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Supramolecular Helix of an Amphiphilic Pyrene Derivative Induced by Chiral Tryptophan through Electrostatic Interactions

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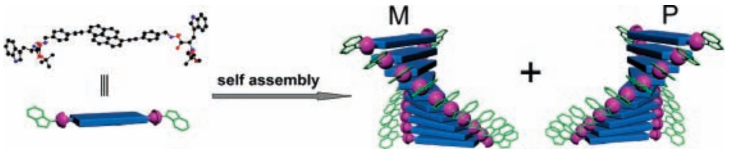
ABSTRACT



An amphiphilic pyrene derivative (PyDNH$_3$) bearing positively charged ammonium cations has been synthesized and characterized. Self-assembly of PyDNH$_3$ in the presence of chiral tryptophan derivatives was investigated in ethanol/water by optical and chiroptical spectra, indicating the formation of helical aggregates. Scanning electron microscope (SEM) images showed the formation of ring-shape structures.

Molecular recognition-driven self-assembly has been widely studied for more than two decades.[1] Especially, in recent years some dye aggregates that could form helical assemblies have led to the development of biomaterials, gels, nanotube materials, chiroptical materials, and highly versatile liquid crystalline materials.[2] Electrostatic interaction, hydrogen bonding, and $\pi-\pi$ stacking interactions play critical roles in successfully controlling the structures and shapes of the aggregations such as columnar, ribbon, and cylindrical architectures.[3] Self-assembly of linear π-conjugated systems has attracted much attention. For example, Ajayaghosh and collaborators reported helicity induction from chiral to achiral molecules in H-bonded supramolecular assemblies in recent years.[4]

Pyrene and its derivatives are the subjects of tremendous investigations because of their interesting optical and elec-

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(1) (a) Lehn, J. M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH Press: New York, 1995. (b) Pedersen, C. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1021. (c) Cram, D. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1009. (d) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijibesma, R. P. *Chem. Rev.* **2001**, *101*, 4071. (e) Ishi-I. T.; Crego-Calama, M.; Timmerman, P.; Reinhoudt, D. N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1924. (f) Berlepsch, H. V.; Kirstein, S.; Böttcher, C. *J. Phys. Chem. B* **2003**, *107*, 9646. (g) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, P. H. J. *Chem. Rev.* **2005**, *105*, 1491. (h) Miyagawa, T.; Yamamoto, M.; Muraki, R.; Onouchi, H.; Yashima, E. J. *J. Am. Chem. Soc.* **2007**, *129*, 3676. (i) George, S. J.; Tomović, Ž.; Smulders, M. M. J.; de Greef, T. F. A.; Leclère, P. E. L. G.; Meijer, E. W.; Schenning, A. P. H. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8206. (j) Shiraki, T.; Morikawa, M.; Kimizuka, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 106.

(2) (a) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384. (b) Palmans, A. R. A.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 2648. (c) Roman, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 63. (d) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449. (e) Prins, L. J.; Huskens, J.; Jong, F. D.; Timmerman, P. *Nature* **1999**, *398*, 498. (f) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039. (g) Ajayaghosh, A.; George, S. J.; Schenning, A. P. H. J. *Top. Curr. Chem.* **2005**, *258*, 83. (h) Ishi-I, T.; Kuwahara, R.; Takata, A.; Jeong, Y.; Sakurai, K.; Mataka, S. *Chem. Eur. J.* **2006**, *12*, 763. (i) Pantoş, G. D.; Wietor, J. L.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2238.

(3) (a) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312. (b) Jolliffe, K. A.; Timmerman, P.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 933. (c) Würther, F.; Thalacker, C.; Sautter, A.; Schärtl, W.; Ibach, W.; Hollricher, O. *Chem. Eur. J.* **2000**, *6*, 3871. (d) Hulvat, J. F.; Stupp, S. I. *Angew. Chem., Int. Ed.* **2003**, *42*, 778. (e) George, S. J.; Ajayaghosh, A.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 3422. (f) Kamikawa, Y.; Kato, T. *Langmuir* **2007**, *23*, 274. (g) Sugimoto, T.; Suzuki, T.; Shinkai, S.; Sada, K. *J. Am. Chem. Soc.* **2007**, *129*, 270. (h) Ajayaghosh, A.; Chithra, P.; Varghese, R. *Angew. Chem., Int. Ed.* **2007**, *43*, 230.

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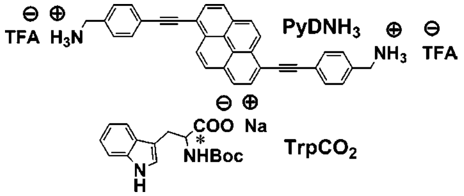
trochemical properties. These materials have high quantum yield, and can be modified by various substituents at the 1-, 6-, and 8-position of the pyrene core, which might tune their absorption and emission spectra.[5] The self-assembly of pyrene and its derivatives into aggregates with controlled nanostructures has attracted significant interest due to the potential applications on optoelectronic devices, sensors, as well as models for photosynthesis.[6] Chiral acids are the common and important structural units in many natural products and drug molecules.[7] In particular, chiral amino acids are not only biologically important but also useful substances for chiral auxiliaries and building blocks in organic synthesis.[8] Integration of these biologically important small molecules and functional organic molecules provides access to supramolecular nanoarchitectures that are capable of converting biomolecular structural information to physicochemical signals. For example, in the group of David K. Smith, excellent low molecular weight gelators were developed that possess a toluene core extended with dendritic amino acid derivatives.[9] Yashima and co-workers also reported hierarchical amplification of chirality information from amino acid derivatives to the dynamic helical polyacetylene.[10] To date, many studies on self-assembly of biological molecules have been focused on biopolymers such as proteins, oligopeptides, and nucleic acids.[11] However, biologically small molecules that graft into chromophores through noncovalent interaction to create functional supramolecular systems also show great potential.

Herein, we describe self-assembly and thermochromic supramolecular behavior of a positively charged pyrene derivative (**PyDNH$_3$**) in the presence of the negatively charged tryptophan derivatives (**TrpCO$_2$**) (Scheme 1). The electrostatic repulsions between the positively charged terminal units of compound **PyDNH$_3$** and the ammonium ion of the amino acid may disturb the attractive interaction because amino acids exist in the zwitterionic form. Therefore, N-protected amino acids with Boc groups were used. For L-**TrpCO$_2$** a negative Cotton effect was observed at the longest wavelength, indicating an M-helical arrangement of the chromophores and the D-**TrpCO$_2$** induced P-helicity under acidic conditions.

Scheme 1. Structure of Compound **PyDNH$_3$** and Chiral Tryptophan **TrpCO$_2$**



Amphiphilic **PyDNH$_3$** consists of an aromatic ethynylpyrene moiety and ammonium group which are linked at both ends of the aromatic core. The synthesis of **PyDNH$_3$** is given in the Supporting Information.[12] **TrpCO$_2$** was obtained according to known literature methods.[13] The resulting molecules were characterized by ^{1}H NMR and ^{13}C NMR and MALDI-TOF mass spectroscopies, which were shown to be in full agreement with the structures presented.

The positively charged **PyDNH$_3$** exhibits good solubility in polar solvents such as ethanol, acetonitrile, and DMSO. **PyDNH$_3$** in ethanol (5×10^{-5} M) shows the monomeric absorption peak with $\lambda_{\max}$ at 394 and 413 nm (for the ethynylpyrene core). It exhibits the emission maxima at 429 and 451 nm with a shoulder at 479 nm upon excitation at 390 nm (Figure S3, Supporting Information). The absorption of **PyDNH$_3$** in ethanol/water (v/v, 8:92) shows similar maxima at 394 and 413 nm. In comparison, the fluorescence was obviously quenched in mixed solvents. The quantum yields (Φ_f) of **PyDNH$_3$** in ethanol and water were measured as $\Phi_f = 0.47$ and 0.04, respectively, with quinine sulfate as standard at 25 °C. These observations support intermolecular chromophore interaction in water and the consequent exciton coupling of the confined chromophores.

Aggregation was observed upon addition of chiral tryptophan to **PyDNH$_3$** solution, which was strongly affected

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(4) (a) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644. (b) Palmans, A. R. A.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8948. (c) George, S. J.; Ajayaghosh, A.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 3422. (d) Ajayaghosh, A.; Vijayakumar, C.; Varghese, R.; George, S. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 456. (e) Ajayaghosh, A.; Varghese, R.; George, S. J.; Vijayakumar, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1141. (f) Ajayaghosh, A.; Varghese, R.; Mahesh, S.; Praveen, V. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7729.

(5) (a) Laurent, A. *Ann. Chim. Phys.* **1837**, *66*, 136. (b) Winnick, F. W. *Chem. Rev.* **1993**, *93*, 587. (c) Sachiko, S.; Tojo, S.; Fujitsuka, M.; Yang, S. W.; Ho, T. I.; Yang, J. S.; Majima, T. *J. Phys. Chem. B* **2006**, *110*, 13296. (d) Rausch, D.; Lambert, C. *Org. Lett.* **2006**, *8*, 5037. (e) Jaska, C. A.; Piers, W. E.; McDonald, R.; Parvez, M. *J. Org. Chem.* **2007**, *72*, 5234.

(6) (a) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100. (c) Seo, Y. J.; Ryu, J. H.; Kim, B. H. *Org. Lett.* **2005**, *7*, 4931. (d) Cuppoletti, A.; Cho, Y.; Park, J. S.; Strässler, C.; Kool, E. T. *Bioconj. Chem.* **2005**, *16*, 528. (e) Li, Y. J.; Li, H.; Li, Y. L.; Liu, H. B.; Wang, S.; He, X. R.; Wang, N.; Zhu, D. B. *Org. Lett.* **2005**, *7*, 4835. (f) Xiao, J. C.; Li, Y. J.; Song, Y. B.; Jiang, L.; Li, Y. L.; Wang, S.; Liu, H. B.; Xu, W.; Zhu, D. B. *Tetrahedron Lett.* **2007**, *48*, 7599.

(7) (a) Coppola, G. M.; Schuster, H. F. *α-Hydroxyl Acids in Enantioselective Syntheses*; VCH: Weinheim, Germany, 1997. (b) Aboul-Enein, H. Y.; Wainer, I. M., Eds. *The Impact of stereochemistry on Drug Development and Use*; John Wiley & Sons: New York, 1997. (c) Challener, C. A., Ed. *Chiral Intermediates*; Ashgate: Hampshire, UK, 2001.

(8) (a) Kuhn, L. A.; Thorpe, M. F. *Protein Flexibility and Folding*; Elsevier: Amsterdam, The Netherlands, 2001. (b) Jons, J. *Amino Acid and Peptide Synthesis*, 2nd ed.; Oxford University Press: Oxford, England, 2002.

(9) (a) Hirst, A. R.; Smith, D. K.; Feiters, M. C.; Geurts, H. P. M.; Wright, A. C. *J. Am. Chem. Soc.* **2003**, *125*, 9010. (b) Hirst, A. R.; Smith. M. C.; Feiters, M. C.; Geurts, H. P. M. *Langmuir* **2004**, *20*, 7070. (c) Huang, B. H.; Hirst, A. R.; Smith, D. K.; Castelletto, V.; Hamley, L. W. *J. Am. Chem. Soc.* **2005**, *127*, 7130. (d) Coates, I. A.; Hirst, A. H.; Smith, D. K. *J. Org. Chem.* **2007**, *72*, 3937.

(10) (a) Saito, M. A.; Maeda, K.; Onouchi, H.; Yashima, E. *Macromolecules* **2000**, *33*, 4616. (b) Maeda, K.; Ishikawa, M.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 15161. (c) Nagai, K.; Sakajiri, K.; Maeda, K.; Okoshi, K.; Sato, T.; Yashima, E. *J. Macromolecules* **2006**, *39*, 5371.

(11) (a) Seeman, N. C. *Acc. Chem. Res.* **1997**, *30*, 357. (b) Ringler, P.; Schulz, G. E. *Science* **2003**, *302*, 106. (c) Zhang, S. *Nat. Biotechnol.* **2003**, *21*, 1171. (d) Hannah, K. C.; Armitage, B. A. *Acc. Chem. Res.* **2004**, *37*, 845. (e) Kim, O. K.; Je, J.; Jernigan, G.; Buckley, L.; Whitten, D. *J. Am. Chem. Soc.* **2006**, *128*, 510.

(12) (a) Lee, J.; Kang, S. U.; Lim, J. O.; Choi, H. K.; Jin, M. K.; Toth, A.; Pearce, L. V.; Tran, R.; Wang, Y.; Szabo, T.; Blumberg, P. M. *Bioorg. Med. Chem.* **2004**, *12*, 371. (b) Leroy-Lhez, S.; Fages, F. *Eur. J. Org. Chem.* **2005**, 2684.

(13) (a) Pastor, I. M.; Västilä, P.; Adolfsson, H. *Chem. Eur. J.* **2003**, *9*, 4031. (b) Nagai, K.; Maeda, K.; Takeyama, Y.; Sakajiri, K.; Yashima, E. *Macromolecules* **2005**, *38*, 5444.

by external conditions such as solvent, chiraltryptophan concentration, and pH. We have investigated the concentration effect of **L-TrpCO$_2$** on the aggregation in ethanol/water. In UV−vis titration experiments, the concentration of **PyDNH$_3$** was kept constant upon addition of **L-TrpCO$_2$** at different ratios. As shown in Figure 1A, the addition of **L-TrpCO$_2$** (0−1.5 × 10^{-3} M) to **PyDNH$_3$** solution (5.0 × 10^{-5} M) led to a decrease in the intensities of the initial absorption bands at 394 and 413 nm with the concomitant growth of an intense red-shifted band at 451 nm through an isosbestic point at 426 nm. These results suggest that J-type assemblies are formed in the solution, which are promoted by the electrostatic and $\pi-\pi$ stacking interactions among the complex.[14] The concentration dependence of the aggregation was also reflected in the fluorescence and induced CD (ICD) spectra. Figure 1B showed the fluorescence spectra for a solution of the complex in ethanol/water at different ratios. When the concentration of **PyDNH$_3$** was kept constant, the fluorescence of the complex showed obvious quenching with increasing concentration of **L-TrpCO$_2$**. CD spectroscopy was helpful for monitoring the definitive interaction between **PyDNH$_3$** and amino acid deirvatives. **PyDNH$_3$** itself was optically inactive, and no CD signal was detected in ethanol/water (Figure 2A). However, upon the addition of chiral tryptophan derivative, the exciton-coupled CD signals with negative (482, 418, 390 nm) and positive (455, 432, 367 nm) Cotton effects were observed in the region of the $\pi-\pi^*$ transition of ethynyl-pyrene. The split-type ICD intensity of the ethynyl-pyrene region increased gradually with increasing concentration of chiral tryptophan and reached a constant value at 30 equiv of **L-TrpCO$_2$** at room temperature. Figure 2B shows the ICD and the absorption spectra of **PyDNH$_3$** in the presence of L- and D-tryptophan in ethanol/water (v/v, 8:92) at [**PyDNH$_3$**]/[**TrpCO$_2$**] = 1:10. The complex exhibited mirror images of the split-type intense ICDs in the π-conjugated ethynyl-pyrene region (300−550 nm), which showed a good relationship between the Cotton effect signals and the absolute configurations of chiral amino acid derivatives. These observations suggest not only that the aggregation of **PyDNH$_3$** in the presence of chiral tryptophan derivatives is strongly affected by amino acid concentration, but also that the complex could form the left- or right-handed helical arrangement based on the configurations of tryptophan derivatives. Under the typical sergeant and soldiers conditions, the complex (**L-**[**TrpCO$_2$**] = 1.0−5.0 × 10^{-5} M; [**PyDNH$_3$**] = 5.0 × 10^{-5} M) did not exhibit any CD siganal (data not shown). Titration of **L-TrpCO$_2$** (5.0 × 10^{-4} M) with **PyDNH$_3$** (1.0−5.8 × 10^{-5} M) resulted in a nonlinear increase of ICD (Figure S5, Supporting Information). These observations support the fact that the complexes exhibited their chirality in the aggregation while all of the positively charged ammonium cations interacted with the negatively charged ions.[15]

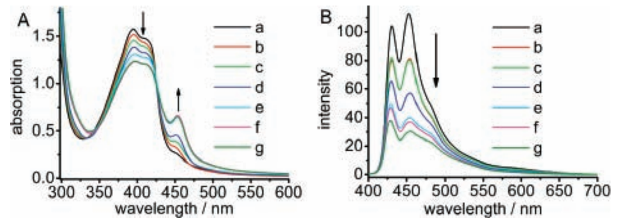

Figure 1. (A) UV−vis absorption and (B) fluorescence spectra (excitation at 390 nm) titration of **L-TrpCO$_2$** to **PyDNH$_3$** in ethanol/water (v/v, 8:92): [**PyDNH$_3$**] = 5 × 10^{-5} M, (a) 0, (b) 2.5 × 10^{-4} M, (c) 5.0 × 10^{-4} M, (d) 7.5 × 10^{-4} M, (e) 1.0 × 10^{-3} M, (f) 1.25 × 10^{-3} M, (g) 1.5 × 10^{-3} M; pH 2.5.

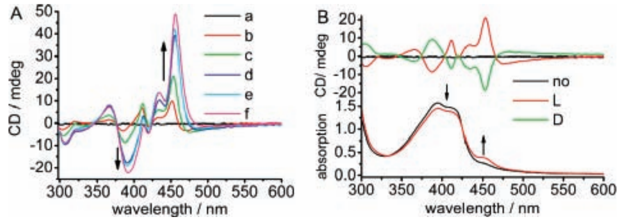

Figure 2. (A) CD spectra titration of **L-TrpCO$_2$** to **PyDNH$_3$** in ethanol/water (v/v, 8:92): [**PyDNH$_3$**] = 5 × 10^{-5} M, [**L-TrpCO$_2$**] = (a) 0, (b) 2.5 × 10^{-4} M, (c) 5.0 × 10^{-4} M, (d) 1.0 × 10^{-3} M, (e) 1.25 × 10^{-3} M, (f) 1.5 × 10^{-3} M; pH 2.5; Figure S4 (Supporting Information) shows the titration curves of **PyDNH$_3$** ($[\theta]_{452}$) with **L-TrpCO$_2$**. (B) CD spectra of complex **TrpCO$_2$/PyDNH$_3$** in ethanol/water (v/v, 8:92): [**PyDNH$_3$**] = 5 × 10^{-5} M, [**L-** or **D-TrpCO$_2$**] = 5.0 × 10^{-4} M; pH 2.5.

Figure 3A,B shows the pH dependence of absorption and fluorescence spectra of aggregation. Increasing the pH of

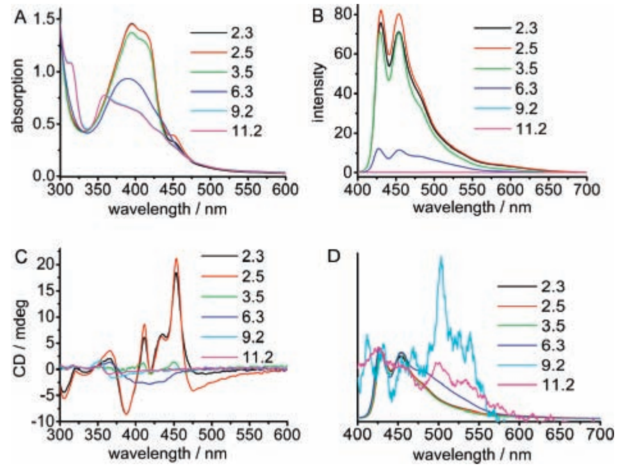

Figure 3. (A) UV−vis absorption, (B) fluorescence spectra, and (C) CD spectra of complex **PyDNH$_3$/L-TrpCO$_2$** in ethanol/water (v/v, 8:92): [**PyDNH$_3$**] = 5 × 10^{-5} M, [**L-TrpCO$_2$**] = 5.0 × 10^{-4} M. (D) Normalized FL spectra.

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[14] (a) Schenning, A. P. H. J.; Jonkheijm, P.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2001**, *123*, 409. (b) Beckers, E. H. A.; Meskers, S. C. J.; Schenning, A. P. H. J.; Chen, Z.; Würthner, F.; Marsal, P.; Beljonne, D.; Cornil, J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2006**, *128*, 649.

the solution from 2.5 to 6.3, the absorption maximum was slightly blue-shifted from 394 to 389 nm. With further addition of NaOH solution to the mixture (pH 9.2, 11.2), the absorption maximum was at 358 nm, accompanied by a slight peak broadening. The largest fluorescence emission was also at a pH around 2.5. Taking the absorption and FL spectra into consideration, we might propose that the complex could precipitate at high pH. From the CD spectra as shown in Figure 3C, the magnitude of the ICD disappeared in basic solution. The experimental results illustrate the maximum J-band absorption at pH around 2.5, which corresponds to the isoelectric point of tryptophan.

To obtain further evidence of the electrostatic interactions between **PyDNH$_3$** and chiral amino acid derivtives, CD spectra were studied as a function of NaCl concentration in solution. The magnitude of the ICD gradually decreased upon successively adding NaCl as shown in Figure S6 (Supporting Information), which corroborated the hypothesis on the electrostatic nature of the interactions between **PyDNH$_3$** and **L-TrpCO$_2$** in aqueous solution.[10]

We studied the morphologies of the complex by SEM. Samples were prepared by casting thin films of the self-assembly complex from ethanol/water solution onto silica slices. Figure S7A (Supporting Information) showed that a complex of ethanol/water ([**PyDNH$_3$**] = 5×10^{-5} M, [**L-TrpCO$_2$**] = 5×10^{-4} M) could form ring-shape aggregations with diameters of several microns. Figure S7B (Supporting Information) displays different morphologies of ring structures and Figure S7C (Supporting Information) shows an isolated ring, whereas compound **PyDNH$_3$** itself from ethanol or ethanol/water (v/v, 8:92) resulted in nanoparticles similar to that previously described[6f] and did not gave any ring structures (Figure S8, Supporting Information). The formation of ring-shape structures might result from the presence of a gas bubble in the solution. The bubble-induced aggregation was the result of a complex process determined by hydrodynamic and surface effects.[16] Dynamic light scattering (DLS) analysis provides direct information about the size of the superstructure in solution. **PyDNH$_3$** (in ethanol), **PyDNH$_3$** (in ethanol/water, v/v, 8:92), and **PyDNH$_3$/L-TrpCO$_2$** (in ethanol/water, v/v, 8:92; pH 2.5) showed broad peaks corresponding to an average hydrodynamic radius (R_h) of approximately 215, 350, and 980 nm, respectively, as shown in Figure S9 (Supporting Information). Combining the SEM and DLS results, one might probably obtain that the chiral amino acid derivative played an important role in controlling the aggregation morphologies of the complex.

A structural model for the spatial arrangement of the ethynyl-pyrene unit in the complex is proposed in Figure 4.

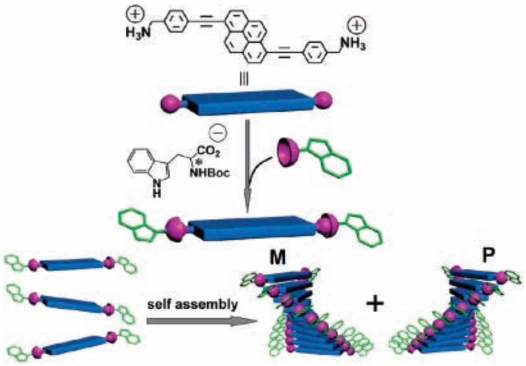

Figure 4. Schematic representation of self-assembly of complex **PyDNH$_3$/TrpCO$_2$**.

The UV−vis, FL, and CD spectra strongly suggest that the configuration of chiral amino acid may hold the key to determine the handedness of the resultant supramolecular assemblies. In ethanol/water, **PyDNH$_3$** was first complexed with chiral amino acid derivatives. Self-assembly of the complex was then initiated by $\pi-\pi$ stacking interaction of ethynyl-pyrene units and hydrophilic and hydrophobic interactions. Mutual rotation in the same direction may reduce steric hindrance between amino acid moieties. Through homochiral recognition of molecules, the complex could twist into a helical arrangement during the self-assembly process.

In summary, we have synthesized an amphiphilic pyrene molecule (**PyDNH$_3$)** and demonstrated the self-assembly and hierarchical helical formation of **PyDNH$_3$** in the presence of chiral amino acid in aqueous solution. By employing the noncovalent combinatorial approach, the biologically small molecules might be the building blocks for the self-assembly. The present study will provide new valuable information for creating a nanoscale chiral architecture that could be developed for designing chiral recognition and nanoscale functional materials.

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Supporting Information Available: Synthetic and experimental details, spectral characterization, and additional spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Fenniri, H.; Deng, B. L.; Ribbe, A. E. *J. Am. Chem. Soc.* **2002**, *124*, 11064.

(16) (a) Judd, R. L.; Lavdas, C. H. *J. Heat Transfer* **1980**, *102*, 461. (b) Schenning, A. P. H. J.; Benneker, F. B. G.; Geurts, H. P. M.; Liu, X. Y.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1996**, *118*, 8549. (c) Vinogradova, O. I. *Colloids Surf. A* **1994**, *82*, 247. (d) Estévez, L. A.; Pino, L. Z.; Cavicchioli, I. A.; Sáez, E. *Chem. Eng. Commun.* **1991**, *105*, 231.