Highlights from the Career of Jeffrey S. Moore

Group Meeting
January 31th, 2013

Christopher R. Jamison

Jeffrey Moore:
Professor of Chemistry and Materials Science

PhD – UIUC, 1989. Advisor: Samuel Stupp

Post Doc. – Caltech. Advisor: Bob Grubbs

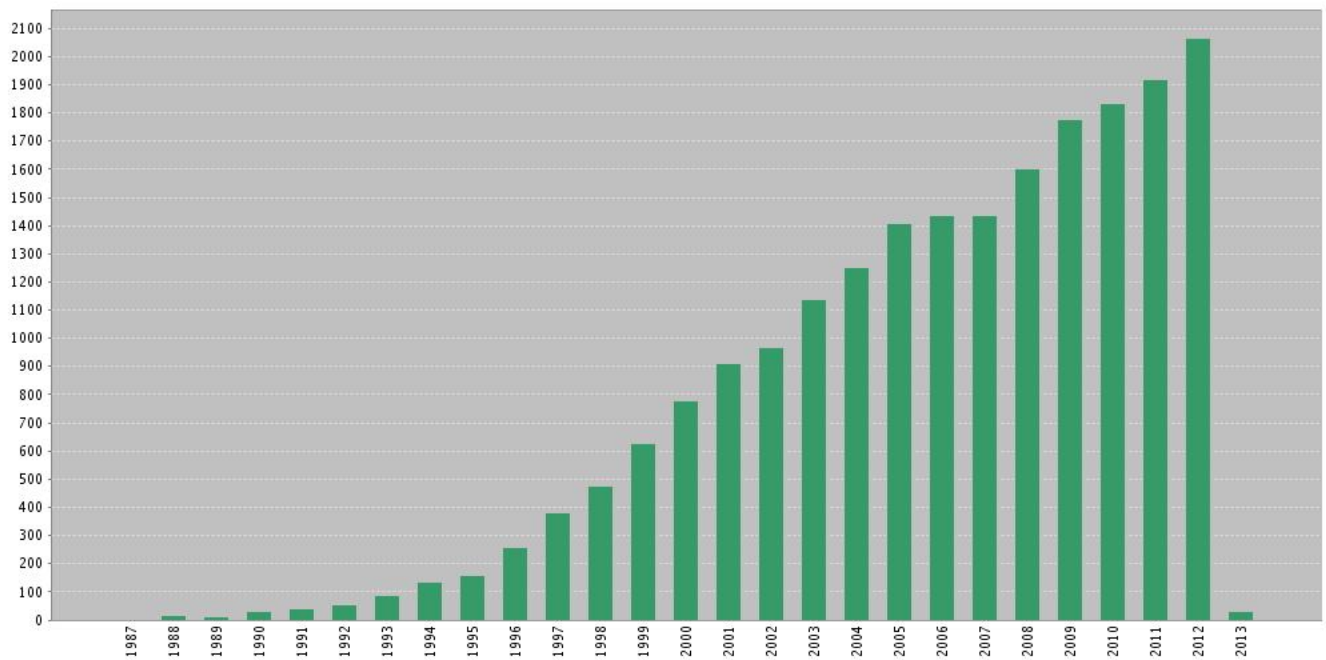
Assitant Prof. – University of Michigan, 1990

Professor – UIUC 1993 – present

Fellow AAAS – 2008

H-Index: 77

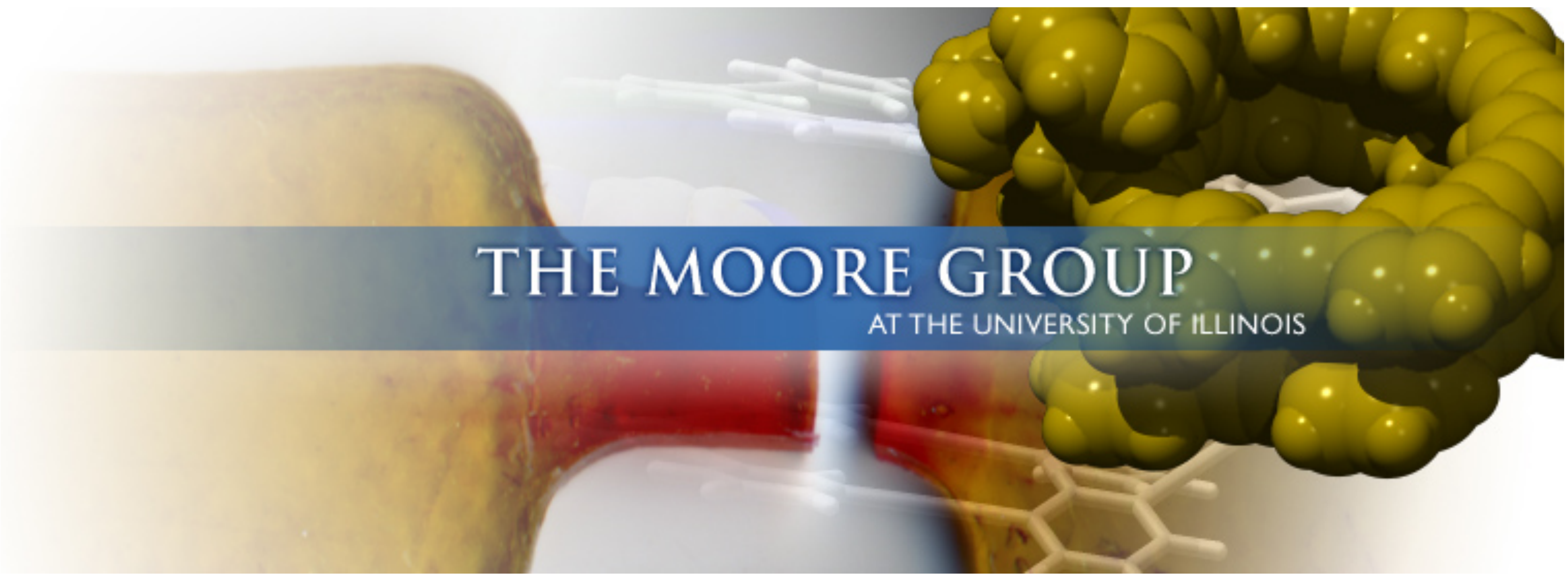
Citations Per Year



Total publications: 318
Total citations: 20,828
Citations per paper: 65.5
H-index: 77

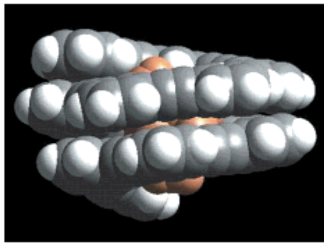
The Moore Group

"In general, our group uses the tools of synthetic and physical organic chemistry to address problems at the interface of chemistry and materials science."

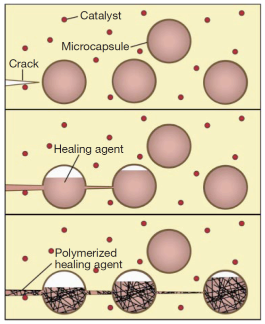


Areas of Research

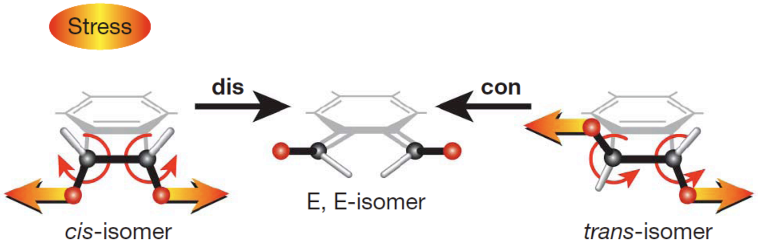
New Macromolecular Architectures



Self-Healing Materials

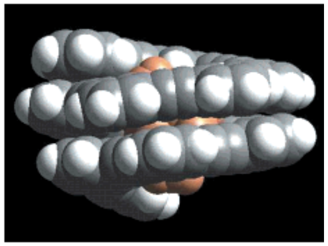


Mechanochemistry



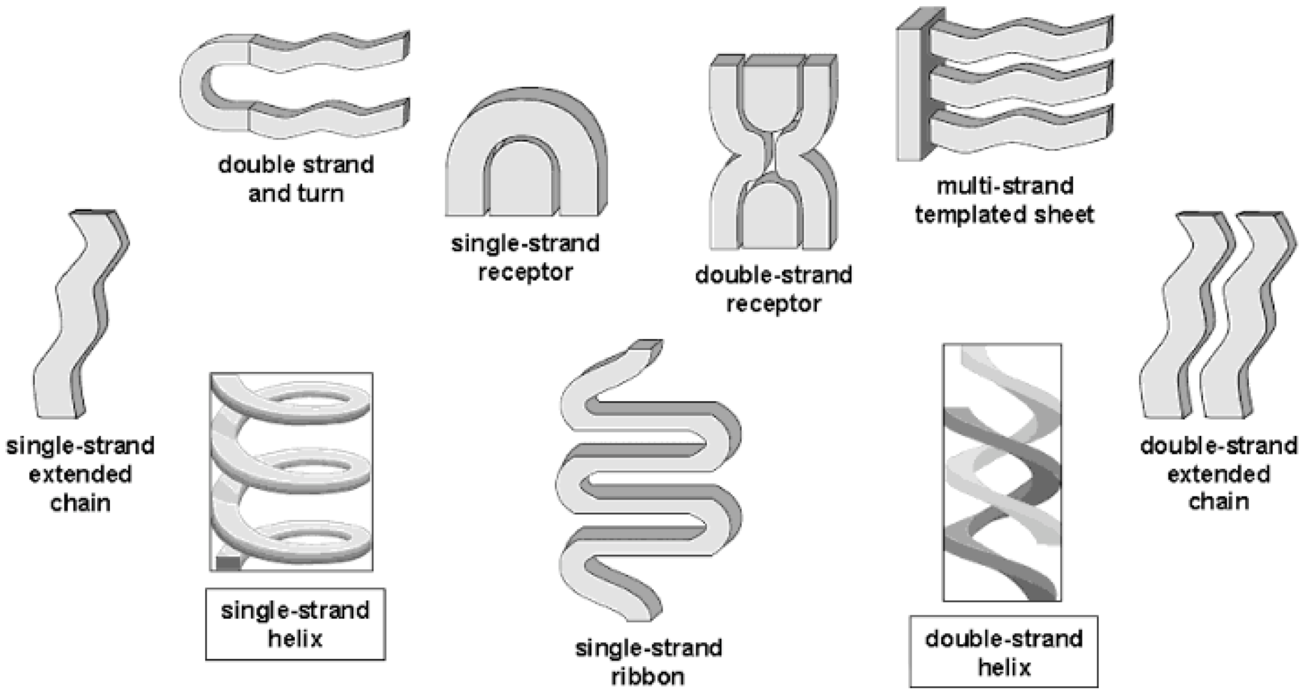
Areas of Research

New Macromolecular Architectures



New Macromolecular Architectures

Non-Biological Foldamers



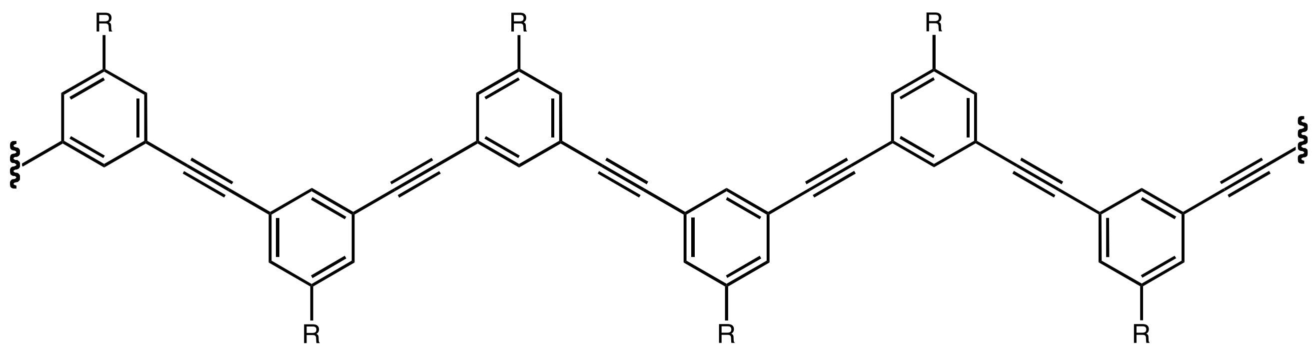
Foldamer

Any oligomer that folds into a conformationally ordered state in solution, the structures of which are stabilized by a collection of noncovalent interactions between nonadjacent monomer units.

Hill, D. J.; *et al. Chem. Rev.* **2001**, 101, 3893-4011

New Macromolecular Architectures

Arylene-Ethynylene Polymers



organic semiconductors

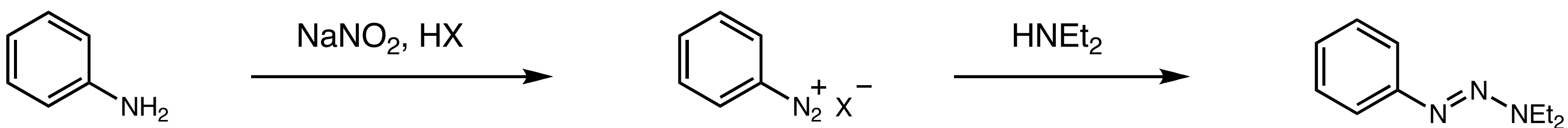
useful optical properties

propensity to self assemble by $\pi-\pi$ interactions

restricted conformational freedom aids in predictable self-assembly

New Macromolecular Architectures

An Aryl Iodide Masking Group

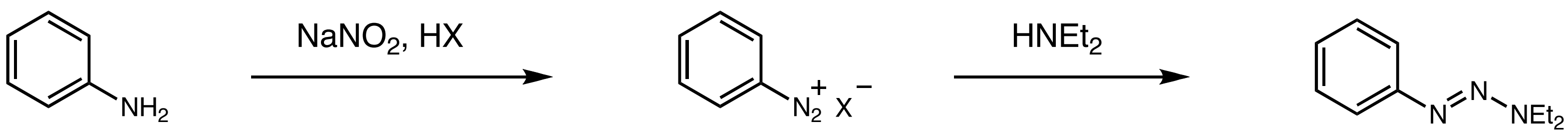


latent iodide
inert to cross-coupling

Moore, J. S.; *et al. Tett. Lett.* **1991**, 32, 2465

New Macromolecular Architectures

An Aryl Iodide Masking Group



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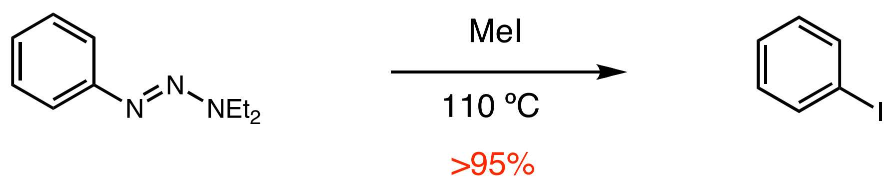
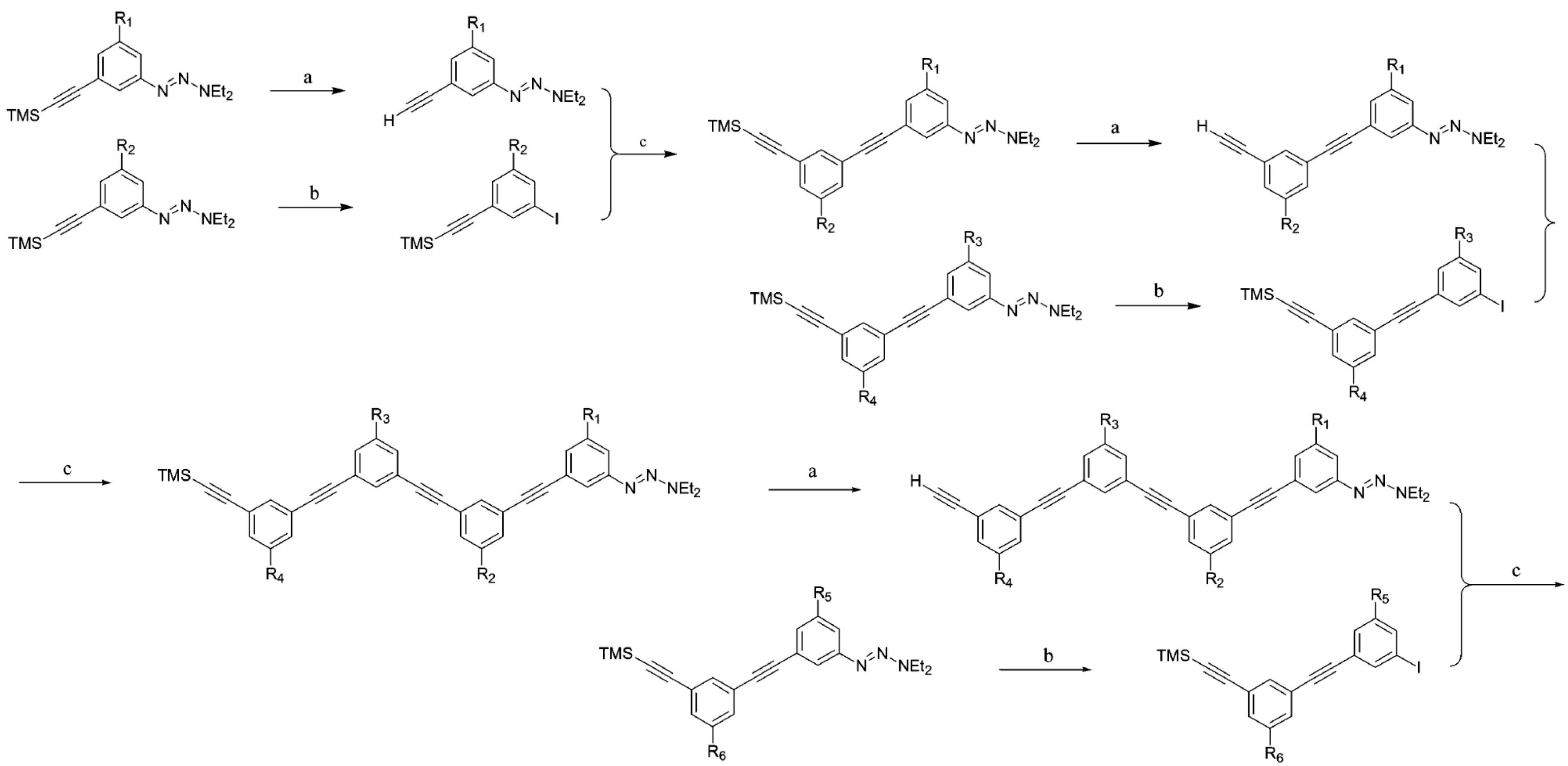


Allows for controlled, step-wise synthesis
of oligomers with precise structue

Moore, J. S.; *et al. Tett. Lett.* **1991**, 32, 2465

New Macromolecular Architectures

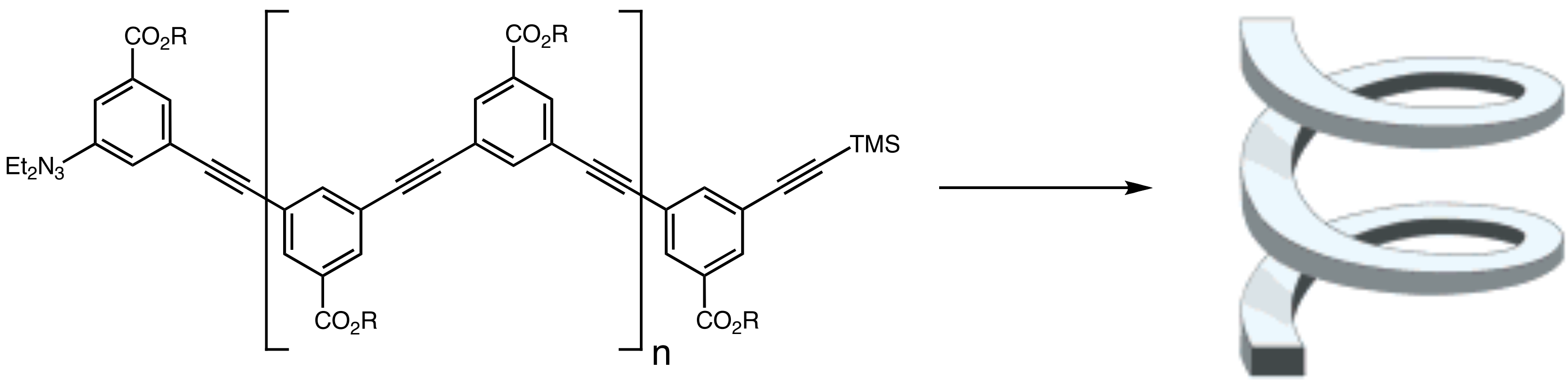
Synthesis of Arylene-Ethynylene Oligomers



Zhao, D.; Moore, J. S. *Chem. Comm.* **2003**, 807

New Macromolecular Architectures

Folding of Arylene-Ethynylene Oligomers into Helices

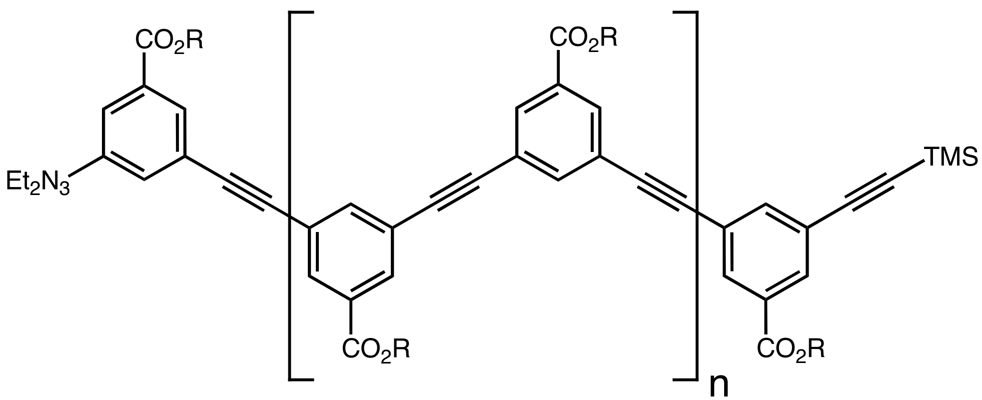


R=$(CH_2CH_2O)_3CH_3$

Nelson, J.; Saven, J.; Moore, J. S.; Wolynes, P. *Science* **1996**, 277, 1793

New Macromolecular Architectures

Folding of Arylene-Ethynylene Oligomers into Helices



$R=(CH_2CH_2O)_3CH_3$

Interested in generating secondary structure without hydrogen bonding to gauge solvophobic contributions

A step toward synthetic polymers with folded achitectures on par with biological macromolecules

Nelson, J.; Saven, J.; Moore, J. S.; Wolynes, P. *Science* **1996**, 277, 1793

New Macromolecular Architectures

Folding of Arylene-Ethynylene Oligomers into Helices

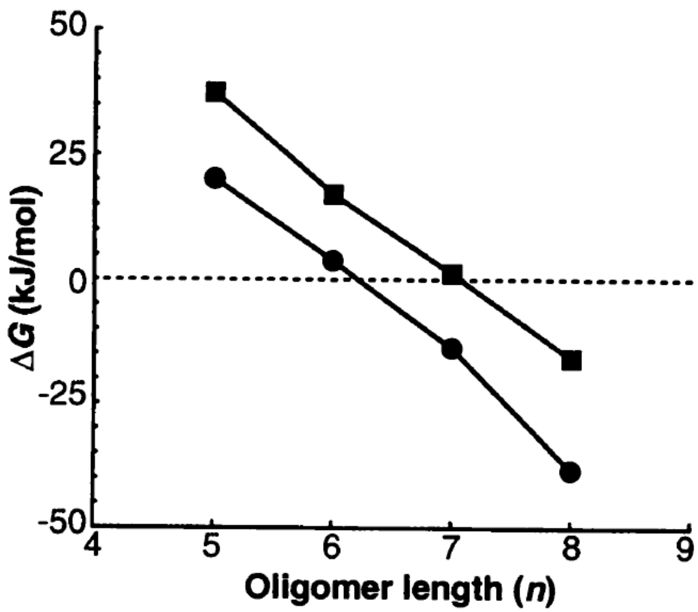


Fig. 2. Estimated free energy of helix formation Δ*G* versus chain length

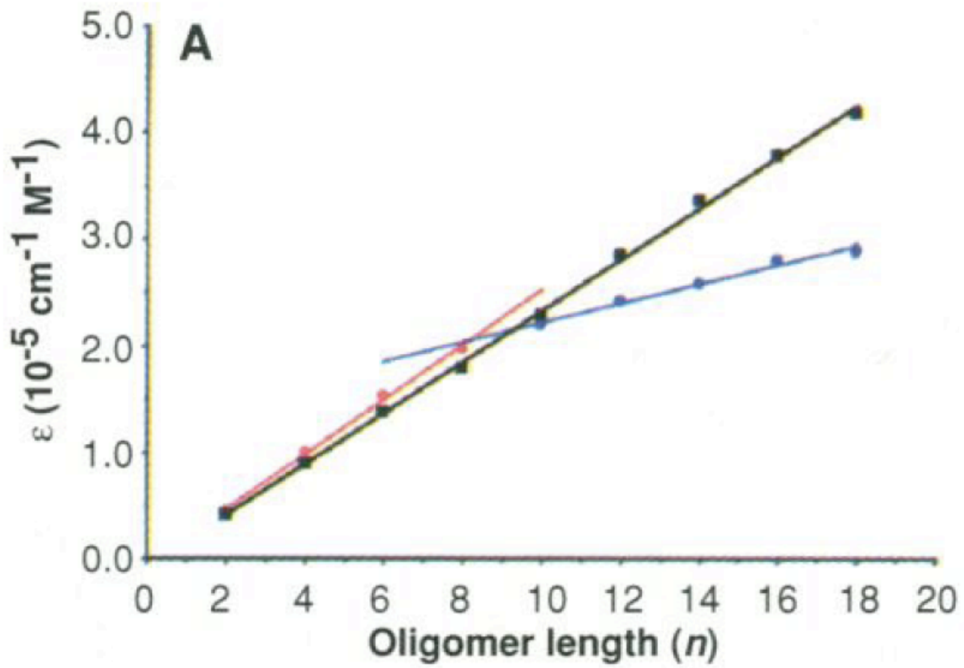
Computational studies predict stable helices are possible for oligomers of at least 8 units

Nelson, J.; Saven, J.; Moore, J. S.; Wolynes, P. *Science* **1996**, 277, 1793

New Macromolecular Architectures

Folding of Arylene-Ethynylene Oligomers into Helices

Fig. 3. (A) The molar extinction coefficient ε (303 nm) chloroform (black) and acetonitrile (red and blue)



Each oligomer's ε was measured over a concentration range to rule out intermolecular associations

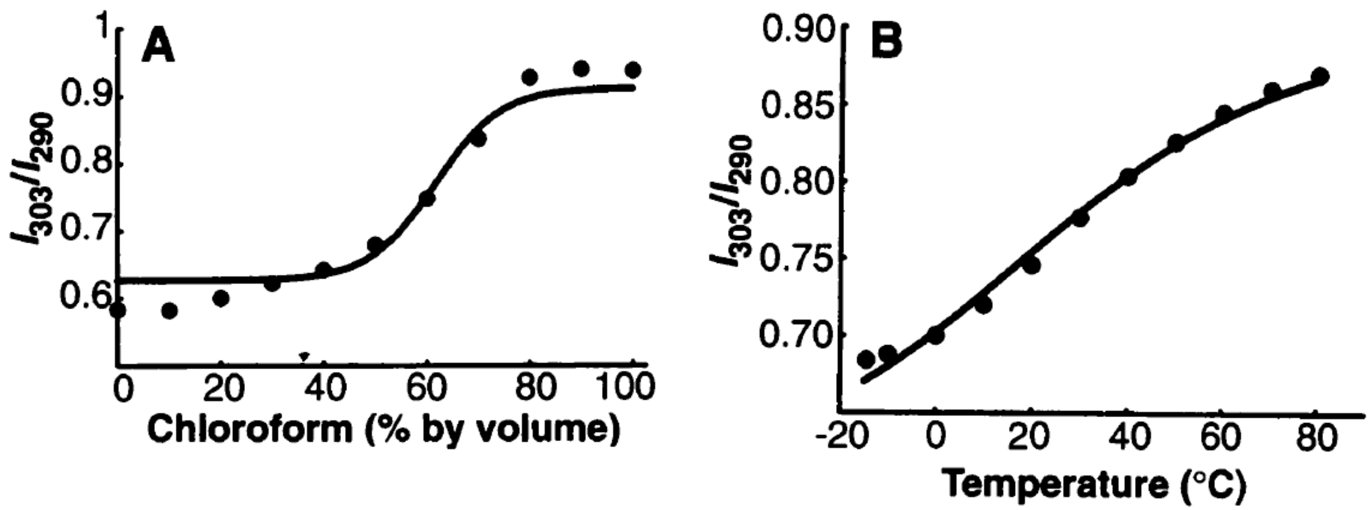
Beer-Lambert Law

$A = \varepsilon c l$

Nelson, J.; Saven, J.; Moore, J. S.; Wolynes, P. *Science* **1996**, 277, 1793

New Macromolecular Architectures

Folding of Arylene-Ethynylene Oligomers into Helices

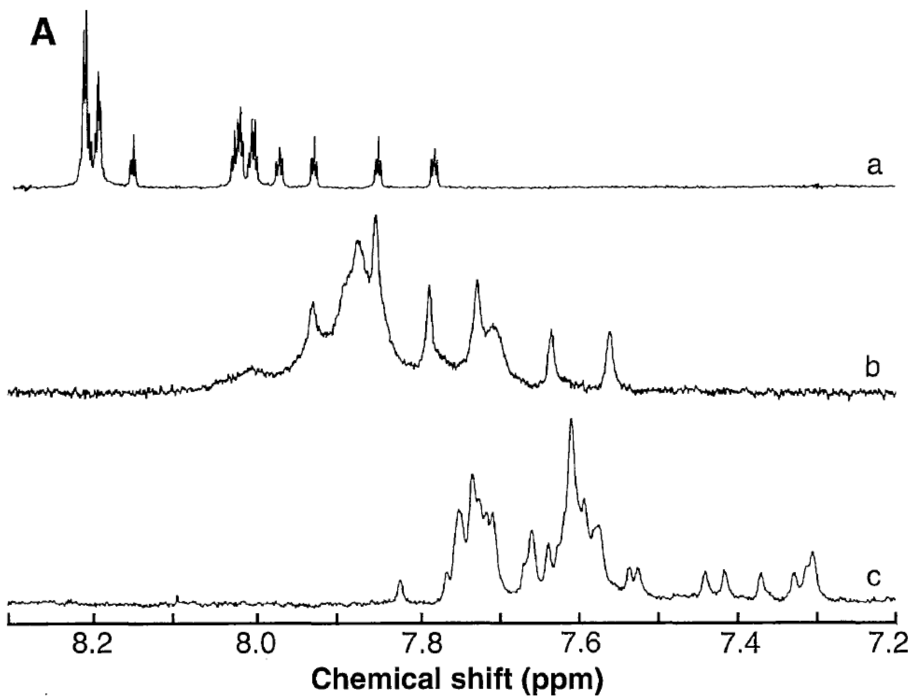


Both heat and chloroform denature the octadecimer helix

Nelson, J.; Saven, J.; Moore, J. S.; Wolynes, P. *Science* **1996**, 277, 1793

New Macromolecular Architectures

Folding of Arylene-Ethynylene Oligomers into Helices



Hexamer

Decimer

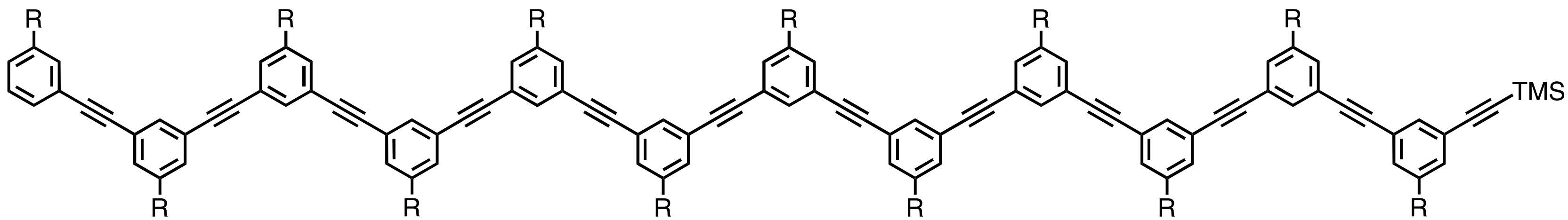
Octadecimer

^{1}H NMR in CD_3CN

Nelson, J.; Saven, J.; Moore, J. S.; Wolynes, P. *Science* **1996**, 277, 1793

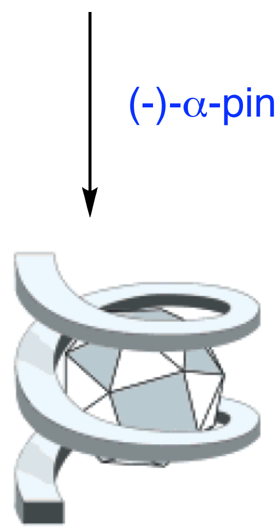
New Macromolecular Architectures

Foldamer-Based Molecular Recognition



1, R = $CO_2(CH_2CH_2O)_3CH_3$

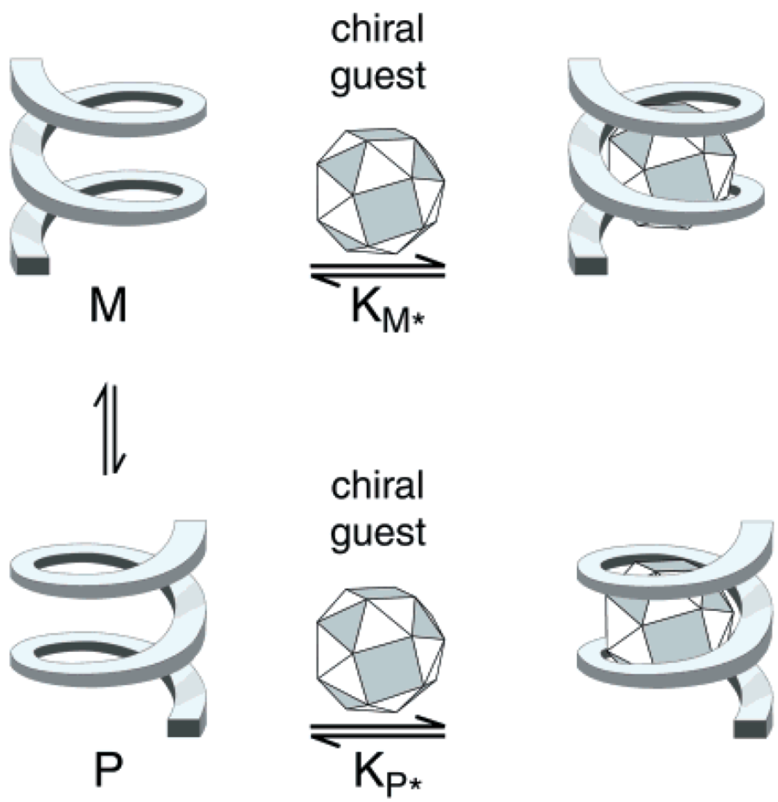
(-)-α-pinene



Prince, R.; Barnes, S.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, 122, 2758

New Macromolecular Architectures

Foldamer-Based Molecular Recognition



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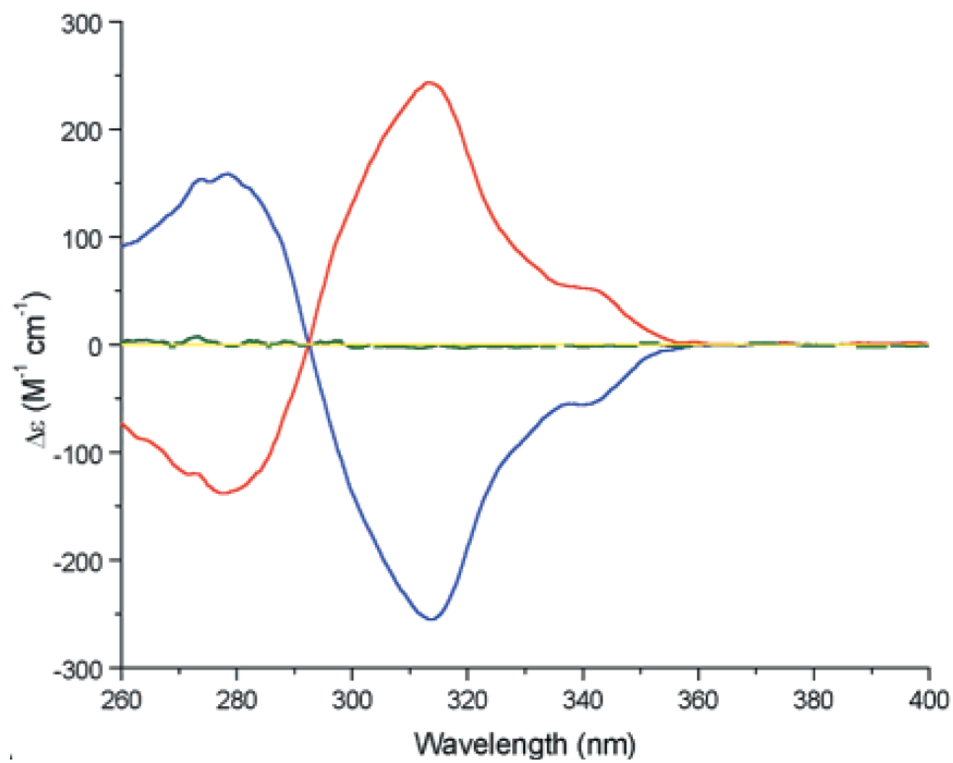
New Macromolecular Architectures

Foldamer-Based Molecular Recognition

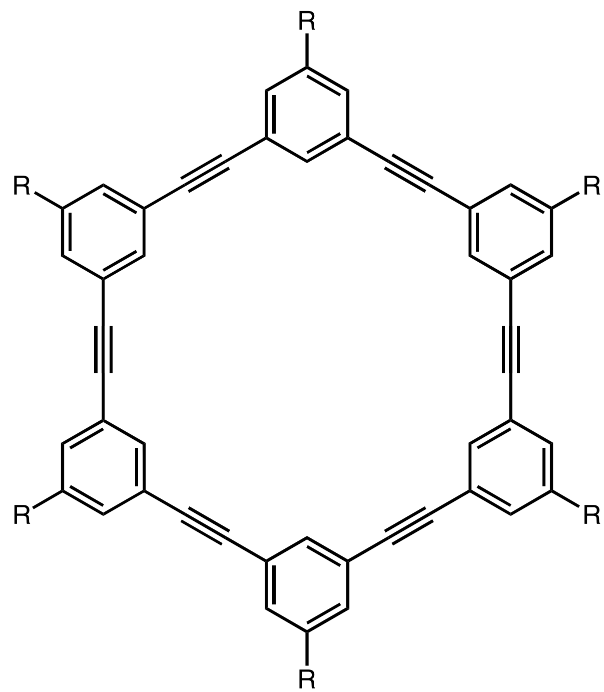


CD spectra. (−)-α-Pinene (yellow line, 420 μM), oligomer **1** (green line) in the presence of 100 equiv of (−)-α- pinene (blue line) and 100 equiv of (+)-α-pinene (red line).

Prince, R.; Barnes, S.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, 122, 2758

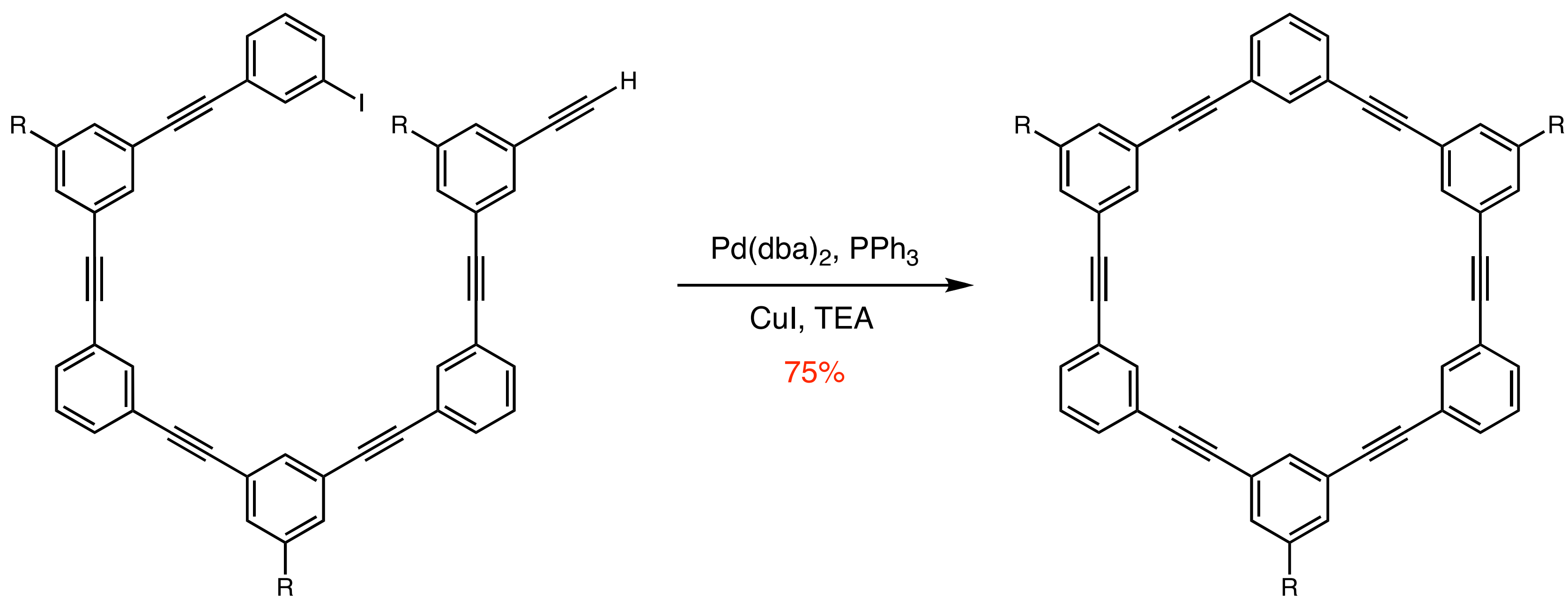
New Macromolecular Architectures

Shape-Persistent Macrocycles



New Macromolecular Architectures

Synthesis of Shape-Persistent Macrocycles

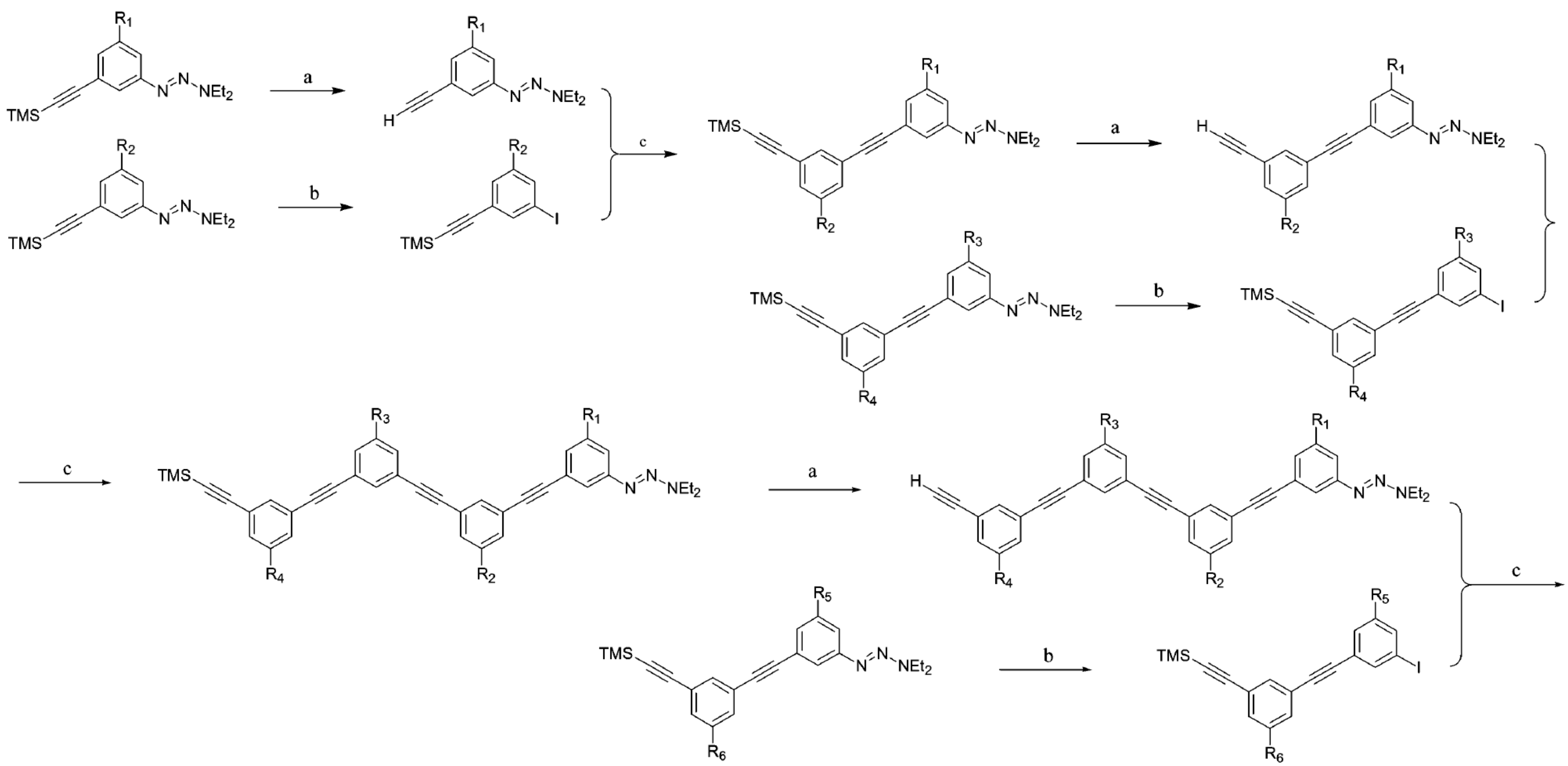


syringe-pump addition

1. Zhang, J.; Moore, J. S. *ACIEE.*, **1992**, 31, 922-923
2. Zhao, D.; Moore, J. S. *Chem. Comm.*, **2003**, 807-818

New Macromolecular Architectures

Synthesis of Shape-Persistent Macrocycles

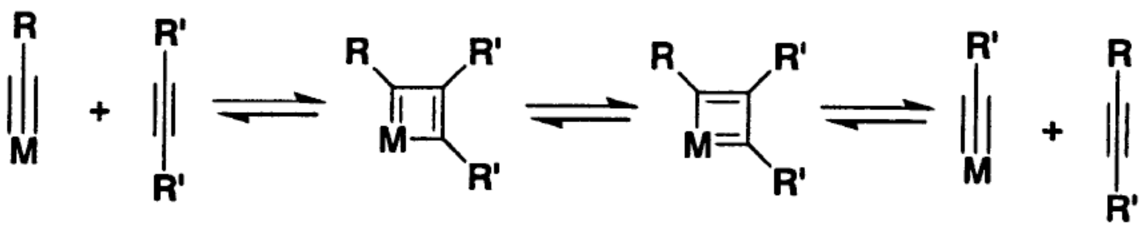


1. Zhang, W.; Moore, J. S. *ACIEE.*, **2006**, 45, 4416-4439
2. Zhao, D.; Moore, J. S. *Chem. Comm.*, **2003**, 807-818

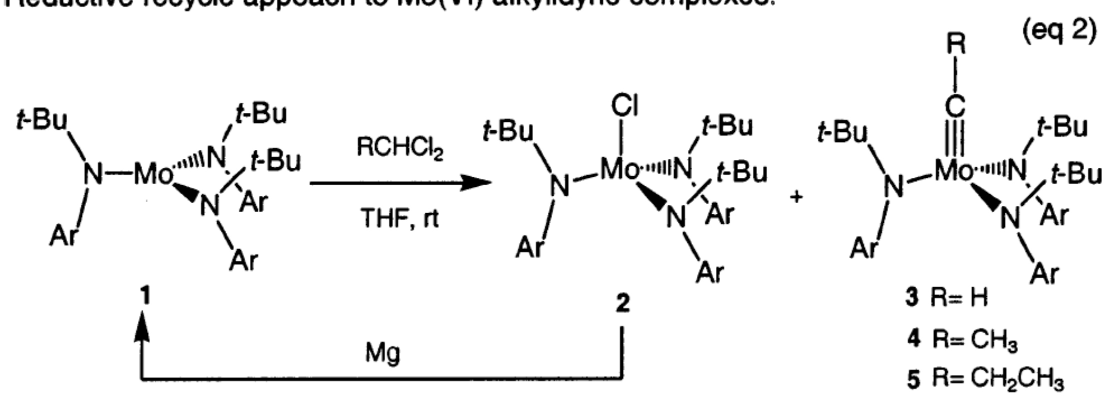
New Macromolecular Architectures

Synthesis of Shape-Persistent Macrocycles

Alkylidyne Mechanism of Alkyne Metathesis



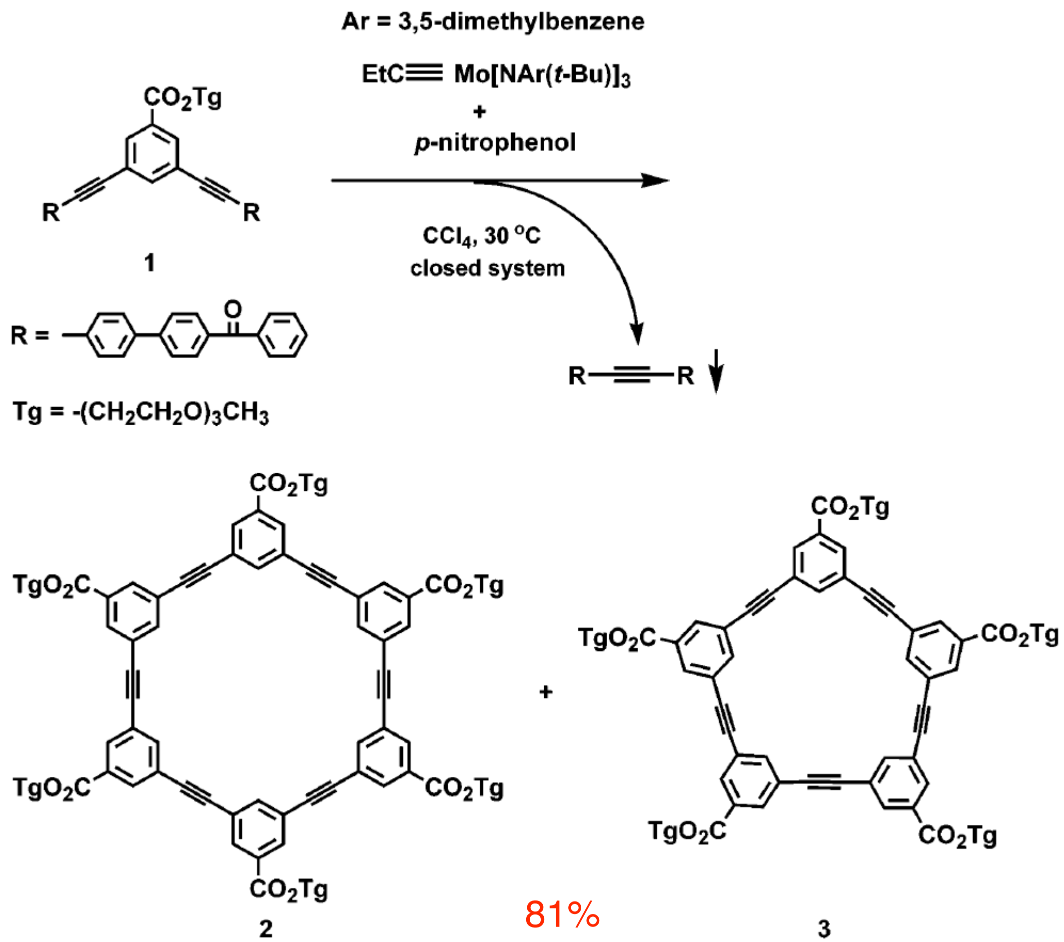
Reductive recycle appoach to Mo(VI) alkylidyne complexes.



Zhang, W.; Kraft, S.; Moore, J. S. *J. Am. Chem. Soc.*, **2004**, 126, 329

New Macromolecular Architectures

Synthesis of Shape-Persistent Macrocycles

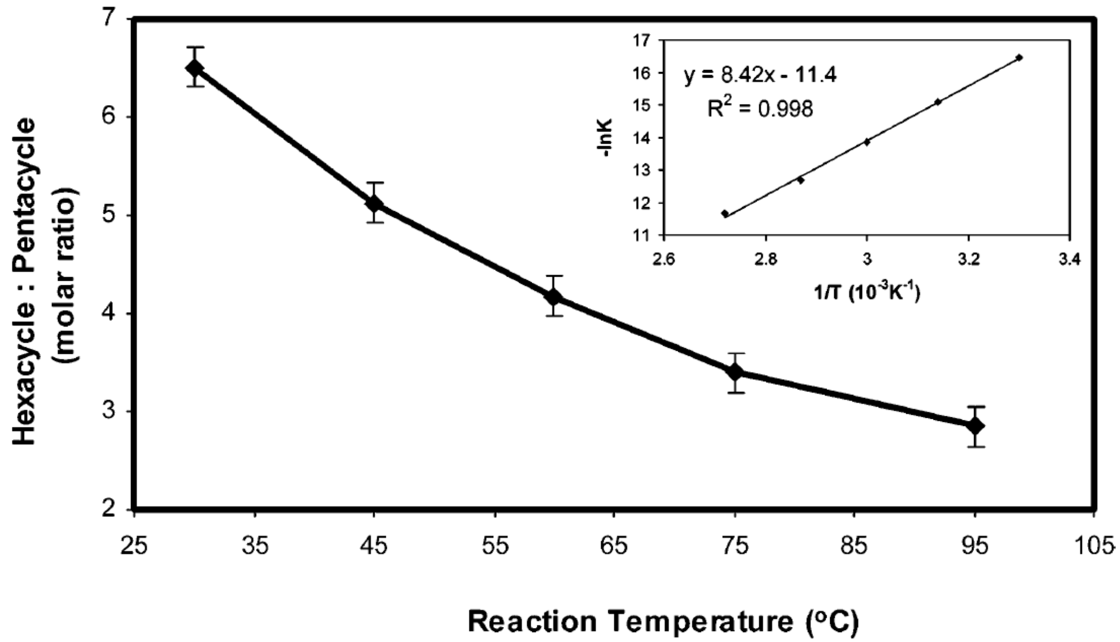


81%

Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2005**, 127, 11863-11867

New Macromolecular Architectures

Synthesis of Shape-Persistent Macrocycles

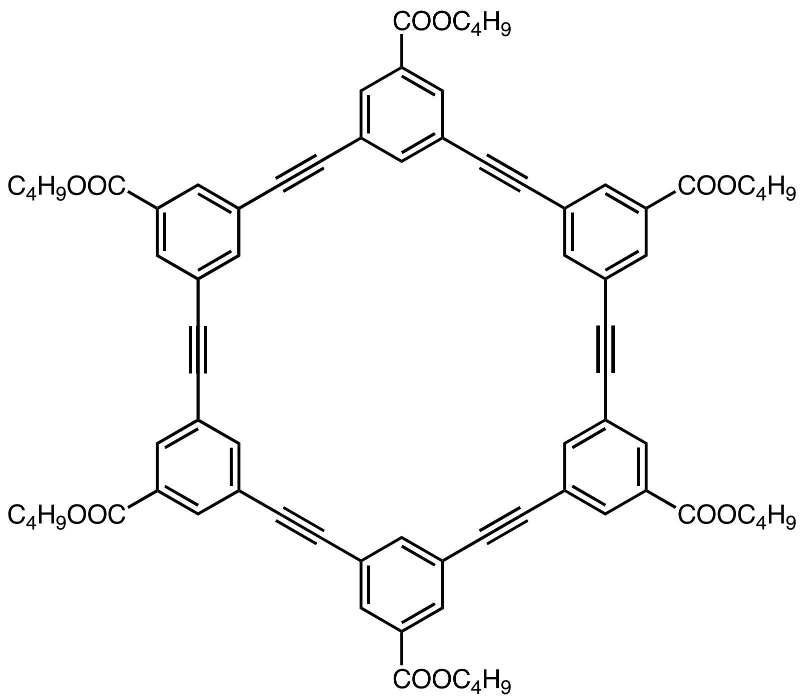


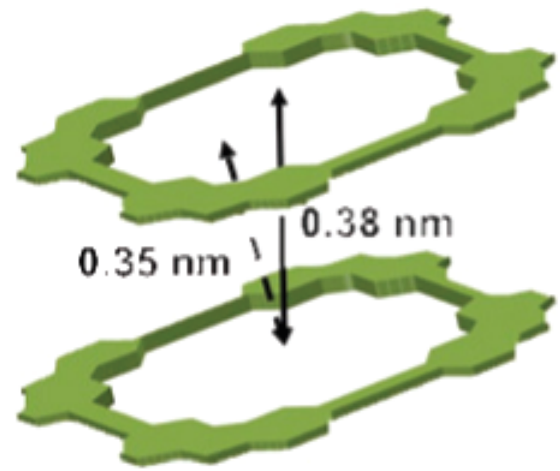
The pentamer is entropically favored despite its higher ring strain and is a larger component of the equilibrium at higher temperatures. ie $\Delta G = \Delta H - T\Delta S$

Zhang, W.; Moore, J. S. *J. Am. Chem. Soc.* **2005**, 127, 11863-11867

New Macromolecular Architectures

Supramolecular Organization of Arylene-Ethynylene Macrocycles

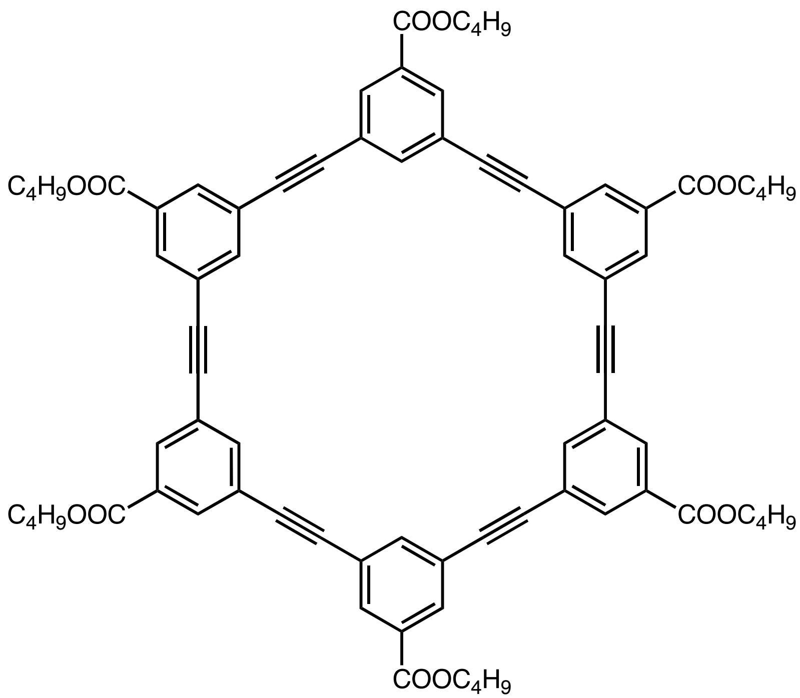


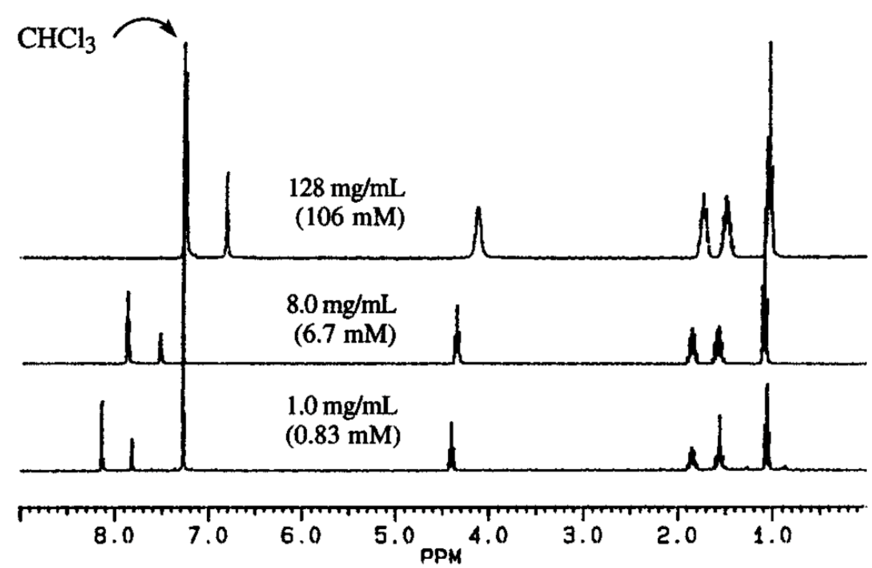


1. Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1992**, 114, 9701-9702
2. Shetty, S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, 118, 1019

New Macromolecular Architectures

Supramolecular Organization of Arylene-Ethynylene Macrocycles





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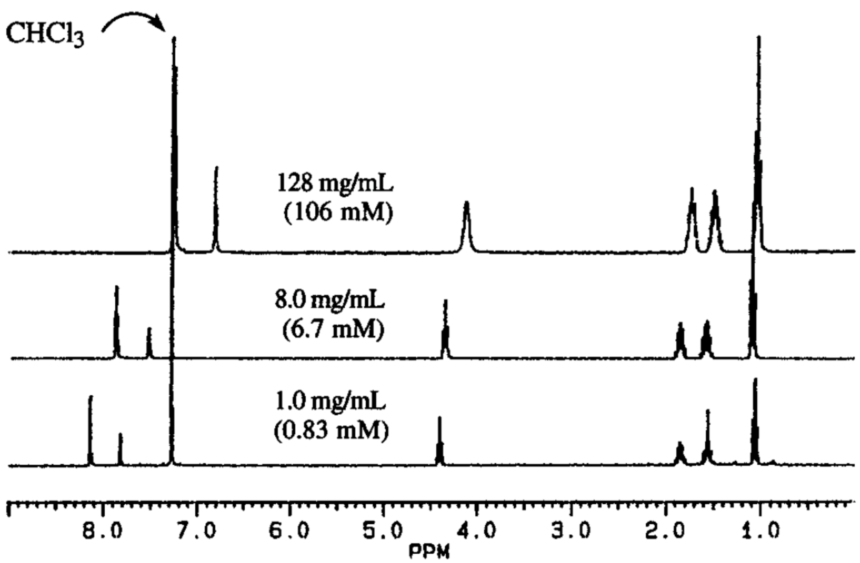

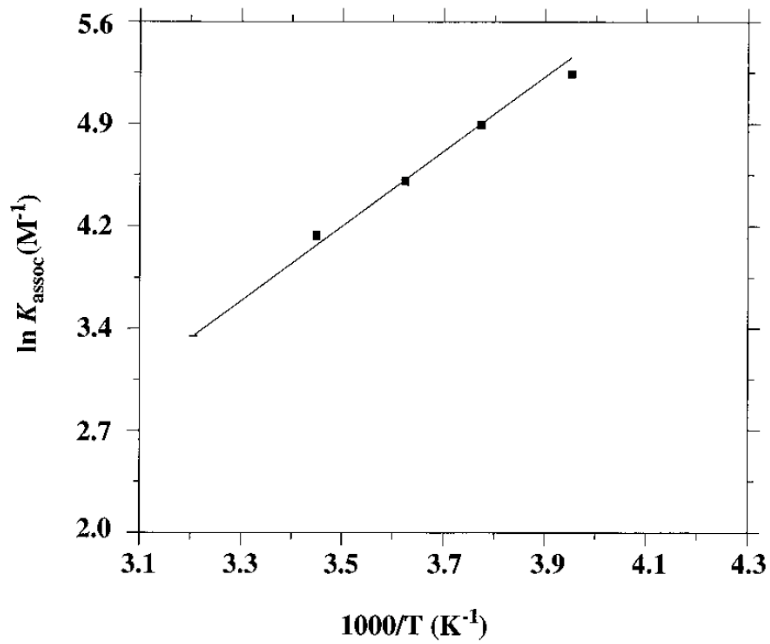

van't Hoff plots of self-association constants (K_{assoc})

$$\ln K = -\Delta H/T + \Delta S/R$$

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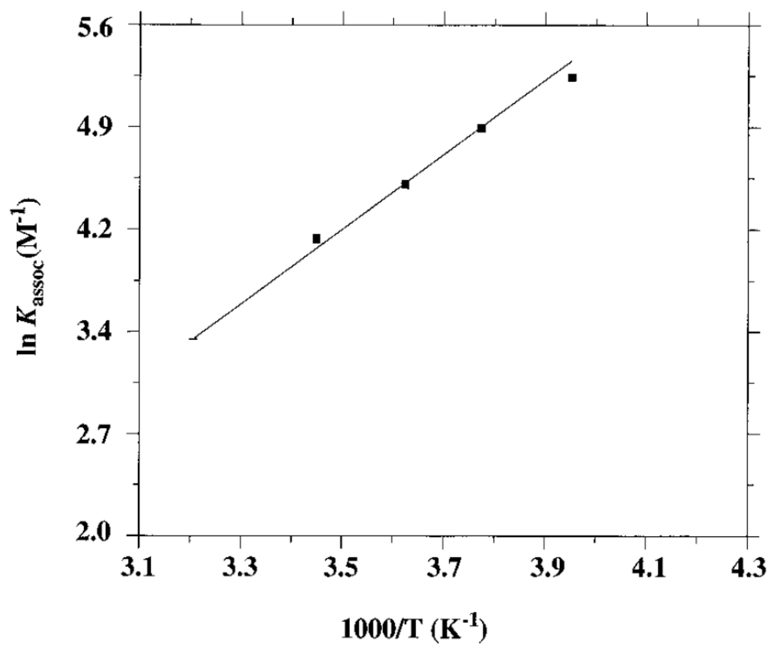
New Macromolecular Architectures

Supramolecular Organization of Arylene-Ethynylene Macrocycles

Thermodynamic Data for Self-Association

K_{assoc} (M^{-1}) [a]	ΔG (kcal/mol)[a]	ΔH (kcal/mol)	ΔS (cal/mol·K)
60	−2.4	−5.0 ± 0.2	−9.2 ± 0.8

Assuming that dimerization is the only significant aggregation state (confirmed by VPO).



van't Hoff plots of self-association constants (K_{assoc})

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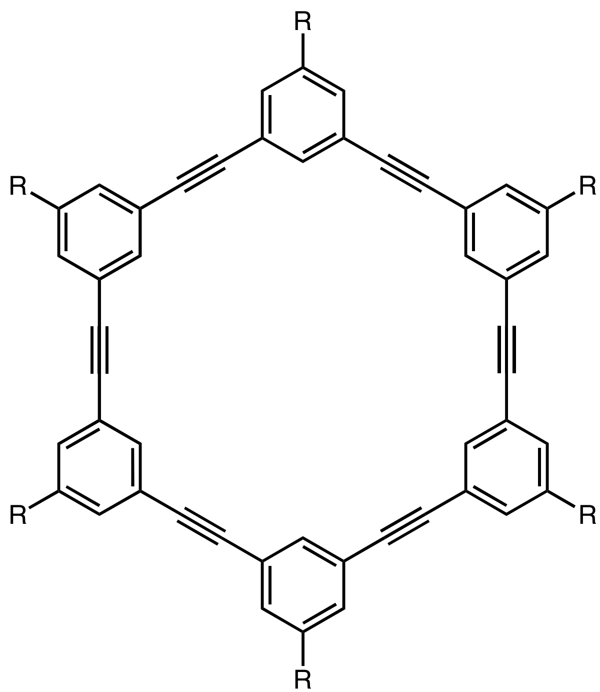
New Macromolecular Architectures

π–Stacking Studies



A model system for studying π–πinteractions

Stacking results in minimal entropic penalty and large enthalpic gain

π–π interactions should be amplified

1. Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1992**, 114, 9701-9702
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New Macromolecular Architectures

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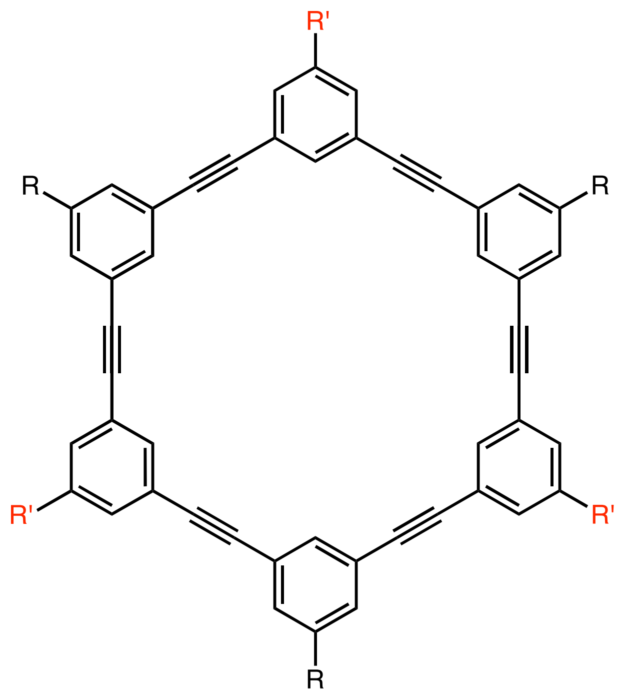

1 R=R'=$CO_2C_4H_9$

2 R=R'=OC_4H_9

3 R=OC_4H_9, R'= $CO_2C_4H_9$

cmpd	K_{assoc} (M^{-1})	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)
1	60	–2.4	–5.0	–9.2
2	0	---	---	---
3	18	–1.7	–5.1	–13.6

1. Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1992**, 114, 9701-9702
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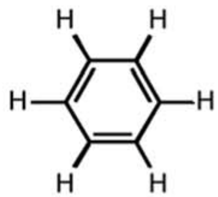
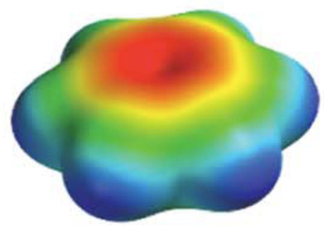
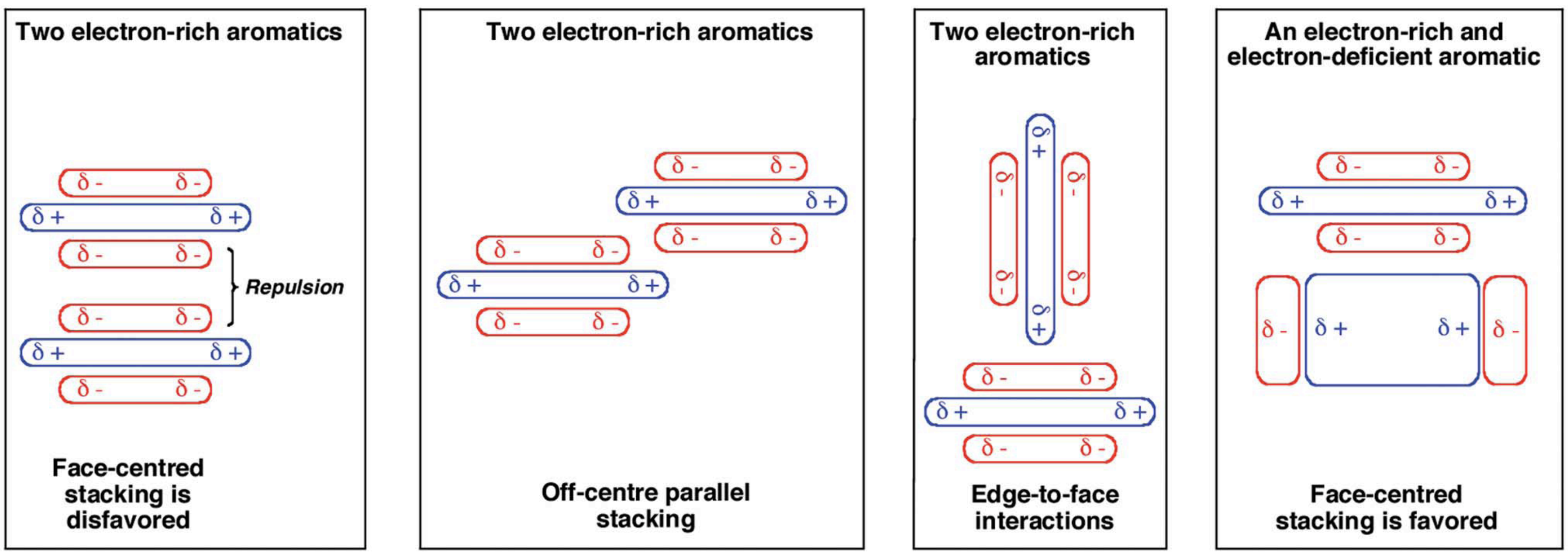
New Macromolecular Architectures

π–Stacking Studies



Benzene

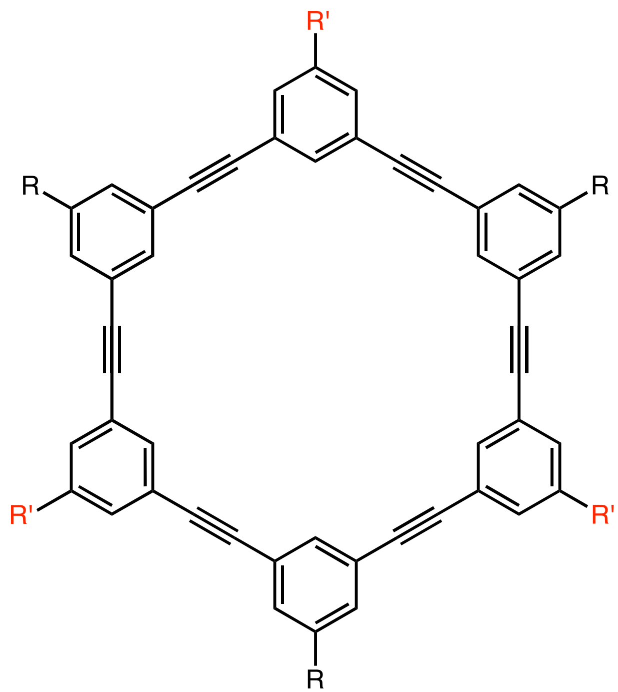




Martinez, C.; Iverson, B. *Chem. Sci.* **2012**, 3, 2191-2201

New Macromolecular Architectures

π–Stacking Studies



1 R=R'=$CO_2C_4H_9$

2 R=R'=OC_4H_9

3 R=OC_4H_9, R'= $CO_2C_4H_9$

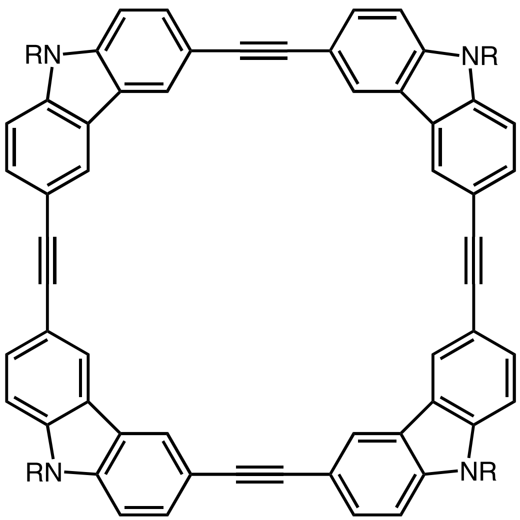
cmpd	K_{assoc} (M^{-1})	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol)
1	60	–2.4	–5.0	–9.2
2	0	---	---	---
3	18	–1.7	–5.1	–13.6

Face-centered stacking is positively affected by van der Waals interactions and negatively affected by quadrupole moment.

1. Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1992**, 114, 9701-9702
2. Shetty, S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, 118, 1019

New Macromolecular Architectures

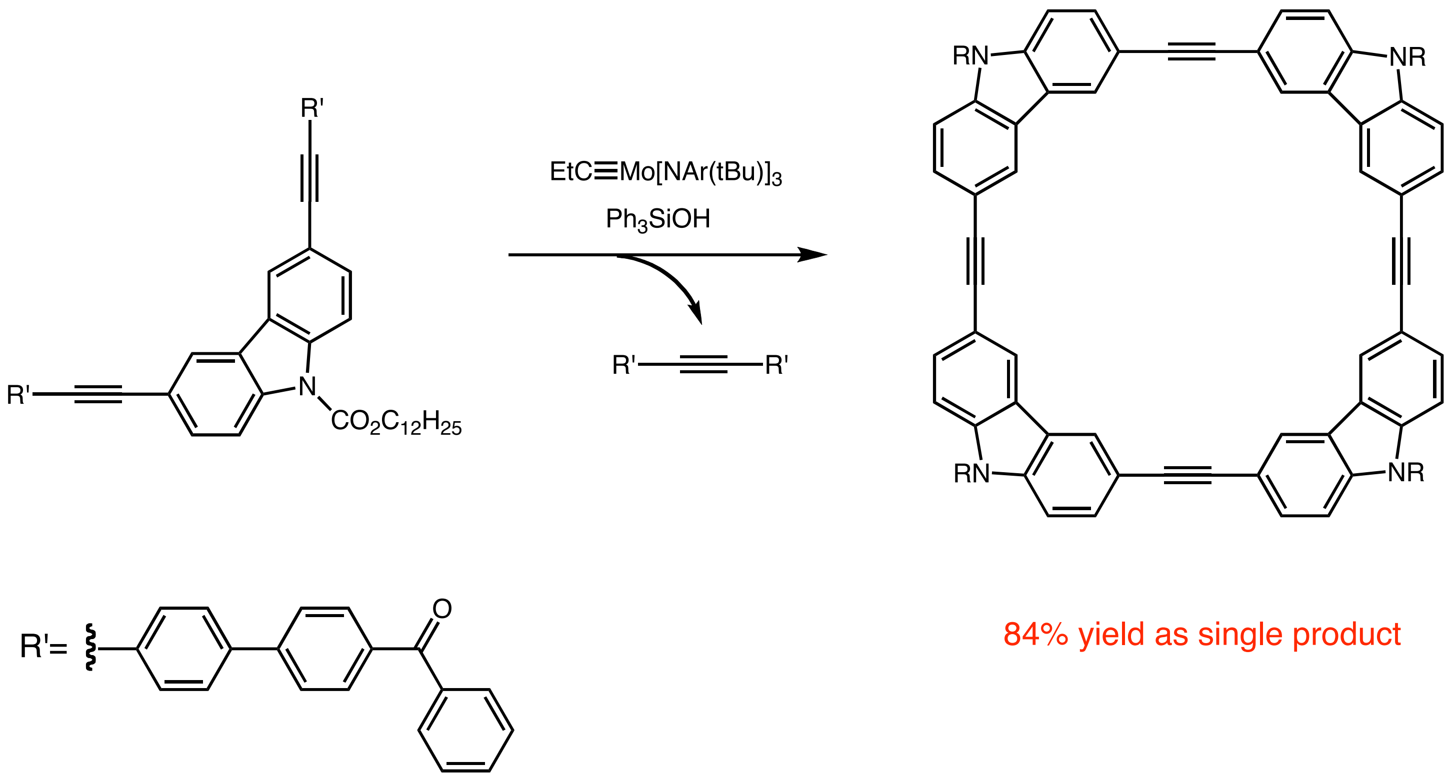
Detection of Explosives with a Nanofibril Film



Moore's group has utilized the supramoleular organization of related carbzole-macrocylces to design materials capable of detecting explosives

New Macromolecular Architectures

Detection of Explosives with a Nanofibril Film



84% yield as single product

Zhang, W. Moore, J. S. *ACIEE* **2006**, 45, 4416-4439

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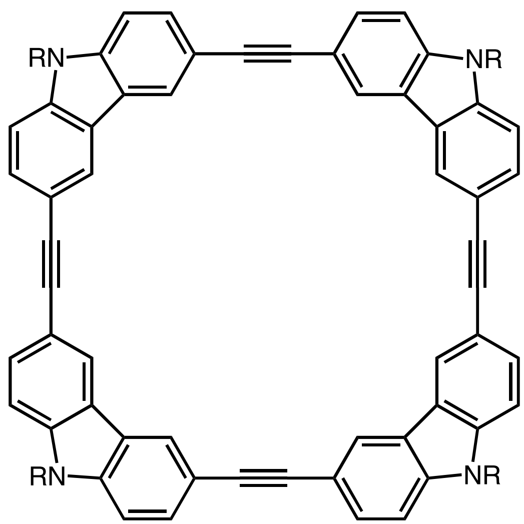
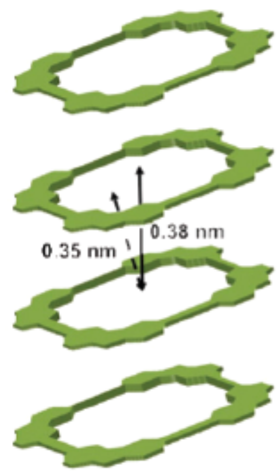
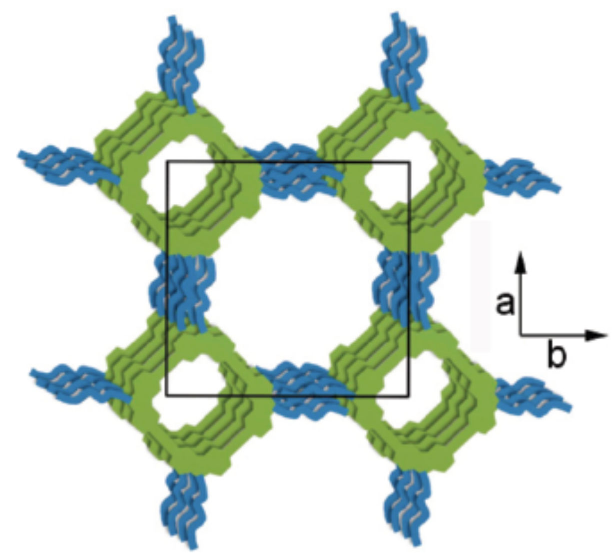




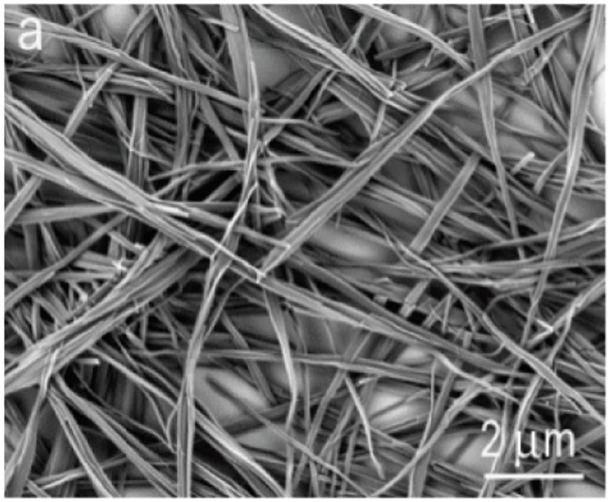


π–π stacking causes the carbazole-based tetracycles to assemble into 1D nanofibrils

1.Naddo, T. *et al. J. Am. Chem. Soc.*, **2007**, 129, 6978-6979.
2. Che, Y. *et al. J. Am. Chem. Soc.*, **2012**, 134-4978.

New Macromolecular Architectures

Detection of Explosives with a Nanofibril Film



SEM image of porous nanofibers generated from piling the fibers by spin-casting

1.Naddo, T. *et al. J. Am. Chem. Soc.*, **2007**, 129, 6978-6979.
2. Che, Y. *et al. J. Am. Chem. Soc.*, **2012**, 134-4978.

New Macromolecular Architectures

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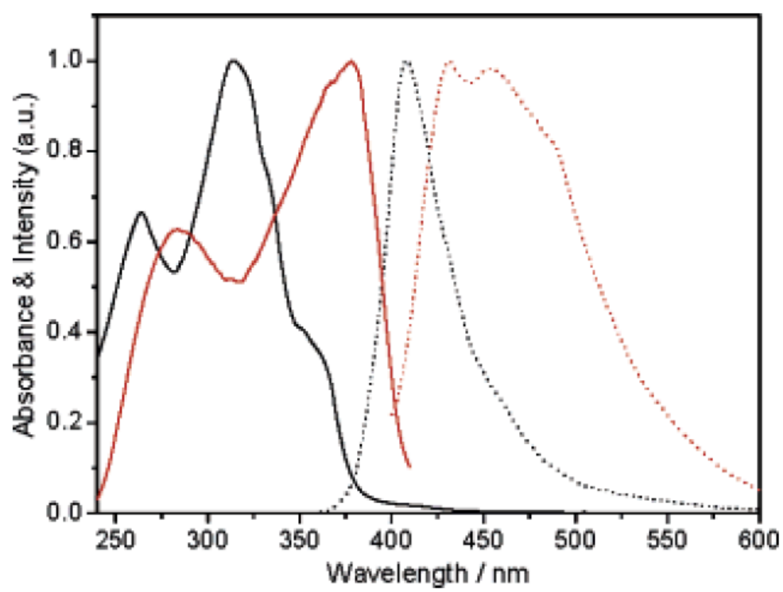

Absorption (solid) and fluorescence (dotted) spectra
solution (black) and dried gel (red)

π–π stacking results in intermolecular electronic coupling as evinced by perturbation of the absorbtion and florescence spectra

The supramolecular assembly behaves somewhat like one large conjugated molecule

Balakrishnan, K. *et al. J. Am. Chem. Soc.*, **2006**, 128, 6576.

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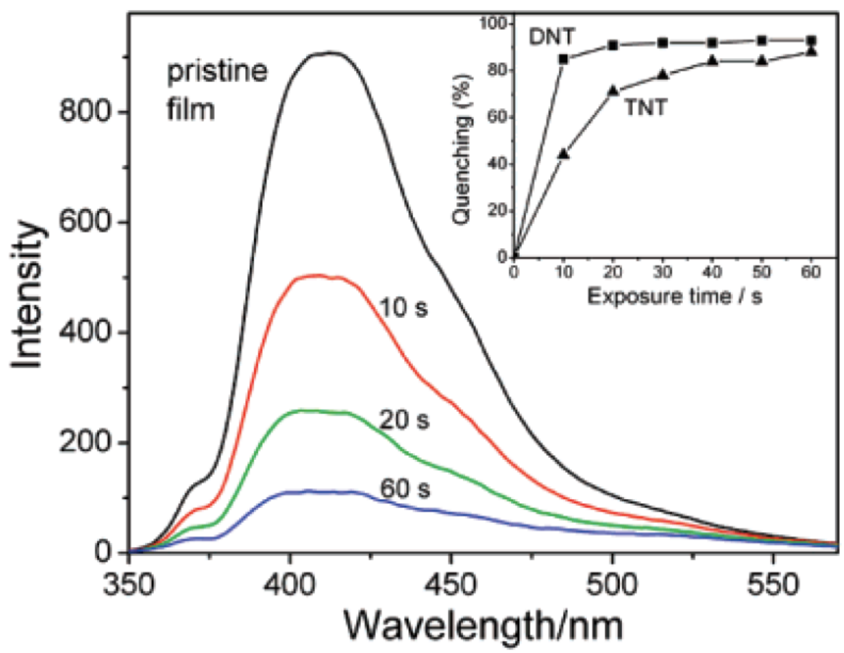

Fluorescence spectra of a 90 nm thick ACTC film upon exposure vapor of TNT (5 ppb) at different times.

1.Naddo, T. *et al. J. Am. Chem. Soc.*, **2007**, 129, 6978-6979.
2. Che, Y. *et al. J. Am. Chem. Soc.*, **2012**, 134-4978.

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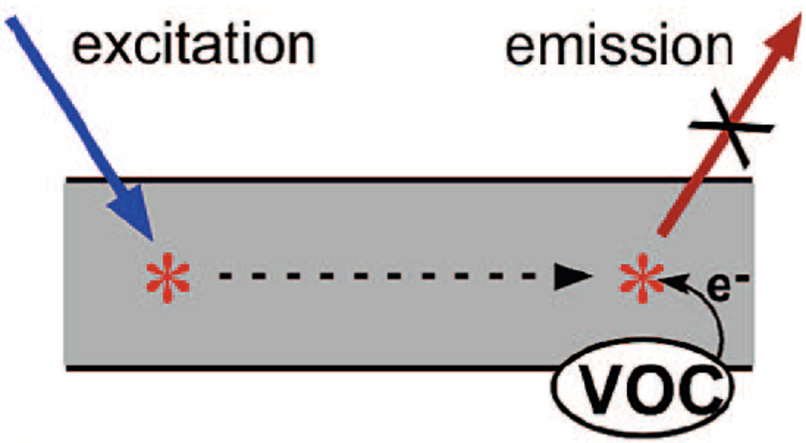

π–π stacking is favorable for long range exciton migration

Fluorescent emmission λ is significantly higher than TNT's absorbtion λ, which precludes quenching by energy transfer

Fluorescence quenching is due to photoinduced electron transfer from the fibril to TNT

1.Naddo, T. *et al. J. Am. Chem. Soc.*, **2007**, 129, 6978-6979.
2. Zhang, L. *et al. Accounts Chem. Res.*, **2008**, 41, 1596.

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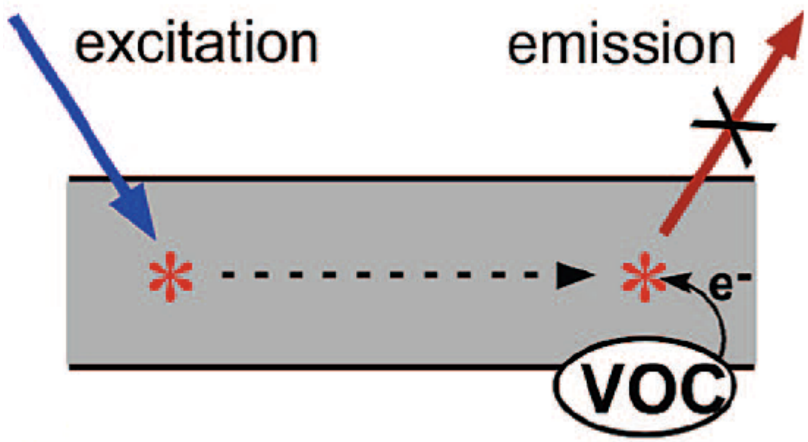

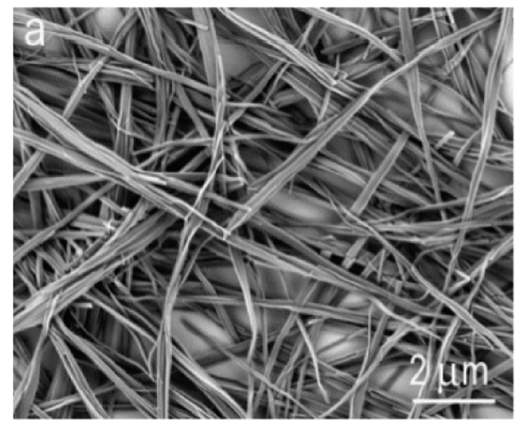

Nanofibers assembled via π–π interactions have high quenching efficiency by both enabling long range exciton migration and diffusion of gaseous TNT

1.Naddo, T. *et al. J. Am. Chem. Soc.*, **2007**, 129, 6978-6979.
2. Zhang, L. *et al. Accounts Chem. Res.*, **2008**, 41, 1596.

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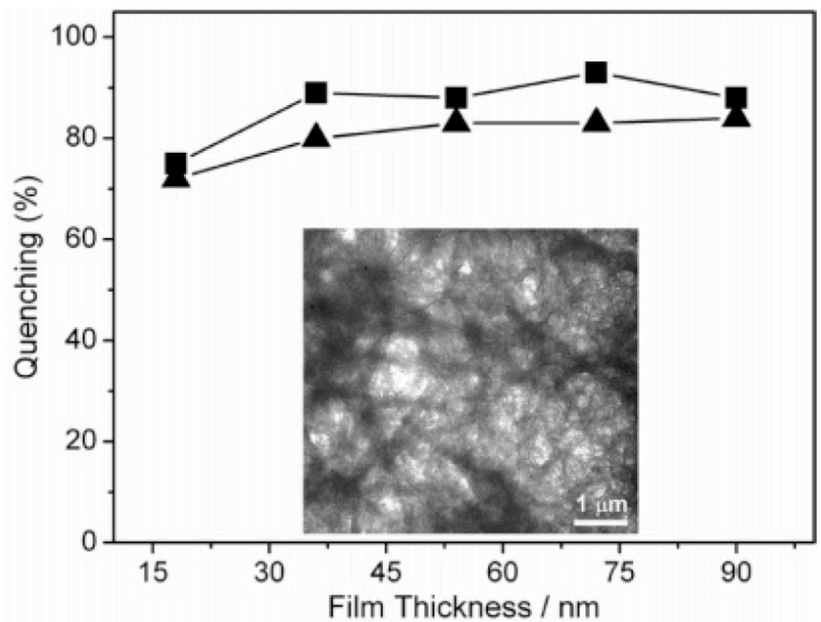

The efficiency of the fluorescence quenching is largely independent of the thickness of the film, a useful property not seen in most thin films

1.Naddo, T. *et al. J. Am. Chem. Soc.*, **2007**, 129, 6978-6979.
2. Zhang, L. *et al. Accounts Chem. Res.*, **2008**, 41, 1596.

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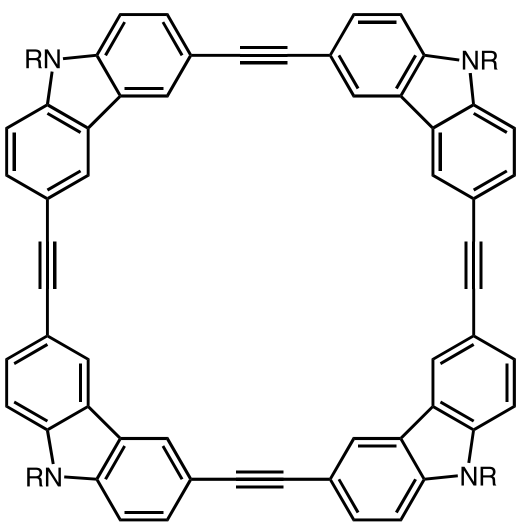
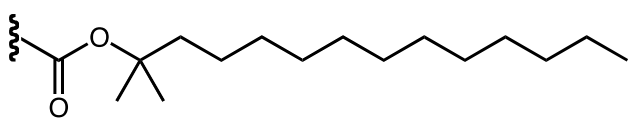


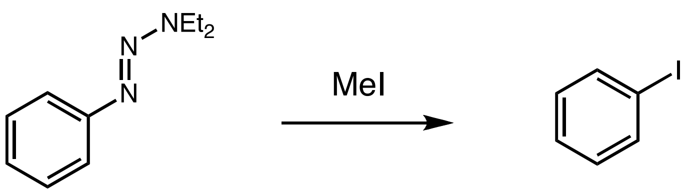
Can selectively detect TNT over other nitroaromatics at a vapor pressure of 20 parts per trillion

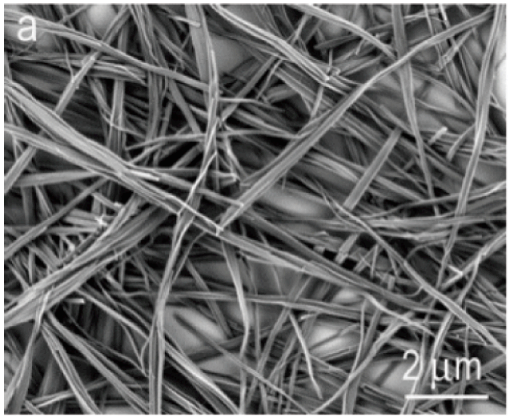
R= 

Che, Y. *et al. J. Am. Chem. Soc.*, **2012**, 134-4978.

Conclusion

A Twenty-One Year Progression





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2012