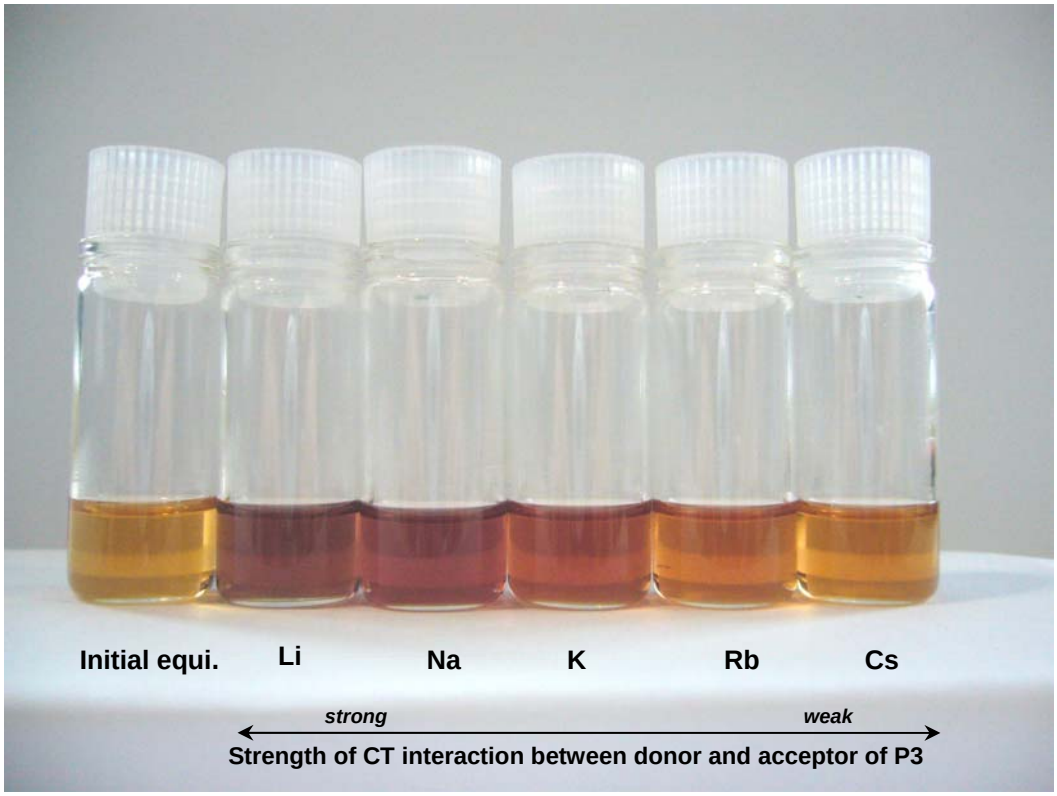


Figure 4-8. Optical evolution of the library of dynamers (as in Figure 4-5) in presence of the different alkali metal ions. Photographs showing the color changes.

Consistent with these effects being associated with the preferred binding of the smaller metal ions in the fold provided by the link **L3** (generated in the course of the constitutional evolution of a mixture of **P1** and **P2**), the amplification of **L3** decreased with increasing ion size (**L1**: **L2**: **L3**: **L4** = 12: 12: 38: 38, 17:17: 33:33 and 20: 20: 30: 30, for K^+, Rb^+ and Cs^+, respectively) (Figure 4-7).

The behavior of this CDPL as a function of the size of alkali metal ions demonstrates a self-sensing property,[4.13] resulting from an adaptation of the CDPL through the constitutional evolution of the system, driven by the recognition of each alkali metal ion. In other words, the system displays the ability to respond to external factors by selective amplification of specific constituents in an adaptive system.

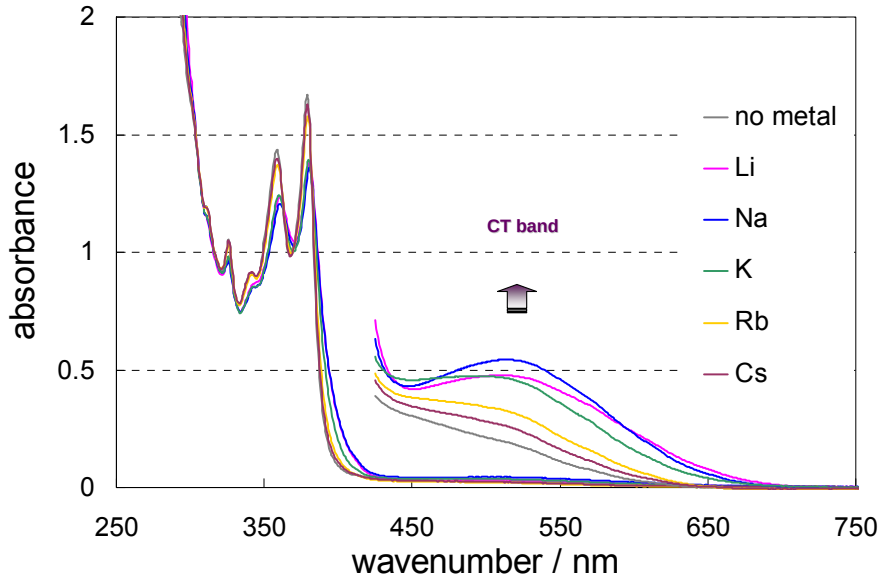


Figure 4-9. Optical evolution of the library of dynamers as in Figure 4-8 corresponding UV-vis spectra.

4. 4 Conclusions

The present CDPL provides an example of adaptive behavior by constitutional recombination in response to the addition of alkali metal ions. Induction of the binding site best suited to a particular metal ion is dependent upon synergistic 1) selection of the optimal components, 2) chain folding and 3) D/A stacking interactions. Moreover, this system is capable of recognizing alkali metal ions along with generation of different optical signals, thus displaying a sensing function due to constitutional modification. Numerous variations may be envisaged, such as extensions to other types of metal ions or to organic guests, incorporation of other components, induction of novel properties, etc. In general terms, a CDPL may display various features which evolve under the pressure of external factors, thus defining a new type of smart material based on change in chemical constitution. Such materials should be able to generate specific responses to external stimuli and thereby to exhibit several different kinds of functions through the implementation of dynamic constitutional variation and adaptation. They point towards the emergence of adaptive materials technologies.

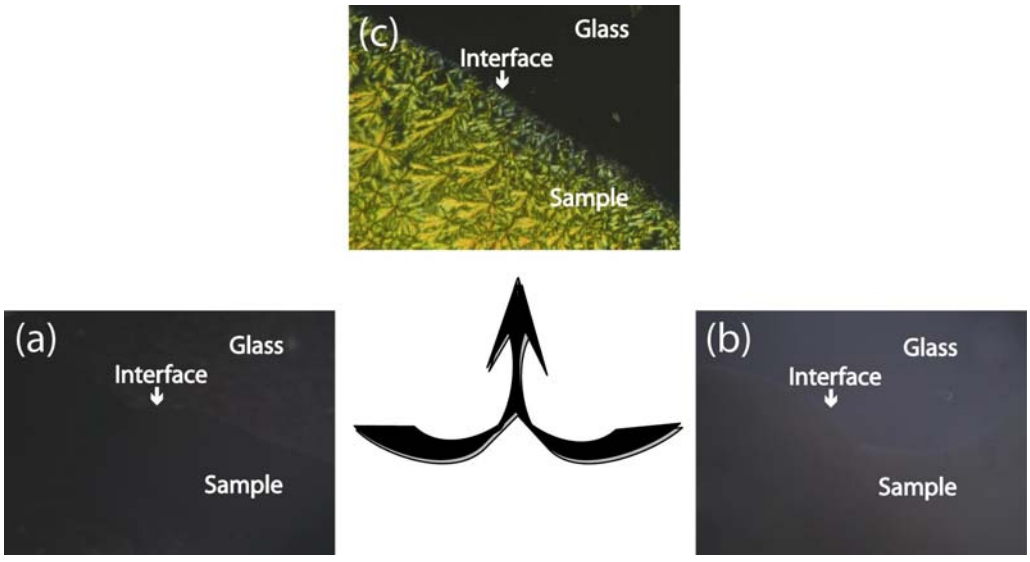
As a perspective of broad concernment, evolution of a biopolymer in nature, such as DNA, RNA and protein has led to their specific constitution and super architecture corresponding to the most stable state. The behavior of the system described here exhibits a process of selection of components to generate the most stable organized architecuture, representing a control of constitution and supramolecular structure selectively driven by self-organization, a factor that may have played an important role in the prebiotic evolution of molecular matter. [4.39]

CHAPTER 5 : Liquid Crystalline Dynamers

The Constitutional Dynamic Polymer Library (CDPL), *Application*

- Crystallization-driven constitutional changes of dynamic polymers in response to neat/solution conditions -

Dynamic polymers (dynamers) based on reversible imine interactions were generated and found to respond to changes in environment between that of the neat material and its solutions, thus displaying adaptive behavior through modification of their constitution in order to maximize the stability of their crystalline mesoscopic state as a function of conditions.



5. 1 Prologue

Properties of polymers can be broadly divided into several categories based upon scale, namely the microscopic, mesoscopic and macroscopic levels. One known means of amplification of a given dynamer of a CDPL (constitutional dynamic polymer library) is by stabilizing its microscopic structure.[5.1, 5.2, 5,3] Although its potential is obvious, little progress has yet been made in utilising mesoscopic properties for dynamer amplification. At the mesoscopic level, properties which determine the morphology of the polymer matrix in space are those reflected in the crystalline, liquid crystalline[5.8, 5.9, 5.10, 5.11] and/or amorphous states of the polymer. A synthetic polymer may be described as crystalline if it contains regions of three-dimensional ordering on nano scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Amplification of a given dynamer of a CDPL under the pressure of a self-organization process,[5.4] such as the formation of an anisotropic phase would be of special interest. In principle, the self-organization of selected member of a CDPL into an anisotropic phase will influence the library composition, favoring those species that can form the most stable (liquid) crystalline domains.[5.5,5.6]

Here we describe our studies of the constitutional dynamic polymers which can adapt to different environmental conditions by stabilizing/unstabilizing the mesoscopic states of the DCL's members, and consequently result in different constitutional expressions. The present study of constitutional dynamic polymers involves consideration of a particularly broad range of features:1) generation of dynamic polymers (dynamers); 2) constitutional dynamics modulated by the reversible imine bonding; 3) dynamic selection of the optimal monomers by adaptation of the environmental condition; 4) amplification and selection processes arising from stabilizing the mesoscopic states of a CDPL's members.

5. 2 Materials Design and Synthesis

The dialdehyde monomers **Ald1** and **Ald3** were synthesized by treatment of 4-hydroxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde, respectively, with 3,6,9,12,15-pentaoxaheptadecane-1,17-diylbis(4-methylbenzenesulfonate) in the presence of K_2CO_3.

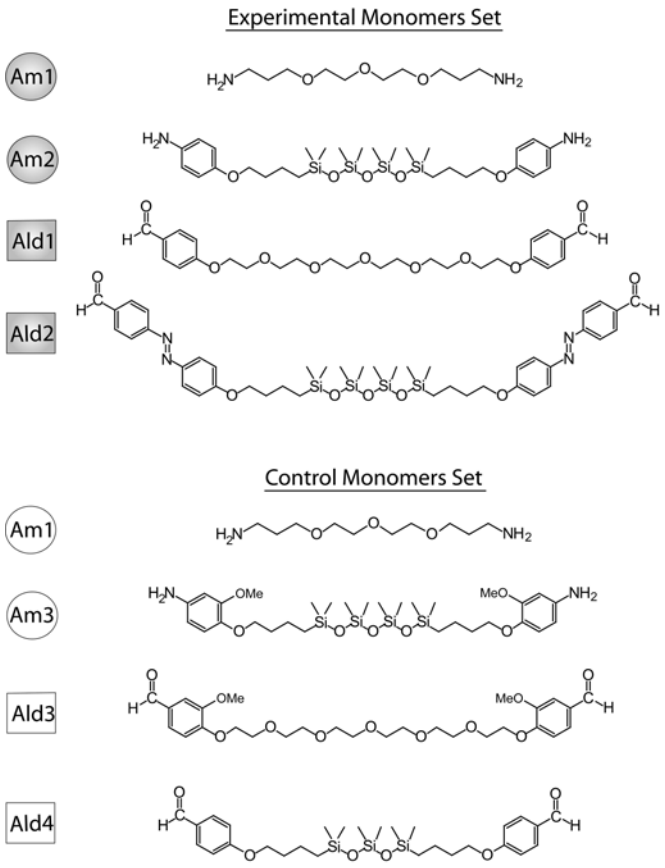


Figure 5-1. (Top) structures of diamines **Am1** and **Am2**, and dialdehydes **Ald1** and **Ald2** of the experimental set; (Bottom) structures of diamines **Am1** and **Am3**, and dialdehydes **Ald3** and **Ald4** of the control set.

The dialdehydes **Ald2** and **Ald4** were obtained, respectively, by coupling 4-(but-3-enyloxy)phenyl-4'-formylazobenzene with octamethyltetrasiloxane, and 4-(but-3-enyloxy)benzaldehyde with hexamethyltrisiloxane using Karstedt's catalyst. Diamine monomers **Am2** and **Am3** were obtained by a similar coupling reaction to that used for **Ald2** by reacting 4-(but-3-enyloxy)-nitrobenzene or 4-(but-3-enyloxy)-2-methoxy-1-nitrobenzene, respectively, with octamethyltetrasiloxane, followed by reduction of their nitro-groups to

amino-moieties by hydrazine monohydrate in the presence of Pd-C catalyst (see experimental section). Figure 5-1 shows the structures of diamines **Am1**-**Am3**, and dialdehydes **Ald1-Ald4** which were used to provide control and experimental polymer sets. The homopolymers **P1-P8**, all linked by reversible imine bonds, were obtained by polycondensation of the corresponding dialdehyde monomers with the corresponding diamine monomers in 1:1 molar ratio in the presence of anhydrous Na_2SO_4 in chloroform for 12h at 60 ºC.

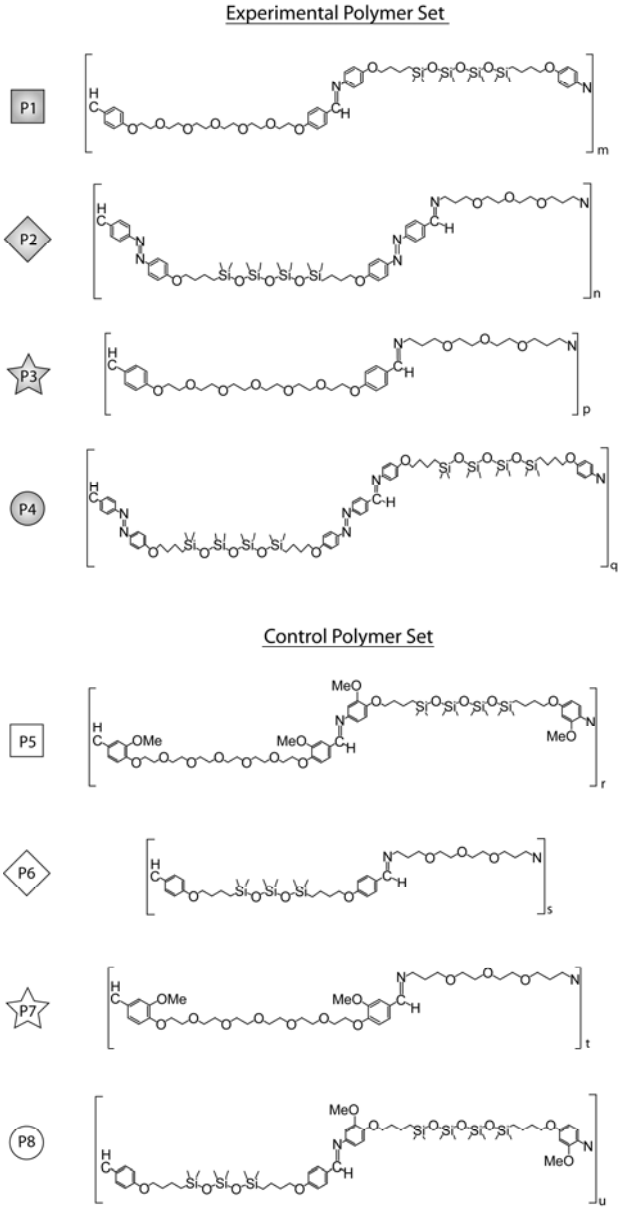


Figure 5-2. (Top) structures of the homopolymers, **P1-P4**, used in the experimental set; (bottom) structures of the homopolymers, **P5-P8**, used in the control set.

Figure 5-2 shows the four homopolymers **P1-P4** used in our experimental studies and the four homopolymers **P5-P8** used in our control experiment studies. **Ald2** has a diazobenzene unit acting to engender liquid crystalline behaviour through their rather strong interactions. The homopolymer **P1**, the condensation product between **Ald1** and **Am2**, was an opaque solid; **P2**, which was formed between **Ald2** and **Am1**, was obtained as a stretchy film; **P3**, derived from **Ald1** and **Am2**, was an oily material; and **P4**, the condensation product from **Ald2** and **Am2**, involving a strong mesogenic moiety of conjugated three benzene rings, was a brittle film (Figure 5-3).

Polycondensation between the monomers **Ald3** and **Am3**, **Ald4** and **Am1**, **Ald3** and **Am1**, and **Ald4** and **Am3** gave, respectively, **P5**, **P6**, **P7** and **P8**, all of which were oily materials at room temperature, as polymers for the control set. ^{1}H-NMR spectroscopy confirmed the formation of all the homopolymers through the appearance of their individual imine proton signals (Figure 5-4). Table 5-1 summarizes the phase transition temperatures and molecular weight (M_n) of the homopolymers **P1-P4**. Of all the polymers in the test set, **P4** melts to give a smectic phase at 125 ºC and has the highest isotropic transition temperature, which was 159.6 ºC, reflecting the presence of the diazobenzene unit acting to engender liquid crystalline behaviour.

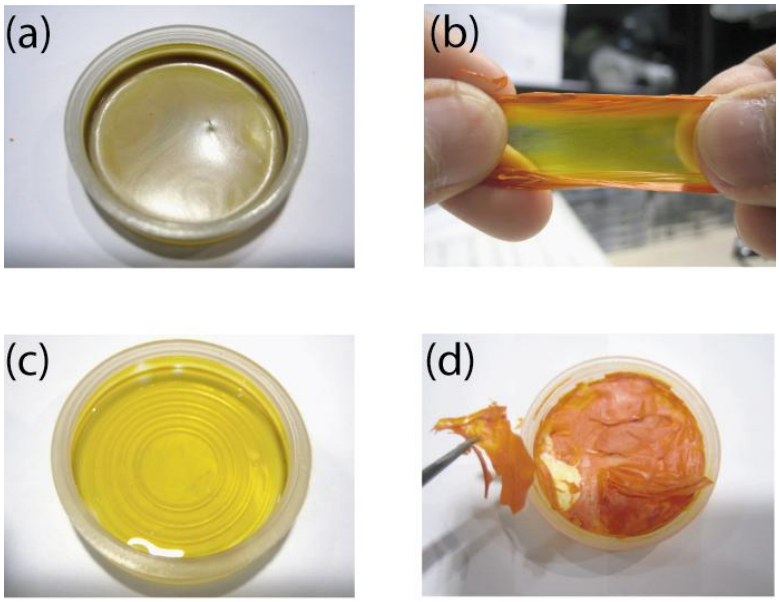


Figure 5-3. Photographs of homopolymers (a) **P1**– opague solid, (b) **P2** –stretchy film, (c) **P3** – oil and (d) **P4** – brittle film.

Table 5-1. Thermal data and molecular weight (Mn) of homopolymers, P1-P4, and polymer blends, B1neat.

Polymer	T_{onset}[a]	M_n[b]
P1	Cr 58.9 S 72.5 I[c]	38,000
P2	Cr 68.4 I	53,000
P3	I≤-40	34,000
P4	Cr 124.1 S 159.6I	54,000
B1$_{neat}$	Cr 131.0 S 154.2I	-

[a] 2nd heating results from differential scanning calorimetry [b] results from equation (4-1) based on NMR integration. [c] Cr = crystal phase, S = smectic phase, I = isotropic liquid.

5. 3 Results and Discussion

The dynamic behavior of the present molecular polymers, due to the reversibility of the imine bonds, was clearly demonstrated by ^{1}H NMR studies of the polymer blends. Polymer blend (**B1$_{sol}$**) was prepared by just mixing the homopolymers **P1** and **P2** in an equimolar ratio (at *ca.* 5mM) for 24 h in deuterated 1,2-dichlorobenzene at 80ºC with 1 mol% acid catalyst. Random copolymer **C1$_{sol}$** was also prepared from the 4 kinds of monomers (**Ald1**, **Ald2**, **Am1** and **Am2**) in equimolar ratios (at *ca.* 5mM) in deuterated 1,4-dichlorobenzene at 80ºC with 1% acid catalyst. ^{1}H-NMR analyses of the resulting polymer blend **B1$_{sol}$** and copolymer **C1$_{sol}$** in deuterated 1,2-dichlorobenzene allowed identification of the various kinds of connections between aldehydes and amines from the signals of the H-C=N protons of imine and aromatic moieties at 6.6-8.8 ppm (Figure 5-4e). The spectrum of blend **B1$_{sol}$** showed four characteristic imine proton signals which were assigned to 1) the connection between **Ald1** and **Am2**, i.e. **P1** domain (at 8.32 ppm and 8.40 ppm); 2) the connection between **Ald2** and **Am1**, i.e. **P2** domain (at 8.26 ppm); 3) a new connection between **Ald1** and **Am1**, i.e. **P3** domain (at 8.14 ppm); and 4) another new connection between **Ald2** and **Am2**, i.e. **P4** domain (at 8.42 ppm and 8.51 ppm). The percentage composition of **P1:P2:P3:P4** domains in the blend **B1$_{sol}$** was about 3:3:2:2 at equiliblium state in solution. The proton signals found in **C1$_{sol}$** were exactly same as those in **B1$_{sol}$** confirming that the homopolymers **P1** and **P2** are constitutional dynamic materials capable of constitutional variation through exchange and reshuffling of their components.

It has previously been shown that temperature, concentration and solvent variations can markedly change the distribution inside a dynamic set of imines.[5.1] Three separate studies of the present system were performed by mixing the homopolymers **P1** and **P2** in an equimolar ratio for 24 hrs with 1% acid catalyst: (i) in deuterated 1,2-dichlorobenzene heated between 25ºC and 100ºC in 25ºC increments; (ii) in deuterated 1,2-dichlorobenzene between 5 mM and 45 mM in 10 mM increments; and (iii) in $CDCl_3$ at 25ºC. In all of the cases, the percentage compositions of **P1:P2:P3:P4** domains in the resultant polymer blends were about 3:3:2:2. which meant that there was no significant change in the selectivity. These results are consistent with the fact that the especially strong link between the electron-donoring **Am1** and the electron-accepting **Ald2** leads to a dominant effect which is not be significantly affected

by the solvent within such ranges of temperature and concentration.

Control polymer blend (**B2$_{sol}$**) was also prepared as the same way as the polymer blend **B1$_{sol}$** by replacing the starting homopolymers to **P5** and **P6**. As expected, components recombination also occurred in the blend **B2$_{sol}$**. Four domains were found in the **B2$_{sol}$** namely links of the types found in **P5**, **P6**, **P7** and **P8**. The percentage composition of **P5:P6:P7:P8** domains in the blend **B2$_{sol}$** was about 2.7:2.7:2.3:2.3 at equilibrium in solution.

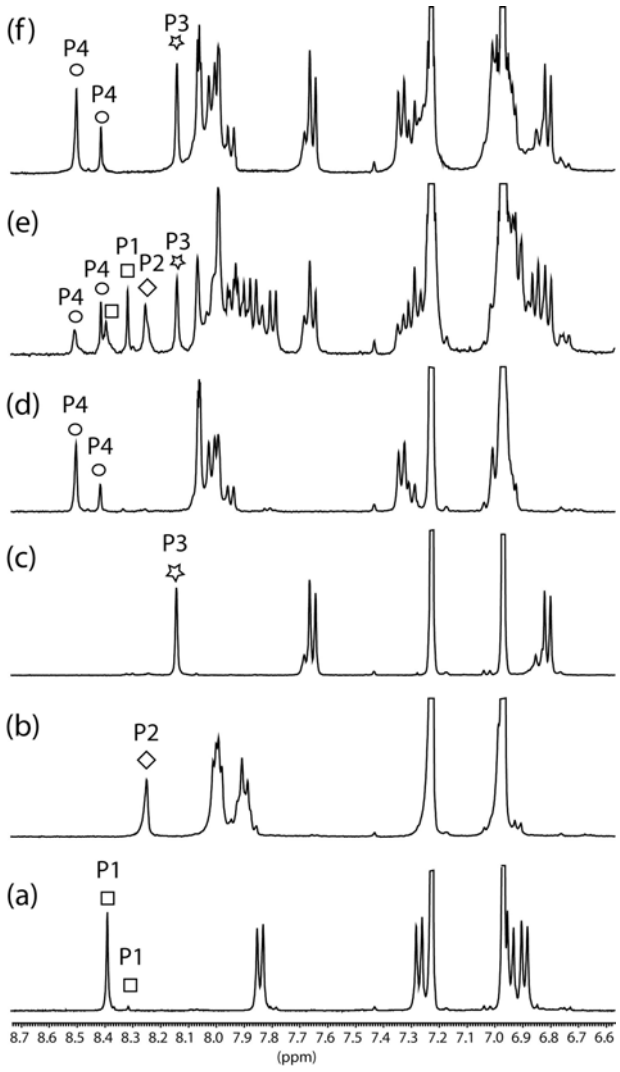


Figure 5-4. Part of the ^{1}H NMR spectra of polymers: (a) **P1**; (b) **P2**; (c) **P3**; (d) **P4**, (e) blend **B1$_{sol}$** and (f) blend **B1$_{neat}$** in deuterated 1,4-dichlorobenzene (ca. 5 mM) showing the H-C=N proton signals of the imine or aromatic entities. The symbols indicate the corresponding characteristic proton signals in the spectra of **B1$_{sol}$** and **B1$_{neat}$** of the reference polymers. [The ^{1}H NMR spectrum was taken within 10 mins of dissolving blend **B1$_{neat}$** in deuterated 1,2-dichlorobenzene].

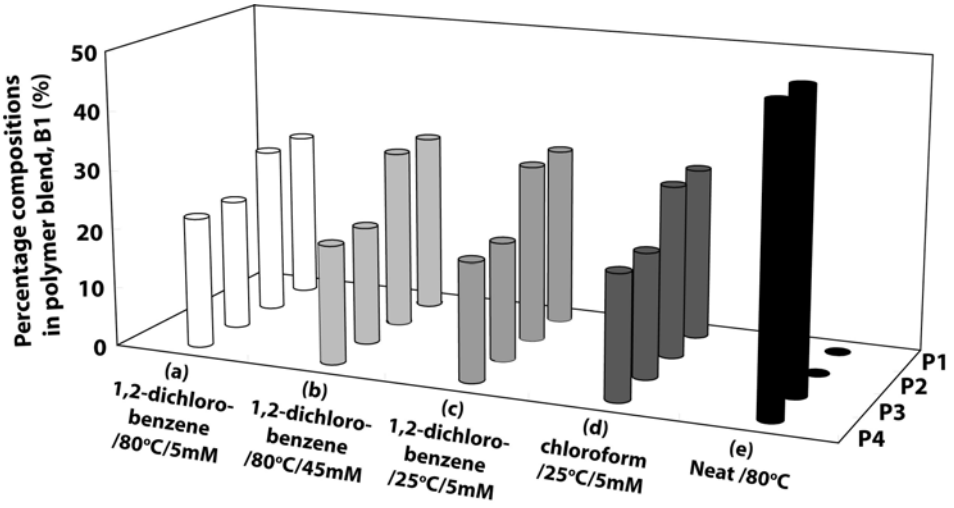
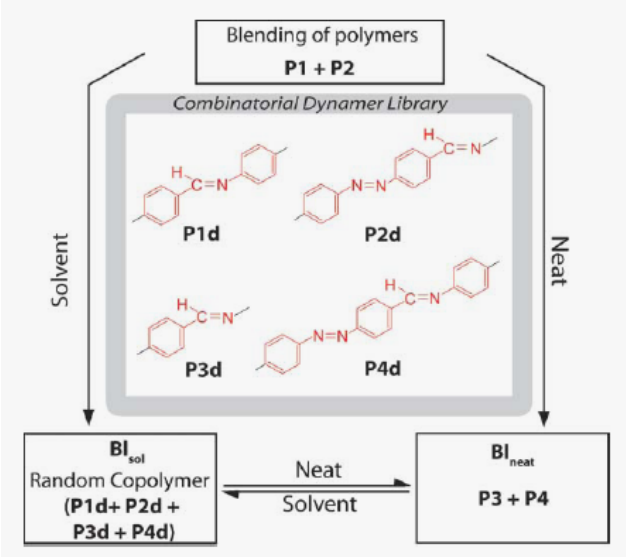


Figure 5-5. Summary of the constitutional dynamic behaviour of of the homopolymers, **P1** and **P2**, under two different kind of stimuli - solvated condition (deuterated 1,2-dichlorobenzene) at 80ºC and neat condition at 80ºC.

Adaptation of the constitutional dynamic behavior of the present polymer system was demonstrated by blending of the homopolymers, **P1** and **P2**, neat, *i.e.* in the absence of solvent (Figure 5-5). Neat polymer blend $\mathbf{B1_{neat}}$ was prepared by simply stirring the homopolymers, **P1** and **P2**, in an equimolar ratio at 80ºC for 24 h. ^{1}H-NMR analyses enabled identification of the different links between aldehydes and amines of the blend $\mathbf{B1_{neat}}$ ($\mathbf{B1_{neat}}$ conditions**:** ^{1}H NMR spectrum was taken within 10 mins of dissolving neat blend polymer). The spectrum of blend $\mathbf{B1_{neat}}$ showed only two characteristic imine proton signals which were assigned to 1) a new connection between **Ald1** and **Am1**, *i.e.* **P3** domain (at 8.14 ppm); and 2) another new connection between **Ald2** and **Am2**, *i.e.* **P4** domain (at 8.42 ppm and 8.51 ppm). An important deduction is that, under neat conditions, the dynamic system reshuffled and exchanged in such a way that **P1** and **P2** domains were completely eliminated from the constitution of the system (Fig. 5f). Random copolymer $\mathbf{C1_{neat}}$ was also prepared from the 4 kinds of monomers (**Ald1**, **Ald2**, **Am1** and **Am2**) in equimolar ratios in neat conditions at 80ºC with 1% acid catalyst. The proton signals found in $\mathbf{C1_{neat}}$ were exactly the same as those in $\mathbf{B1_{neat}}$ confirming that the blending reaction in $\mathbf{B1_{sol}}$ had reached its equilibrium. Control polymer blend ($\mathbf{B2_{neat}}$) was prepared as the same way as the polymer blend $\mathbf{B1_{neat}}$ by replacing the starting homopolymers to **P5** and **P6**. In this case, however, no significant constitutional adaptation was found in the blend $\mathbf{B2_{neat}}$ when comparing with that of the $\mathbf{B2_{sol}}$.

Four domains were found in the $\mathbf{B2_{neat}}$ namely those of **P5**, **P6**, **P7** and **P8** types. The percentage composition of **P5:P6:P7:P8** domains in the blend $\mathbf{B2_{neat}}$ was about 2.8:2.8:2.2:2.2.

The parent dynamers, **P1** and **P2,** showed adaptive constitutional behavior in solution as well as in their neat forms. The dynamic character of the resulting polymer blends, $\mathbf{B1_{sol}}$ or $\mathbf{B1_{neat}}$, was demonstrated by their constitutional interconversion upon dissolution (+stimulus solvent) or solvent removal by evaporation (+stimulus neat). Deuterated chloroform was used to dissolve the blend $\mathbf{B1_{neat}}$ at *ca.* 10 mM; after 24 h (long enough for equilibration) the chloroform mixture was dried out to give the neat polymer blend. During the course of the experiment, ^{1}H-NMR spectra were used to identify the constitutional changes of the polymer blend. Figure 5-6 shows the four cycles of constitutional changes in the polymer samples in solution (+stimulus solvent) and when neat (+stimulus neat). The results showed five distinctive features of this adaptive behavior: 1) when neat, the offspring dynamers adapted, reshuffled and exchanged their monomers in such a way that only **P3** and **P4** links were present, *i.e.* **P1** and **P2** domains were completely extinguished; 2) in solution, the offspring dynamers re-adapted, reshuffled and re-exchanged their monomers in such a way that the four imine domains of **P1, P2, P3** and **P4** types were produced in a ratio of 3:3:2:2; 3) the half-life of the adaptive behaviors under the solvated at r. t. and neat conditions at 80 °C is about 150 minutes; and 4) this constitutional dynamic interconversion was completely reversible.



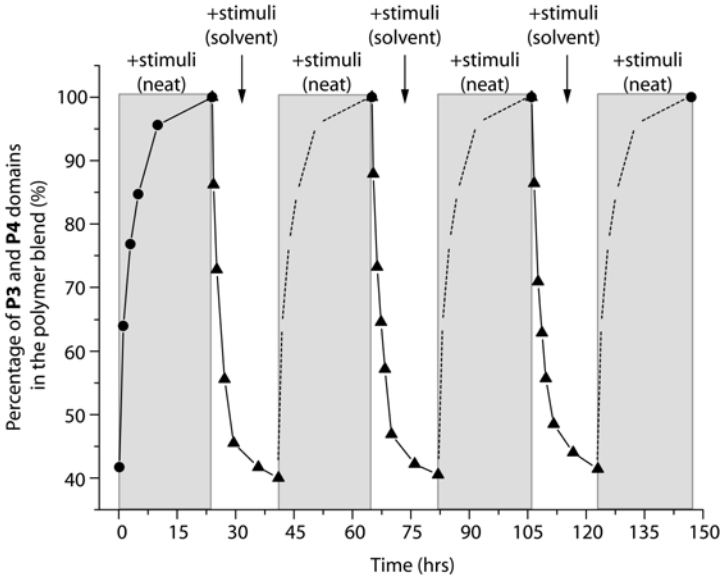


Figure 5-6. Constitutional interconversion of the polymer blend, **B1**, during applying $CDCl_3$ (+stimuli solvent) and under neat condition (+stimuli neat). The percentage of **P3** and **P4** domains are calculated from the integration from the ^1H NMR of blends in $CDCl_3$ (ca. 10 mM).

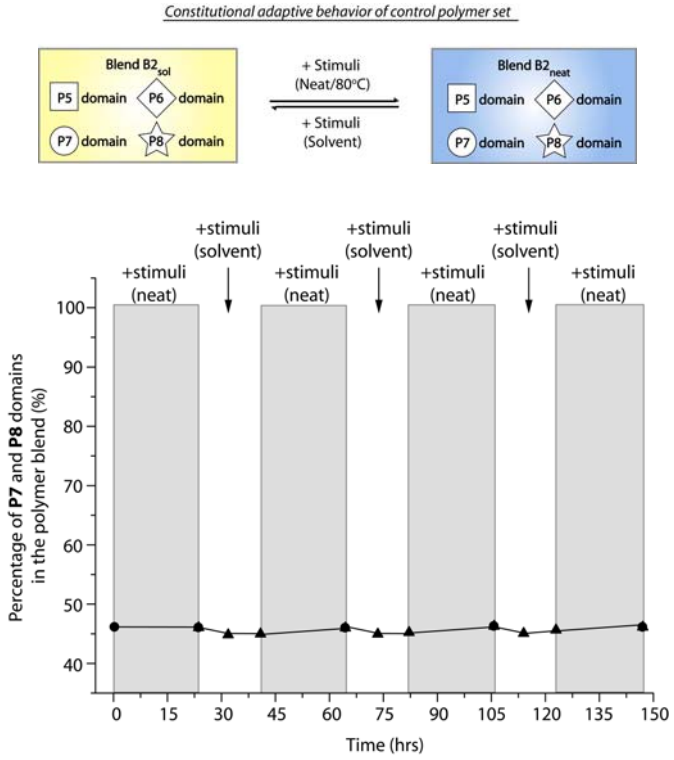


Figure 5-7. Constitutional interconversion of the control polymer blend, **B2**, in $CDCl_3$ (+stimulus solvent) and under neat conditions (+stimulus neat). The percentage of **P7** and **P8** domains are calculated from the integration from the ^1H NMR peaks of the blends in $CDCl_3$ (ca. 10 mM).

The same experiments were performed using the control polymer blend (**B2$_{neat}$**) by preparing first a *ca* 10 mM solution in $CDCl_3$ (+stimulus solvent), then, after 24 hours, evaporating this solution to dryness (+stimulus neat). Figure 5-7 shows the four cycles of the constitutional changes of the control polymer blend during these processes. The results showed that there was no constitutional adaptive ability of the control polymer blend. The percentage composition of the four domains **P5:P6:P7:P8** domains in the control blend remained the same at about 2.8:2.8:2.2:2.2. The constitutional evolution of the dynamic polymer systems can be explained by influence of the mesogenic domains involving the conjugated rigid three benzene rings of **P4** in the CDPL (Figure 5-5). The sole existence of **P3** and **P4** domains in the polymer blend processed under neat conditions is a good starting point to understand the adaptive phenomenon of the systems. Neat, at 80ºC, CDPL members containing **P1**, **P2** and **P3** domains would favour the formation of isotropic liquids while the **P4** domain would favour the formation of a crystalline solid, *i.e.* a thermodynamically more stable phase. We conclude that this strong driving force shifted the equilibria within the CDPL to favour **P4** domains, thus agonistically producing **P3** domains. Figure 5-8 clearly shows that both neat parent dynamers, **P1** and **P2**, existed as isotropic liquids at 80ºC while an anisotropic phase grew up after bringing them into contact under the same conditions.

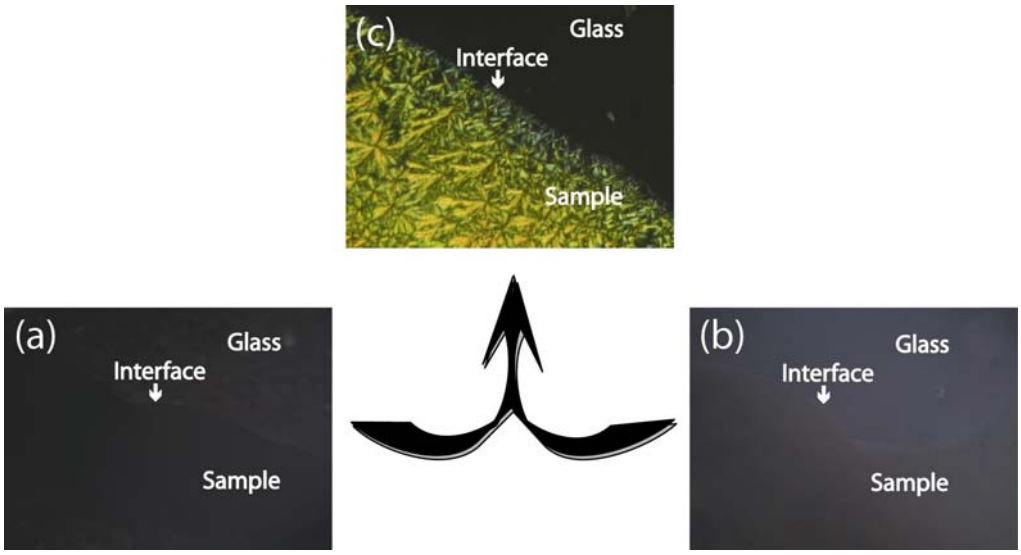


Figure 5-8. Photographs taken by polarized light microscopy in transmission mode (x40) at 80ºC (a) isotropic phase of the homopolymer **P1** at 80ºC, (b) isotropic phase of the homopolymer **P2** at 80ºC and (c) anisotropic phase of the polymer blend **B1$_{neat}$** at 80ºC.

In comparison, when the polymer blend $\mathbf{B1_{neat}}$ was dissolved in an organic solvent, the influence of the mesogenic centres was modified. Consequently, the dynamic system re-adapted, reshuffled and re-exchanged its monomers in such a way that all four imine domains of **P1, P2, P3** and **P4** types became present. The results of the control experiments support this argument. Due to the fact that all members of the control set CDPL, **P5-P8**, existed as isotropic liquids at 80ºC, this amorphous state of the polymer blend $\mathbf{B2_{neat}}$ was as random as the polymer blend $\mathbf{B2_{sol}}$**.** The absence of the diazobenzene unit led to no overwhelming influence favouring the formation of an especially stable liquid crystalline phase under maximally concentrated (neat) conditions.

The homopolymers **P3** and **P4** were cast separately onto a mica surface from CH_2Cl_2 solutions. Figure 5-9 shows the topographical AFM images of the two homopolymers cast separately: **P3** exhibited the tendency to aggregate in globules on the mica surface (Figure 5-9 left) while **P4** formed a fragmented layer on the substrate (Figure 5-9 right). The average height (h) of the **P3** globules was 6 nm while the **P4** broken layer was found to have an average height of 2 nm. In contrast, when the blend $\mathbf{B1_{neat}}$ was cast on mica from CH_2Cl_2 solutions, globular aggregates were found lying on top of a fragmented layer. Figure 5-10 shows a AFM topographical image of blend $\mathbf{B1_{neat}}$. The phase image in Figure 5-10 reveals a different contrast of the two observed architectures (*i.e.* the fragmented layer and the globular aggregates), providing evidence for different viscoelastic properties. Furthermore, the dimensions and in particular the height of the observed architectures in the AFM topographical image of blend $\mathbf{B1_{neat}}$ were comparable with the ones measured for the homopolymers shown in Figure 5-9: the globules' height in blend $\mathbf{B1_{neat}}$ was measured to be 5 nm while the height of the fragments was found to be 2 nm. Therefore the globular aggregates found for the blend $\mathbf{B1_{neat}}$ can be ascribed to the homopolymer **P3** and the fragmented layer to the homopolymer **P4**.

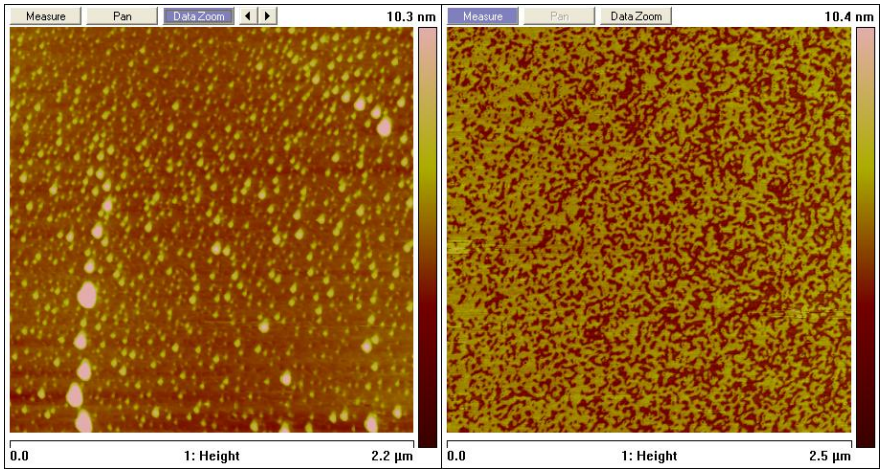


Figure 5-9. Intermittent contact AFM topographical images of 0.4 mM in CH_2Cl_2 solutions cast on mica: (left) the homopolymer **P3** and (right) the homopolymer **P4**.

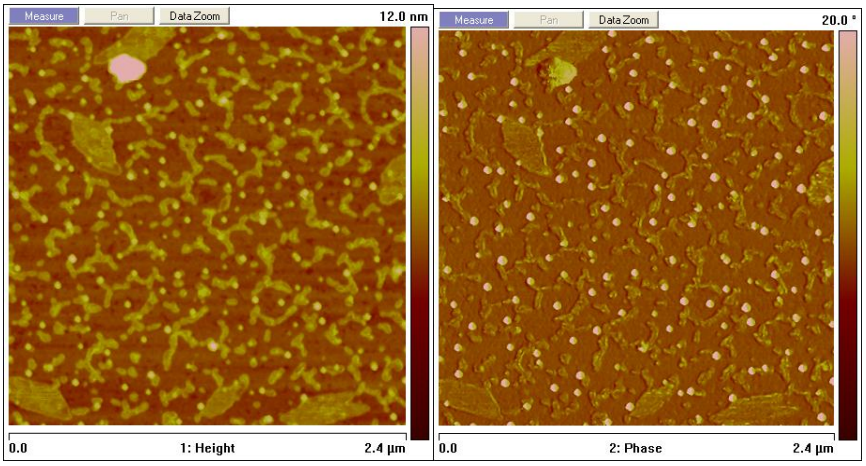


Figure 5-10. Intermittent contact AFM images of the blend $\mathbf{B1}_{\mathbf{neat}}$ with 0.4 mM in CH_2Cl_2 solution cast on mica at RT: (left) topographical image; (right) phase image.

5.4 Conclusions

The processes described here present several aspects of adaptive behavior in a system of covalent dynamic polymers in response to a change in physical state (Figure 5-6).

(1) The parent dynamers **P1** and **P2** generated two offspring dynamer blends, a random copolymer $\mathbf{Bl_{sol}}$ when mixed in solution, and a mixture $\mathbf{Bl_{neat}}$ of the two polymers **P3** and **P4** in neat conditions.

(2) This adaptive behavior is retained in the generation of the offspring systems $\mathbf{B1_{sol}}$ and $\mathbf{Bl_{neat}}$, which can be reversibly switched over several dissolution–evaporation cycles.

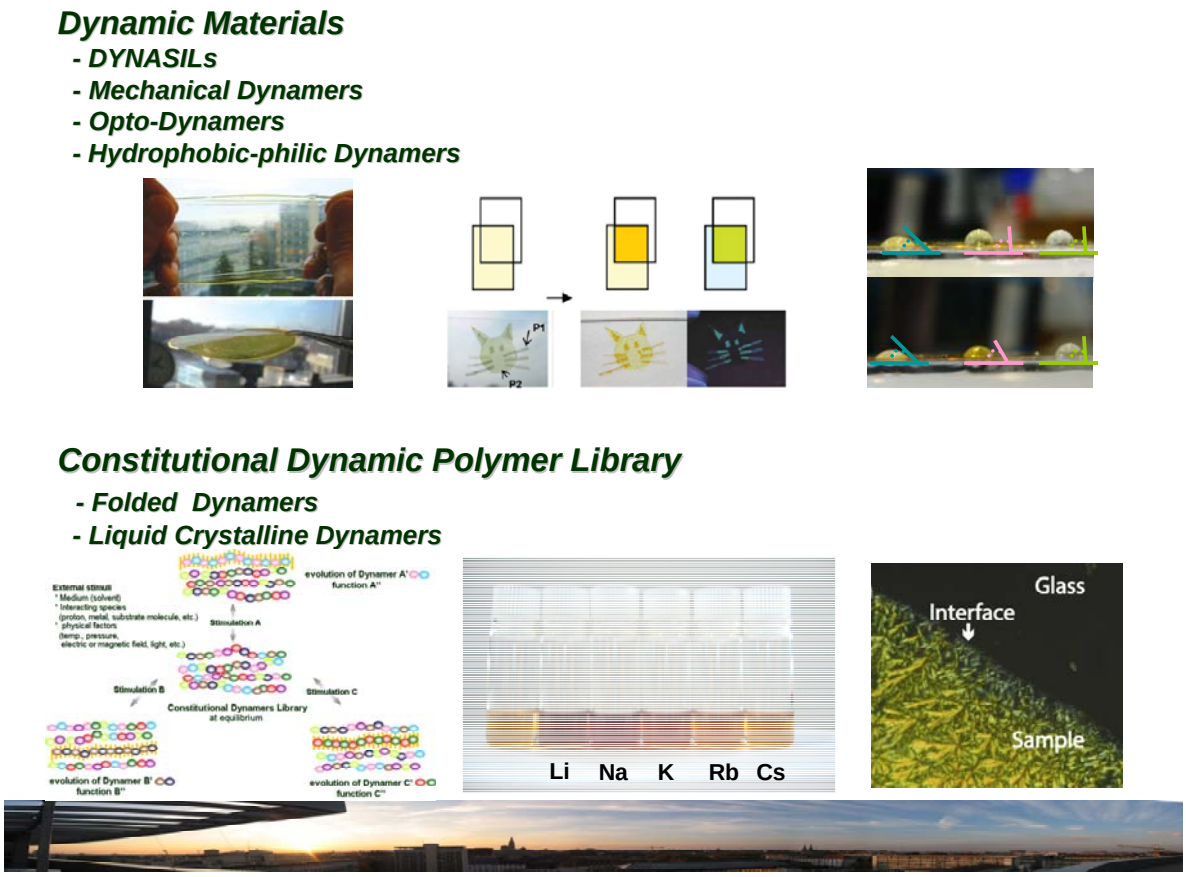
(3) Formation of $\mathbf{Bl_{sol}}$ from (**P1** + **P2**) or from $\mathbf{Bl_{neat}}$ amounts to a randomization giving a copolymeric material containing all four monomeric components **Am1**, **Am2**, **Ald1** and **Ald2**.

(4) Formation of $\mathbf{Bl_{neat}}$ from the $\mathbf{Bl_{sol}}$ random copolymer in the neat state upon solvent removal amounts to a derandomization giving a mixture of only the polymers **P3d** and **P4d**. This implies a process of self-selection under the pressure of the formation of an organized phase, the crystalline copolymer **P4**.

(5) The system described here represents a constitutional dynamic material displaying adaptive behavior by constitutional dynamic interconversion between two constitutional states in response to a change in physical stimuli (‘‘solution’’ or ‘‘neat’’ conditions).

The present results demonstrate the possibility of generating dynamic imine polymers which are able to show constitutional dynamics by reshuffling of the members in the polymer chains by exchange of dialdehyde and diamines monomers. More importantly, the dynamics of the dynamers can adapt to different environmental condition by stabilizing/destablizing the mesomorphic states of CDPL’s members.

CHAPTER 6 : Conclusions and Outlook



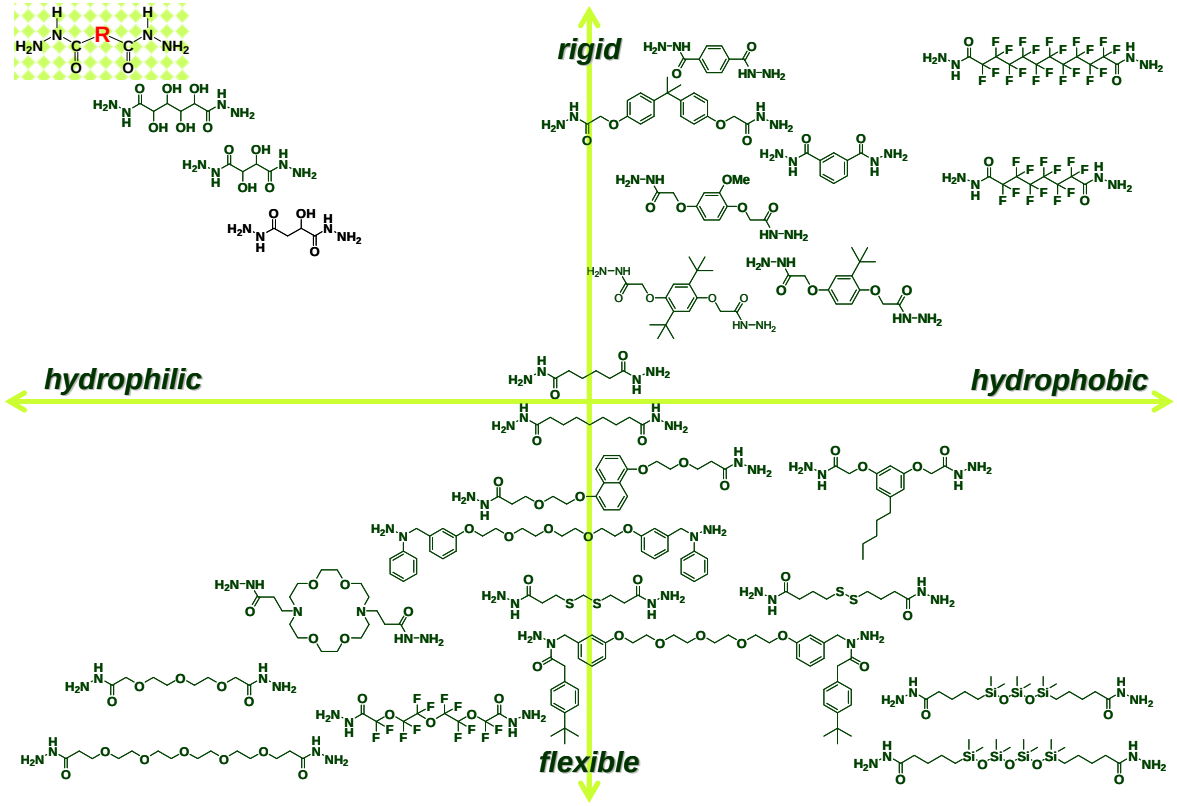
A number of important conclusions can be drawn from the development of various aspects of dynamer chemistry described in this thesis.

The first development was of various *DYNASILs* involving an oligodimethylsiloxane based on reversible acylhydrazone, hydrazone and imine bonds and forming oil, gum and film-like materials, capable both of undergoing component exchange due to their dynamic nature as well as of showing the properties of conventional polydimethylsiloxane polymers such as flexibility (low Tg), heat stability, and hydrophobicity.

Based on these systems, dynamers showing a variety of mechanical behaviour and different properties along the hydrophobic/hydrophilic spectrum were developed. Thus, the properties of the *DYNASILs* could be varied from mechanically soft to hard and from hydrophobic to hydrophilic by incorporation of different monomeric components into the

original polymer through dynamic exchange process based on CDC (Constitutional Dynamic Chemistry).

Dynamic optical materials, termed optodynamers, also showed color and fluorescence changes through bond exchange and component recombination, exhibiting the potential for applications as molecular sensors or photoactive devices through the modulation of their electronic (redox modifications, conductivity) and magnetic properties.



The structure of bis-hydrazide and bis-hydrazine monomers synthesized until now are shown here with the axis of hardness, and a hydrophilicity. By these monomers, almost all the analogue of conventional polymers in industry can be synthesized and dynamers with new function such as ion transport, electrical and double dynamic can be also designed. The monomers library may enable us to design functional smart dynamic materials on market in near future.

And then we successfully extended DCC (Dynamic Combinatorial Chemistry) into a dynamic polymer study (Scheme 4-1 in Chapter 4), demonstrating the concept of CDPL

(Constitutional Dynamic Polymer Library) for multifunctional adaptive materials through studies of dynamer folding and mesomorphism. The present CDPL involved dynamer folding driven by the double supramolecular interactions of alkali metal coordination and D/A stacking interactions and exhibited adaptive behavior by constitutional recombination, with the recognition of alkali metal ions generating different optical signals (displaying a sensing function) due to constitutional modification. Numerous variations may be envisaged, such as extensions to other types of metal ions or to organic guests, incorporation of other components, leading to induction of novel properties.

Another CDPL system was observed through the mesomorphism of the dynamer, termed a "liquid crystalline" dynamer. The adaptive behavior of these systems was the result of a process of self-selection leading to the formation of a (liquid) crystalline phase in response to different environmental conditions (changes in physical stimuli due to being under ''solution'' or ''neat''conditions), which stabilize/destabilize the mesomorphic states of the CDPL members. The present study can be applied to methodologies for crystallization control in general polymer science (polyester, polyamide etc…) through chemical exchange reaction, which drives the constitutional evolution of polymers and results in controlling crystallinity, crystalline ratio and rate in a new way in comparison to a conventional physical treatment such as an annealing.

These properties of dynamic polymers are thus illustrative of the potential and various features which evolve under the pressure of external factors, defining a new type of smart material based on change in chemical constitution. Such materials should be able to generate specific responses to external stimuli and thereby to exhibit several different kinds of functions through the implementation of dynamic constitutional variation and adaptation. We envisage that they point towards the emergence of adaptive materials science and technologies.

CHAPTER 7: Experimental Part

7. 1 General Method and Materials

Chemical reagents were purchased from commercial suppliers (ABCR, Acros, Aldrich, Fluka, Gelest and TCI) and used without further purifications unless otherwise noted.

Solvent. Water was deionized by using Millipore Elix 10 (reverse osmosis). Anhydrous DMF and MeOH were purchased from the Aldrich. DCM was dried either over phosphorus pentachloride or by passing through a column of activated alumina. THF was dried either over sodium in the presence of benzophenone or by passing through a column of activated alumina. Metal salts were dried by gentle heating (60°C) under vacuum for a few hours.

Glass ware. All non-aq. reactions were performed under argon or nitrogen atmosphere. Solvents were removed by concentration in a rotary evaporator and drying under high vacuum.

Thin layer chromatography (TLC) was performed with silica supported on aluminium sheets (Silica gel 60 F254, Merck) or neutral alumina supported on aluminium sheets (Aluminium oxide 60 F254, Merck). **Flash Column chromatography** was carried out using silica gel (Si 60, 40-63 mm, Merck) or neutral alumina (Aluminium oxide 90 active neutral, Activity stage I, Merck) on a classical glass column. Amine, hydrazine and hydrazide compounds were detected by staining with anisaldehyde solution (p-anisaldehyde, AcOH and conc. H_2SO_4 in 95% ethanol) and all aromatic compounds were visualized with a UV lamp.

^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz. Chemical shifts are given in ppm. Residual solvent peaks were taken as reference ($CHCl_3$: 7.26 ppm, d6-DMSO: 2.50 ppm, CD_3CN: 1.94 ppm and CD_3OD: 3.31 ppm). The coupling constants J are given in Hz and the resonance multicity is described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qt), sextet (st), doublet of doublet (dd), doublet of doublet of doublet (ddd), doublet of triplet (dt), multiplet (m) and broad (br). The assigned proton is written in italic. All spectra were recorded at 25°C, unless otherwise noted. When noted, spectra were recorded on a 500 MHz Bruker Avance 500 spectrometer at 500 MHz.

^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at 100 MHz. All spectra were measured in broadband decoupled conditions. Chemical shifts are quoted in ppm, referenced to the appropriate solvent peak ($CHCl_3$: 77.0 ppm, d6-DMSO: 39.52 ppm, CD_3CN: 1.24 ppm and CD_3OD: 49.05 ppm). For the mixtures of solvent, the calibration was done using the residual solvent. peak of: CD_3CN in the case of CD_2Cl_2/CD_3CN mixtures and d6-DMSO in the case of CD_2Cl_2/DMSO mixtures.

2D NMR (COSY, ROESY, NOESY) experiments were recorded either on a Bruker Avance 400 spectrometer or, when noted, on a 500 MHz Bruker Avance 500 spectrometer.

Mass spectrometry. LC/MS was performed using reverse phase HPLC (C18 solid phase, 5 mm particles size, 2.1 x 5 mm column, eluent: MeOH with 0.01% TFA, 0.7 mL/min flow, diode array detector) combined with a Thermo MSQ quad electrospray mass spectrometer using positive detection mode. **High Resolution ElectroSpray Ionization Mass Spectrometry (HR-ESI-MS) analyses** were performed on a Bruker Micro TOF mass spectrometer at the Service de Spectrometrie de Masse, Universite Louis Pasteur. The given value represents the largest peak. The observed pattern was always confirmed to the theoretical pattern. The molecular ion (*M*) is reported in *m/z* units

Absorption spectra were recorded on a Varian CARY 3 spectrophotometer in UV-Visible range. A 1 cm width cuvette was used except otherwise noted. Wavelengths are reported in nm and ε in $M^{-1}.cm^{-1}$.

Fluorescence measurements were performed on a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer equipped with a sample holder for solid state.

X-ray crystallography was performed at the Service de Radiocristallographie, Universite Louis Pasteur. The crystals were placed in oil and a single crystal was selected, mounted on a glass fiber and placed in a low temperature nitrogen stream. The X-ray diffraction data were collected on a Nonius-Kappa-CCD diffractometer with a graphite monochromatized Mo-Ka radiation (l=0.71073 A).

Elemental analyses were performed at the Service de Microanalyse, Universite Louis Pasteur. Data are given in percentage.

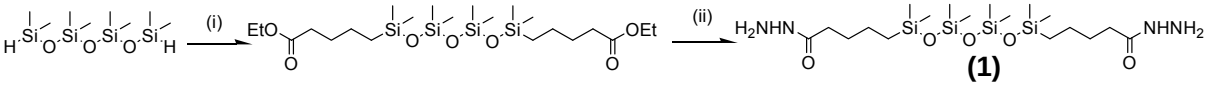
Differential Scanning Calorimetry (DSC) were performed at a rate of 10 °C/min.

Gel permeation chromatography were measured by analytical department in Mitsui chemicals inc., Japan or by the Service de GPC, Centre National de la Recherche Scientifique, CNRS, Strasbourg to determine molecular weights.

7. 2 Synthetic Procedure and Characterization

CHAPTER 2

1,7-bis(5-hydrazino-5-oxopentyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (1)



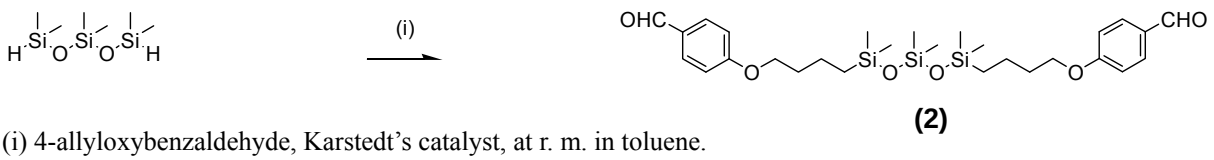
(1)

(i) ethyl pent-4-enoate, Karstedt's catalyst, at r. m. in toluene; (ii) hydrazine monohydrate, refluxed in EtOH.

To a solution of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (5.00 g, 17.69 mmol) and Karstedt catalyst[1] (100ppm/Si-Hmol) in toluene (80 ml) was slowly added ethyl pent-4-enoate (5.35 g, 41.74 mmol) using a pressure-equalizing additional funnel at room temperature under Ar atmosphere, then the mixture was stirred for one night. The reaction was monitored by ^{1}H NMR analysis. After the reaction was complete, toluene and excess amount of ethyl pent-4-enoate was removed by evaporation, and the residue was passed through a short silica gel column (eluent: ethyl acetate) to separate the Karstedt catalyst. The volatiles were then removed in vacuo to give the purified intermediate (9.00g, 16.70 mmol) 94% yield as a transparent and colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 4.12 (q, ^{3}J = 7.0Hz, 4H), 2.29 (t, ^{3}J = 7.3Hz, 4H), 1.65 (qui, ^{3}J = 7.6Hz, 4H), 1.35 (tt, ^{3}J = 7.6Hz, ^{3}J '= 8.2Hz, 4H), 1.25 (t, ^{3}J = 7.0Hz, 6H), 0.54 (t, ^{3}J = 8.3 Hz, 4H), 0.06 (s, 12H), 0.01 (s, 12H).

To a solution of imtermediate (9.00 g, 16.70 mmol) in EtOH (100 ml) was added dropwise hydrazine monohydrate (8.36 g, 166.99 mmol), followed by refluxing for 2 days under Ar atmosphere. The volatiles were removed under vacuo and the residue was purified by column chromatography on silica gel (eluent: EtOH/dichloromethane, 1:4) to give the desired compound **(1)** in 59% yield as a transparent and colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.15 (br, 2H), 3.92 (br, 4H), 2.16 (t, ^{3}J = 7.8Hz, 4H), 1.66 (qui, ^{3}J = 7.4Hz, 4H), 1.35 (tt, ^{3}J = 7.4Hz, ^{3}J '= 8.2Hz, 4H), 0.54 (t, ^{3}J = 8.2Hz, 4H), 0.06 (s, 12H), 0.02 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 174.23, 34.47, 29.27, 23.19, 18.14, 1.34, 0.31; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{46}N_4O_5Si_4Li_1$ $[M+Li]^+$ 517.2700, found 517.2693; elemental analysis calcd (%) for $C_{18}H_{46}N_4O_5Si_4$: C 42.31, H 9.07, N 10.97; found: C 41.71, H 9.33, N 10.64.

1,5-bis(3-(4-formylphenoxy)propyl)-1,1,3,3,5,5-hexamethyltrisiloxane (2)

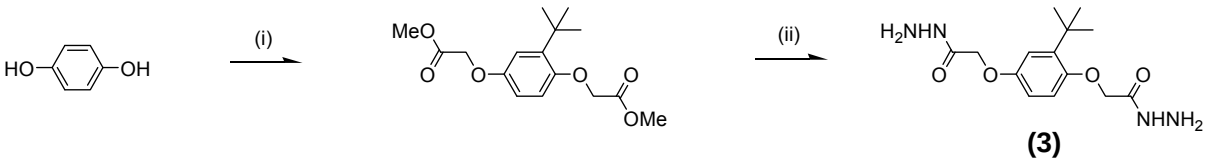


(2)

(i) 4-allyloxybenzaldehyde, Karstedt's catalyst, at r. m. in toluene.

To a solution of 1,1,3,3,5,5-hexamethyltrisiloxane (4.26 g, 20.43 mmol) and Karstedt catalyst[1] (100 ppm/Si-H mol) in toluene(80 ml) was slowly added 4-(but-3-enyloxy)benzaldehyde (9.00 g, 51.08 mmol) using a pressure-equalizing additional funnel over 30 min at room temperature under Ar atmosphere, then the mixture was stirred for one night. The reaction was monitored by ^{1}H NMR analysis. After the reaction was complete, toluene was evaporated and the residue was subjected to column chromatography on silica gel (eluent: cyclehexane/DCM, 1:3) to give desired compound **(2)** (4.51 g, 8.46 mmol) in 41% yield as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 9.87 (s, 2H), 7.82 (d, ^3J = 8.8Hz, 4H), 6.98 (d, ^3J = 8.8Hz, 4H), 3.99 (t, ^3J = 6.7Hz, 4H), 1.89-1.81 (tt, ^3J = 6.8Hz, $^3J'$ = 8.8Hz, 4H), 0.69 (t, ^3J = 8.8Hz, ^2J = 3.2Hz, 4H), 0.12 (s, 12H), 0.05 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 190.95, 164.41, 132.12, 129.90, 114.88, 68.16, 32.68, 19.88, 18.07, 1.45, 0.35; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{44}O_6Si_3Li_1$ $[M+Li]^+$ 567.2601, found 567.2664; elemental analysis calcd (%) for $C_{26}H_{40}O_6Si_3$: C 58.61, H 7.57; found: C 58.46, H 7.93.

***tert*-butyl-2,5-bis(2-hydrazino-2-oxoethoxy)benzene (3)**



(3)

(i) methyl bromoacetate, K_2CO_3, at 80 °C in DMF; (ii) hydrazine monohydrate, at r. m. in MeOH.

tert-butylhydroquinone (19.93 g, 120 mmol) and methyl bromoacetate (26 ml, 275 mmol) were added to a suspension of K_2CO_3 (44.3 g, 321 mmol) in acetone (150 ml) and the stirred mixture was heated to reflux for 12 h under Ar atmosphere. The mixture was taken up in H_2O (200 ml) / $CHCl_3$ (300 ml). The organic layer was washed with H_2O (200 ml) 4 times, dried

over Na_2SO_4 and the solvents were evaporated to dryness. The crude product was roughly purified by column chromatography on silica gel (eluent: CH_2Cl_2) affording roughly purified imtermediate (26.1 g, 84 mmol) in 70% yield as a light orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 6.97 (d, $^{>3}J$ = 2.4 Hz, 1H), 6.59–6.65 (m, 2H), 4.60 (s, 2H), 4.58 (s, 2H), 3.81 (s, 6H), 1.39 (s, 9H).

The intermediate (11.05 g, 35.6 mmol) in MeOH (40 ml) was added dropwise into a stirred mixture of hydrazine monohydrate (57.4 g, 1.15 mol) in MeOH (100 ml) at room temperature. The mixture was stirred for 1 h under Ar atmosphere, then the MeOH was removed in vacuo giving a two phases solution. The upper phase of the solution was roughly purified by column chromatography on silica gel (eluent: $CHCl_3$/MeOH, 10:1) to give crude product as a viscous oil. The crude product was recrystallized from mixture of $CHCl_3$ and n-hexane, followed by purification of column chromatography on silica gel (eluent: $CHCl_3$/MeOH, 10:1) affording the desired compound **(3)** (7.08 g, 22.8 mmol) in 64 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.98 (br, 1H), 7.74 (br, 1H), 6.89 (d, $^{>3}J$ = 2.9 Hz, 1H), 6.70 (d, ^3J = 8.8 Hz, 1H), 6.69 (dd, ^3J = 8.8 Hz, $^{>3}J$ = 2.9 Hz, 1H), 4.52 (s, 2H), 4.47 (s, 2H), 3.96 (br, 4H), 1.35 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 169.16, 152.12, 151.49, 140.82, 115.37, 114.37, 111.54, 68.47, 67.63, 35.04, 30.04; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{22}N_4O_4Li_1$ $[M+Li]^+$ 317.1796, found 317.1763; elemental analysis calcd (%) for $C_{28}H_{46}N_8O_9$: C 52.65, H 7.26, N 17.54; found: C 52.38, H 7.05, N 17.81.

1.10-bis(4-formyl-3-methoxyphenoxy)decane (4)

(4)

(i) 4-hydroxy-2-methoxybenzaldehyde, K_2CO_3, at 80 °C in DMF.

To a suspension of K_2CO_3 (4.60 g, 33.3 mmol), KI (110.0mg, 0.7 mmol) and 4-hydroxy-2-methoxybenzaldehyde (3.00 g, 19.7 mmol) in DMF (40 ml) and was added 1.10-dibromodecane (2.00 g, 6.7 mmol) under nitrogen atmosphere. The mixture was allowed to heat to 80 °C and stirred for 24 h. The reaction was monitored by silica gel

TLC(eluent:5v% ethyl acetate in $CHCl_3$). After completion of the reaction, to the reaction mixture was added 40 ml of $CHCl_3$, and then the resulting precipitate was removed by filtration. The filtrate was evaporated under reduced pressure, and the residue was subjected to a silica gel column chromatography to give product **(4)** (1.52 g) in 52 % yield as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.31 (s, 2H), 7.83 (d, ^3J = 8.7Hz, 2H), 6.56 (dd, ^3J = 1.8 Hz, *J'* = 8.7 Hz, 2H), 6.47 (d, *J* = 1.9 Hz, 2H), 4.05 (t, ^3J = 6.5 Hz, 4H), 3.93 (s, 6H), 1.83 (qui, ^3J = 6.5 Hz, 4H), 1.49 (m, 4H), 1. 38 (b, 8H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 188.46, 165.94, 163.76, 130.88, 119.06, 106.30, 98.50, 68.56, 55.73, 29.60, 29.46, 29.22, 26.10; HRMS (ESI): *m/z* calcd for $C_{26}H_{34}O_6Na_1$ $[M+Na]^+$ 465.2248, found 465.2200; elemental analysis calcd (%) for $C_{26}H_{34}O_6$: C, 70.56, H, 7.74; found: C 70.51, H 7.53.

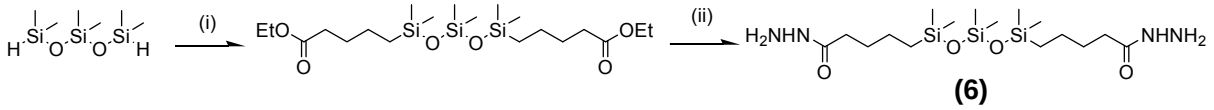
bis(2-(4-formyl-3-methoxyphenoxy)ethyl)ether (5)

(5)

(i) 4-hydroxy-2-methoxybenzaldehyde, K_2CO_3, at 80 °C in DMF.

4-hydroxy-2-methoxybenzaldehyde (2.33 g, 15.3 mmol) and 2–chloroethoxyether (1.05 g, 7.3 mmol) were added to a suspension of K_2CO_3 (5.19 g, 37.6 mmol) and NaI (3.07 g, 20.5 mmol) in DMF (20 mL) and the stirred mixture was heated to 90 °C for 17 h under argon atmosphere. The mixture was taken up in H_2O (500 ml) and extracted with $CHCl_3$ (100 ml) 5 times. The combined organic layer (about 500 ml) was washed with H_2O (100 ml) twice, dried over Na_2SO_4 and the solvents were evaporated to dryness to give a slightly orange powder (2.52 g). The powder was recrystallized from mixture of $CHCl_3$ and acetone to give the desired compound **(5)** (1.91 g, 5.1 mmol) in 70 % yield as a white powder. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 10.16 (s, 2H), 7.66 (d, ^3J = 8.8 Hz, 2H), 6.69 (d, ^3J = 2.4 Hz, 2H), 6.67 (dd, *J* = 8.8 Hz, *J'* = 2.4 Hz, 2H), 4.27 (t, ^3J = 4.4 Hz, 4H), 3.88 (s, 6H), 3.86 (t, ^3J = 4.4 Hz, 4H); elemental analysis calcd (%) for $C_{20}H_{22}O_7$: C 64.16, H 5.92; found: C 63.97, H 5.76.

1,5-bis(5-hydrazino-5-oxopentyl)-1,1,3,3,5,5- hexamethyltrisiloxane (6)



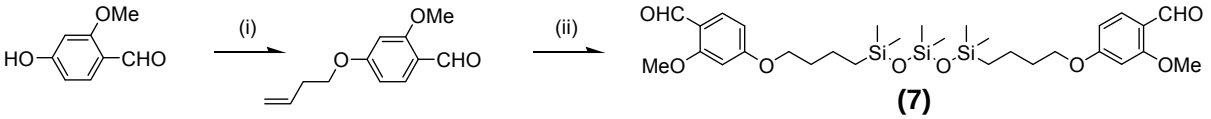
(6)

(i) ethyl pent-4-enoate, Karstedt's catalyst, at r. m. in toluene; (ii) hydrazine monohydrate, refluxed in EtOH.

To a solution of 1,1,3,3,5,5,-hexamethyltrisiloxane (6.44 g, 30.88 mmol) and Karstedt catalyst[1] (100 ppm/Si-H mol) in toluene (100 mL) was slowly added ethyl pent-4-enoate (9.50 g, 74.12 mmol) using a pressure-equalizing additional funnel at room temperature under Ar atmosphere, then the mixture was stirred overnight. The reaction was monitored by ^{1}H NMR analysis. After the reaction was complete, toluene and excess amount of ethyl pent-4-enoate was removed by evaporation, and the residue was passed through a short silica gel column (eluent: EtOAc) to remove the Karstedt's catalyst. The volatiles were then removed under reduced pressure to give the compound in 94% yield as a transparent and colorless oil. The intermediate was used for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 4.13 (q, ^{3}J = 7.0 Hz, 4H), 2.29 (t, ^{3}J = 7.3 Hz, 4H), 1.64 (qui, ^{3}J = 7.6 Hz, 4H), 1.35 (tt, ^{3}J = 7.6 Hz, ^{3}J '= 8.2 Hz, 4H), 1.25 (t, ^{3}J = 7.0 Hz, 6H), 0.54 (t, ^{3}J = 8.2 Hz, 4H), 0.05 (s, 12H), 0.00 (s, 6H).

To a solution of intermediate (10.00 g, 21.50 mmol) in EtOH (100 mL) was added dropwise hydrazine monohydrate (10.70 g, 213.74 mmol), and the mixture was then refluxed for 2 days under Ar atmosphere. The volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: EtOH/DCM, 1:8) to afford the desired product **(6)** in 60 % yield as a transparent and colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (br, 2H), 3.92 (br, 4H), 2.17 (t, ^{3}J = 7.8 Hz, 4H), 1.67 (qui, ^{3}J = 7.4 Hz, 4H), 1.36 (tt, ^{3}J = 7.4 Hz, ^{3}J '= 8.2 Hz, 4H), 0.54 (t, ^{3}J = 8.2 Hz, 4H), 0.05 (s, 12H), 0.01 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 174.28, 34.38, 29.27, 23.16, 18.16, 1.39, 0.27; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{40}N_4O_4Si_3Li_1$ $[M+Li]^+$ 443.2512, found 443.2480; elemental analysis calcd (%) for $C_{14}H_{40}N_4O_2Si_3$: C 44.00, H 9.23, N 12.83, found: C 43.82, H 9.59, N 12.71.

1.5-bis((4-formyl-3-methoxyphenoxy)butyl) 1,1,3,3,5,5-hexamethyltrisiloxane (7)



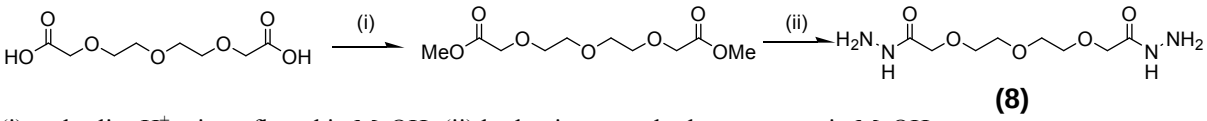
(7)

(i) 4-bromobut-1-ene, K_2CO_3, at 80 °C in DMF; (ii) 1,1,3,3,5,5-hexamethyltrisiloxane, Karstedt's catalyst, at r. m. in toluene.

To a suspension of 4-hydroxy-2-methoxybenzaldehyde (3.00 g, 19.72 mmol) and K_2CO_3 (10.90 g, 78.87 mmol) in DMF (30ml) was added 4-bromobut-1-ene (5.32 g, 39.41 mmol) under N_2 atmosphere at room temperature. The mixture was heated at 80 °C overnight and then filtered, and the filtrate was concentrated under reduced pressure. The residue was placed in DCM (50 ml) and the solution was washed with brine (20 ml × 3) and dried over anhydrous Na_2SO_3. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: DCM) to afford 4-(but-3-enyloxy)-2-methoxybenzaldehyde as a white solid in 54 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 10.28 (s, 1H), 7.81 (d, ^3J = 8.8 Hz, 1H), 6.55 (d, ^3J = 8.8 Hz, $^{>3}J$ = 2.0 Hz, 1H), 6.45 (s, $^{>3}J$ = 2.0 Hz, 1H), 5.94-5.84 (m, 1H), 5.21-5.12 (m, 2H), 4.08 (t, ^3J = 6.4 Hz, 2H), 2.56 (q, ^3J = 6.4 Hz, 2H).

To a solution of 1,1,3,3,5,5-hexamethyltrisiloxane (0.50 g, 2.40 mmol) and Karstedt catalyst[1] (100ppm/Si-Hmol) in toluene (20 mL) was added 4-(but-3-enyloxy)-2-methoxybenzaldehyde (1.09 g, 3.30 mmol) using dropping funnel at room temperature under Ar atmosphere, then the mixture was stirred overnight. The reaction was monitored by ^{1}H NMR analysis. After the solvent was removed by evaporation, the resulting residue was chromatographed over silica gel (eluent: pentane/DCM, 1:1 → 1:3), giving compound **(7)** in 81 % yield as a transparent and colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 10.28 (s, 2H), 7.80 (d, ^3J = 8.3 Hz, 2H), 6.54 (d, ^3J = 8.8 Hz, $^{>3}J$ = 2.0 Hz, 2H), 6.43 (s, $^{>3}J$ = 2.0 Hz, 2H), 4.02 (t, ^3J = 6.4 Hz, 4H), 1.82 (qui, ^3J = 6.8 Hz, 4H), 1.51 (qui, ^3J = 6.8 Hz, 4H), 0.60 (t, ^3J = 8.3 Hz, 4H), 0.09 (s, 12H), 0.03 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 188.45, 165.96, 163.76, 130.86, 119,04, 106.31, 98.47, 68.19, 55.71, 32.71, 19.89, 18.08, 1.46, 0.36; HRMS (ESI): *m*/*z* calcd for $C_{30}H_{48}O_8N_3Na_1$ $[M+Na]^+$ 643.2549, found 643.2538; elemental analysis calcd (%) for $C_{30}H_{48}O_8Si_3$: C 58.03, H 7.79, found: C 57.91, H 7.61.

Triethylene glycol bishydrazide (8)



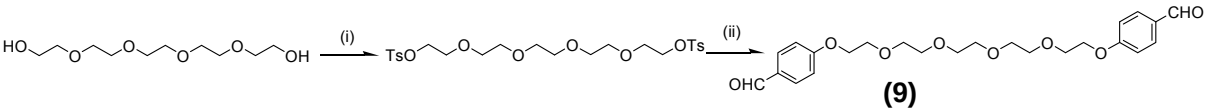
(8)

(i) amberlite-H^+ rein, refluxed in MeOH; (ii) hydrazine monohydrate, at r. m. in MeOH.

To a solution of 3,6,9,-trioxaundecanedioic acid (10.00 g, 45.01 mmol) in MeOH(100 ml) was added amberlite IR 120-H^+ form resin (5 g) as acid catalyst under N_2 atmosphere and the mixture was refluxed overnight. After the solvent was removed under reduced pressure and the residue was placed in 100 ml of DCM, and then the solution was washed with saturated $NaHCO_3$ aq. solution(30 ml × 3), brine (30 ml × 2), dried over anhydrous Na_2SO_4. Evaporation of the solvent provided the intermediate, which was used for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 4.15 (s, 4H), 3.74 (s, 4H), 3.76-3.67 (m, 8H).

To a solution of the intermediate (8.46 g, 33.81 mmol) in MeOH (100 mL) was added dropwise hydrazine monohydrate (16.92 g, 338.00 mol) at room temperature under Ar atmosphere and the mixture was then stirred overnight. After the volatiles were evaporated, the residue was purified by column chromatography on silica gel (eluent: DCM/EtOH, 3:2) to afford the product **(8)** as a transparent and colorless oil in 54 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 8.64 (br, 2H), 4.10 (s, 4H), 3.72-3.65 (m, 8H), 3.48 (br, 4H); ^{13}C NMR ($CDCl_3$): δ ppm = 170.22, 71.19, 70.45, 70.30; LCMS : m/z (%); HRMS (ESI): *m*/*z* calcd for $C_8H_{18}O_5N_4Na_1$ $[M+Na]^+$ 273.1169, found 273.1194.

1,16-bis(3-(4-formylphenoxy)tetraethylene glycol (9)



(9)

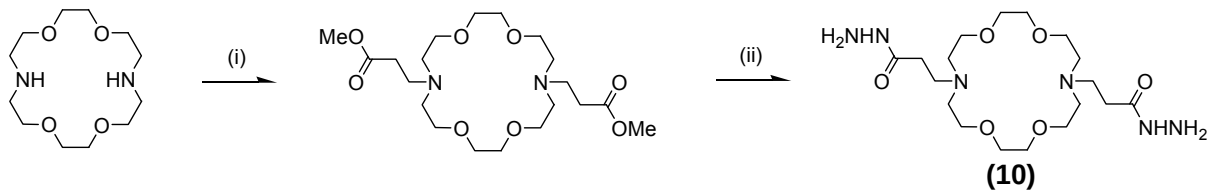
(i) tosyl chloride, triethylamine at r. m. in DCM; (ii) 4-hydroxy-benzaldehyde, K_2CO_3, at 80°C in DMF.

To a solution of tetraethylene glycol (5.00 g, 25.74 mmol) and tosyl chloride (7.36 g, 38.61

mmol) in DCM (100 ml) at 0 °C under N_2 atmosphere was added through a dropping funnel triethylamine (7.81 g, 77.22 mmol). The mixture was allowed to warm slowly to room temperature and stirred overnight, and then washed with 1N HCl aqueous solution(30 ml × 3), saturated aqueous $NaHCO_3$ (30 ml × 3) and brine (30 ml × 2) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: DCM → 80 % EtOAc in DCM) to afford tetraethylene grycol bistosylate as a white solid in 80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.80 (d, ^3J = 8.2 Hz, 4H), 7.35 (d, ^3J = 8.3 Hz, 4H), 4.15 (t, ^3J = 5.4 Hz, 4H), 3.68 (t, ^3J = 4.9 Hz, 4H), 3.61 (s, 4H), 3.58 (s, 4H), 2.44 (s, 6H).

To a suspension of 4-hydroxybezaldehyde (2.43 g, 19.90 mmol) and K_2CO_3 (5.50 g, 39.79 mmol) in DMF (50 ml) was added tetraethylene glycol bistosylate (4.00 g, 7.96 mmol) under N_2 atmosphere at room temperature. The resulting mixture was heated at 80 °C overnight and then filtered, and the filtrate was concentrated under reduced pressure. The residue was placed in DCM (100 ml) and the solution was washed with brine (30 ml × 3) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: pentane/DCM, 1: 1 → 1:3) to afford the product **(9)** as a white solid in 78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 9.86 (s, 2H), 7.81 (d, ^3J = 8.4 Hz, 4H), 7.00 (d, ^3J = 8.4 Hz, 4H), 4.19 (t, ^3J = 4.8 Hz, 4H), 3.87 (t, ^3J = 4.8 Hz, 4H), 3.73-3.67 (s, 8H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 190.87, 163.93, 132.05, 130.18, 114.97, 71.02, 70.79, 69.59, 67.87; HRMS(ESI): *m*/*z* calcd for $C_{24}H_{30}O_7Na_1$ ［M+Na］$^+$ 469.2071, found 469.2039; elemental analysis calcd (%) for $C_{24}H_{30}O_8$: C, 47.84, H, 10.92, found: C, 47.75, H, 11.02,

Kryptofix 22 bishydrazide (10)



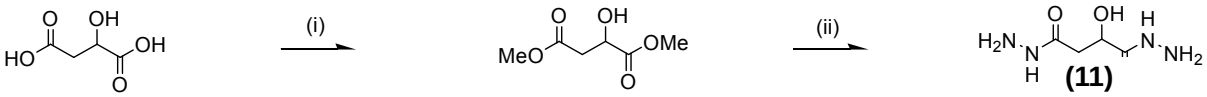
(10)

(i) methyl acrylate, at r.t. in MeOH; (ii) hydrazine monohydrate, at r. m. in MeOH.

To a solution of kryptofix 22(1,7,10,16-tetraoxa-4,13-diazacyclooctadecan) (5 g, 19.05mmol) in MeOH (100 ml) was added slowly methyl acrylate at room temperature under Ar atmosphere. The reaction mixture was stirred overnight and monitored for ^{1}H NMR. After the completion of the reaction, the volatiles were evaporated to afford the crude intermediate quantitatively, which was used for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 3.66 (s, 6H), 3.59-3.56 (m, 14H), 2.86 (t, ^3J = 7.3 Hz, 4H), 2.76 (t, ^3J = 5.8 Hz, 8H), 2.46 (t, ^3J = 7.3 Hz, 4H).

To a solution of the intermediate (7.74 g, 19.01 mmol) in MeOH (60 ml) was added dropwise hydrazine monohydrate (8.92 g, 178.19 mol) at room temperature under Ar atmosphere and the mixture was then stirred overnight. After the volatiles were evaporated, the residue was purified by recrystallization from water to afford the product **(10)** as a white solid in 64 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 9.43 (br, 2H), 4.00 (br, 4H), 3.64 (s, 8H), 3.57 (t, ^3J = 4.9 Hz, 8H), 2.67 (t, ^3J = 5.4 Hz, 4H), 2.36 (t, ^3J = 5.4 Hz, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 172.34, 70.80, 69.07, 54.24, 50.80, 32.73; HRMS(ESI): *m*/*z* calcd for $C_{18}H_{38}N_6O_6Si_3$ $[M+H]^+$ 457.2745, found 457.2681; elemental analysis calcd (%) for $C_{18}H_{31}N_6O_6$: C, 49.75, H, 8.81, N, 19.34: found: C, 49.55, H, 8.74, N, 19.24.

2-hydroxysuccinohydrazide (11)

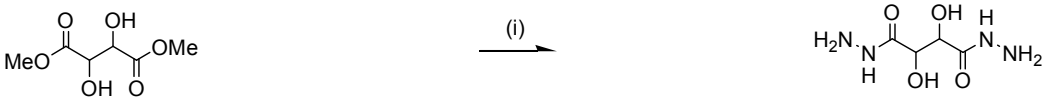


(i) amberlite-H^+ rein, refluxed in MeOH; (ii) hydrazine monohydrate, at r. m. in MeOH

To a solution of hydroxybutanedioic acid (malic acid) (1.00 g, 7.46 mmol) in MeOH (20 ml) was added amberlite IR 120-H^+ form resin (1 g) as acid catalyst under N_2 atmosphere and the mixture was refluxed overnight. After the solvent was removed under reduced pressure and the residue was placed in 20 ml of DCM, and then the organic solution was washed with saturated $NaHCO_3$ aq. solution(10 ml × 3), brine (10 ml × 2), dried over anhydrous Na_2SO_4. Evaporation of the solvent provided dimethyl 2-hydroxysuccinate in 82 % yield, which was used for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 3.66 (s, 6H), 4.69-4.65 (m, 1H), 2.92-2.78 (m, 2H).

To a solution of dimethyl 2-hydroxysuccinate (0.60 g, 3.70 mmol) in MeOH (20 ml) was added dropwise hydrazine monohydrate (1.85 g, 37.00 mmol) at room temperature under Ar atmosphere. The product precipitated readily after the addition of hydrazine monohydrate. The reaction mixture was stirred overnight and then the product was filtered, washed with MeOH and DCM and dried in vacuo at 60 °C for 12 hr to afford the monomer **(11)** as a white solid in 83 % yield. ^{1}H NMR (400 MHz, D_2O): δ ppm = 4.47-4.44 (m, 1H), 2.64-2.43 (m, 2H); ^{13}C NMR (400 MHz, D_2O): δ ppm = 173.43, 171.24, 67.76, 38.29; HRMS(ESI): *m*/*z* calcd for $C_4H_{10}N_4O_3Li_1$ $[M+Li]^+$ 169.0908, found 169.0907; elemental analysis calcd (%) for $C_4H_{10}N_4O_3$: C, 29.63, H, 6.22, N, 34.55: found: C, 29.05, H, 6.04, N, 35.03.

2,3-dihydroxysuccinohydrazide (12)



(12)

(i) hydrazine monohydrate, at r. m. in MeOH

To a solution of 2,3-dihydroxy butanedioic acid dimethylester(tartaric acid) (1.00 g, 5.61 mmol) in MeOH (20 ml) was added dropwise hydrazine monohydrate (2.81 g, 56.10 mmol) at room temperature under Ar atmosphere. The product precipitated readily during the addition of hydrazine monohydrate. The reaction mixture was stirred overnight and then the product was filtered, washed with MeOH and DCM and dried in vacuo at 60 °C for 12 hr to afford the monomer **(12)** as a white solid in 87 % yield. ^{1}H NMR (400 MHz, D_2O): δ ppm = 4.62 (s, 2H); ^{13}C NMR (400 MHz, D_2O): δ ppm = 171.82, 71.91; HRMS(ESI): *m*/*z* calcd for $C_4H_{10}N_4O_4Li_1$ $[M+Li]^+$ 185.0857, found 185.0846.

General method for the synthesis of polyhydrazone polymers

The bis-hydrazide(s) and the dialdehyde(s) at concentrations around 1 M each were dissolved in 1 : 1 stoichiometry in $CHCl_3$ and heated to 60 °C for 24 h. The solution was poured into a

petri dish of 50 mm diameter made of fluoroplastic, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared and then kept at 60 °C in vacuo for 24 h. About 140 mg of the total amounts of monomers were used to obtain the polymer film of around 0.04–0.06 mm thickness. The film thus obtained was used as such for the study of its mechanical properties. It usually contained trace amounts of $CHCl_3$, as determined by ^1H NMR.

General procedures for exchange reactions by incorporation of monomer into polyhydrazone polymer

To a solution of the polymer in $CHCl_3$ (the concentration was around 30 mM) were added equimolar amounts of the bis-hydrazide and the dialdehyde on the basis of repeating unit of the polymer, followed by addition of 2 mol% pentadecafluorooctanoic acid(with respect to the resulting total acylhydrazone bonds). The solution was heated to 60 °C for 24 h and then poured into a petri dish followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared, and then in vacuo for 24 h at the same temperature.

General procedures for the physical blending polymers

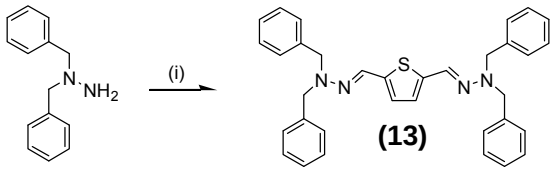
The polymer on the basis of repeating unit of the polymer were added to a solution of the polymer in $CHCl_3$, The solution was heated to 60 °C for 24 h and then poured into a petri dish followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared, and then in vacuo for 24 h at the same temperature.

Proton NMR determination of the kinetics for monomer incorporation into polymer P1

In a NMR tube was dissolved the polymer **P1** (5.0 mg) in 1 mL of a 1 : 1 mixing solution of DMSO-d_6 : CD_2Cl_2. To this solution was added either equimolar amounts of the bis-hydrazide and the dialdehyde or polymer, followed by addition of 2 mol% pentadecafluorooctanoic acid per the resulting total acylhydrazone bonds. The solution was heated to 60°C and then proton NMR was recorded.

CHAPTER 3

Compound (13)



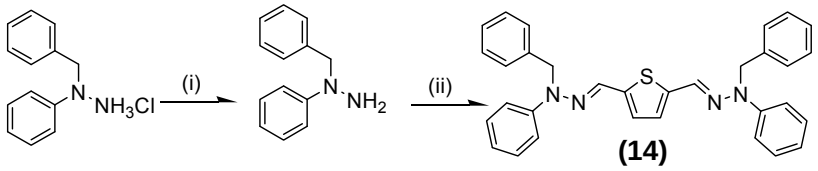
(i) 2,5-thiophenedicarboxyaldehyde, at r. m. in $CHCl_3$

N,N-dibenzylhydrazine was (1.5 g) was recrystallized from hot n-heptane (20 mL) to give purified compound as a colorless crystal (0.31 g).

2,5-thiophenedicarboxyaldehyde was purchased from Aldrich. The compound (2.0 g) was recrystallized from hot water (20 mL), followed by active carbon treatment to give the purified compound as a white powder (1.55 g).

The purified N,N-dibenzylhydrazine (129 mg, 0.61 mmol) and the purified 2,5-thiophenedicarboxyaldehyde (42 mg, 0.3 mmol) was dissolved in $CHCl_3$ (0.6 mL) and the mixture was stirred at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$/n-heptane, 2:1) affording desired compound (**13)** (103 mg) in 64% yield as a pale yellow powder. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.37-7.25 (m, 22H), 6.71 (s, 2H), 4.50 (s, 8H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 529.2420; found 529.2374; elemental analysis calcd (%) for $C_{34}H_{32}N_4S$: C 77.24, H 6.10, N 10.60; found: C 77.02, H 6.11, N 10.42.

Compound (14)

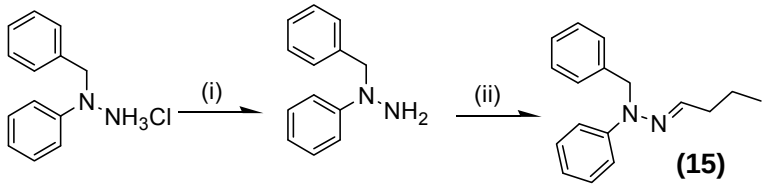


(i) NaOH aq. sol., at r.t.; (ii) 2,5-thiophenedicarboxyaldehyde, at r. m. in $CHCl_3$

An aqueous solution of N-benzyl-N-phenylhydrazine hydrochloride (2.35 g), purchased from Alfa Aezar, was neutralized with 1N-NaOH aqueous solution, followed by extraction with $CHCl_3$. The solution was dried over Na_2SO_4 and the solvent were evaporated to dryness to give a crude product (1.75 g). The crude was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CN$, 50:1) affording purified product (0.22 g) as a white powder.

The purified N-benzyl-N-phenylhydrazine (202 mg, 1.02 mmol) and 2,5-thiophenedicarboxyaldehyde (70 mg, 0.50 mmol) was dissolved in $CHCl_3$ (10 mL) and the mixture was stirred at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CN$, 50:1) affording desired compound **(14)** (282 mg) in 56% yield as dark tango oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.78 (s, 2H), 7.42-7.32 (m, 12H), 7.27 (t, *J* = 7.33 Hz, 2H), 7.19 (d, *J* = 7.28 Hz, 4H), 7.00 (s, 2H), 6.97-6.90 (m, 2H), 5.31 (s, 4H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 501.2107; found 501.2070; elemental analysis calcd (%) for $C_{32}H_{28}N_4S$: C 76.77, H 5.64, N 11.19; found: C 76.70, H 5.41, N 11.00.

1-benzyl-2-butylidene-1-phenylhydrazine (15)



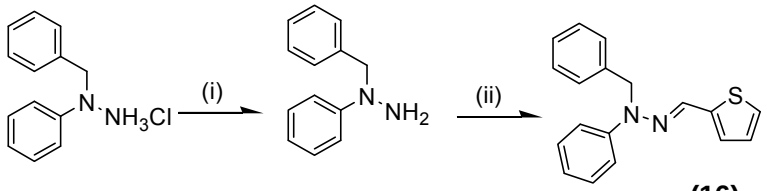
(15)

(i) NaOH aq. sol., at r.t.; (ii) butyraldehyde, at r. m. in $CHCl_3$

The purified N-benzyl-N-phenylhydrazine (119 mg, 0.6 mmol) and butyraldehyde (64 mg, 0.89 mmol) was dissolved in $CHCl_3$ (0.6 mL) and the mixture was stirred at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$) affording the compound **(15)** (129 mg) in 51% yield as colorless oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.33 (t, *J* = 7.46 Hz, 2H), 7.26-7.23 (m, 5H), 7.13 (d, *J* = 7.31

Hz, 2H), 6.97-6.61 (m, 2H), 5.10 (s, 2H), 2.22 (dt, *J* = 7.22, *J'* = 5.29 Hz, 2H), 1.45 (sext., *J* = 7.34 Hz, 2H), 0.84 (t, *J* = 7.37 Hz, 3H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 253.1699; found 253.1706; elemental analysis calcd (%) for $C_{17}H_{20}N_2$: C 80.91, H 7.99, N 11.10; found: C 80.96, H 7.99, N 11.14.

1-benzyl-1-phenyl-2-(thiophen-2-ylmethylene)hydrazine (16)

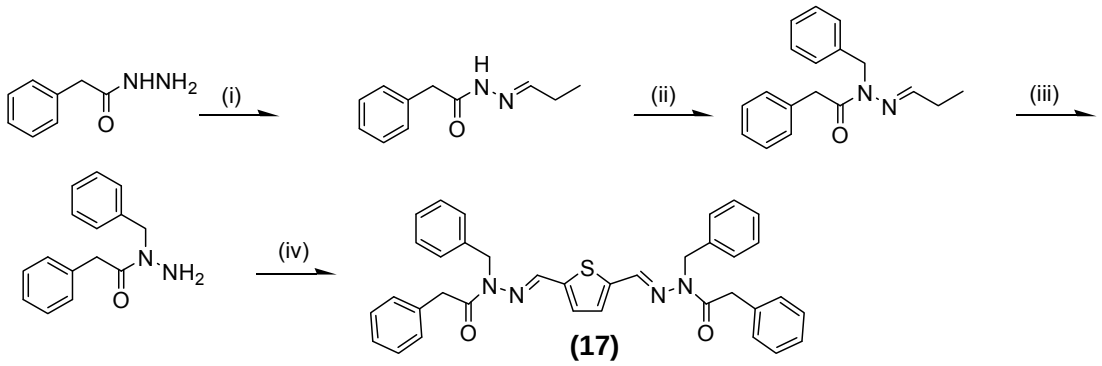


(16)

(i) NaOH aq. sol., at r.t.; (ii) 2-thiophenecarboxyaldehyde, at r. m. in $CHCl_3$

The purified N-benzyl-N-phenylhydrazine (198 mg, 1.0 mmol) and 2-thiophenecarboxyaldehyde (144 mg, 1.28 mmol) was dissolved in $CHCl_3$ (1 mL) and the stirred mixture was kept at room temperature for 3 h under argon atmosphere, followed by evaporation of $CHCl_3$ at room temperature with slight argon stream. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3$) affording the compound **(16)** (250 mg) in 85% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.84 (s, 1H), 7.44 (d, *J* = 5.07 Hz, 1H), 7.41-7.10 (m, 10H), 7.02 (dd, *J* = 5.05, *J'* = 3.56 Hz, 1H), 6.95-6.87 (m, 1H), 5.29 (m, 2H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 293.1107; found 293.1003; elemental analysis calcd (%) for $C_{18}H_{16}N_2S$: C 73.94, H 5.52, N 9.58; found: C 73.94, H 5.50, N 9.63.

Compound (17)



(17)

(i) propionaldehyde, at r. t. in CH_2Cl_2; (ii) benzyl bromide, K_2CO_3, at 60°C in DMF; (iii) O-methylhydroxylamine, HCl aq. sol., at r. m. in DMF; (iv) AcOH, H_2O at 80 °C in THF.

Phenylacetic acid hydrazide (2.32 g, 0.015 mol) and propionaldehyde (1.56 mg, 0.027 mol) was dissolved in the mixture of CH_2Cl_2 (20 mL) and $CHCl_3$ (10 mL) with Na_2SO_4, and the stirred mixture was kept at room temperature for 1 day under argon atmosphere, followed by filtration and evaporation of $CHCl_3$ at room temperature with slight argon stream, affording crude intermediate 2-phenyl-*N'*-propylideneacetohydrazide (2.93 g) as white solid. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 11.14, 10.92 (s, 1H), 7.52-7.15 (m, 6H), 3.83 (s, 1H), 3.44 (s, 1H), 2.27-2.19 (m, 2H), 1.32-0.67 (m, 3H).

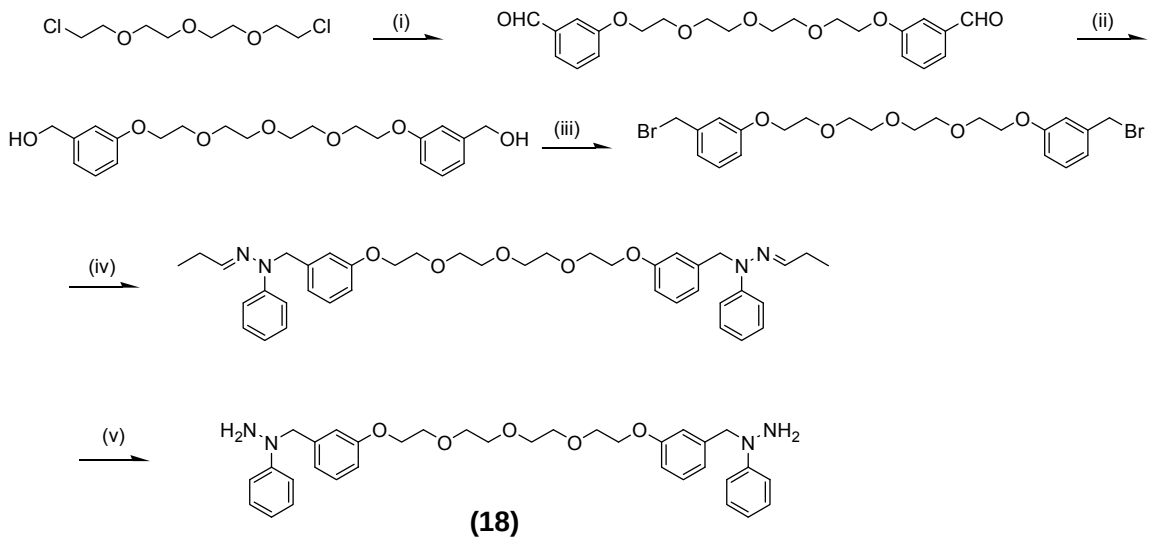
2-phenyl-*N'*-propylideneacetohydrazide (1.90 g) and benzyl bromide (0.86 g, 0.005 mol) were added to a suspension of K_2CO_3 (3.20 g, 0.023 mol) in DMF (6 mL) and the stirred mixture was heated to 60 °C for 4 h under argon atmosphere, followed by filtration and evaporation of DMF. The crude product was roughly purified by column chromatography on silica gel (eluent: $CH_2Cl_2/C_2H_5OCOCH_3$, 30:1) affording the compound *N*-benzyl-2-phenyl-*N'*-propylideneacetohydrazide (0.91 g). ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.40-7.19 (m, 8H), 7.16 (t, *J* = 4.54 Hz, 1H), 7.10 (d, *J* = 8.22 Hz, 2H), 5.09 (s, 1H), 4.13 (s, 1H), 2.22 (dq, *J* = 7.40, 4.51 Hz, 2H), 0.98 (t, *J* = 7.42 Hz, 2H).

N-benzyl-2-phenyl-*N'*-propylideneacetohydrazide (0.42 g) and O-methylhydroxylamine hydrochloride (0.50g, 6 mmol) were dissolved in DMF (8 mL), then 1N-HCl aqueous solution (2.3 g) was added. The stirred mixture was kept at room temperature for 2 h under argon atmosphere. The mixture was taken up in 0.5N-NaOH aqueous solution (25 mL) / $CHCl_3$ (80

mL). The organic layer was washed with H_2O (500 mL) 2 times, dried over Na_2SO_4 and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CN$, 10:1) affording purified compound *N*-benzyl-2-phenylacetohydrazide (0.24 g) as colorless crystal. ^1H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.40-7.14 (m, 10H), 4.70 (s, 2H), 4.49 (br, 2H), 3.93 (s, 2H).

N-benzyl-2-phenylacetohydrazide (147 mg, 0.61 mmol) and the purified 2,5-thiophenedicarboxyaldehyde (42 mg, 0.30 mmol) was dissolved in the mixture of $CHCl_3$ (0.4 mL) and MeOH (0.2 mL) with acid type ion-exchange resin (Amberlyst^{TM} 15, 1.5 mg), then the stirred mixture was kept at 60 °C for 5 h under argon atmosphere, followed by evaporation of the solvents. The residue was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CN$, 25:1) affording the compound **(17)** (160 mg). Furthermore, the compound (160 mg) was recrystallized from the mixture of $CHCl_3$ (1.6 g) and MeOH (1.9 g) to give yellow crystal (90 mg) in 51 % yield. ^1H NMR (400 MHz, [D_6]DMSO): δ ppm = 8.02 (s, 2H), 7.39 (d, *J* = 7.07 Hz, 4H), 7.33- 7.20 (m, 14H), 7.15 (d, *J* = 7.07 Hz, 4H), 5.23 (s, 4H), 4.22 (s, 4H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 585.2319; found 585.2300; elemental analysis calcd (%) for $C_{36}H_{28}N_4O_2S$: C 73.95, H 5.52, N 9.58; found: C 74.11, H 5.51, N 9.65.

Compound (18)



(18)

(i) 3–Hydroxybenzaldehyde, at 60°C in DMF; (ii) $NaBH_4$, at 0°C in MeOH; (iii) PBr_3, at 0°C in DCM; (iv) 1-phenyl-2-propylidenehydrazine, K_2CO_3, at 80 °C in DMF; (v) O-methylhydroxylamine, HCl aq. sol., at r. m. in DMF.

3–Hydroxybenzaldehyde (12.23 g, 0.10 mol) and bis[2–(2–chloroethoxy)ethyl]ether (9.37 g, 0.040 mol) were added to a suspension of K_2CO_3 (17.45 g, 0.126 mol) and NaI (1.20 g, 0.008 mol) in DMF (60 mL) and the stirred mixture was heated to 90 °C for 21 h under argon atmosphere. The mixture was taken up in H_2O (200 mL) / $CHCl_3$ (300 mL). The organic layer was washed with H_2O (200 mL) 4 times, dried over Na_2SO_4 and the solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: $CH_2Cl_2/C_2H_5OCOCH_3$, 3:1) affording the intermediate (8.43 g, 0.021 mol) in 49% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 9.98 (s, 2H), 7.55-7.50 (m, 4H), 7.42 (d, *J* = 2.94 Hz, 2H), 7.33-7.26 (m, 4H), 4.18 (t, *J* = 4.67 Hz, 4H), 3.77 (t, *J* = 4.51 Hz, 4H), 3.63-3.53 (m, 8H); elemental analysis calcd (%) for $C_{22}H_{26}O_7$: C 65.66, H 6.51; found: C 65.14, H 6.50.

Powder of $NaBH_4$ (3.78g, 0.10 mol) was added gradually into a stirred mixture of the intermediate (8.00 g, 0.020 mol) in MeOH (300 mL) at 0 °C. The mixture was kept stirred for 20 min at 0 °C after the addition, followed by for 1 h at 25 °C. HCl aqueous solution (1N, 170 mL) was added carefully into the stirred mixture at 0 °C, then MeOH was removed from the mixture solution in vacuo. The residue was taken up in H_2O (300 mL) and extracted with $CHCl_3$ (200 mL) 3 times. The $CHCl_3$ solution combined was dried over Na_2SO_4 and the solvents were evaporated to give the crude intermediate (7.05 g, 0.017 mol) in 87% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22 (t, *J* = 7.92 Hz, 2H), 6.91-6.86 (m, 4H), 6.80 (d, *J* = 6.95 Hz, 2H), 5.16 (t, *J* = 5.79 Hz, 2H), 4.47 (d, *J* = 5.80 Hz, 4H), 4.06 (t, *J* = 4.78 Hz, 4H), 3.74 (t, *J* = 4.51 Hz, 4H), 3.63-3.52 (m, 8H).

PBr_3 (5.42g, 0.020 mol) in CH_2Cl_2 (35 mL) was added dropwise into a solution of the intermediate (7.05 g, 0.017 mol) in CH_2Cl_2 (250 mL) at 0 °C. The mixture was kept stirred for 1 h at 0 °C after the addition, followed by for 18 h at 25 °C. H_2O (100 mL) was added to the mixture at 0 °C, then NaOH aqueous solution (1N, 320 mL) was added carefully until pH of the mixture reached to around 10. The organic layer was separated after adding NaCl aqueous solution (saturated, 175 mL) and dried over Na_2SO_4. Solvents were evaporated to afford the intermediate (8.77 g, 0.016 mol) in 95% yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.27 (t, *J* = 8.00 Hz, 2H), 7.04-7.00 (m, 4H), 6.92-6.87 (m, 2H), 4.66 (s, 4H), 4.08 (t, *J* = 4.75 Hz, 4H), 3.74 (t, *J* = 4.53 Hz, 4H), 3.61-3.55 (m, 8H).

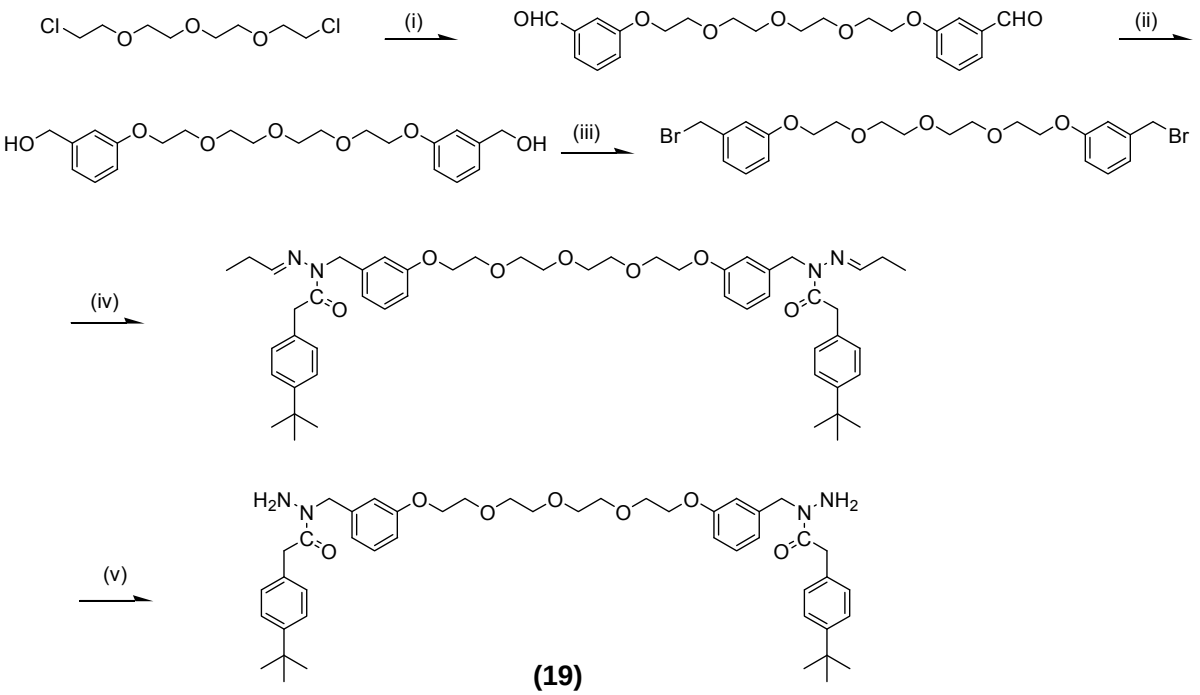
Propionaldehyde (7.0 g, 0.121 mol) was added dropwise into a solution of phenylhydrazine

(10.8 g, 0.10 mol) in CH_2Cl_2 (50 mL) at 25 °C, followed by adding Na_2SO_4 (20 g). After stirred for 1 h at 25 °C, Na_2SO_4 was isolated by filtration. The filtrate mixture was evaporated to afford the compound 1-phenyl-2-propylidenehydrazine (14.2 g, 0.096 mol) in 96% yield as mixture of the *E* and *Z* isomers. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 9.59 and 9.02 (s, 1H), 7.18-6.32 (m, 6H), 2.26-2.18 (m, 2H), 1.08-1.02 ppm (m, 3H).

The intermediate (2.08 g, 0.004 mol) and 1-phenyl-2-propylidenehydrazine (2.37 g, 0.016 mol) were added to a suspension of K_2CO_3 (1.26 g, 0.009 mol) in DMF (12 mL) and the stirred mixture was heated to 60 °C for 3 h under argon atmosphere. The mixture was taken up in H_2O (400 mL), then extracted with $CHCl_3$ (100 mL) twice. The combined $CHCl_3$ solution was dried over Na_2SO_4 and the solvent was evaporated to dryness. The residue (4.12g, a hard red oil) was roughly purified by column chromatography on silica gel (eluent: $CHCl_3$/AcOEt, 20:1) affording the intermediate (1.10 g, 1.7 mmol) in 42 % yield as a orange oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22-7.18 (m, 10H), 6.86 (t, *J* = 4.76 Hz, 2H), 6.79-6.75 (m, 4H), 6.67–6.64 (m, 4H), 5.01 (s, 4H), 4.00-3.98 (m, 4H), 3.68–3.66 (m, 4H), 3.54–3.45 (m, 8H), 2.25 (dq, *J* = 7.44, *J'* = 4.76 Hz, 4H), 0.98–1.02 (t, *J* = 7.45 Hz, 6H).

The intermediate (750 mg, 1.13 mmol) and *O*-Methoxylamine hydrochloride (0.97 g, 11.6 mmol) were dissolved in the mixture of DMF (7 mL) and HCl aqueous solution (1N, 3.5 mL). The solution was stirred for 2 h at 25 °C, then taken up in $CHCl_3$ (400 mL). After adding NaOH aqueous solution (0.5N, 40 mL) to the bilayer solution, the organic layer was washed with H_2O (400 mL) 3 times followed by dryness with Na_2SO_4. Crude product (590 mg) was obtained after evaporation. Column chromatographies were performed 3 times on silica gel (eluent: CH_2Cl_2/CH_3CN, 3:1) to afford pure compound **(18)** (260 mg, 0.44 mmol) in 39 % yield as a faintly yellow oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22 (t, *J* = 7.95 Hz, 2H), 7.13 (dd, *J* = 8.70, 7.23 Hz, 4H), 6.96 (d, *J* = 7.94 Hz, 4H), 6.86-6.84 (m, 4H), 6.80 (d, *J* = 7.12 Hz, 2H), 6.62 (t, *J* = 7.20 Hz, 2H), 4.58 (s, 4H), 4.36 (br, 4H), 4.01 (dd, *J* = 4.4 Hz, *J'* = 4.9 Hz, 4H), 3.68 (dd, *J* = 4.4 Hz, *J'* = 4.9 Hz, 4H), 3.58-3.52 (m, 8H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 587.3228; found 587.3224; elemental analysis calcd (%) for $C_{34}H_{42}N_4O_5$: C 68.54, H 7.10, N 9.40; found: C 68.97, H 7.23, N 9.27.

Compound (19)



(19)

(i) 3–Hydroxybenzaldehyde, at 60°C in DMF; (ii) $NaBH_4$, at 0°C in MeOH; (iii) PBr_3, at 0°C in DCM; (iv) 2-(4-tert-butylphenyl)-N'-propylideneacetohydrazide, K_2CO_3, at 80 °C in DMF; (v) O-methylhydroxylamine HCl salt, at r. m. in DMF.

Synthesis of (**19)** was carried out in the same manner described in the scheme of monomer synsthesis of **(18)** previously. Methyl *p-tert*-butylphenylacetate (12.38 g, 0.06 mol) in MeOH (15 mL) was added dropwise into a stirred mixture of hydrazine monohydrate (15 g, 0.3 mol) in MeOH (40 mL) at room temperature. The mixture was stirred at 50 °C for 2 h followed by cooled to 0 °C to give precipitate. After adding H_2O (200 mL), the precipitate was isolated by filtration to give 2-(4-*tert*-butylphenyl)acetohydrazide (8.67 g). ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 9.19 (s, 1H), 7.31 (d, *J* = 8.25 Hz, 2H), 7.18 (d, *J* = 8.22 Hz, 2H), 4.20 (s, 2H), 3.30 (br, 2H), 1.27 (s, 9H).

Propionaldehyde (3.48 g, 0.06 mol) was added dropwise into a stirred mixture of 2-(4-*tert*-butylphenyl)acetohydrazide (8.24 g, 0.04 mol) in CH_2Cl_2 (50 mL) at 25 °C, followed by adding Na_2SO_4 (10 g). After stirred for 1 h at 25 °C, Na_2SO_4 was isolated by filtration. The filtrate mixture was evaporated to afford 2-(4-tert-butylphenyl)-*N'*-propylideneacetohydrazide (9.85 g). ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 11.14, 10.93 (s, 1H), 7.54-7.17 (m, 6H),

3.78 (s, 1H), 3.39 (s, 1H), 2.28-2.18 (m, 2H), 1.07-1.00 (m, 3H).

The intermediate (2.34 g, 0.0044 mol) and 2-(4-tert-butylphenyl)-*N'*-propylideneacetohydrazide (4.95 g, 0.02 mol) were added to a suspension of K_2CO_3 (9.03 g, 0.065 mol) in DMF (12 mL) and the stirred mixture was heated to 60 °C for 4 h under argon atmosphere. The solid portion of the mixture was isolated by filtration and the solution was evaporated. The residue (8.34 g) was roughly purified twice by column chromatography on silica gel (eluent: CH_2Cl_2/CH_3CN, 5:1) affording the intermediate compound (1.10 g, 1.28 mmol) in 29 % yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.33 (d, *J* = 8.26 Hz, 4H), 7.24 (d, *J* = 8.25 Hz, 4H), 7.20-7.13 (m, 4H), 6.78 (d, *J* = 8.08 Hz, 2H), 6.67-6.65 (m, 4H), 5.03 (s, 4H), 4.09 (s, 4H), 3.98 (dd, *J* = 5.43, *J'* = 3.74 Hz, 4H), 3.71 (dd, *J* = 5.29, *J'* = 3.73 Hz, 4H), 3.59-3.53 (m, 8H) 2.21 (dq, *J* = 7.40, *J'* = 4.46 Hz, 4H), 1.26 (s, 18H), 0.99 (t, *J* = 7.40 Hz, 6H).

The intermediate (0.43 g, 0.5 mmol) and *O*-Methoxylamine hydrochloride (0.84 g, 10 mmol) were dissolved in DMF (4 mL). The solution was stirred for 4 h at 25 °C, then taken up in $CHCl_3$ (30 mL). After adding NaOH aqueous solution (0.5N, 30 mL) to the solution, the organic layer was evaporated. The residue (0.36 g) was purified three times by column chromatography on silica gel (eluent: CH_2Cl_2/CH_3CN/MeOH, 100:50:1) affording purified compound **(19)** (105 mg, 0.13 mmol) in 29 % yield as a colorless oil. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.31 (d, *J* = 8.21 Hz, 4H), 7.24-7.19 (m, 6H), 6.84 (d, *J* = 8.36 Hz, 2H), 6.81-6.79 (m, 4H), 4.65 (s, 4H), 4.50 (br, 4H), 4.08 (dd, *J* = 5.32, *J'* = 4.06 Hz, 4H), 3.88 (s, 4H), 3.76 (dd, *J* = 5.39, *J'* = 4.19 Hz, 4H), 3.64-3.56(m, 8H), 1.30 (s, 18H); FAB HRMS: *m/z* calcd for $[M+H]^+$: 783.4691; found 783.4645; elemental analysis calcd (%) for $C_{46}H_{62}N_4O_7$: C 70.56, H 7.98, N 7.16; found: C 70.43, H 8.11, N 6.73.

General method for the synthesis of polymers

Equimolar amounts of the bis-hydrazine and the dialdehyde at concentrations around 0.04 M each were dissolved in the mixture of $CHCl_3$ and THF(8 : 2 in volume ratio; for the polymer **P1**) or $CHCl_3$ (for the polymer **P2**, **P3, P4**), followed by addition of pentadecafluorooctanoic

acid in 0.1 molar ratio with respect to the resulting total hydrazone bonds. The solution was heated to 60 °C for 12 h, then poured into a petri dish of 50 mm diameter made of fluoroplastic, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared and then kept at 60 °C in vacuo for 12 h. About 200 mg of the total amounts of monomers were used to obtain the polymer film of around 0.04–0.06 mm thickness.

Polymer P1

^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.22-7.00 (br, 10H), 6.73 (br, 5H), 6.63 (br, 5H), 4.96 (br, 4H), 3.92 (br, 4H), 3.61 (br, 4H), 3.45 (br, 8H), 2.15 (br, 4H), 1.56(br, 2H)

Polymer P2

^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.96 (br, 2H), 7.33-7.12 (m, 12H), 6.75-6.64 (m, 6H), 5.12 (br, 4H), 4.14 (br, 4H), 3.92 (br, 4H), 3.63 (br, 4H), 3.48 (br, 8H), 1.14(br, 18H)

Polymer P3

^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 7.78-7.71 (br, 2H), 7.36-7.18 (m, 10H), 6.92-6.69 (m, 10H), 5.18 (br, 4H), 3.94 (br, 8H), 3.61 (br, 4H), 3.43(br, 8H)

Preparation of polymer thin layers

Polymer thin layers were prepared using a 2 wt% THF solution of the polymer by spin-coating onto 5 cm square quartz plates, which was rinsed with acetone prior to use. The spin-speed and the period were 500 rpm and 60 sec, respectively. These layers were subsequently dried *in vacuo* at 60 °C for 12 hr.

CHAPTER 4

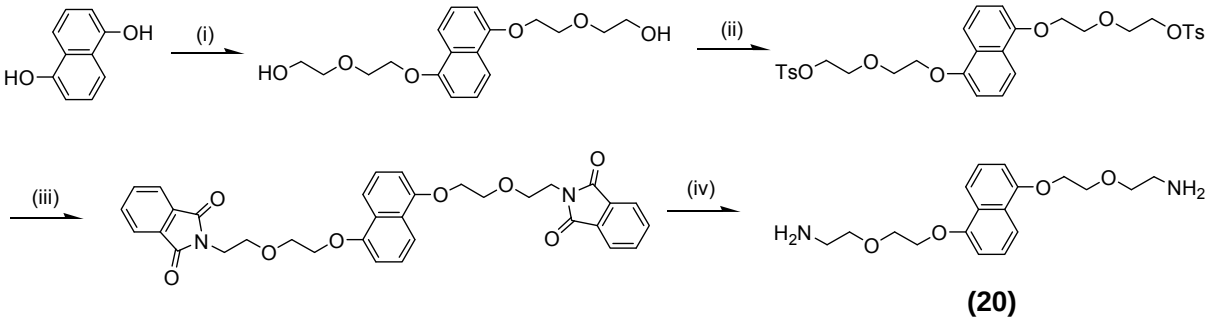
General method for the synthesis of polymers

Condensation polymerization reaction was carried out by the following procedure. Equimolar amounts of the diamine and the dialdehyde at a concentration of around 0.05 M each were dissolved in $CHCl_3$, followed by the addition of anhydrous $MgSO_4$. The reaction mixture was heated at 60 °C for 24 h under N_2 atomsphere, then poured into a petri dish after the filtelation of $MgSO_4$. The solvent was slowly evaporated under atm/60 °C temp. until most of the solvent had disappeared and the resulting polymer film or oil then was kept at 60 °C in vacuo for 12 h.

General Procedure for the exchange reaction in constitutional dynamers library

Polymers and deuterated trifluoroacetic acid (2 mol % per imine unit) were dissolved in a mixing solution of CD_2Cl_2 and CD_3CN(8 : 2) and the constitutional dynamic mixture was stirred for 12 hours at r.t.. After the constitutions of the polymers were equilibrated well, each metal ion (LiOTf, NaOTf, KOTf, RbOTf and CsOTf) in CD_3CN was added to the reaction mixture and ^{1}H-NMR spectra were recorded to determine the constitutional distribution of the dynamer library after the resulting mixture was reached to the other equilibrium completely by the stirring for 6 hrs.

Synthesis of diamine monomer AmD (donor) (20)



(20)

(i) 2-(2-chloroethoxy)ethanol, K_2CO_3, at 80°C in DMF; (ii) tosyl chloride, triethylamine at r. m. in DCM; (iii) potassium phthalimide at 120 °C in DMF; (iv) hydrazine monohydrate, refluxed in EtOH.

To a suspension of 1,5-dihydroxynaphtalene (6.00 g, 37.46 mmol), K_2CO_3 (31.06 g, 224.73 mmol) and KI (0.31 g, 1.87 mmol) in DMF (50ml) was added 2-(2-chloroethoxy)ethanol (14.00 g, 112.39 mmol) under N_2 atmosphere at room temperature. The resulting mixture was heated at 80 °C for 12 h and then filtered, and the filtrate was concentrated under reduced pressure. The residue was placed in DCM (100 ml) and the solution was washed with brine (50 ml × 3) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: EtOH/DCM, 5 : 95) to afford the intermediate as a brownish solid in 75 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.87 (d, ^3J = 8.5 Hz, 2H), 7.36 (t, ^3J = 8.0 Hz, 2H), 6.85 (d, ^3J = 7.6 Hz, 2H), 4.30 (t, ^3J = 4.8 Hz, 4H), 3.99 (t, ^3J = 4.8 Hz, 4H), 3.77 (br, 4H), 3.73 (br, 4H), 2.19 (br, 2H).

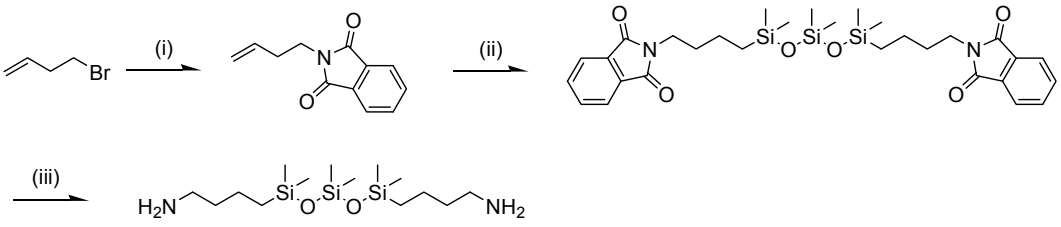
To a solution of intermediate (9.40 g, 27.94 mmol) and tosyl chloride (15.98 g, 83.66 mmol) in DCM (200ml) at 0 °C under N_2 atmosphere was added through a dropping funnel over a period of 1 hr triethylamine (14.14 g, 139.74 mmol). The mixture was allowed to warm slowly to room temperature and stirred for 12 h, and then washed with 1N HCl aqueous solution(50 ml × 3), saturated aqueous $NaHCO_3$ (50 ml × 3) and brine (50 ml × 2) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: DCM→ 10 % EtOAc in DCM) to afford the compound as a brownish solid in 78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.83 (d, ^3J = 8.4 Hz, 2H), 7.77 (d, ^3J = 8.0 Hz, 4H), 7.34 (t, ^3J = 8.4 Hz, 2H), 7.22 (d, ^3J = 8.0 Hz, 4H), 6.79 (d, ^3J = 7.6 Hz, 2H), 4.27 (t, ^3J = 4.8 Hz, 4H), 3.96 (t, ^3J = 4.4 Hz, 4H), 3.79 (t, ^3J = 4.8 Hz, 4H), 3.73 (br, 4H), 2.33 (s, 6H).

To a solution of intermediate (5.00 g, 7.75 mmol) in DMF (50 ml) was added potassium phthalimide (4.31 g, 23.27 mmol) at room temperature under N_2 atmosphere. The reaction mixture was heated at 120 °C for 12 h and then poured into 200 ml of water. The resulting mixture was extracted with DCM (50 ml × 3) and the combined extracts was washed with brine (50 ml × 3), dried over anhydrous Na_2SO_3 and concentrated under pressure. The resulting residue was chromatographed over silica gel (eluent: DCM → 10 % ethyl acetate in DCM) to give intermediate as a yellowish solid in 61 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.81-7.78 (m, 2H, 4H), 7.64 (m, 4H), 7.31 (t, ^3J = 8.0 Hz, 2H), 6.78 (d, ^3J = 7.6 Hz, 2H), 4.18 (t, ^3J = 4.4 Hz, 4H), 3.89 (t, ^3J = 4.4 Hz, 4H), 3.80 (m, 2H, 2H); elemental analysis

calcd (%) for $C_{34}H_{30}N_2O_8$: C, 68.68, H, 5.09, N, 4.71: found: C, 68.62, H, 5.08, N, 4.61.

To a solution of intermediate (2.82 g, 4.74 mmol) in EtOH (100 mL) was added dropwise hydrazine monohydrate (1.89 g, 37.94 mmol) and the mixture was then refluxed for 24 h under N_2 atmosphere. The resulting solid was filtered off and the volatiles were removed under vacuo. The residue was chromatographed over alumina (eluent: 2 % MeOH in DCM → 5 % MeOH in DCM) to give the desired compound **AmD (20)** in 22% yield as a white solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ ppm = 7.73 (d, ^3J = 8.4 Hz, 2H), 7.39 (t, ^3J = 8.0 Hz, 2H), 7.00 (d, ^3J = 7.7 Hz, 2H), 4.26 (t, ^3J = 4.8 Hz, 4H), 3.86 (t, ^3J = 4.4 Hz, 4H), 3.50 (t, ^3J = 5.6 Hz, 4H), 2.69 (t, ^3J = 5.6 Hz, 4H), 1.35 (br, 4H); ^{13}C NMR (400 MHz, [D$_6$]DMSO): δ ppm = 153.78, 125.89, 125.33, 113.67, 105.88, 73.26, 68.68, 67.64, 41.31; LCMS: m/z (%): 335.35 (100) $[M+H]^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{27}N_2O_4$ $[M+H]^+$ 335.1965, found 335.1992,

Synthesis of diamine monomer AmSi (21)



(21)

(i) potassium phthalimide at 120 °C in DMF; (ii) 1,1,3,3,5,5-hexamethyltrisiloxane, Karstedt's catalyst, at r. m. in toluene; (iii) hydrazine monohydrate, refluxed in EtOH.

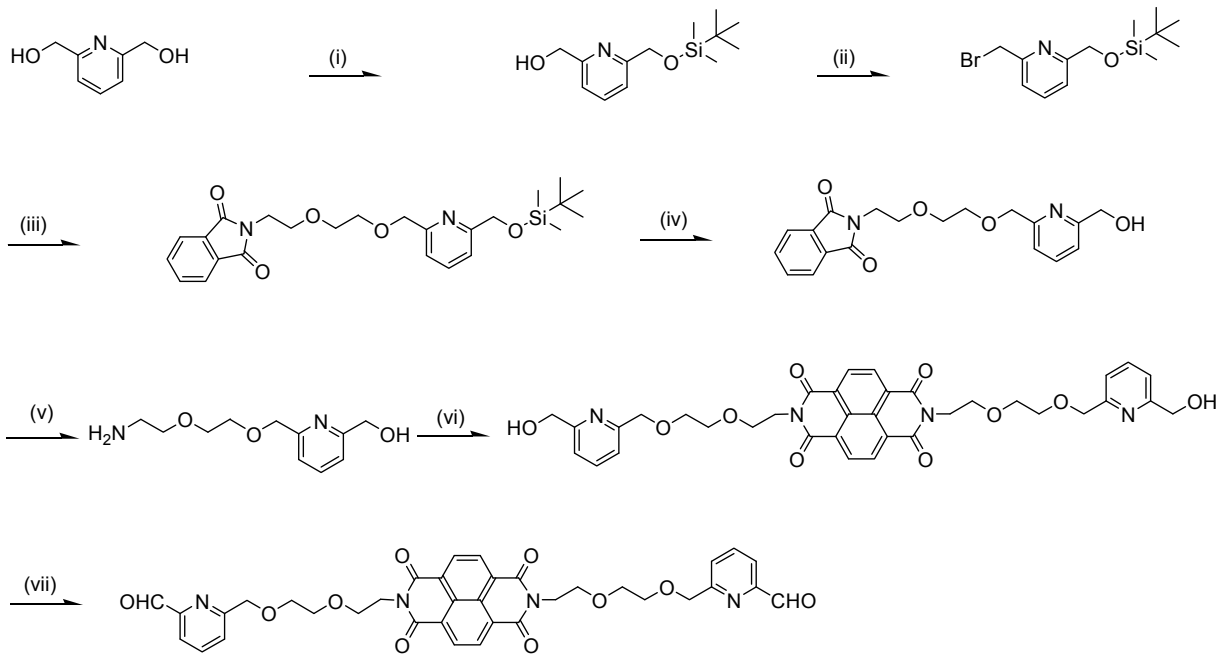
To a solution of 4-bromobut-1-ene (4.00 g, 29.63 mmol) in DMF (50 ml) was added potassium phthalimide (8.23 g, 44.44 mmol) at room temperature under N_2 atmosphere. The reaction mixture was heated at 100 °C for 48 h and then poured into 100 ml of water. The mixture was extracted with DCM (50 ml × 3) and the combined extracts was washed with brine (50 ml × 3), dried over anhydrous Na_2SO_3 and concentrated under pressure. The resulting residue was chromatographed over silica gel (eluent: pentane/DCM, 3 : 7) to give 2-(but-3-enyl)isoindoline-1,3-dione as a white solid in 69 % yield. ^{1}H NMR (400 MHz,

$CDCl_3$): δ ppm = 7.85-7.83 (m, 2H), 7.72-7.69 (m, 2H), 5.84-5.74 (m, 1H), 5.09-5.00 (m, 2H), 3.78 (t, ^3J = 6.8 Hz, 2H), 2.47-2.42 (m, 2H).

To a solution of 1,1,3,3,5,5-hexamethyltrisiloxane (0.94 g, 4.52 mmol) and Karstedt catalyst[1] (100ppm / Si-Hmol) in toluene (20 mL) was added 2-(but-3-enyl)isoindoline-1,3-dione (2.00 g, 9.96 mmol) using a pressure-equalizing additional funnel at room temperature under Ar atmosphere, then the mixture was stirred for 24h. The reaction was monitored by ^{1}H NMR analysis. After the solvent was removed by evaporation, the resulting residue was chromatographed over silica gel (eluent: pentane/DCM, 3 : 5 → 1 : 4), affording desired compound in 93 % yield as a transparent and colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.86-7.81 (m, 4H), 7.70-7.68 (m, 4H), 3.67 (t, ^3J = 7.3 Hz, 4H), 1.69 (qui, ^3J = 7.8 Hz, 4H), 1.37 (qui, ^3J = 8.3 Hz, 4H), 0.57 (t, ^3J = 7.6 Hz, 4H), 0.04 (s, 12H), 0.00 (s, 6H).

To a solution of intermediate (2.40 g, 9.46 mmol) in EtOH (50 mL) was added dropwise hydrazine monohydrate (2.05 g, 14.20 mmol) and the mixture was then refluxed for 1 day under N_2 atmosphere. The resulting solid was filtered off and the volatiles were removed under reduced pressure. The residue was purified by Kougell distillation to afford the desired compound **AmSi (21)** as a transparent and colorless oil in 38 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.86-7.81 (m, 4H), 7.70-7.68 (m, 4H), 3.67 (t, ^3J = 7.3 Hz, 4H), 1.69 (qui, ^3J = 7.8 Hz, 4H), 1.37 (qui, ^3J = 8.3 Hz, 4H), 0.57 (t, ^3J = 7.6 Hz, 4H), 0.04 (s, 12H), 0.00 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 42.07, 37.67, 20.64, 18.22, 1.41, 0.30; LCMS: m/z (%): 351.38 (100) $[M+H]^+$; HRMS(ESI): *m/z* calcd for $C_{14}H_{39}N_2O_2Si_3$ $[M+H]^+$ 351.2314, found 351.2331; elemental analysis calcd (%) for $C_{14}H_{38}N_2O_2Si_3$: C, 47.84, H, 10.92, N, 7.99: found: C, 47.35, H, 11.22, N, 7.88.

Synthesis of dialdehyde monomer AlA (22)



(22)

(i) imidazole, TBSCl, at r. t. in DMF; (ii) carbon tetrabromide, triphenylphosphine, at r.m. in diethyl ether; (iii) 2-(2-(2-hydroxyethoxy)ethyl)isoindoline-1,3-dione, NaH, at r. m. in DMF; (iv) AcOH, H_2O at 80 °C in THF, (v) hydrazine monohydrate, refluxed in EtOH; (vi) 1,4,5,8- naphthalenetetracarboxylic acid anhydride, at 120 °C in DMF; (vii) Dess–Martin periodinane, at r. m. in DCM.

To a solution of 2,6 –dihydroxymethyl pyridine (20.00 g, 143.73 mmol) and imidazole (5.42 g, 79.61 mmol) in DMF (200 mL) at 0 °C under N_2 atmosphere was added dropwise over a period of 1h a solution of TBSCl (12.02g, 79.75 mmol) in DMF (50 mL). The reaction mixture was allowed to warm to ambient temperature and stirred overnight. After the solvent was removed, the residue was placed in 200 ml of DCM. The organic solution was washed with aq. 1N HCl solution (50 ml × 2), saturated aq. NaHCO3 solution (50 ml × 2) and brine (50 ml × 2) and dried over Na_2SO4. The solvent was evaporated under reduced pressure and the crude mixture was purified by silica gel chromatography(eluent: 10 → 50 % EtOAc in DCM) to afford 2-Hydroxymethyl-6-(tert-buthyldimetthylsilyloxymethyl)pyridine as a colorless liquid in 42 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.70 (t, ^3J = 7.8 Hz, 1H), 7.42 (d, ^3J = 7.8 Hz, 1H), 7.10 (d, ^3J = 7.8 Hz, 1H), 4.84 (s, 2H), 4.73 (s, 2H), 3.80 (br, 1H), 0.97 (s, 9H), 0.13 (s, 6H).

To a solution of carbon tetrabromide (10.91 g, 32.90 mmol) and mono-protected diol (7.58 g, 29.91 mmol) in diethyl ether (100 mL) was added through a dropping funnel a solution of triphenylphosphine (9.81 g. 37.40 mmol) in diethyl ether (50 mL) at r.m. under N_2 and the reaction mixture was stirred for 12 h, during which time a white precipitate (triphenylphosphine oxide) formed. The precipitate was removed off by vacuum filtration and the filtrate was concentrated under reduced pressure to give a crude orange oil. The product was purified by silica gel column chromatography (heptane → 50 % DCM in heptane), giving bromomethyl-6-(tert-butyldimethylsilyloxymethyl) pyridin as a pale yellow oil in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 8.05 (t, ^3J = 7.8 Hz, 1H), 7.79 (d, ^3J = 7.8 Hz, 1H), 7.65 (d, ^3J = 7.8 Hz, 1H), 5.17 (s, 2H), 4.85 (s, 2H), 1.30 (s, 9H), 0.46 (s, 6H).

To a solution of phthalic anhydride (7.01 g, 47.56 mmol) in DMF (100 mL) was added 2-(2-aminoethoxy)ethanol and the mixture was then heated at 120 °C overnight. The solvent was removed under vacuum, and the residue was chromatographed over silica gel (eluent: EtOAc/DCM, 3 : 2) to gave 2-(2-(2-hydroxyethoxy)ethyl)isoindoline-1,3-dione as a white solid in 80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.87-7.85 (m, 2H), 7.73-7.71 (m, 2H), 3.92 (t, ^3J = 5.4 Hz, 2H), 3.75 (t, ^3J = 5.8 Hz, 2H), 3.69 (t, ^3J = 4.4 Hz, 2H), 3.61 (t, ^3J = 4.0 Hz, 2H).

To a suspension of sodium hydride (946.0 mg, 60% in mineral oil, 23.65 mmol) in DMF (50 ml) was added 2-(2-(2-hydroxyethoxy)ethyl)isoindoline-1,3-dione (5.06 g, 21.50 mmol), and the mixture was stirred at room temperature. After 1 h, a solution of bromomethyl-6-(tert-butyldimethylsilyloxymethyl) pyridin (7.48g, 23.65 mmol) in DMF (20 ml) was added to the reaction mixture, and then the resulting mixture was stirred at room temperature for 24 h. The solid was filtered off by a celite treatment and the solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography (eluent: 15% EtOAc in DCM) to yield 2-(2-(2-((6-((tert-butyldimethylsilyloxy)methyl)pyridin-2-yl)methoxy)ethoxy)ethyl) isoindoline -1,3-dione (5.5 g, 54 %) as a transparent and colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.87-7.85 (m, 2H), 7.74-7.72 (m, 2H, 1H), 7.44 (d, ^3J = 7.4 Hz, 1H), 7.32 (d, ^3J = 7.4 Hz, 1H), 4.84 (s, 2H), 4.62 (s, 2H), 3.95 (t, ^3J = 5.8 Hz, 2H), 3.80 (t, ^3J = 5.8 Hz, 2H), 3.74-3.68 (m, 2H, 2H), 0.99 (s, 9H), 0.14 (s, 6H).

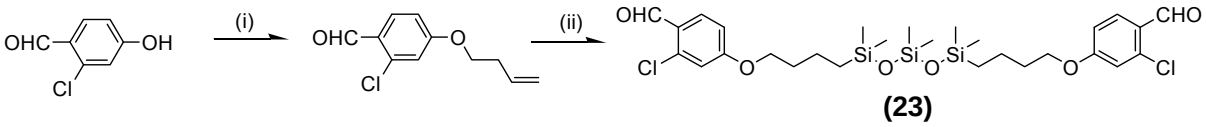
A 2-(2-(2-((6-((tert-butyldimethylsilyloxy)methyl) pyridin-2-yl)methoxy)ethoxy)ethyl) isoindoline-1,3-dione (5.50 g, 11.69 mmol) in a mixing solution of acetic acid (40 mL), water (30 mL) and THF (30 mL) was heated at 80 °C overnight. After the solvent was evaporated, the residue was dissolved in EtOAc (70 ml) and the organic solution was washed with saturated aqueous $NaHCO_3$ (20 mL × 3), brine (20 ml × 2) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the remaining residue was chromatographed over silica gel (eluent: EtOAc) to afford 2-(2-(2-((6-(hydroxymethyl)pyridin-2-yl)methoxy)ethoxy)ethyl)isoindoline-1,3-dione as a colorless in 78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.84-7.82 (m, 2H), 7.73-7.69 (m, 2H, 1H), 7.37 (d, ^3J = 7.4 Hz, 1H), 7.14 (d, ^3J = 7.4 Hz, 1H), 4.74 (s, 2H), 4.65 (s, 2H), 3.93 (t, ^3J = 5.8 Hz, 2H), 3.78 (t, ^3J = 5.8 Hz, 2H), 3.73-3.67 (m, 2H, 2H).

To a solution of 2-(2-(2-((6-(hydroxymethyl)pyridin-2-yl)methoxy)ethoxy) ethyl)isoindoline-1,3-dione (3.25 g, 9.12 mmol) in EtOH (50 mL) was added dropwise hydrazine monohydrate (2.50 g, 49.94 mmol) and the mixture was then refluxed for 1 day under N_2 atmosphere. The resulting solid was filtered off and the volatiles were removed by rotary evaporator. The residue was placed in DCM and the resulting precipitate was filtered off again and the filtrate was evaporated under reduced pressure. The residue was used to next step without further purification (transparent and colorless oil in 93 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.68 (t, ^3J = 7.8 Hz, 1H), 7.36 (d, ^3J = 7.4 Hz, 1H), 7.15 (d, ^3J = 7.4 Hz, 1H), 4.74 (s, 2H), 4.70 (s, 2H), 3.76-3.68 (m, 2H, 2H), 3.55 (t, ^3J = 5.4 Hz, 2H), 2.90 (t, ^3J = 5.4 Hz, 2H).

To a solution of 1,4,5,8- naphthalenetetracarboxylic acid anhydride (1.08g, 4.04 mmol) in DMF was slowly added (6-((2-(2-aminoethoxy)ethoxy)methyl)pyridin-2-yl)methanol (1.92 g, 8.49 mmol) at room temperature under N_2. The reaction mixture was heated to 120 °C and stirred overnight. After the completion of the reaction, the mixture was concentrated under reduced pressure. Purification of the crude compound by a silica gel column chromatography, eluting with 5 % EtOH in DCM, provided the desired product as a pale yellow solid (980 mg, in 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 8.67 (s, 4H), 7.57 (t, ^3J = 7.8 Hz, 2H), 7.23 (d, ^3J = 7.4 Hz, 2H), 7.07 (d, ^3J = 7.8 Hz, 2H), 4.64 (s, 4H), 4.55 (s, 4H), 4.49 (t, ^3J = 5.8 Hz, 4H), 3.91 (t, ^3J = 5.8 Hz, 4H), 3.77-3.69 (m, 4H, 4H).

The intermediate (0.70 g, 1.02 mmol) and Dess–Martin periodinane (1.08 g, 2.56 mmol) were stirred in DCM (50 mL) for 12h. The reaction mixture was washed with 1 N Na_2CO_3 aq. solution(20 mL × 3), brine (20 ml × 2) and dried over anhydrous Na_2SO4. After the solvent was removed under reduced pressure, the residue was recrystallized in EtOAc to afford the compound **AlA (22)** as a yellow solid in 88 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 9.98 (s, 2H), 8.70 (s, 4H), 7.84-7.79 (m, 2H, 2H), 7.65 (d, ^3J = 7.4 Hz, $^{>3}J$ = 2.4 Hz, 2H), 4.67 (s, 4H), 4.49 (t, ^3J = 5.4 Hz, 4H), 3.90 (t, ^3J = 5.8 Hz, 4H), 3.80-3.72 (m, 4H, 4H); ^{13}C NMR ($CDCl_3$): δ ppm = 192.99, 166.13, 162.26 159.077, 137.65, 130.23, 125.88, 125.25, 124.98, 119.79, 72.50, 69.60, 69.52, 66.74, 46.50; HRMS (ESI): *m*/*z* calcd for $C_{36}H_{32}N_4O_{10}Li_1$ $[M+Li]^+$ 687.2274, found 687.2233; elemental analysis calcd (%) for $C_{36}H_{32}N_4O_{10}$: C, 63.52, H, 4.74, N, 8.23, found: C, 63.12, H, 4.95, N, 8.25.

Synthesis of dialdehyde monomer AlSi (23)



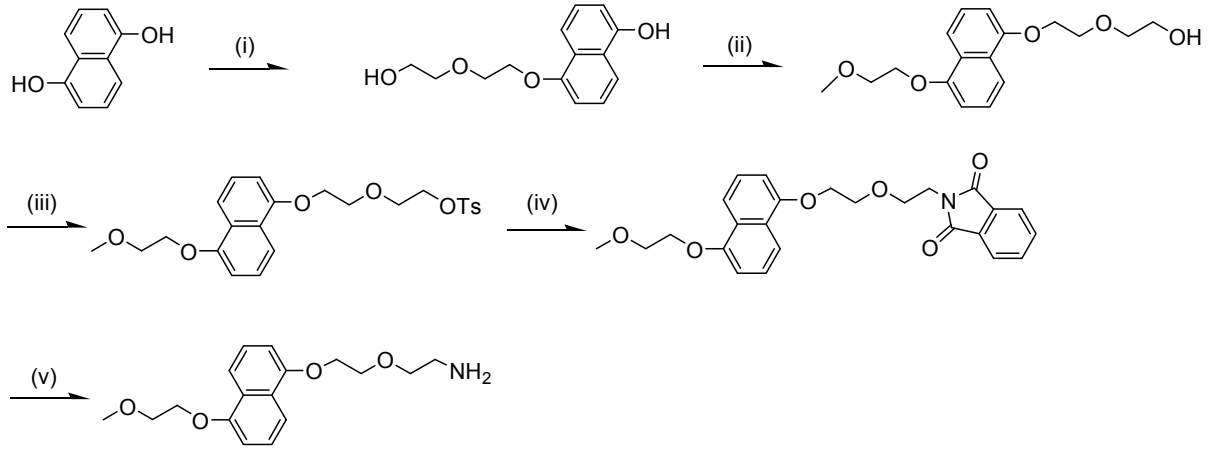
(23)

(i) 4-bromobut-1-ene, K_2CO_3, at 80 °C in DMF; (ii) 1,1,3,3,5,5-hexamethyltrisiloxane, Karstedt's catalyst, at r. m. in toluene.

To a suspension of 2-chloro-4-hydroxybenzaldehyde (0.50 g, 3.19 mmol) and K_2CO_3 (1.32 g, 9.57 mmol) in DMF (10ml) was added 4-bromobut-1-ene (0.86 g, 6.39 mmol) under N_2 atmosphere at room temperature. The mixture was heated at 80 °C for 12 h and then filtered, and the filtrate was concentrated under reduced pressure. The residue was placed in DCM (20 ml) and the solution was washed with brine (10 ml × 3) and dried over anhydrous Na_2SO_3. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: pentane/DCM, 3 : 4) to afford 4-(but-3-enyloxy)-2 -chlorobenzaldehyde as a white solid in 98 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 10.33 (s, 1H), 7.80 (d, ^3J = 8.8 Hz, 1H), 6.93 (s, $^{>3}J$ = 2.4 Hz, 1H), 6.90 (d, ^3J = 8.8 Hz, $^{>3}J$ = 2.0 Hz, 1H), 5.93-5.83 (m, 1H), 5.21-5.13 (m, 2H), 4.08 (t, ^3J = 6.8 Hz, 2H), 2.59 (q, ^3J = 6.8 Hz, 2H).

To a solution of 1,1,3,3,5,5-hexamethyltrisiloxane (0.33 g, 1.56 mmol) and Karstedt catalyst (100ppm/Si-Hmol) in toluene (20 mL) was added 4-(but-3-enyloxy)-2-chlorobenzaldehyde (0.69 g, 3.30 mmol) using a pressure-equalizing additional funnel at room temperature under Ar atmosphere, then the mixture was stirred for 12h. The reaction was monitored by ^{1}H NMR analysis. After the solvent was removed by evaporation, the resulting residue was chromatographed over silica gel (eluent: pentane/DCM, 1 : 1 → 1 : 4), giving compound **AlSi (23)** in 62 % yield as a transparent and colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 10.32 (s, 2H), 7.89 (d, ^{3}J = 8.3 Hz, 2H), 6.91 (s, $^{>3}J$ = 2.0 Hz, 2H), 6.88 (d, ^{3}J = 8.8 Hz, $^{>3}J$ = 2.0 Hz, 2H), 4.02 (t, ^{3}J = 6.4 Hz, 4H), 1.83 (qui, ^{3}J = 7.4 Hz, 4H), 1.51 (qui, ^{3}J = 7.8 Hz, 4H), 0.59 (t, ^{3}J = 8.3 Hz, 4H), 0.08 (s, 12H), 0.03 (s, 6H). ^{13}C NMR (400 MHz, $[D_6]$DMSO): δ ppm = 188.72, 164.40, 139.86, 131.13, 125.97, 115.77, 114.16, 68.58, 32.52, 19.84, 18.02, 1.45, 0.35; LCMS: m/z (%): 681.58 (100) $[M+H]^+$; HRMS (ESI): *m/z* calcd for $C_{28}H_{42}Cl_2O_6Si_3Li_1$ $[M+Li]^+$ 635.1821, found 635.1771; elemental analysis calcd (%) for $C_{28}H_{42}Cl_2O_6Si_3$: C, 53.40, H, 6.72, found: C, 53.21, H, 6.62.

Synthesis of a mono-amine analogue, mono- AmD for a model oligomer; AmM3 (24)



(24)

(i) 2-(2-chloroethoxy)ethanol, K_2CO_3, at 80°C in DMF; (ii) 1-bromo-2-methoxyethane, K_2CO_3, at 80°C in DMF; (iii) tosyl chloride, triethylamine at r. m. in DCM; (iv) potassium phthalimide at 120 °C in DMF; (v) hydrazine monohydrate, refluxed in EtOH.

To a suspension of 1,5-dihydroxynaphtalene (10.00 g, 62.43 mmol), K_2CO_3 (10.40 g, 75.24

mmol) and KI (0.52 g, 3.12 mmol) in DMF (80 ml) was added 2-(2-chloroethoxy)ethanol (7.78 g, 62.45 mmol) under N_2 atmosphere at room temperature. The resulting mixture was heated at 80 °C for 12 h and then filtered, and the filtrate was concentrated under reduced pressure. The residue was placed in DCM (100 ml) and the solution was washed with brine (50 ml × 3) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: DCM/EtOAc, 1 : 1) to afford 5-(2-(2-hydroxyethoxy)ethoxy)naphthalen-1-ol as a brownish solid in 23 % yield. ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 10.03 (br, 1H), 7.70 (d, ^3J = 8.3 Hz, 1H), 7.61 (d, ^3J = 8.3 Hz, 1H), 7.32 (t, ^3J = 8.3 Hz, 1H), 7.27 (t, ^3J = 8.3 Hz, 1H), 6.94 (d, ^3J = 7.8 Hz, 1H), 6.89 (d, ^3J = 7.8 Hz, 1H), 4.63 (br, 1H), 4.24 (t, ^3J = 4.4 Hz, 2H), 3.88 (t, ^3J = 4.4 Hz, 2H), 3.58-3.55 (m, 4H).

To a suspension of 5-(2-(2-hydroxyethoxy)ethoxy)naphthalen-1-ol (2.00 g, 8.06 mmol) and K_2CO_3 (4.67 g, 24.17 mmol) in DMF (20 ml) was added 1-bromo-2-methoxyethane (2.24 g, 16.12 mmol) under N_2 atmosphere at room temperature. The resulting mixture was heated at 80 °C for 12 h and then filtered, and the filtrate was concentrated under reduced pressure. The residue was placed in DCM (50 ml) and the solution was washed with brine (50 ml × 3) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: DCM/EtOAc, 3 : 2) to afford desired compound as a white solid in 88 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.91 (d, ^3J = 8.3 Hz, 1H), 7.87 (d, ^3J = 8.3 Hz, 1H), 7.36 (tt, ^3J = 8.3 Hz, 1H, 1H), 6.86 (d, ^3J = 7.4 Hz, 2H), 4.32-4.28 (m, 4H), 4.01 (t, ^3J = 4.9 Hz, 2H), 3.90 (t, ^3J = 4.9 Hz, 2H), 3.80-3.74 (m, 4H), 3.51 (s, 3H).

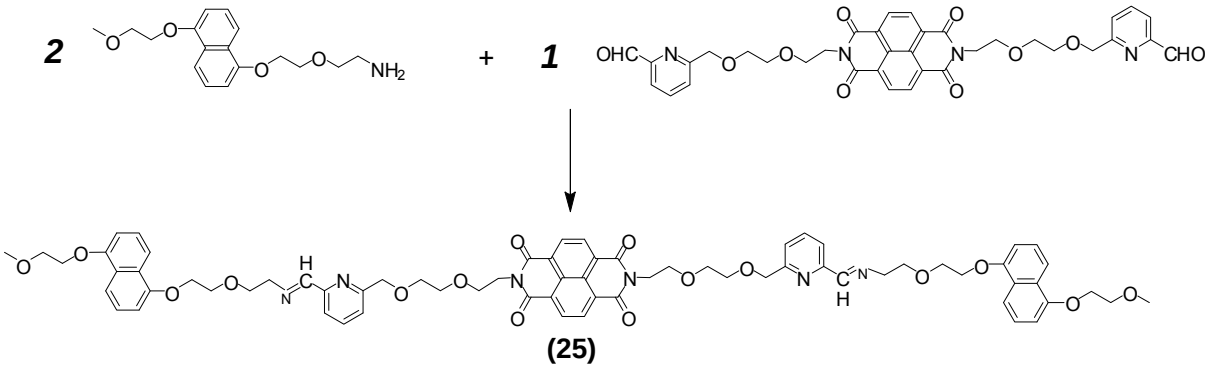
To a solution of intermediate (2.16 g, 7.05 mmol) and tosyl chloride (2.02 g, 10.58 mmol) in DCM (30 ml) at 0 °C under N_2 atmosphere was added through a dropping funnel triethylamine (2.14 g, 21.15 mmol). The mixture was allowed to warm slowly to room temperature and stirred overnight, and then washed with 1N HCl aqueous solution(10 ml × 3), saturated aqueous $NaHCO_3$ (10 ml × 3) and brine (10 ml × 2) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the remaining residue was chromatographed over silica gel (eluent: DCM → 10 % EtOAc in DCM) to afford desired compound as a yellowish solid in 86 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.91 (d, ^3J = 8.3 Hz, 1H), 7.82 (d, ^3J = 8.8 Hz, 1H), 7.78 (d, ^3J = 7.8 Hz, 2H), 7.35 (t, ^3J = 8.3 Hz, 2H), 7.24 (d, ^3J = 7.8 Hz,

2H), 6.86 (d, ^3J = 7.3 Hz, 1H), 6.81 (d, ^3J = 7.8 Hz, 1H), 4.29 (t, ^3J = 4.9 Hz, 2H), 4.23-4.18 (m, 4H), 3.92-3.89 (m, 4H), 3.83 (t, ^3J = 4.4 Hz, 2H), 3.51 (s, 3H), 2.35 (s, 3H).

To a solution of intermediate (2.80 g, 6.08 mmol) in DMF (20 ml) was added potassium phthalimide (1.69 g, 9.12 mmol) at room temperature under N_2 atmosphere. The reaction mixture was heated at 120 °C for 12 h and then poured into 50 ml of water. The resulting mixture was extracted with DCM (20 ml × 3) and the combined extracts was washed with brine (10 ml × 3), dried over anhydrous Na_2SO_3 and concentrated under pressure. The resulting residue was chromatographed over silica gel (eluent: 10 % EtOAc in DCM → 30 % EtOAc in DCM) to give product as a yellowish solid in 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.84 (d, ^3J = 8.8 Hz, 1H), 7.78-7.75 (m, 2H, 1H), 7.64-7.62 (m, 2H), 7.29 (t, ^3J = 7.4 Hz, 2H), 6.83 (d, ^3J = 7.3 Hz, 1H), 6.78 (d, ^3J = 7.8 Hz, 1H), 4.28 (t, ^3J = 4.9 Hz, 2H), 4.22 (t, ^3J = 4.9 Hz, 2H), 3.99-3.94 (m, 4H), 3.91-3.88 (m, 4H), 3.51 (s, 3H).

To a solution of intermediate (2.00 g, 4.59 mmol) in EtOH (50 mL) was added dropwise hydrazine monohydrate (2.30 g, 45.93 mmol) and the mixture was then refluxed overnight under N_2 atmosphere. The resulting solid was filtered off and the volatiles were removed under reduced pressure. The residue was placed in DCM and the resulting precipitate was then filtered off and the filtrate was evaporated. The residue was purified by recrystallization from water, affording the desired product **mono-AmD (24)** as a white solid in 63 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.90 (dd, ^3J = 8.3 Hz, 2H), 7.35 (t, ^3J = 7.8 Hz, 2H), 6.86 (d, ^3J = 7.8 Hz, 2H), 4.30 (tt, ^3J = 4.4 Hz, 2H, 2H), 3.96 (t, ^3J = 4.9 Hz, 2H), 3.89 (t, ^3J = 4.9 Hz, 2H), 3.65 (t, ^3J = 4.9 Hz, 2H), 3.51 (s, 3H); ^{13}C NMR ($CDCl_3$): δ ppm = 154.52, 154.46, 126.94, 125.23, 125.19, 114.86, 114.72, 105.88, 105.84, 73.82, 71.26, 69.71, 68.05, 67.95, 59.46, 42.04; LCMS: m/z (%): 306.31 (100) $[M+H]^+$; HRMS (ESI): *m*/*z* calcd for $C_{17}H_{24}N_1O_4$ $[M+H]^+$ 306.1700, found 306.1743.

Synthesis of model oligomer of dynamer P3 for X-ray crystallographic analysis (25)

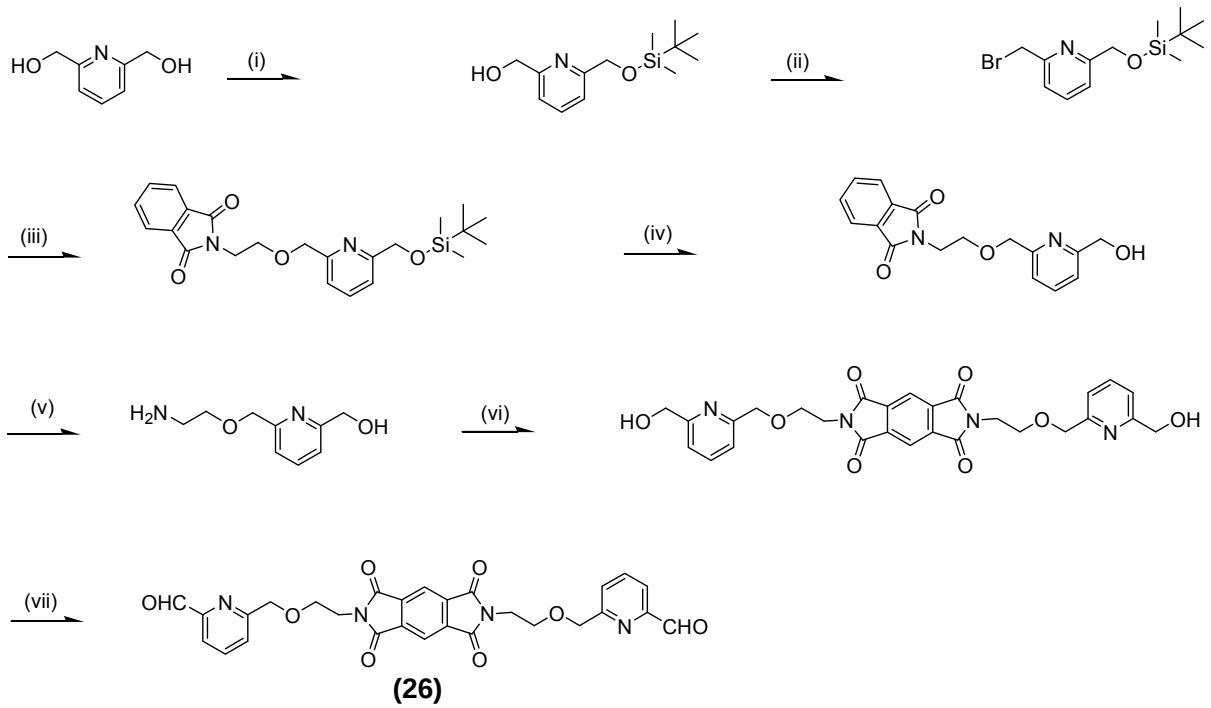


Mono-amine **(24)** and the dialdehyde **AlA (22)** were dissolved in $CHCl_3$, followed by the addition of anhydrous $MgSO_4$. The reaction mixture was heated to 60 °C for 24 h under N_2 atomsphere, and then the solvent was evaporated after the filtration of $MgSO_4$, affording the title compound. A solution of NaOTf or KOTf (2 eq.) in CD_3CN was added to a solution of oligomer of dynamer in $CHCl_3$ and slow evaporation of the mixing solution of CD_3CN and $CHCl_3$ yielded crystals of the Na^+ or K^+ complex of the model oligomer of dynamer suitable for structure determination by X-ray crystallographic analysis.

Table 7-1. Crystallographic data, details of data collection and structure refinement parameters for trimer(oligomer of P3) with NaOTf or KOTf

Compound	**trimer with NaOTf**	**trimer with KOTf**
Chemical formula	$C_{72}H_{76}F_6N_6Na_2O_{23}S_2$	$C_{72}H_{74}F_6K_2N_6O_{22}S_2$
M (g mol^{-1})	1617.47	1631.69
Temperature, (K)	293(2)	173(2)
Wavelength, (Å)	0.71073	0.71073
Crystal system	*Triclinic*	*Triclinic*
Space group	*P-1*	*P-1*
a(Å)	9.4185(8)	10.7351(4)
b(Å)	11.2053(15)	10.7761(5)
c(Å)	19.525(3)	18.2716(10)
α(°)	82.785(4)	81.963(2)
β(°)	79.497(7)	87.340(3)
γ(°)	68.680(6)	61.615(2)
V(Å^3)	1883.5(4)	1840.83(15)
Z	1	1
D_c (g cm^{-3})	1.424	1.472
μ (mm^{-1})	0.178	0.281
F(000)	840	848
Goodness-of-fit on F^2	1.002	1.025
Final *R1, wR*$_2$ [I>2σ(I)]	0.1249, 0.3042	0.0570, 0.1410
R1, *wR*$_2$ (all data)	0.3257, 0.4106	0.1129, 0.1689
Largest diff. peak and hole (eÅ^{-3})	0.336, -0.248	0.600, -0.443

Synthesis of dialdehyde monomer (26)



(26)

(i) imidazole, TBSCl, at r. t. in DMF; (ii) carbon tetrabromide, triphenylphosphine, at r.m. in diethyl ether; (iii) 2-(2-hydroxyethyl)isoindoline-1,3-dione, NaH, at r. m. in DMF; (iv) AcOH, H_2O at 80 °C in THF, (v) hydrazine monohydrate, refluxed in EtOH; (vi) 1,2,4,5- benzenetetracarboxylic dianhydride, at 120 °C in DMF; (vii) Dess–Martin periodinane, at r. m. in DCM.

To a solution of 2,6 –dihydroxymethyl pyridine (20.00 g, 143.73 mmol) and imidazole (5.42 g, 79.61 mmol) in DMF (200 mL) at 0 °C under N_2 atmosphere was added dropwise over a period of 1h a solution of TBSCl (12.02g, 79.75 mmol) in DMF (50 mL). The reaction mixture was allowed to warm to ambient temperature and stirred overnight. After the solvent was removed, the residue was placed in 200 ml of DCM. The organic solution was washed with aq. 1N HCl solution (50 ml × 2), saturated aq. NaHCO3 solution (50 ml × 2) and brine (50 ml × 2) and dried over Na_2SO4. The solvent was evaporated under reduced pressure and the crude mixture was purified by silica gel chromatography(eluent: 10 → 50 % EtOAc in DCM) to afford 2-Hydroxymethyl-6-(tert-buthyldimetthylsilyloxymethyl)pyridine as a colorless liquid in 42 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.70 (t, ^3J = 7.8 Hz, 1H), 7.42 (d, ^3J = 7.8 Hz, 1H), 7.10 (d, ^3J = 7.8 Hz, 1H), 4.84 (s, 2H), 4.73 (s, 2H), 3.80 (br, 1H), 0.97 (s, 9H), 0.13 (s, 6H).

To a solution of carbon tetrabromide (10.91 g, 32.90 mmol) and mono-protected diol (7.58 g, 29.91 mmol) in diethyl ether (100 mL) was added through a dropping funnel a solution of triphenylphosphine (9.81 g. 37.40 mmol) in diethyl ether (50 mL) at r.m. under N_2 and the reaction mixture was stirred for 12 h, during which time a white precipitate (triphenylphosphine oxide) formed. The precipitate was removed off by vacuum filtration and the filtrate was concentrated under reduced pressure to give a crude orange oil. The product was purified by silica gel column chromatography (heptane → 50 % DCM in heptane), giving bromomethyl-6-(tert-butyldimethylsilyloxymethyl) pyridin as a pale yellow oil in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 8.05 (t, ^3J = 7.8 Hz, 1H), 7.79 (d, ^3J = 7.8 Hz, 1H), 7.65 (d, ^3J = 7.8 Hz, 1H), 5.17 (s, 2H), 4.85 (s, 2H), 1.30 (s, 9H), 0.46 (s, 6H).

To a suspension of sodium hydride (0.77 g, 60% in mineral oil, 19.12 mmol) in DMF (40 ml) was added a solution of 2-(2-hydroxyethyl)isoindoline-1,3-dione (3.60 g, 18.83 mmol) in DMF (20 ml), and the mixture was stirred at room temperature under N_2 atmosphere. After 1 h, a solution of bromomethyl-6- (tert-butyldimethylsilyloxymethyl) pyridin (6.00g, 18.96 mmol) in DMF (20 ml) was added to the reaction mixture, and then the resulting mixture was stirred at room temperature for 24 h. The solid was filtered off by a celite treatment and the solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography (eluent: EtOAc/DCM, 1:1) to yield 2-(2-((6-((tert-butyldimethylsilyloxy)methyl)pyridin-2-yl)methoxy)ethyl)isoindoline-1,3-dione as a transparent and colorless oil in 56 % yeild. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.86-7.84 (m, 2H), 7.72-7.71 (m, 2H), 7.63 (t, ^3J = 7.4 Hz, 1H), 7.37 (d, ^3J = 7.8 Hz, 1H), 7.23 (d, ^3J = 7.4 Hz, 1H), 4.78 (s, 2H), 4.61 (s, 2H), 3.98 (t, ^3J = 5.9 Hz, 2H), 3.81 (t, ^3J = 5.4 Hz, 2H), 0.94 (s, 9H), 0.10 (s, 6H).

A 2-(2-((6-((tert-butyldimethylsilyloxy)methyl)pyridin-2-yl)methoxy)ethyl)isoindoline-1,3-dione (4.48 g, 10.50 mmol) in a mixing solution of acetic acid (40 mL), water (30 mL) and THF (30 mL) was heated at 80 °C overnight. After the solvent was evaporated, the residue was dissolved in EtOAc (60 ml) and the organic solution was washed with saturated aqueous $NaHCO_3$ (20 mL × 3), brine (20 ml × 2) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the remaining residue was chromatographed over silica gel (eluent: EtOAc/DCM, 4:1) to afford 2-(2-((6-(hydroxymethyl)pyridin-2-yl)

methoxy)ethyl)isoindoline-1,3-dione as a colorless in 92 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.87-7.86 (m, 2H), 7.73-7.72 (m, 2H), 7.62 (t, ^{3}J = 7.4 Hz, 1H), 7.29 (d, ^{3}J = 7.4 Hz, 1H), 7.10 (d, ^{3}J = 7.8 Hz, 1H), 4.71 (s, 2H), 4.66 (s, 2H), 3.99 (t, ^{3}J = 5.4 Hz, 2H), 3.84 (t, ^{3}J = 5.9 Hz, 2H).

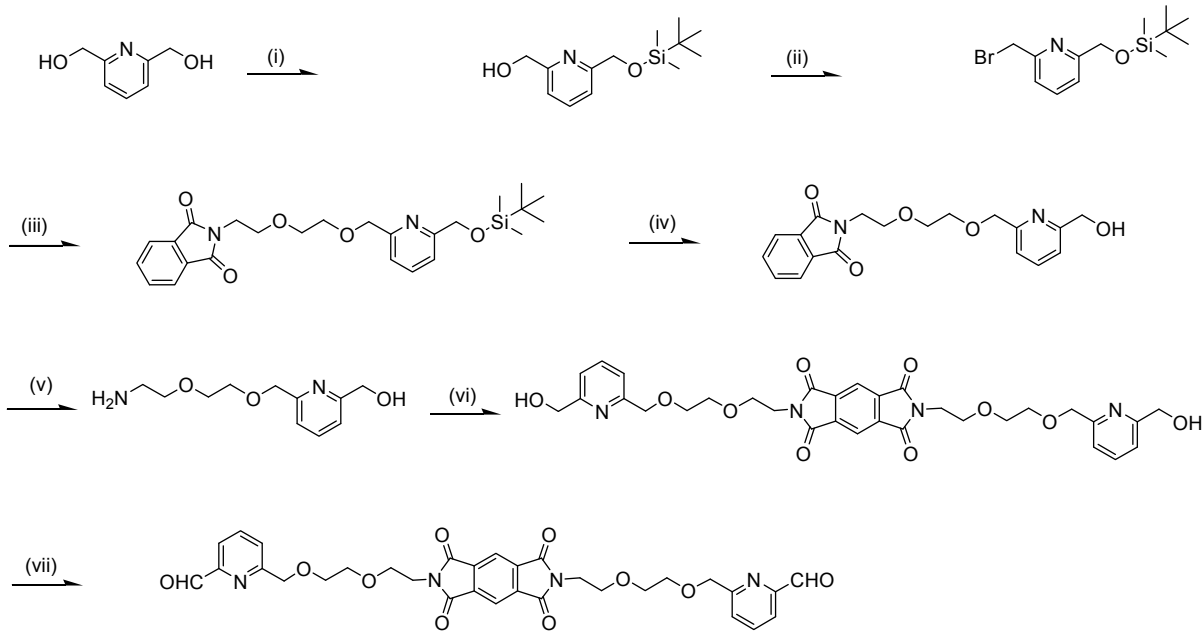
To a solution of 2-(2-((6-(hydroxymethyl)pyridin-2-yl)methoxy)ethyl)isoindoline-1,3-dione (2.63 g, 8.42 mmol) in EtOH (50 mL) was added dropwise hydrazine monohydrate (2.40 g, 48.03 mmol) and the mixture was then refluxed overnight under N_2 atmosphere. The resulting solid was filtered off and the volatiles were removed by rotary evaporator. The residue was placed in DCM and the resulting precipitate was filtered off again and the filtrate was evaporated under reduced pressure. The product (6-((2-aminoethoxy)methyl) pyridin-2-yl)methanol thus obtained was used for next step without further purification (transparent and colorless oil in 98 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 7.69 (t, ^{3}J = 7.8 Hz, 1H), 7.36 (d, ^{3}J = 7.3 Hz, 1H), 7.15 (d, ^{3}J = 7.8 Hz, 1H), 4.74 (s, 2H), 4.67 (s, 2H), 3.61 (t, ^{3}J = 5.4 Hz, 2H), 2.94 (t, ^{3}J = 5.4 Hz, 2H).

To a solution of 1,2,4,5-benzenetetracarboxylic dianhydride (0.47 g, 2.14 mmol) in DMF (30 ml) was slowly added (6-((2-aminoethoxy)methyl) pyridin-2-yl)methanol (0.80 g, 4.39 mmol) at room temperature under N_2. The reaction mixture was heated to 120 °C and stirred overnight. After the completion of the reaction, the mixture was concentrated under reduced pressure. Purification of the crude compound by a silica gel column chromatography, eluting with 5 % EtOH in DCM, provided the desired product as a white solid (896 mg, in 77 % yield). ^{1}H NMR (400 MHz, [D_6]DMSO): δ ppm = 8.21 (s, 2H), 7.70 (t, ^{3}J = 7.8 Hz, 2H), 7.31 (d, ^{3}J = 7.8 Hz, 2H), 7.15 (d, ^{3}J = 7.8 Hz, 2H), 4.52 (s, 4H), 4.46 (s, 4H), 3.88 (t, ^{3}J = 5.4 Hz, 2H), 3.75 (t, ^{3}J = 5.4 Hz, 2H).

The intermediate (0.89 g, 1.63 mmol) and Dess–Martin periodinane (1.73 g, 4.07 mmol) were stirred in DCM (50 mL) for 12h. The reaction mixture was washed with saturated $NaHCO_3$ aq. solution (20 ml × 3), brine (20 ml × 2) and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was chromatographed over silica gel, eluting 20 % EtOAc in DCM, to afford the product **(26)** as a white solid in 59 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 9.99 (s, 2H), 8.29 (s, 2H), 7.87-7.82 (m, 4H), 7.62 (d, ^{3}J = 6.8 Hz, $^{>}J$ = 1.5 Hz, 2H), 4.74 (s, 4H), 4.07 (t, ^{3}J = 5.4 Hz, 4H), 3.90 (t, ^{3}J = 5.4 Hz, 4H); ^{13}C

NMR (400 MHz, $CDCl_3$): δ ppm = 193.36, 166.21, 159.02 152.20, 137.91, 137.39, 125.62, 120.68, 118.55, 73.27, 67.83, 38.34; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{22}N_4O_8Li_1$ $[M+Li]^+$ 549.1593, found 549.1646.

Synthesis of dialdehyde monomer (27)

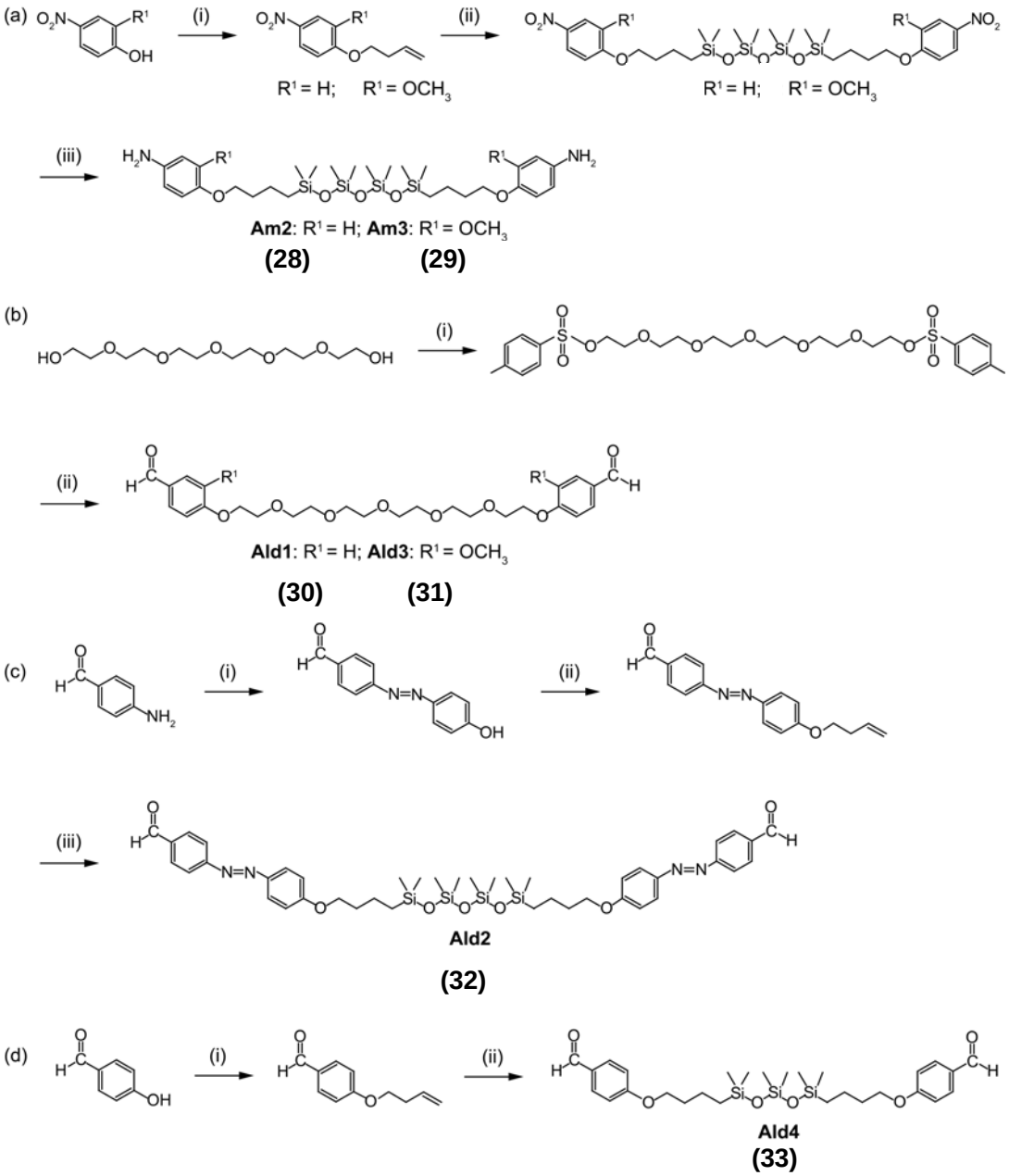


(27)

(i) imidazole, TBSCl, at r. t. in DMF; (ii) carbon tetrabromide, triphenylphosphine, at r.m. in diethyl ether; (iii) 2-(2-(2-hydroxyethoxy)ethyl)isoindoline-1,3-dione, NaH, at r. m. in DMF; (iv) AcOH, H_2O at 80 °C in THF, (v) hydrazine monohydrate, refluxed in EtOH; (vi) 1,2,4,5- benzenetetracarboxylic dianhydride, at 120 °C in DMF; (vii) Dess–Martin periodinane, at r. m. in DCM.

Synthesis of **(27)** was carried out in the same manner described in the scheme of monomer synsthesis of (**22)** and **(26)** previously. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm = 10.00 (s, 2H), 8.17 (s, 2H), 7.90-7.82 (m, 4H), 7.66 (d, ^3J = 7.8 Hz, 2H), 4.68 (s, 4H), 3.98 (t, ^3J = 5.4 Hz, 4H), 3.81 (t, ^3J = 5.9 Hz, 4H), 3.74-7.70 (m, 8H); ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm = 193.45, 166.19, 159.62, 152.19, 137.80, 137.26, 125.59, 120.55, 118.25, 73.63, 70.51, 70.21, 67.82, 38.17; elemental analysis calcd (%) for $C_{32}H_{30}N_4O_{10}$: C, 60.95, H, 4.80, N, 8.88, found: C, 60.80, H, 4.76, N, 8.66.

CHAPTER 5



(a)(i) 4-bromo-1-butene, K_2CO_3, refluxed in acetone, 12 h; (ii) 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 2 drops of Karstedt's catalyst stirred in toluene, 12 h; (iii) 10 % Pd-C, hydrazine monohydrate stirred in methanol, 12 h. (b)(i) triethylamine, *p*-toluenesulfonyl chloride, stirred in dry CH_2Cl_2, 24 h; (ii) 4-hydroxybenzaldehyde or vanillin, K_2CO_3 in anhyd. DMF, 80ºC, 12 h. (c)(i) ref [5.7] (ii) 4-bromo-1-butene, K_2CO_3 in anhyd. DMF, 80ºC, 12 h; (iii) 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 2 drops of Karstedt's catalyst stirred in toluene, 12 h. (d)(i) 4-bromo-1-butene, K_2CO_3 in anhyd. DMF, 80ºC, 12 h; (ii) 1,1,3,3,5,5-hexamethyltrisiloxane, 2 drops of Karstedt's catalyst stirred in toluene, 12 h.

Synthesis of diamines monomer (Am2) (28)

4-(but-3-enyloxy)-nitrobenzene**:** A mixture of 4-nitrophenol (5 g, 35.9 mmol), 4-bromo-1-butene (7.28 g, 53.9 mmol), K_2CO_3 (7.5 g, 53.9 mmol) and 100 ml acetone was reflux with stirring under nitrogen for overnight. The white solids in the reaction mixture were then filtered by the filter paper. The filtrate acetone was then reduced to 0 ml. The oily crude product was then purified by extraction the diethyl ether (100 ml) phase with water (3 X 100 ml). The organic phase was collected and concentrated. Brown oil was obtained (80 %). ES-MS (+ve mode): m/z 194 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 8.21 (d, *J* = 9.26 Hz, 2H), 6.97 (d, *J* = 9.27 Hz, 2H), 5.91 (tdd, *J* = 17.02, 10.25, 6.72 Hz, 1H), 5.19 (dddd, *J* = 16.27, 10.26, 2.90, 1.52 Hz, 2H), 4.13 (t, *J* = 6.66 Hz, 2H), 2.61 (q, *J* = 6.67 Hz, 2H). Anal. Calcd. for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.20; H, 5.73; N, 7.23.

Tetradimethylsiloxanes-α,ω-bis[4-(but-3-enyloxy)-nitrobenzene]**:**4-(But-3-enyloxy)-nitrobenz ene (2 g, 10.31 mmol) was added to a 20 mL of toluene 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (1.33 g, 4.71 mmol). 2 drops of Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene) was then added to the solution mixture. The reaction was stirred at room temperature under nitrogen for overnight. The reaction mixture was concentrated, giving crude brown oil which was then purified by silica gel column chromatography to give brown oil (98%). ES-MS (+ve mode): m/z 670 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 8.21(d, *J* = 9.30 Hz, 4H), 6.96 (d, *J* = 9.27 Hz, 4H), 4.08 (t, *J* = 6.39 Hz, 4H), 1.96-1.75 (m, 4H), 1.67-1.46 (m, 4H), 0.72-0.55 (m, 4H), 0.11 (m, 24H). Anal. Calcd. for $C_{28}H_{48}N_2O_9Si_4$: C, 50.27; H, 7.23; N, 4.19. Found: C, 50.33; H, 7.30; N, 4.12.

Tetradimethylsiloxanes-α,ω-bis[4-(butyloxy)-aminobenzene]**:**Tetradimethylsiloxanes-α,ω-bis [4-(buten-4-oxy)-nitrobenzene] (1.667 g, 2.49 mmol) and 10 % Pd-C (0.32 g) were added to a 40 mL of methanol. Then hydrazine monohydrate (1.25 g, 25 mmol) was slowly added to the solution mixture. The reaction was stirred at room temp under N_2 for overnight. The reaction mixture was concentrated, giving yellow oil **(28)** (100 %). ES-MS (+ve mode): m/z 610 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 6.79 (d, *J* = 8.81 Hz, 4H), 6.65 (d, *J* = 8.81 Hz, 4H), 3.93 (t, *J* = 6.50 Hz, 4H), 1.95-1.72 (m, 4H), 1.56 (tt, *J* = 9.36, 6.53 Hz, 4H),

0.77-0.55 (m, 4H), 0.14 (m, 24H). Anal. Calcd. for $C_{28}H_{52}N_2O_5Si_4$: C, 55.22; H, 8.61; N, 4.60. Found: C, 55.11; H, 8.70; N, 4.62.

Synthesis of diamines monomer (Am3) (29)

The product was synthesized in the same procedure described for **Am2** in *part (a) – (c)* with replacing the starting materials from 4-nitrophenol to 4-nitroguaiacol.

3-methoxy-4-(but-3-enyloxy)-nitrobenzene: yield: 84 %. ES-MS (+ve mode): m/z 224 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 7.92 (dd, *J* = 8.92, 2.61 Hz, 1H), 7.77 (d, *J* = 2.56 Hz, 1H), 6.93 (d, *J* = 8.94 Hz, 1H), 5.92 (dd, *J* = 17.16, 10.33 Hz, 1H), 5.29-5.11 (m, 2H), 4.18 (t, *J* = 6.97 Hz, 2H), 3.97 (s, 3H), 2.74-2.60 (m, 2H). Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.22; H, 5.94; N, 6.31.

Tetradimethylsiloxanes-α,ω-bis[3-methoxy-4-(but-3-enyloxy)-nitrobenzene]: yield: 98 %. ES-MS (+ve mode): m/z 729 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 7.91 (dd, *J* = 8.91, 2.62 Hz, 2H), 7.76 (d, *J* = 2.59 Hz, 2H), 6.91 (d, *J* = 8.94 Hz, 2H), 4.13 (t, *J* = 6.70 Hz, 4H), 3.95 (s, 6H), 2.02-1.86 (m, 4H), 1.64-1.48 (m, 4H), 0.72-0.58 (m, 4H), 0.10 (m, 24H). Anal. Calcd. for $C_{30}H_{52}N_2O_{11}Si_4$: C, 53.85; H, 8.44; N, 4.19. Found: C, 54.01; H, 8.39; N, 4.08.

(Am3) (29): yield: 100 %. ES-MS (+ve mode): m/z 669 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 6.74 (d, J = 8.40 Hz, 2H), 6.32 (d, J = 2.56 Hz, 2H), 6.23 (dd, J = 8.38, 2.60 Hz, 2H), 3.94 (t, J = 6.80 Hz, 4H), 3.82 (s, 6H), 3.33 (br, 4H), 1.90-1.77 (m, 4H), 1.58-1.43 (m, 4H), 0.68-0.56 (m, 4H), 0.08 (m, 24H). Anal. Calcd. for $C_{30}H_{56}N_2O_7Si_4$: C, 53.85; H, 8.44; N, 4.19. Found: C, 54.01; H, 8.39; N, 4.08.

Synthesis of dialdehydes monomer (Ald1) (30)

3,6,9,12,15-Pentaoxaheptadecane-1,17-diylbis(4-methylbenzenesulfonate): A mixture of

hexaethylene glycol (3 g, 10.6 mmol) and triethylamine (10.7 g, 110 mmol) in 50 ml dry CH_2Cl_2 was kept at 0 °C under N_2. Solid *p*-toluenesulfonyl chloride (31.8 mmol) was slowly added to the mixture which was kept under 5 °C. The reaction mixture was stirred under nitrogen for 24 hour at room temp. The reaction mixture was then washed with pH 1 HCl (aq) 150 ml X 5. The filtrate CH_2Cl_2 was then collected and reduced to 0 ml. The oily crude product was then purified by silica gel chromography by using ethylacetate:CH_2Cl_2(1:1). Colorless oil was obtained (60 %). ES-MS (+ve mode): m/z 592 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 7.81 (d, *J* = 8.18 Hz, 4H), 7.35 (d, *J* = 8.18 Hz, 4H), 4.21-4.14 (m, 4H), 3.73-3.67 (m, 4H), 3.65-3.61 (br, 8H), 3.62-3.57 (br, 8H), 2.46 (s, 6H). Anal. Calcd. for $C_{26}H_{38}O_{11}S_2$: C, 52.87; H, 6.48. Found: C, 52.74; H, 6.42.

4,4'-[3,6,9,12,15-pentaoxaheptadecane-1,17-diylbis(oxy)]dibenzaldehyde: **(Ald1) (30):** A mixture of 3,6,9,12,15-pentaoxaheptadecane-1,17-diylbis(4-methylbenzenesulfonate) (2.7 g, 4.57 mmol), 4-hydroxybenzaldehyde (1.67 g, 13.7 mmol), K_2CO_3 (3.8 g, 27.4 mmol) and 30 ml anhydrous DMF was heat at 80 °C with stirring under nitrogen for overnight. The solids in the reaction mixture were then filtered. The filtrate was then concentrated. The crude product was then purified by silica gel chromography by using pure CH_2Cl_2, then pure ethylacetate, then MeOH to wash out the product. Colorless solid **(31)** was then obtained (74%). ES-MS (+ve mode): m/z 491 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 9.90 (s, 2H), 7.84 (d, *J* = 8.78 Hz, 4H), 7.04 (d, *J* = 8.77 Hz, 4H), 4.28-4.15 (m, 4H), 3.96-3.83 (m, 4H), 3.80-3.57 (m, 16H). Anal. Calcd. for $C_{26}H_{34}O_9$: C, 63.66; H, 6.99. Found: C, 63.53; H, 6.77.

Synthesis of dialdehydes monomer (Ald2) (32)

4-(but-3-enyloxy)phenyl-4'-formylazobenzene: A mixture of 4'-formyl-4-hydroxyphenylazobenzene, (4.07 g, 18 mmol), 4-bromo-1-butene (4.85 g, 36 mmol), K_2CO_3 (10 g, 72 mmol) and 30 ml anhydrous DMF was heated at 80 °C with stirring under nitrogen for overnight. The solids in the reaction mixture were then filtered by the filter paper. The filtrate DMF was then reduced to 0 ml. The crude product was then purified by silica chromography by using pet heptane:acetone (5:1). Orange solid was then obtained (93%). ES-MS (+ve mode): m/z 281 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm =10.17 (s,

1H), 8.14 (d, *J* = 8.66 Hz, 2H), 8.07 (d, *J* = 8.66 Hz, 2H), 8.01 (d, *J* = 9.06 Hz, 2H), 7.19 (d, *J* = 9.05 Hz, 2H), 5.98 (m, 1H), 5.29-5.08 (m, 2H), 4.23 (t, *J* = 6.62 Hz, 2H), 2.62 (q, *J* = 6.65 Hz, 2H). Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.99; H, 5.73; N, 9.93.

Tetradimethylsiloxanes-α,ω-bis[4-(butyloxy)phenyl-4'-formylazobenzene] **(Ald2) (32):** 4-(But-3-enyloxy)phenyl-4'-formylazobenzene, (0.7373 g, 2.63 mmol) was added to a 6 mL of toluene 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (0.35 g, 1.25 mmol). 2 drops of Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene) was then added to the solution mixture. The reaction was stirred at room temperature under nitrogen for overnight. The reaction mixture was concentrated, giving crude red oil which was then purified by silica gel column chromatography [heptane:CH_2Cl_2:acetone (3:2:0.2)] to give red solid (98%). ES-MS (+ve mode): m/z 843 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 10.15 (s, 2H), 8.12 (d, *J* = 8.64 Hz, 4H), 8.04 (d, *J* = 8.63 Hz, 4H), 7.99 (d, *J* = 9.04 Hz, 4H), 7.15 (d, *J* = 9.03 Hz, 4H), 4.17 (t, *J* = 6.37 Hz, 4H), 1.98-1.81 (m, 4H), 1.64 (tt, *J* = 9.38, 6.50 Hz, 4H), 0.79-0.66 (m, 4H), 0.15 (m, 24H). Anal. Calcd. for $C_{42}H_{58}N_4O_7Si_4$: C, 59.82; H, 6.93; N, 6.64. Found: C, 59.54; H, 6.95; N, 6.60.

Synthesis of dialdehydes monomer (Ald3) (31)

The product was synthesized by using the procedure described for **Ald1 (30)** in *part (a) – (b)* with replacing the reagent from 4-hydroxybenzaldehyde to vanillin.

4,4'-[3,6,9,12,15-pentaoxaheptadecane-1,17-diylbis(oxy)]bis-(3-methoxybenzaldehyde) **(Ald3) (31):** yield: 95 %. ES-MS (+ve mode): m/z 551 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 9.86 (s, 2H), 7.50-7.36 (m, 4H), 7.02 (d, *J* = 8.15 Hz, 2H), 4.27 (t, *J* = 7.06 Hz, 4H), 3.98-3.81 (m, 10H), 3.85-3.57 (m, 16H). Anal. Calcd. for $C_{28}H_{38}O_{11}$: C, 61.08; H, 6.96. Found: C, 60.86; H, 7.07.

Synthesis of dialdehydes monomer (Ald4) (33)

4-(but-3-enyloxy)-benzaldehyde: A mixture of 4-hydroxybenzaldehyde (2.19 g, 17.9 mmol), 4-bromo-1-butene (3.64 g, 27.0 mmol), K_2CO_3 (3.75 g, 27 mmol) and 30 ml anhydrous DMF was heated at 80ºC with stirring under nitrogen for overnight. The reaction mixture was then reduced to 0 ml. The crude solid was extracted with CH_2Cl_2. The solid precipitates were filtered out. The organic phase was collected and concentrated. Crude yellow oil was obtained and purified by silica gel column chromatography by using heptane:CH_2Cl_2(2:3). Colorless oil was obtained (86 %). ES-MS (+ve mode): m/z 177 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 9.90 (s, 1H), 7.85 (d, *J* = 8.66 Hz, 2H), 7.02 (d, *J* = 8.62 Hz, 2H), 6.00-5.84 (m, 1H), 5.29-5.09 (m, 2H), 4.12 (t, *J* = 6.65 Hz, 2H), 2.60 (q, *J* = 6.66 Hz, 2H). Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.86; H, 6.99.

Tridimethylsiloxanes-α,ω-bis[4-(butyloxy)-benzaldehyde] **(Ald4) (33)** 4-(but-3-enyloxy)-benzaldehyde (1.81 g, 10.31 mmol) was added to a 20 mL of toluene 1,1,3,3,5,5-hexamethyltrisiloxane (0.98 g, 4.71 mmol). 2 drops of Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex in xylene) was then added to the solution mixture. The reaction was stirred at room temperature under nitrogen for overnight. The reaction mixture was concentrated, giving yellow oil which was then purified by silica gel column chromatography by using heptane:CH_2Cl_2(2:3) then CH_2Cl_2 to give colorless oil (98%). ES-MS (+ve mode): m/z 561 $[M+H]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm = 9.89 (s, 2H), 7.84 (d, *J* = 8.84 Hz, 4H), 7.00 (d, *J* = 8.73 Hz, 4H), 4.06 (t, *J* = 6.42 Hz, 4H), 1.94-1.78 (m, 4H), 1.65-1.46 (m, 4H), 0.69-0.56 (m, 4H), 0.11 (m, 18H). Anal. Calcd. for $C_{28}H_{44}O_6Si_3$: C, 59.96; H, 7.91. Found: C, 59.34; H, 7.97.

General procedure for the preparation of the dynamic imine polymers

Condensation polymerization reaction was performed by mixing diamine (**Am1** or **Am2** or **Am3**) (0.20 mmol), dialdehyde (**Ald1** – **Ald4**) (0.20 mmol) and anhydrous Na_2SO_4 (2 mmol) in 4 ml $CHCl_3$. The reaction mixture was stirred and at 60 °C under N_2 for 24 hrs. The solution mixture was then concentrated after the filtration of Na_2SO_4. Polymer was obtained

by casting in a petri dish (2.5 cm diameter), by redissolving the polymer product in CH_2Cl_2 and then letting the solution slowly evaporate under atm/50 °C temp.

Polymer P1 (**Ald1/Am2**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$):δ ppm = 8.41 (s, 2H), 7.82 (d, *J* = 8.69 Hz, 4H), 7.20 (d, *J* = 8.77 Hz, 4H), 6.99 (d, *J* = 8.63 Hz, 4H), 6.92 (d, *J* = 8.80 Hz, 4H), 4.24-4.16 (m, 4H), 3.98 (t, *J* = 6.51 Hz, 4H), 3.92-3.86 (m, 4H), 3.78-3.63 (m, 16H), 1.94-1.74 (m, 4H), 1.62-1.47 (m, 4H), 0.72-0.54 (m, 4H), 0.10 (m, 24H). Mn. = 38000 $gmol^{-1}$.

Polymer P2 (**Ald2/Am1**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$):δ ppm = 8.36 (s, 2H), 7.98-7.88 (m, *J* = 8.67, 5.31 Hz, 8H), 7.86 (d, *J* = 8.56 Hz, 4H), 7.01 (d, *J* = 9.03 Hz, 4H), 4.06 (t, *J* = 6.41 Hz, 4H), 3.75 (t, *J* = 6.52 Hz, 4H), 3.71-3.66 (m, 4H), 3.65-3.56 (m, 8H), 2.03 (quin, *J* = 6.48 Hz, 4H), 1.93-1.79 (m, 4H), 1.62-1.48 (m, 4H), 0.73-0.57 (m, 4H), 0.10 (m, 24H). Mn. = 53000 $gmol^{-1}$.

Polymer P3 (**Ald1/Am1**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$):δ ppm = 8.22, 8.20 (s, 2H), 7.69-7.57 (m, 4H), 6.96-6.87 (m, 4H), 4.20-4.07 (m, 4H), 3.92-3.81 (m, 4H), 3.78-3.63 (m, 24H), 3.63-3.53 (m, 8H), 2.04-1.93 (m, 4H). Mn. = 34000 $gmol^{-1}$.

Polymer P4 (**Ald2/Am2**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$):δ ppm = 8.55, 8.37 (s, 2H), 8.02 (d, *J* = 8.42 Hz, 4H), 7.96 (d, *J* = 6.50 Hz, 4H), 7.94 (d, *J* = 6.56 Hz, 4H), 7.29-7.25 (m, 4H), 7.02 (d, *J* = 8.57 Hz, 4H), 6.95 (d, *J* = 8.59 Hz, 4H), 4.06 (t, *J* = 6.33 Hz, 4H), 4.00 (t, *J* = 6.41 Hz, 4H), 1.96-1.75 (m, 8H), 1.62-1.50 (m, 8H), 0.71-0.54 (m, 8H), 0.10 (m, 48H). Mn = 54000 $gmol^{-1}$.

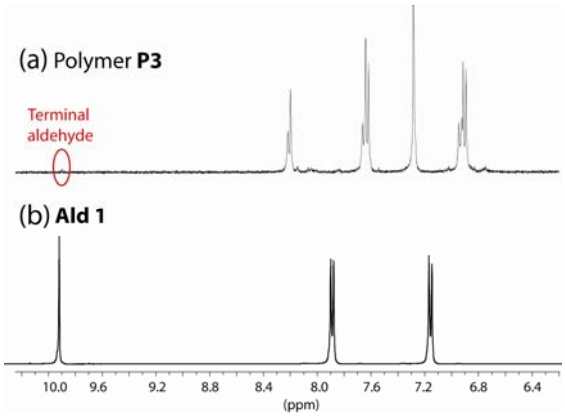
Polymer P5 (**Ald3/Am3**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$): δ ppm 8.40 (s, 2H), 7.60 (d, *J* = 1.68 Hz, 2H), 7.32 – 7.25 (m, 2H), 6.97 (d, *J* = 8.23 Hz, 2H), 6.90 (d, *J* = 8.50 Hz, 2H), 6.88 (d, *J* = 2.31 Hz, 2H), 6.79 (dd, *J* = 8.46, 2.28 Hz, 2H), 4.25 (t, *J* = 5.10 Hz, 4H), 4.05 (t, *J* = 6.88 Hz, 4H), 4.01 (s, 6H), 3.98 – 3.92 (m, 4H), 3.91 (s, 6H), 3.75 – 3.65 (m, 16H), 1.95 – 1.84 (m, 4H), 1.63-1.53 (m, 4H), 0.68-0.54 (m, 4H), 0.18-0.01 (m, 24H).

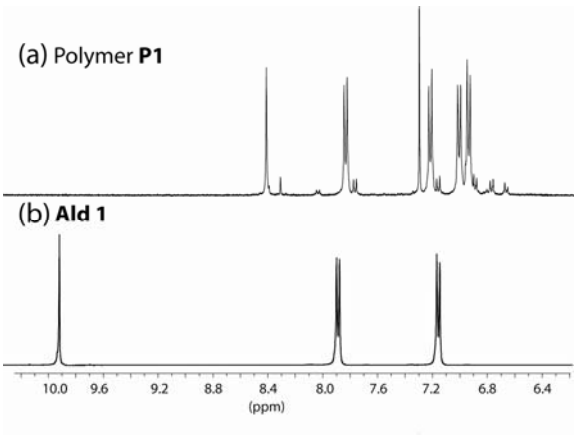
Polymer P6 (**Ald4/Am1**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$): δ ppm 8.22 (s, 2H), 7.65 (d, *J* = 8.75 Hz, 4H), 6.91 (d, *J* = 8.73 Hz, 4H), 3.99 (t, *J* = 6.45 Hz, 4H), 3.73-3.50 (m, 14H), 2.00 (m, 4H), 1.89-1.75 (m, 4H), 1.54-1.44 (m, 6H), 0.68-0.54 (m, 4H), 0.18-0.01

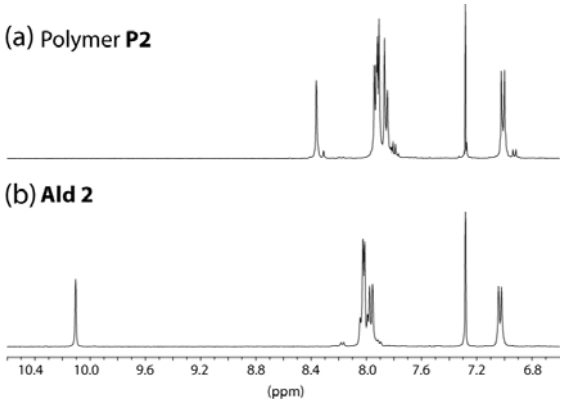
(m,18H).

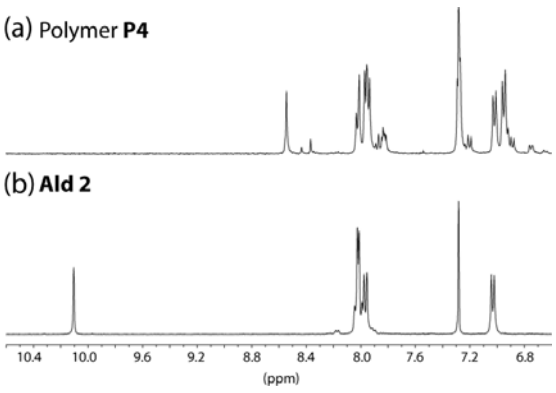
Polymer P7 (**Ald3/Am1**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$): δ ppm 8.20 (s, 2H), 7.41 (d, *J* = 1.72 Hz, 2H), 7.12 (dd, *J* = 8.19, 1.79 Hz, 2H), 6.92 (d, *J* = 8.22 Hz, 2H), 4.22 (t, *J* = 5.16 Hz, 4H), 3.97-3.85 (m, 8H), 3.80-3.51 (m, 28H), 2.07-1.92 (m, 4H), 1.67 (s, 6H).

Polymer P8 (**Ald4/Am3**): ^{1}H-NMR spectrum (400 MHz, 5 mM, $CDCl_3$): δ ppm 8.42 (s, 2H), 7.83 (d, *J* = 8.78 Hz, 2H), 6.97 (d, *J* = 8.76 Hz, 4H), 6.90 (d, *J* = 8.53 Hz, 4H), 6.87 (d, *J* = 2.31 Hz, 2H), 6.78 (dd, *J* = 8.48, 2.41 Hz, 2H), 4.04 (m, 8H), 3.91 (s, 6H), 1.87 (m, 8H), 1.63-1.53 (m, 8H), 0.68-0.54 (m, 8H), 0.18-0.01 (m, 42H).









Detection of the molecular weight of polymer P3 by its terminal group in ^{1}H-NMR at 1 mM in $CDCl_3$

Integration of the very small remaining ^{1}H-NMR signal for terminal aldehyde protons gave a molecular weight of 34000 $gmol^{-1}$ (~50 repeating units) for **P3**. On the other hand, this signal was not observable for **P1**, **P2** and **P4**. The ratio between the signals of their new imine proton and of the α-CH_2 of silioxane moiety for **P1, P2** and **P4**, α-CH_2 of oligo ethylene oxa moiety was exactly 2:4, indicating that polymerization was proceeded beyond the NMR detection limit. The molecular weights of these polymers were roughly estimated as ≥50,000 $gmol^{-1}$ (using on ^{1}H-NMR detection limit of 1 mol %). GPC measurements on polymers **P1-P4** showed only peaks corresponding to monomers(their molecular weight were below 1000 $gmol^{-1}$) due to dissociation on dilution.

Synthesis of polymer blend – (a) $B1_{sol}$

Homopolymers **P1** (0.005 mmol), **P2** (0.005 mmol) and pentadecafluorooctanoic acid (2 x 10^{-7} mol, 1 % per imine unit) were dissolved in 1.00 ml of deuterated 1,2-dichlorobenzene. The mixture was kept at 80ºC for 24 hrs. ^{1}H-NMR was used to identify the composition in the mixture. **(b) $B2_{sol}$:** the polymer blend $B2_{sol}$ was synthesized by using the procedure described for $B1_{sol}$, with replacing the starting homopolymers from **P1** and **P2** to **P5** and **P6**.

Synthesis of polymer blend – (a) $B1_{neat}$

Homopolymers **P1** (0.005 mmol), **P2** (0.005 mmol) and pentadecafluorooctanoic acid (2 x 10^{-7} mol, 1 % per imine unit) were dissolved in 1.00 ml of dichloromethane. The mixture was dried up immediately at 80ºC in vacuum oven for 24 hrs. ^{1}H-NMR was used to identify the composition in the neat polymer blend. **(b) $B2_{neat}$:** the polymer blend $B2_{neat}$ was synthesized by using the procedure described for $B1_{sol}$, with replacing the starting homopolymers from **P1** and **P2** to **P5** and **P6**.

Constitutional interconversion between $B1_{sol}$ or $B1_{neat}$

Homopolymers **P1** (0.1 mmol), **P2** (0.1 mmol) and pentadecafluorooctanoic acid (4 x 10^{-6} mol) were dissolved in $CDCl_3$ at 10 mM at r. m. for 24 hrs ($B1_{sol}$). The mixture was dried up

immediately at 80ºC in vacuum oven for 24 hrs (**B1$_{neat}$**). During the course of experiment, ^{1}H NMR was used to identify the composition of the polymer blend by dissolving the polymer blend (0.005 g) in 0.50 ml of $CDCl_3$. (The ^{1}H NMR spectrum was taken within 10 mins after the polymer blend dissolved). After 24 hours, the composition of the polymer blend was well equilibrated, 0.50 ml of deuterated chloroform was applied to dissolve the polymer blend (0.005 g). The mixture was kept at room temperature for 24 hours in an NMR tube. During the course of experiment ^{1}H-NMR was used to identify the composition of it. After 24 hours, the chloroform mixture was well equilibrated, it was then dried up to neat at 80ºC in vacuum oven for 24 hrs. ^{1}H NMR was used to identify the composition of the polymer blend. These cycles were then repeated for four times.

CHAPTER 8: References

CHAPTER 1

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