

# Literature Report

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# Tricomponent Supramolecular Multiblock Copolymers with Tunable Composition via Sequential Seeded Growth

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## Research Background

- **1999:** Undergraduate Researcher in the group of Dr. A. Ajayaghosh Photosciences and Photonics Unit, Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology, NIST (CSIR) (formerly RRL), Trivandrum, India
- **March 2003 – May 2003:** Guest Researcher in the group of **Prof. Dr. E. W. (Bert) Meijer** Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, The Netherlands
- **2000-2004:** Ph.D. Researcher in the group of Dr. A. Ajayaghosh Photosciences and Photonics Unit, Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology, NIST (CSIR) (formerly RRL), Trivandrum, India
- **December 2004 – June 2008:** Post Doctoral Associate in the group of **Prof. Dr. E. W. (Bert) Meijer** and Dr. Albert Schenning Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, The Netherlands
- **August 2008-June 2014:** Faculty Fellow, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, India
- **2014-2020:** Associate Professor, New Chemistry Unit, JNCASR, Bangalore, India
- **2020-present:** Full Professor, New Chemistry Unit, JNCASR, Bangalore, India
- **2020- present:** Chair, New Chemistry Unit (NCU), JNCASR.

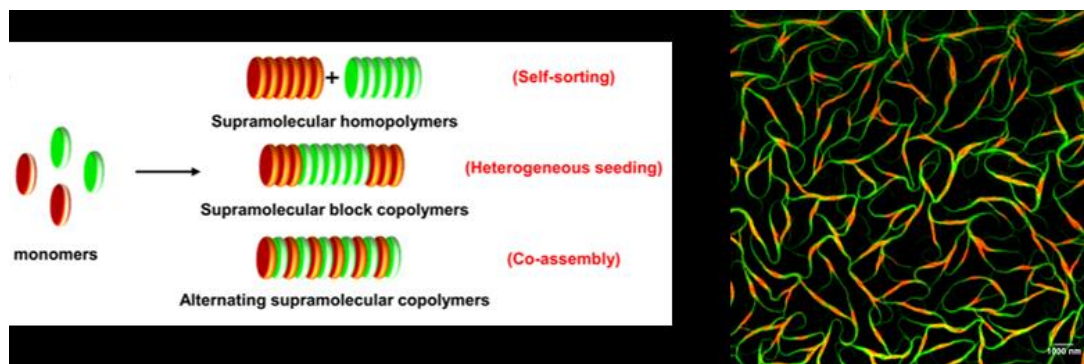
# Literature Source



## Research Area

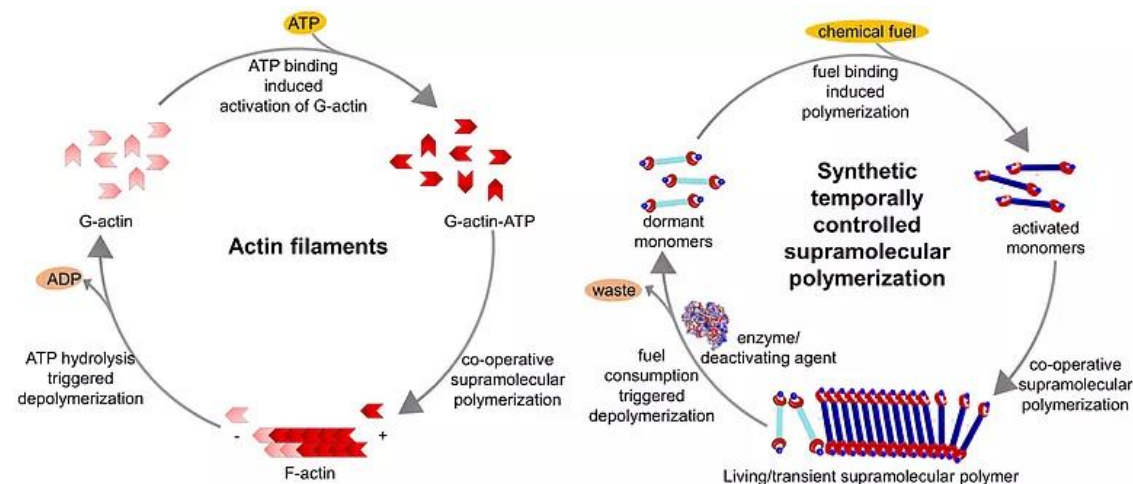
- Supramolecular Chemistry and Organic Materials
- Supramolecular Polymers
- Organic Phosphors
- Circularly Polarized Luminescent (CPL) materials

### Multicomponent Supramolecular Polymerization



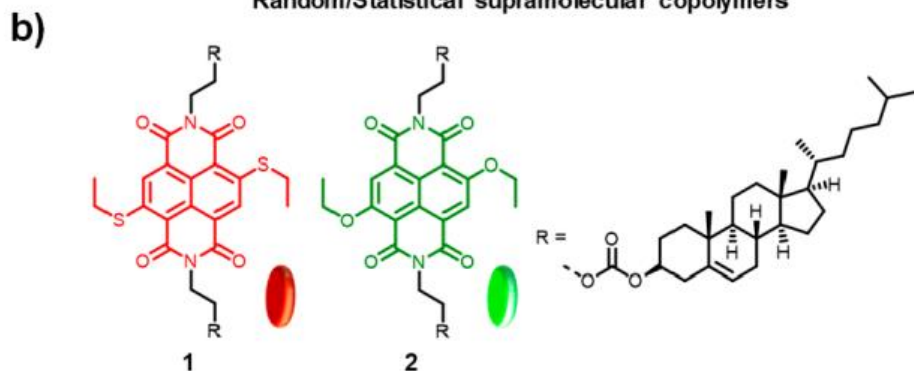
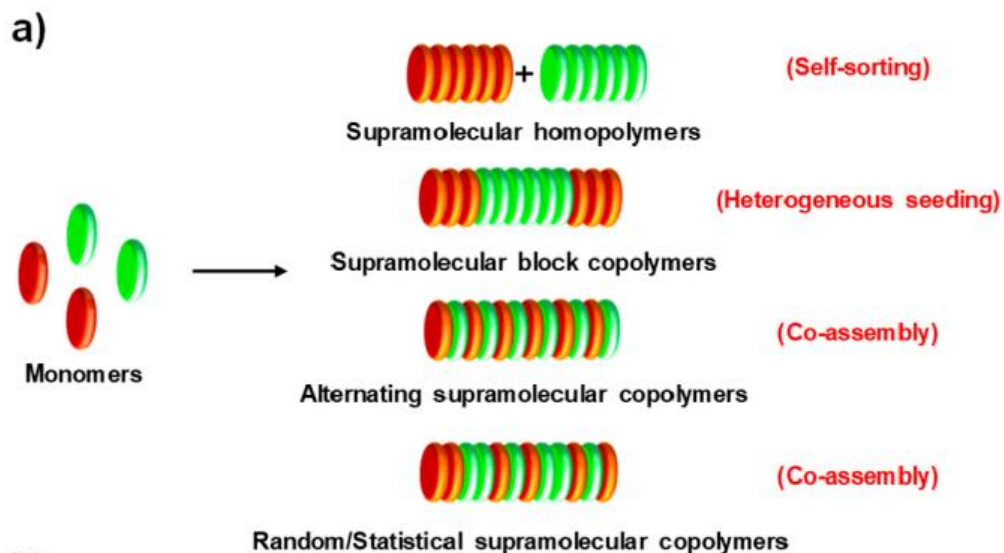
*J. Am. Chem. Soc.* **2020**, *142*, 7606-7617.

### Bioinspired Fuel-driven Living and Transient Supramolecular Polymerization

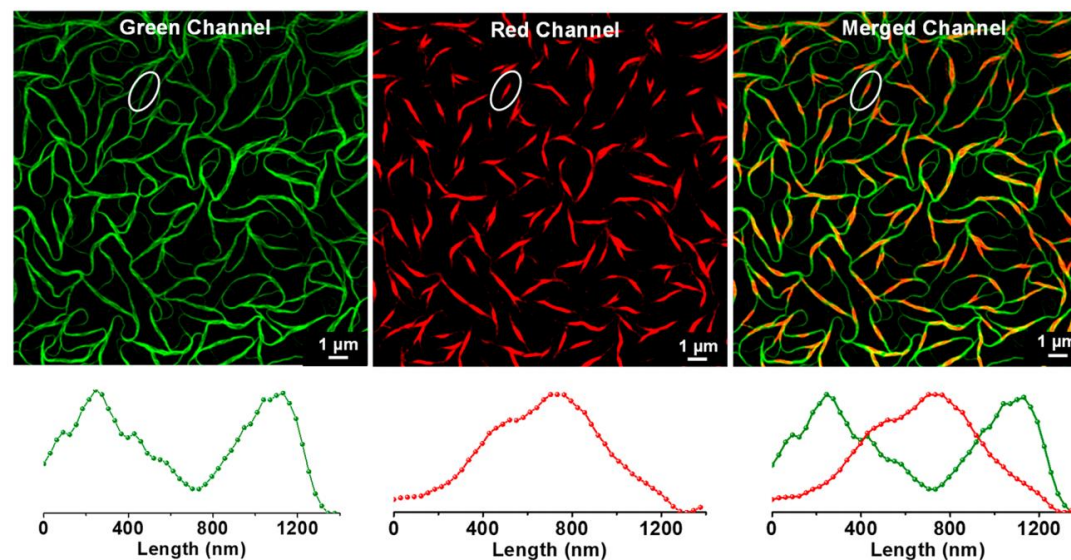
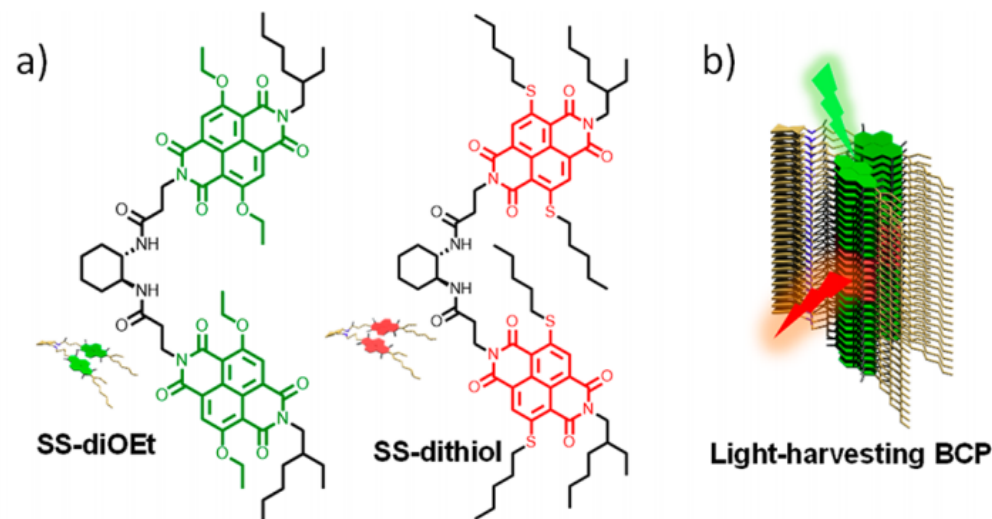


*Nat. Commun.* **2018**, *9*, 1295; *Nat. Commun.* **2014**, *5*, 5793.

# Introduction



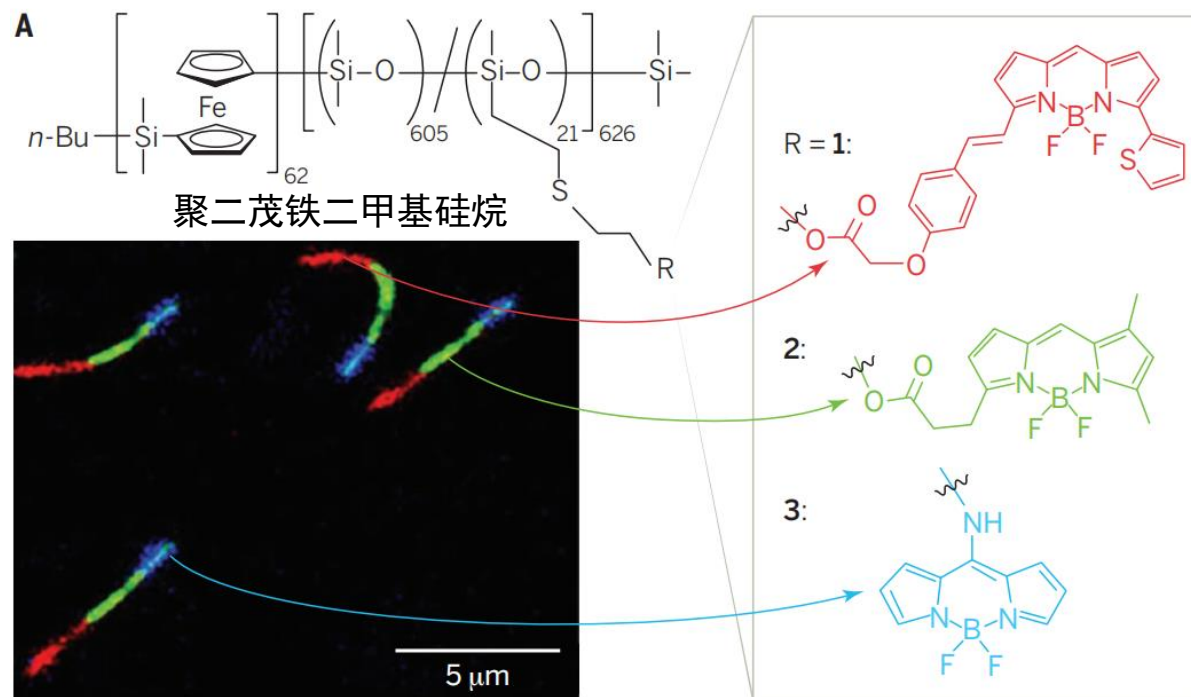
通过序列控制、多组分自组装得到的自分类、嵌段和随机超分子共聚物



合成功能性轴向有机异质结构的协同超分子嵌段共聚物

# Comparison

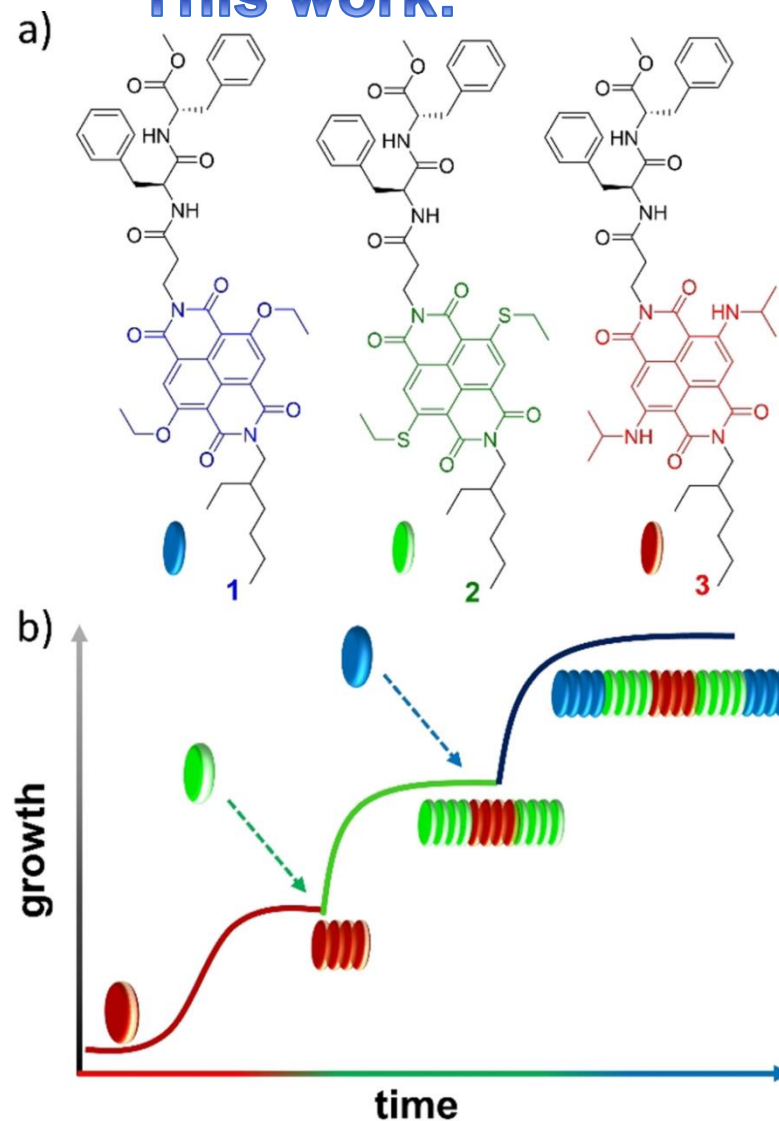
## Previous pioneering work:



### Crystallization-driven self-assembly (CDSA)

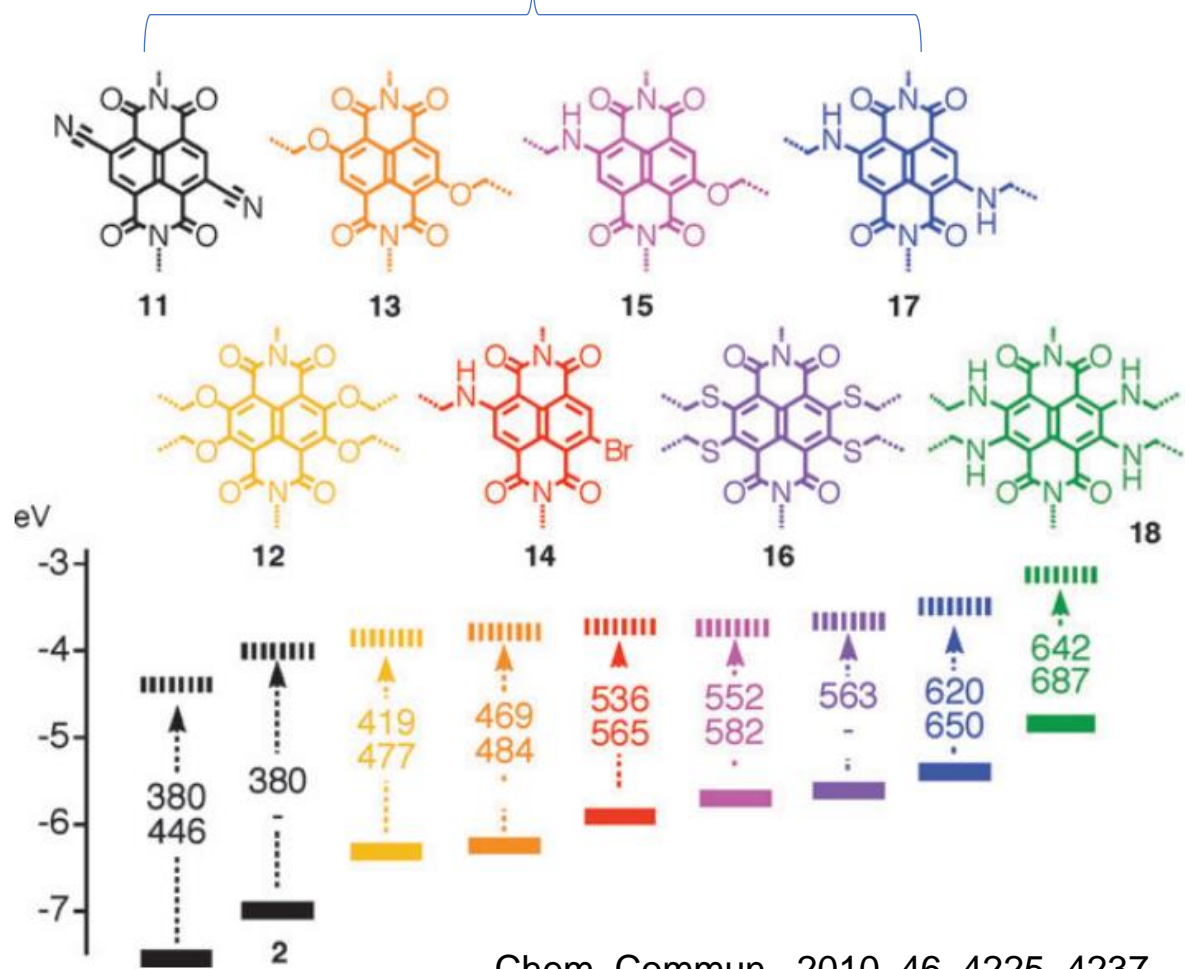
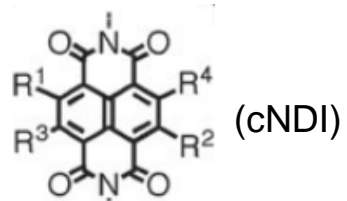
以结晶、半结晶聚合物作为成核链段，结晶作为驱动力形成零维、一维、二维及多维复杂结构。

## This work:

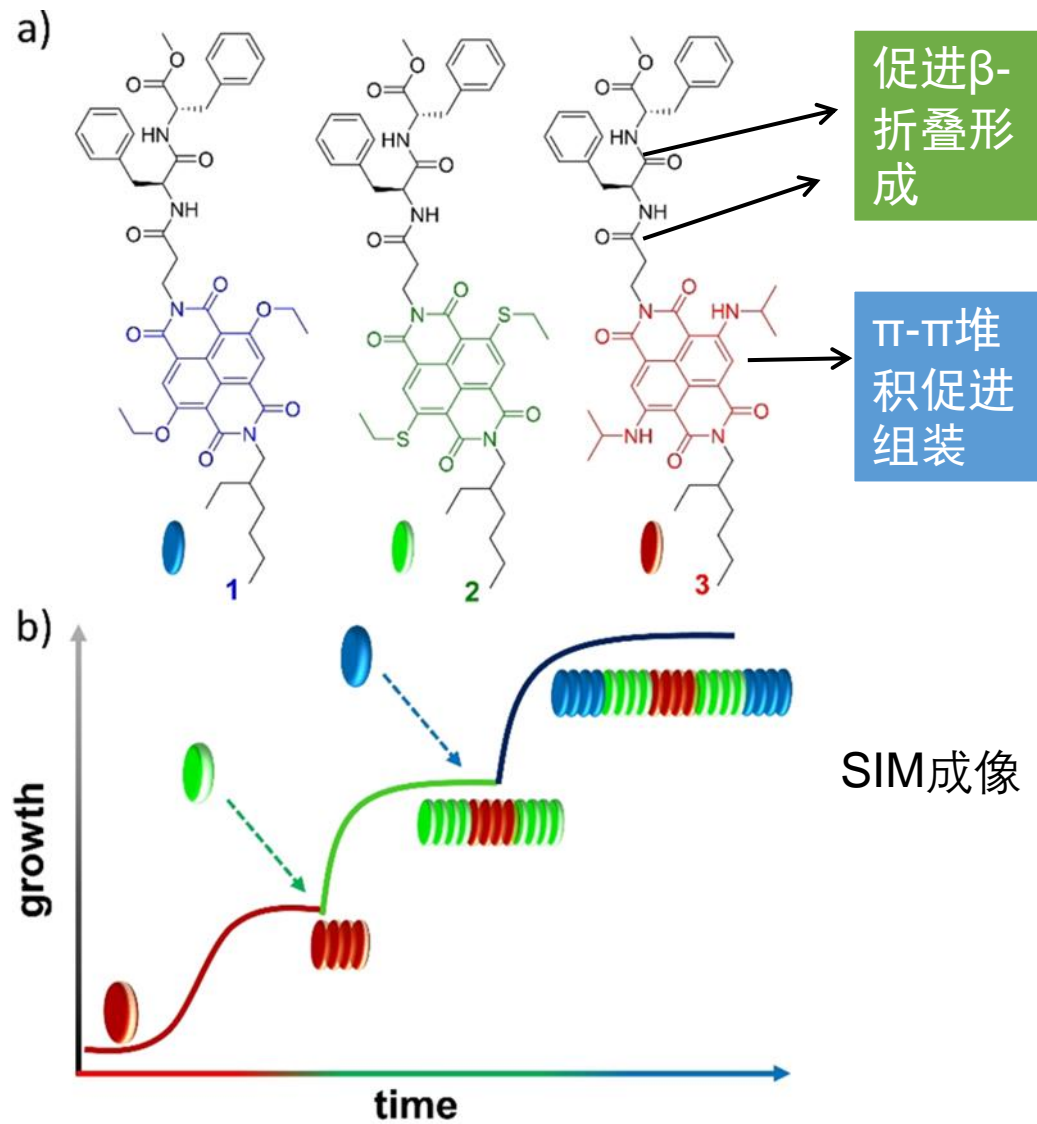


利用分子体系自组装的动力学特性，将体系置于动力学控制的亚稳态，进而在体系中加入种子或引发分子实现链增长类型的超分子聚合过程。

# Design of Monomers

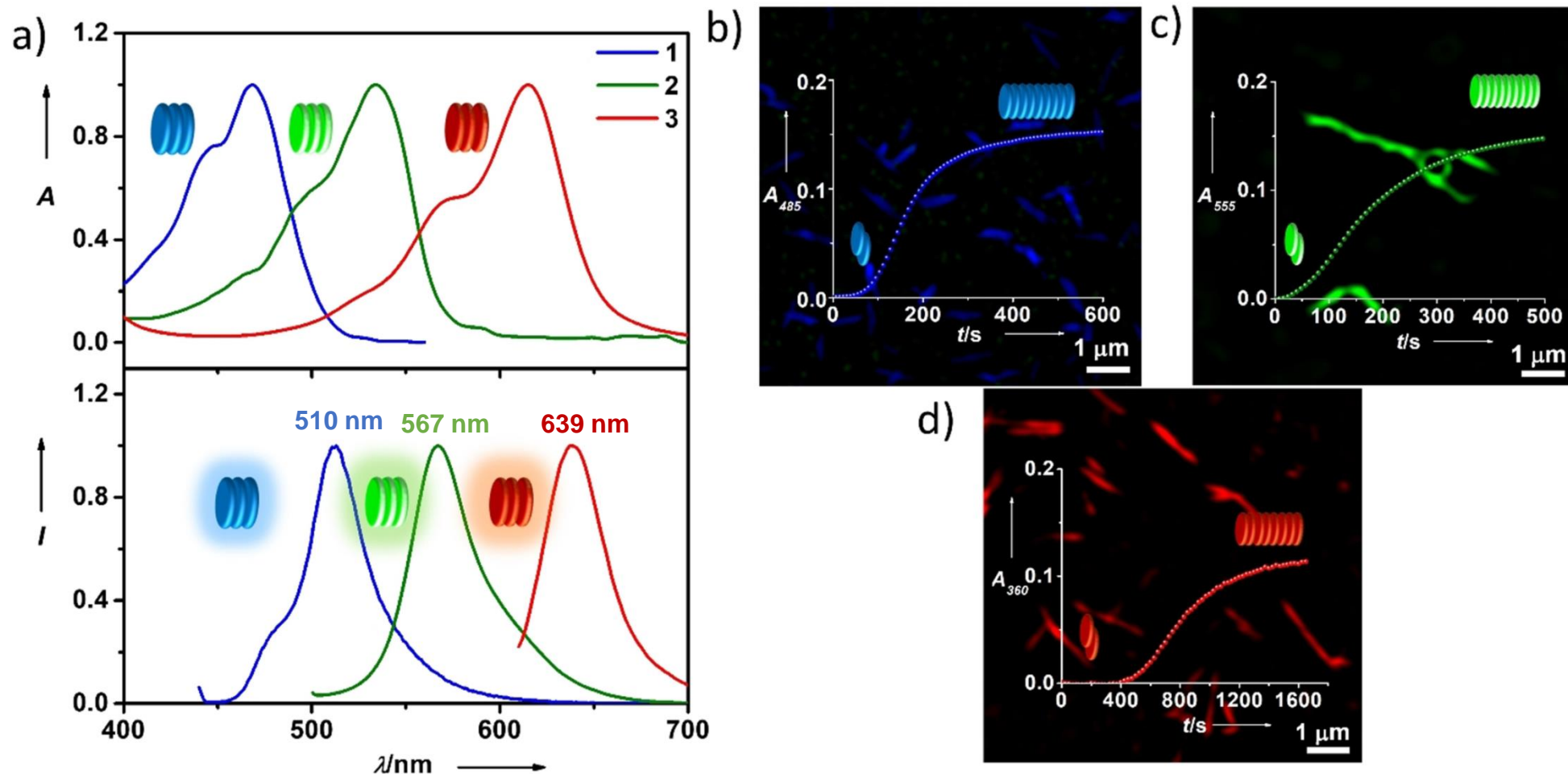


Chem. Commun., 2010, 46, 4225–4237





# Pathway Complexity of Monomers 1, 2, and 3

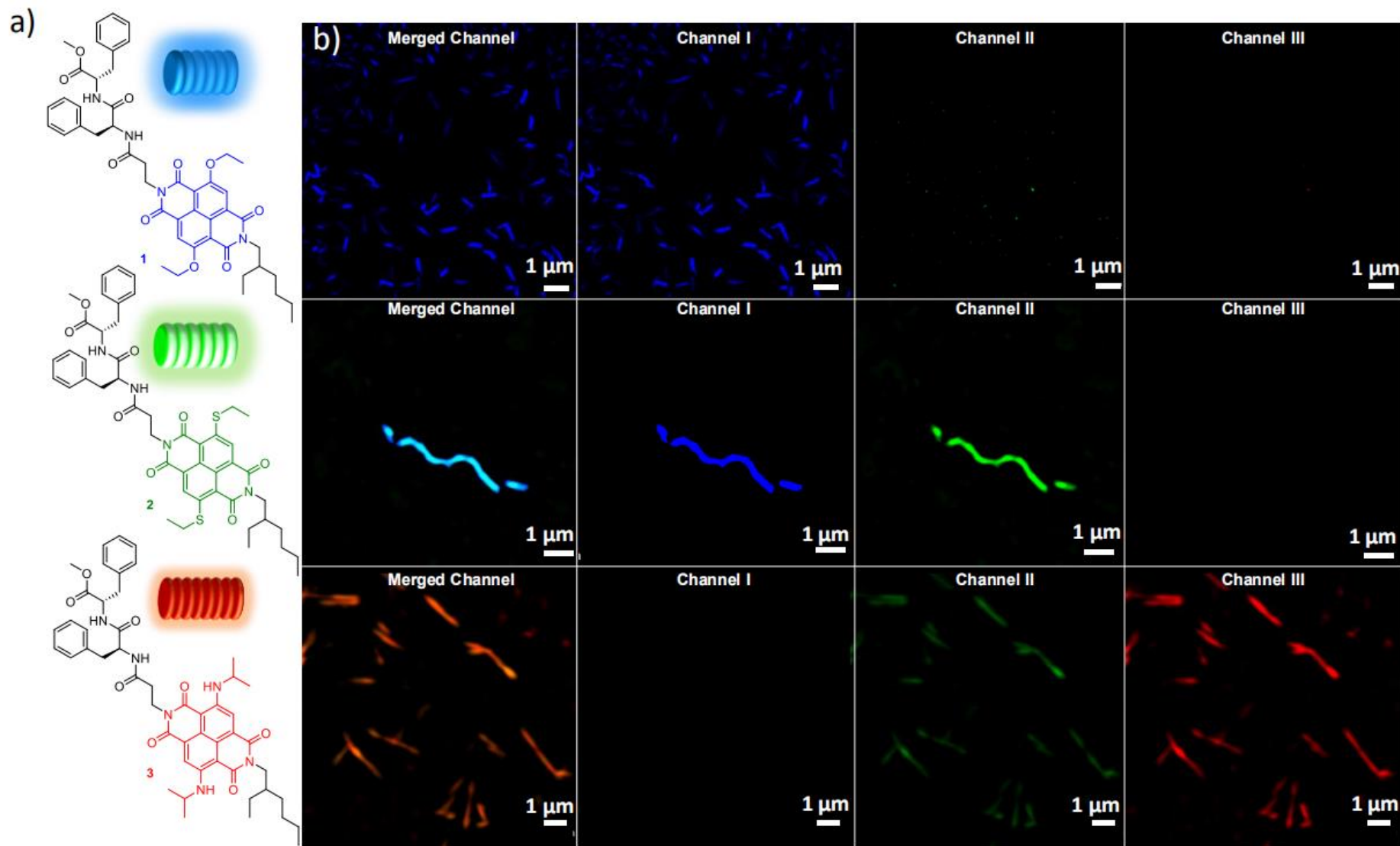


**Figure 2.** a) Normalized absorption and emission spectra of supramolecular homopolymers of **1** (blue), **2** (green) and **3** (red) with distinct absorption and emission profiles ( $[1] = [2] = [3] = 1.5 \times 10^{-5}$  M, TCE/MCH, 10/90 (v/v)). The emission spectra of monomer **1** ( $\lambda_{ex} = 430$  nm), **2** ( $\lambda_{ex} = 530$  nm) and **3** ( $\lambda_{ex} = 600$  nm). b) Time dependent absorbance changes (monitored at 475 nm for **1**, 555 nm for **2** and 360 nm for **3**), which exhibits kinetically controlled cooperative supramolecular polymerization of the monomers. In the background of figures b–d, it shows the SIM images (inset) of the corresponding assemblies imaged through Channel I, Channel II, and Channel III, respectively which shows the presence of blue, green and red emitting supramolecular polymers ( $[1] = [2] = [3] = 1.5 \times 10^{-5}$  M, TCE/MCH, 10/90 (v/v), Channel I:  $\lambda_{ex} = 488$  nm,  $\lambda_{coll} = 495$ – $575$ ; Channel II:  $\lambda_{ex} = 561$  nm,  $\lambda_{coll} = 570$ – $650$ , Channel III:  $\lambda_{ex} = 642$  nm,  $\lambda_{coll} = 655$ – $800$  nm).





# Pathway Complexity of Monomers 1, 2, and 3



$\lambda_{\text{ex}}$   
 $\lambda_{\text{coll}}$

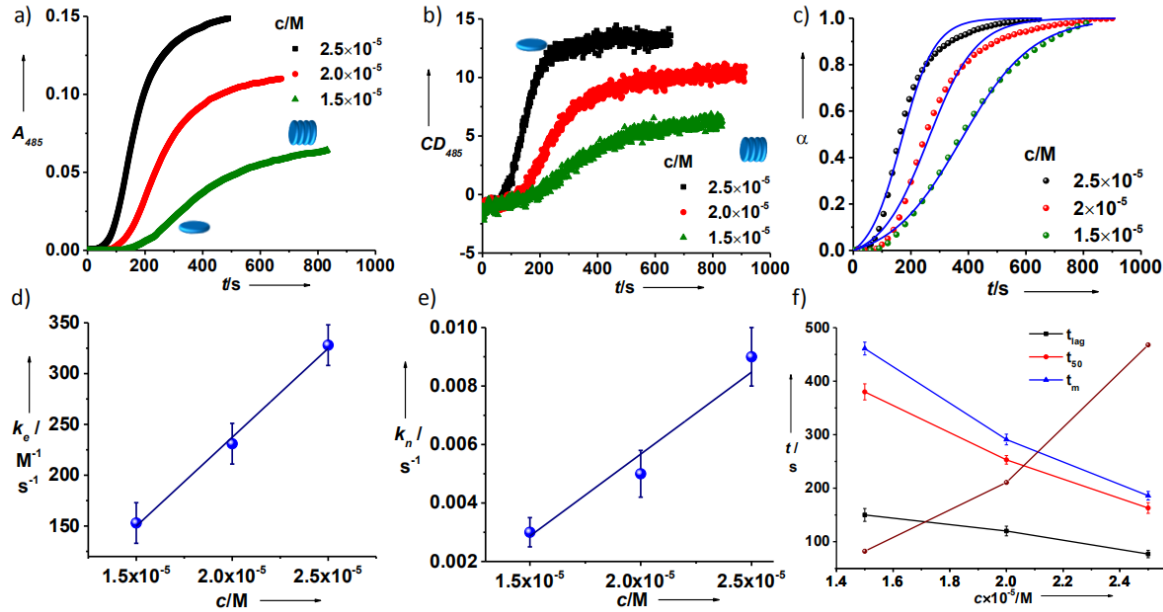
488 nm  
495–575 nm

561 nm  
570–650 nm

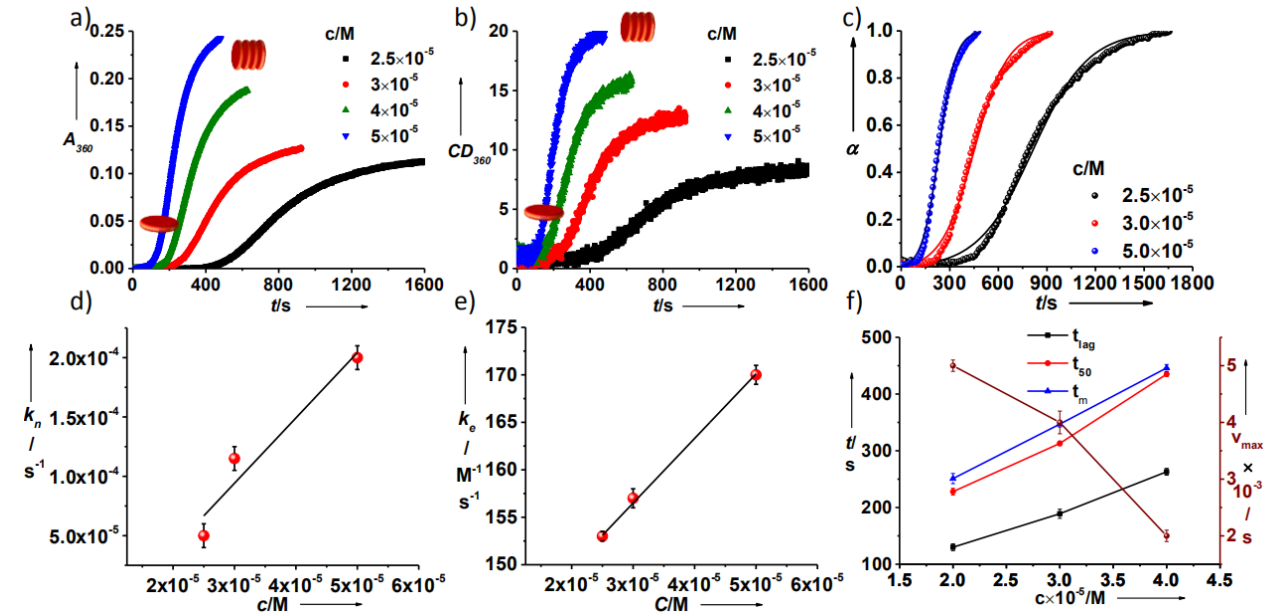
642 nm  
655–800 nm



# Pathway Complexity of Monomers 1 and 3



1



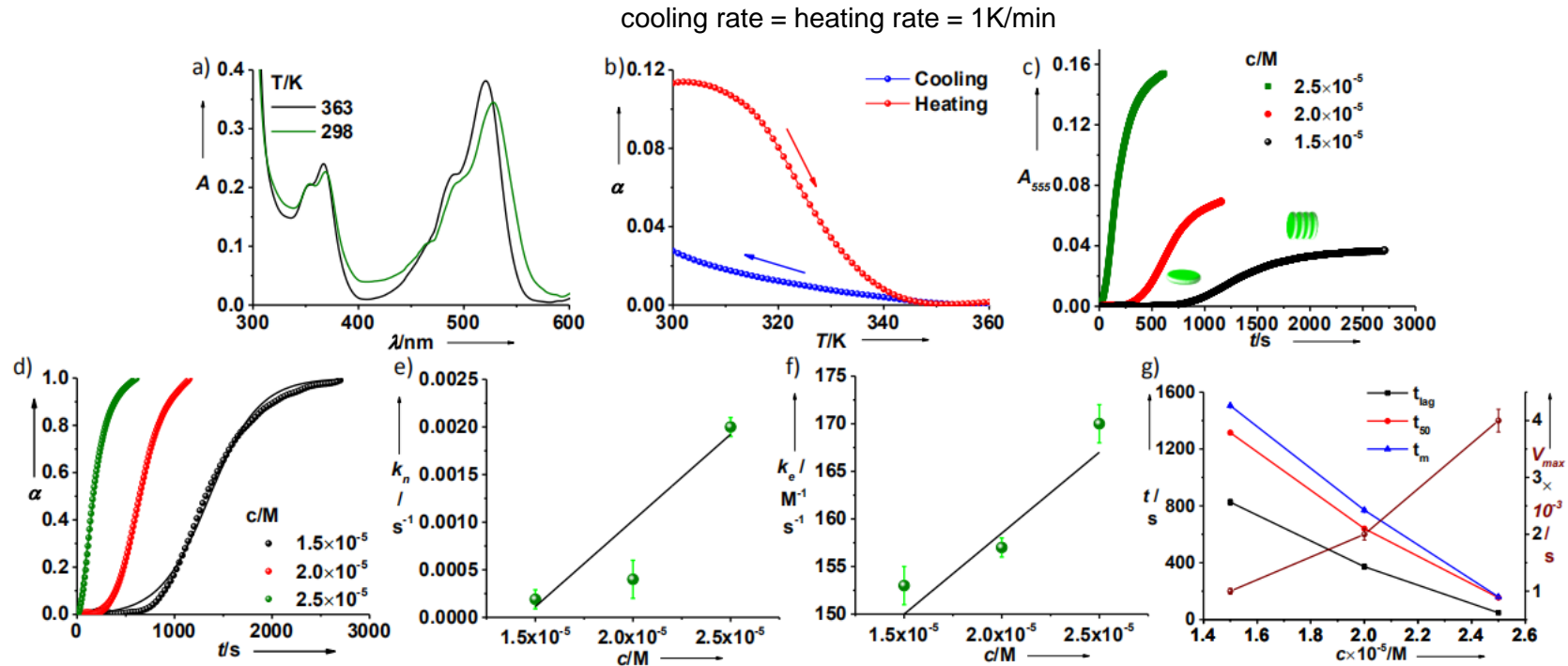
3

$k_n$  (Nucleation rate constant),  $k_e$  (Elongation rate constant)

- 超分子均聚过程遵循协同成核生长机制（Watzky-Finke 自催化模型）。
- 亚稳态转化为热力学稳定的均聚态所需的时间随着浓度的降低而增加。



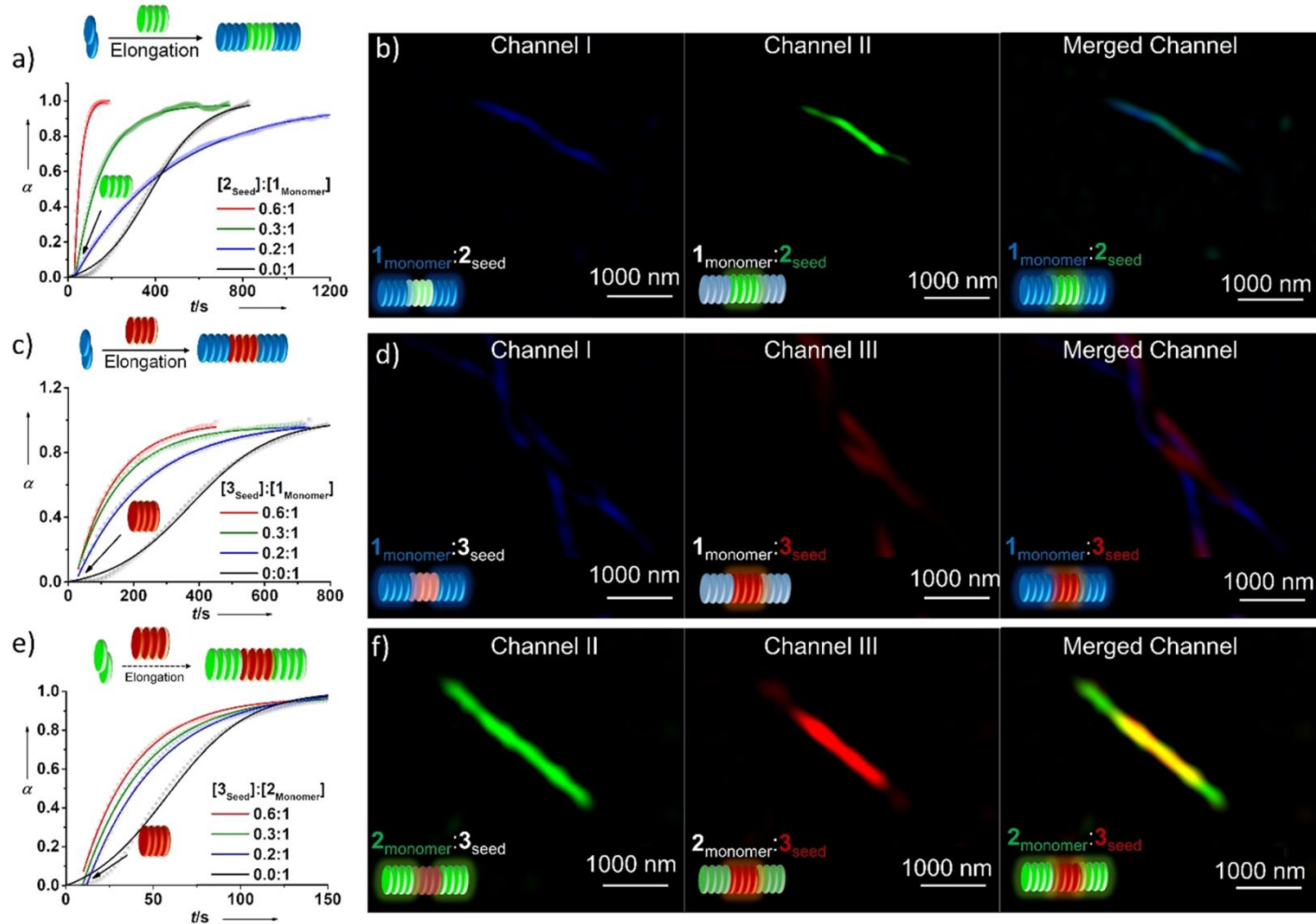
# Pathway Complexity of Monomers 2



- 超分子均聚过程遵循协同成核生长机制（Watzky-Finke 自催化模型）。
- 亚稳态转化为热力学稳定的均聚态所需的时间随着浓度的降低而增加



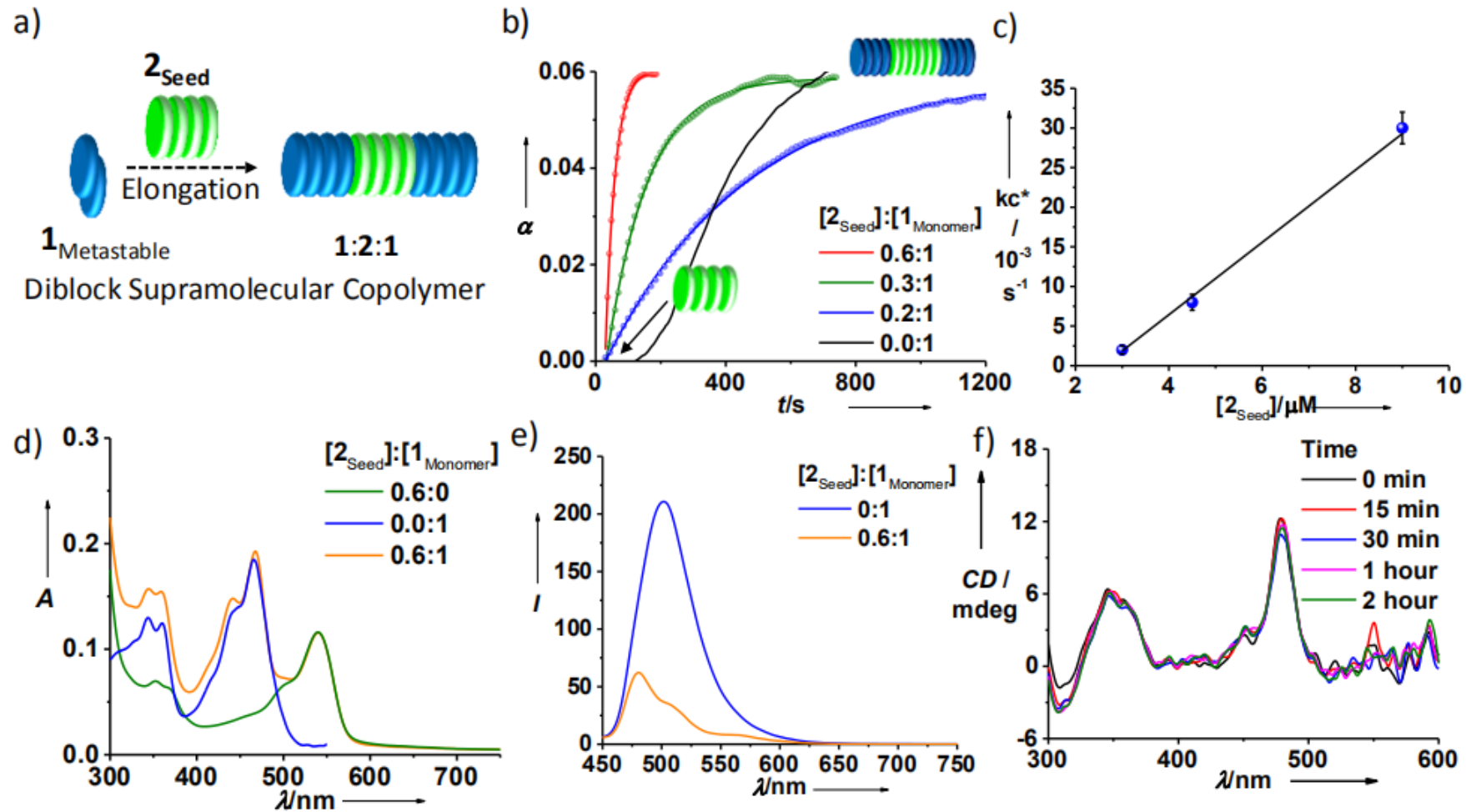
# Two-Component Supramolecular Block Copolymers



**Figure 3.** Time course of supramolecular polymerization on the addition of a)  $2_{\text{seed}}$  into the metastable state of **1** (monitored using absorbance changes at 485 nm) c)  $3_{\text{seed}}$  into the metastable state of **1** (monitored using absorbance changes at 485 nm) and e)  $3_{\text{seed}}$  into the metastable state of **2** (monitored using absorbance changes at 555 nm) ( $[1] = [2] = [3] = 1.5 \times 10^{-5} \text{ M}$ , TCE/MCH, 10/90 (v/v)). The spontaneous growth of the monomers of **1** and **2**, without a lag phase, hints towards the heterogeneous seeding process. These experiments are performed for various monomer to seed ratios ( $[S]:[M]$ ), which shows that the rate of growth of the second monomer decreases with a decrease in seed concentration, reiterating the seed-induced supramolecular polymerization process. SIM images of the synthesized two components supramolecular BCPs of b)  $2_{\text{seed}}:1_{\text{monomer}}$  (0.6:1) imaged through channel I, and channel II, d)  $3_{\text{seed}}:1_{\text{monomer}}$  (0.6:1) in channel I and channel III and f)  $2_{\text{seed}}:3_{\text{monomer}}$  (0.6:1) in channel II and channel III, which shows the presence of connected green-blue, red-blue and yellow-blue segments, respectively (Channel I:  $\lambda_{\text{ex}} = 488 \text{ nm}$ ,  $\lambda_{\text{coll}} = 495\text{--}575$ ; Channel II:  $\lambda_{\text{ex}} = 561 \text{ nm}$ ,  $\lambda_{\text{coll}} = 570\text{--}650$ , channel III:  $\lambda_{\text{ex}} = 642 \text{ nm}$ ,  $\lambda_{\text{coll}} = 655\text{--}800 \text{ nm}$ ).



# Two-Component Supramolecular Block Copolymers

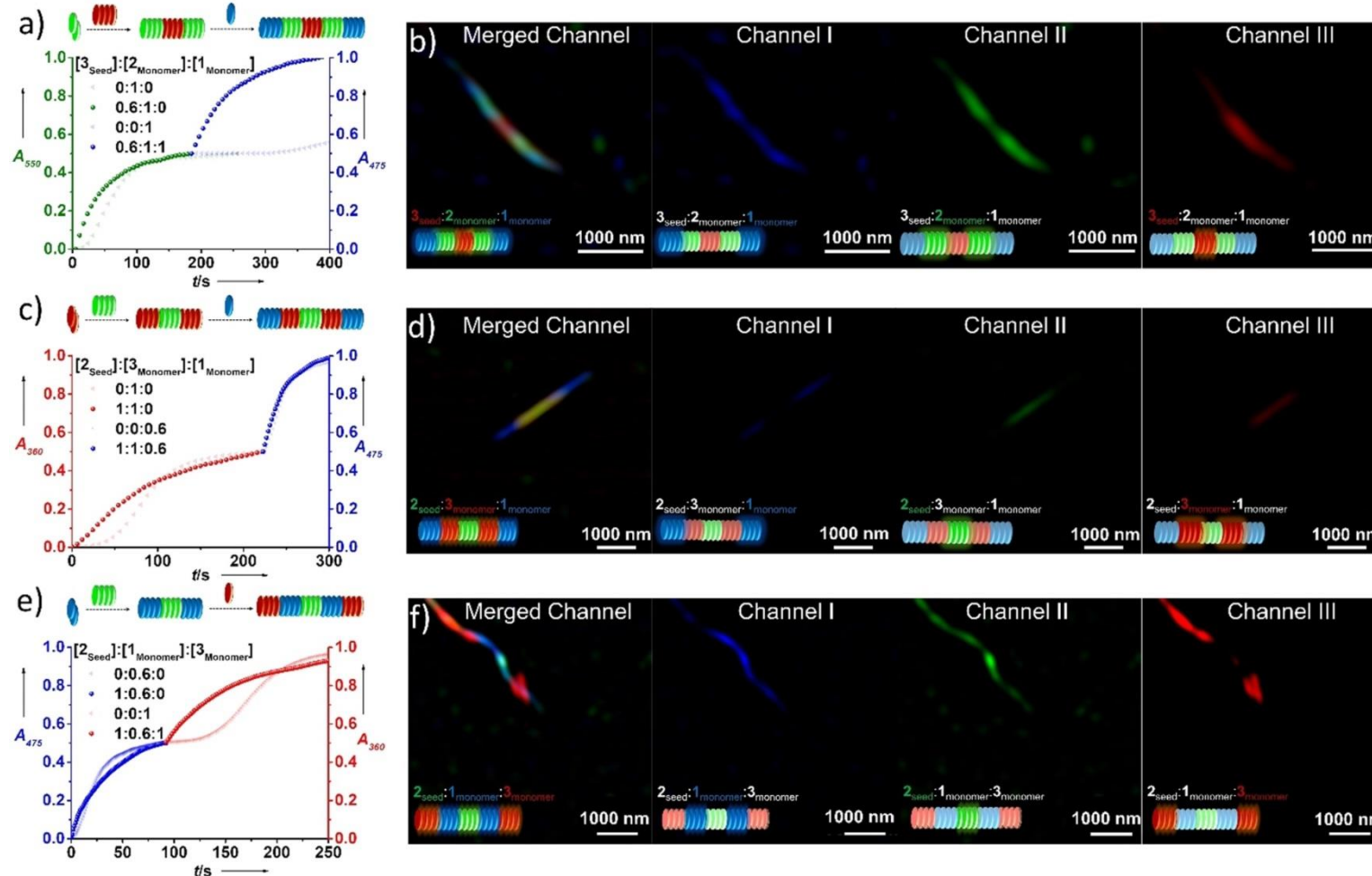


通过改变种子添加量可以控制种子超分子聚合动力学。

动力学控制下形成具有不同荧光 cNDI 单体的轴向异质结构超分子嵌段聚合物。



# Three-Component Supramolecular BCPs with Tunable Microstructure



与预测序列一致

**Figure 4.** Synthesis of tricomponent supramolecular BCPs. Time course of supramolecular polymerization on sequential addition of a)  $2_{\text{monomer}}$  and  $1_{\text{monomer}}$  to  $3_{\text{seed}}$  (TCE/MCH, 10/90 (v/v),  $[1_{\text{monomer}}] = [2_{\text{monomer}}] = 1.5 \times 10^{-5}$  M), c)  $3_{\text{monomer}}$  and  $1_{\text{monomer}}$  to  $2_{\text{seed}}$  (TCE/MCH, 6/94 (v/v),  $[3_{\text{monomer}}] = 2.5 \times 10^{-5}$  M,  $[1_{\text{monomer}}] = 1.5 \times 10^{-5}$  M) and e)  $1_{\text{monomer}}$  and  $3_{\text{monomer}}$  to  $2_{\text{seed}}$  (TCE/MCH, 6/94 (v/v),  $[1_{\text{monomer}}] = 1.5 \times 10^{-5}$  M,  $[3_{\text{monomer}}] = 2.5 \times 10^{-5}$  M) to result in tricomponent supramolecular BCPs with sequences of  $3_{\text{seed}}:2_{\text{monomer}}:1_{\text{monomer}}$ ,  $2_{\text{seed}}:3_{\text{monomer}}:1_{\text{monomer}}$  and  $2_{\text{seed}}:1_{\text{monomer}}:3_{\text{monomer}}$  respectively. SIM images of b)  $3_{\text{seed}}:2_{\text{monomer}}:1_{\text{monomer}}$ , d)  $2_{\text{seed}}:3_{\text{monomer}}:1_{\text{monomer}}$  and f)  $2_{\text{seed}}:1_{\text{monomer}}:3_{\text{monomer}}$  tricomponent block sequences in channel I, channel II, channel III and merged channel showing presence green-red-blue, red-green-blue, green-blue-red segments, respectively (Channel I:  $\lambda_{\text{ex}} = 488$  nm,  $\lambda_{\text{coll}} = 495\text{--}575$ ; Channel II:  $\lambda_{\text{ex}} = 561$  nm,  $\lambda_{\text{coll}} = 570\text{--}650$ , channel III:  $\lambda_{\text{ex}} = 642$  nm,  $\lambda_{\text{coll}} = 655\text{--}800$  nm).



## Conclusion



- 通过连续顺序添加种子的方法构建了三组分嵌段共聚物。
- 通过光谱信息表征了其动力学途径，符合Watzky-Finke 自催化模型。
- 通过SIM成像验证了得到的嵌段共聚物与预测序列的一致性。



- 对于不同成分组装的动态过程，特别是奇特结构的形成，不同单体的分辨存在挑战，能否也通过合成构建具有不同荧光的核取代PBI，从而分辨不同单体，进而有利于动态过程的观察。