Angewandte
Chemie

Self-Assembly

The Introduction of π–π Stacking Moieties for Fabricating Stable Micellar Structure: Formation and Dynamics of Disklike Micelles**

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Amphiphiles can self-organize into micellar structures with defined sizes and shapes[1,2] that may be used in applications such as templates for making nanostructured materials and mimicking biomineralization processes. Engineering robustness is required to make these applications practical, as the micellar structures are inherently dynamic and fluid. Enhancing the intermolecular interactions among the aggregates is one possible method for stabilizing the micellar structures. This approach may rely on generating a strong association among its assembling units through a combination of different interactions, including van der Waals interactions and hydrogen bonding.[3–5] Herein, we report the introduction of a strong π–π stacking moiety into bolaamphiphiles[6] so as to increase the robustness of the self-organized entities, thus providing a new approach to fabricating organic nanostructured materials.

The diaryldiketopyrrolopyrrole (DPP) dye is a recently developed technical pigment with remarkable properties such as a high fade-proof nature, extraordinary thermal stability, and very low solubility as a consequence of strong intermolecular interactions.[7] We attempted to introduce a DPP dye as a strong π–π stacking moiety into bolaamphiphiles, and hoped that such a bolaamphiphile might give rise to a stable micellar nanostructure with light-emitting properties. For this

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[**] We thank the major state basic research development program (G2000078102) and the National Natural Science Foundation of China (20334010, 20473045) for financial support. The Flemish and Belgian governments, as well as the University of Leuven, supported this work with a bilateral grant (BIL02/03), the grant IAP-V-4, and a postdoctoral fellowship to Y.F., respectively. M.S. thanks F. W. O. Vlaanderen for a postdoctoral fellowship. Professor Lei Jiang and Huan Liu of the Institute of Chemistry, Chinese Academy of Sciences are thanked for their help with FE-SEM measurements.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200500980
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purpose, a series of bolaamphiphiles bearing diaryldiketopyrrolopyrrole units with different spacer lengths were synthesized, namely, 2,5-bis(*n*-(1-pyridinium)alkyl)-3,6-bis-(2-thienyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole ditosylate salts, abbreviated as DPP-*n*, where *n* ($n = 7$, 11, 15) corresponds to the number of methylene units in the alkyl chain spacer.

For DPP-11, for example, there exists a critical micelle concentration (cmc) at 5.5×10^{-5} M, as indicated by the plot of the conductivity as a function of the concentration (Figure 1).

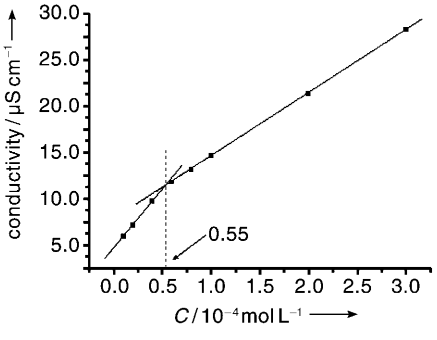

Figure 1. Dependence of the solution conductivity of DPP-11 on concentration; the cmc is around 5.5×10^{-5} M.

When the concentration is above this critical value the bolaamphiphiles self-organize into micelles in aqueous solution. The formation of a micellar structure is also supported by ^{1}H NMR spectroscopic analysis. As seen in Figure 2, the ^{1}H NMR signals of the aromatic rings from the two terminal pyridinium groups as well as from the rigid unit are well resolved below its cmc. However, all the ^{1}H NMR signals become broad and weak when the concentration is above its cmc. The change in the ^{1}H NMR signals of the thienyl residues in the rigid moiety is even greater than that of the two terminal pyridinium groups. This change can be rationalized by the restricted motion of the amphiphilic molecule in the associated state.[3,8] The segregation of the hydrophobic and hydrophilic parts of the molecule during the self-assembly in water results in the thienyl groups residing in the inner part of the micelles and the terminal pyridinium groups at the outer part of the micelles. Therefore, interaction between the water and the pyridinium groups is stronger than that with the thienyl residues, thus leading to increased local mobility and less line broadening of the NMR signals.

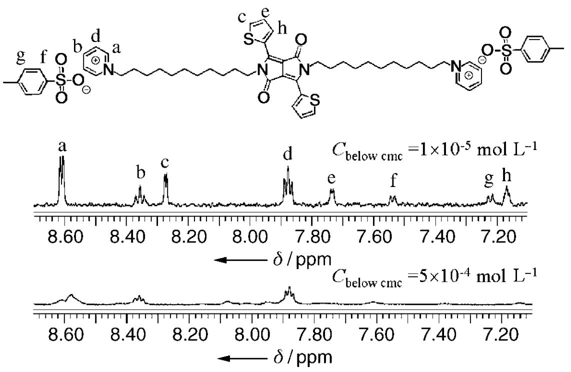

Figure 2. ^{1}H NMR spectra of DPP-11 in D_2O with concentrations lower and higher than its cmc.

We found that if the concentration of the DPP-11 solution was above the cmc the solution turned from bright red to dark purple. We anticipated that the color change was indicative of the formation of micelles, which was further supported by spectroscopic studies: We first identified the UV/Vis spectral absorption bands of the DPP-11 monomer and aggregate. As shown in Figure 3, there are two absorption bands around 514 and 540 nm in dilute aqueous solution (below the cmc, dotted curve) or in the good solvent, methanol (dashed curve). These bands are assigned to the monomer of DPP-11. In concentrated solution (above the cmc), a new absorption band appears around 601 nm (solid curve), which is attributed to the aggregate state of DPP-11. The bathochromic shift of the absorption bands is caused by the strong π–π stacking of the diketopyrrolopyrrole units in the amphiphiles upon self-assembly into micellar structures. Interestingly, in contrast with the normal formation of micelles that reaches equilibrium in a very short time, we found that DPP-11 requires a relatively long period to self-assemble, thus allowing the dynamic process to be monitored (Figure 4). Only absorption bands at around 514 and 540 nm corresponding to the monomer absorption exist at the beginning. The monomer absorption becomes weaker and weaker over time and concomitantly the absorption band of the aggregate around 601 nm appears and then becomes greater and greater, thus indicating the formation of micelles and the increase in their numbers. There is an isosbestic point around 560 nm. Figure 4b shows that the absorption change of DPP-11 almost reaches a plateau after about 10 minutes, thus suggesting an equilibrium situation.

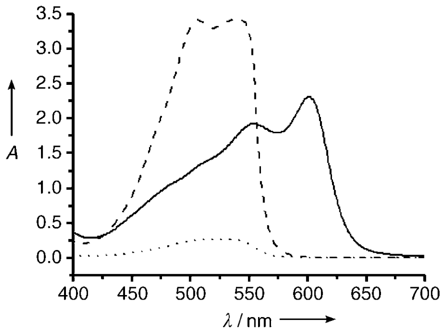

Figure 3. Concentration-dependent UV/Vis spectra of DPP-11: in methanol at 1.0×10^{-4} M (dashed line); in aqueous solution at 1.0×10^{-4} M, above the cmc (solid line); in aqueous solution at 1.0×10^{-5} M, below the cmc (dotted line).

To determine whether the aggregation is temperature-dependent in solution we carried out systematic experiments of the variation of the UV/Vis spectrum with temperature. As shown in Figure 5, the UV/Vis absorption experiment indeed shows that the aggregate can disassemble as the temperature increases and reassemble as the temperature decreases. The increase and decrease of the characteristic absorption bands of the aggregates (601 nm) and monomers of the DPP-11

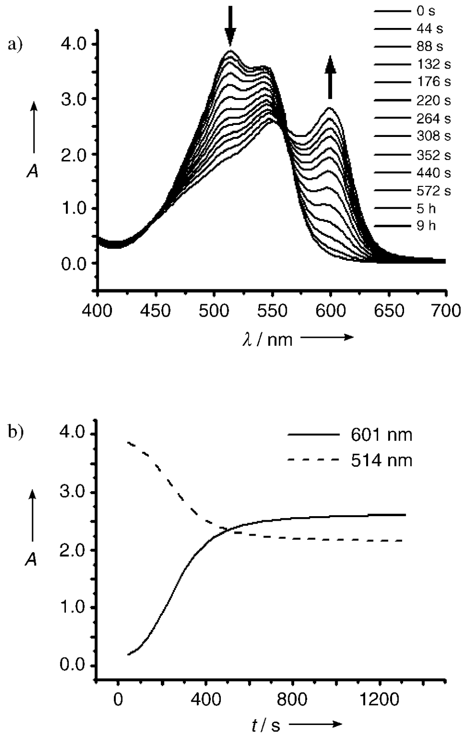

Figure 4. a) Time-resolved absorbance of DPP-11 in aqueous solution at a concentration of 1.0×10^{-4} M. b) The change in the absorbance with time at 601 nm (solid line) and 514 nm (dashed line).

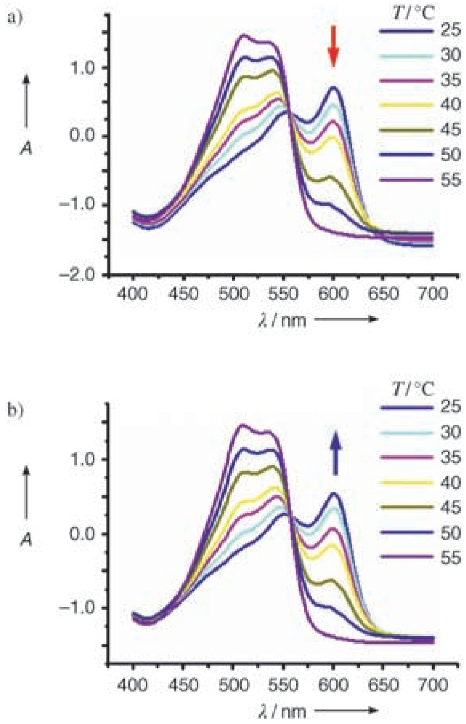

Figure 5. Temperature-dependent UV/Vis spectra of DPP-11 in aqueous solution at 1.0×10^{-4} M. The temperature increase (a) and decrease (b) are in intervals of 5 °C.

molecules (514 nm) show aggregation is a reversible process. At the same time, the reversible phenomena also indicate the DPP-11 molecules experience self-assembly through supramolecular interactions.

The micelles formed in aqueous solution could be adsorbed on freshly cleaved mica sheets and visualized by ex situ atomic force microscopy (AFM). As exhibited in Figure 6, DPP-11 forms disklike micelles with diameters ranging from several hundreds of nanometers to one micrometer. Adjacent disklike micelles partially overlap, and the overlapping parts stack together to form double layers, triple layers, or even multilayers. The section analysis (Figure 6b) shows that the disk has an average thickness of about 3.7 nm. This value agrees well with the length of a single DPP-11 molecule, thus suggesting that the disks form a monolayer structure with the thickness of a single molecule. Although the self-assembly of the amphiphiles is mainly driven by the hydrophobic effect, once the disklike micelle forms, the π–π stacking interaction becomes another dominating factor that enhances the stability of the disks. This is the reason why we can readily observe the micellar structure by ex situ AFM: the micellar structure formed in this way is stable enough toward the drying process. When looking more closely at the disks we found that there were uniform stripes with a width of about 10 nm (Figure 6c, d). These stripes have a preferred orientation within one disk, although the orientation can be different in different disks. Thus, the surface disklike micelle is a combination of micro- and nanostructures, which can be explained in terms of a compromise between the different intermolecular interactions. The intermolecular π–π stacking in the middle part of the aggregate forces the molecules to pack closely, while the repulsive interaction of the positively charged head groups has the reverse effect. We believe that the repulsion between the charged head groups may be enhanced as a consequence of water evaporation during the drying process. A compromise between these two types of

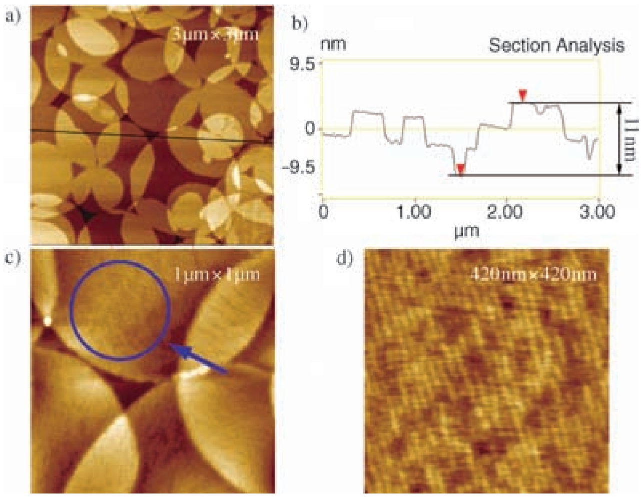

Figure 6. Ex situ AFM images of DPP-11 micellar structures adsorbed on a mica sheet: a) large area image; b) section analysis of (a); c) and d) magnified images.

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interaction could lead to crystallization of the amphiphiles, which is responsible for the formation of the observed stripelike structure.

The disklike micellar structure in the dry state as revealed by ex situ AFM should also reflect its associated structure in solution. This speculation is supported by the following experimental facts. First, in situ AFM studies demonstrate the presence of similar disks as those observed by ex situ AFM, thus excluding the possibility that the disks are formed during the air-drying process. Second, the disks can also be observed when adsorbed onto hydrophilic quartz slides. This fact indicates that formation of the disks is not induced by the mica substrate, and that the disklike micelles formed in the aqueous solution are robust enough to resist the effect of the substrate. Third, the UV/Vis absorption bands for the adsorbates on both a mica sheet and quartz slide are almost the same as that for the micellar suspension, which indicates the micelles are resistant to the transferring and drying processes. Fourth, the enhanced stability is also supported by AFM studies at elevated temperature. The disks undergo no apparent changes until the substrate is heated to 80 °C, after which they gradually melt as the temperature is further increased.

In addition, an appropriate length of the flexible spacers is also necessary for such bolaamphiphile to self-organize into the disklike micellar structure. We performed similar studies on DPP-7 and DPP-15, but failed to obtain self-assembled structures for these two bolaamphiphiles where the spacers are shorter and longer than DPP-11, respectively. Neither the concentration/conductivity plot nor the UV/Vis spectra for DPP-7 show any distinct phase transition, thus indicating that this compound can not form micellar structures in aqueous solution. Analysis of the adsorbate on a hydrophilic substrate by AFM showed no regular structures were formed. The self-assembly of DPP-15 is inhibited by its poor solubility, since the increase in the spacer length decreases its solubility in water significantly.

In summary, interesting disklike micelles have been obtained by self-assembly of a novel bolaamphiphile, and the dynamics of disk formation have been investigated. The disklike micelles can maintain their monomolecule-layered structures even when being transferred to hydrophilic substrates, thus showing their high stability as a result of the introduction of a strong π–π stacking moiety into the amphiphile. Although micelles are inherently dynamic and fluid, they can be stabilized by enhancing the intermolecular interactions, thus providing a new approach for the fabrication of organic nanostructured materials.

Experimental Section

A commercial multimode Nanoscope IV AFM was used to characterize the surface structure. In situ AFM: The substrate was mounted under a liquid cell and the solution injected into the cell. After leaving the solution to stand for at least 30 minutes to reach equilibrium, it was scanned in the tapping mode. Ex situ AFM: The substrate was incubated in the solution for at least 30 minutes, before a sample was removed from the solution and air-dried. The sample was then scanned in the tapping mode. UV/Vis spectra were measured with a HITACHI U-3010 spectrophotometer. A weighed amount of DPP-11 was dissolved in a minimum quantity of methanol (a good solvent for DPP-11) and then the solution injected into a certain volume of water. The UV/Vis spectrum was then recorded immediately by capturing one spectrum every 44 s. ^{1}H NMR spectroscopic analysis (600 MHz) was performed in deuterium oxide. The substrates used in the AFM studies were commercial mica and quartz slides. Before each use, the mica was freshly cleaved, and the quartz slides treated with piranha solution (concentrated sulfuric acid and 30% H_2O_2 (7:3)) to obtain a hydrophilic surface.

The three bolaamphiphiles DPP-7, DPP-11, and DPP-15 were synthesized in an analogous way. The synthesis of DPP-11 is presented as an example. 3,6-Bis-(2-thienyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole (DPP) was synthesized as reported before.[9] 7-Bromo-1-heptanol was obtained by monobromination of 1,7-heptanediol with HBr, and 15-bromo-1-pentadecanol was prepared by cleaving ω-pentadecalactone with H_2SO_4/HBr, followed by reduction with borane·methyl sulfide complex (2 M solution in THF).

2,5-Bis-(11-hydroxyundecyl)-3,6-bis-(2-thienyl)-1,4-dioxopyrrolo-[3,4-*c*]pyrrole (**1**): 11-Bromo-1-undecanol (1.7 g, 6.8 mmol), K_2CO_3 (1 g, 7.2 mmol), and NaI (1 g, 6.7 mmol) were added to a solution of DPP (1 g, 3.3 mmol) in dry DMF (40 mL). The mixture was stirred at 60 °C for 18 h. After cooling the mixture to room temperature, it was poured into water and extracted with ethyl acetate. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product (0.6 g, 28%) was obtained by column chromatography (SiO_2, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, tetramethylsilane (TMS)): $\delta = 8.92$ (d, ^3J(H,H) = 4.2 Hz, 2H,), 7.64 (d, ^3J(H,H) = 4.2 Hz, 2H), 7.28 (t, ^3J(H,H) = 4.2 Hz, 2H), 4.07 (t, ^3J(H,H) = 7.2 Hz, 4H), 3.64 (t, ^3J(H,H) = 3.6 Hz, 4H), 1.29–1.74 ppm (m, 36H).

2,5-Bis-(11-tosyloxyundecyl)-3,6-bis-(2-thienyl)-1,4-dioxopyrrolo-[3,4-*c*]pyrrole (**2**): Tosyl chloride (TosCl; 0.6 g, 3 mmol) and 4-dimethylaminopyridine (0.6 g, 4.9 mmol) were added to a solution of **1** (0.6 g, 0.9 mmol) in dichloromethane (140 mL). The mixture was stirred at room temperature for 24 h, and then the solvent evaporated in vacuo. The product (0.16 g, 19%) was obtained by column chromatography (SiO_2, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.92$ (d, ^3J(H,H) = 4.2 Hz, 2H), 7.80 (d, ^3J(H,H) = 8.7 Hz, 4H), 7.64 (d, ^3J(H,H) = 4.2 Hz, 2H), 7.34 (d, ^3J(H,H) = 8.7 Hz, 4H), 7.28 (t, ^3J(H,H) = 4.2 Hz, 2H), 3.99–4.09 (m, ^3J(H,H) = 7.2 Hz, 8H), 2.44 (s, 6H), 1.29–1.74 ppm (m, 36H).

DPP-11: Dry pyridine (4 mL) was added to a solution of **2** (0.165 g, 0.17 mmol) in dry chloroform (10 mL). The solution was refluxed under nitrogen for 20 h. After cooling the mixture to room temperature, it was added dropwise to toluene (150 mL). The resulting red precipitate (0.18 g, 93%) was purified by two precipitations by adding a solution of the product in methanol to diethyl ether. ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS): $\delta = 9.07$ (d, ^3J(H,H) = 6.0 Hz, 4H; 2-H, 6-H Py), 8.80 (d, ^3J(H,H) = 4.2 Hz, 2H; 3-H Th), 8.58 (t, ^3J(H,H) = 7.2 Hz, 2H; 4-H Py), 8.14 (t, ^3J(H,H) = 7.2 Hz, 4H; 3-H 5-H Py), 8.10 (d, ^3J(H,H) = 4.2 Hz, 2H; 5-H Th), 7.47 (d, ^3J(H,H) = 8.1 Hz, 4H; 2-H, 6-H Tos), 7.40 (t, ^3J(H,H) = 4.2 Hz, 2H; 4-H Th), 7.10 (d, ^3J(H,H) = 8.1 Hz, 4H; 3-H, 5-H Tos), 4.57 (t, ^3J(H,H) = 7.2 Hz, 4H; CH_2Py), 3.99 (t, ^3J(H,H) = 7.2 Hz, 4H; CH_2DPP), 2.50 (t, ^3J(H,H) = 1.7 Hz, 6H; CH_3 Tos), 1.88 (m, 4H; CH_2CH_2Py), 1.62 (m, 4H; CH_2CH_2DPP), 1.20 ppm (m, 28H; $CH_2CH_2(CH_2)_7CH_2CH_2$).

DPP-7: ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS): $\delta = 9.07$ (d, ^3J(H,H) = 6.0 Hz, 4H; 2-H 6-H Py), 8.80 (d, ^3J(H,H) = 4.2 Hz, 2H; 3-H Th), 8.58 (t, ^3J(H,H) = 7.2 Hz, 2H; 4-H Py), 8.14 (t, ^3J(H,H) = 7.2 Hz, 4H; 3-H 5-H Py), 8.10 (d, ^3J(H,H) = 4.2 Hz, 2H; 5-H Th), 7.47 (d, ^3J(H,H) = 8.1 Hz, 4H; 2-H, 6-H Tos), 7.40 (t, ^3J(H,H) = 4.2 Hz, 2H; 4-H Th), 7.10 (d, ^3J(H,H) = 8.1 Hz, 4H; 3-H; 5-H Tos), 4.57 (t, ^3J(H,H) = 7.2 Hz, 4H; CH_2Py), 3.99 (t, ^3J(H,H) = 7.2 Hz, 4H; CH_2DPP), 2.50 (t, ^3J(H,H) = 1.7 Hz, 6H; CH_3 Tos), 1.90 (m, 4H; CH_2CH_2Py), 1.62 (m, 4H; CH_2CH_2DPP), 1.37 ppm (m, 12H; $CH_2CH_2(CH_2)_7CH_2CH_2$).

DPP-15: ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS): $\delta = 9.07$ (d, ^3J(H,H) = 6.0 Hz, 4H; 2-H, 6-H Py), 8.80 (d, ^3J(H,H) = 4.2 Hz, 2H; 3-H Th), 8.58 (t, ^3J(H,H) = 7.2 Hz, 2H; 4-H Py), 8.14 (t, ^3J(H,H) = 7.2 Hz, 4H; 3-H 5-H Py), 8.10 (d, ^3J(H,H) = 4.2 Hz, 2H; 5-H Th), 7.47 (d, ^3J(H,H) = 8.1 Hz, 4H; 2-H, 6-H Tos), 7.40 (t, ^3J(H,H) = 4.2 Hz, 2H; 4-H Th), 7.10 (d, ^3J(H,H) = 8.1 Hz, 4H; 3-H; 5-H Tos), 4.57 (t, ^3J(H,H) = 7.2 Hz, 4H; CH_2Py), 3.99 (t, ^3J(H,H) = 7.2 Hz, 4H; CH_2DPP), 2.50 (t, ^3J(H,H) = 1.7 Hz, 6H; CH_3 Tos), 1.90 (m, 4H; CH_2CH_2Py), 1.62 (m, 4H; CH_2CH_2DPP), 1.20 ppm (m, 44H; $CH_2CH_2(CH_2)_7CH_2CH_2$).

Received: March 17, 2005
Revised: May 20, 2005
Published online: July 1, 2005

Keywords: bolaamphiphiles · micelles · nanostructures · noncovalent interactions · self-assembly

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