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Hierarchical self-assembly of *p*-terphenyl derivative with dumbbell-like amphiphilic and rod-coil characteristics

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ABSTRACT

As water is gradually added, a *p*-terphenyl derivative with dumbbell-like amphiphilic and rod-coil characteristics can hierarchically self-assemble to metastable rectangle columns architecting sheets first and then to stable quasi-hexagonal columns architecting rolled sheets, and finally to rod-like nanostructures in MeOH/H_2O solution. Interestingly, the formed sheet, rolled sheet, and nanorod possess blue-light emitting property.

Molecular self-assembly recently has attracted considerable attention for its use in the design and fabrication of nanostructures, leading to the development of advanced materials;[1] and many efforts have always been focused on designing new building blocks for exploration of novel properties and functions.[2] Bolaamphiphile and rod-coil molecules have been extensively studied as important building blocks in self-assembly research. The former, containing a hydrophobic skeleton and two hydrophilic heads on both ends, can form a variety of nanostructures in solution, such as monolayer vesicles, fibers, and tubules;[3] and the latter imparts microphase separation of the rod and coil blocks into ordered periodic structures in nanoscale dimensions due to the mutual repulsion of the dissimilar blocks.[4] Contrary to the conventional bolaamphiphile with flexible alkyl chains as hydrophobic spacer, the dumbbell-like amphiphile with rigid hydrophobic spacer, especially that which possesses rod-coil characteristic, was scarcely investigated, though combination of multi-supramolecular driving forces in one molecule would lead to more abundant and special nanostructures and mesophases.[5] Recently, Tschierske's group thoroughly and systematically studied the thermotropic liquid crystalline behavior of the bolaamphiphiles with biphenyl spacer and a lateral grafting hydrophobic chain,[6,7] following their previous research on the lyotropic liquid crystalline behavior of *p*-terphenyl amphiphiles with a lateral hydrophilic group.[8] For such molecules with multi-driving force, however, we are more interested in their self-assembling behavior in solution, especially the direct preparation of nanostructure materials from them. Herein, we designed and synthesized a novel symmetrical building block **A**, which possessed the characteristics of both dumbbell-like amphiphile and rod-coil molecule. It consisted of three parts, that is, rigid *p*-terphenyl core, hydrophilic trihydroxymethyl and amide groups on each end, and coil-like alkoxy chain on both sides of the core (Scheme 1 and Fig. S1). Interestingly, it could hierarchically self-assemble into various nanostructures in MeOH/H_2O solution depending on the amount of water, and its self-assembling behavior was completely different from that of the general bolaamphiphiles and rod-coil molecules.[3,4] In addition, the formed sheet, rolled sheet, and nanorod have blue-emitting property.

The synthetic route of compound **A** is outlined in Scheme 1. 4-Dihydroxybroanylbenzoic acid (**1**) was synthesized by a reported method.[9] 1,4-Dibromo-2,5-didodecyloxybenzene (**2**) was easily synthesized according to the reported procedure.[10] Compound **3** was synthesized by Pd-catalyzed Suzuki cross-coupling reaction in 68% yield from **1** and **2**. And compound **A** was obtained in 60% yield by the amidation reaction of tri(hydroxymethyl)aminomethane (Tris) with the acyl chloride of **3** at 0 °C in dimethyl acetamide (DMA).

Compound **A** is soluble in MeOH up to 4 mg/mL and insoluble even in hot water. When water was added gradually (one drop per 5 s by using a 1 mL syringe) to 1 mL solution of **A** in MeOH (2 mg/mL) with stirring, the mixture became cloudy within minutes or hours as described in Table 1, depending on the amount

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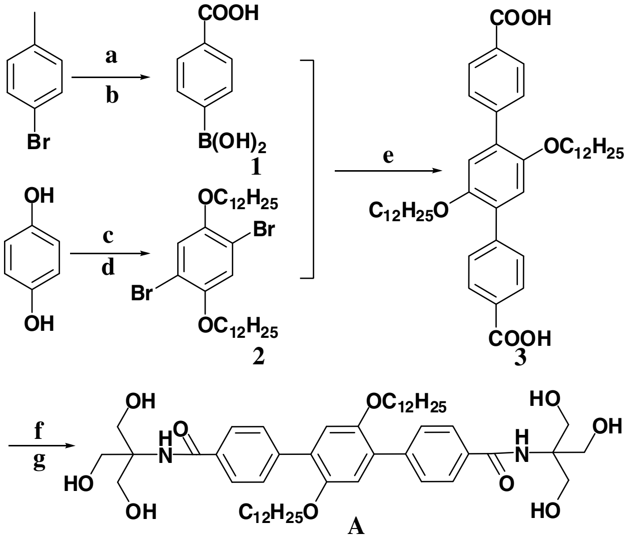

Scheme 1. Synthetic route of compound **A**. Reagents and conditions: (a) (1) Mg/I_2, THF, reflux 12 h; (2) $B(OMe)_3$, −78 °C, 4 h/ rt, 12 h; (3) H^+/H_2O, 30 min, 70%; (b) $KMnO_4$, H_2O/OH^-, 24 h, 60%; (c) 1-bromododecane, acetone, Na_2CO_3, reflux, 8 h, 75%; (d) Br_2, CCl_4, rt, 12 h, 94%; (e) 2 M Na_2CO_3, $Pd(PPh_3)_4$, dioxane/EtOH, reflux 72 h, 68%; (f) $SOCl_2$, $CHCl_3$, 12 h, 82%; (g) tri(hydroxymethyl)aminomethane, DMA, 0 °C,4 h/ rt, 12 h, 60%.

of water. After 24 h, the superstratum was monitored by TEM and SEM, and remarkably different morphologies were observed as shown in Figures 1, S2, and S3.

It is evidently demonstrated that the amount of water added determines the morphologies of the self-assembled arrays. For **A1**, the morphology was sheet-like (Fig. 1a); and in **A2**, some rod-like nanostructures appeared and coexisted with the sheets (Fig. 1b). In **A3**, however, only regular rods with the width from ca. 80 nm to 200 nm and the length up to several micrometers were formed, and the end of the rod is solid instead of being hollow (Figs. 1c and S2). From the coexistence phenomenon of sheets and rods, we can infer that a transition state of rolled sheet would exist, through which the rod can be transformed from sheet. For that, a series of control experiments were conducted and as expected, stable rolled sheets were found when a large amount of water was used as in **A4** and **A5** (Figs. 1d, e, and S3). In addition, when 0.1 or 0.2 mL more water was added into **A3** after 24 h, no rolled sheet was found by TEM, which further supported our presumption that rolled sheet is a 'frozen' transition state. Furthermore, to investigate the effect of time on the morphologies, TEM observations were conducted, respectively, three days later and 2 weeks later, and no difference in morphology was found for the same sample. We noted such self-assembling phenomena, especially the formation of the regular solid nanorod, are distinctly different from those of usual bolaamphiphiles,[3] even those with rigid naphthalene diimide or azobenzen spacer.[11]

Table 1
Conditions and morphologies of self-assembled nanostructures formed from compound **A** in $MeOH/H_2O$ solution

	A1	A2	A3	A4	A5
Water (mL)[a]	0.1	0.2	0.3	0.4	0.5
Time[b]	—[c]	12 h	5 h	5 min	1 min
Morphology (Fig.)	Sheet (1a)	Rod, sheet (1b)	Rod (1c)	Rolled sheet (1d and e)	Rolled sheet (S2)

[a] The amount of water added.
[b] Time of precipitate emergence.
[c] No precipitate appears in 2 weeks.

A1 was spin-coated on a glass slide (1 cm × 1 cm), and then X-ray powder diffraction was conducted. The three peaks in the small-angle region (Fig. 2a) can be indexed as 10-, 01-, 11-reflections of a rectangular 2D lattice based on the reciprocal spacings of 10-:11- is $1{:}2^{1/2}$. The lattice parameters amount to $a = 2.8$ nm

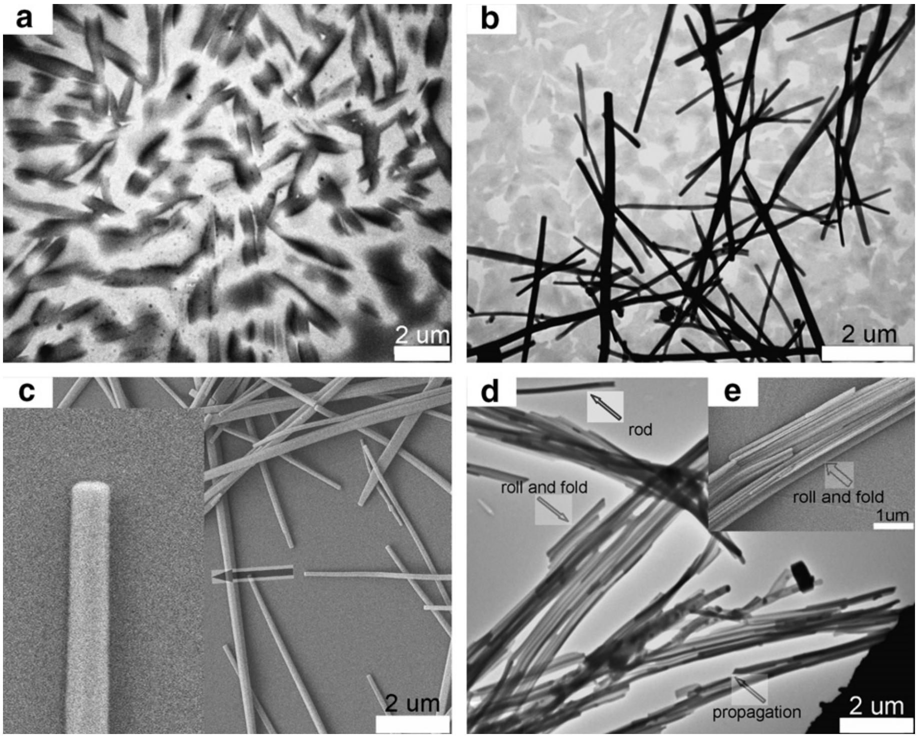

Figure 1. Electron microscopy pictures of self-assembled sheets (a, TEM); sheet and rod (b, TEM); nanorods and its end (inset) (c, SEM); and rolled or folded sheet (d, TEM; e, SEM) formed in **A1**, **A2**, **A3**, and **A4**, respectively, listed in Table 1, respectively.

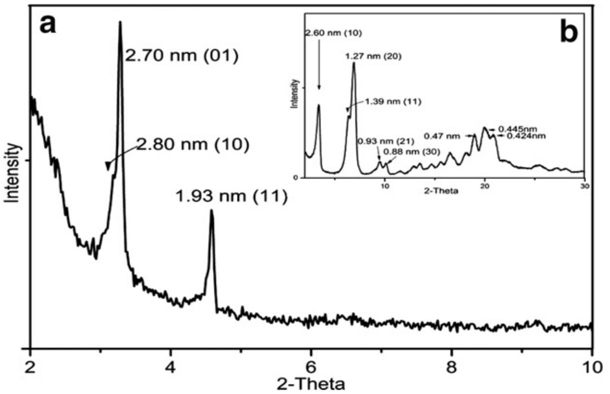

Figure 2. Power X-ray diffractograms of the self-assembled aggregates from **A1** (a) and **A3** (b) listed in Table 1.

and $b = 2.7$ nm. Meanwhile, the diffractogram of the dried assemblies of **A3** and **A4** shows five reflection peaks in this region. Their reciprocal spacings are close to the ratio $1:(3^{1/2}):(4^{1/2}):(7^{1/2}):(9^{1/2})$, and so they can be indexed as 10-, 11-, 20, 21-, and 30-reflections of a quasi-hexagonal columnar structure with lattice parameter $a_{hex} = 2.9$ nm for **A3** and 3.0 nm for **A4**.[12] The representative graph of **A3** is shown in Figure 2b, and their lattice spacings are listed in Table S1. The diffractogram of the crystal of compound A from hot saturated MeOH/H_2O (v/v = 4:1) solution showed no reflections in the small-angle region ($2\theta < 4$), which excluded the possibility of crystallization of the samples (Fig. S4). Noticeably, as the amount of water increases, the packing model of molecule **A** transforms from the metastable rectangle into a more stable quasi-hexagonal columnar structure. Similar phase transition was also observed by Tschierske et al. in the mesophase of bolaamphiphile liquid crystal depending on the length of grafting alkyl chain.[6] Next, we try to clarify what kind of driving force leads to the formation of columnar structure rather than classic monomolecular layer-based vesicles or tubular structure formed by general bolaamphiphiles[3,13] and how the molecule**s** are packed in such columns.

p-Terphenyl is a well-known luminescent species in the near UV region,[14] which can be employed in monitoring the self-assembling process.[15] Compound **A** shows three absorption maxima at 250 nm, 281.4 nm, and 333.8 nm, and the molar extinction coefficient at 281.4 nm, standing for the *p*- terphenyl,[14] is ca. 23774 M^{-1} cm^{-1}. Water (0.5–2 mL) was added to five samples of 2 mL methanol solution of **A** (0.05 mM), respectively, and the change in absorption spectra was recorded and is shown in Figure 3. When the amount of water was more than 1.5 mL, the maxima absorption at 281.4 nm red-shifted to 285.8 nm and then to 287.4 nm, and the bands became broad. Additionally, we also recorded the change in absorption spectra with time of curve d (i.e., the amount of water is 1.5 mL, Fig. 3 inset). As time goes by, the intensity of absorption decreases and the maxima absorption band shows a little red-shift in 30 mins. Hence, it is reasonable to consider that π-stacking of *p*-terphenyl and hydrophobic effects of the *p*-terphenyl groups themselves and the long alkyl chains attached to them are the main driving force of the different self-assembling structures.

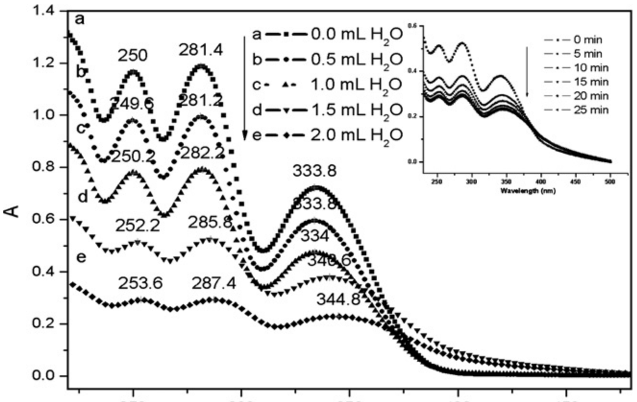

Figure 3. Absorption spectra of **A** in MeOH/H_2O solution with different amounts of water, and the change of d with time (inset).

FT-IR spectra of **A1**–**A4** (Fig. S5) all showed two peaks at 1641 and 1531 cm^{-1} for the amide I and II bands, supporting the existence of the amide hydrogen-bonds.[13a,b] Because the amide's hydrogen-bonds can exist in high polar solvent (e.g., *N*-methylpyrrolidone) and even aqueous solution, it is also reasonable to consider that the amide's hydrogen-bond should be one of the driving forces for the different assembling structures.[13]

STM technology was used to further investigate the driving force of self-assembly and the molecular packing of compound **A** (Fig. 4a). As expected, it forms a uniform and well-ordered quasi-rectangle network adlayer in a scale of 50 nm (Fig. S6), which can be regarded as alternative hydrophobic and hydrophilic domains. The particular bright bar corresponds to the *p*-terphenyl skeleton due to its larger electronic density. The length of the bar is measured to be 1.4 ± 0.2 nm and is consistent with the size of *p*-terphenyl core based on the CPK model of monomolecule (Fig. S1). The distance between two adjacent parallel *p*-terphenyl groups is ca. 1.64 nm, corresponding to length of alkoxy group on the *p*-terphenyl. The packing model is proposed in Figure 4b. The microphase separation of the hydrophobic and hydrophilic parts in compound **A** can be evidently seen in the STM picture, though the interaction between the long alkoxy group and the highly oriented pyrolytic graphite (HOPG) substrate is another important factor in the formation of such a self-assembled pattern. In contrast, bolaamphiphiles formed lamellar arrays on HOPG in general,[16] and network structure is often formed from the assembly of two or more kinds of molecules.[17]

Based on the above-mentioned results, we consider that the dumbbell-like amphiphiles are prone to form a rectangle or hexagonal framework due to the size mismatch of hydrophilic heads and the terphenyl core with long side alkoxy chains when the self-assembly is mainly driven by hydrophobic effect and π-stacking of terphenyl; and the long alkoxy chains fill exactly in the space between the terphenyl groups to stabilize such a framework. Inspired by Tschierske's[7a] molecule packing model in the columnar structure of liquid crystal, a possible molecular packing model of the columns is proposed in Figure 5.

At last, the formation mechanism of self-assembled arrays featuring a variety of morphologies will be discussed. In the initial stage of self-assembly, the rectangle columns with hydroxy-containing hydrophilic domains and alkoxy and terphenyl-based hydrophobic domains are dispersed on the sheet surface. Such domains play a role like 'glue' on the sheet and therefore it can be iconically regarded as a two-faced sticky paper. As the amount of water increases, the rectangle columns are transformed to more stable hexagonal columns; at the same time, the sheets begin to roll tightly into solid bars. The process is shown in Figure 6. As for the general bolaamphiphiles, however, the surface of their self-assembled entities would be uniform, non-sticky and compatible with solvent system, which makes them unlikely to roll into solid rod, but liable to form monomolecular layer-based tubular or vesicle structure.[3] Yao and co-workers[18] first reported the formation of submicrotubes from rolled sheet-like structure, however, no report on the formation of the organic solid nanorods via the mechanism on rolling up self-assembled sheets was given till now to the best of our knowledge.

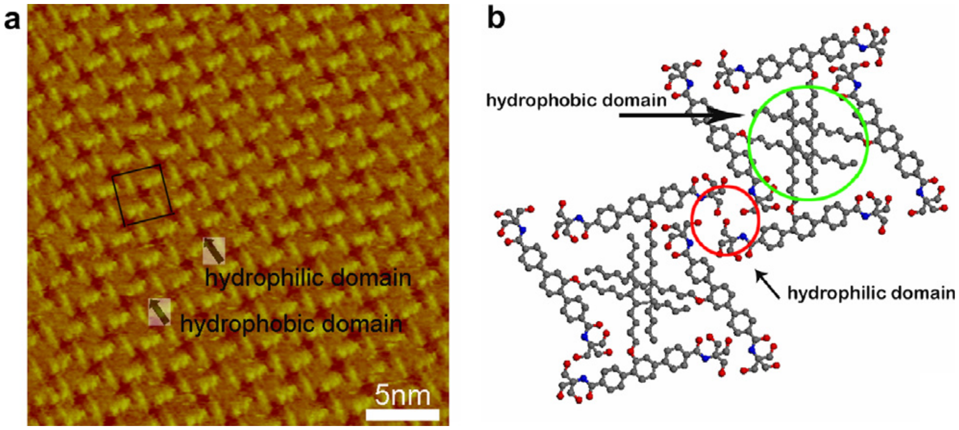

Figure 4. STM images of the well-ordered assembly of **A** on HOPG (a) and the corresponding packing model, alkoxy groups on the periphery are omitted for simplification (b). Tunnelling conditions: E_{bias} 619.2 mv, set point 753 pA.

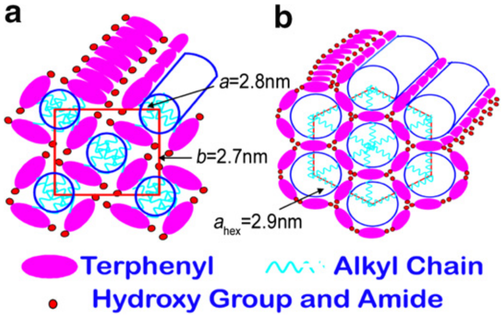

Figure 5. Possible molecule packing model in rectangle (a) and quasi-hexagonal (b) columnar structure, in which four and six terphenyls enclosed a column of alkoxy chains, respectively.

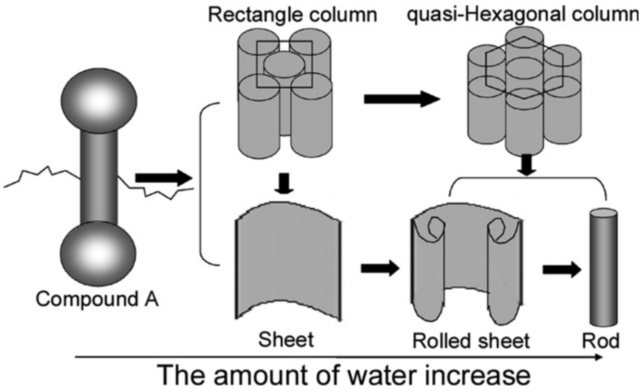

Figure 6. The schematic map of the self-assembling process from **A** to sheet, then rolled sheet and finally rod.

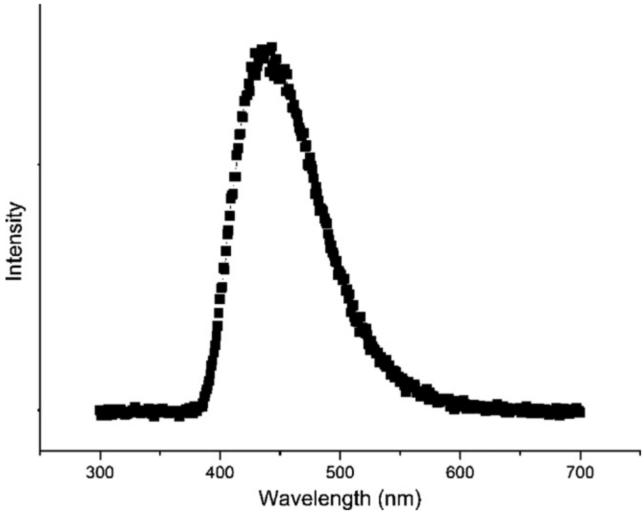

Figure 7. The photoluminescence (PL) spectrum of the formed nanorod in **A3** (excitation 330 nm).

The superstratum in **A1–A5** was spin-coated on a quartz plate. Their photoluminescence (PL) spectra have the same maximum emission wavelength of ca. 438 nm (the typical spectrum of A**3** is shown in Fig. 7). Such results indicated that the formed sheets, rolled sheets, and nanorods can emit blue light, though we cannot observe blue-emitting nanorods directly. We consider such blue-emitting sheet, especially nanorods would be a promising photoluminescent material.

In summary, we have designed and synthesized a *p*-terphenyl derivative **A** combining the structure characteristics of dumbbell-like amphiphile with rod-coil molecule, and studied its hieratical assembly behavior. Driven by hydrophobic effect, π-stacking of terphenyl, and the hydrogen-bonding of amide, compound **A** first packed into rectangle and then to quasi-hexagonal columnar structure in MeOH/H_2O solution with the increasing amount of water; and the corresponding morphology of self-assemblies transformed from sheets to rolled-up sheets, and finally to rods via a rolling and propagating process instead of vesicles formed from the usual bolaamphiphilic compound. Interestingly, all the formed sheets, rolled sheets, and nanorods possess a blue-emitting property.

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Supplementary data

Supplementary data (general experimental procedure and the corresponding characterization are available) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.07.048.

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