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# Helical structures architecture of L-{2-(4-hydroxy-phenyl)-1-[(pyren-1-ylmethyl)-carbamoxyl]-ethyl}-carbamic acid *tert*-butyl ester

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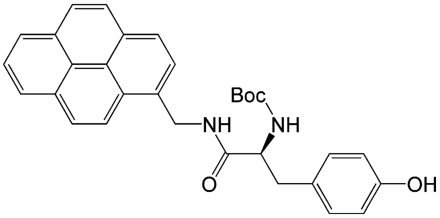
**Abstract**—A new pyrenemethylamine substituted L-Boc-tyrosine derivative was synthesized and characterized. UV–vis, FL, CD, and light scattering experiments proved that the chiral molecules were able to self-assemble for formation of new aggregate structure. The SEM and AFM images indicated that the helical wires could be fabricated by π–π stacking interaction between adjacent pyrene molecules.

The self-assembly of small molecules into a chiral supramolecular architecture on a nanoscale is of great interest due to their potential applications in studies of biological sensors, information storage technology, light energy conversion, and optical devices.[1] Organic supramolecular systems have been formed on a nanometer scale through concerted weak interactions. Hydrogen-bonding, π–π stacking, van der Waals forces, and metal–ligand interactions played central roles in controlling the structures and shapes of the aggregations such as columnar, ribbon, and cylindrical architectures.[2] Several research groups have incorporated chiral moieties in self-assembling organic molecules (such as OPV, porphyrin, thiophene, merocyanine, and perylene derivatives) with the objective of forming chiral supramolecular structures.[3] Pyrene is a well-known chromophore and has been incorporated into self-assembled systems.[4]

Here we would like to report the result of helix transition during the self-assembly of L-{2-(4-hydroxy-phenyl)-1-[(pyren-1-ylmethyl)-carbamoxyl]-ethyl}-carbamic acid *tert*-butyl ester (**PLBT**) through π–π stacking interaction to form perfect helical structures and the optical, chiroptical, and morphological properties that can be modulated by employing different solvents as the key factor for biasing the organization of **PLBT** (Scheme 1). In brief, **PLBT** was readily prepared[5] by an EDCI-mediated condensation reaction of 1-pyrenemethylamine hydrochloride and L-Boc-tyrosine in the presence of 4-(dimethylamino)-pyridine and characterized by IR, $^{1}$H NMR, $^{13}$C NMR, and MS-TOF mass spectrometry. **PLBT** was easily soluble in THF and 1,4-dioxane.

UV–vis absorption spectra are sensitive to interchromophore distance and orientation and have been widely used to study π–π stacking chromophore.[6] **PLBT** in THF solution ($1 \times 10^{-3}$ and $1 \times 10^{-4}$, $1 \times 10^{-5}$ M) at room temperature exhibited absorption spectra with $\lambda_{max}$ at 342 nm and other three peaks at 267, 276, and 326 nm, respectively, which was attributed to the π–π* transition moment of the planar pyrene chromophore



**Scheme 1.** Structure of **PLBT** under investigation.

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*Keywords*: Self-assembly; Chiral; Stacking; Aggregation.

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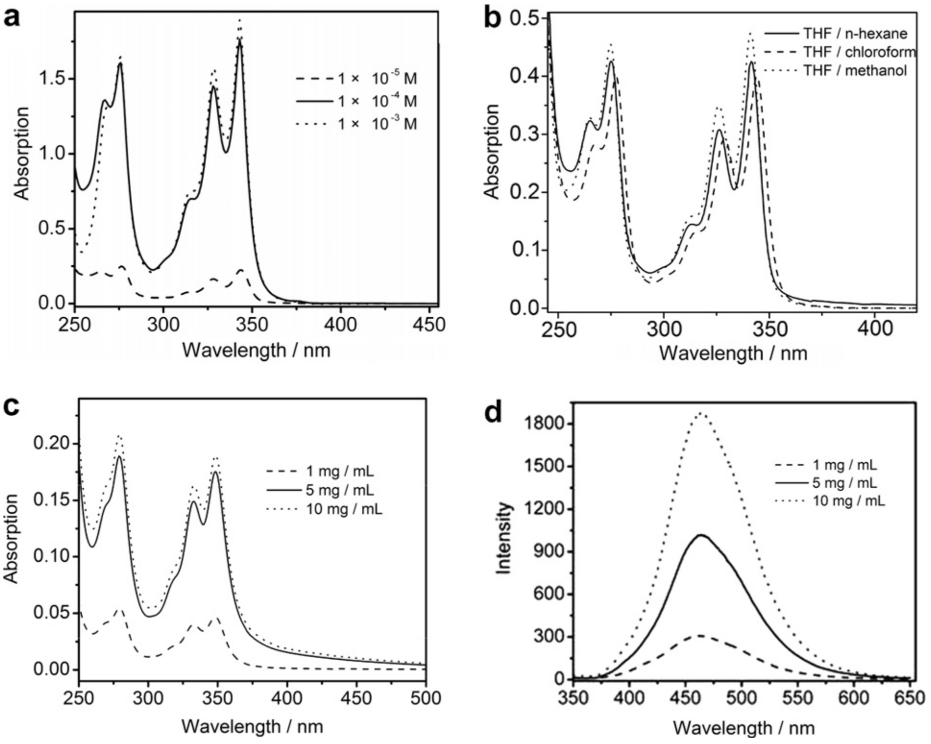

**Figure 1.** (a) UV–vis absorption spectra of **PLBT**: $1 \times 10^{-4}$ and $1 \times 10^{-5}$ M, 1 cm path length; $1 \times 10^{-3}$ M, 1 mm path length. (b) UV–vis absorption of **PLBT** in THF/*n*-hexane (v/v, 1:9), THF/chloroform (v/v, 1:9) and THF/methanol (v/v, 1:9) at room temperature, $c = 2 \times 10^{-5}$ M. (c) Solid-state UV–vis spectra of **PLBT**, as thin films spin-coated from THF solutions. (d) Solid-state emission spectra as thin films spin-coated from THF solutions. Excitation wavelength: 332 nm.

(Fig. 1a).[7] Significant variation of solvent polarity (*n*-hexane, chloroform, and methanol) led to negligible shift (Fig. 1b). These results clearly indicated that the pyrene unit was in monomeric form. The spectra of **PLBT** thin films prepared on quartz slices exhibited clear absorption at 279, 332, and 348 nm, which were the characteristic band of pyrene unit. The red-shift of 6 nm for the absorption of films was probably due to the strong interaction between individual molecules in the densely packed films (Fig. 1c).

As shown in Figure 2a, when the ratio of water:THF was greater than 80:20 in the mixture, the absorption bands of **PLBT** at 326, 342 nm were red-shifted by nearly 10 nm relative to the absorption band in pure THF or water of content less than 80% in the solution and the spectra became broader. Meanwhile, the order of intensity centered at 352 and 337 nm vibronic transitions was reversed, which was indicative of π–π stacking in pyrene units.[8] The red-shift spectra indicated that the aggregation process resulted in the formation of J-type structures.[9]

The fluorescence spectrum of **PLBT** in THF solution exhibited emission maxima at 376 and 395 nm, together with a broad shoulder at 413 nm with excitation wavelength at 326 nm, which is characteristic of monomeric fluorescence of pyrene. This indicates that **PLBT** disperses as a monomeric state in THF as supported by absorption spectra. However, the emission maximum in THF/$H_2O$ showed to be red-shifted and the fluorescence was obviously quenched. In addition, the new band centered at 460 nm was observed, which was assigned to the excimer formation of pyrene units (Fig. 2b). Fluorescence spectra of **PLBT** film on quartz slices spin-coated from the THF solution also show a broad band at 460 nm corresponding to excimer of the pyrene (Fig. 1d).[10] These variations of the absorption and emission spectra revealed that **PLBT** molecules formed aggregates through π–π stacking interaction.[11]

To investigate the possible expression of chirality within the aggregates and thus gain more information on the structure of the assemblies, circular-dichroism (CD) spectroscopy was performed (Fig. 2a).[12] Solutions of **PLBT** in THF were circular-dichroism-inactive at wavelengths longer than 250 nm, thus it was not possible to transfer chiral information from the stereogenic centers to the pyrene unit. However, **PLBT** in THF/$H_2O$ (above 80% water content) showed exciton-coupled bisignate CD signal with negative ($\lambda = 354$, 338, and 288 nm) and positive ($\lambda = 326$, 316, and 274 nm) cotton effects in the region of the $\pi$–$\pi^*$ transition of pyrene, unambiguously confirming that self-assembly architecture took a handed helical conformation.

To get more insight into the self-assembly behavior of **PLBT**, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were carried out. After evaporation of a mixture solvent of **PLBT**, the superstructures of **PLBT** could be observed. SEM images (Fig. 3c–e) showed that **PLBT** from THF/*n*-hexane, THF/metha-

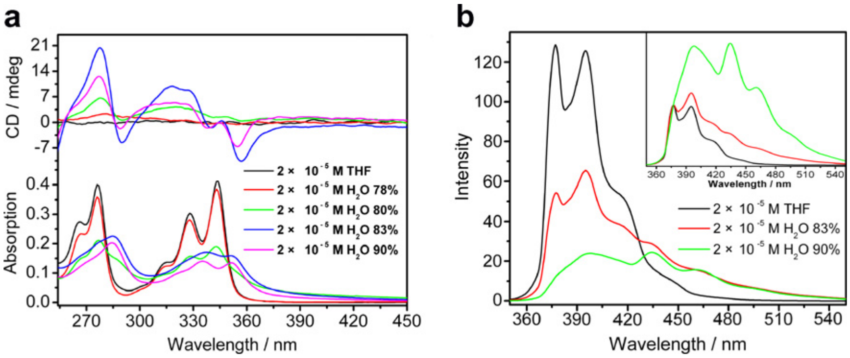

**Figure 2.** (a) UV–vis absorption and CD spectra of **PLBT** in THF, THF/$H_2O$ (v/v, 22:78, 20:80, 17:83, 10:90) at room temperature. (b) Emission spectra of **PLBT** in THF, THF/$H_2O$ (v/v, 17:83, 10:90) ($c = 2 \times 10^{-5}$ M). $\lambda_{ex} = 326$ nm (THF); $\lambda_{ex} = 336$ nm (THF/$H_2O$); inset: the normalized spectra.

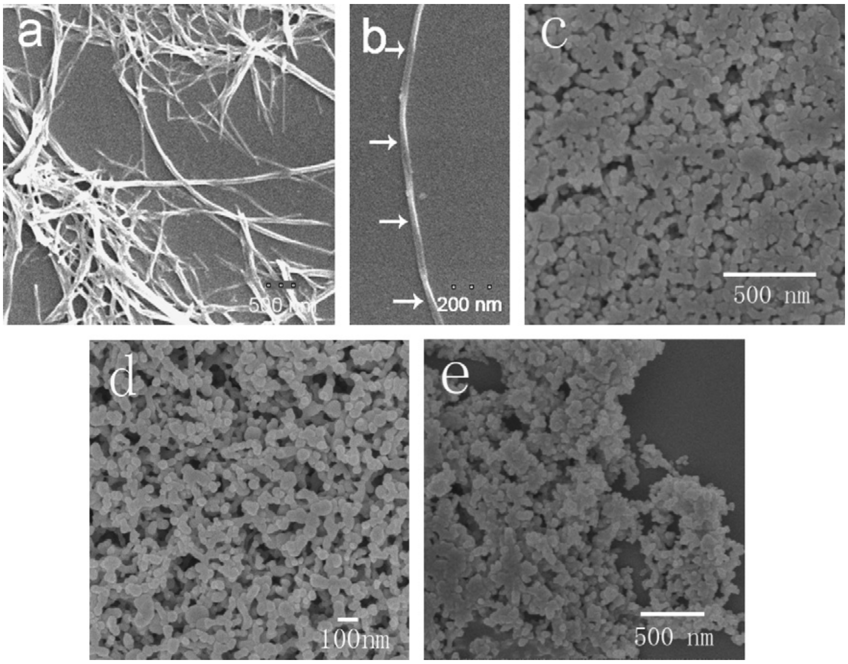

**Figure 3.** SEM images: (a) helical nanowires upon evaporation of its THF/$H_2O$ (v/v, 1:9) solution. (b) An isolated helical wire. (c) Ball-like nanoparticles upon natural evaporation of THF/hexane solution. (d) Ball-like nanoparticles upon natural evaporation of THF/methanol solution. (e) Ball-like nanoparticles upon natural evaporation of THF/$CHCl_3$ solution (concentration: $6 \times 10^{-5}$ M) at ambient temperature.

nol, and THF/$CHCl_3$ could form ball-like nanoparticles with diameters in the range of 20–100 nm. The SEM image (Fig. 3a) shows that **PLBT** from THF/$H_2O$ could form a series of entangled helical wires with diameters in the range of 20–100 nm and lengths of several micrometers. Figure 3b shows an isolated helical nanowire. These results qualitatively supported the view that the helical sense of aggregation was profoundly associated with the CD sign.

Figure 4 shows the AFM images of **PLBT** cast from its dilute solutions in THF/$H_2O$ (v/v, 1:9). The self-assemblies adopted left-handed helical structures, which was in agreement with the CD spectra. The initially formed 1D aggregates with a left-handed twist might wind in the positive direction during the higher-order assembly to result in an ultimate left-handed twist, as could be seen as the large wires of **PLBT** (Fig. 4a). A zoom-in image (Fig. 4b) shows an individual wire separated from a bundle. Careful analysis of the single wire shows the morphology of a left-handed wire of 120 ± 5 nm in width and 27 ± 2 nm in height on the mica surface. Figure 4c and d shows the height and the corresponding phase images of aggregated **PLBT**, respectively. Regular movements of AFM tip through the long axis of assembly with variable pitch length and height profile were characteristic of twisted helical wire-like assemblies of different size that were intertwined.

Dynamic laser light scattering (DLLS) analyses were also performed for the aggregation behavior of **PLBT** in solution.[13] Dissolving a **PLBT** solution in THF into

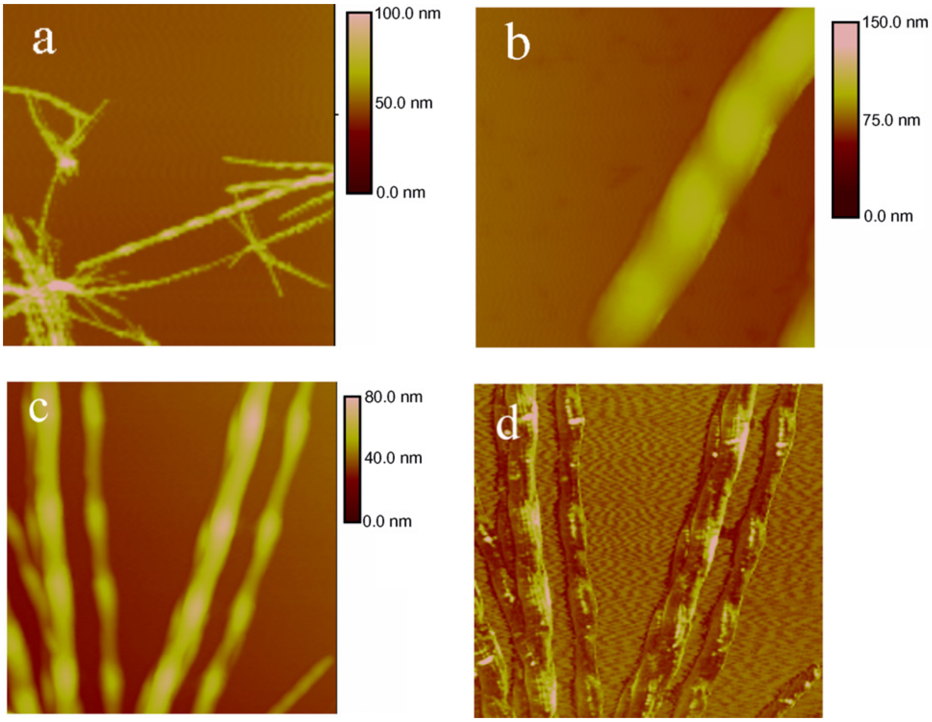

**Figure 4.** AFM images: (a) height image of helical nanowires (6.08 × 6.08 μm), (b) height image of a typical nanowire (600 × 600 nm), (c) magnified height images of wire-like nanostructures (1.04 × 1.04 μm), (d) the corresponding phase image. Samples were prepared in THF/$H_2O$ (v/v, 1:9, $c = 6 \times 10^{-5}$ M) and transferred to freshly cleaved mica by drop-casting under room temperature.

ultrapure water gave a final THF/water ratio of 1:9 (v/v). DLLS experiments were performed with the solution of **PLBT** with concentration of 3 mg/L over a scattering angular range of 30–120°. The CONTIN analysis of the autocorrelation function shows a broad peak corresponding to an average hydrodynamic radius ($R_h$) of approximately 237 nm (Fig. 5a). The formation of cylindrical micelles was confirmed by using the Kratky plot, which shows a linear angular dependence on the intensity of the light scattered by the aggregates (Fig. 5b).

In our experiment, on the basis of the different optical, chiroptical, and morphological properties of **PLBT** in different solvent, it was clear that the spatial arrangements of pyrene in the assembly of molecule **PLBT** were remarkably changed when water was added into the THF solution. When **PLBT** molecules were dissolved in THF, they could disperse into the solution and no aggregation was formed. So no helical wires were observed. However, in a mixture of THF/$H_2O$, the aggregation was initiated by the strong π–π stacking interaction between adjacent pyrene molecules. Mutual rotation in the same direction may reduce steric hindrance between the bulky and hydrophilic L-Boc-tyrosine moieties that are exposed to the aqueous environment. Through homochiral recognition of molecules, molecule **PLBT** could self-sort into L nanostructures during self-assembly (Fig. 6).

In summary, our work represents a typical fabrication of self-assembly from a chiral small molecule to helical supramolecule aggregates by employing different sol-

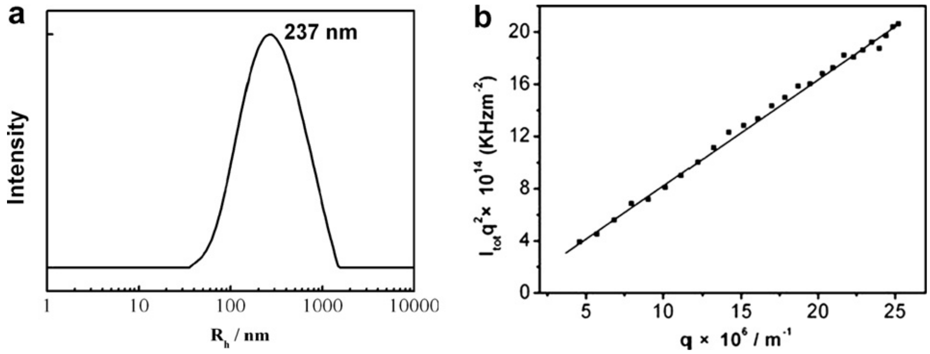

**Figure 5.** (a) Dynamic laser light scattering (DLLS) of **PLBT** (3 mg/L) in THF/$H_2O$ (v/v, 1:9) (from CONTIN analysis of the autocorrelation function) at a scattering angle of 30°. (b) Kratky plot and linear fit of **PLBT** (3 mg/L).

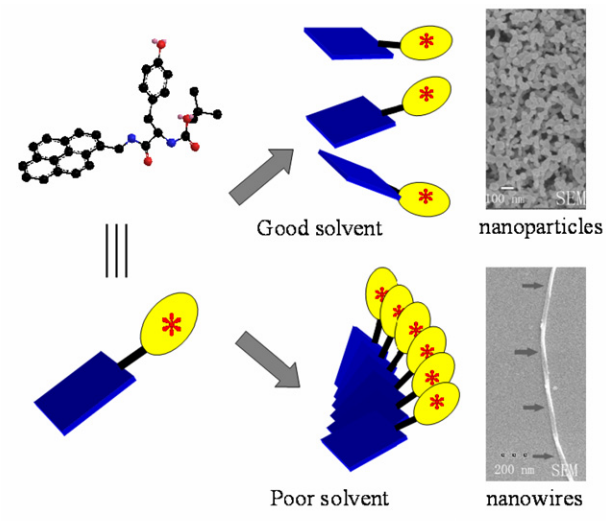

**Figure 6.** Schematic representation of self-assembly of compound **PLBT**.

vents and this approach also shows an interesting result for producing large quantities helical nanowires with perfect structure. This might be a simple way to pack organic molecules into supermolecular structures on a nanoscale of controlled morphology and should be helpful for the future design of nanoscopic functional self-assembly.[14]

## Acknowledgments

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