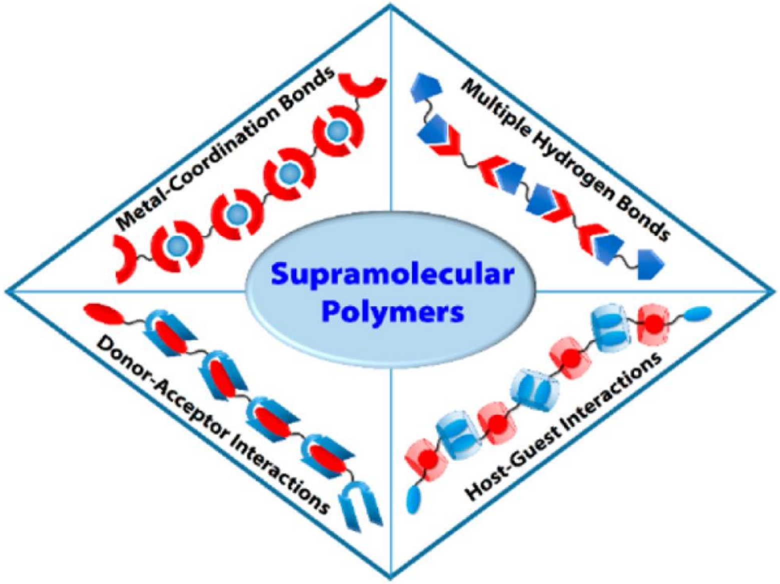
Supramolecular Polymers: Characterization, Preparation and Applications



Aida, T.; Meijer, E. W.; Stupp, S. I. *Science* **2012**, *335*, 813.

Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, *41,* 6042.

Yang, L.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Rev.* **2015**, *115,* 7196.

Rest, C.; Kandanelli, R.; Fernandez, G. *Chem. Soc. Rev.* **2015**, *44,* 2543.

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SUPERVISOR: GUANGBIN DONG

DATE: FEB 10. 2015

Characterization of Supramolecular Polymers

General Rule:

- **The characterization of a supramolecular polymer cannot be realized with a *single* method; a convincing conclusion relies on *the combination of several different techniques*.**

- **the *average molar mass* is especially useful (high *degree of polymerization (DP)* is required)**

Several Methods:

- ***Theoretical estimation* of molecular weight from *binding constant***
- **Size exclusion chromatography (SEC)**
- **Viscometry**
- **Light scattering (SLS and DLS)**
- **Vapor pressure osmometry (VPO)**
- **Mass spectrometry & NMR spectroscopy**
- **Scanning probe microscopy and electron microscopy (AFM & STM)**
- **AFM-based *single molecule force spectroscopy* (SMFS)**
- **Asymmetric Flow Field-Flow Fractionation (AF4)**

Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41,* 5922.

Yang, L.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Rev.* **2015**, *115,* 7196.

Characterization of Supramolecular Polymers

- ***Theoretical estimation—qualitative information***

  Thermodynamic equilibrium

  Isodesmic model (simplest):
  assumes that the association of the end-groups of the monomers does *not change* during the supramolecular polymerization process

  $$DP \sim (K_aC)^{1/2}$$

  K_a: equilibrium constant between monomers

  C: total monomer concentration

  K_a could be obtained through NMR titrations, isothermal titration calorimetry and UV-vis spectroscopy

- **Size exclusion chromatography (SEC)**

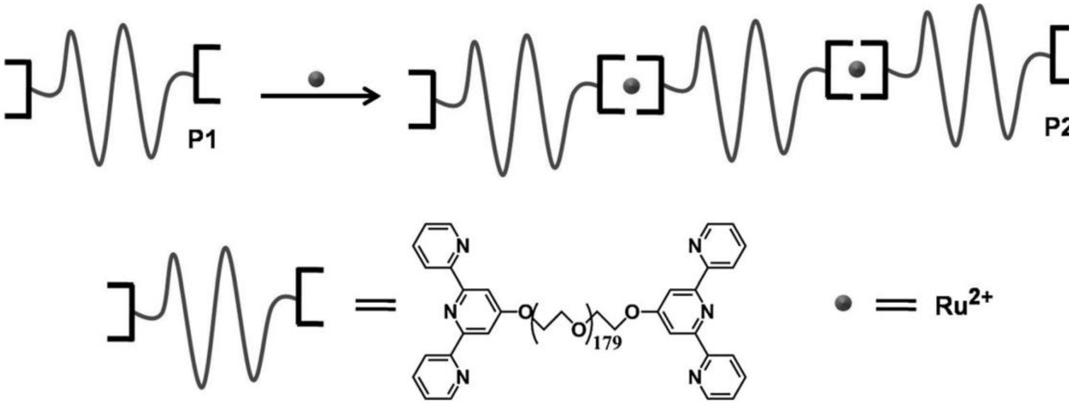
  Especially gel permeation chromatography (GPC)

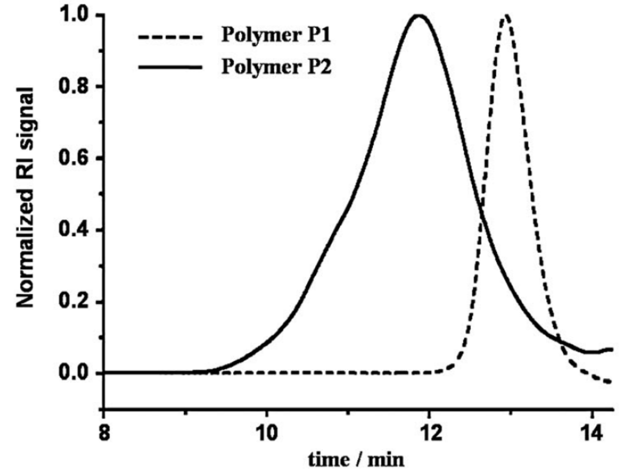
  molar mass distribution of a polymer (require a standard curve)

  - **Not suitable for supramolecular polymer when the DP is highly dependent on the concentration (dilution)**
  - **Works well for systems with slow association and disassociation kinetics (e.g. multiple H-bonding and metal-coordination systems)**

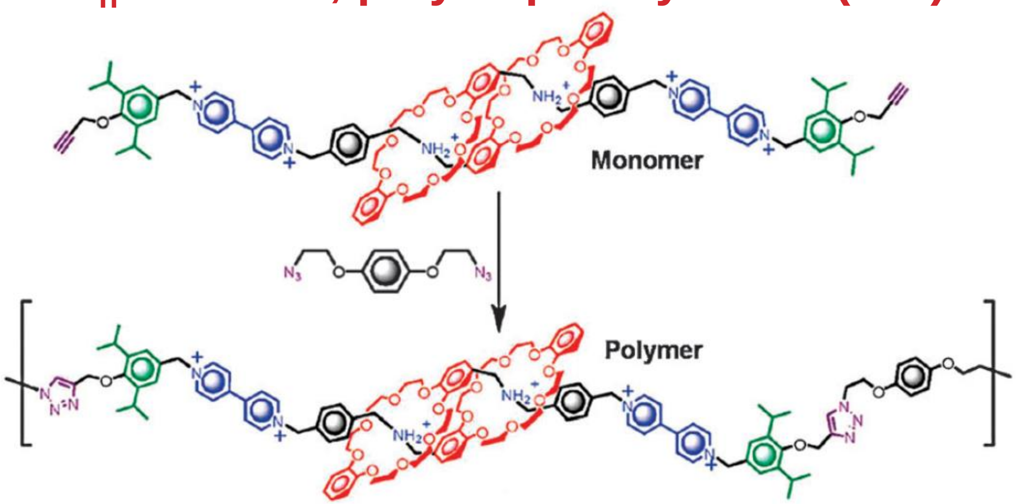
Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012***, 41,* 5922.

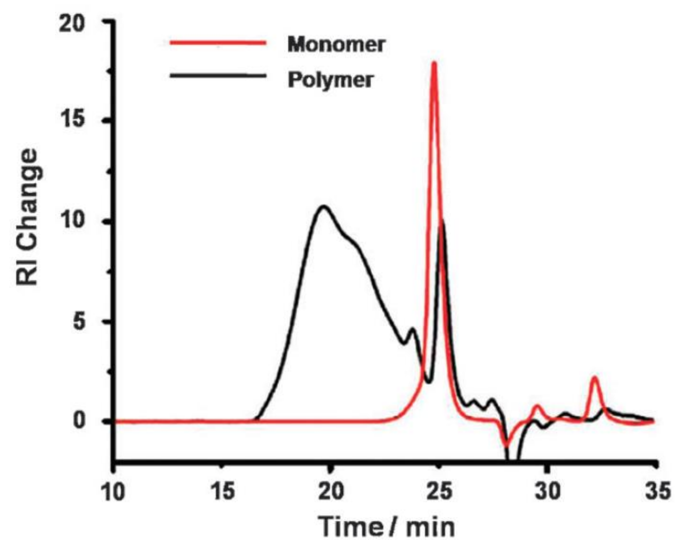
Characterization of Supramolecular Polymers





- M_n=138 kDa; polydispersity index (PDI) of 1.55; DP=15





- M_n=32.9±2.5 kDa ; PDI=1.85

Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41,* 5922.

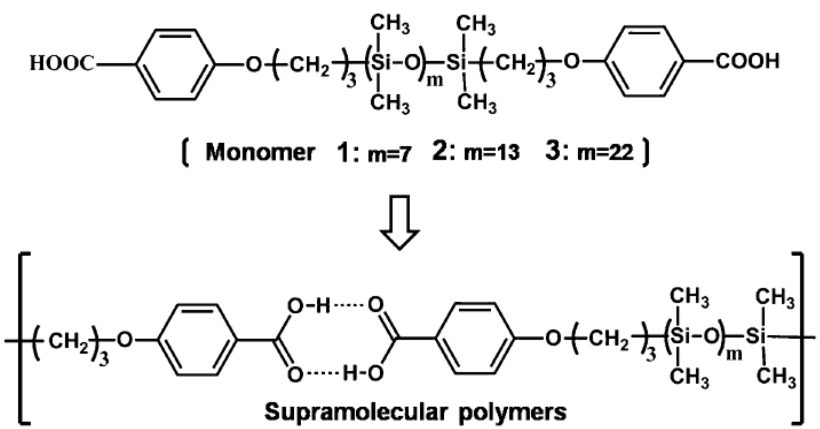
Characterization of Supramolecular Polymers

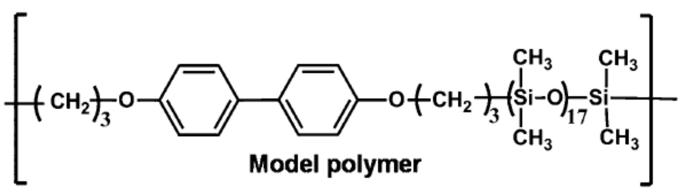
- ***Viscometry—Classical method***

Mark–Houwink equation

$[\eta]=KM^a$ **K, a: empirical constants**

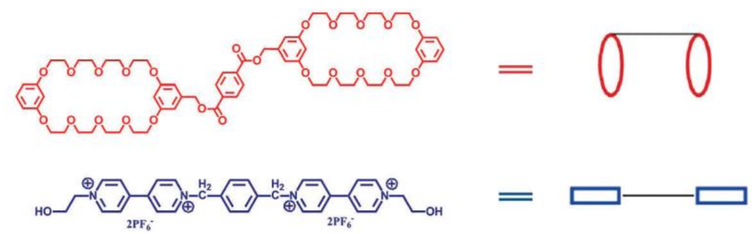
***Difficulty*: find a suitable *covalent model* for dynamic system to obtain these parameters**

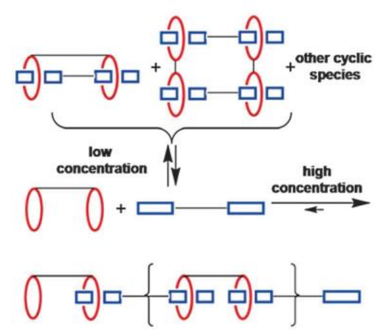


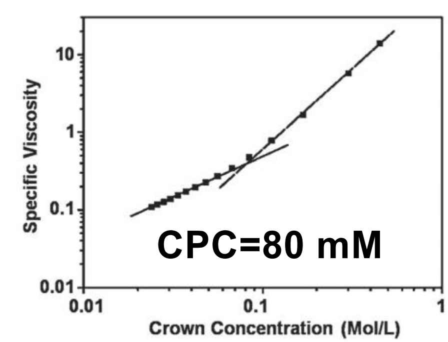


- **Deduce the *critical polymerization concentration* (CPC)**

Supramolecular polymerization with a ring–chain mechanism







Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41,* 5922.

Abed, S.; Boileau, S.; Bouteiller, L. *Polymer* **2001**, *42,* 8613.

Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 2836.

Characterization of Supramolecular Polymers

- <u>**Light scattering (SLS and DLS)**</u>
  - **Static light scattering (SLS)**

  Measure the molecular mass of polymers– determine M_w
  Not always applicable **for supramolecular polymers**

  - **Dynamic light scattering (DLS)**

  Measure the *size distribution* of small particles or aggregates

- <u>**Vapor pressure osmometry (VPO)**</u>

  Determination of M_n

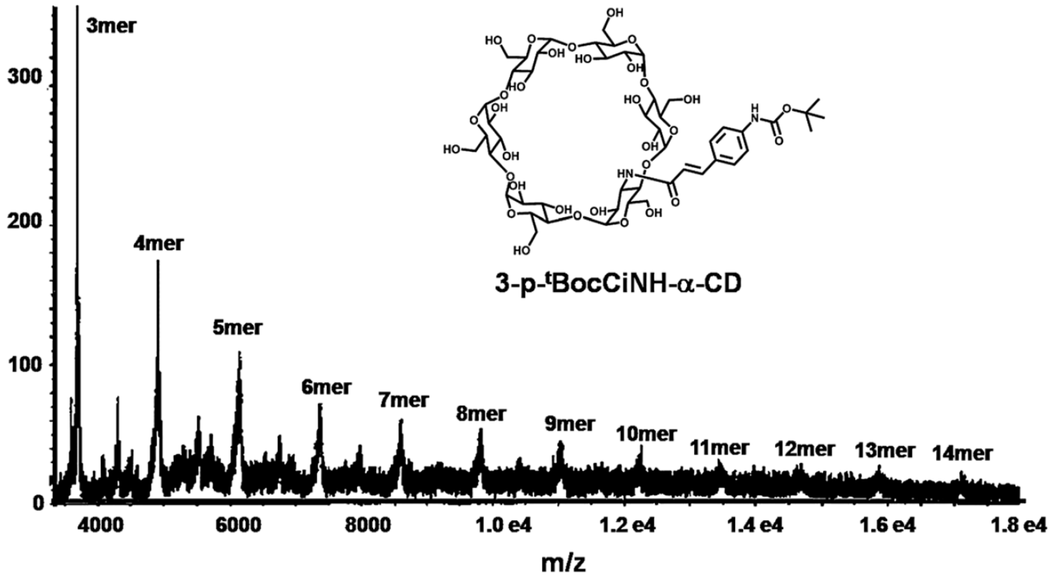
  - **The vapor pressure of a solution is lower than that of the pure solvent (same T and pressure)**
  - **Raoult's law-- the M_n and the vapor pressure can be related**

Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41*, 5922.

Characterization of Supramolecular Polymers

- **<u>Mass spectrometry & NMR spectroscopy</u>**

  - **MALDI-TOF-MS: Soft ionization method**
  - **turbo ion spray TOF MS---up to 14mer**



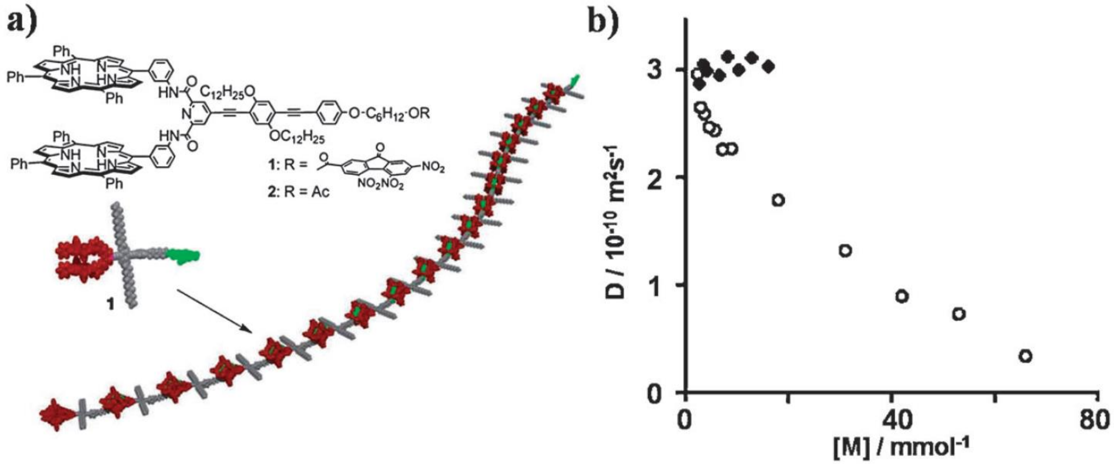
Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012***, 41,* 5922.

Characterization of Supramolecular Polymers

- <u>**Mass spectrometry & NMR spectroscopy**</u>
  - **[1]H-NMR– useful in determining polymers M_n by end-group analysis**
  - **For supramolecular polymers, need many assumptions; usually used for qualitative analysis**

    Increasing conc. of monomer, broader peaks generated– suggesting formation of supramolecular polymers

  - **Diffusion ordered [1]H-NMR spectroscopy (DOSY):**



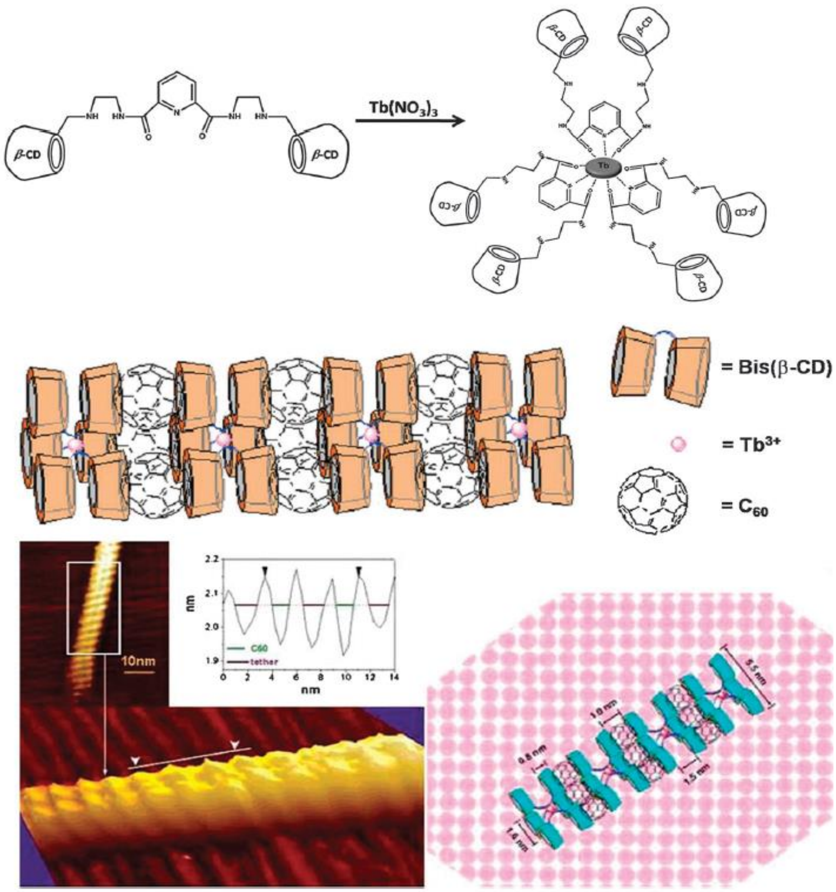
Increasing conc. of monomer, decreasing diffusion coefficient– suggesting formation of supramolecular polymers

Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41,* 5922.

Haino, T.; Watanabe, A.; Hirao, T.; Ikeda, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 1473.

Characterization of Supramolecular Polymers

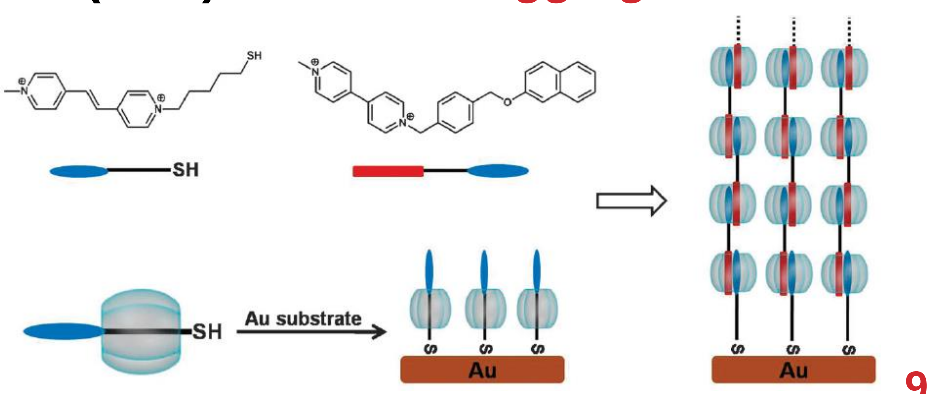
- <u>**Scanning probe microscopy and electron microscopy (AFM & STM)**</u>
  - **Scanning tunneling microscopy (STM): image the sample at the atomic scale --- characterizing a rigid and big supramolecular polymer (dilute sample)**



- **Atomic force microscopy (AFM) imaging the *morphology of surfaces* and providing a *three dimensional surface* profile**

Determine growth height for surface grafted supramolecular polymers

- **Transmission electron microscopy (TEM) -- *visualize aggregates***



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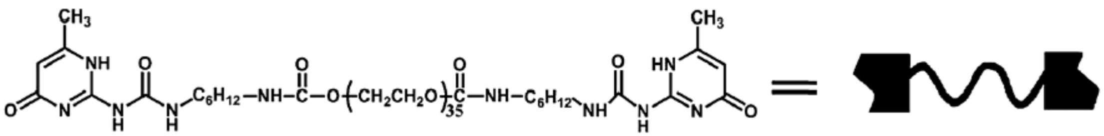
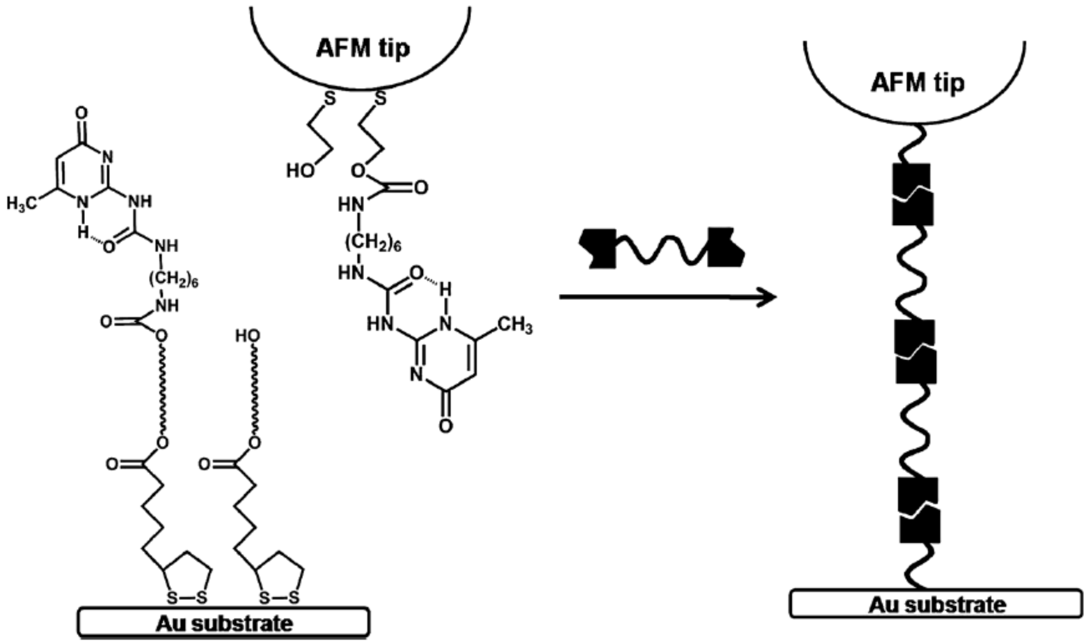
Characterization of Supramolecular Polymers

- **AFM-based *single molecule force spectroscopy* (SMFS)**
  - **Single molecule force spectroscopy (SMFS)**
    AFM as a highly *sensitive force sensor*
  - **Application in polymer research: entropic and enthalpic *elasticity* of a *single polymer chain*; force-induced conformational transition, etc.**





Stretching lengths: >150 nm => DP up to 15

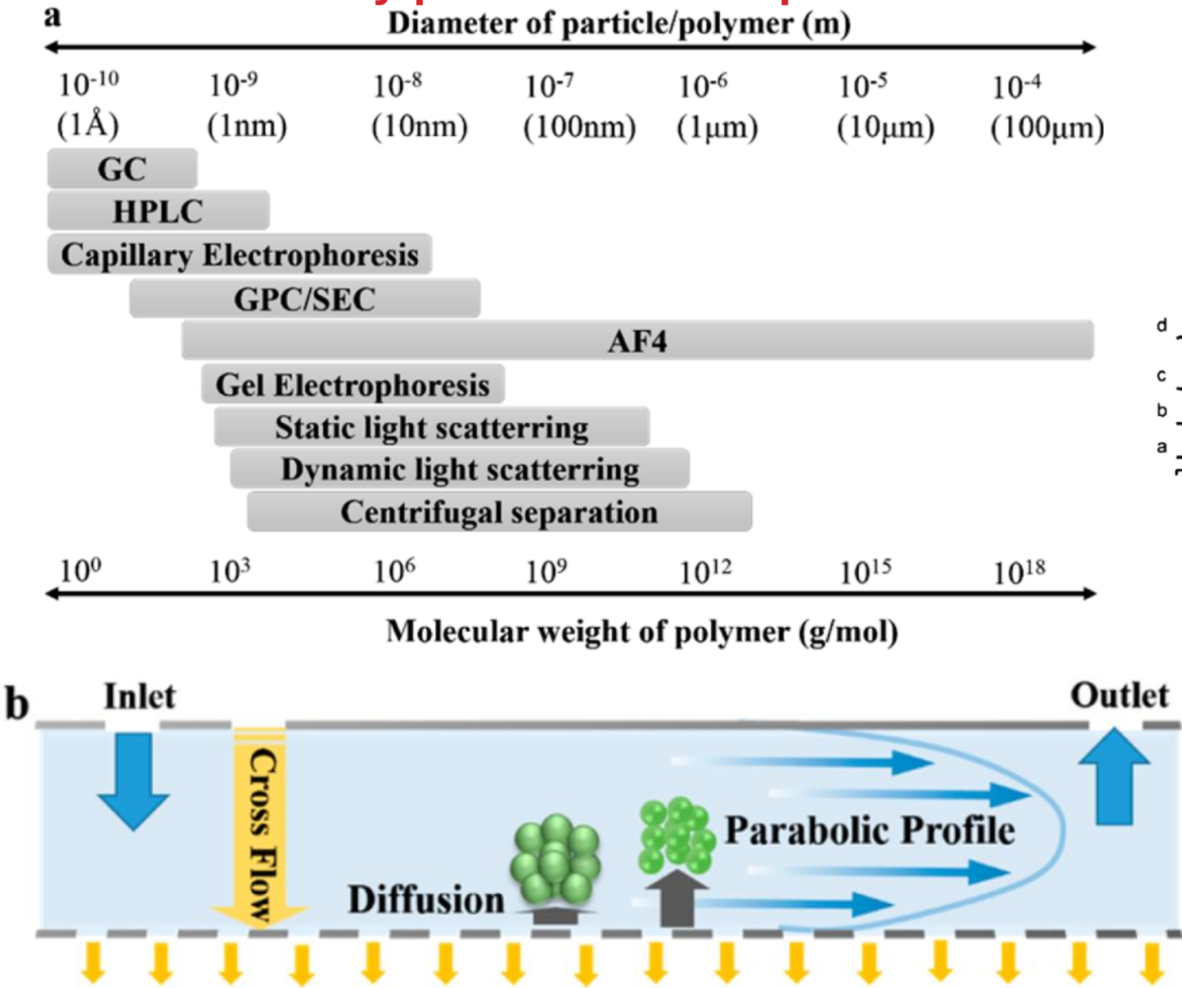
Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41,* 5922.

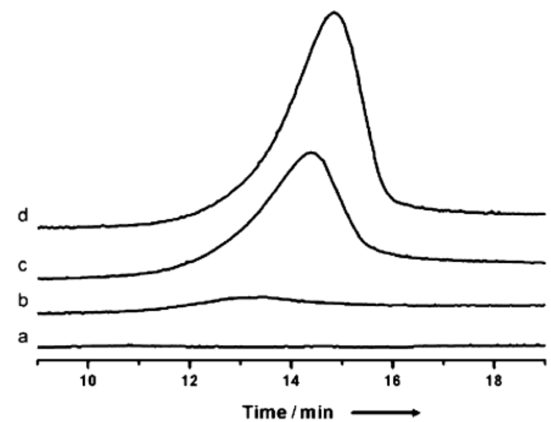
Zou, S.; Schönherr, H.; Vancso, G. J. *Angew. Chem. Int. Ed.* **2005**, *44,* 956.

Characterization of Supramolecular Polymers

- **<u>Asymmetric Flow Field-Flow Fractionation (AF4)</u>**

No stationary phase--- mild seperation





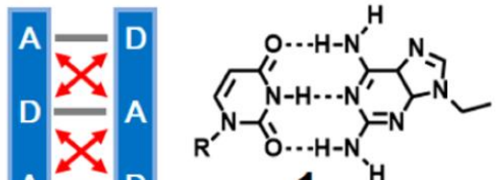
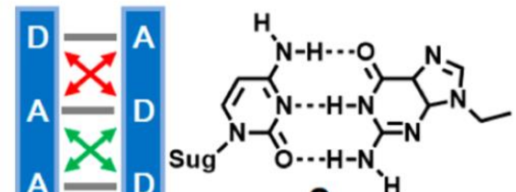
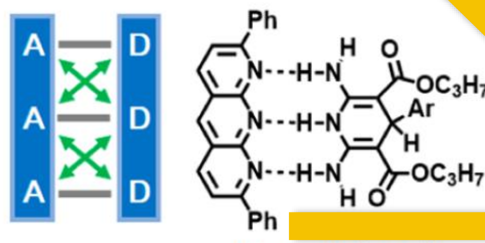
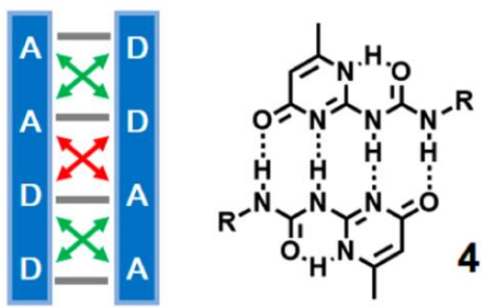
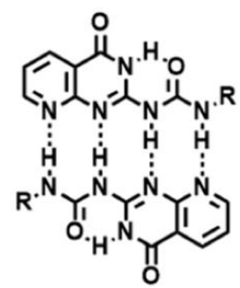
velocity gradient **-- separates the sample according to their *size* (smaller molecules elute first) –opposite to GPC**

Yang, L.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Rev.* **2015**, *115,* 7196.

Driving forces for Supramolecular Polymers

- **Multiple Hydrogen Bonds------ *5-30 kJ/mol***
- **Metal Coordination Bonds**
- **Host-Guest Interactions**
- **Aromatic Donor-Acceptor Interaction**
- **Multiple Driving Force**

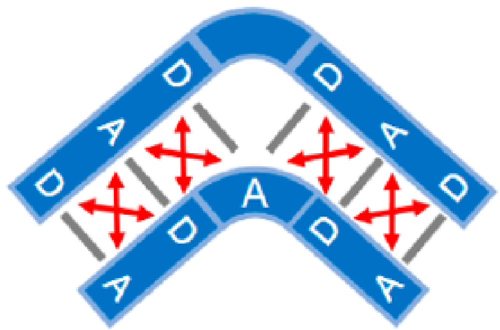
Multiple Hydrogen Bonds

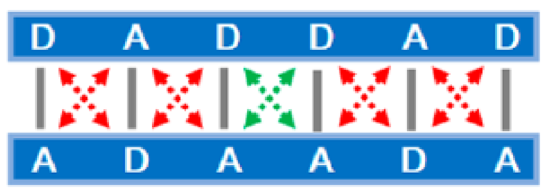
Type	Example
Triple	 **1** $K_a = 10^2\ M^{-1}$  **2** $K_a = 10^4 - 10^5\ M^{-1}$  **3** $K_a \geq 10^5\ M^{-1}$
Quadruple	 **4** $K_a = 10^7\ M^{-1}$ Upy-Upy in $CHCl_3$  **5** $K_a = 10^7\ M^{-1}$ DeAP-DeAP in $CDCl_3$

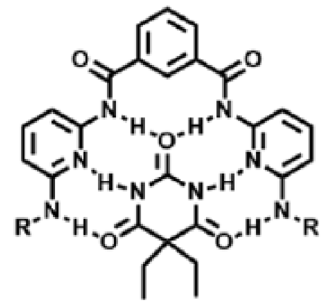
attractive *secondary* electrostatic interactions

Multiple Hydrogen Bonds

Sextuple

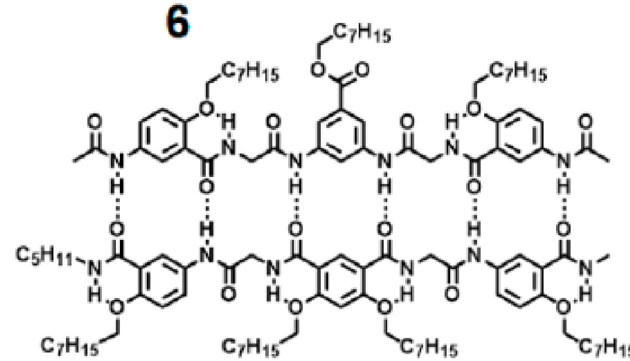






6

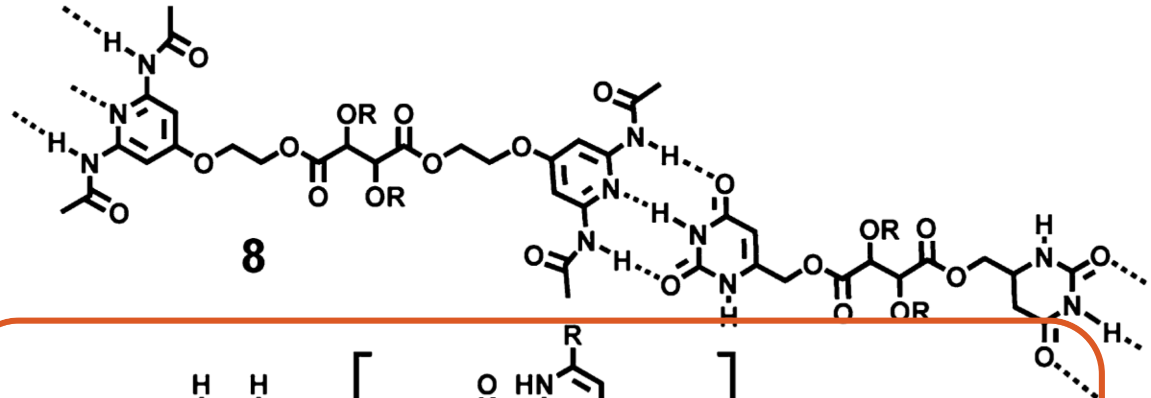
$K_a = 10^6\ M^{-1}$
in $CDCl_3$



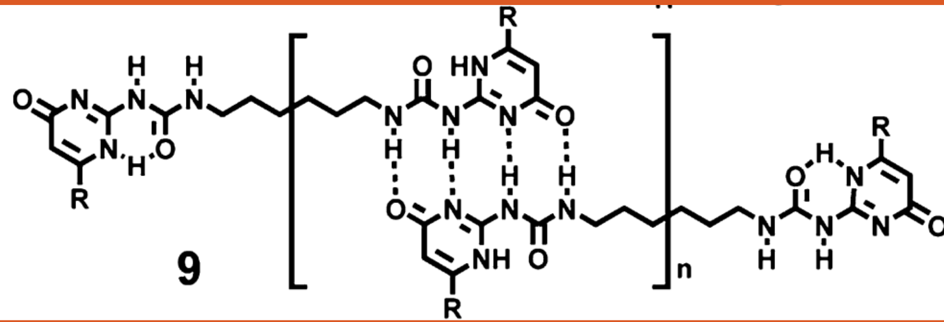
7

$K_a = 10^9\ M^{-1}$
in $CHCl_3$

Multiple Hydrogen Bonds



8



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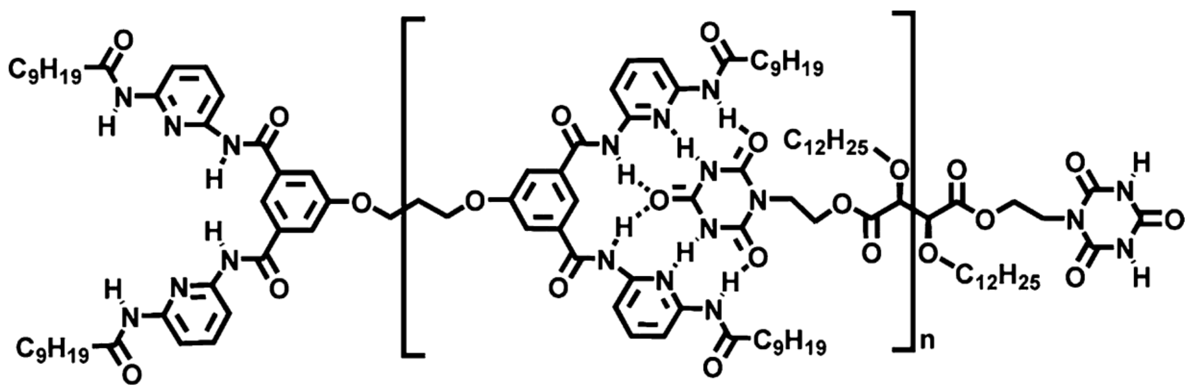


10

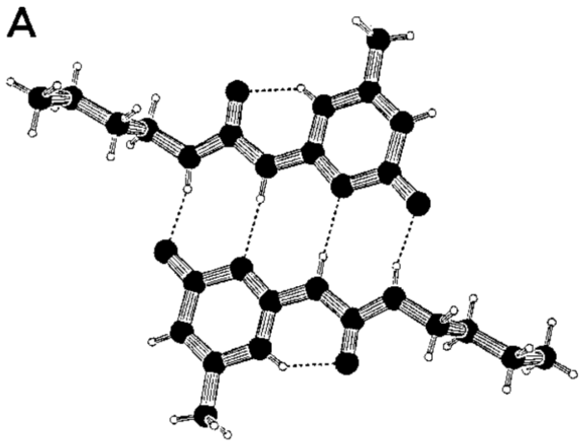
First example :
Bifunctional diamidopyridines and uracil derivatives

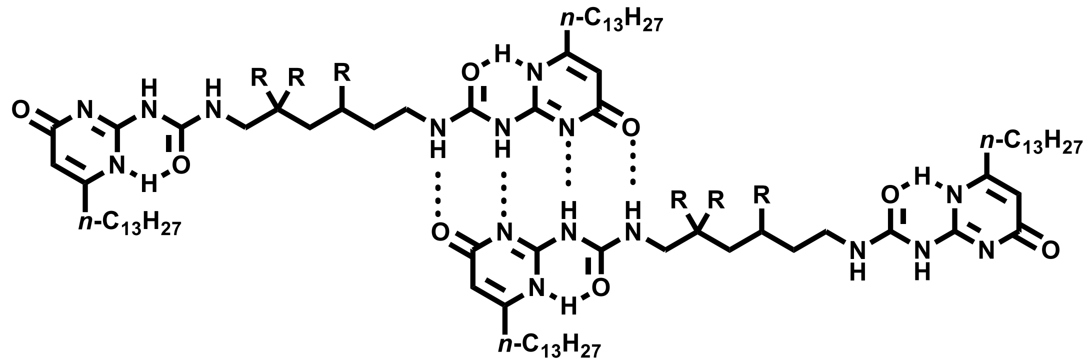
Homodimerizing: Mm can be tuned by solvent and concentration

Sextuple arrays—Rigid fiber and gel were observed in different solvent.

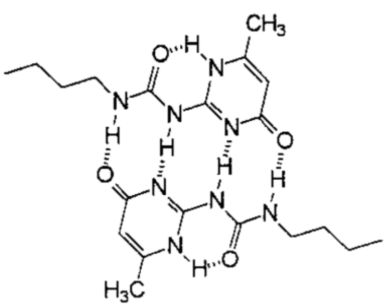
Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* **1990,** *2,* 254.
Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.
Kolomiets, E.; Buhler, E.; Candau, S. J.; Lehn, J. M. *Macromolecules* **2006**, *39*, 1173.

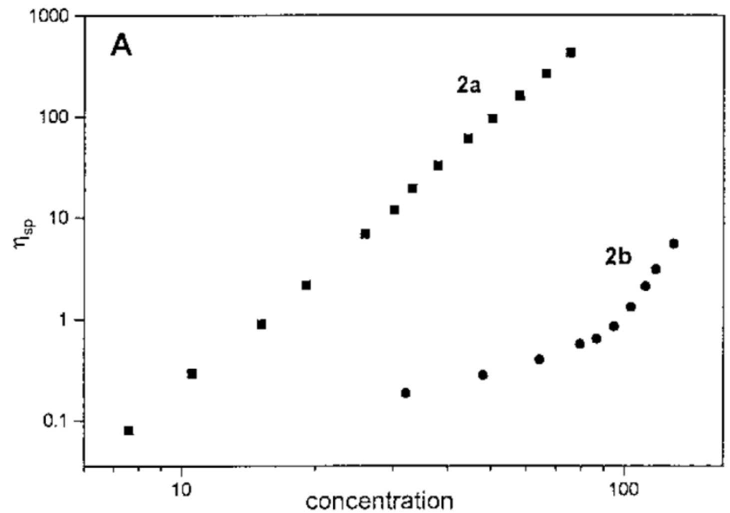
Multiple Hydrogen Bonds– Upy System





2a: R=H
2b: R=CH_3





K_{dim}> 10^6 M^{-1} in $CHCl_3$

- **Fits Cate’s model for reversibly breakable polymers above overlap conc.**
- **2b is more prone to form rings**

Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.

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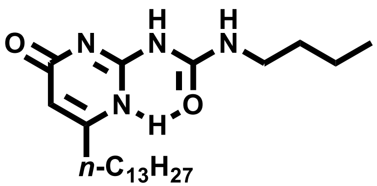
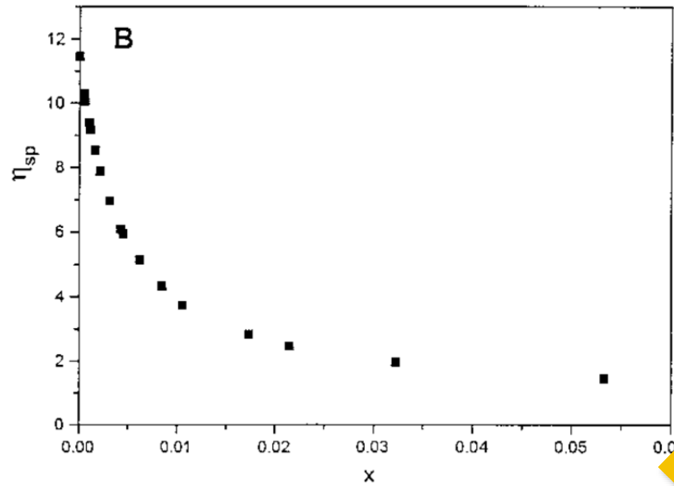
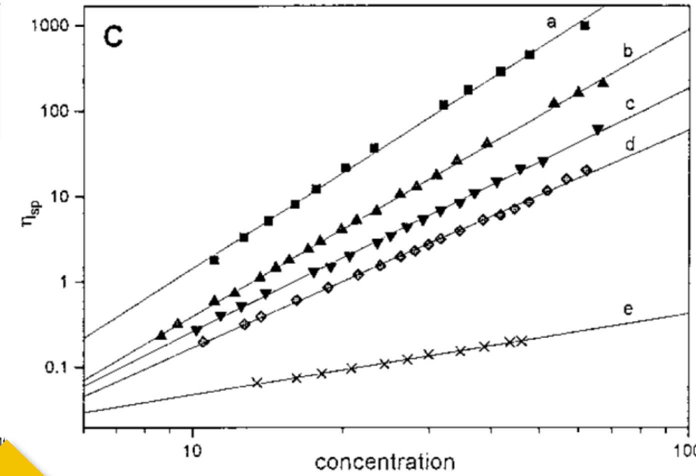
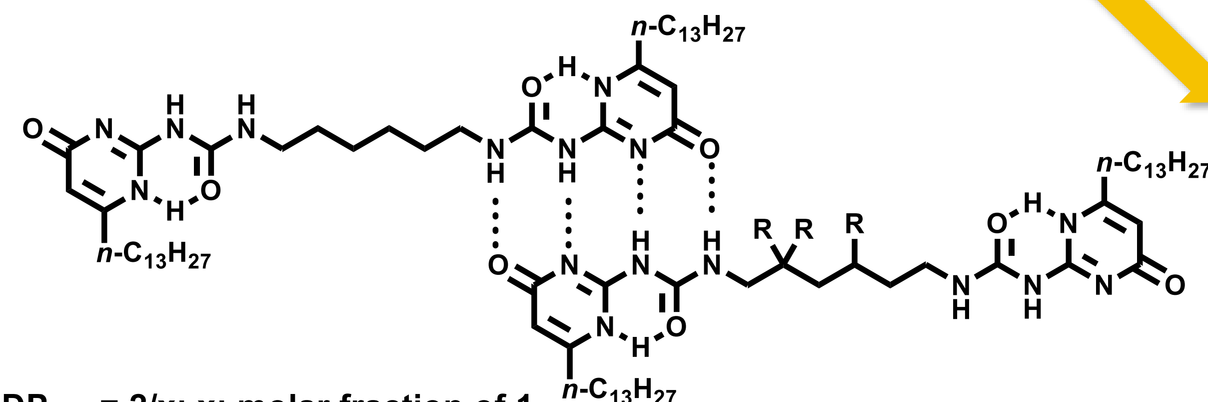


1: ***Chain Stopper***







DP$_{max}$= 2/x; x: molar fraction of 1

2a

$$DP = \frac{2 \cdot ([2] + [1])}{[1] - \frac{1}{4K_{dim}}\left[1 - \sqrt{1 + 8K_{dim}([1] + 2 \cdot [2])}\right]}$$

- **Average molar mass: $5{\times}10^5$ g/mol**
- **reversible association process**
- **no uncontrolled multidirectional gelation**

Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.

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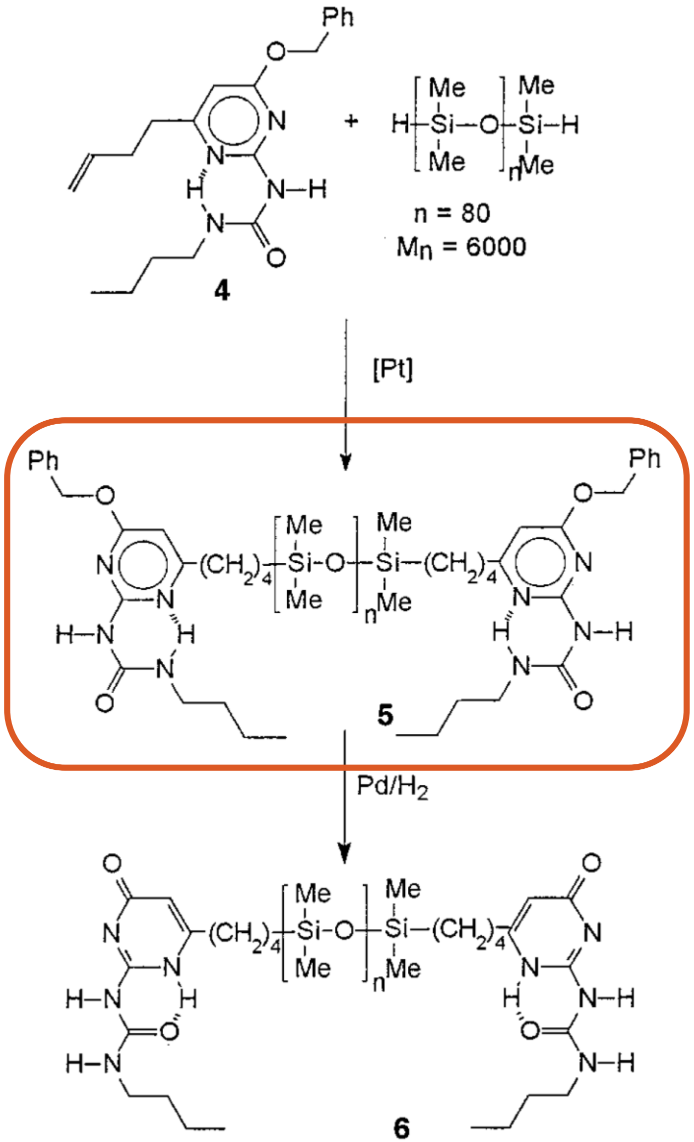
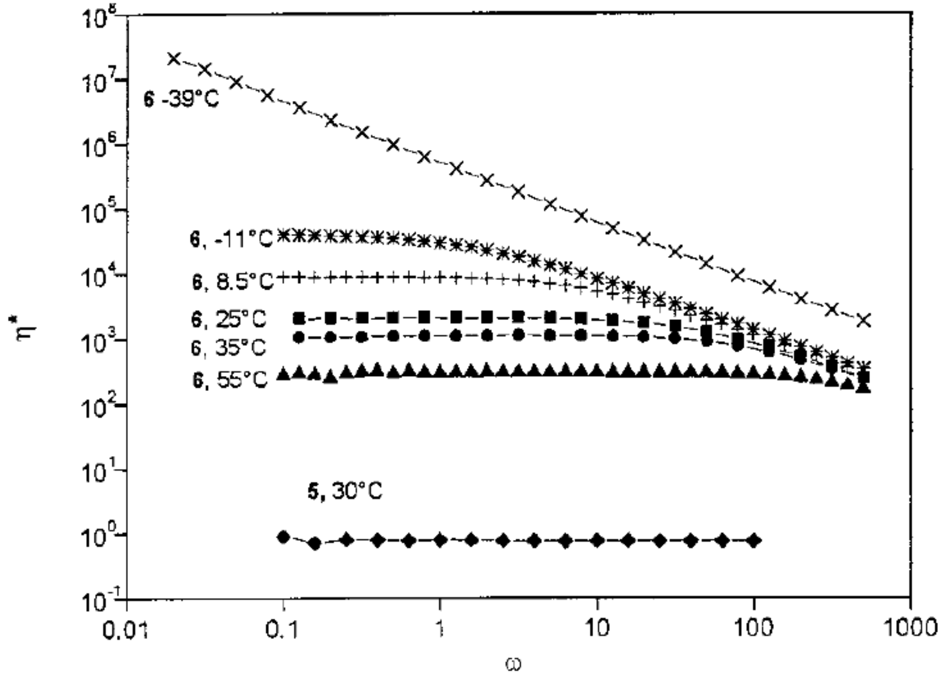
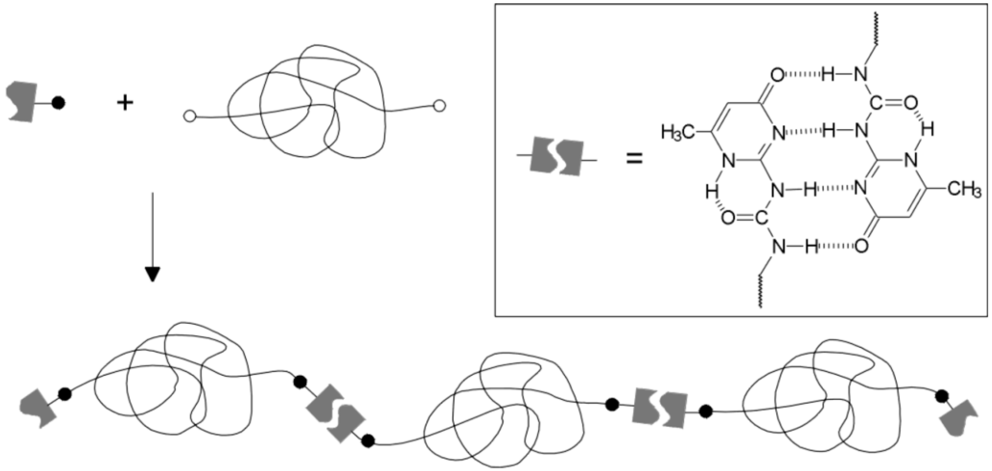




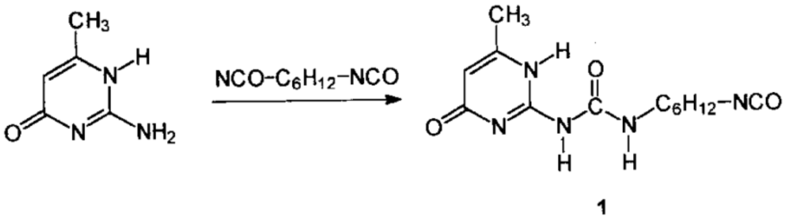
- **polymer-like viscoelastic behavior**
- **Increasing T, increasing rate of chain breaking**
- **thermoplastic behavior**

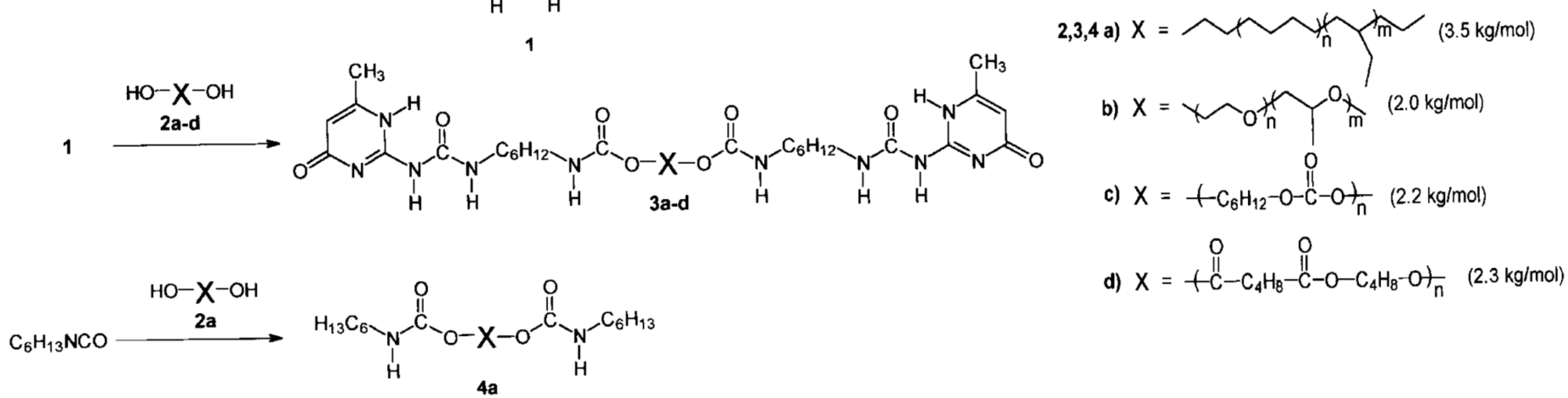
Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.

Multiple Hydrogen Bonds– Upy System



- **Soft rubber**
- **Physical crosslink formed by small clusters**

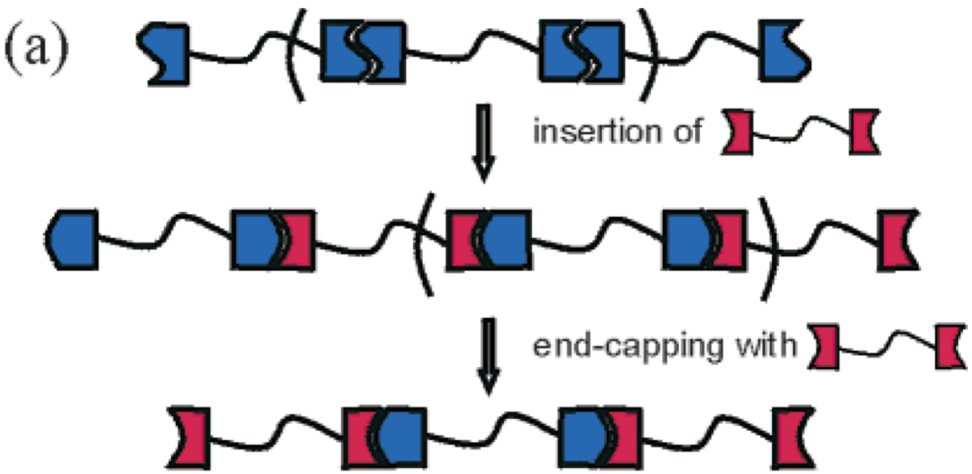




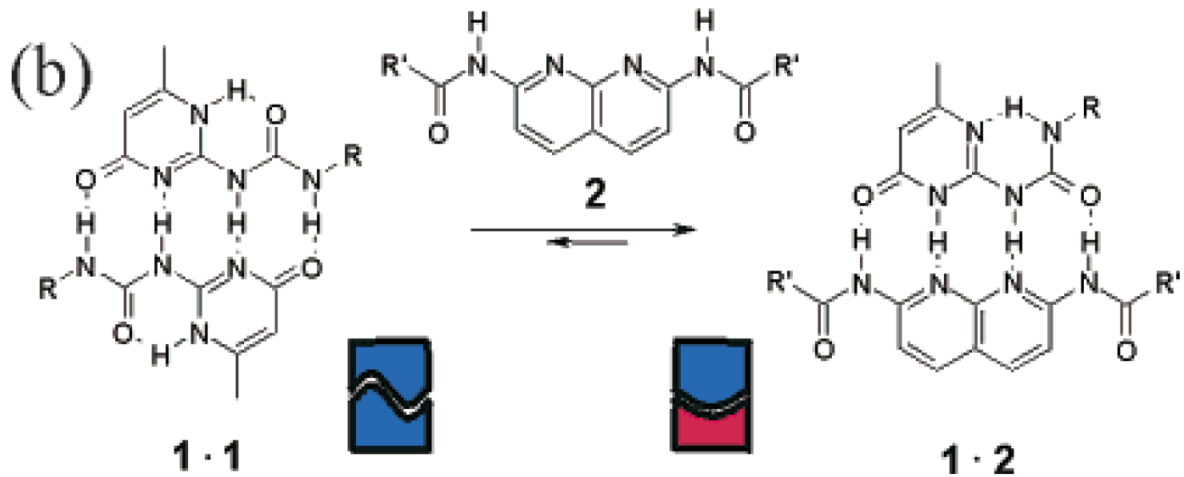
Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874.

Multiple Hydrogen Bonds– Upy System

Supramolecular Copolymers



- **simply mixing components in solution results in different degrees of comonomer incorporation**

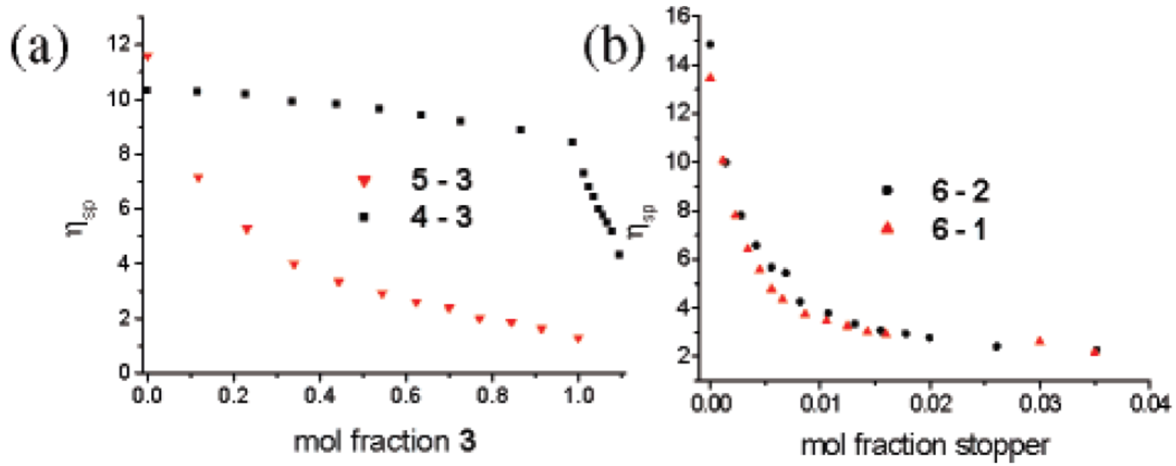


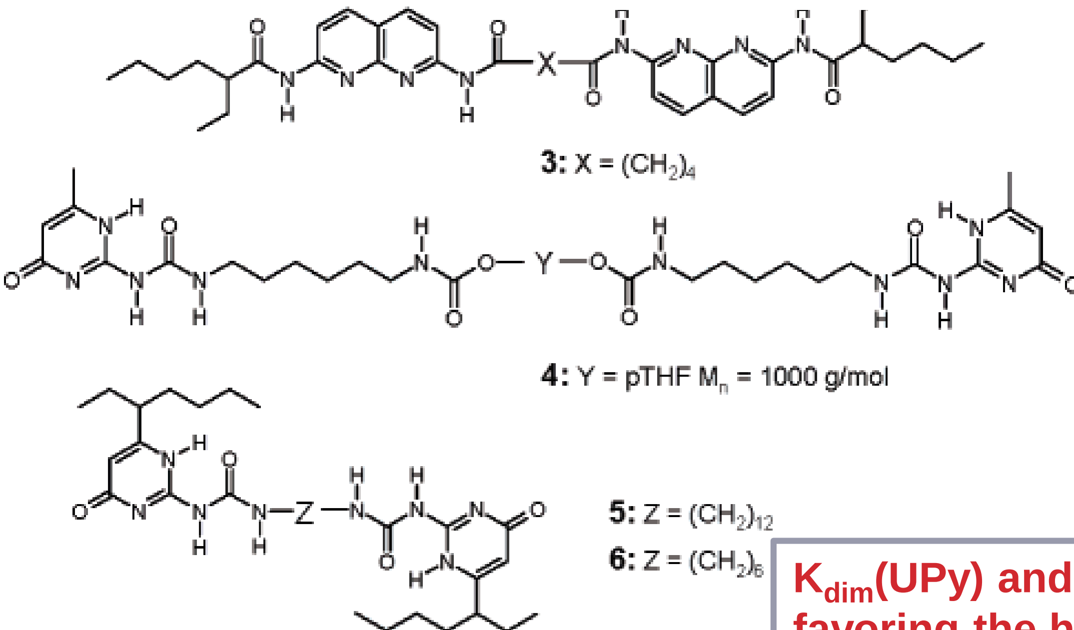
Ligthart, G. B. W. L.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 810.

Multiple Hydrogen Bonds– Upy System

Supramolecular Copolymers

- 3 incorporated to 4 until a strictly alternating copolymer at 1:1 ratio of monomers
- 3 acts as end cappers when ratio is beyond 1:1, reducing the length of copolymer



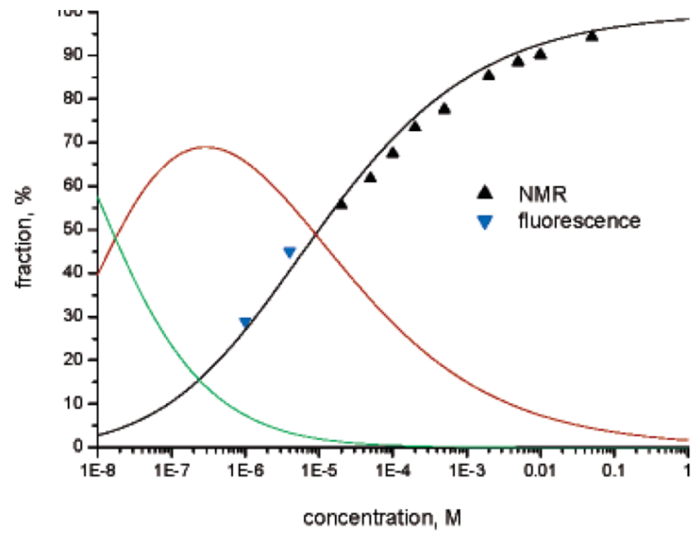


3: X = $(CH_2)_4$

4: Y = pTHF M_n = 1000 g/mol

5: Z = $(CH_2)_{12}$

6: Z = $(CH_2)_6$

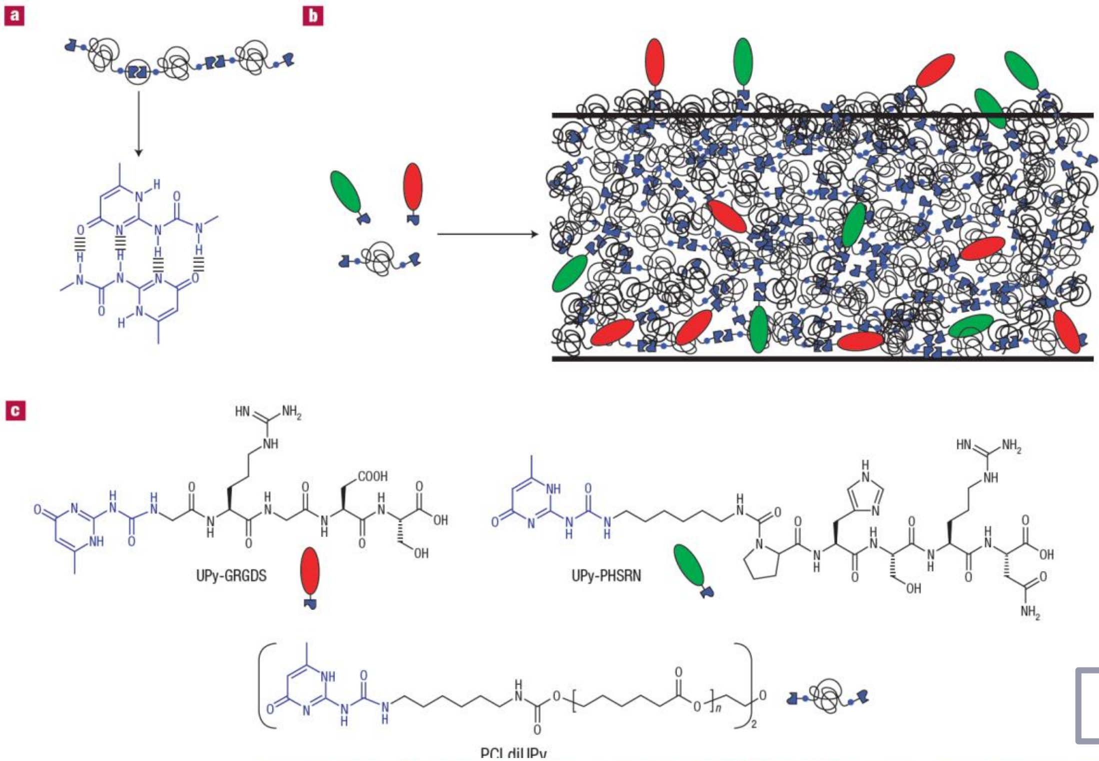


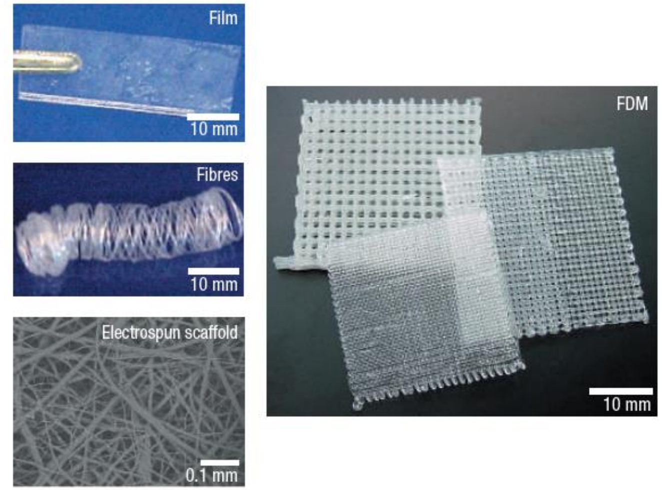
K_{dim}(UPy) and K_a(UPy-Napy) (6×10^7 and 5×10^6 M^{-1}), favoring the heterodimer above 10^{-5} M

Ligthart, G. B. W. L.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 810.

Multiple Hydrogen Bonds– Upy System

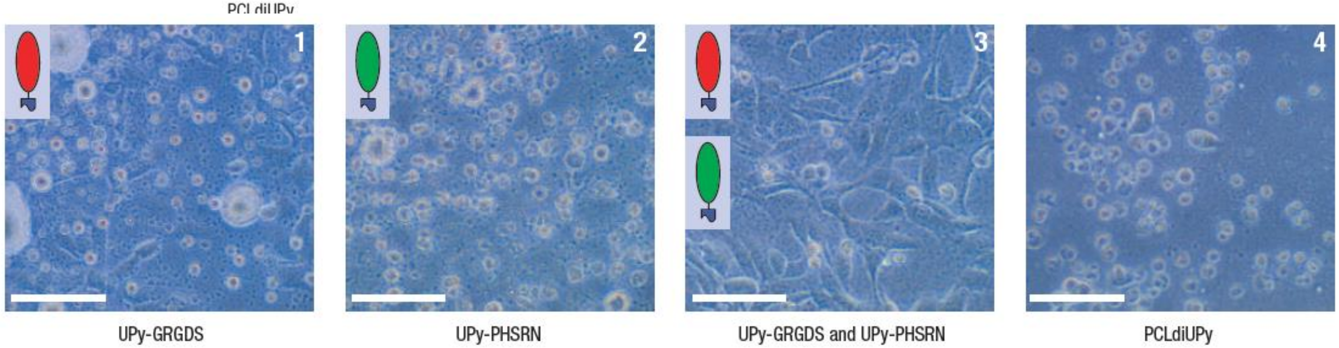
Biomedical Applications





High processability

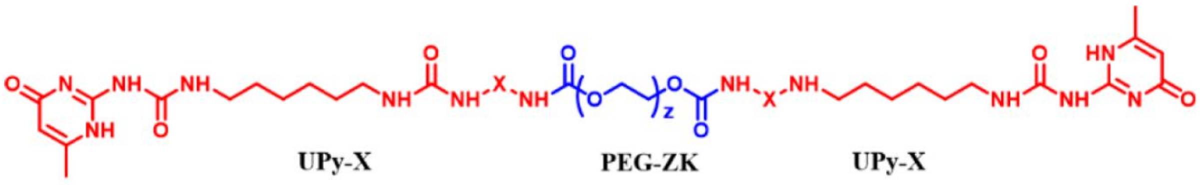
Cell adhesion and spreading



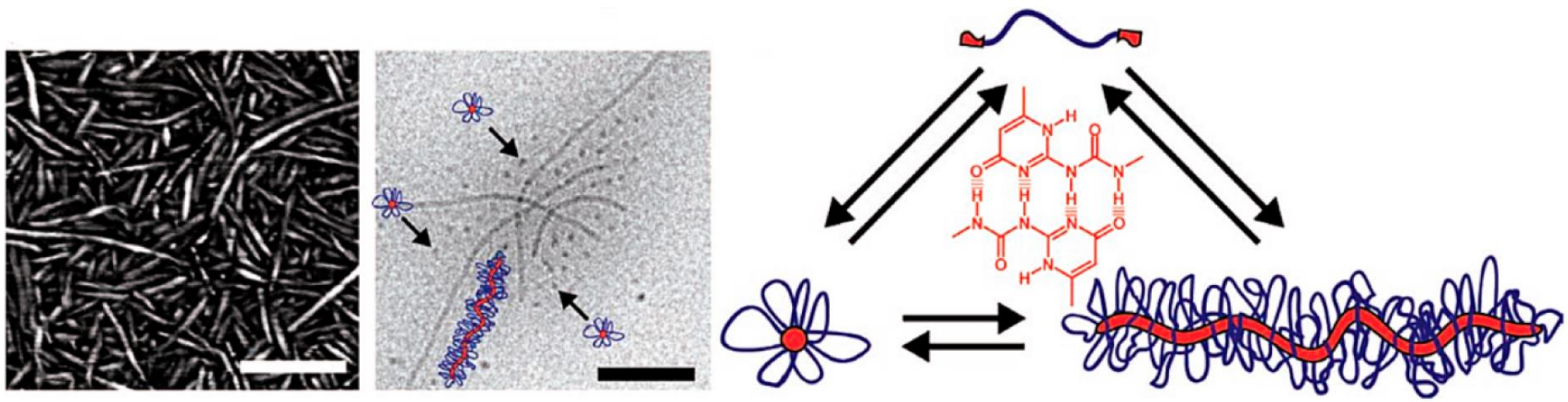
Dankers, P. Y. W.; Harmsen, M. C.; Brouwer, L. A.; Van Luyn, M. J. A.; Meijer, E. W. *Nat Mater* **2005***, 4,* 568.

Multiple Hydrogen Bonds– Upy System

Biomedical Applications



102

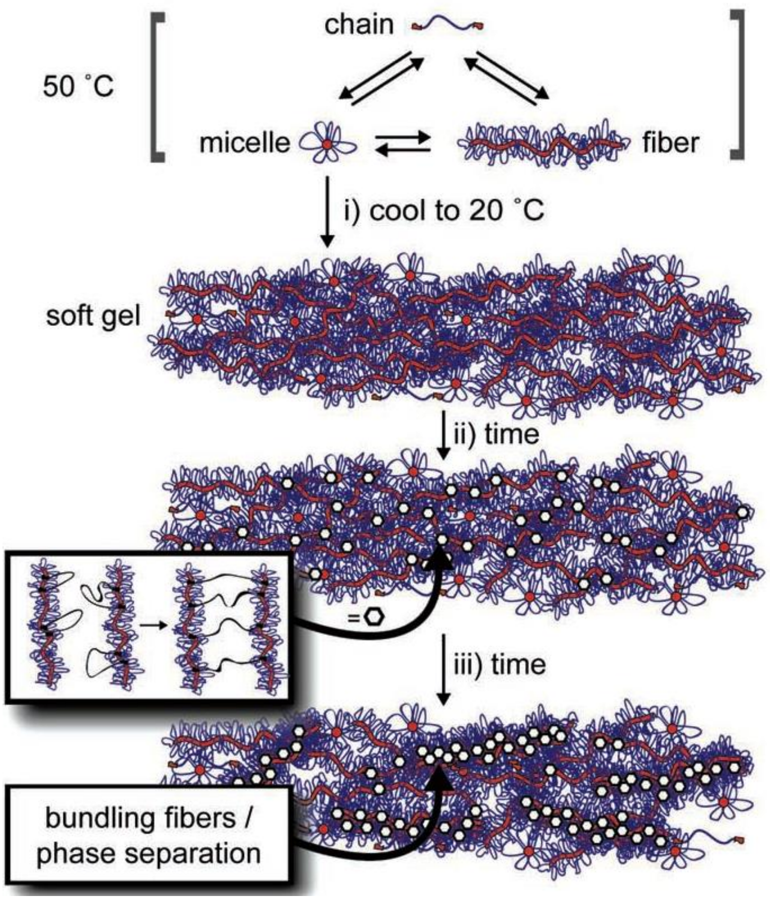


Formation of a hydrogel

Dankers, P. Y. W.; Hermans, T. M.; Baughman, T. W.; Kamikawa, Y.; Kieltyka, R. E.; Bastings, M. M. C.; Janssen, H. M.; Sommerdijk, N. A. J. M.; Larsen, A.; van Luyn, M. J. A.; Bosman, A. W.; Popa, E. R.; Fytas, G.; Meijer, E. W. *Adv. Mater.* **2012***, 24,* 2703*.*

Multiple Hydrogen Bonds– Upy System

Biomedical Applications

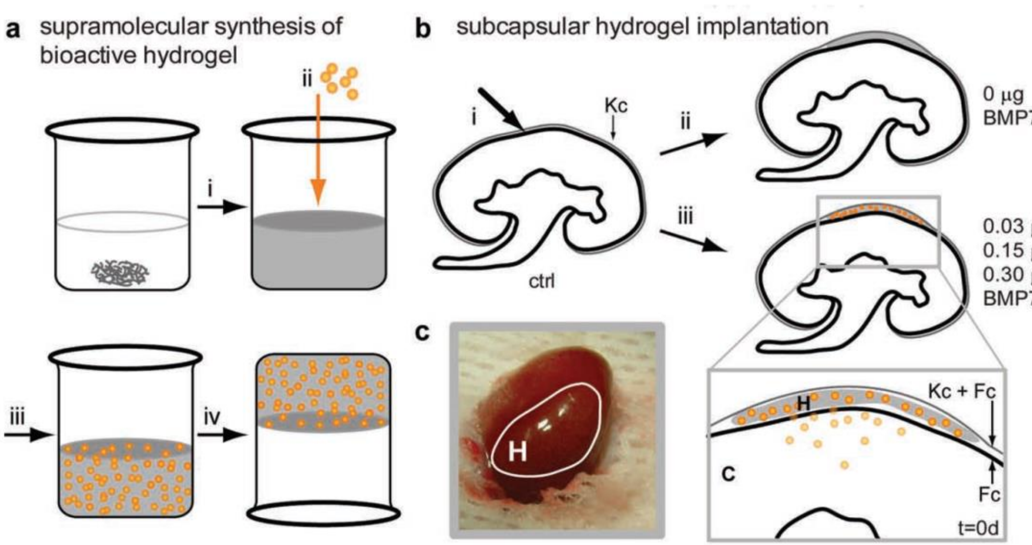


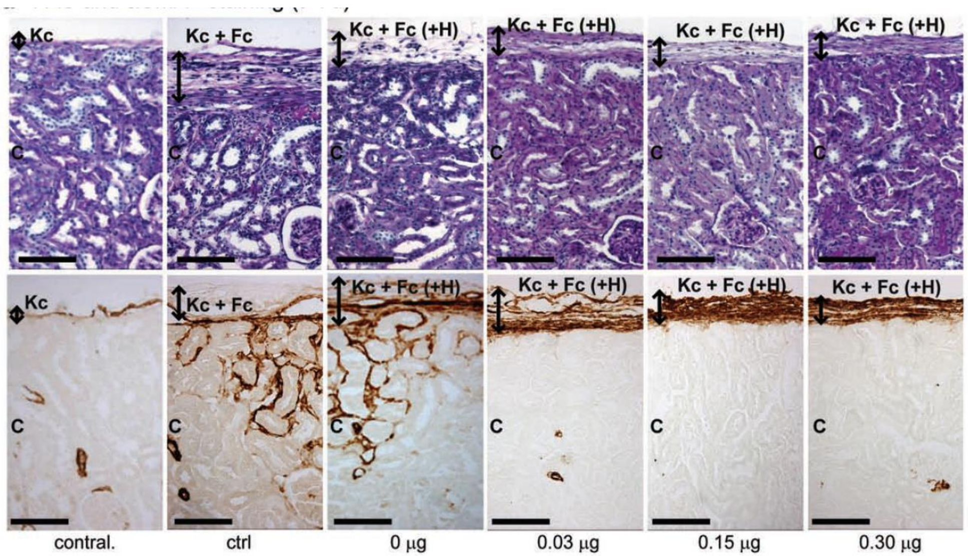
Formation of a hydrogel

Dankers, P. Y. W.; Hermans, T. M.; Baughman, T. W.; Kamikawa, Y.; Kieltyka, R. E.; Bastings, M. M. C.; Janssen, H. M.; Sommerdijk, N. A. J. M.; Larsen, A.; van Luyn, M. J. A.; Bosman, A. W.; Popa, E. R.; Fytas, G.; Meijer, E. W. *Adv. Mater.* **2012**, *24,* 2703.

Multiple Hydrogen Bonds– Upy System

Biomedical Applications



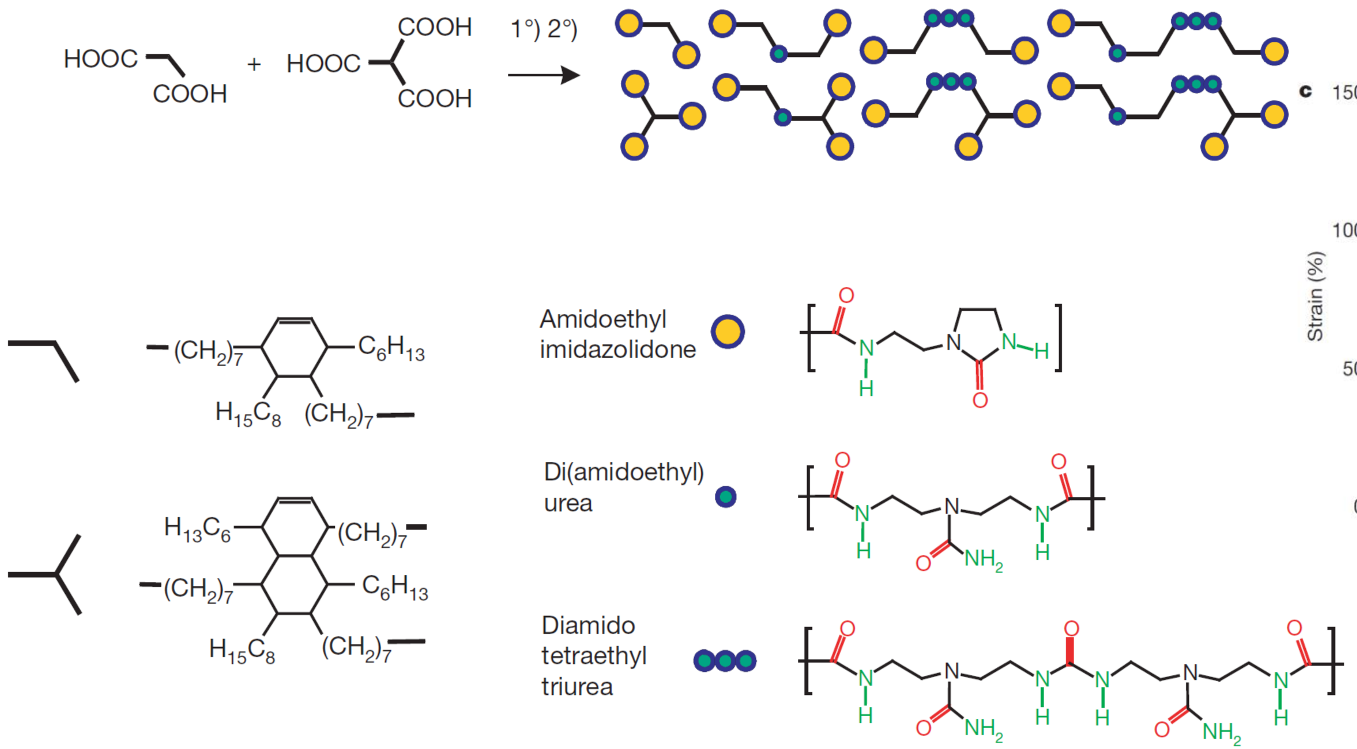


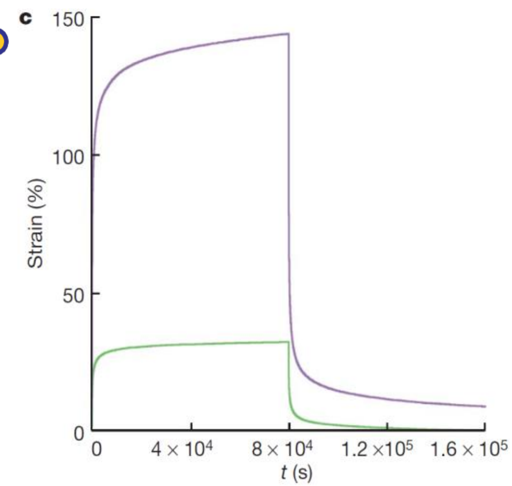
Protein delivery

Dankers, P. Y. W.; Hermans, T. M.; Baughman, T. W.; Kamikawa, Y.; Kieltyka, R. E.; Bastings, M. M. C.; Janssen, H. M.; Sommerdijk, N. A. J. M.; Larsen, A.; van Luyn, M. J. A.; Bosman, A. W.; Popa, E. R.; Fytas, G.; Meijer, E. W. *Adv. Mater.* **2012***, 24,* 2703*.*

Multiple Hydrogen Bonds

Self-healing Materials





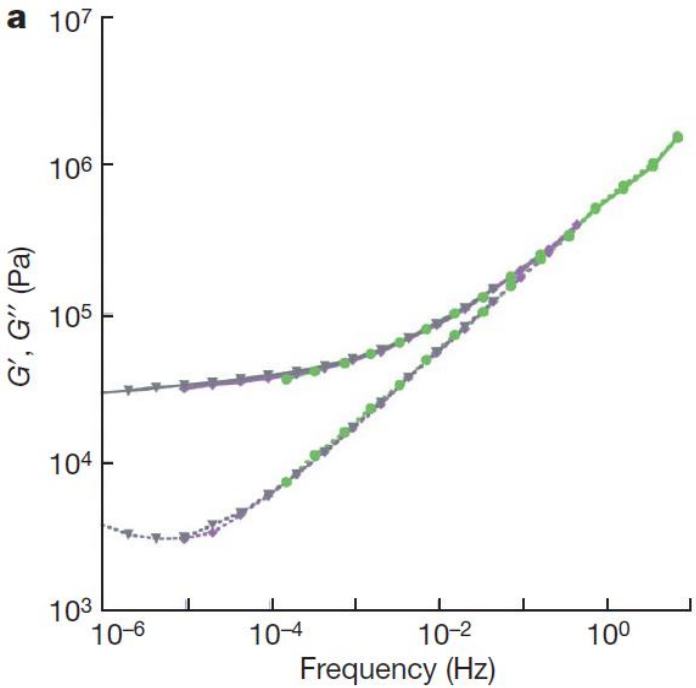
- **Oligomers according to NMR study**
- **Posessing polymer-like properties**

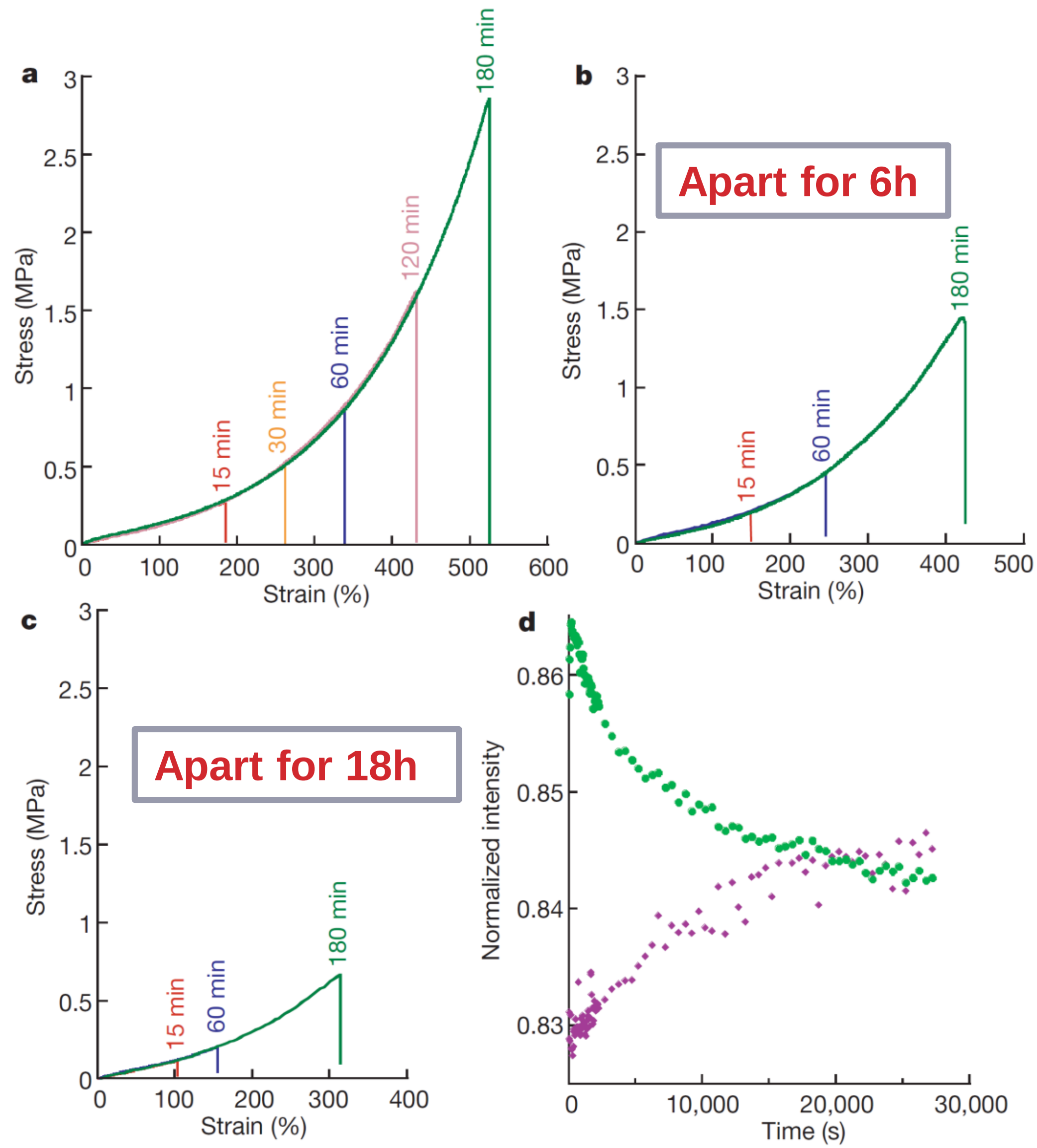
Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451,* 977.

Multiple Hydrogen Bonds

Self-healing Materials

Low frequency: elastic rubbery; high frequency: glass transition



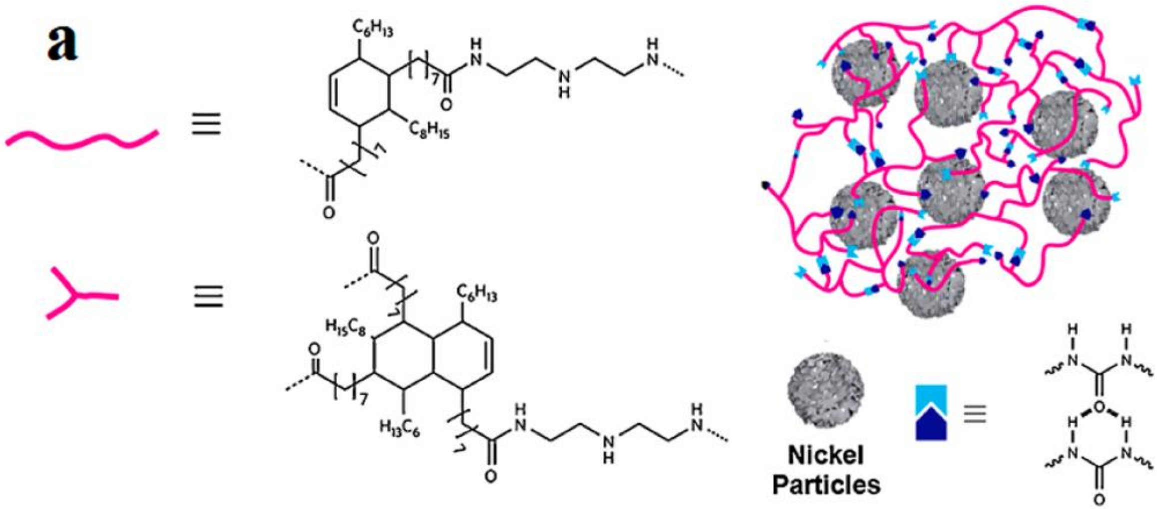


Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451,* 977.

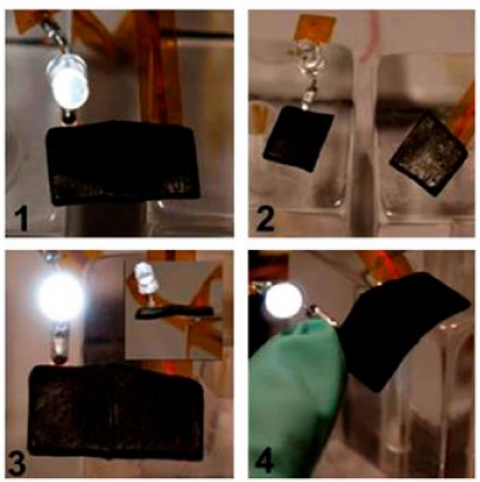
Multiple Hydrogen Bonds

Self-healing Materials in electronic skin

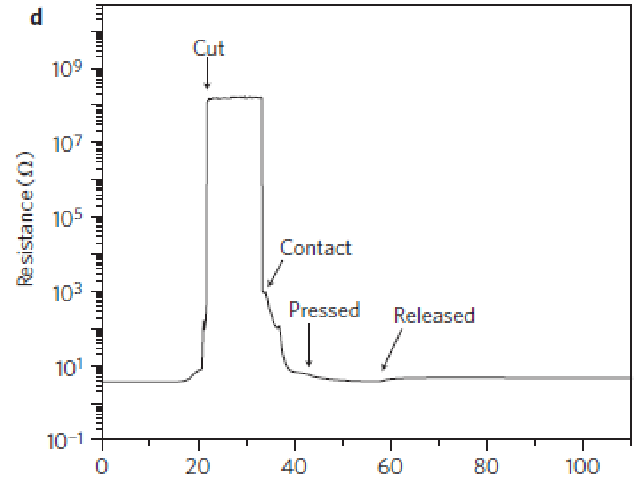
a



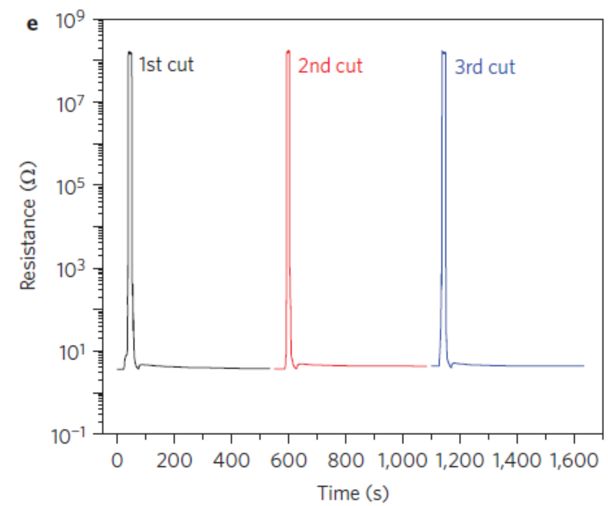
b



d



e

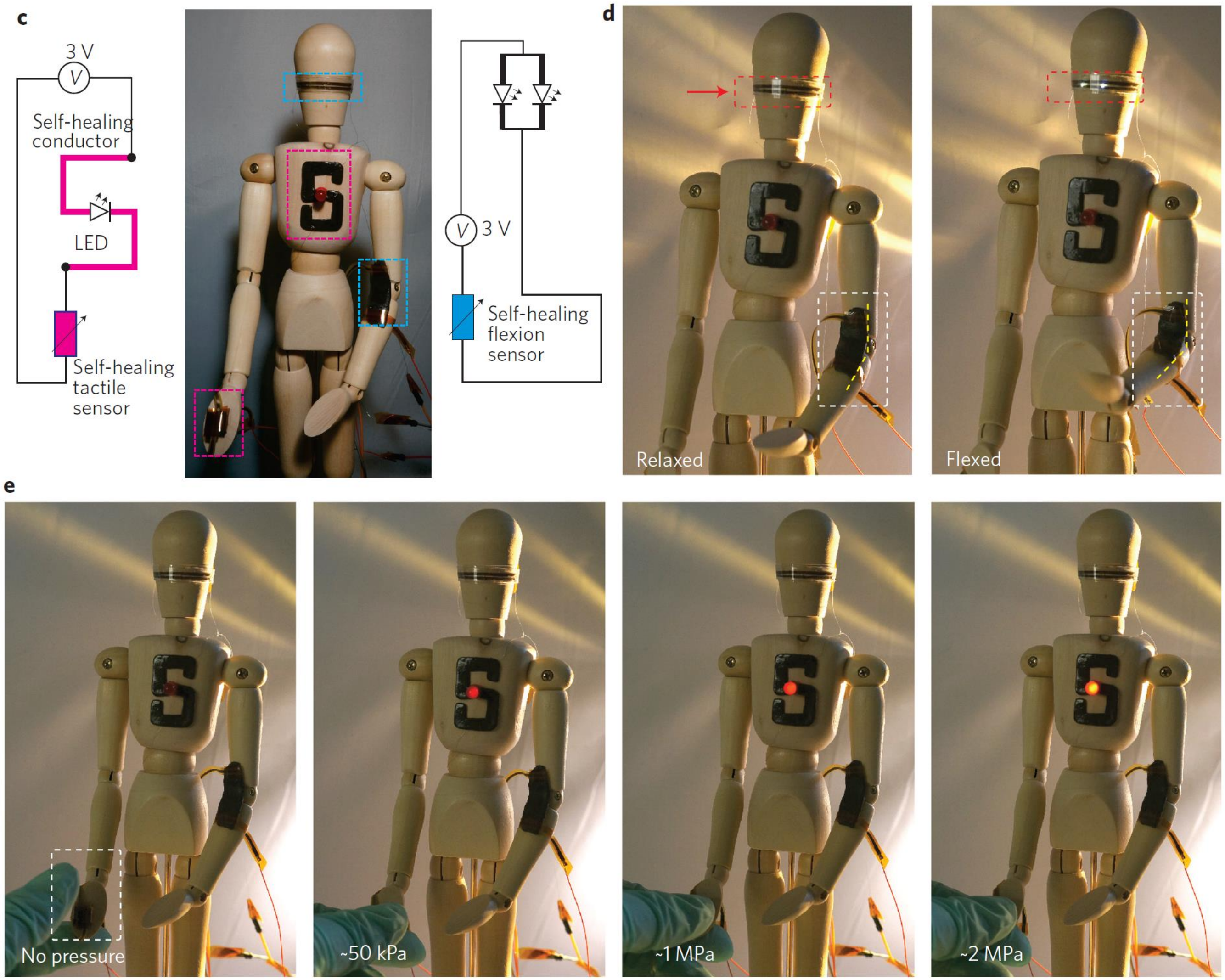


Room temperature self-healing composite with good conductivity

Tee, B. C. K.; Wang, C.; Allen, R.; Bao, Z. *Nat Nano* **2012,** *7*, 825.

Multiple Hydrogen Bonds

Self-healing Materials in electronic skin

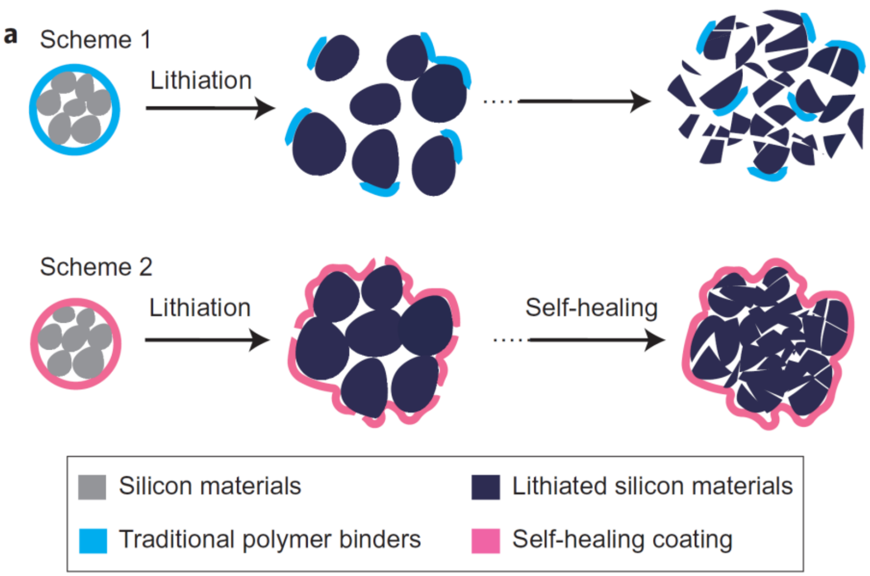


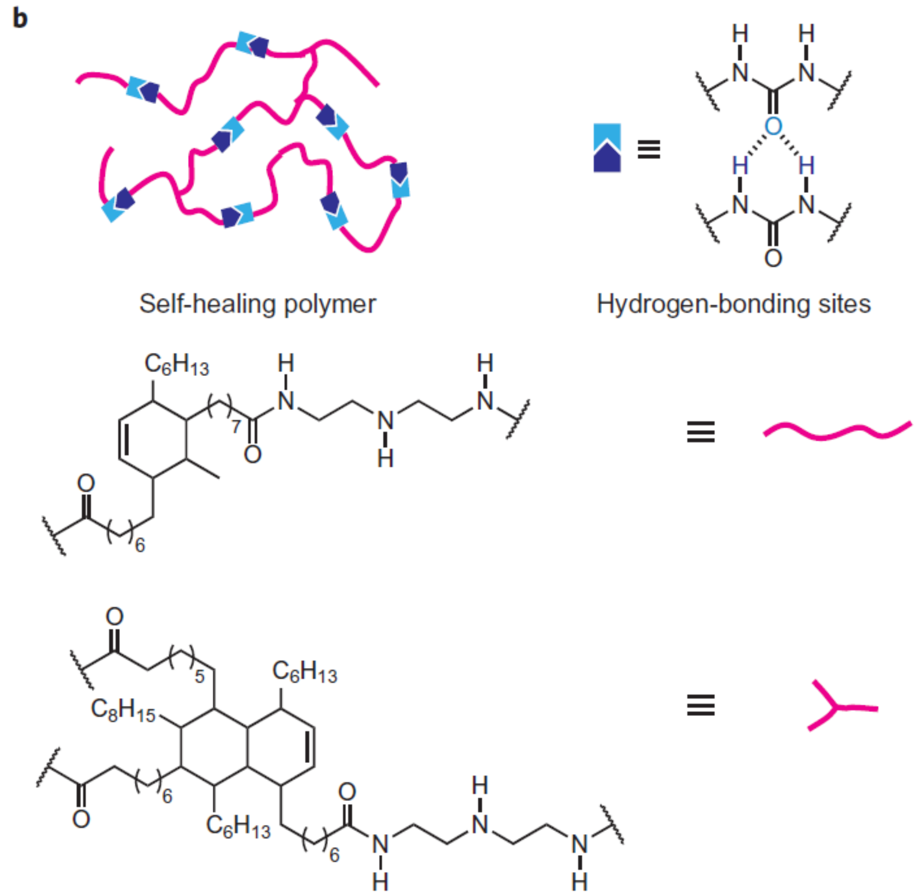
In combination with flexion and tactile sensors

Tee, B. C. K.; Wang, C.; Allen, R.; Bao, Z. *Nat Nano* **2012,** *7*, 825.

Multiple Hydrogen Bonds

Self-healing Materials in lithium-ion battery



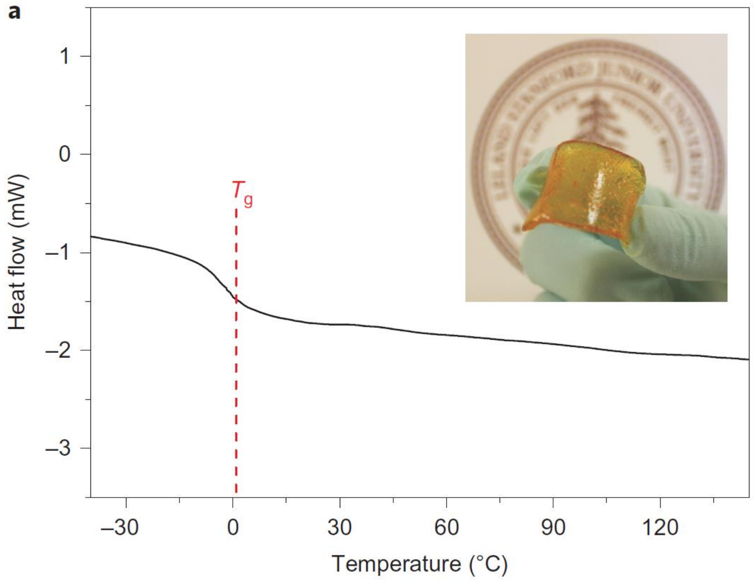


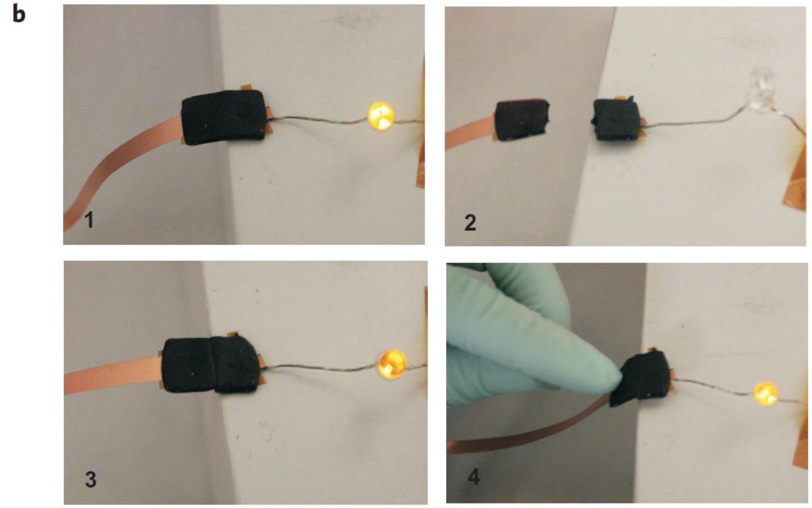
Amorphous material with low glass transition temperature

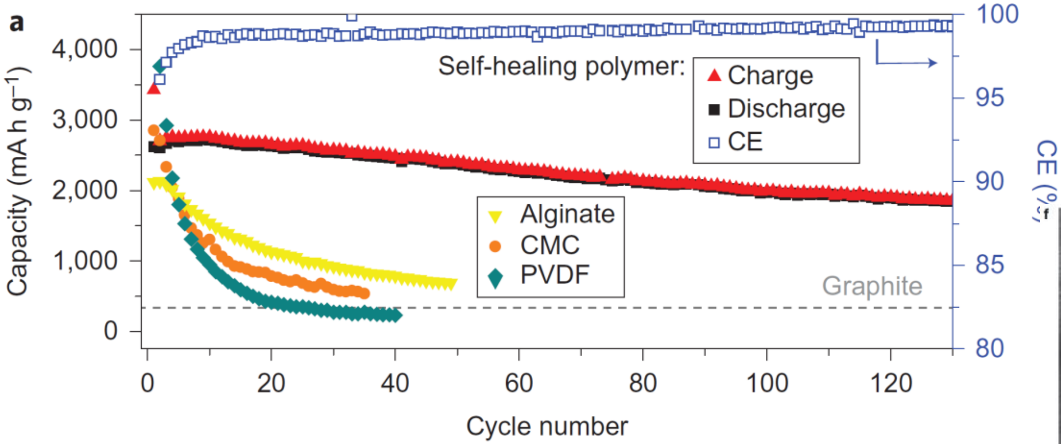
Wang, C.; Wu, H.; Chen, Z.; McDowell, M. T.; Cui, Y.; Bao, Z. *Nat. Chem.* **2013**, *5,* 1042.

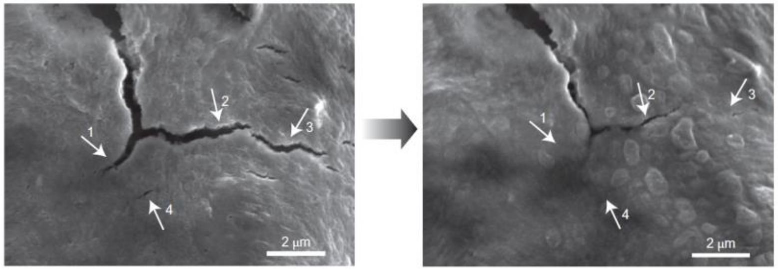
Multiple Hydrogen Bonds

Self-healing Materials in lithium-ion battery









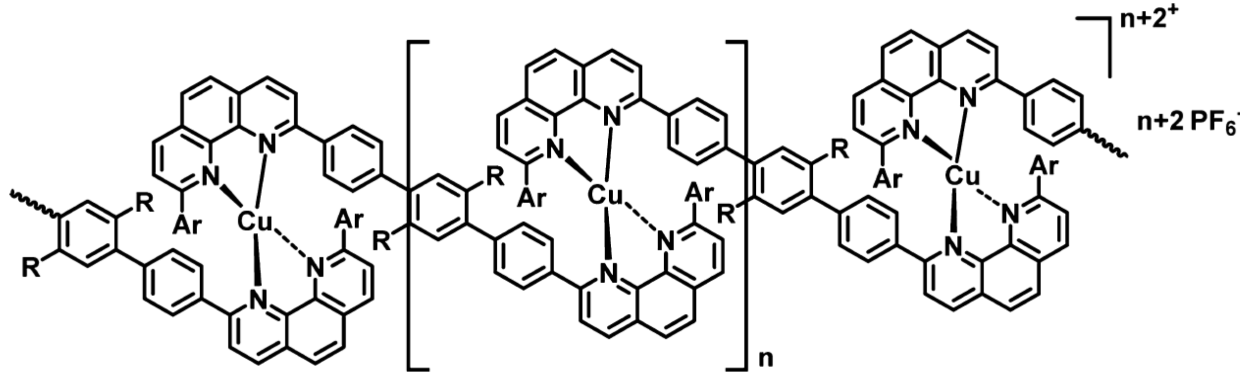
Wang, C.; Wu, H.; Chen, Z.; McDowell, M. T.; Cui, Y.; Bao, Z. *Nat. Chem.* **2013**, *5,* 1042.

Metal-Coordination Bonds

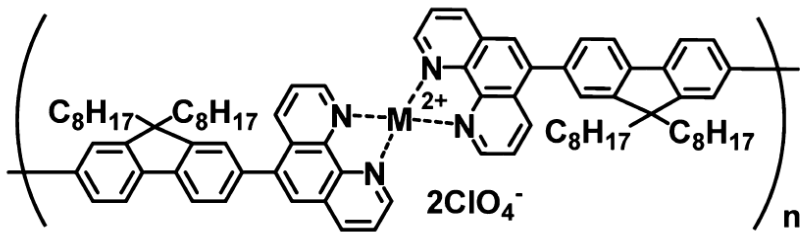
- **<u>Metallosupramolecular polymers (MSPs)</u>**

  Reversible metal-ligand interaction

First Report: stable MSP in noncoordinative solvent



17



18 M = Cu^{2+}, Ni^{2+}

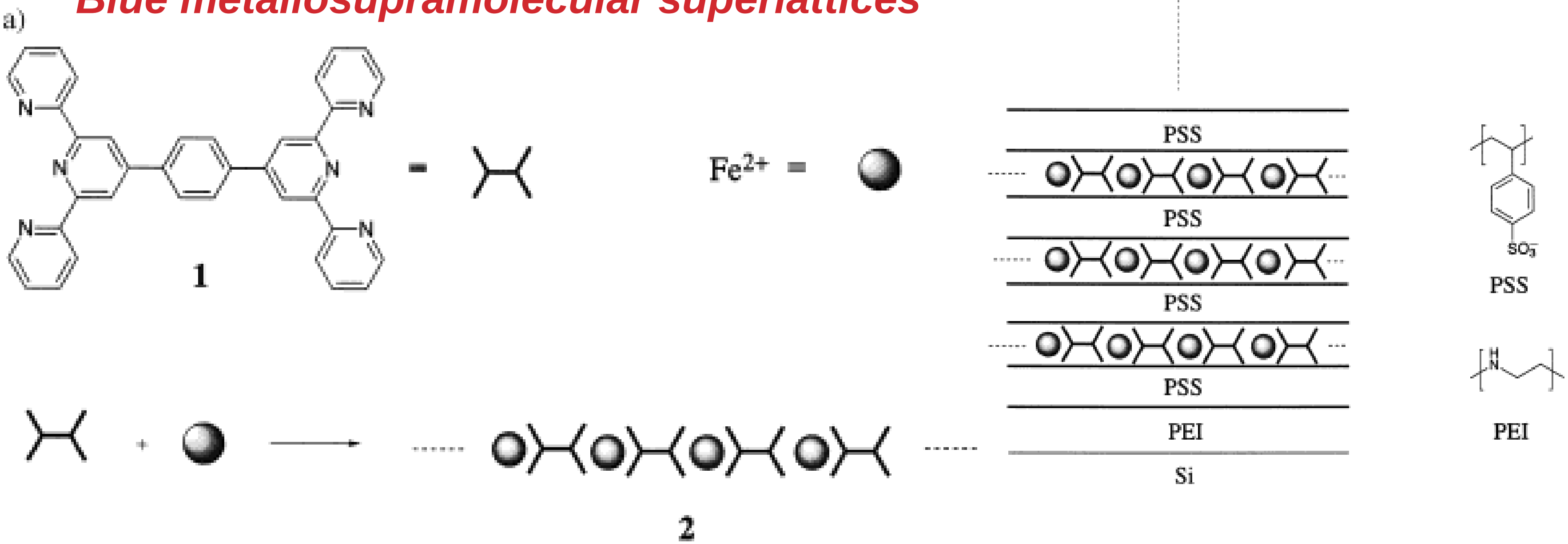
Green electrochromic material

Velten, U.; Rehahn, M. *Chem. Commun.* **1996**, *2639.*
Hossain, M. D.; Sato, T.; Higuchi, M. *Chemistry – An Asian Journal* **2013**, *8,* 76.

Metal-Coordination Bonds

- **<u>Metallosupramolecular polymers (MSPs)</u>**

Blue metallosupramolecular superlattices



Postively charged metallosupramolecular coordination polyelectrolyte absorbed by negatively charged PSS

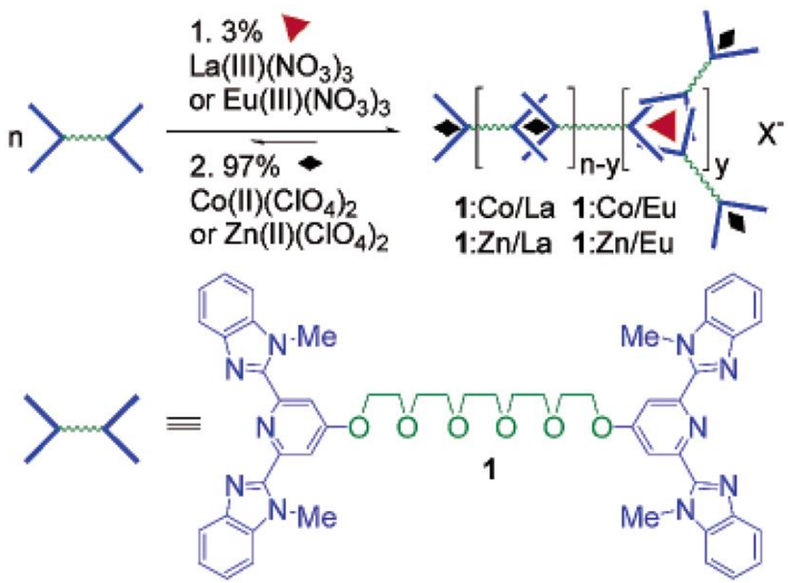
TPY-metal system:
Stability: Fe(II)> Ni(II)> Co(II)> Cu(II)
Extra metal ions will lead to significant decrease in viscosity

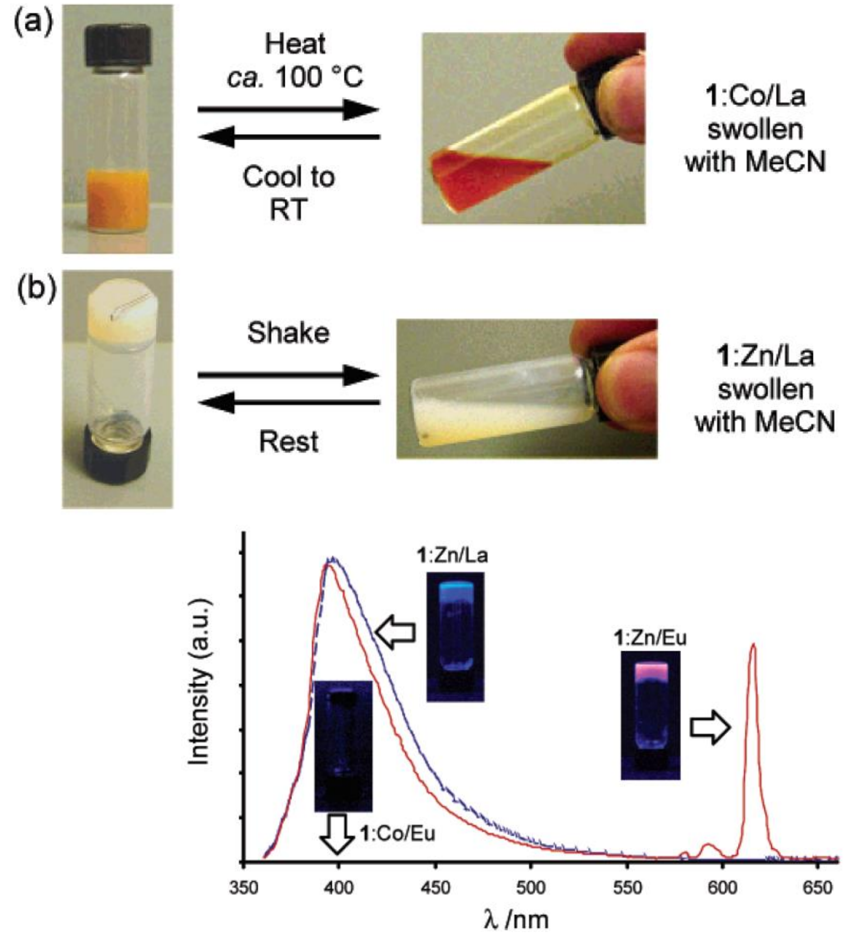
Schütte, M.; Kurth, D. G.; Linford, M. R.; Cölfen, H.; Möhwald, H. *Angew. Chem. Int. Ed.* **1998**, *37,* 2891.
Schmatloch, S.; van den Berg, A. M. J.; Alexeev, A. S.; Hofmeier, H.; Schubert, U. S. *Macromolecules* **2003**, *36,* 9943.

Metal-Coordination Bonds

- **<u>Metallosupramolecular polymers (MSPs)</u>**

Environmentally responsive cross-linking MSPs





lanthanide metal-centered emission

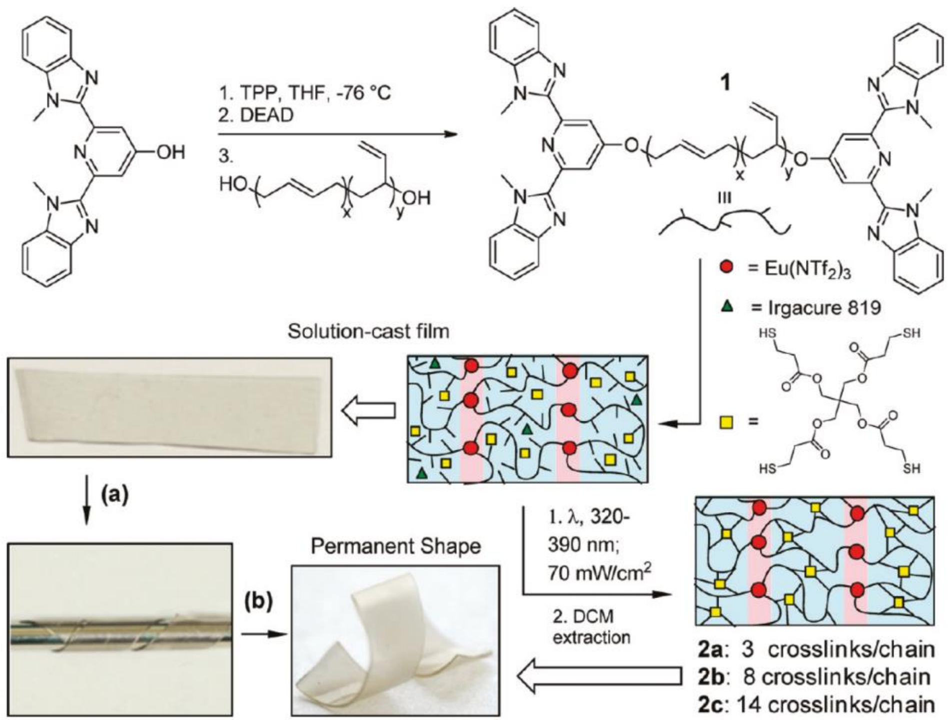
Beck, J. B.; Rowan, S. J. *J. Am. Chem. Soc.* **2003**, *125,* 13922.

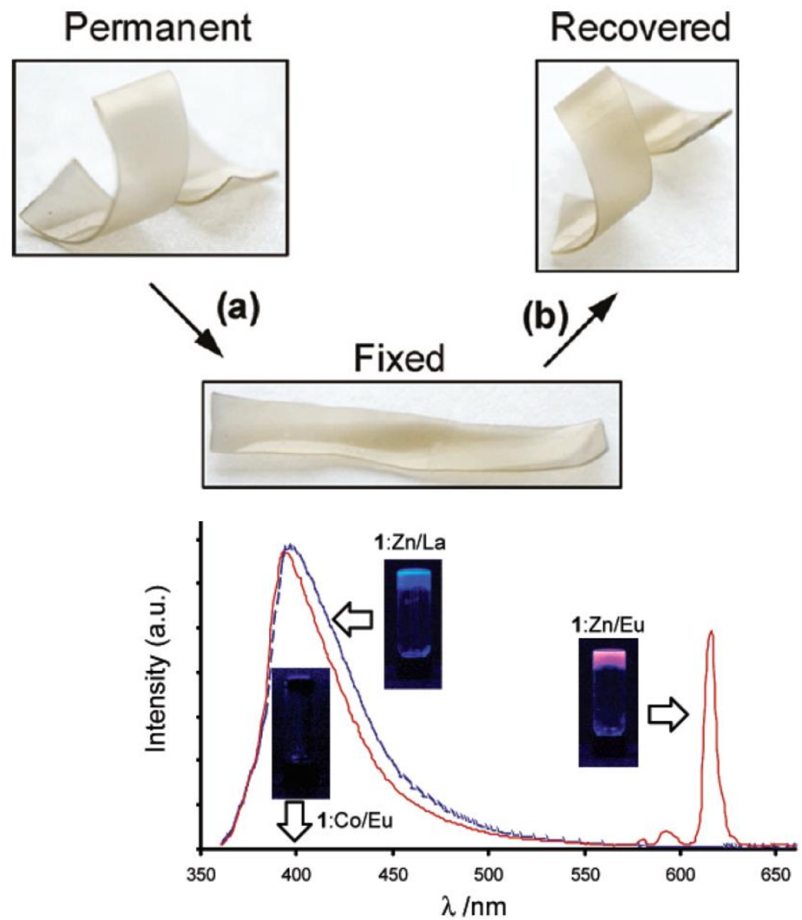
Kumpfer, J. R.; Rowan, S. J. *J. Am. Chem. Soc.* **2011**, *133,* 12866.

Metal-Coordination Bonds

- **Metallosupramolecular polymers (MSPs)**

Environmentally responsive cross-linking MSPs





lanthanide metal-centered emission

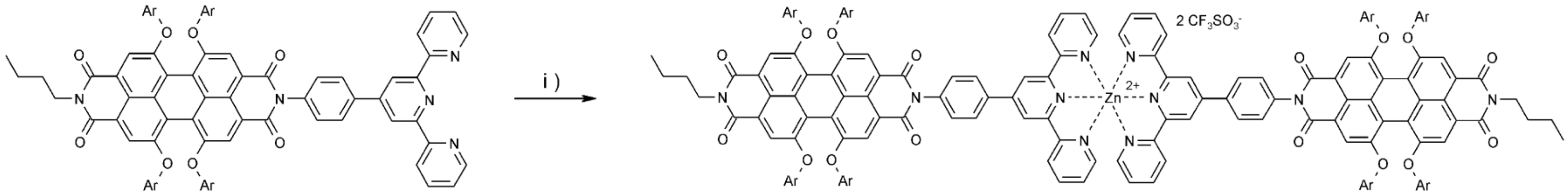
Beck, J. B.; Rowan, S. J. *J. Am. Chem. Soc.* **2003***, 125,* 13922.

Kumpfer, J. R.; Rowan, S. J. *J. Am. Chem. Soc.* **2011***, 133,* 12866.

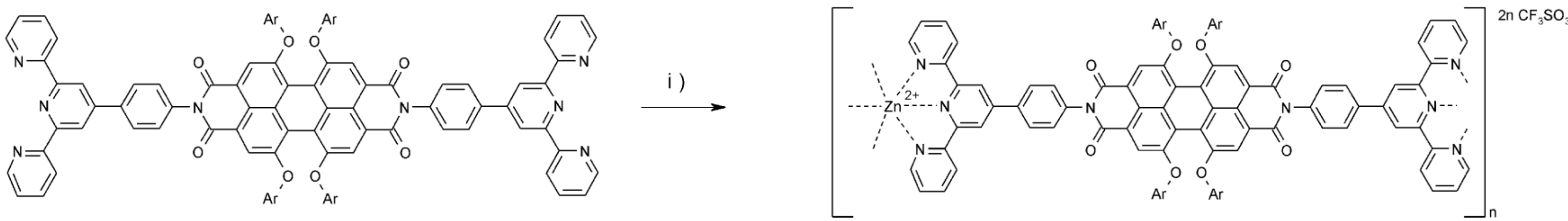
Metal-Coordination Bonds

- **<u>Metallosupramolecular polymers (MSPs)</u>**

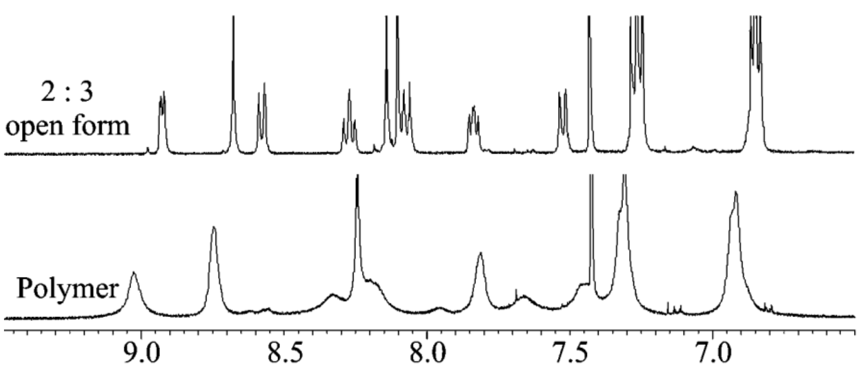
Photoluminescent supramolecular polymers

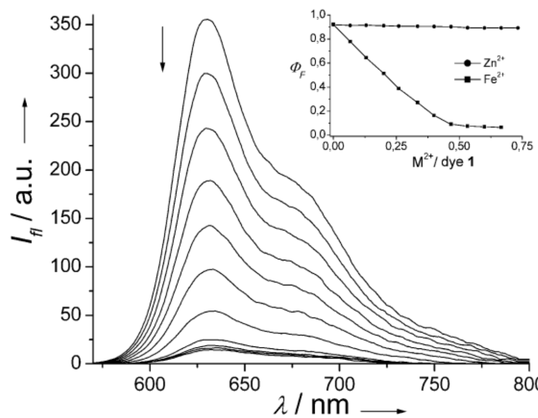


1 2



3 4





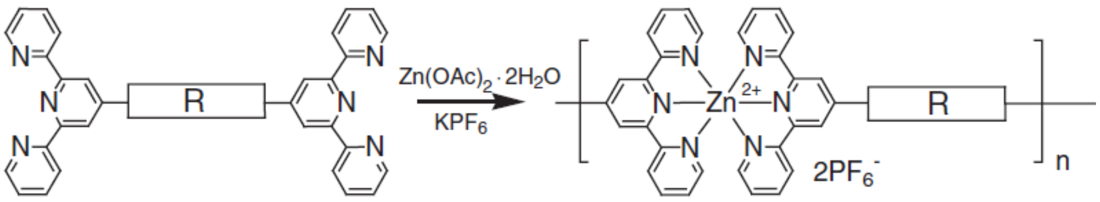
Dobrawa, R.; Wurthner, F. *Chem. Commun.* **2002**, 1878.

Different metal has different energy transfer process within rigid-rod polymers

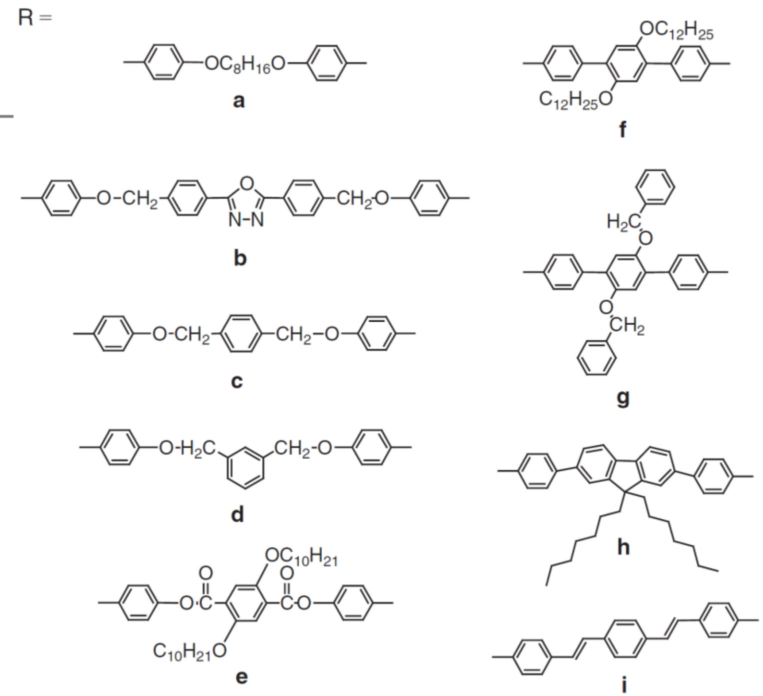
Metal-Coordination Bonds

- <u>**Metallosupramolecular polymers (MSPs)**</u>

Self-assembled electroluminescent polymers



1a–1i **2a–2i**



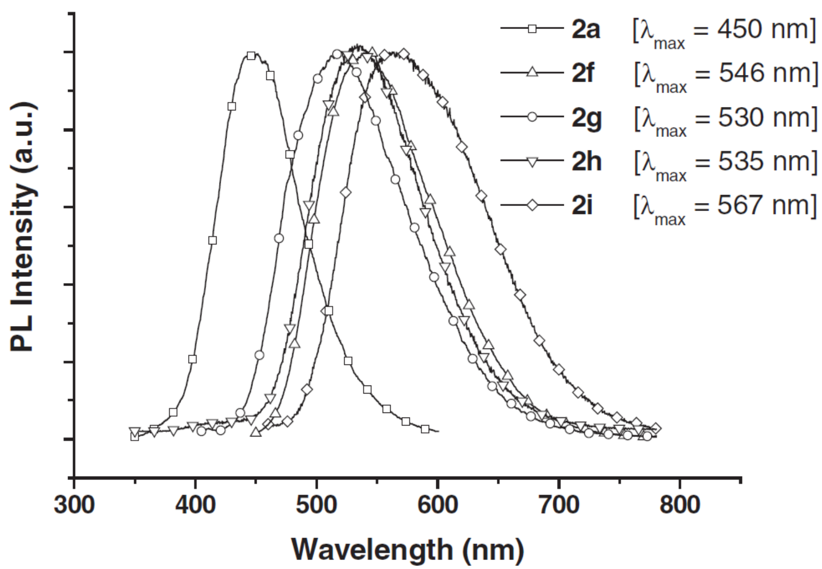


Fig. 3. Emission spectra of **2a**, **2f**, **2g**, **2h**, and **2i** as thin films.

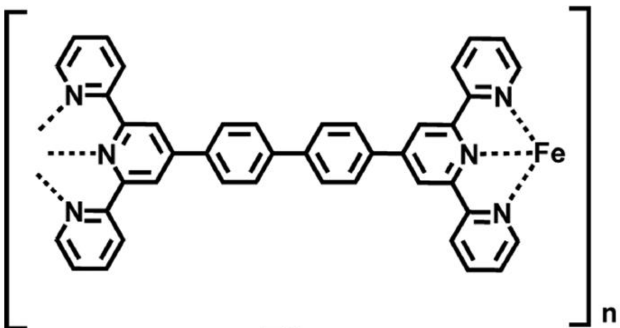
- **Violet to yellow light emission**
- **Readily available self-assemble reactions**
- **Promising PLED**

Yu, S. C.; Kwok, C. C.; Chan, W. K.; Che, C. M. *Adv. Mater.* **2003**, *15,* 1643.

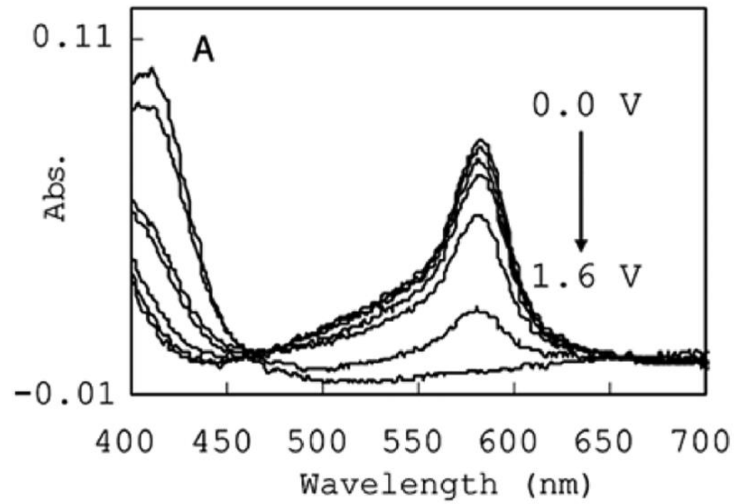
Metal-Coordination Bonds

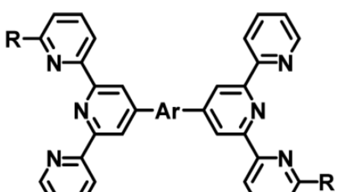
- **<u>Metallosupramolecular polymers (MSPs)</u>**

Electrochromic materials



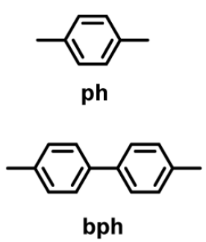
76



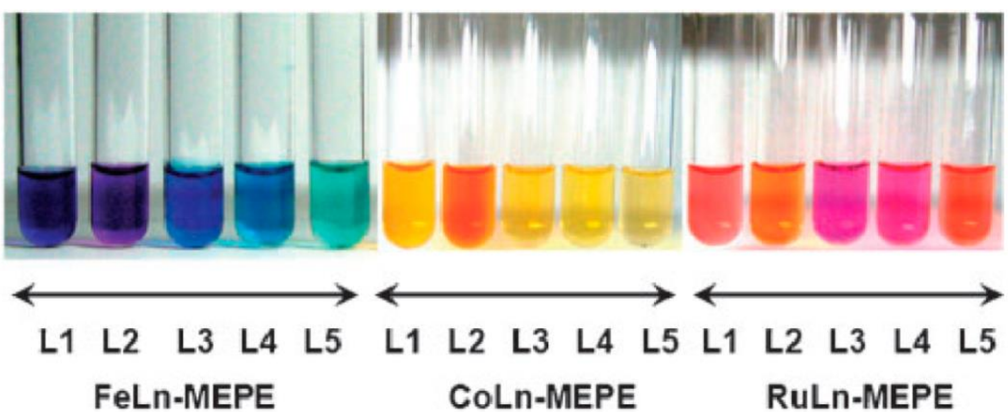


Ln

Ln	R	Ar
L1	H	ph
L2	H	bph
L3	OMe	ph
L4	OMe	bph
L5	Br	ph



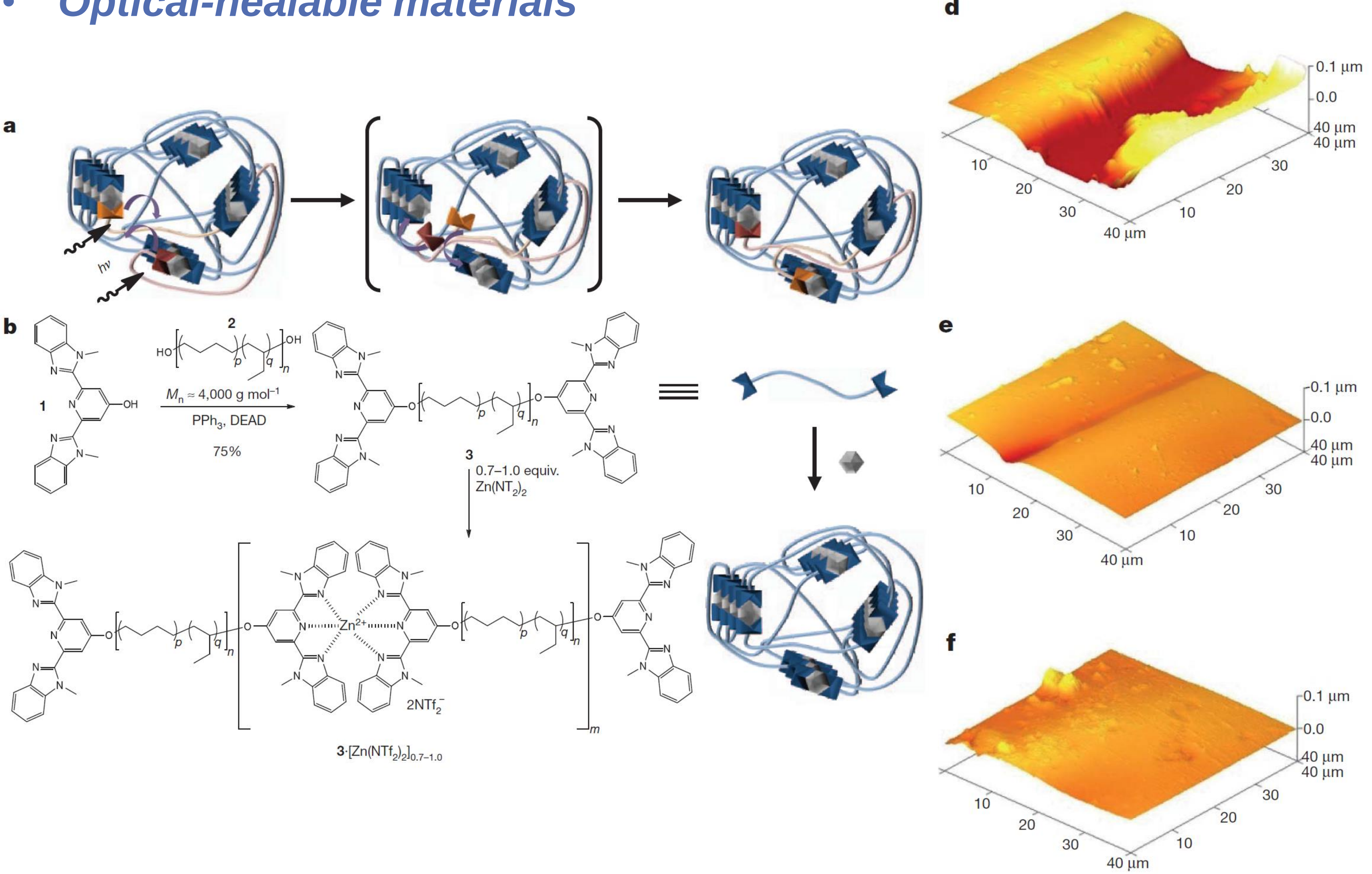
ITO slide completely colorless at 1.6 V



Han, F. S.; Higuchi, M.; Kurth, D. G. *Adv. Mater.* **2007**, *19,* 3928.

Metal-Coordination Bonds

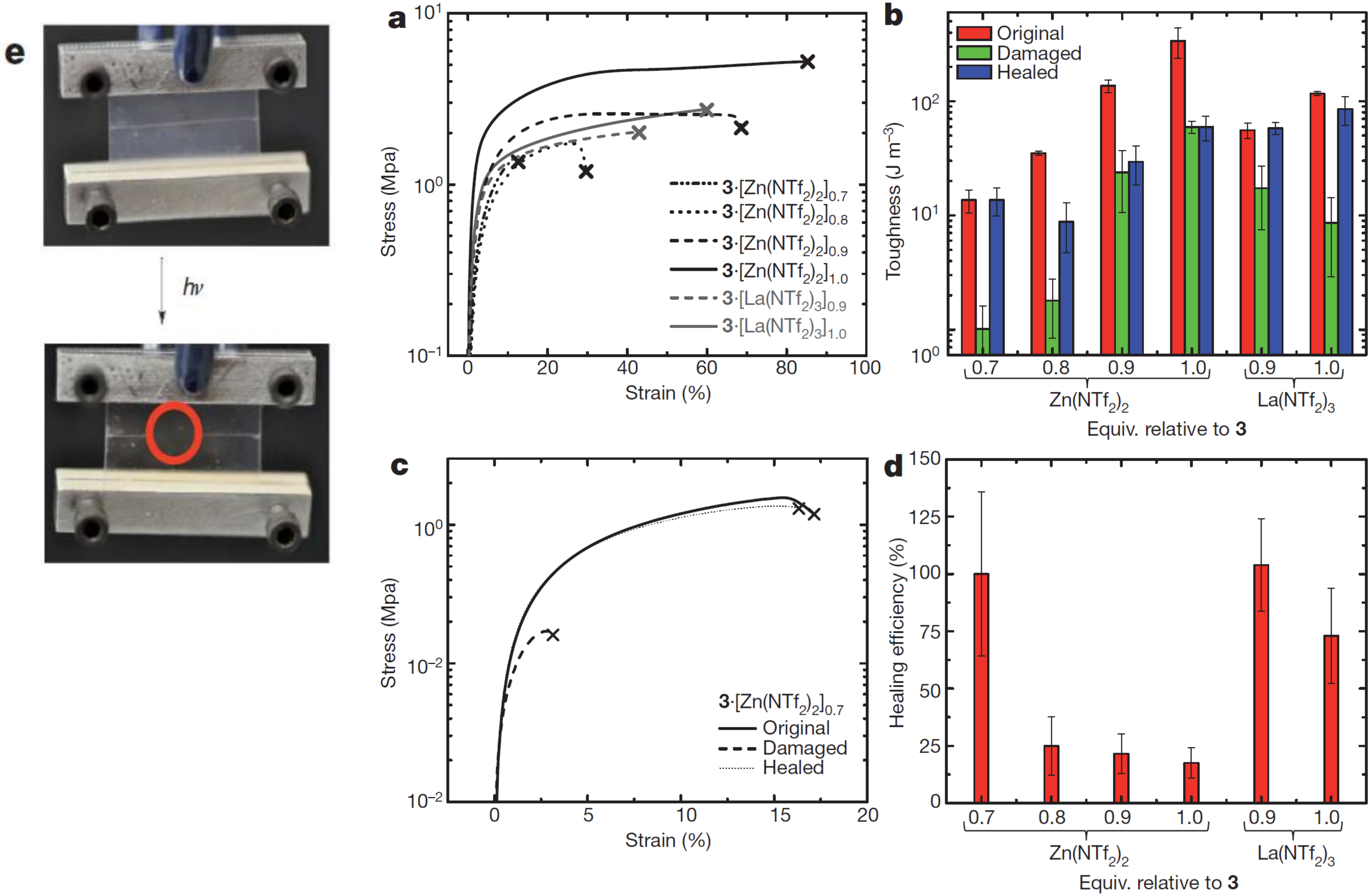
- ***Optical-healable materials***



Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. *Nature* **2011**, *472,* 334.

Metal-Coordination Bonds

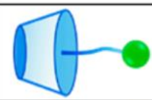
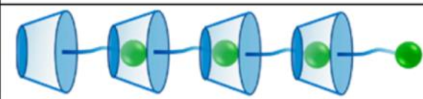
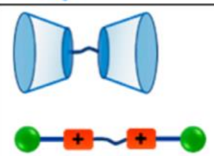
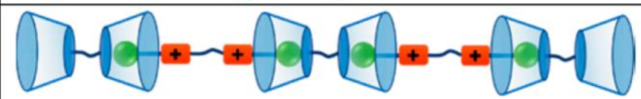
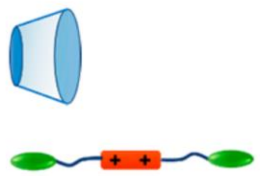
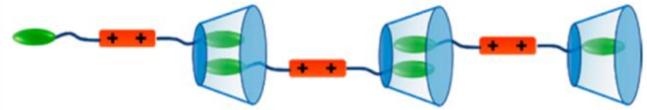
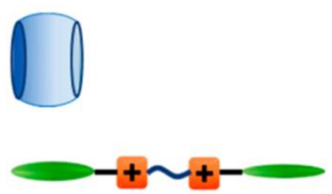
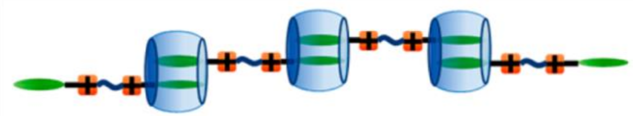
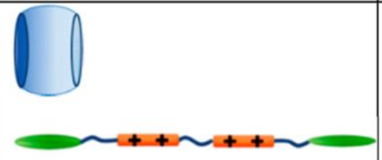
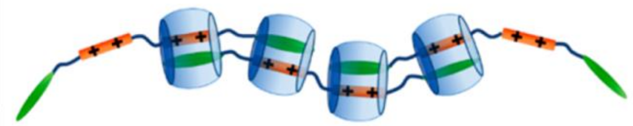
- ***Optical-healable materials***



Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. *Nature* **2011**, *472,* 334.

Host-Guest Interactions

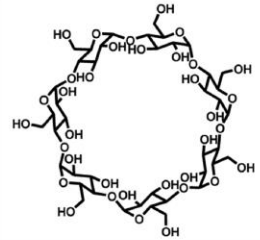
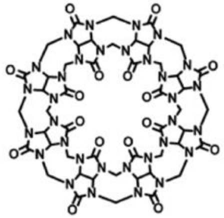
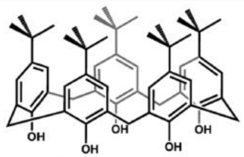
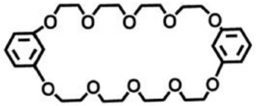
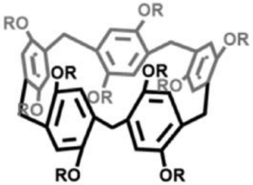
- **<u>Representative Types of Host-Guest Monomers</u>**

Type	Monomer	Supramolecular Polymers
AB		
AA/BB		
Host/BB		
		
Host/ABBA		

Yang, L.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Rev.* **2015**, *115,* 7196.

Host-Guest Interactions

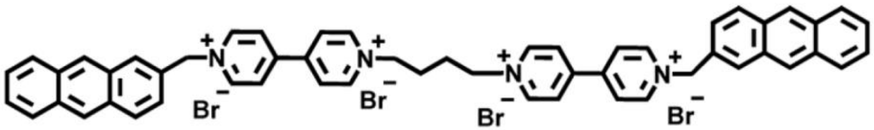
- **Representative Types of Host-Guest Monomers**

host molecules	molecular structures	typical guest molecules
β-cyclodextrin		adamantane, coumarin
cucurbit[8]uril		methyl viologen, charged naphthalene, anthracene and alkane
calixarene		charged alkane, viologen
crown ether		viologen, charged amine
pillararene		charged imidazole and DABCO

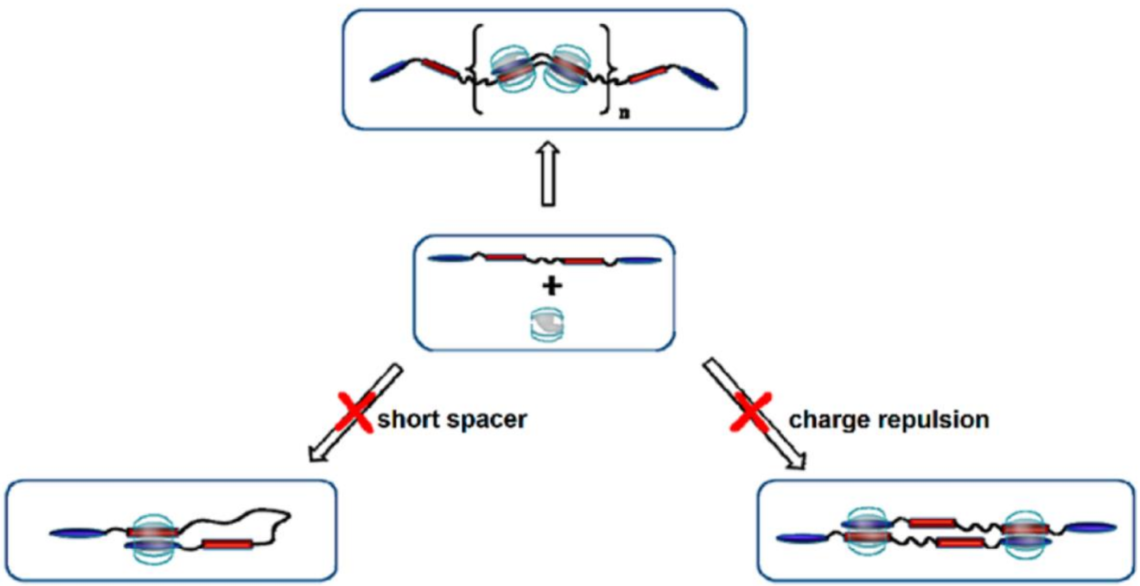
Yang, L.; Tan, X.; Wang, Z.; Zhang, X. *Chem. Rev.* **2015***, 115,* 7196.

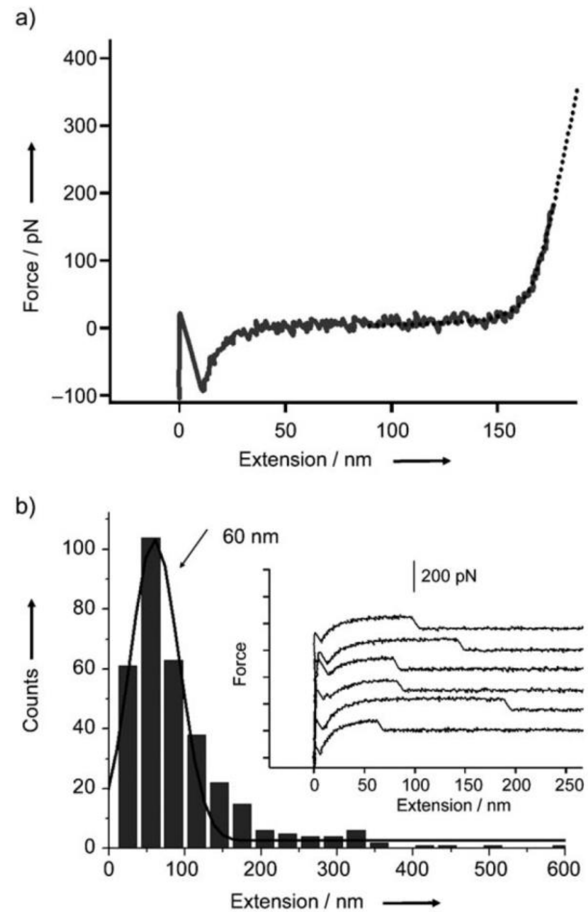
Host-Guest Interactions

- **Cucurbit[8]uril-Based ABBA type**



25





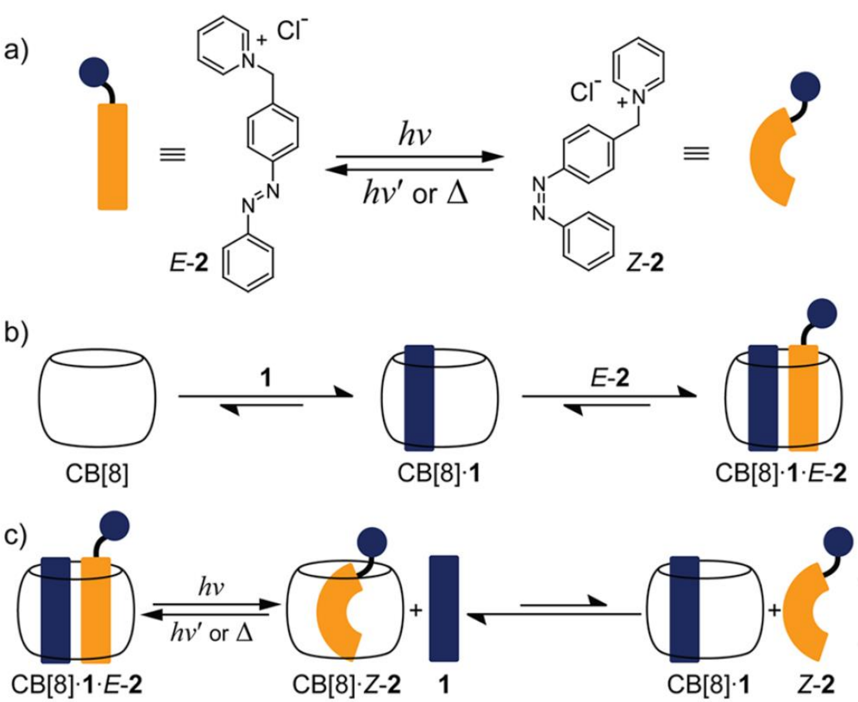
Short and charged linkage is important for the supramolecular polymer formation

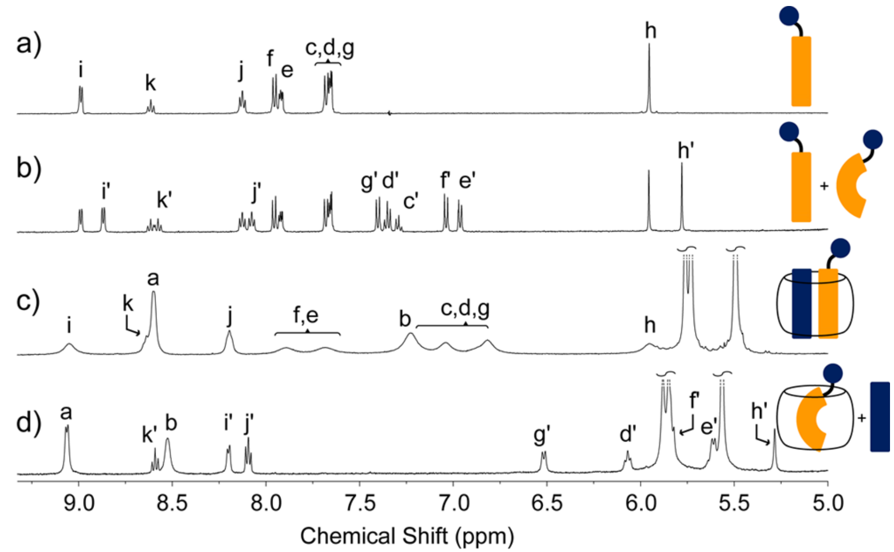
SMFS characterization: Kuhn length of 2.2±0.1 nm; segment elasticity (1.25±0.05)×10^3 pN/nm, larger than covalent polymer

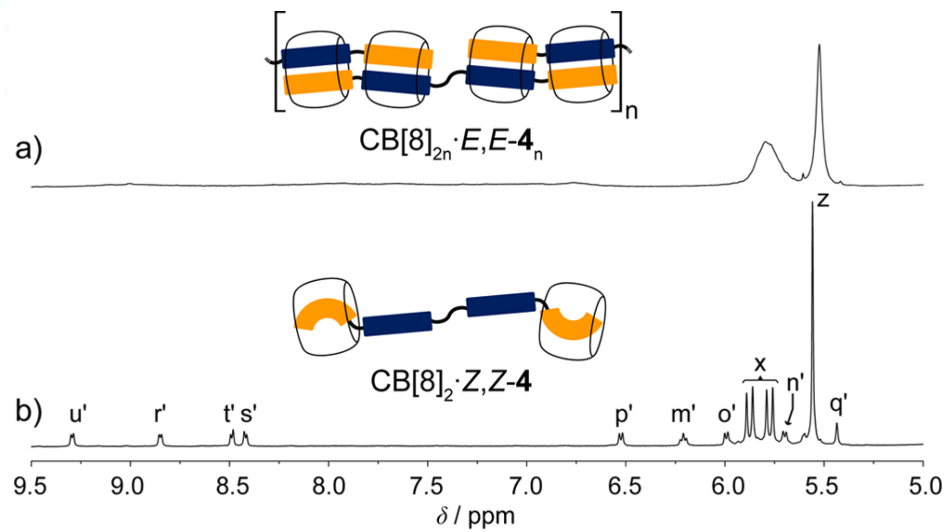
Liu, Y.; Yu, Y.; Gao, J.; Wang, Z.; Zhang, X. *Angew. Chem. Int. Ed.* **2010**, *49,* 6576.

Host-Guest Interactions

- **<u>Photoswitchable Cucurbit[8]uril-Based</u>**





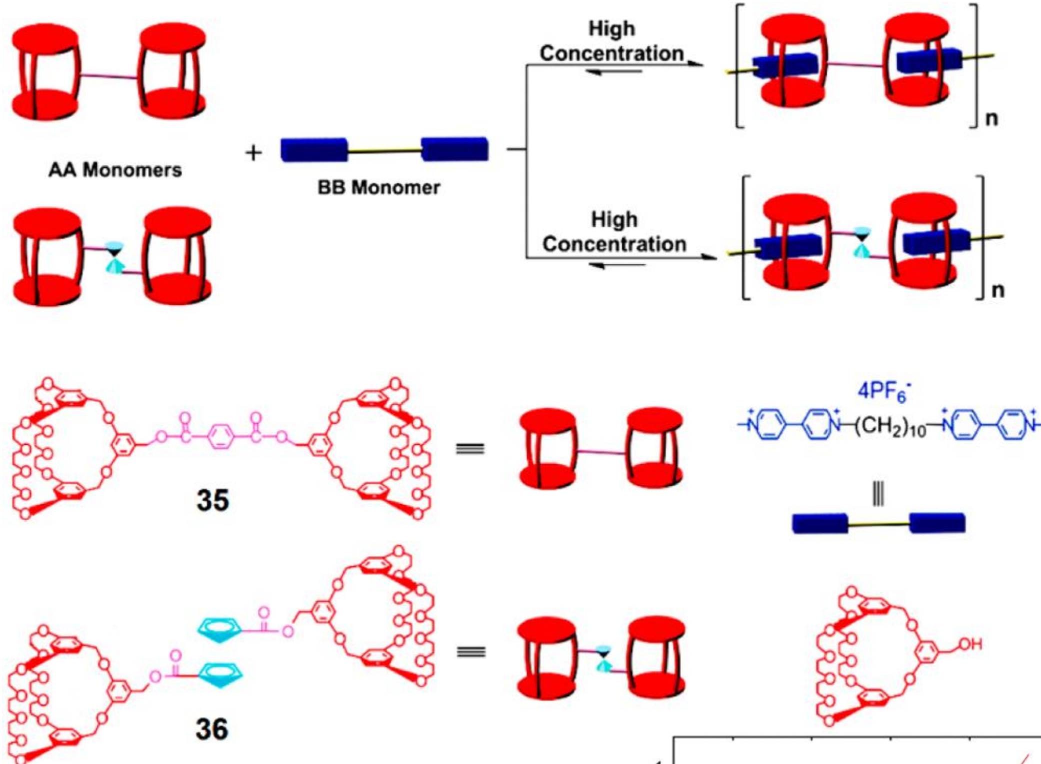


- **Changes in diffusion coefficient from DOSY experiments**
- **Reappearance of the H signal in the blue segment**
- **Deduction in size confirmed by SANS**

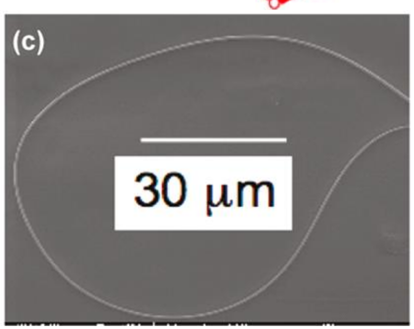
del Barrio, J.; Horton, P. N.; Lairez, D.; Lloyd, G. O.; Toprakcioglu, C.; Scherman, O. A. *J. Am. Chem. Soc.* **2013**, *135*, 11760.

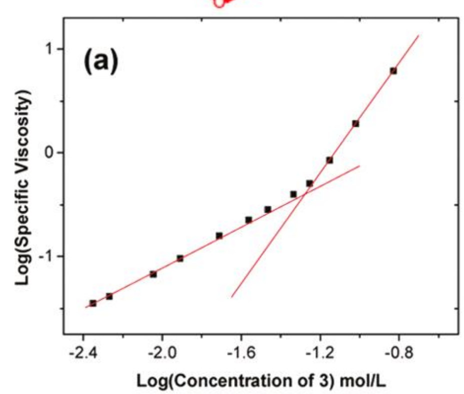
Host-Guest Interactions

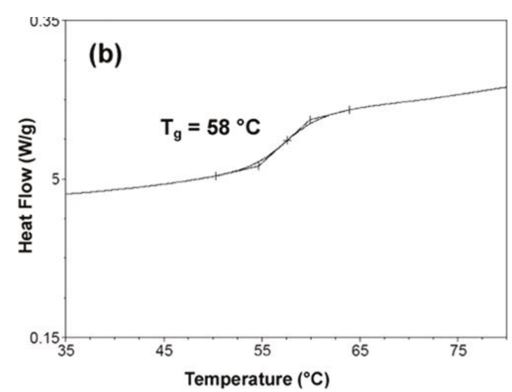
- <u>**Crown ether-Based AA-BB type**</u>



- **35 has a smaller $[M]_{crit}$ suggesting less cyclic structure in the mixture---less flexibility**
- **Much higher specific viscosity then normal crown ether based SPs, higher binding constant**
- **Robust enough to form film through normal dry spinning method**



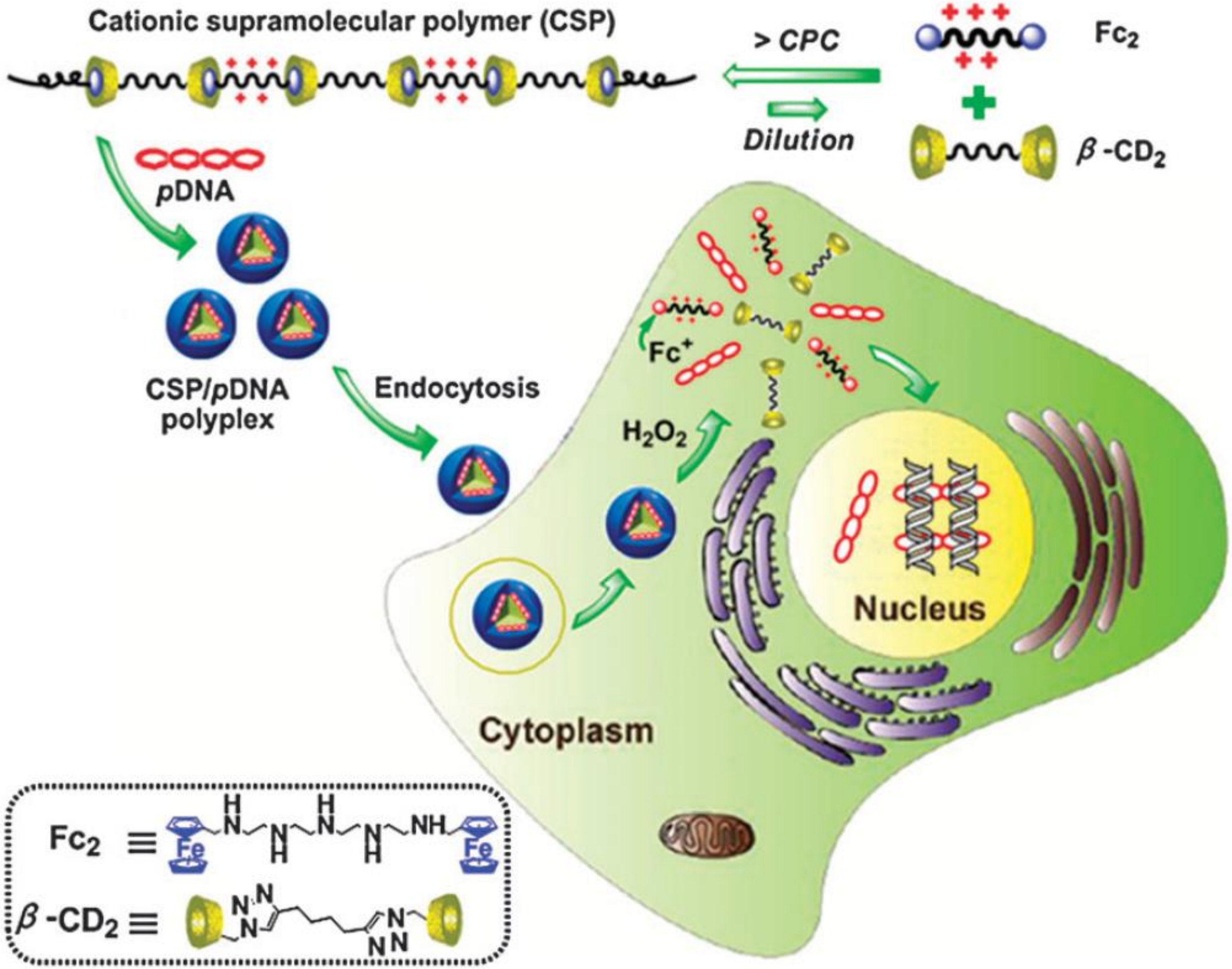




Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133,* 2836.

Host-Guest Interactions

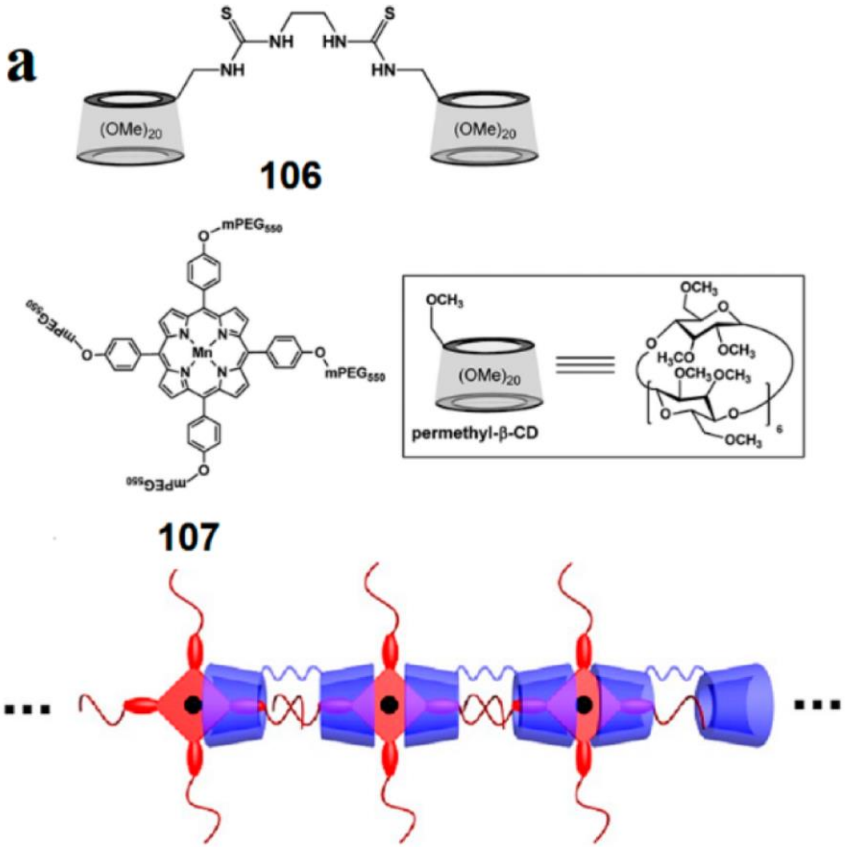
- **<u>B-cyclodextrin-Based supramolecular polymers</u>**

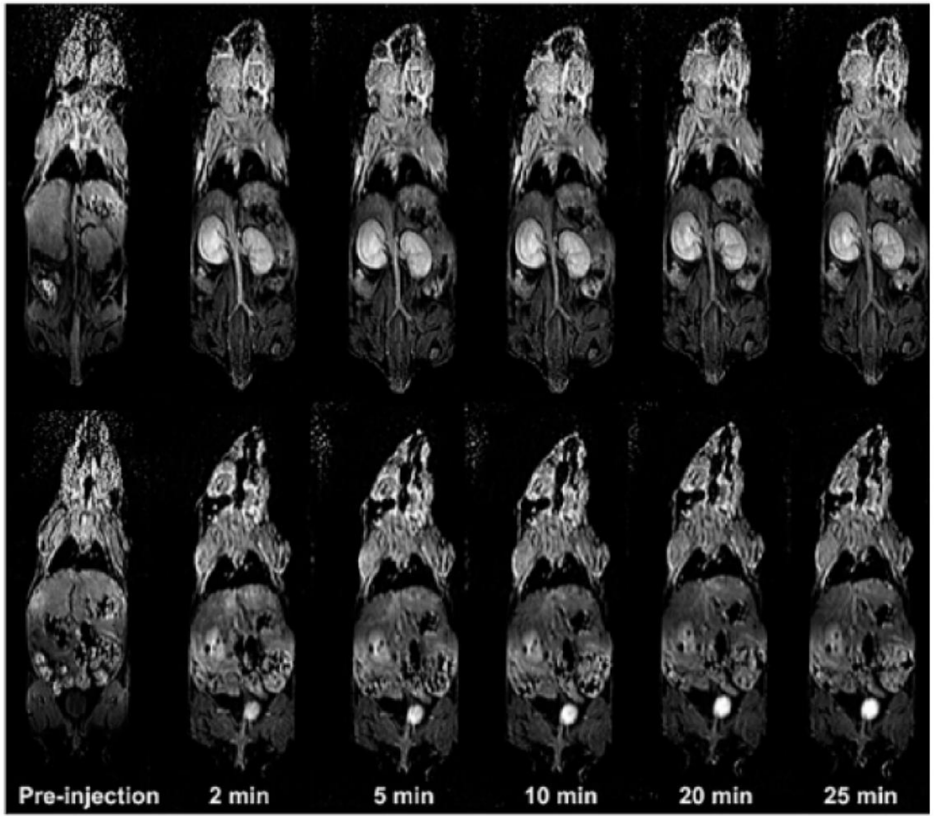


Dong, R.; Su, Y.; Yu, S.; Zhou, Y.; Lu, Y.; Zhu, X. *Chem. Commun.* **2013**, *49,* 9845.

Host-Guest Interactions

- **B-cyclodextrin-Based supramolecular polymers**



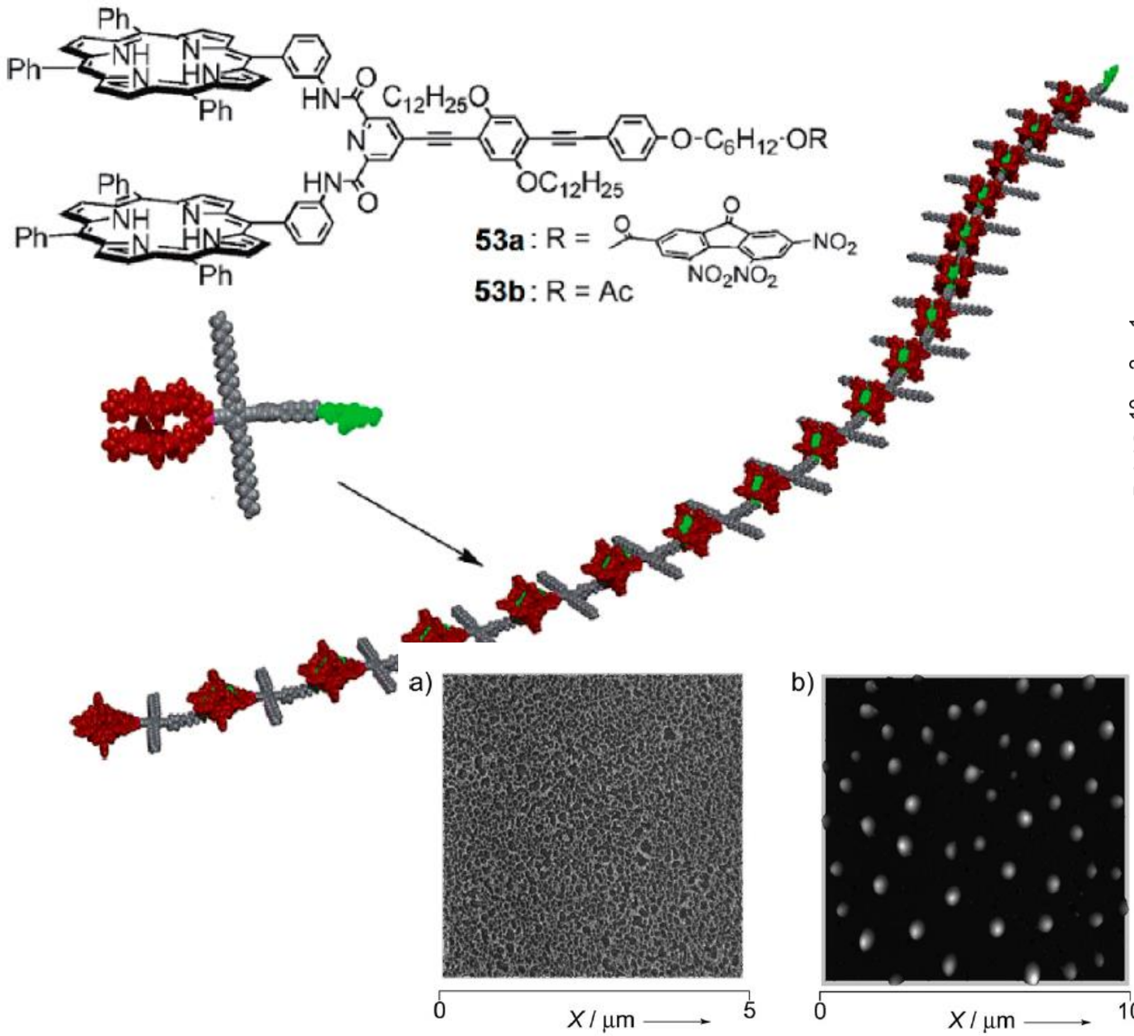


2D coronal T_1-weighted MR images of the mice

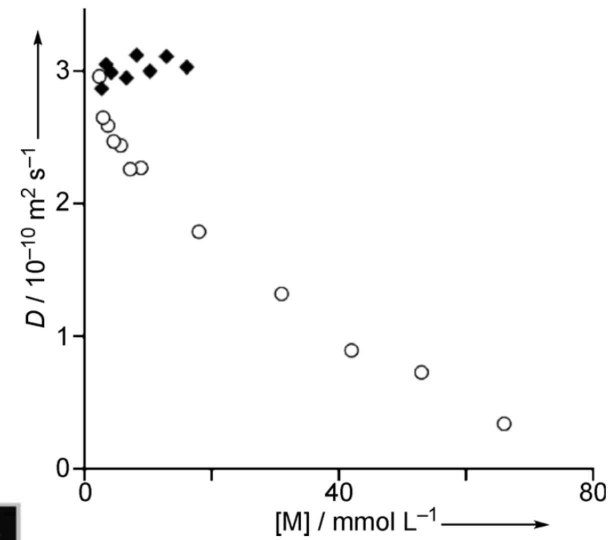
Sun, M.; Zhang, H.-Y.; Liu, B.-W.; Liu, Y. *Macromolecules* **2013***, 46,* 4268.

Aromatic Donor-Acceptor Interaction

- **Bisporphyrin tweezer via charge-transfer interaction**



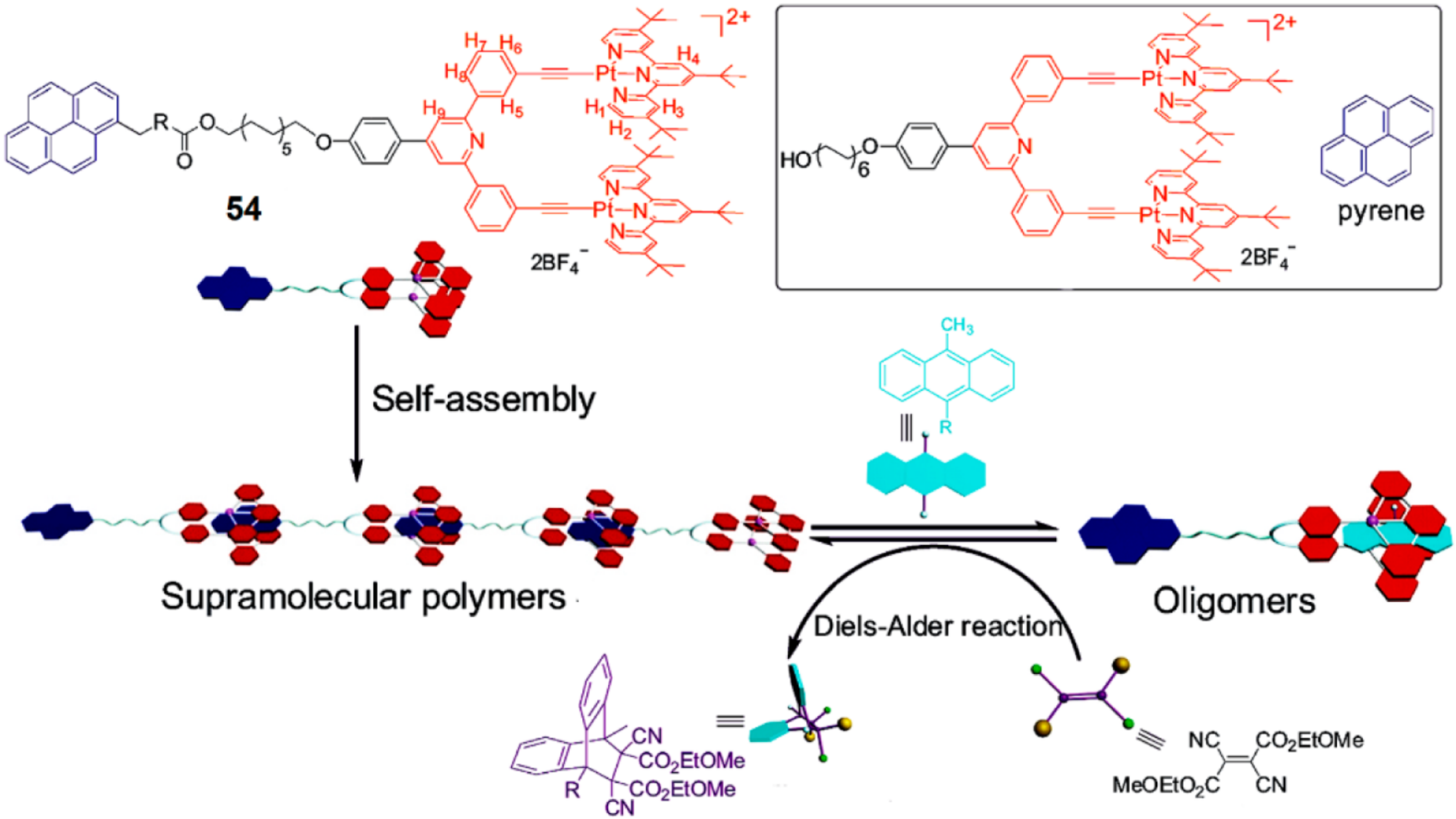
With electron-poor planar aromatic guests



Haino, T.; Watanabe, A.; Hirao, T.; Ikeda, T. *Angew. Chem. Int. Ed.* **2012**, *51,* 1473.

Aromatic Donor-Acceptor Interaction

- **Bis[alkynylplatinum(II)] Terpyridine Molecular Tweezer**



With electron-rich planar aromatic guests

Tian, Y.-K.; Shi, Y.-G.; Yang, Z.-S.; Wang, F. *Angew. Chem. Int. Ed.* **2014**, *53,* 6090.

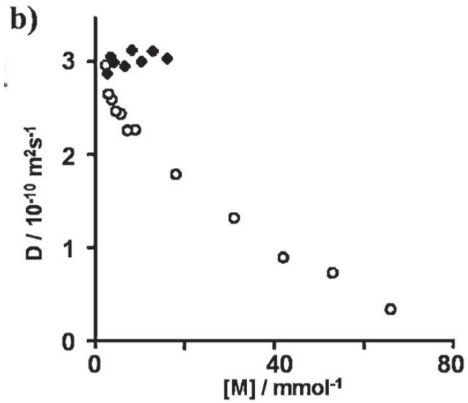
Thanks for your attention!

- **Q1**

Q1: We have talked about many characterization methods for supramolecular polymers, here are some easy review on them, please fill in the blank.

Instability of the structure upon dilution is the biggest challenge for utilizing GPC to characterize supramolecular polymers.

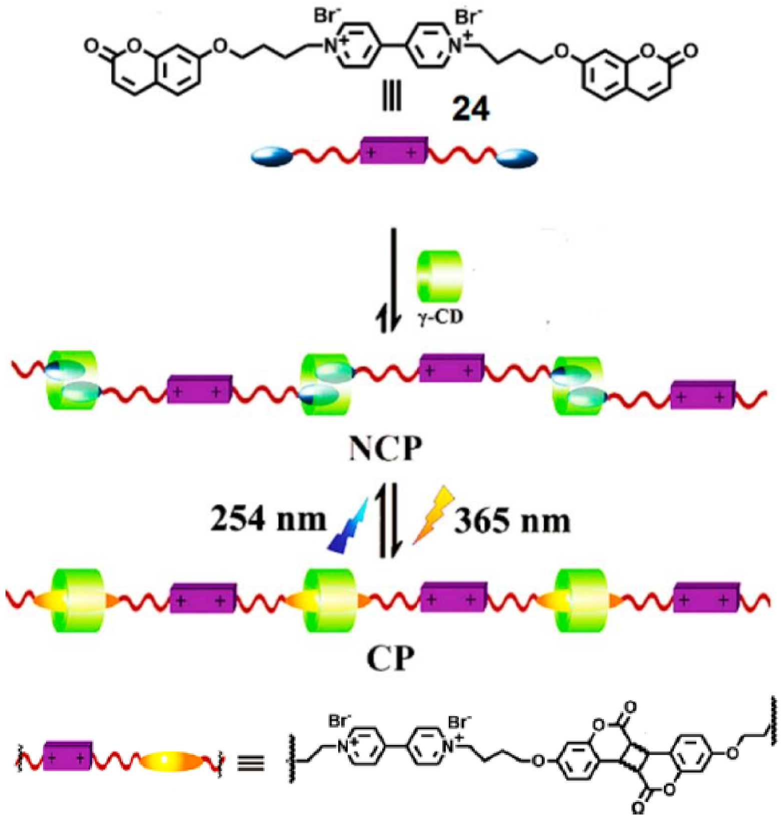
Small (large or small in size) elutes out first in Asymmetric Flow Field-Flow Fractionation (AF4).



According to this graph, circle (rectangular or circle) curve belongs to a supramolecular polymer.

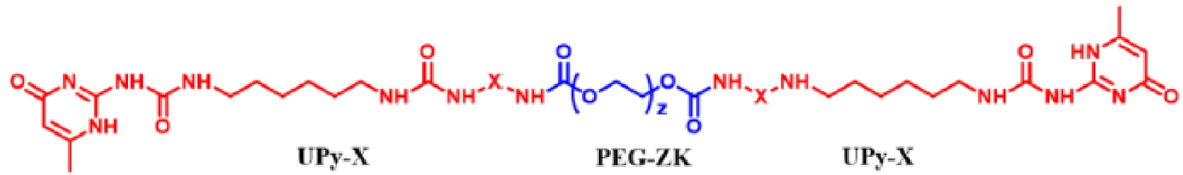
- **Q2**

Q2: Please figure out what happened after shining light on the supramolecular polymers. (Draw out the reaction)



- **Q3**

Q3: Please propose a route to synthesis following monomer. (starting material A can be used as polymer directly)



A