Self-Assembly

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Supramolecular Amphiphiles Based on a Water-Soluble Charge-Transfer Complex: Fabrication of Ultralong Nanofibers with Tunable Straightness**

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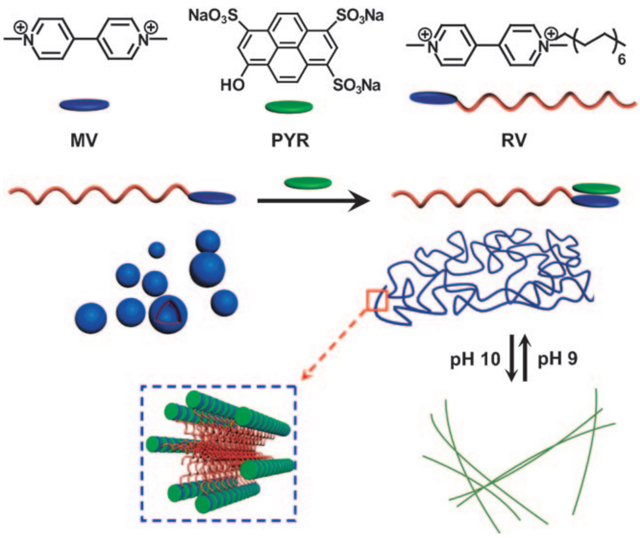
Charge-transfer complexes are formed by the weak association of two molecules or molecular subgroups, one of which acts as an electron donor and the other as an electron acceptor.[1] The formation of charge-transfer complexes is always driven by a combination of charge-transfer interactions and other noncovalent interactions, such as host–guest interactions and hydrophobic interactions.[2] One characteristic of charge-transfer complexes is their high charge-carrier densities, which lead to high conductivity. From this point of view, one-dimensional nanostructures that facilitate the directional movement of charge carriers are extremely important for the promising application of charge-transfer complexes as organic nanowires in electronic and optoelectronic nanodevices.[3] Typically, charge-transfer complexes are prepared by solid-phase reactions or self-assembly in nonpolar solvents (but rarely in water) because of the generally low solubility of the charge-transfer components.[4] Examples of water-soluble organic charge-transfer complexes based on viologen and pyrene derivatives have been reported for applications such as glucose sensors and guanosine triphosphate (GTP) detectors.[5] Inspired by their easy preparation and the use of water as an environmentally friendly solvent, we wondered if we could directly obtain nanoscale materials based on one-dimensional charge-transfer complexes by self-assembly in aqueous solution. However, this concept is very challenging, since the accurate stoichiometry and detailed supramolecular structure of the charge-transfer complex would not be fully revealed. Moreover, the complex formation is simultaneously affected by Coulombic attractions and charge-transfer interactions, but the dominant driving force is unclear, thus strongly hindering further application in supramolecular soft materials.

Supramolecular amphiphiles are amphiphilic building blocks that are assembled by noncovalent interactions.[6] Herein, we attempt to extend the concept of "supramolecular amphiphiles" for the fabrication of one-dimensional ultralong nanofibers on the basis of the water-soluble charge-transfer complex formation between viologen derivatives and the 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (PYR). Notably, the straightness of the nanofiber can be tuned by changing the pH of the reaction solution. Furthermore, the detailed supramolecular structure is revealed, and the dominant driving force of the viologen–PYR complex is clarified. As shown in Scheme 1, a viologen-containing amphiphile (RV) was designed and synthesized. PYR is a water-soluble pyrene derivative, and is a strong electron donor. PYR and RV are expected to form a supramolecular amphiphile driven by the charge-transfer-complex formation between the PYR and the viologen. One advantage is that the supramolecular PYR–RV complex can be readily prepared by the direct mixing of PYR and RV in aqueous solution.



Scheme 1. Schematic representation of the preparation of the pH-responsive nanofibers.

When dissolved in aqueous solution, RV itself self-assembles into an aggregate because of its amphiphilic nature. The aggregation of RV at a concentration of 1.0×10^{-4} M in pH 9 buffer solution was studied by transmission electron microscopy (TEM). Figure 1a shows how RV self-assembles into sphere-like structures. The clear contrast between the dark periphery and the gray central part indicates that the spheres are typically vesicle-like structures with hollow centers. TEM images show that the average size of the vesicles is about 300 nm, which is consistent with the value of 310 nm determined by dynamic laser scattering

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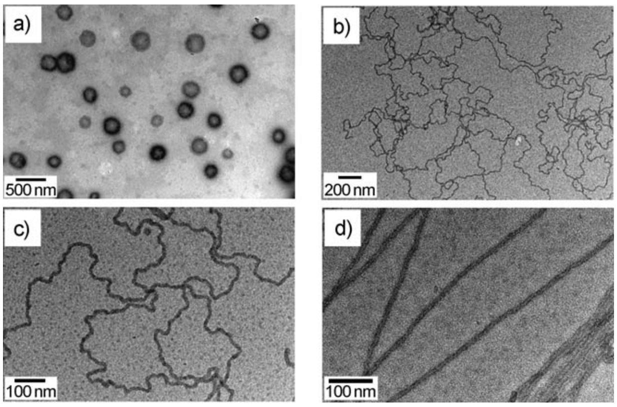

Figure 1. TEM images of a) RV and b, c) PYR–RV in pH 9 buffer solution; d) TEM image of PYR–RV in pH 10 buffer solution. The concentration of RV is 1×10^{-4} M in each case.

(DLS) experiments (Figure S1 in the Supporting Information).

It should be noted that the vesicles transformed into one-dimensional nanofibers when an equivalent amount of PYR was added into the RV solution. As shown in Figure 1 b, the PYR–RV supramolecular amphiphile self-assembles into a one-dimensional wormlike structure. From the magnified image of this structure, no clear contrast between the edge and central part is observed, thus indicating that the wormlike structures are solid nanofibers. Moreover, the nanofibers have a large length/diameter ratio: they exhibit a uniform diameter of about 14 nm, and their length reaches tens of micrometers.

To understand the mechanism of the transformation from vesicles to nanofibers, a series of complexes with different PYR/RV ratios were prepared. When the PYR/RV ratio was 1:10, the vesicles broke into pieces of membranes (Figure S2 in the Supporting Information). As the PYR component increased, the membranes became longer and narrower. At a PYR/RV ratio of 2:3, wormlike nanowires appeared, which coexisted with the membranes. When the PYR/RV ratio reached 1:1, uniform wormlike nanostructures were observed. It should be pointed out that further increases in the PYR/RV ratio did not bring any significant changes to the nanofibers. A plausible explanation is that when the PYR/RV molar ratio is larger than 1:1, all the RV molecules were complexed and therefore no further structural changes could be generated.

Since PYR is itself pH-responsive, we wondered if this property could be brought to the supramolecular amphiphile, and a 1.0×10^{-4} M solution of the PYR–RV complex in pH 10 buffer was prepared. Figure 1 d shows the self-assembled structures of the PYR–RV complex. Notably, the curly wormlike nanofibers were straightened. Contrary to the random wormlike nanofibers, the straight nanofibers prefer to hierarchically aggregate into bundles (Figure S3 in the Supporting Information). The diameter of the nanofibers is still about 14 nm, which is the same as that of the curly nanofibers, and suggests that the molecular packing framework should remain unchanged. When the pH value was changed to 9, the straight nanofibers became curly again, thus indicating that the process is reversible. At pH 9 and pH 10, the lengths of the nanofiber are nearly the same, ranging from about several micrometers to about 20 micrometers.

The formation of nanofibers relies on appropriate molecular packing and specific directional noncovalent interactions, such as π–π interactions and hydrogen bonding.[7] We used different characterization techniques to help elucidate how the nanofibers are formed. We specifically wished to identify whether Coulombic attractions and charge-transfer interactions were the dominant driving force in the formation of the complex between viologen groups and PYR molecules. We also wanted to examine the viologen–PYR packing motif that favors the one-dimensional nanostructures. Considering the low solubility of the PYR–RV complex, we synthesized methyl viologen (MV) as a model compound to investigate the complex formation between the viologen group and the PYR molecule. MV (an electron acceptor) and PYR (an electron donor) were mixed in water in a 1:1 ratio, and the resulting spectroscopic changes were observed. Both the fluorescence quenching in the emission spectra and the red shifts of the peaks in the UV/Vis spectra are indicative of charge-transfer complex formation (Figure S4 in the Supporting Information). Furthermore, mass spectroscopy supports the formation of charge-transfer complex between MV and PYR. A peak at m/z 641.02 is observed, which corresponds to the PYR^{3-}–MV^{2+} complex (Figure S5 in the Supporting Information), and indicates that PYR and MV indeed form a charge-transfer complex with 1:1 stoichiometry, thus supporting the previously reported assumption.[6]

^{1}H NMR spectroscopy was used to provide information on the intermolecular interactions that occur during complex formation. As shown in Figure 2 a, upon formation of the charge-transfer complex, it was observed that all the resonances of the protons on MV and PYR were shifted upfield. It is noted that the protons at the center of the molecule exhibited larger shifts than those at the edges of molecules (Figure S7 in the Supporting Information). This effect arises from the aromatic π electrons that are situated above or below the respective protons, thus strongly suggesting the face-to-face packing of PYR and MV. Interestingly, for PYR, the central protons adjacent to the hydroxy group exhibit larger shifts than those near the sulfonate groups. This effect possibly occurs because the sulfonate groups are electron-withdrawing and thus have a local effect as well as reducing the electron-donating properties of the PYR unit as a whole. This effect could lead to reduced interaction with the MV units at these positions, and therefore the reduced shift. The packing fashion could be further confirmed by nuclear Overhauser effect spectroscopy (NOESY), since the typical distance between the charge-transfer donor and acceptor is 3–5 Å, which is in the detectable range of NOE signals. As shown in Figure 2 b, the cross-peaks m2–p4 and m1–p6 were observed, which are consistent with our packing model in which PYR and MV adopt a one-dimensional face-to-face packing feature.

To more directly understand the packing structure on the basis of intermolecular interactions, a single crystal of the complex was successfully grown. As shown in Figure 3, the asymmetric unit contains one PYR^{3-} ion, one MV^{2+} ion, one Na^+ ion, and six water molecules. The overall PYR^{3-}/MV^{2+}

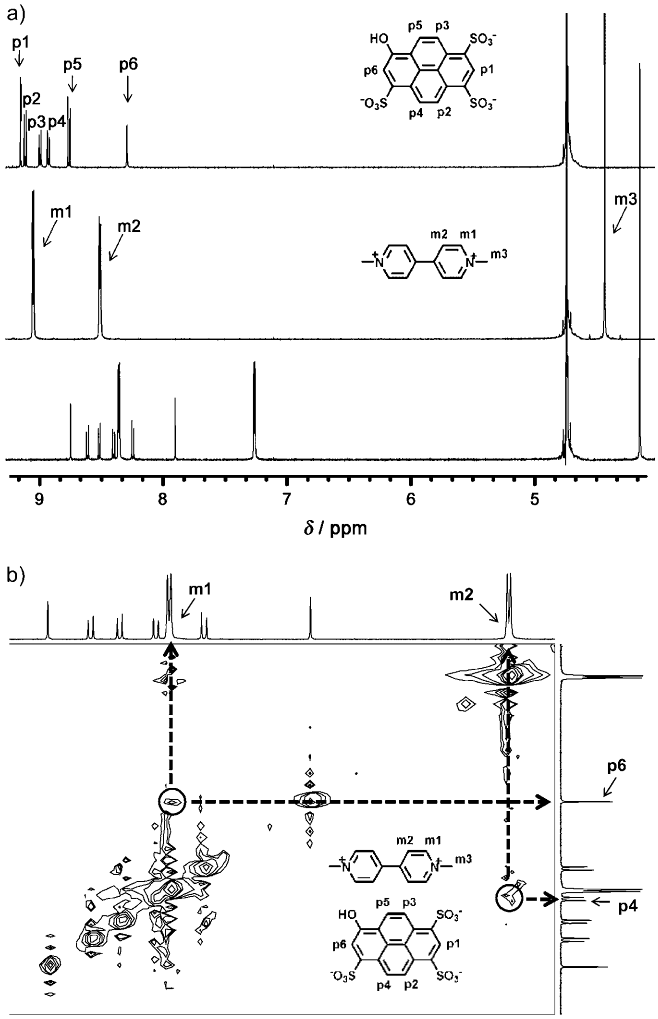

Figure 2. a) ^1H NMR spectra (D_2O) of PYR, MV, and PYR–MV; b) NOESY spectrum (D_2O) of PYR–MV.

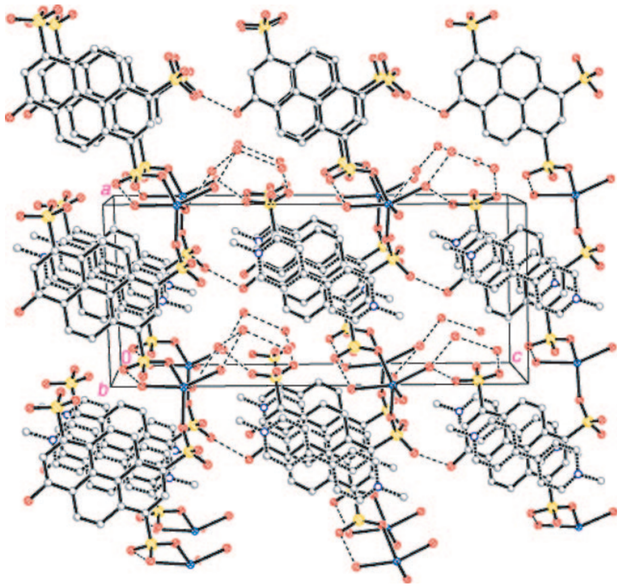

Figure 3. Packing view of a single crystal of the PYR–MV complex. Solid bonds PYR; dashed bonds MV; dashed line hydrogen bonding; black C; red O; blue N, Na; yellow S.

stoichiometry is 1:1, which further confirms the formation of a specific 1:1 charge-transfer complex. The PYR and MV molecules are arranged in alternating layers that are almost parallel, thus confirming the tilted face-to-face packing motif. The distance between the donor and acceptor molecules is about 3.5 Å, which suggests strong donor–acceptor interactions between PYR and MV.

After resolution of the structure, we could determine whether Coulombic attractions or charge-transfer interactions were the dominant driving force for the complex formation. For a long time, the formation of charge-transfer complexes was thought to be simply driven by Coulombic attractions. However, this assumption cannot explain all the experimental results, for example, the 1:1 face-to-face packing and ultralong nanofiber formation. To investigate the complex formation, isothermal titration calorimetry (ITC) experiments were performed. As shown in Figure 4, diaminodiphenyl hydrochloride (BN) was chosen as a control compound. BN and MV have the same charges and similar molecular structures, so they should have similar Coulombic attractions with PYR. However, BN is not a good electron acceptor, so there should be no charge-transfer interactions between BN and PYR. By comparing the binding constants of PYR–BN and PYR–MV, we were able to deduce the interaction that is the dominant driving force. As shown in Figure 4, the binding constant (K_1) of PYR–BN is about $1280\,\text{M}^{-1}$. In contrast, PYR and MV exhibit strong interactions and the binding constant (K_2) is about $1\times10^4\,\text{M}^{-1}$, which is consistent with the value calculated from the emission spectra. According to the energy terms, the Gibbs free energy ΔG is proportional to $\ln K$. Therefore, the Gibbs free energy change of the PYR–BN system is still about 75 % of that of the PYR–MV system. By assuming a linear free-energy relationship, which is a commonly applied assumption, the interaction is calculated to be 75 % electrostatic and 25 % charge transfer. The results indicate that although the Coulombic attraction is the main driving force, charge-transfer interaction also plays an important role.

With the face-to-face packing fashion in mind, we tried to explain the transformation mechanism between vesicles and nanofibers. We proposed that PYR molecules complex with viologen headgroups to form one dimensional face-to-face stacking arrays. Therefore, the curvature may become rigid and oriented, and the length/diameter ratio becomes larger. Finally, at the 1:1 stoichiometry, when almost all the viologen groups are complexed, uniform ultralong nanofibers are obtained. In the nanofiber, the soft alkyl chain prefers to stay in the interiors because of its hydrophobic nature. The rigid and hydrophilic PYR–viologen arrays lie on the surface of the nanofiber. In addition, the pH increase would increase the ionization of the hydroxy group on PYR. Therefore, the electric charges of the PYR–viologen arrays on the surface of the nanofibers increase, which results in an enhancement of the charge repulsion. The repulsive forces at the nanofiber surface also increase, thus inducing the transformation from curly nanofibers to straight nanofibers.

In conclusion, ultralong nanofibers are obtained from a supramolecular amphiphile based on a water-soluble charge-transfer complex with a 1:1 PYR/MV stoichiometry. The

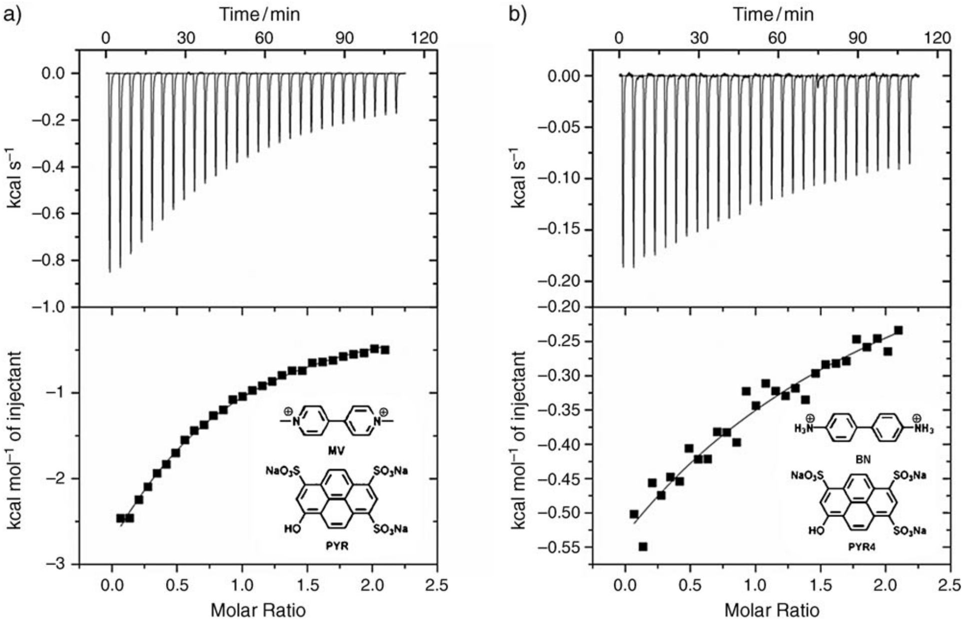

Figure 4. ITC binding experiment. Titration of a) MV and b) BN into a solution of PYR (1×10^{-4} M) with 20×10 µL aliquots at $T=25$ °C in pH 3 buffer solution.

formation of the complex is driven by combined interactions including Coulombic attractions, charge-transfer interactions, and the hydrophobic effect. The straightness of the nanofiber can be tuned by changing the pH of the system. Compared with conventional materials based on charge-transfer complexes, the easy and environmentally friendly preparation of the water-soluble charge-transfer complex is advantageous. It is hoped that such a method may be extended to fabricate tunable self-assembling materials for electronic and optoelectronic devices. Moreover, it could be used as a model system for understanding amyloid fibril formation and neurodegenerative diseases.

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[1] a) D. S. Acker, R. J. Harder, W. R. Hertler, W. Mahler, L. R. Melby, R. E. Bensin, W. E. Mochel, *J. Am. Chem. Soc.* **1960**, *82*, 6408; b) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Bensin, W. E. Mochel, *J. Am. Chem. Soc.* **1962**, *84*, 3374; c) J. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948.

[2] a) R. Keller-Griffith, H. Ringsdorf, *Colloid Polym. Sci.* **1986**, *264*, 924–935; b) H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **1988**, *100*, 117; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113; c) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.–W. Spiess, S. D. Hudson, H. Duan, *Nature* **2002**, *419*, 384; d) D. Janietz, *J. Mater. Chem.* **1998**, *8*, 265; e) M. Manickam, M. Belloni, S. Kumar, S. V. Varshney, D. S. S. Rao, P. R. Ashton, J. A. Preece, N. Spencer, *J. Mater. Chem.* **2001**, *11*, 2790; f) N. Tchebotareva, K. Müllen, *J. Am. Chem. Soc.* **2003**, *125*, 9734; g) E. Peeters, P. A. Van Hal, S. C. J. Meskers, R. A. J. Janssen, E. W. Meijer, *Chem. Eur. J.* **2002**, *8*, 4470; h) K. Naka, H. Itoh, Y. Chujo, *Langmuir* **2003**, *19*, 5496; i) E. H. A. Beckers, S. C. J. Meskers, A. P. H. Schenning, Z. J. Chen, F. Würthner, P. Marsal, D. Beljonne, J. Cornil, R. A. J. Janssen, *J. Am. Chem. Soc.* **2006**, *128*, 649; j) K. Xiao, I. N. Ivanov, A. A. Puretzky, Z. Liu, D. B. Geohegan, *Adv. Mater.* **2006**, *18*, 2184.

[3] a) S. Cui, Y. L. Li, Y. B. Guo, H. B. Liu, Y. L. Song, J. L. Xu, J. Lv, M. Zhu, D. B. Zhu, *Adv. Mater.* **2008**, *20*, 309; b) H. L. Peng, C. B. Ran, Z. F. Liu, Y. Z. Long, Z. M. Wang, Z. Q. Yu, H. L. Sun, Y. G. Wei, S. Gao, Z. J. Chen, E. Q. Chen, *J. Phys. Chem. C* **2008**, *112*, 11001; c) S. Wan, J. Guo, J. Kim, H. Ihee, D. L. Jiang, *Angew. Chem.* **2008**, *120*, 8958; *Angew. Chem. Int. Ed.* **2008**, *47*, 8826; d) L. Wang, J. Kim, T. Ishizuka, Y. Honsho, A. Saeki, S. Seki, H. Ihee, D. L. Jiang, *J. Am. Chem. Soc.* **2009**, *131*, 7287.

[4] a) H. B. Liu, J. B. Li, C. S. Lao, C. S. Huang, Y. L. Li, Z. L. Wang, D. B. Zhu, *Nanotechnology* **2007**, *18*, 495704; b) S. Cui, H. B. Liu, L. B. Gan, Y. L. Li, D. B. Zhu, *Adv. Mater.* **2006**, *18*, 2918; c) Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S Seki, S. Tagawa, M. Taniguchi, T. Kawai, T. Aida *Science* **2006**, *314*, 1761; d) T. Akutagawa, T. Ohta, T. Hasegawa, T. Nakamura, C. Christensen, J. Becher, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5028.

[5] a) E. B. De Borba, C. L. C. Amaral, M. J. Politi, R. Villalobos, M. S. Baptista, *Langmuir* **2000**, *16*, 5900; b) P. P. Neelakandan, M. Hariharan, D. Ramaiah, *J. Am. Chem. Soc.* **2006**, *128*, 11334; c) S. Gamsey, A. Miller, M. M. Olmstead, C. Beavers, L. C. Hirayama, S. Pradhan, R. A. Wessling, B. Singaram, *J. Am. Chem. Soc.* **2007**, *129*, 1278; d) R. Sasaki, S. Murata, *Langmuir* **2008**, *24*, 2387.

[6] a) Y. P. Wang, H. P. Xu, X. Zhang, *Adv. Mater.* **2009**, *21*, 2489; b) Y. P. Wang, N. Ma, Z. Q. Wang, X. Zhang, *Angew. Chem.* **2007**, *119*, 2881; *Angew. Chem. Int. Ed.* **2007**, *46*, 2823; c) C. Wang, S. C. Yin, S. L. Chen, H. P. Xu, Z. Q. Wang, X. Zhang, *Angew. Chem.* **2008**, *120*, 9189; *Angew. Chem. Int. Ed.* **2008**, *47*, 9049; d) T. M. Hermans, M. A. C. Broeren, N. Gomopoulos, A. F. Smeijers, B. Mezari, E. N. M. Van Leeuwen, M. R. J. Vos, P. C. M. M. Magusin, P. A. Hilbers, M. H. P. Van Genderen, N. A. J. M. Sommerdijk, G. Fytas, E. W. Meijer, *J. Am. Chem. Soc.* **2007**, *129*, 15631; e) Y. J. Jeon, P. K. Bharadwaj, S. Choi, J. W. Lee, K. Kim, *Angew. Chem.* **2002**, *114*, 4654; *Angew. Chem. Int. Ed.* **2002**, *41*, 4474; f) X. Zhang, Z. J. Chen, F. Würthner, *J. Am. Chem. Soc.* **2007**, *129*, 4866.

[7] a) F. M. Menger, *Angew. Chem.* **1991**, *103*, 1104; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1086; b) B. Song, S. L. Chen, Z. Q. Wang, X. Zhang, *Adv. Mater.* **2007**, *19*, 416; c) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491; d) T. Shiraki, M. Morikawa, N. Kimizuka, *Angew. Chem.* **2008**, *120*, 112; *Angew. Chem. Int. Ed.* **2008**, *47*, 106; e) L. C. Palmer, S. I. Stupp, *Acc. Chem. Res.* **2008**, *41*, 1674; f) B. K. Cho, H. J. Kim, Y. W. Chung, B. I. Lee, M. Lee, *Adv. Polym. Sci.* **2008**, *219*, 69; g) A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644; h) S. Lenhert, L. Zhang, J. Mueller, H. P. Wiesmann, G. Erker, H. Fuchs, L. Chi, *Adv. Mater.* **2004**, *16*, 619.