JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

A Supramolecular Cross-Linked Conjugated Polymer Network for Multiple Fluorescent Sensing

Xiaofan Ji, Yong Yao, Jinying Li, Xuzhou Yan, and Feihe Huang*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, P. R. China

Supporting Information

ABSTRACT: A supramolecular cross-linked network was fabricated and demonstrated to act as a multiple fluorescent sensor. It was constructed from a fluorescent conjugated polymer and a bisammonium salt cross-linker driven by dibenzo[24]crown-8/secondary ammonium salt host−guest interactions. Compared with the conjugated polymer, the network has weak fluorescence due to the aggregation of polymer chains. Thanks to the multiple stimuli-responsiveness of host−guest interactions, the fluorescence intensity of the system can be enhanced by four types of signals, including potassium cation, chloride anion, pH increase, and heating. Hence, the network can serve as a cation sensor, an anion sensor, a pH sensor, and a temperature sensor. It can be used in both solution and thin film. Interestingly, exposure of a film made from this supramolecular cross-linked network to ammonia leads to an increase of fluorescence, making it a good candidate for gas detection.

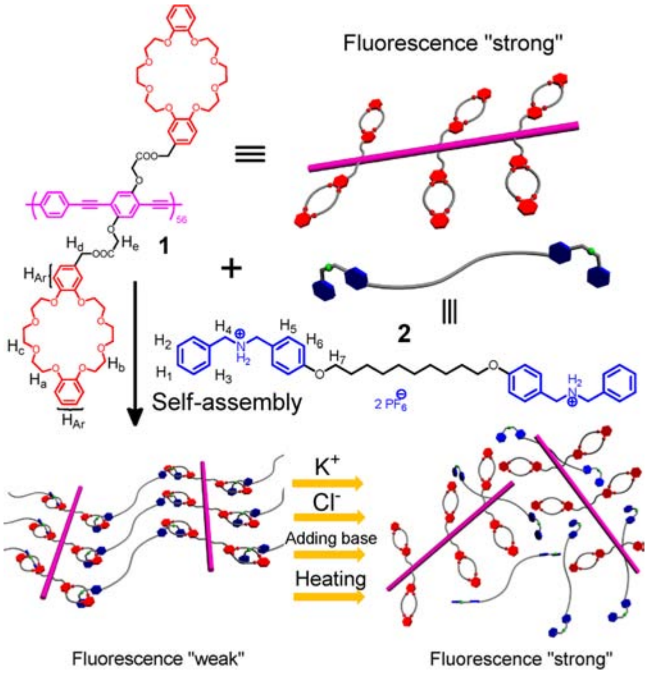
Supramolecular cross-linked polymer networks, prepared from covalent polymeric backbones tied together by noncovalent interactions, have received much attention in recent years due to the mechanical or photophysical properties obtained from the polymeric chains and also the reversibility and stimuli-responsiveness contributed by noncovalent interactions used in cross-linking.[1] The stimuli-responsiveness of cross-linking motifs can endow supramolecular cross-linked networks with plenty of unique applications, such as controlled release,[2] self-healing,[3] and fluorescent sensors.[4] Nowadays, much attention has been paid to fluorescent sensors based on supramolecular cross-linked networks on account of their high selectivity and sensitivity, especially the ones whose polymeric backbones are fluorescent conjugated polymers.[4] An important advantage of conjugated polymers is the obvious change of fluorescence intensity in different states: the individual conjugated polymers exhibit strong fluorescence, while their aggregates formed by noncovalent cross-linking show weak or quenched fluorescence,[4b,c,h] making them suitable fluorescent sensors for detecting signals that can influence the state of aggregation. Up to now, considerable efforts have been dedicated to fluorescent sensors based on conjugated polymer networks.[4] For example, Swager and co-workers reported the first sensory system which utilized the fluorescence difference of conjugated polymers in different states, and it was used for detecting potassium ion.[4b] Kakuchi and co-workers recently developed a fluorescent sensory network whose conjugated polymer chains were cross-linked through hydrogen bonding to probe anions that can disrupt the cross-linking.[4k] Conjugated polymer networks based on organometallic cross-links had also been studied.[5] However, all reported conjugated polymer networks based on supramolecular cross-links can only probe one or two types of signals.[4] Consequently, it is challenging to develop a conjugated polymer network based on supramolecular cross-links to detect multiple signals.

Noncovalent interactions with multiresponsiveness have been widely used in the construction of smart or adaptive materials, such as supramolecular gels with multiple stimuli responsive properties.[6] Therefore, our strategy is to select a kind of noncovalent interaction with multiresponsiveness to serve as supramolecular cross-linker. Thus, the disassembly of the conjugated polymer network will be triggered by multiple stimuli. Crown ethers,[7] the first generation of supramolecular macrocyclic hosts, have been considered as a fascinating platform to prepare multiresponsive materials.[6a,b] It is well-known that dibenzo[24]crown-8 (DB24C8) and its complementary guest dibenzylammonium salt (DBA) form a 1:1 threaded structure, which is responsive to quadruple stimuli (K^+, Cl^-, pH, or temperature change).[6b,c,8,9b] Herein, we prepared a supramolecular cross-linked polymer network by mixing a poly(phenylene-ethynylene) (PPE) polymer with pendent DB24C8 groups and a bisammonium salt cross-linker. The network will form when the DB24C8 units interact with the secondary ammonium salt moieties, causing the aggregation of polymer main chains and leading to a sharp decrease of fluorescence intensity compared to that of the PPE polymer.[4b] Collapse will happen to the network after treatment with K^+ or Cl^-; correspondingly recovery of the fluorescence intensity will occur. Moreover, the network is also responsive to pH and temperature changes.[3b,7p] Hence, this system can be utilized as four types of sensors: a cation sensor, an anion sensor, a pH sensor, and a temperature sensor (Scheme 1). The system can be used in both solution and thin film. Interestingly, exposure of a film made from this network to ammonia leads to an increase of fluorescence from the film, making it a good candidate for gas sensing.

Polymer **1** (M_n = 70.6 kDa and PDI = 1.77) was synthesized by a Pd-catalyzed cross-coupling reaction of 1,4-diethynylbenzene and diiodo-diDB24C8-substituted benzene derivative **3** (Supporting Information (SI), Scheme S1). There were about

Received: November 4, 2012
Published: December 21, 2012

Scheme 1. Cartoon Representation of the Formation of a Supramolecular Cross-Linked Conjugated Polymer Network and Its Disassembly Induced by Different Signals



112 DB24C8 units (56 repeat units) per single polymer chain for **1** as calculated based on the GPC data. The cross-linker **2** is a bisammonium salt linked by a long flexible alkyl chain.[7a] A supramolecular cross-linked polymer network will form upon the addition of **2** to **1** in $CHCl_3/CH_3CN$ (1:1, *v*/*v*).

To investigate the formation of the supramolecular cross-linked network, NMR spectroscopy, fluorescence titration spectroscopy, and scanning electron micrography (SEM) were carried out. First, proton NMR spectra gave direct evidence for the complexation of polymer **1** and cross-linker **2** in solution.[3b] As shown in Figure 1, spectra of polymer **1**, cross-linker **2**, and a mixture of **1** and **2** were examined. Upfield shifts were observed for aromatic protons H_1, H_2, H_3, H_5, and H_6 and benzyloxymethylene protons H_7 of **2** after complexation. However, the benzyl protons H_4 of **2** shifted downfield after mixing, in accordance with a previously reported complexation system of DB24C8/DBA.[9] Moreover, the slow exchange feature made the protons of the DB24C8 unit and the DBA moiety split into two sets of signals, the complexed and uncomplexed ones. These distinct changes in chemical shifts indicated the occurrence of host−guest interactions between DB24C8 and DBA, inducing the formation of a supramolecular cross-linked polymer network.

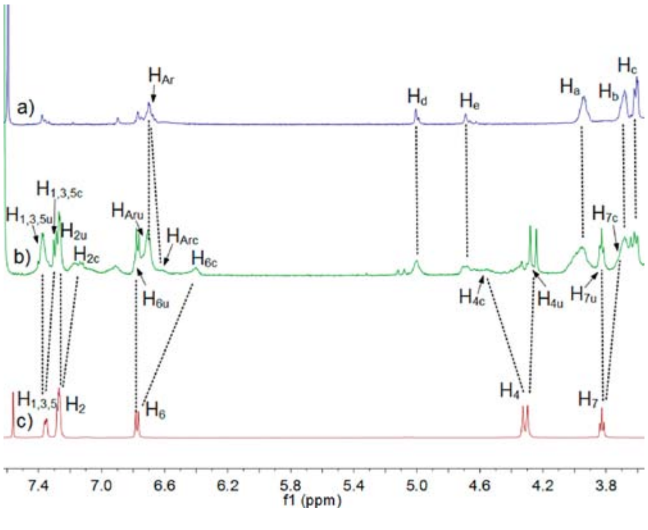


Figure 1. Partial ^1H NMR spectra (500 MHz, 1:1 $CDCl_3/CD_3CN$, 298K): (a) polymer **1**; (b) a mixture of 2.00 μM polymer **1** (0.224 mM crown ether units) and 20.0 μM cross-linker **2** (40.0 μM ammonium moieties); (c) cross-linker **2**. Here "c" and "u" denote complexed and uncomplexed moieties, respectively.

Fluorescence titration experiments were carried out to investigate the fluorescence response of the conjugated polymer **1** to cross-linker **2**. Figure 2 shows the fluorescence spectra of conjugated polymer **1** upon addition of cross-linker **2**. As the concentration of cross-linker **2** increased, the fluorescence intensity of polymer **1** decreased gradually, and the inherent blue band of the PPE shifted to longer wavelengths: from 440 to 447 nm, in accordance with aggregation-induced planarization of the polymer chains.[10] In addition, the photographs in Figure 2 show that the brightness of the solution was also reduced. Obviously, it is the complexation of the DB24C8 units and the DBA moieties that results in the aggregation of PPE chains and causes the reduction of the fluorescence intensity. However, the fluorescence intensity of polymer **1** was not totally quenched. The reason was that the long alkyl chain which links the two bisammonium salt units confine the compactness of the conjuagted polymer chain aggregation. These results showed that the supramolecular cross-linked polymer network constructed by host−guest interactions between the DB24C8 units and the DBA moieties exhibits weak fluorescence compared to its PPE chains.

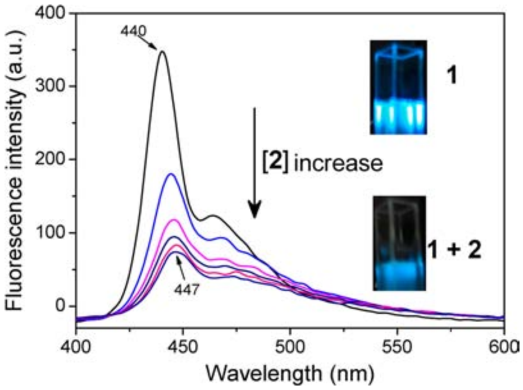


Figure 2. Fluorescence spectra of **1** (2.0 μM) in $CHCl_3/CH_3CN$ (1:1, *v*/*v*) with different concentrations of **2**, from top to bottom: 0.0; 20; 40; 80; 100; 150 μM. λ_{exc} = 355 nm.

To test the morphology of the supramolecular cross-linked polymer network, SEM studies were carried out. Figure 3b shows an interconnected porous 3D structure, indicating the formation of the supramolecular cross-linked network owing to the aggregation of PPE chains through host−guest interactions. The phenomenon illustrated that the presence of cross-linkers not only realized the conversion from the linear polymer to supramolecular network, but also brought about the change in the microscopic structure (Figure 3a,b).

All the above results confirmed the formation of the supramolecular cross-linked network from **1** and **2**. It was

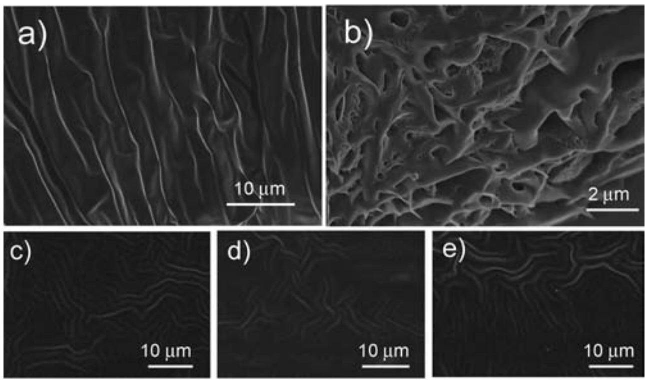


Figure 3. SEM images: (a) polymer **1**; (b) a mixture of 2.00 μM polymer **1** (0.224 mM crown ether units) and 20.0 μM cross-linker **2** (40.0 μM ammonium moieties); (c) after adding TBACl (40.0 μM) to mixture b; (d) after adding KPF_6 (40.0 μM) to mixture b; (e) after adding Et_3N (40.0 μM) to mixture b.

also shown that the fluorescence of the supramolecular network is weaker than that of conjugated polymer **1**. It is well-known that the complexation of DB24C8 and DBA can be controlled by potassium cation (K^+),[8b] chloride anion (Cl^-),[9b] pH change,[3b,7p,8c] and temperature change,[8a] since the DB24C8 unit forms a more stable 1:1 complex with K^+, Cl^- forms a tight ion pair with DBA, Et_3N converts the secondary ammonium to the corresponding secondary amine, and heating causes the disassembly by reducing the binding constant.[3b,6b,7p,9b] Hence, the fluorescence of the system will be strengthened by these different types of signals. We used TBACl, KPF_6, triethylamine (Et_3N), and heating to control the host−guest interactions, which resulted in the transition from the supramolecular cross-linked network to linear polymer and the increase of fluorescence intensity. Figure 4 shows that the fluorescence intensity of the network system increased upon the addition of TBACl, KPF_6, or Et_3N or heating. As shown in Figure 3b−e, the morphology of the mixture of **1** and **2** changed from interconnected porous 3D structure to fibers with parallel arrangement after treatment by TBACl, KPF_6, and Et_3N. The parallel arrangement is generated by the $\pi-\pi$ interactions between polymer main chains. In the process of sample preparation, the polymer chains gathered closer and closer with the evaporation of solvents, giving sufficient distance for the $\pi-\pi$ interactions between polymer chains. The ^1H NMR experiment also demonstrated this disassembly process (SI, Figures S7−S10). Therefore, this network system can function as a multiple fluorescent sensor. In addition, inspired by recent work about multiresponsive gels,[6e] this network was demonstrated to be able to function as an XOR gate (SI, Figures S11 and S12). If a single input (K^+ or Cl^-) is set, the fluorescence increases by disassembly of the network. However, if both inputs (K^+ and Cl^-) are present, KCl precipitates and the network reassembles, causing decreased fluorescence.

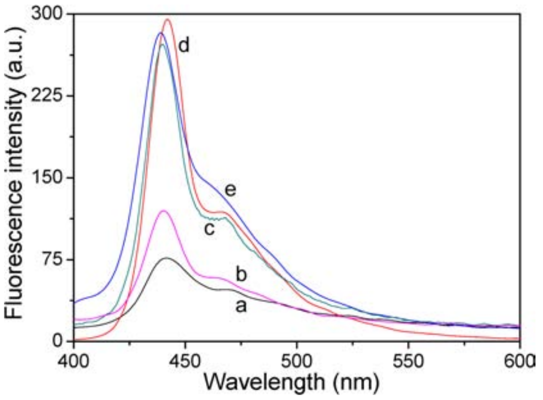


Figure 4. Fluorescence emission spectra of (a) the mixture of **1** (2.0 μM) and **2** (100 μM), and after treatment with (b) heating at 50 °C; (c) KPF_6 (200 μM); (d) TBACl (200 μM); (e) Et_3N (200 μM).

Besides in solution the fluorescence intensity changes of polymer **1** in the presence of cross-linker **2** and the network system under external signals can also be observed in thin film. Thin films of polymer **1** and the mixture of **1** and **2** were prepared by spin-casting solutions in $CHCl_3/CH_3CN$ (1:1, ν/ν) onto glass slides. Figure 5a shows that the fluorescence intensity of polymer **1** in a thin film decreased under the existence of cross-linker **2**. Moreover, as shown in Figure 5b,c, the thin films displayed a visually clear fluorescence color change from a film of polymer **1** to a film of a mixture of **1** and **2**: from bright blue to pale blue. In addition, the thin film of the supramolecular cross-linked network can be applied as a gas sensor to detect alkaline gases because the complexation of DB24C8 and DBA will be destroyed by base.[3b,4a,i,7p] When a thin film of the network was exposed to the vapor of ammonia vapor (Figure 5e), the ammonium unit of cross-linker **2** was deprotonated, destroying the network structure and giving rise to an increase of fluorescence intensity (Figure 5d).

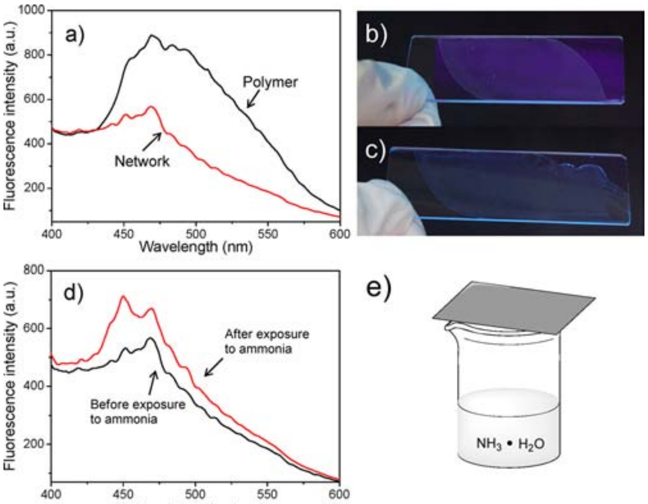


Figure 5. (a) Fluorescence emission spectra of thin solid films of 2.00 μM polymer **1** (0.224 mM crown ether units) and a mixture of 2.00 μM polymer **1** and 20.0 μM cross-linker **2** (40.0 μM ammonium moeties) spin-cast from $CHCl_3/CH_3CN$ (1:1, ν/ν) solutions; (b) photograph of a film of polymer **1**, illuminated at 365 nm; (c) photograph of a film of a mixture of **1** and **2** with a molar ratio of 1:10, illuminated at 365 nm; (d) fluorescence emission spectra of thin films of the mixture, before and after exposure to ammonia for 10 min; (e) cartoon representation of exposure of a film made from the supramolecular network to ammonia.

In conclusion, we developed a novel supramolecular cross-linked network based on the host−guest interactions between the pendent DB24C8 units of a conjugated polymer and the DBA moieties of a bisammonium cross-linker. The network exhibited weak fluorescence compared to the conjugated polymer because of the aggregation of polymer main chains.

Owing to the multiresponsiveness of the host−guest interactions, the network structure can be destroyed by multiple signals, leading to the enhancement of the fluorescence. Therefore, the system can serve as a multiple fluorescent sensor. Moreover, exposure of a film of the supramolecular cross-linked network to ammonia leads to an increase of the fluorescence from the film, endowing the system with a function in gas detecting. It is the combination of supramolecular chemistry and conjugated polymer science that gave birth to the supramolecular cross-linked network with remarkable features, and we believe that the novel network system will pave the way for designing and preparing advanced sensor materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, synthesis of **1**, NMR spectra, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

fhuang@zju.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (20834004, 91027006, and 21125417), the Fundamental Research Funds for the Central Universities (2012QNA3013), Program for New Century Excellent Talents in University, Zhejiang Provincial Natural Science Foundation of China (R4100009), and Open Project of State Key Laboratory of Supramolecular Structure and Materials.

■ REFERENCES

(1) (a) Fleury, G.; Schlatter, G.; Brochon, C.; Travelet, C.; Lapp, A.; Lindner, P.; Hadziioannou, G. *Macromolecules* **2007**, *40*, 535−543. (b) Lieleg, O.; Claessens, M. M. A. E.; Bausch, A. R. *Soft Matter* **2010**, *6*, 218−225. (c) Suzuki, M.; Hanabusa, K. *Chem. Soc. Rev.* **2010**, *39*, 455−463. (d) Steed, J. W. *Chem. Soc. Rev.* **2010**, *39*, 3686−3699. (e) Piepenbrock, M.-O. M.; Lloyd, G. O.; Clarke, N.; Steed, J. W. *Chem. Rev.* **2010**, *110*, 1960−2004. (f) Seiffert, S.; Sprakel, J. *Chem. Soc. Rev.* **2012**, *41*, 909−930.

(2) (a) Zhu, Z.; Wu, C.; Liu, H.; Zou, Y.; Zhang, X.; Kang, H.; Yang, C. J.; Tan, W. *Angew. Chem., Int. Ed.* **2010**, *49*, 1052−1056. (b) Li, X. M.; Li, J. Y.; Gao, Y.; Kuang, Y.; Shi, J. F.; Xu, B. *J. Am. Chem. Soc.* **2010**, *132*, 17707−17709. (c) Li, X.; Kuang, Y.; Shi, J.; Gao, Y.; Lin, H. C.; Xu, B. *J. Am. Chem. Soc.* **2011**, *133*, 17513−17518. (d) Park, M. H.; Joo, M. K.; Choi, B. G.; Jeong, B. *Acc. Chem. Res.* **2012**, *45*, 424−433.

(3) (a) Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451*, 977−980. (b) Zhang, M.; Xu, D.; Yan, X.; Chen, J.; Dong, S.; Zheng, B.; Huang, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 7011−7015.

(4) (a) Chen, L.; McBranch, D. W.; Wang, H.-L.; Helgeson, R.; Wudl, F.; Whitten, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 12287−12292. (b) Kim, J.; McQuade, D. T.; McHugh, S. K.; Swager, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3868−3872. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574. (d) Jiang, H.; Zhao, X.; Schanze, K. S. *Langmuir* **2006**, *22*, 5541−5543. (e) Nelson, T. L.; O'Sullivan, C.; Greene, N. T.; Maynor, M. S.; Lavigne, J. J. *J. Am. Chem. Soc.* **2006**, *128*, 5640−5641. (f) Satrijo, A.; Swager, T. M. *J. Am. Chem. Soc.* **2007**, *129*, 16020−16028. (g) Kim, I.-B.; Phillips, R.; Bunz, U. H. F. *Macromolecules* **2007**, *40*, 814−817. (h) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339−1386. (i) Esser, B.; Swager, T. M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8872−8875. (j) Zhao, X.; Schanze, K. S. *Chem. Commun.* **2010**, *46*, 6075−6077. (k) Sakai, R.; Nagai, A.; Tago, Y.; Sato, S.; Nishimura, Y.; Arai, T.; Satoh, T.; Kakuchi, T. *Macromolecules* **2012**, *45*, 4122−4127.

(5) Weder, C. *Chem. Commun.* **2005**, 5378−5389.

(6) (a) Yan, X.; Xu, D.; Chi, X.; Chen, J.; Dong, S.; Ding, X.; Yu, Y.; Huang, F. *Adv. Mater.* **2012**, *24*, 362−369. (b) Dong, S.; Zheng, B.; Xu, D.; Yan, X.; Zhang, M.; Huang, F. *Adv. Mater.* **2012**, *24*, 3191−3195. (c) Zheng, B.; Wang, F.; Dong, S.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 1621−1636. (d) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 6042−6065. (e) Qi, Z.; Malo de Molina, P.; Jiang, W.; Wang, Q.; Nowosinski, K.; Schulz, A.; Gradzielski, M.; Schalley, C. A. *Chem. Sci.* **2012**, *3*, 2073−2082.

(7) (a) Yamaguchi, N.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 143−147. (b) Gibson, H. W.; Yamaguchi, N.; Jones, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 3522−3533. (c) Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2004**, *126*, 14738−14739. (d) Tian, H.; Wang, Q. *Chem. Soc. Rev.* **2006**, *35*, 361−374. (e) Huang, F.; Nagvekar, D. S.; Zhou, X.; Gibson, H. W. *Macromolecules* **2007**, *40*, 3561−3567. (f) Wang, F.; Han, C.; He, C.; Zhou, Q.; Zhang, J.; Wang, C.; Ling, N.; Huang, F. *J. Am. Chem. Soc.* **2008**, *130*, 11254−11255. (g) Wang, F.; Zheng, B.; Zhu, K.; Zhou, Q.; Zhai, C.; Li, S.; Li, N.; Huang, F. *Chem. Commun.* **2009**, 4375−4377. (h) Ge, Z.; Hu, J.; Huang, F.; Liu, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 1798−1802. (i) Jiang, W.; Han, M.; Zhang, H.; Zhang, Z.; Liu, Y. *Chem.—Eur. J.* **2009**, *15*, 9938−9945. (j) Jiang, W.; Schalley, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 10425−10429. (k) Jiang, W.; Schäfer, A.; Mohr, P. C.; Schalley, C. A. *J. Am. Chem. Soc.* **2010**, *132*, 2309−2320. (l) Ma, X.; Tian, H. *Chem. Soc. Rev.* **2010**, *39*, 70−80. (m) Wang, F.; Zhang, J.; Ding, X.; Dong, S.; Liu, M.; Zheng, B.; Li, S.; Wu, L.; Yu, Y.; Gibson, H. W.; Huang, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1090−1094. (n) Yan, X.; Zhou, M.; Chen, J.; Chi, X.; Dong, S.; Zhang, M.; Ding, X.; Yu, Y.; Shao, S.; Huang, F. *Chem. Commun.* **2011**, *47*, 7086−7088. (o) Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurney, R. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 9260−9327. (p) Dong, S.; Luo, Y.; Yan, X.; Zheng, B.; Ding, X.; Yu, Y.; Ma, Z.; Zhao, Q.; Huang, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1905−1909. (q) Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 2836−2839. (r) Ji, X.; Zhu, K.; Yan, X.; Ma, Y.; Li, J.; Hu, B.; Yu, Y.; Huang, F. *Macromol. Rapid Commun.* **2012**, *33*, 1197−1202. (s) Ji, X.; Li, J.; Chen, J.; Chi, X.; Zhu, K.; Yan, X.; Zhang, M.; Huang, F. *Macromolecules* **2012**, *45*, 6457−6463. (t) Avestro, A.; Belowich, M. E.; Stoddart, J. F. *Chem. Soc. Rev.* **2012**, *41*, 5881−5895. (u) Liu, Y.; Wang, Z.; Zhang, X. *Chem. Soc. Rev.* **2012**, *41*, 5922−5932. (v) Li, S.; Xiao, T.; Lin, C.; Wang, L. *Chem. Soc. Rev.* **2012**, *41*, 5950−5968. (w) Zhu, K.; Vukotic, V. N.; Loeb, S. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 2168−2172. (x) Zhu, K.; Vukotic, V. N.; Noujeim, N.; Loeb, S. J. *Chem. Sci.* **2012**, *3*, 3265−3271. (y) Vukotic, V. N.; Loeb, S. J. *Chem. Soc. Rev.* **2012**, *41*, 5896−5906.

(8) (a) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem.—Eur. J.* **1996**, *2*, 709−728. (b) Gibson, H. W.; Wang, H.; Slebodnick, C.; Merola, J.; Kassel, W. S.; Rheingold, A. L. *J. Org. Chem.* **2007**, *72*, 3381−3393. (c) Wu, J.; Leung, K. C.-F; Benítez, D.; Han, J.-Y; Cantrill, S. J.; Fang, L.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 7470−7474.

(9) (a) Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 7001−7004. (b) Gibson, H. W.; Jones, J. W.; Zakharov, L. N.; Rheingold, A. L.; Slebodnick, C. *Chem.—Eur. J.* **2011**, *17*, 3192−3206.

(10) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652−654.