Self-Assembly

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Superamphiphiles Based on Directional Charge-Transfer Interactions: From Supramolecular Engineering to Well-Defined Nanostructures**

*Kai Liu, Chao Wang, Zhibo Li, and Xi Zhang**

Dedicated to Professor Jiacong Shen on the occasion of his 80th birthday

Superamphiphiles are amphiphiles that are formed on the basis of noncovalent interactions,[1] which may include π–π interactions,[2] hydrogen bonding,[3] charge-transfer interactions,[4] and electrostatic interactions.[5] Superamphiphiles with various architectures can be fabricated, and they can be either small organic molecules or polymers. Because superamphiphiles are synthesized through noncovalent interactions, time-consuming organic synthesis can be avoided to some extent. In addition, building blocks with functional moieties, can be easily incorporated into the superamphiphiles, thus allowing for the fabrication of functional supramolecular nanostructures.[6] Among the various noncovalent interactions that can be used as driving forces for the fabrication of superamphiphiles, charge-transfer interactions between electron-deficient and electron-rich building blocks are especially attractive. The face-to-face packing mode in the charge-transfer complex facilitates the formation of one-dimensional nanostructures.

An interesting aspect is that some charge-transfer complexes are highly directional.[7] For example, naphthalene diimide and naphthalene[8] prefer a face-centered packing arrangement, in which the long axes of the two aromatic rings are nearly parallel.[9] Using this unique feature, we attempted to employ this directional charge-transfer interaction to fabricate superamphiphiles of various architectures and to establish the relationship between molecular and supramolecular structures, thus leading to further development of supramolecular engineering. Different building blocks were designed and synthesized, as shown in Figure 1. These include bolaamphiphiles that contain electron-rich naphthalene (BNAPH and IBNAPH) and electron-deficient naphthalene diimide (BNDI) groups. BNAPH and IBNAPH refer to the 1,5- and 2,6-substitutions, respectively. It was hypothesized that when BNDI was complexed with BNAPH, an X-shape superamphiphile would be formed, and the self-assembly of this superamphiphile would lead to one-dimensional nanostructures, because of the face-centered packing of naphthalene and naphthalene diimide and the 1,5-substitution of the

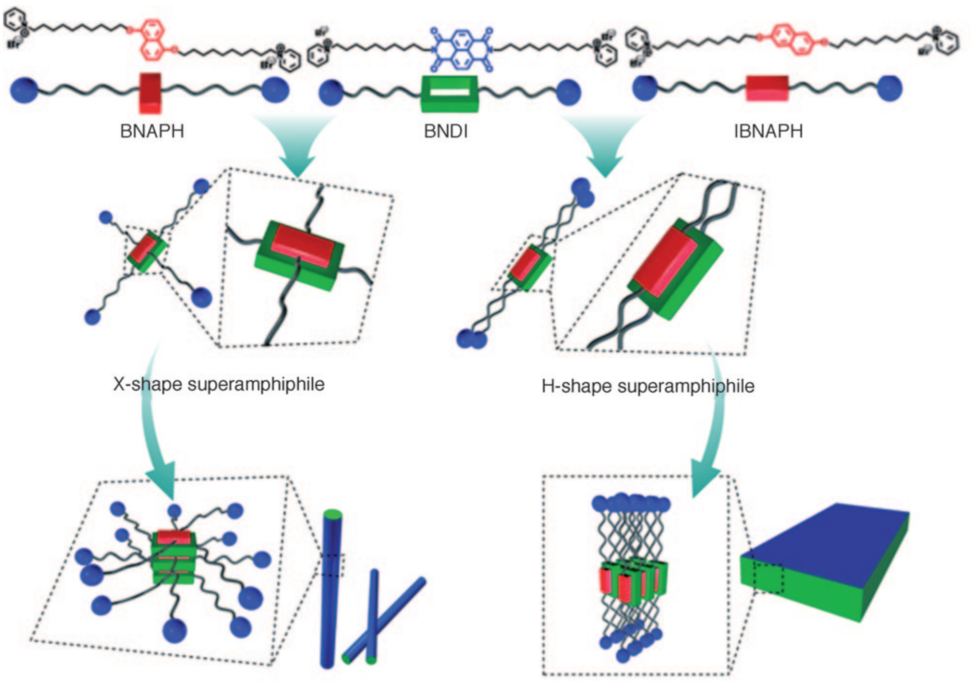

Figure 1. Schematic representation of the X- and H-shape superamphiphiles and their assembly into one-dimensional and two-dimensional nanostructures, respectively.

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[*] K. Liu, C. Wang, Prof. X. Zhang
Key Lab of Organic Optoelectronics & Molecular Engineering
Department of Chemistry, Tsinghua University
Beijing 100084 (China)
Fax: (+86) 10-6277-1149
E-mail: xi@mail.tsinghua.edu.cn
Prof. Z. B. Li
Institute of Chemistry, Chinese Academy of Sciences (China)

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two alkyl chains on the naphthalene. However, the complexation of BNDI and IBNAPH would form an H-shape superamphiphile for the 2,6-substitution of the two alkyl chains on the naphthalene, which favors the formation of two-dimensional membranes.

We wanted to understand how the building blocks themselves self-assemble in water before complexation. From Figure 2a, it can be seen that the critical micelle concentration (CMC) of the BNDI was determined to be 3.1×10^{-4} M using concentration-dependent conductivity. Cryo-TEM images, as shown in Figure 2b, indicate that the BNDI self-assembles into one-dimensional nanostructures with a diameter of 3.5 nm (see Figure S1a in the Supporting Information). There is no sharp contrast between the periphery and central parts, thus indicating that the one-dimensional nanostructures are solid nanofibers. Similarly, the CMC of BNAPH was determined to be 9.0×10^{-4} M, which is shown in Figure 2c. In addition, it was found that BNAPH forms micellar aggregates (Figure 2d) with a diameter of about 14.7 nm (Figure S1b).

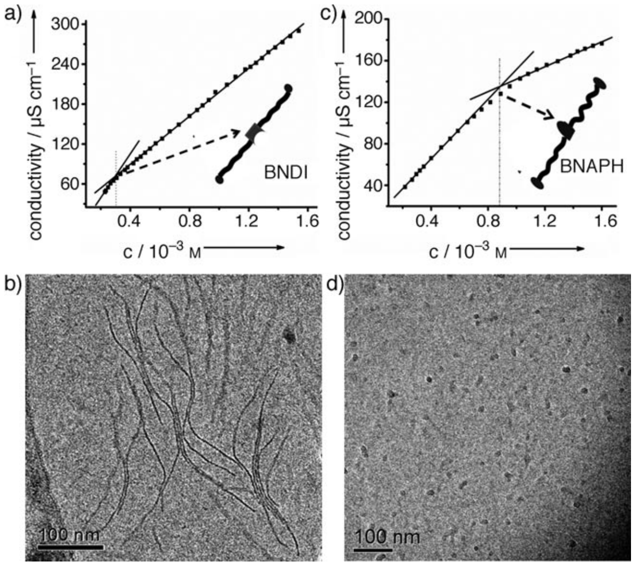

Figure 2. The concentration-dependent conductivity of a) BNDI and c) BNAPH; cryo-TEM images of b) BNDI, d) BNAPH. The CMCs were determined to be 3.1×10^{-4} M and 9.0×10^{-4} M, for BNDI and BNAPH, respectively. The solution concentrations for the cryo-TEM experiments were 1.0×10^{-3} M for BNDI, and 2.0×10^{-3} M for BNAPH.

To confirm that BNDI and BNAPH form charge-transfer complexes, we have carried out UV/Vis absorption, fluorescence emission, and temperature-dependent ^{1}H NMR spectroscopic measurements to provide evidence. BNDI and BNAPH were mixed in water at a 1:1 ratio; the resulting solution had a plum color, which is typical of the naphthalene diimide–naphthalene charge-transfer complex (Figure 3a). A new and broad absorption band between 450 nm and 700 nm was detected after complexation, which is a characteristic of charge-transfer interactions (Figure 3b). In addition, both the fluorescence emission of naphthalene diimide and naphthalene were quenched after complexation (Figure S2). As the temperature was increased, both protons on the naphthalene diimide and naphthalene aromatic groups underwent downfield resonance shifts after being complexed. Thus, this observation indicated the charge-transfer interactions between the two aromatic groups were weakened (Figure S3 and Chart S1). All these data indicate that naphthalene diimide and naphthalene form charge-transfer complexes,[7-9] which are responsible for the formation of the superamphiphile.

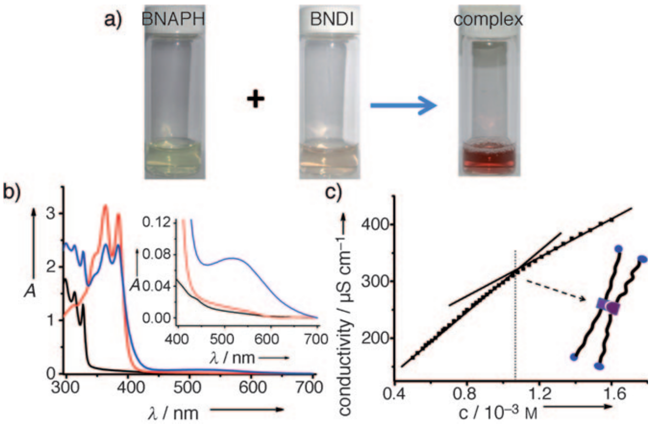

Figure 3. a) Photographs of the BNAPH, BNDI, and BNDI–BNAPH 1:1 complex solutions showing their colors. The concentrations of BNDI and BNAPH were both 2.0×10^{-3} M. b) UV/Vis absorption spectra of BNDI (red), BNAPH (black), and the BNDI–BNAPH 1:1 complex (blue). The concentrations of BNDI and BNAPH were both 2.0×10^{-3} M. Inset: Magnification of the charge-transfer band. c) Concentration-dependent conductivity of the BNDI–BNAPH 1:1 complex. The CMC of the BNDI–BNAPH complex was determined to be 1.1×10^{-3} M.

We have observed that the concentration-dependent conductivity of a BNDI–BNAPH superamphiphile is different from that of the BNDI and BNAPH amphiphiles. From Figure 3c, it can be seen that a new transition point appears at a concentration of 1.1×10^{-3} M, which corresponds to the CMC of the superamphiphile formed by charge-transfer complexes of BNDI and BNAPH. It should be noted that the CMC of the superamphiphile is higher than that of the two building blocks (3.1×10^{-4} M and 9.0×10^{-4} M, respectively). The enhanced CMC of the superamphiphile can be explained by a decreased area of the hydrophobic part and an increased area of the hydrophilic part, therefore changing its amphiphilicity.

To test whether the superamphiphiles formed between BNDI and BNAPH are X-shaped, we used ^{1}H NMR spectroscopy and nuclear Overhauser effect spectroscopy (NOESY) to gain structural information.[7-9] From Figure 4a, it can be seen that all the resonances of the protons on naphthalene and naphthalene diimide were shifted upfield. The protons of n1, n2, and n3 underwent much larger resonances shifts compared with that of m1 (Figure S4), hence suggesting that the protons of naphthalene are located at the center of the charge-transfer complex, while those of the naphthalene diimide are located at the edge.[4b] Considering that the surface area of naphthalene diimide is larger than naphthalene, a face-centered stacking geometry is

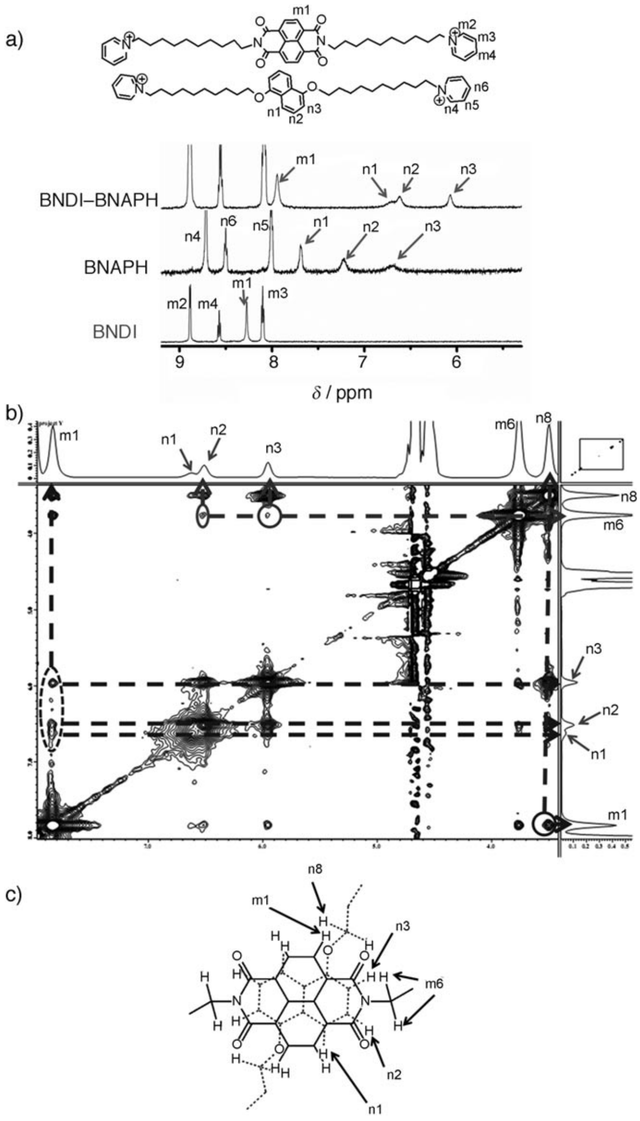

Figure 4. a) ^{1}H NMR spectra of the BNDI–BNAPH complex, BAPH, and BNDI in D_2O solutions. b) 2D NOESY spectrum of the BNDI–BNAPH complex in a D_2O solution. c) Proposed packing arrangement of naphthalene and naphthalene diimide in a charge-transfer complex (some protons that displayed NOE effects are marked).

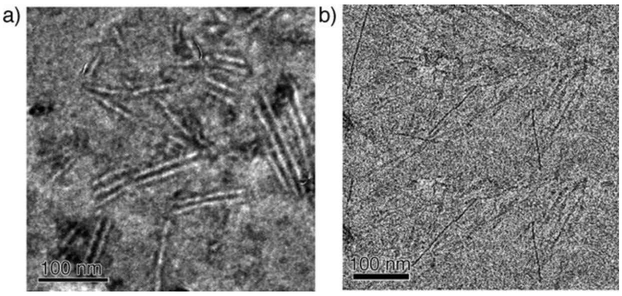

Figure 5. a) TEM and b) cryo-TEM images of the BNDI–BNAPH assembly. The solution concentrations for the TEM experiments were 4.0×10^{-3} M for both BNDI and BNAPH.

proposed (Figure 4c). In addition, the resonance shifts of n2 and n3 are nearly equal and indicate that the two protons in the charge-transfer complex are in a similar environment, which further supports the face-centered packing arrangement. We further confirmed face-centered stacking geometry using NOESY. From Figure 4b, it can be seen that the cross-peaks of the protons on naphthalene and naphthalene diimide, that is, m1–n1, m1–n2, and m1–n3, indicate the close contact of the two aromatic rings, because the detectable limit of NOE signals was less than 5 Å. In addition, the cross-peaks m1–n8, m6–n2, and m6–n3 strongly suggest the face-centered packing arrangement, which is shown in Figure 4c. Therefore, the evidence indicates that the intended X-shape superamphiphile was formed.

Microscopy observations indicate that one-dimensional nanorods are formed by the self-assembly of the X-shape superamphiphiles of BNDI–BNAPH. As shown in Figure 5a, nanorods are seen clearly, however, we are not sure if the structure is influenced by negative staining of phosphotungstic acid. To arrive at convincing conclusions, we employed cryo-TEM to observe the assemblies, and as shown in Figure 5b, straight nanorods with a width of 3.7 nm indeed are formed. The straightness may arise from the face-centered packing of naphthalene and naphthalene diimide aromatic surfaces, which is highly directional and perpendicular to the aromatic surfaces.[8,9] The self-assemblies that can be formed by X-shape superamphiphiles of BNDI–BNAPH are different from the ones of the building blocks, BNDI and BNAPH, hence indicating that superamphiphiles can be used as building blocks for the fabrication of highly-ordered structures.

To understand if well-defined nanostructures can be fabricated by rational design of molecular building blocks, we have replaced the 1,5-substituted naphthalene with 2,6-substituted naphthalene and comparatively studied the outcome. The CMC of the BNDI–IBNAPH superamphiphile was measured to be 1.1×10^{-3} M (Figure S7b), which is similar to that of the X-shape superamphiphile. From the Supporting Information it can be seen that we have employed different methods to confirm that BNDI and IBNAPH formed H-shape superamphiphiles based on their directional charge-transfer interactions. In contrast to the X-shape superamphiphile, this H-shape superamphiphile self-assembles into two-dimensional nanosheets, which can be seen in TEM (Figure 6a) and were confirmed by cryo-TEM (Figure 6b). The cryo-TEM is not as clear as expected because of the low contrast between the assembly and the icy layer. The formation of twodimensional nanosheets is also indicated clearly by AFM (Figure 6c). Section analysis of AFM images shows that the thickness of a single layer of the nanosheet is about 3.3 nm (Figure S11). In addition, XRD indicates the existence of a layered structure in the nanosheet with a *d* spacing of 3.45 nm (Figure 6d).

In conclusion, we have demonstrated the feasibility of obtaining well-defined nanostructures by using the supramolecular engineering of superamphiphiles. By elaborately tuning the structures of the building blocks, X-shape or H-shape superamphiphiles were successfully assembled, which can be used to create tunable supramolecular nanostructures. The preference for rod versus sheet formation should be a

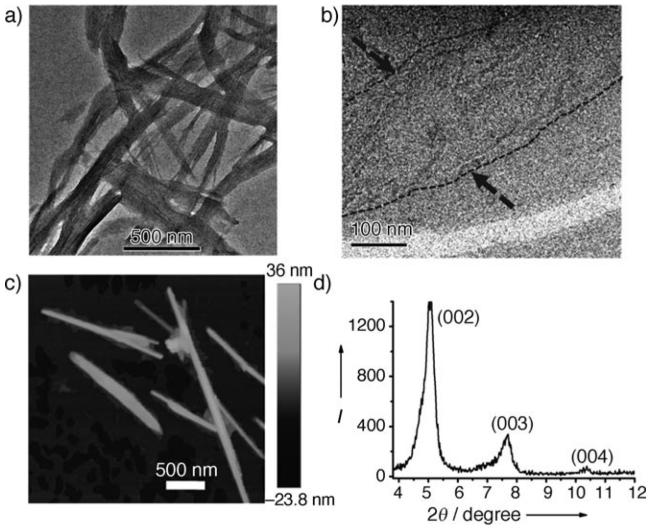

Figure 6. a) TEM, b) cryo-TEM (the contour of the assembly is marked by dotted lines), and c) tapping-mode AFM images of the BNDI–IBNAPH assembly; d) XRD scan of the BNDI–IBNAPH assembly. The concentrations of the solutions were 4.0×10^{-3} M for both BNDI and IBNAPH.

delicate balance between energetic contributions of tail orientation relative to the core units, deviations relative to the free energy minimum in the unaggregated state, and the relative free energy benefits obtained from the different aggregated structures. If the formation of superamphiphiles is regarded as a first-order self-assembly, it is probable that superamphiphiles can function as building blocks for the construction of highly-ordered assemblies by further second-order self-assembly. The advance of superamphiphiles will not only enrich the family of conventional amphiphiles that are formed based on covalent bonds, but will also provide a new bridge between the colloidal and supramolecular sciences. In addition, functional groups may be introduced into the superamphiphile and thus provide a new avenue for the assembly of functional supramolecular nanostructures.

Experimental Section

^{1}H NMR spectra were obtained by using a JOEL JNM-ECA300 apparatus and a JOEL JNM-ECA600 apparatus (for the temperature-dependent ^{1}H NMR and 2D NOESY spectra); ESI–MS spectra were recorded using a PE Sciex API 3000 apparatus.

UV/Vis spectra were measured using a HITACHI U-3010 spectrophotometer; fluorescence spectra were obtained by using a HITACHI F-7000 apparatus (slit: 5.0 nm, scanning rate: 240 nm min^{-1}).

AFM was performed using tapping-mode in air on a commercial multimode Nanoscope IVAFM. For sample preparation, a few drops of the solution were placed on a silicon surface and were incubated for 2 h under moist conditions; excess solution was removed by absorption onto filter paper and the sample was air-dried.

TEM measurements were carried out on a JEMO 2010 electron microscope operating at an acceleration voltage of 120 kV. The samples were prepared by drop-casting the aqueous solution on the carbon-coated copper grid and were then negatively stained with a uranyl acetate or phosphotungstic acid solution. Cryo-TEM samples were prepared in a controlled environment vitrification system (CEVS) at 28 °C. The vitrified samples were stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined by a JEM2200FS TEM (200 kV) at about −174 °C.

For XRD measurements, a few drops of the solution were placed on a silicon surface, and the solvent was evaporated at room temperature. The sample was used for XRD measurements. The Bragg peak λ was extracted from the XRD data and the layer thickness d could be obtained according to the Bragg equation $d=\lambda/2\sin\theta$, $\lambda=0.15405$ nm.

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[1] a) X. Zhang, C. Wang, *Chem. Soc. Rev.* **2011**, *40*, 94; b) Y. P. Wang, H. P. Xu, X. Zhang, *Adv. Mater.* **2009**, *21*, 2849.

[2] a) B. Song, Z. Q. Wang, S. L. Chen, X. Zhang, Y. Fu, M. Smet, W. Dehaen, *Angew. Chem.* **2005**, *117*, 4809; *Angew. Chem. Int. Ed.* **2005**, *44*, 4731; b) L. Zang, Y. Che, J. S. Moore, *Acc. Chem. Res.* **2008**, *41*, 1596; c) H. Shao, J. Seifert, N. C. Romano, M. Gao, J. J. Helmus, C. P. Jaroniec, D. A. Modarelli, J. R. Parquette, *Angew. Chem.* **2010**, *122*, 7854; *Angew. Chem. Int. Ed.* **2010**, *49*, 7688; d) H. Shao, T. Nguyen, N. C. Romano, D. A. Modarelli, J. R. Parquette, *J. Am. Chem. Soc.* **2009**, *131*, 16374; e) F. Würthner, *Chem. Commun.* **2004**, 1564; f) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491; g) J. K. Klosterman, Y. Yamauchi, M. Fujita, *Chem. Soc. Rev.* **2009**, *38*, 1714; h) X. Zhang, Z. J. Chen, F. Würthner, *J. Am. Chem. Soc.* **2007**, *129*, 4886; i) X. Zhang, S. Rehm, M. M. Safont-Sempere, F. Würthner, *Nat. Chem.* **2009**, *1*, 623; j) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; k) C. J. Zhong, W. S. V. Kwan, L. L. Miller, *Chem. Mater.* **1992**, *4*, 1423; l) S. Wan, J. Guo, J. Kim, H. Ihee, D. L. Jiang, *Angew. Chem.* **2008**, *120*, 8958; *Angew. Chem. Int. Ed.* **2008**, *47*, 8826; m) R. J. Li, W. P. Hu, Y. Q. Liu, D. B. Zhu, *Acc. Chem. Res.* **2010**, *43*, 529; n) Y. B. Wang, H. B. Fu, A. D. Peng, Y. S. Zhao, J. S. Ma, Y. Ma, J. N. Yao, *Chem. Commun.* **2007**, 1623; o) L. Jiang, X. Yao, H. X. Li, Y. Y. Fu, L. Chen, Q. Meng, W. P. Hu, L. Jiang, *Adv. Mater.* **2010**, *22*, 376; p) R. S. K. Kishore, O. Kel, N. Banerji, D. Emery, G. Bollot, J. Mareda, A. G-Casado, P. Jonkheijm, J. Huskens, P. Maroni, M. Borkovec, E. Vauthey, N. Sakai, S. Matile, *J. Am. Chem. Soc.* **2009**, *131*, 11106.

[3] a) N. Kimizuka, T. Kawasaki, T. Kunitake, *J. Am. Chem. Soc.* **1993**, *115*, 4387; b) N. Kimizuka, T. Kawasaki, K. Hirata, T. Kunitake, *J. Am. Chem. Soc.* **1998**, *120*, 4094; c) 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; d) R. J. Williams, A. M. Smith, R. Collins, N. Hodson, A. K. Das, R. V. Ulijn, *Nat. Nanotechnol.* **2009**, *4*, 19; e) P. D. Thornton, R. J. Mart, R. V. Ulijn, *Adv. Mater.* **2007**, *19*, 1252.

[4] a) 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; b) C. Wang, Y. S. Guo, Y. P. Wang, H. P. Xu, X. Zhang, *Angew. Chem.* **2009**, *121*, 9124; *Angew. Chem. Int. Ed.* **2009**, *48*, 8962; c) C. Wang, Y. S. Guo, Y. P. Wang, H. P. Xu, X. Zhang, *Chem. Commun.* **2009**, 5380.

[5] a) A. Harada, K. Kataoka, *Macromolecules* **1995**, *28*, 5294; b) A. V. Kabanov, S. V. Vinogradov, Y. G. Suzdaltseva, V. Y. Alakhov, *Bioconjugate Chem.* **1995**, *6*, 639; c) A. Harada, K. Kataoka, *Science* **1999**, *283*, 65; d) Y. P. Wang, P. Han, H. P. Xu, Z. Q. Wang, X. Zhang, A. V. Kabanov, *Langmuir* **2010**, *26*, 709.

[6] a) Y. P. Wang, N. Ma, Z. Q. Wang, X. Zhang, *Angew. Chem.* **2007**, *119*, 2881; *Angew. Chem. Int. Ed.* **2007**, *46*, 2823; b) C. Wang, Q. S. Chen, H. P. Xu, Z. Q. Wang, X. Zhang, *Adv. Mater.* **2010**, *22*, 2553; c) C. Wang, Q. S. Chen, Z. Q. Wang, X. Zhang, *Angew. Chem.* **2010**, *122*, 8794; *Angew. Chem. Int. Ed.* **2010**, *49*, 8612; d) S. K. M. Nalluri, B. J. Ravoo, *Angew. Chem.* **2010**, *122*, 5499; *Angew. Chem. Int. Ed.* **2010**, *49*, 5371; e) Y. Tang, L. P. Zhou, J. X. Li, Q. Luo, X. Huang, P. Wu, Y. G. Wang, J. Y. Xu, J. C. Shen, J. Q. Liu, *Angew. Chem.* **2010**, *122*, 4012; *Angew. Chem. Int. Ed.* **2010**, *49*, 3920; f) S-H. Hsu, M. D. Yilmaz, C. Blum, V. Subramaniam, D. N. Reinhoudt, A. H. Velders, J. Huskens, *J. Am. Chem. Soc.* **2009**, *131*, 12567.

[7] a) H. Ringsdorf, J. Venzmer, *Angew. Chem.* **1988**, *100*, 117; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 113; b) V. Percec, M. Glodde, T. K. Berra, 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; c) J. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948; d) 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; e) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Bensin, W. E. Mochel, *J. Am. Chem. Soc.* **1962**, *84*, 3374; f) S. Ghosh, S. Ramakrishnan, *Angew. Chem.* **2005**, *117*, 5577; *Angew. Chem. Int. Ed.* **2005**, *44*, 5441; g) S. Ghosh, S. Ramakrishnan, *Angew. Chem.* **2004**, *116*, 3326; *Angew. Chem. Int. Ed.* **2004**, *43*, 3264; h) X. Zhao, M.-X. Jia, X.-K. Jiang, L.-Z. Wu, Z.-T. Li, G.-J. Chen, *J. Org. Chem.* **2004**, *69*, 270; i) W. Pisula, M. Kastler, D. Wasserfallen, J. W. F. Robertson, F. Nolde, C. Kohl, K. Müllen, *Angew. Chem.* **2006**, *118*, 834; *Angew. Chem. Int. Ed.* **2006**, *45*, 819; j) A. Friggeri, O. Gronwald, K. J. C. Van Bommel, S. Shinkai, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2002**, *124*, 10754; k) Y. L. Liu, Y. Yu, J. Gao, Z. Q. Wang, X. Zhang, *Angew. Chem.* **2010**, *122*, 6726; *Angew. Chem. Int. Ed.* **2010**, *49*, 6576; l) Y. H. Ko, E. Kim, I. Hwang, K. Kim, *Chem. Commun.* **2007**, 1305.

[8] a) G. J. Gabriel, B. L. Iverson, *J. Am. Chem. Soc.* **2002**, *124*, 15174; b) J. Q. Nguyen, B. L. Iverson, *J. Am. Chem. Soc.* **1999**, *121*, 2639; c) V. J. Bradford, B. L. Iverson, *J. Am. Chem. Soc.* **2008**, *130*, 1517; d) J. J. Reczek, B. L. Iverson, *Macromolecules* **2006**, *39*, 5601; e) S. Bhosale, A. L. Sisson, P. Talukdar, A. Fürstenberg, N. Banerji, E. Vauthey, G. Bollot, J. Mareda, C. Röger, F. Würthner, N. Sakai, S. Matile, *Science* **2006**, *313*, 84; f) P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S. Kawano, N. Fujita, S. Shinkai, *Angew. Chem.* **2006**, *118*, 1622; *Angew. Chem. Int. Ed.* **2006**, *45*, 1592; g) J. G. Hansen, N. Feeder, D. G. Hailton, M. J. Gunter, J. Becherand, J. K. M. Sanders, *Org. Lett.* **2000**, *2*, 449; h) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond, J. K. M. Sanders, *Angew. Chem.* **2004**, *116*, 1993; *Angew. Chem. Int. Ed.* **2004**, *43*, 1959; i) S. V. Bhosale, C. H. Jani, S. J. Langford, *Chem. Soc. Rev.* **2008**, *37*, 331; j) H. Tanaka, S. Litvinchuk, D. H. Tran, G. Bollot, J. Mareda, N. Sakai, S. Matile, *J. Am. Chem. Soc.* **2006**, *128*, 16000; k) S. A. Vignon, T. Jarrosson, T. Iijima, H.-R. Tseng, J. K. M. Sanders, J. F. Stoddart, *J. Am. Chem. Soc.* **2004**, *126*, 9884; l) M. R. Molla, A. Das, S. Ghosh, *Chem. Eur. J.* **2010**, *16*, 10084.

[9] a) R. S. Lokey, B. L. Iverson, *Nature* **1995**, *375*, 303; b) M. S. Cubberley, B. L. Iverson, *J. Am. Chem. Soc.* **2001**, *123*, 7560; c) G. Koshkakaryan, L. M. Klivansky, D. Cao, M. Snauko, S. J. Teat, J. O. Struppe, Y. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 2078; d) J. J. Reczek, K. R. Villazor, V. Lynch, T. M. Swager, B. L. Iverson, *J. Am. Chem. Soc.* **2006**, *128*, 7995; e) D. G. Hamilton, J. E. Davies, L. Prodi, J. K. M. Sanders, *Chem. Eur. J.* **1998**, *4*, 608.