ChemComm

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COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c3cc00059a

Received 5th December 2012,
Accepted 9th January 2013

DOI: 10.1039/c3cc00059a

www.rsc.org/chemcomm

Supra-amphiphiles formed by complexation of azulene-based amphiphiles and pyrene in aqueous solution: from cylindrical micelles to disklike nanosheets†

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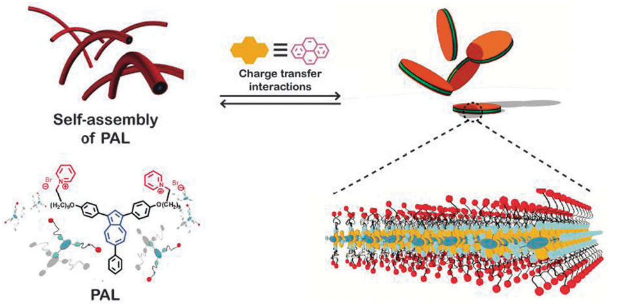
We have fabricated supra-amphiphiles by charge-transfer complexation of azulene-based amphiphiles and pyrene in water, and the self-assembled nanostructures can reversibly change between cylindrical micelles and disklike nanosheets in response to interaction with guest molecules.

Self-assembly involves spontaneous formation of well-defined structures from various chemical building blocks. Among the building blocks for self-assembly, amphiphiles that contain both hydrophilic and hydrophobic parts are widely used building blocks.[1] In contrast to conventional amphiphiles that are formed by covalent bonding, supra-amphiphiles refer to amphiphiles that are formed by different noncovalent interactions.[2] The major advantage of supra-amphiphiles is that different functional groups with stimuli-responsiveness can be easily attached to the amphiphiles by noncovalent synthesis, thus avoiding tedious chemical synthesis to some extent. In the meantime, it may endow the assemblies with desirable functions, thus allowing for the fabrication of adaptive supramolecular nanostructures. The study of supra-amphiphiles with diversified topologies can not only enrich the traditional field of colloid and interface science, but also bring a new horizon to supramolecular science.

Herein, for the first time we attempted to fabricate supra-amphiphiles with azulene-based oligomers of amphiphiles and pyrene as building blocks by charge-transfer (CT) interactions.[3] In this regard, we wanted to load directly one equivalent of water-insoluble pyrene into the hydrophobic interior of the amphiphiles without use of organic solvent. Technically, this is difficult, because the existing strong homo-association of the aromatic segments of amphiphiles will lead to the precipitation of pyrene in aqueous media. To solve this problem, Y-shaped aromatic segments of the amphiphiles are designed in order to avoid the strong homo-association between them, and the azulene moiety is introduced as a core of the Y-shaped aromatic segment to increase the hetero-association with pyrene. It should be noted that azulene, a bicyclic aromatic system fused with an electron-rich five-membered and an electron-poor seven-membered ring, exhibits a dipole moment of 1.08 D and a higher CT association constant than naphthalene.[4] In addition, it has been widely used as a basic unit of conjugated polymers and oligomers[5] with conductive[6] and optical[7] properties. In this work, we have designed and synthesized a Y-shaped bola-amphiphile bearing an azulene moiety (PAL) (see ESI†).[8] As shown in Scheme 1, pyrene, a water-insoluble molecule, can be mixed with PAL in aqueous media which is expected to form supra-amphiphiles driven by hydrophobic and CT interactions, allowing for preparation of the complexes directly in water. Moreover, the self-assemblies may be changed reversibly in response to interaction with guest molecules. In contrast to the external stimuli such as pH, light, redox and temperature, introduction of pyrene and its interaction with PAL allows us to provide a tool for structural evolution of the assemblies, which is promising for application in smart nanoscale materials.[9]

The formation of supra-amphiphiles is confirmed by UV-visible and fluorescence spectroscopy. Upon adding pyrene in THF to an aqueous solution of PAL (1 : 1 molar ratio of PAL/pyrene), the resulting mixture was initially turbid, which then yielded a transparent solution with color changed from light green to green after 36 hours. The change of the solution color



Scheme 1 Amphiphiles consisting of azulene-based oligomer complexes with pyrene through CT interactions. The self-assembled structure is transformed from cylindrical micelles to nanosheets by adding pyrene.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc00059a

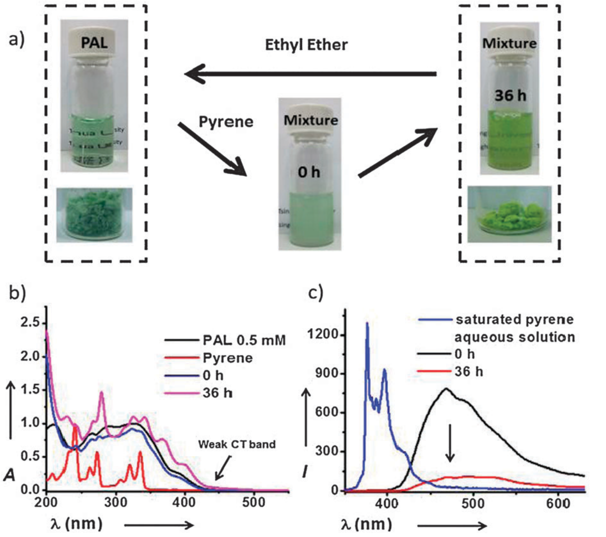

Fig. 1 (a) Photographs of PAL, initial addition of pyrene, and the equilibrated complex; (b) UV/Vis absorption spectra of PAL, pyrene in THF, the resulting solution before (0 h) and after complexation (36 h); (c) emission spectra of the pyrene and resulting solution before (0 h) and after complexation (36 h) (excitation wavelength: 335 nm). The PAL solution concentration is 5×10^{-4} M; the concentration of pyrene in THF is 2×10^{-2} M. The molar ratio of PAL and pyrene in the solution is 1 : 1.

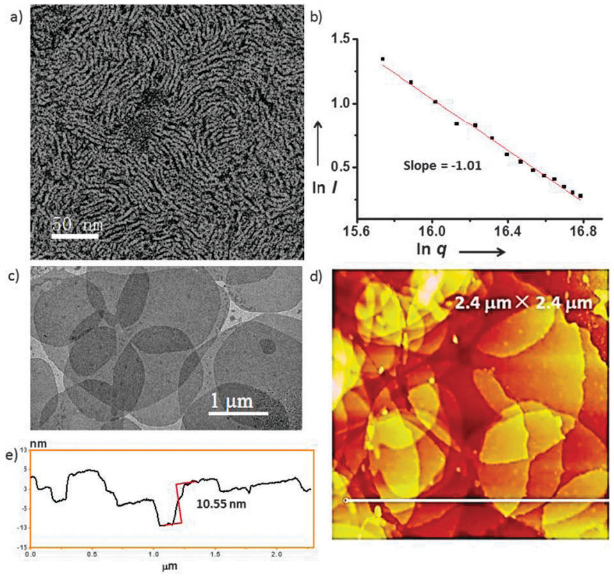

Fig. 2 (a) TEM image of PAL assembly with negative staining (1.5 wt% uranyl acetate); (b) vector-dependent scattering intensities of the PAL assemblies; (c) TEM image of the PAL–pyrene co-assembly; (d) tapping-mode AFM image of the PAL–pyrene complexes adsorbed on a carbon-coated grid; (e) section analysis of (d).

was also confirmed by lyophilization (Fig. 1a). It was supposed that addition of water-insoluble pyrene into aqueous solution quickly led to a suspension of particles in water, which then slowly formed complexes with PAL. There was no clear absorption of pyrene when it is added initially into the PAL solution (Fig. 1b). After 36 hours, the transparent solution showed absorption bands belonging to pyrene, indicating that pyrene and PAL have formed some complexes in the hydrophobic region. Notably, the complex exhibits a broad absorption band between 430 and 550 nm which corresponds to the characteristic absorption of the CT complexes.[10,11] Concomitantly, significant quenching of the emission between 400 nm and 600 nm which is ascribed to the excimer of pyrene was detected after complexation (Fig. 1c).[12] It is important to note that the CT interactions are influenced by temperature. When temperature increased, the absorbance above 430 nm weakened and the absorption bands peaked at 369 nm and 395 nm also decreased and exhibited blue-shifts, indicating the gradual destruction of the CT complexes (Fig. S4, ESI†). Therefore, the combination of UV-visible and fluorescence spectroscopy supports the formation of CT complexes indeed. Removal of the pyrene from the aqueous phase was performed by addition of ethyl ether, leading to restoration of the solution colour (Fig. S5, ESI†). In addition, adding more than one equivalent of pyrene led to a white precipitate of pyrene at the bottom of the solution and no further increase of that absorption, further supporting that the complex has a molar ratio of 1 : 1 (Fig. S6, ESI†).

Different methods were employed to study the self-assembling structures before and after CT complexation. As indicated by transmission electron microscopy (TEM), PAL molecules self-assemble in aqueous media to form cylindrical micelles of 3–5 nm in diameter (Fig. 2a). Static light scattering (SLS) measurements of angular dependent scattering intensities further provided evidence. A linear dependence between the Napierian logarithm of I and that of q and the slope value was −1.01, which is consistent with that predicted for one-dimensional nanostructures (−1.0) (Fig. 2b).[13] After complexation, the CT complex displayed a disklike structure (Fig. 2c). The adjacent disklike micelles partially overlapped and stacked together with diameters ranging from a few hundreds of nanometers to several micrometers, much larger than those obtained for PAL alone. The selected area electron diffraction (SAED) pattern was obtained for the multiple-layered stacking nanosheets (Fig. S10, ESI†). It displayed two Debye–Scherrer ring patterns around the discrete diffraction spots, which confirms that the PAL–pyrene assemblies are crystalline. The outer ring corresponded to a distance of 0.39 nm, which should be attributed to the π–π stacking distance between PAL and pyrene. The stacking of the disklike structure is clearly observed by atomic force microscopy (AFM, Fig. 2d). Section analysis revealed that the total thickness of three nanosheets was 10.55 nm, therefore the average thickness of a single layer was 3.52 nm (Fig. 2e). This value is a little bit smaller than that of the molecule at full stretch (*ca.* 4.13 nm by CPK modeling studies), indicating that the disklike aggregates are single-layered nanosheets.

X-ray diffraction (XRD) was used to provide structural information before and after complexation. Before complexation, the sharp reflection peak that was indexed to the (020) reflection of PAL corresponded to a layered structure with a *d*-spacing of 3.56 nm in the bulk state (Fig. 3a), which was further proved by the small angle X-ray diffraction (SAXD) experiment (Fig. S11a, ESI†). Therefore, this indicates that the cylindrical micelles formed by PAL in water are not stable against the drying process (see ESI,† part 6). The cylindrical micelles become thin films in the bulk state. However, after complexation, the disklike structures formed by self-assembly of PAL–pyrene complexes are rather stable not only in solution but also in the bulk state. SAXD measurement of the *d*-spacing of single-layered disklike nanosheets afforded a

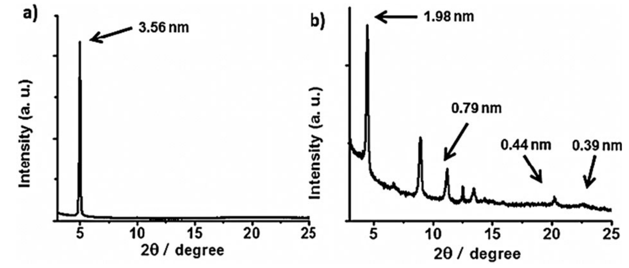

Fig. 3 XRD pattern of (a) PAL and (b) PAL–pyrene complexes.

negative result (Fig. S11b, ESI†), whereas the crystalline order in the other two dimensions was obtained. As supposed that PAL and pyrene are packed together, the presence of a reflection at d = 0.79 nm suggests the formation of extended heteroassociated π–π stacks composed of alternating donors and acceptors.[14] The reflections at d = 0.39 nm and 0.44 nm, as observed in SAED measurement, are probably due to the intermolecular π–π stacking and the characteristic of the average spacing of molecules in this system (Fig. 3b). A d-spacing of 1.98 nm, which is attributed to the rearrangement of PAL–pyrene complexes in another direction, was also observed. Single crystal structure of a model compound, 1,3-bis(4-butoxyphenyl)-6-phenyl-azulene (BPA), was provided for evidence (Fig. S12, ESI†). It reveals that BPA molecules have to adopt a tilting head-to-tail packing fashion along the (001) direction of the cell lattice because the characteristic Y-shaped aromatic segments cannot pack closely together. Notably, this d-spacing is close to that of 1.98 nm which was observed in the XRD measurement of PAL–pyrene complexes. This suggests that complexation of pyrene with PAL may adopt the characteristic head-to-tail packing fashion along this direction. In addition, the packing of BPA molecules is driven by weak edge-to-face π–π interactions, because the adjacent phenyl rings are tilted toward the plane of the azulene groups in the lattice. Therefore, the Y-shaped aromatic segments of PAL cannot effectively stack with each other by strong π–π interactions. Consequently, such a structure may favor incorporation of pyrene into PAL by more stronger CT interactions, which allows for fabrication of supra-amphiphiles without using organic solvent.[3a]

In conclusion, we have successfully fabricated supra-amphiphiles based on a CT complex between PAL and pyrene in aqueous media. The formation process of the supra-amphiphiles is well monitored, and it is found that the self-assembled nanostructures can reversibly change between cylindrical micelles and disklike nanosheets in response to interaction with guest molecules. Compared with cylindrical micelles of PAL in aqueous solution, self-assembly of supra-amphiphiles leads to disklike micelles with crystalline order. Thus, it is highly anticipated that this line of research may enrich the realm of supramolecular engineering and provide a new avenue for fabricating self-assembling materials for organic electronics.

We acknowledge the financial support from the National Basic Research Program (2013CB834502), the Foundation of Innovative Groups of NSFC (21121004), and an NSFC-DFG joint grant (TRR 61) as well as the Tsinghua University Initiative Scientific Research Program (2009THZ02230). We thank Ms Ling Hu (Tsinghua University) for TEM and electron diffraction measurements. We also acknowledge Prof. Zhibo Li, Mr Yu Liu (Institute of Chemistry, CAS), Mr Kai Liu, and Mr Yu Yi (Tsinghua University) for helpful discussion.

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10 A weak, broad absorbance corresponding to characteristic S_0–S_1 transition of the azulene unit between 615 and 640 nm (Fig. S1, ESI†) was not changed before and after complexation (see ref. 10), which was consistent with the recent result reported by J. F. Stoddart *et al.* that the S_0–S_1 transition of the azulene unit is not involved in the charge transfer process (see ref. 3*e*). Therefore, we did not show the absorbance over 550 nm for clarity.

11 Fitting the longest wavelength profile to a Gaussian band shape allows us to split the CT band form the overall absorption.

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