Self-Assembly

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Supramolecular Hydrogels and High-Aspect-Ratio Nanofibers through Charge-Transfer-Induced Alternate Coassembly**

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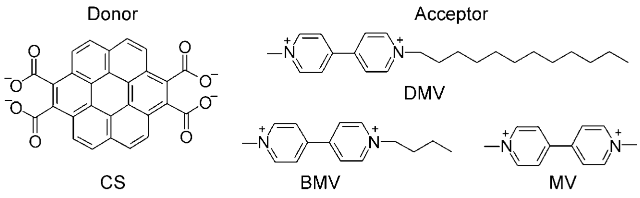
Weak charge-transfer interactions between electron-rich and electron-deficient aromatic molecules[1] have been extensively used for the design of various supramolecular assemblies in solution, such as rotaxanes,[2] catenanes,[3] and foldamers.[4] The conformation of various donor–acceptor (D–A) polymers in solution has been tuned by charge-transfer interactions in synergy with either solvophobic[5] or ion-binding[6] interactions. In addition, extended solid-phase assemblies of alternate donor and acceptor molecules for device applications were attained by cocrystallization[7] and liquid-crystalline mesophase coassembly.[8] Columnar mesophases of alternate donor and acceptor molecules have enhanced columnar organization and higher charge-carrier mobilities compared to their individual components.[8d] 1D self-assembled nanowires based on organic π-conjugated systems have attracted a great deal of attention in recent years in the field of organic and supramolecular electronics.[9,10] Several approaches, which make use of hydrogen-bonding and π-stacking interactions, have been used to design self-assembled fibers of donor–acceptor arrays, and create supramolecular p–n heterojunctions for photovoltaics.[11] However, use of charge-transfer interactions for the design of two-component, alternate 1D supramolecular fibers of donor and acceptor molecules in solution is difficult to achieve, as the orthogonal self-assembly (phase separation) of individual components may prevent their efficient coassembly, and hence a careful design of monomers is required.[8f,12] 1D charge-transfer nanofibers are expected to exhibit better conductivity caused by the directional movement of their high-density charge carriers and a well-ordered, stronger π-stacked architecture as a result of better π overlapping of face-to-face-packed aromatic molecules.[8f,13] These observations prompted us to investigate whether nanofibers of alternate donor and acceptor molecules coassembled through charge-transfer interactions can be constructed using supramolecular chemistry design principles. Herein, we show that high-aspect-ratio cylindrical micelles and hydrogels of a donor–acceptor charge-transfer complex can be constructed by self-assembly in water. Although a variety of peptide[14] and rod–coil[15] amphiphiles, as well as sugar derivatives,[16] have been reported to form hydrogels,[17] this is the first report of hydrogel formation that exploits charge-transfer interactions between chromophores.

We synthesized a donor–acceptor pair, a coronene tetracarboxylate tetrapotassium salt (CS), and a dodecyl-functionalized methyl viologen derivative (DMV) for the design of coassembled nanostructures (Scheme 1). After benzene, coronene is the simplest sixfold symmetrical aromatic molecule. Diimide, tetraester, and imidoester derivatives of coronene are known to be liquid crystalline, with high thermal and air stability.[18] Strong intermolecular interactions between the extended planar aromatic cores of these derivatives are expected to result in higher charge-carrier mobilities and hence can emerge as an alternative to the well-studied class of perylene bisimide (PBI) molecules for potential electron-transport materials.[19] We have recently reported the use of CS for the noncovalent functionalization and solubilization of graphene through charge-transfer (CT) interactions.[20] We selected CS as the aromatic donor molecule in this study since it is highly soluble in water and shows blue emission ($\lambda_{max} = 435$ nm). We selected viologen derivatives as the electron acceptor counterpart as these derivatives are well-known electron acceptors and have been extensively used for the design of stimuli-responsive supramolecular systems.[21] Hence, the unsymmetric amphiphile DMV was used as the acceptor molecule, which would not only allow CT interactions with coronene, but also trigger the self-assembly of the resultant D–A pair through hydrophobic interactions. In addition, we have used both the butyl methyl



Scheme 1. Molecular structures of aromatic donor (CS) and acceptors (DMV, BMV, and MV).

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viologen derivative BMV and methyl viologen MV as model compounds in order to gain a deeper insight into the molecular arrangement of the chromophores in the D–A pair. CS was synthesized by a twofold oxidative benzogenic Diels–Alder reaction of perylene with *N*-ethyl maleimide and subsequent hydrolysis with KOH in methanol.[22] DMV and BMV were synthesized according to literature procedures.[22] The charge-transfer interactions of CS with viologens were studied by optical spectroscopy, NMR, and single-crystal X-ray crystallography. Self-assembly of D–A pairs were characterized by AFM, field-emission scanning electron microscopy (FE-SEM), and TEM.

To examine the feasibility of CT interactions between CS and viologens, we carried out detailed optical spectroscopic measurements. Since the acceptor amphiphile DMV self-assembles in water (as evident from dynamic light scattering studies, see below), all donor–acceptor mixtures were prepared by the injection of a solution of DMV in methanol (in which the viologens do not interact), to an aqueous solution containing free CS molecules (the resulting solution contained 10% v/v methanol in water). Although this sample preparation method was followed to ensure the efficient formation of D–A complexes, further optical spectroscopic studies showed that DMV self-assembly in water was sufficiently dynamic to reorganize and form D–A CT complexes upon addition of CS molecules.[22] The absorption spectrum of CS (10% v/v methanol in water, 1×10^{-4} M) exhibits a strong absorption at 314 nm and a weak band at 351 nm, which is characteristic of noninteracting anionic coronene molecules.[20,22] A noticeable red shift of the CS absorption maxima (ca. 5 nm with one equivalent of DMV) with a concomitant decrease in the absorbance and a broadening of the absorption band was observed with increasing DMV concentration,[22] thus indicating a strong ground-state intermolecular interaction between donor and acceptor molecules. Moreover, the absorption changes were accompanied by the appearance of a new weak, broad band centered around 500 nm, which unambiguously proves the occurrence of CT interactions between CS and DMV.[22] Remarkably, the intensity of this red-shifted absorption was more prominent after the addition of one equivalent of DMV, thus suggesting a 1:1 stoichiometry for the D–A complexes.[23] Further evidence for CT interactions is provided by fluorescence measurements, which show significant quenching of the coronene emission in the CS–DMV mixtures.[22] Although CS shows intense blue fluorescence with emission maxima at 435 nm and 462 nm, the emission intensity of the mixture containing 1 equivalent of DMV is reduced by a factor of 10. The changes in absorption and emission properties upon CT complex formation could also be easily visualized with the naked eye.[22] Spectroscopic studies in buffer solutions (pH 9) have shown similar changes to those described above.[22]

Since the 1:1 CS–DMV CT complex structurally resembles a noncovalent amphiphile with polar ionic groups on one end and a hydrophobic dodecyl chain on the other, a typical surfactant-like self-assembly of a higher order between the CT complexes can be envisaged to occur in water. Appearance of scattering-induced changes in the absorption spectrum upon formation of CT complexes together with light scattering experiments, which showed a broad distribution curve, provided preliminary evidence of higher-order aggregates in solution.[22] Remarkably, a gradual increase in the concentration of a 1:1 CS–DMV CT complex makes the solution visibly viscous and finally results in a transparent, dark-red hydrogel (Figure 1 a). In a typical gelation experiment, an aqueous solution of the CS–DMV complex was heated until the components no longer interacted, and the solution was recooled to room temperature. The gel was formed within a few minutes, as confirmed by the inverted vial method (the critical gel concentration of the CS–DMV hydrogel was 7.96 mM). AFM analysis of the CS–DMV hydrogel showed the formation of an entangled network of very long fibers 10–15 μm in length and 100–300 nm in diameter (Figure 1 b). The hydrogels thus formed were stable for several months and showed the characteristic CT absorption at 500 nm, whereas fluorescence was quenched completely (Figure 1 c), thus indicating that the gel fibers are indeed formed by 1D assembly of CT complexes.

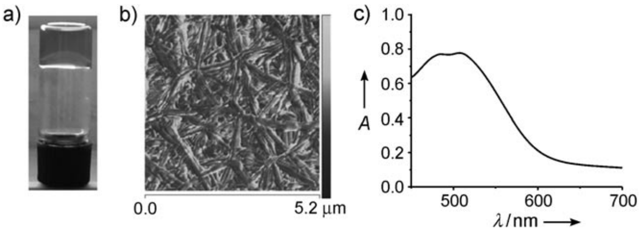

Figure 1. Physical appearance and characterization of CS–DMV hydrogels (7.9 mM). a) Photograph of the hydrogel, b) phase AFM image of the gel on a glass substrate, and c) absorption spectrum showing the CT band of the gel measured in a 1 mm cuvette.

To obtain a better insight into CT interactions and the molecular organization of coronene and viologens in the self-assembled CT complexes, two model compounds MV and BMV were synthesized and their interaction with CS were studied by both NMR spectroscopy and single-crystal X-ray diffraction. Strong CT interactions of both MV and BMV with CS became evident from optical spectroscopic studies, which showed absorption and fluorescence changes similar to those of DMV (see above).[22] Decisive proof for charge-transfer interactions is provided by ^{1}H NMR studies of the model viologen (MV) with CS in D_2O. As shown in Figure 2 a, all aromatic proton signals of the acceptor MV (H_{MV1} and H_{MV2}) undergo a significant upfield shift upon formation of the CT complex. Interestingly, the central protons of MV (H_{MV2}) are significantly upfield-shifted (from $\delta = 8.45$ to 3.89 ppm) relative to the terminal protons (H_{MV1}) (from $\delta = 8.98$ to 6.47 ppm), thus suggesting a face-to-face stacking for the donor and acceptor molecules. The aromatic π electrons of CS therefore induce a pronounced shielding of H_{MV2}. At the same time, closely associated doublets of the coronene aromatic protons (H_{CS1} and H_{CS2}) also undergo a similar, albeit smaller, upfield shift (around 1 ppm), which leads to well separated doublets ($\delta = 8.18$ and 7.97 ppm) upon interaction with MV. Face-to-face stacking in CT complexes could be further supported by NOESY experiments, which showed

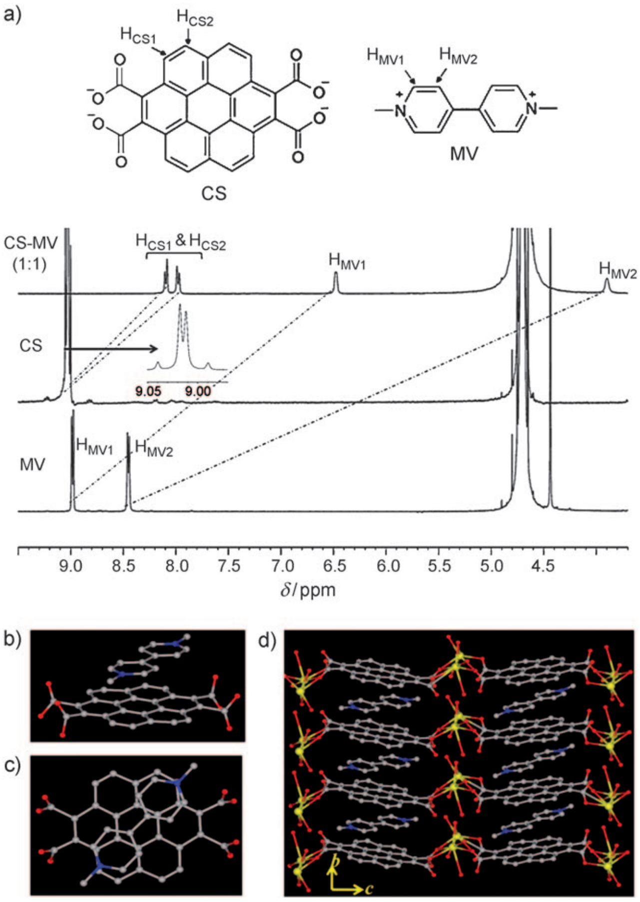

Figure 2. ^{1}H NMR and single-crystal X-ray diffraction studies of the CT complexes between CS and MV. a) Partial ^{1}H NMR spectra of CS, MV, and CS–MV (D_2O, 1.6×10^{-2} M). Molecular orientation of CS and MV in the crystal structure, viewed along the b) crystallographic *a* axis and c) *b* axis. d) Side view of the extended π-columnar stacks of CS–MV cocrystals bridged by potassium ions. Hydrogen atoms are omitted for clarity.

through-space interactions between the H_{MV1} terminal protons and the H_{CS1} and H_{CS2} protons of CS.[22] No NOE interaction was found for the central H_{MV2} protons, thus suggesting a diagonal face-to-face arrangement for the donor and acceptor molecules (see below). ^{1}H NMR studies of BMV (0.2×10^{-2} M),gave similar results to MV upon interaction with CS, thus suggesting a face-to-face stacking arrangement of the chromophores even in a bilayer-type packing.[22] Interestingly, as the concentration of the BMV-CS CT complex increases, the aromatic resonance signals shift further upfield and is accompanied by a simultaneous broadening of the signals, which is characteristic of strong intermolecular association that leads to higher-order self-assembly of the CT complexes.[22]

Single-crystal X-ray diffraction studies of CS and MV cocrystals provided further unequivocal evidence for the formation of the D–A CT complex. Single crystals were grown by dissolving a mixture of CS and MV (1:1) in a water/DMSO mixture (1:1 v/v) and maintaining it at 60 °C. Dark-red crystals were formed slowly, and were shown by ^{1}H NMR spectroscopy to contain CS and MV in a 1:1 ratio, which indicated strong CT interactions similar to those in solution and in DMV gels.[22] Remarkably, simple mechanical grinding of a 1:1 mixture of CS and DMV also quickly resulted in a red powder, consistent with D–A CT interactions.[22] Single-crystal X-ray analysis of the CS–MV cocrystals revealed an alternate face-to-face coassembly of CS with MV (Figure 2b–d). The MV molecules are positioned between the CS chromophores in a diagonal orientation as evident from Figure 2b,c. π-Stacking columns formed by the alternate coassembly of face-stacked donor and acceptor aromatic units are arranged along the crystallographic *b* axis with a face-to-face distance around 3.4 Å (Figure 2d). Detailed analysis of the cocrystals showed an overall formula of $[(\mathrm{MV})\{\mathrm{K_2(CS)}(\mu\text{-}\mathrm{OH_2})(\mathrm{H_2O})_4\}]\cdot 2\,\mathrm{H_2O}$. The crystals can also be viewed as a 1D chain of CS bridged by potassium ions, into which the MV dications are intercalated through π–π and charge-transfer interactions.[22] Furthermore, co-crystals grown from solution containing CS and two equivalents of MV showed a similar arrangement, thus suggesting a preference for a 1:1 stoichiometry. Unfortunately, attempts to cocrystallize CS and BMV, which would have given a better insight into the orientation of chromophores in a bilayer-like assembly, were not successful.

Detailed microscopic studies have provided an insight into the hierarchical self-assembly of the DMV-CS CT complexes into 1D nanofibers and hydrogels (Figure 3). Dynamic light scattering and FE-SEM studies showed that the DMV molecule can self-assemble in aqueous solution into spherical objects with an average diameter of 250 nm because of its amphiphilic character (Figure 3a).[22] In addition, TEM analysis suggests that the spherical objects are formed by the vesicular self-assembly of DMV amphiphiles.[22] Remarkably, detailed TEM[22] and AFM studies (Figure 3d) of 1:1 DMV-CS complexes in water (1×10^{-4} M) showed long nanofibers 50–150 nm in width and several micrometers in length, thus indicating a highly directional 1D self-assembly process. The self-assembly can be envisaged to involve a 1D bilayer-type packing, assisted by hydrophobic interactions, of the supramolecular charge-transfer amphiphile along the π–π stacking direction of the chromophore. Interestingly, TEM analysis of the fibers, which were negatively stained with uranyl acetate, revealed the presence of thinner, 10–15 micrometer-long fibers with a uniform diameter of 6 nm (Figure 3b,c), which is close to twice the length of the CT amphiphile, including the aromatic segments and the dodecyl chains (CPK modeling showed a length of 2.8 nm, Figure 3g), thus confirming a bilayer packing. Furthermore, AFM cross-sectional analysis of the isolated fibers showed a height of 6–7 nm, which suggests that the CT amphiphiles in the bilayer are arranged in a radial fashion that results in 1D cylindrical micelles (Figure 3e,f). The surface charges on these individual cylindrical micelles might act as “glue” for their lateral association through Coulombic interactions to give nanofibers 50–150 nm in width, as visible in TEM without staining, and AFM.[22] The laterally associated nanofibers could further coil with each other to give fiber bundles as indicated by the height of 13-14 nm of twin fiber bundles (Figure 3f), which is twice the diameter of a cylindrical micelle. Thus the microscopic studies demonstrate that the CT amphiphiles first self-assemble into high-aspect-ratio cylindrical micelles that subsequently form laterally associated fiber bundles. At higher concentrations the resulting fibrous structures further coil and entangle, which results in hydrogelation. The hierarchical self-assembly of CS–DMV amphiphiles into cylindrical micelles and 1D nanofibers is shown in Figure 3g. Remarkably, temperature-dependent spectroscopic studies have shown that the self-assembly of CS–DMV CT complexes in water are completely thermoreversible, unlike many of the reported aqueous self-assembled π-conjugated systems that are not dynamic because of strong hydrophobic interactions.[9b]

In conclusion, we have demonstrated an alternate coassembly of a novel class of a donor–acceptor noncovalent amphiphilic pair into very long cylindrical micelles and hydrogels. This two-component hierarchical self-assembly process is different from previously reported peptide and rod–coil amphiphile-based hydrogels. The dynamic nanofibers, which have radially charged surfaces and embedded fluorescent chromophores, might be versatile scaffolds for mineralization and sensing. Furthermore we are currently exploring how the two-component nature of the hydrogels could be exploited to make them responsive to stimuli such as guests or light, by appropriate modifications of the donor or acceptor molecular structure.

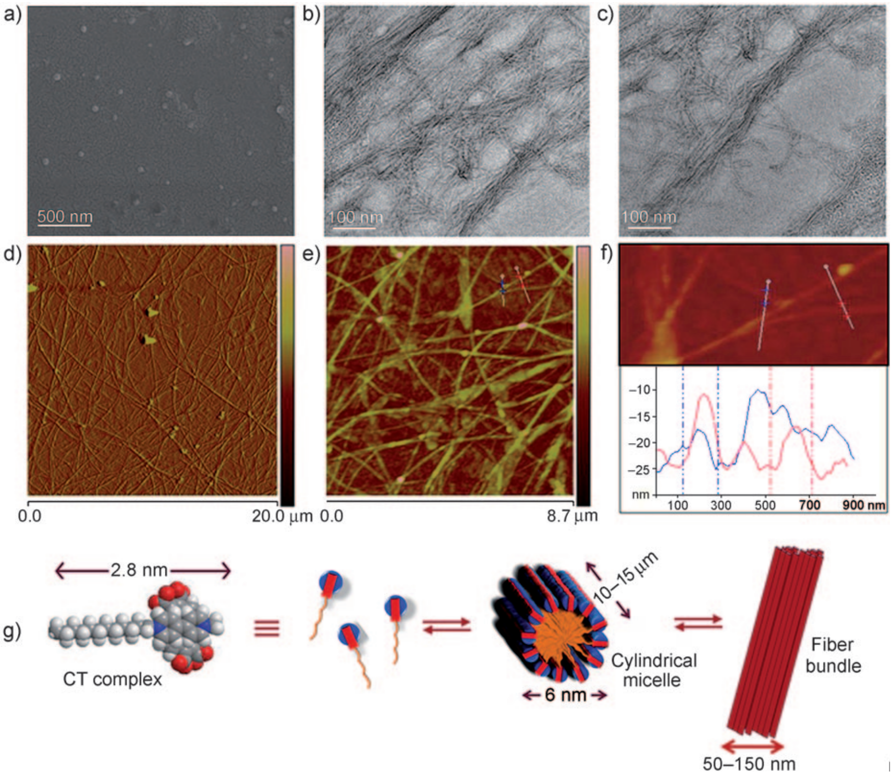

Figure 3. Microscopic studies of the CS–DMV (1×10^{-4} M) CT complex in water. a) FE-SEM image of the spherical objects formed from DMV in water (1×10^{-4} M) on a glass substrate. b), c) TEM images of CS–DMV (1:1) complex on carbon-coated copper grids, sample was stained with uranyl acetate (1 wt% in water). d) AFM amplitude and e) height images of the CS–DMV (1:1) complex on a glass substrate; color scale shows the decrease in height of the object from top to bottom. f) AFM height analysis of the isolated fibers, red and blue curves show the height profile of the fibers indicated by the lines in (e) and (f). g) Schematic representation of the hierarchical self-assembly of the CS–DMV CT amphiphile into cylindrical micelles and fiber bundles.

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[1] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525 – 5534.

[2] a) V. Balzani, M. G-Lopez, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405 – 414; b) C. A. Schalley, K. Beizai, F. Vögtle, *Acc. Chem. Res.* **2001**, *34*, 465 – 476.

[3] a) A. R. Pease, J. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433 – 444; b) H. Y. Au-Yeung, G. D. Pantos, J. K. M. Sanders, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10466; c) H. Y. Au-Yeung, G. D. Pantoş, J. K. M. Sanders, *J. Am. Chem. Soc.* **2009**, *131*, 16030 – 16032; d) V. Balzani, A. Credi, M. Venturi, *Chem. Soc. Rev.* **2009**, *38*, 1542 – 1550.

[4] a) R. S. Lokey, B. L. Iverson, *Nature* **1995**, *375*, 303; b) A. J. Zych, B. L. Iverson, *J. Am. Chem. Soc.* **2000**, *122*, 8898 – 8909; c) V. J. Bradford, B. L. Iverson, *J. Am. Chem. Soc.* **2008**, *130*, 1517 – 1524.

[5] S. De, S. Ramakrishnan, *Macromolecules* **2009**, *42*, 8599 – 8603.

[6] a) S. Ghosh, S. Ramakrishnan, *Angew. Chem.* **2005**, *117*, 5577; *Angew. Chem. Int. Ed.* **2005**, *44*, 5441; b) S. Ghosh, S. Ramakrishnan, *Angew. Chem.* **2004**, *116*, 3326; *Angew. Chem. Int. Ed.* **2004**, *43*, 3264.

[7] a) B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1988**, *100*, 1605 – 1608; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1547 – 1550; b) J.-Y. Ortholand, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1989**, *101*, 1402 – 1404; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1394 – 1395; c) D. G. Hamilton, J. E. Davies, L. Prodi, J. K. M. Sanders, *Chem. Eur. J.* **1998**, *4*, 608 – 620; d) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond, J. K. M. Sanders, *Angew. Chem.* **2004**, *116*, 1993 – 1996; *Angew. Chem. Int. Ed.* **2004**, *43*, 1959 – 1962; e) G. Koshkakaryan, L. M. Klivansky, D. Cao, M. Snauko, S. J. Teat, J. O. Struppe, Y. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 2078 – 2079.

[8] a) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119 – 1122; b) 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 – 387; c) L. Y. Park, D. G. Hamilton, E. A. McGehee, K. A. McMenimen, *J. Am. Chem. Soc.* **2003**, *125*, 10586 – 10590; d) W. Pisula, M. Kastler, D. Wasserfallen, J. W. F. Robertson, F. Nolde, C. Kohl, K. Müllen, *Angew. Chem.* **2006**, *118*, 834 – 838; *Angew. Chem. Int. Ed.* **2006**, *45*, 819 – 823; e) J. J.

Reczek, K. R. Villazor, V. Lynch, T. M. Swager, B. L. Iverson, *J. Am. Chem. Soc.* **2006**, *128*, 7995–8002; f) J.-Y. Wang, J. Yan, L. Ding, Y. Ma, J. Pei, *Adv. Funct. Mater.* **2009**, *19*, 1746–1752.

[9] For reviews on supramolecular π-conjugated systems, see: a) A. P. H. J. Schenning, E. W. Meijer, *Chem. Commun.* **2005**, 3245–3258; b) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491–1546; c) A. Ajayaghosh, S. J. George, A. P. H. J. Schenning, *Top. Curr. Chem.* **2005**, *258*, 83–118; d) A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644–656; e) F. Würthner, *Chem. Commun.* **2004**, 1564–1579.

[10] a) A. Ajayaghosh, S. J. George, *J. Am. Chem. Soc.* **2001**, *123*, 5148–5149; b) A. P. H. J. Schenning, P. Jonkheijm, E. Peeters, E. W. Meijer, *J. Am. Chem. Soc.* **2001**, *123*, 409–416; c) S. J. George, A. Ajayaghosh, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem.* **2004**, *116*, 3504–3507; *Angew. Chem. Int. Ed.* **2004**, *43*, 3422–3425; d) J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii, T. Aida, *Science* **2004**, *304*, 1481–1483; e) V. Percec, M. R. Imam, T. K. Bera, V. S. K. Balagurusamy, M. Peterca, P. A. Heiney, *Angew. Chem.* **2005**, *117*, 4817–4823; *Angew. Chem. Int. Ed.* **2005**, *44*, 4739–4745; f) J. Puigmartí-Luis, V. Laukhin, Á. P. del Pino, J. Vidal-Gancedo, C. Rovira, E. Laukhina, D. B. Amabilino, *Angew. Chem.* **2007**, *119*, 242–245; *Angew. Chem. Int. Ed.* **2007**, *46*, 238–241; g) B.-K. An, S. H. Gihm, J. Won Chung, C. R. Park, S.-K. Kwon, S. Y. Park, *J. Am. Chem. Soc.* **2009**, *131*, 3950–3957; h) X. Feng, W. Pisula, T. Kudernac, D. Wu, L. Zhi, S. De Feyter, K. Müllen, *J. Am. Chem. Soc.* **2009**, *131*, 4439–4448; i) D. González-Rodríguez, P. G. A. Janssen, R. Martín-Rapún, I. De Cat, S. De Feyter, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2010**, *132*, 4710–4719.

[11] a) J. V. van Herrikhuyzen, A. Syamakumari, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2004**, *126*, 10021–10027; b) F. Würthner, Z. Chen, F. J. M. Hoeben, P. Osswald, A. P. H. J. Schenning, P. P. A. M. Van der Schoot, E. W. Meijer, E. H. A. Beckers, S. C. J. Meskers, R. A. J. Janssen, *J. Am. Chem. Soc.* **2004**, *126*, 10611–10618; c) E. H. A. Beckers, S. C. J. Meskers, A. P. H. J. Schenning, Z. Chen, F. Würthner, P. Marasal, D. Beljonne, J. Cornil, R. A. J. Janssen, *J. Am. Chem. Soc.* **2006**, *128*, 649–657; d) P. Jonkheijm, N. Stutzmann, Z. Chen, D. M. de Leeuw, E. W. Meijer, A. P. H. J. Schenning, F. Würthner, *J. Am. Chem. Soc.* **2006**, *128*, 9535–9540.

[12] a) C. Wang, S. Yin, S. Chen, H. Xu, Z. Wang, X. Zhang, *Angew. Chem.* **2008**, *120*, 9189–9192; *Angew. Chem. Int. Ed.* **2008**, *47*, 9049–9052; b) C. Wang, Y. Guo, Y. Wang, H. Xu, R. Wang, X. Zhang, *Angew. Chem.* **2009**, *121*, 9124–9127; *Angew. Chem. Int. Ed.* **2009**, *48*, 8962–8965; c) Y. P. Wang, H. P. Xu, X. Zhang, *Adv. Mater.* **2009**, *21*, 2849–2864; d) U. Maitra, P. V. Kumar, N. Chandra, L. J. D'Souza, M. D. Prasanna, A. R. Raju, *Chem. Commun.* **1999**, 595–596; e) P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S. Kawano, N. Fujita, S. Shinkai, *Angew. Chem.* **2006**, *118*, 1622–1625; *Angew. Chem. Int. Ed.* **2006**, *45*, 1592–1595.

[13] a) T. Kitamura, S. Nakaso, N. Mizoshita, Y. Tochigi, T. Shimomura, M. Moriyama, T. Kato, *J. Am. Chem. Soc.* **2005**, *127*, 14769; b) Y. Tatewaki, T. Hatanaka, R. Tsunashima, T. Nakamura, M. Kimura, H. Shirai, *Chem. Asian J.* **2009**, *4*, 1474–1479; c) I. Danila, F. Riobé, J. P-Luis, Á. P. del Pino, J. D. Wallis, D. B. Amabilino, N. Avarvari, *J. Mater. Chem.* **2009**, *19*, 4495–4504; d) J. Puigmartí-Luis, Á. P. del Pino, V. Laukhin, L. N. Feldborg, C. Rovira, E. Laukhinaac, D. B. Amabilino, *J. Mater. Chem.* **2010**, *20*, 466–474.

[14] a) J. D. Hartgerink, E. Beniash, S. I. Stupp, *Science* **2001**, *294*, 1684–1688; b) H. Cui, T. Muraoka, A. G. Cheetham, S. I. Stupp, *Nano Lett.* **2009**, *9*, 945–951.

[15] a) E. Lee, J.-K. Kim, M. Lee, *Angew. Chem.* **2008**, *120*, 6475–6478; *Angew. Chem. Int. Ed.* **2008**, *47*, 6375–6378; b) J.-H. Ryu, M. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 14170–14171.

[16] a) S. Kiyonaka, K. Sugiyasu, S. Shinkai, I. Hamachi, *J. Am. Chem. Soc.* **2002**, *124*, 10954–10955; b) J. H. Jung, G. John, M. Masuda, K. Yoshida, S. Shinkai, T. Shimizu, *Langmuir* **2001**, *17*, 7229–7232; c) N. Kameta, K. Yoshida, M. Masuda, T. Shimizu, *Chem. Mater.* **2009**, *21*, 5892–5898.

[17] a) U. Maitra, S. Mukhopadhyay, A. Sarkar, P. Rao, and S. S. Indi, *Angew. Chem.* **2001**, *113*, 2341–2343; *Angew. Chem. Int. Ed.* **2001**, *40*, 2281–2283; b) J. C. Tiller, *Angew. Chem.* **2003**, *115*, 3180–3183; *Angew. Chem. Int. Ed.* **2003**, *42*, 3072–3075; c) L. A. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201–1217; d) J. F. Hulvat, M. Sofos, K. Tajima, S. I. Stupp, *J. Am. Chem. Soc.* **2005**, *127*, 366–372; e) P. K. Vemula, G. John, *Chem. Commun.* **2006**, 2218–2220; f) K. M. Anderson, G. M. Day, M. J. Paterson, P. Byrne, N. Clarke, J. W. Steed, *Angew. Chem.* **2008**, *120*, 1074–1078; *Angew. Chem. Int. Ed.* **2008**, *47*, 1058–1062; g) Y. Chen, X.-H. Pang, C.-M. Dong, *Adv. Funct. Mater.* **2010**, *20*, 579–586; h) P. Dastidar, S. Okabe, K. Nakano, K. Iida, M. Miyata, N. Tohnai, M. Shibayama, *Chem. Mater.* **2005**, *17*, 741–748.

[18] a) U. Rohr, P. Schlichting, A. Böhm, M. Gross, K. Meerholz, C. Bräuchle, K. Müllen, *Angew. Chem.* **1998**, *110*, 1463–1467; *Angew. Chem. Int. Ed.* **1998**, *37*, 1434–1437; b) S. Alibert-Fouet, I. Seguy, J.-F. Bobo, P. Destruel, H. Bock, *Chem. Eur. J.* **2007**, *13*, 1746.

[19] Z. An, J. Yu, B. Domercq, S. C. Jones, S. Barlow, B. Kippelen, S. R. Marder, *J. Mater. Chem.* **2009**, *19*, 6688–6698.

[20] A. Ghosh, K. V. Rao, S. J. George, C. N. R. Rao, *Chem. Eur. J.* **2010**, *16*, 2700–2704.

[21] a) U. Rauwald, O. A. Scherman, *Angew. Chem.* **2008**, *120*, 4014–4017; *Angew. Chem. Int. Ed.* **2008**, *47*, 3950–3953; b) H. D. Nguyen, D. T. Dang, J. L. J. van Dongen, L. Brunsveld, *Angew. Chem.* **2010**, *122*, 907–910; *Angew. Chem. Int. Ed.* **2010**, *49*, 895–898; c) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson, F. Huang, *Angew. Chem.* **2010**, *122*, 1108–1112; *Angew. Chem. Int. Ed.* **2010**, *49*, 1090–1094.

[22] See the Supporting Information.

[23] The increase of DMV concentrations to above 1 equivalent showed further broadening of the absorption spectrum and fluorescence quenching, which might be due to the Coulombic interactions between donor and acceptor molecules.