

Self-Assembly and Characterization of A Novel Hydrogen-Bonded Nanostructure

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Received: November 6, 2003; In Final Form: March 11, 2004

A novel hydrogen-bonded supramolecular system of a [60]fullerene derivative with perylene bisimide was synthesized and characterized. ¹H NMR spectra confirmed the existence of strong hydrogen-bonding interaction between compounds **1** and **5**. Transmission electron microscopy images of **1**·**5** aggregates showed spherical particles having a mean diameter of 50 nm. The photocurrent response of the film was measured, and a steady and rapid anodic photocurrent response was obtained.

Introduction

In the past few years, new photoelectric materials containing conjugated organic molecules have attracted commercial and scientific interest.¹ Design and self-assembly of organic molecules into functional superstructures is a main goal in supramolecular chemistry. Control of hydrogen bonding has attracted much attention in the design of various molecular assemblies by virtue of the directionality and specificity.² Well-defined nanosized aggregates should be very useful for the development of novel functional materials and nanoelectronic devices. Hydrogen-bonding assemblies are most promising to fabricate a controllable molecular array and shape for efficient intermolecular energy and electron transfer between donor and acceptor units.^{3,4} The ready availability of [60]fullerene and its derivatives as novel electropool π -systems has increasingly invited exploration of their outstanding physical and chemical properties.⁵ Of particular interest is the hydrogen-bonding assembly by organic molecules of organofullerene molecules containing [60]fullerene, combination of the pyridine unit and carboxylic acid moiety to provide stable hydrogen-bonded molecular assemblies.

In this paper we discuss the self-assembly and characterization of [60]fullerene derivative **1** and perylene bisimide **5** to form a novel hydrogen-bonded supramolecular system in which three amino functionalities of the [60]fullerene moiety positioned on the assembly interact with perylene bisimide via amino–carboxylic acid interaction (Chart 1). Many organic systems have been developed that exhibit reasonable light-harvesting efficiencies, and much has been shown about the energy and electron transfer. And these systems provide effective means to convert photons to electrons.⁶ We hope that the aggregate obtained by complexation of **1** and **5** through hydrogen bonding would be a good candidate for efficient intermolecular energy and electron transfer.

Results and Discussion

The [60]fullerene derivative **1** bearing a 2,6-diacylaminopyridine unit was prepared as previously reported.⁷ The synthesis

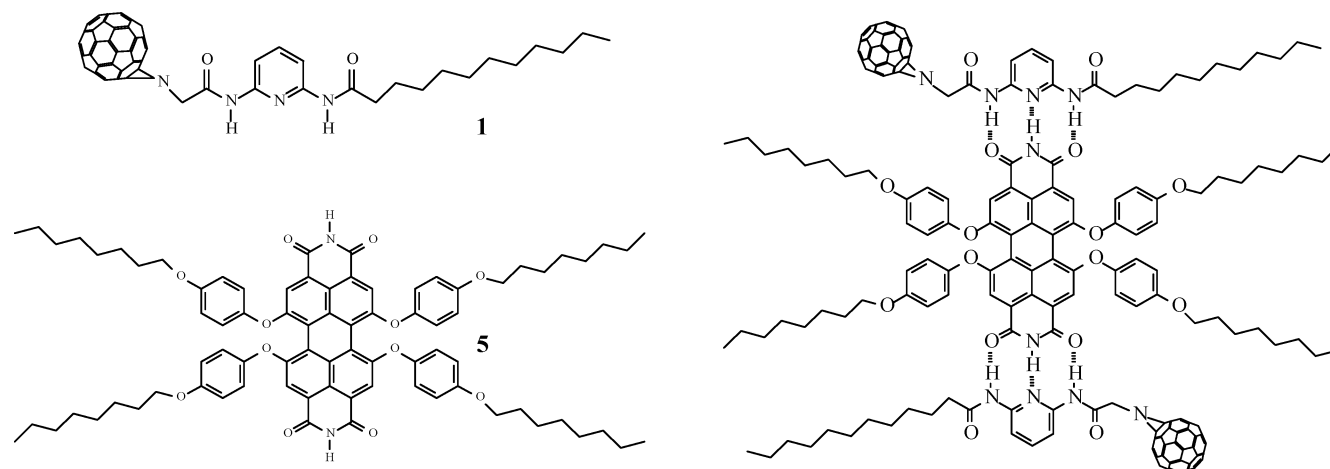
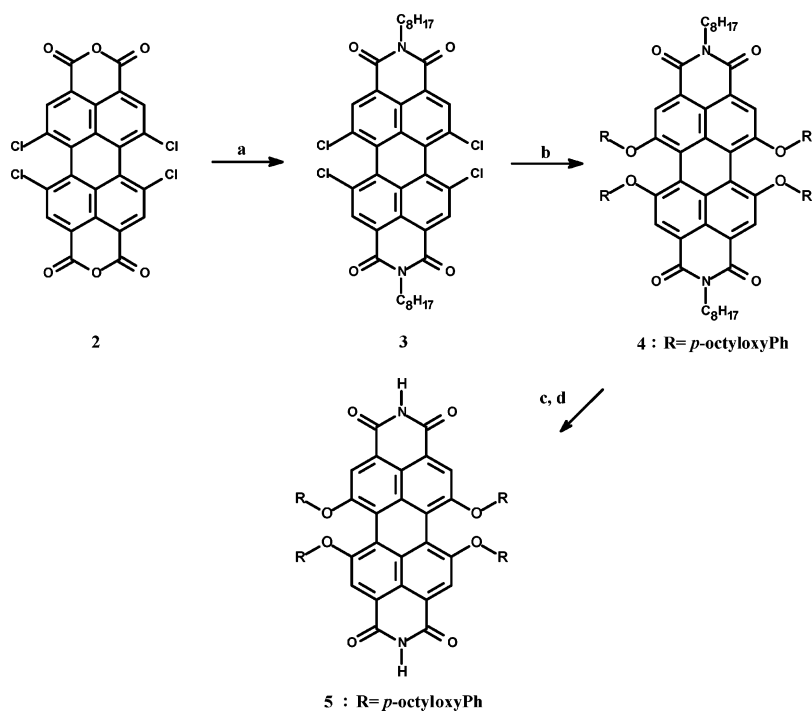
of the perylene bisimide **5** is sketched in Scheme 1. Briefly, 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (**2**) was converted to the corresponding *n*-octyl bisimide **3** using *n*-octylamine. Subsequently, compound **4** was prepared by the nucleophilic substitution of the four chlorine atoms using 4-(*n*-octyloxy)phenol. The perylene bisimide **5** was synthesized by cleavage of the bisimide **4** and reaction with ammonium acetate, according to known methods.⁸

The formation of the hydrogen-bonding self-assembly of **1** and **5** was demonstrated by ¹H NMR spectroscopic studies. Upon complexation of compound **5** by compound **1**, the imide proton signal of **5** underwent a significant downfield shift of several parts per million in the NMR titration experiment since the electron densities of the protons involved in hydrogen bonds were decreased and consequently their NMR signals were shifted to lower magnetic fields. The interaction of **5** with compound **1** was investigated by ¹H NMR spectroscopic titration carried out in CDCl₃. For the ¹H NMR studies, the concentration of **5** was kept constant and the change in the chemical shift was followed as a function of increasing concentration of **1**. The NMR titration experiments revealed a significant downfield shift of the amidic proton signal because of complexation of **1** (Figure 1). The peak at $\delta = 8.39$ ppm was assigned to the N–H protons of compound **5**. When compound **5** (1×10^{-5} M) was blended with 0.5 equiv of compound **1** in CDCl₃, the chemical shift for the proton resonance of the amidic protons of compound **5** changed from 8.39 to 8.73 ppm. When compound **5** (1×10^{-5} M) was blended with 1, 1.5, and 2 equiv of compound **1** in CDCl₃, the chemical shift for the proton resonance of the amidic protons of **5** changed from 8.39 to 8.94, 9.23, and 9.47 ppm, respectively. We also measured a mixture solution of compound **5** (1×10^{-5} M) and 2.5 equiv of compound **1** in CDCl₃, and found that the chemical shift for the proton resonance of the amidic protons of compound **5** changed from 8.39 to 9.69 ppm. These changes are characteristic of the formation of a multiple-point hydrogen-bonding complex. As shown in Figure 2, analysis of the downfield shift of the amidic protons of compound **5** as a function of increasing concentration of **1** provided support for the 1:2 binding model. These results showed that strong hydrogen bonding took place between **1** and **5**, and these assembly motifs exhibited a significantly high stability.

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CHART 1: Superstructure of Self-Assembly of [60]Fullerene Derivative 1 with Perylene Bisimide 5 by Hydrogen Bonding**SCHEME 1: Synthesis of Perylene Compounds^a**

^a Reagents and conditions: (a) *n*-octylamine, propionic acid, reflux, 24 h; (b) 4-(*n*-octyloxy)phenol, K₂CO₃, *N*-methyl-2-pyrrolidinone (NMP), reflux, argon, 24 h; (c) KOH, 2-propanol/water, reflux, argon, 42 h; (d) ammonium acetate, propionic acid, reflux, 24 h.

As shown in Figure 3, the FT-IR spectra of **1** and **5** in CH₂-Cl₂ showed the free NH stretching band at 3344 and 3173 cm⁻¹, respectively. The NH stretching band of the mixture of **1** and **5** (2:1 stoichiometry) in CH₂Cl₂ was observed at 3280 cm⁻¹, which is consistent with the formation of hydrogen bonding between **1** and **5**. These results indicated that a three-point hydrogen bonding between **1** and **5** is formed.

In UV/vis titration experiments, the concentration of **5** was kept constant upon addition of **1** in chloroform at different ratios. The absorption spectrum of **1** has a weak peak at 423 nm which is characteristic of a [6,6]-closed fullerene structure and no absorption at wavelengths $\lambda > 450$ nm.⁷ As shown in the UV/vis spectra (Figure 4), although no obvious shifts of **5** upon addition of **1** are observed, absorption intensities of 1:1 and 1:2 complexes of **5** with **1** exhibit distinct changes due to hydrogen-bonding interaction of **1**•**5**. A similar phenomenon was mentioned by Würthner et al.⁴

As shown in Figure 5a, pure perylene bisimide **3** showed intense fluorescence, and the fluorescence of compounds **4** and **5** showed significant quenching compared with that of compound **3**. Pure perylene bisimides **4** and **5** showed weak fluorescence. This is due to the *p*-octyloxy group of compounds **4** and **5**, leading to strong fluorescent quenching.^{3a,8f} We also found that when compound **5** was added with compound **1** in CHCl₃ at different ratios ([**1**]:[**5**] = 1:1 or 2:1 stoichiometry), the fluorescence of **5** was quenched slightly by the organofullerene (Figure 5b). These results indicated there was intramolecular and intermolecular charge transfer between the octyloxy group and perylene bisimide moiety and between the perylene bisimide and the organofullerene in these systems.

Photocurrent generation of a perylene bisimide **5** and [60]-fullerene derivative **1** film ([**1**]:[**5**] = 2:1 stoichiometry) deposited onto an ITO electrode was measured at 63.2 mW/cm² white light irradiation. A steady and rapid anodic 0.07 μ A

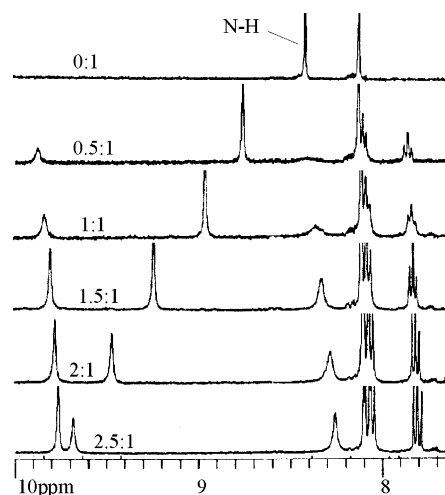


Figure 1. Partial ^1H NMR spectra of the **1·5** supramolecular system in different concentration ratios in CDCl_3 at room temperature. The concentration of **5** was kept constant at 1×10^{-5} M.

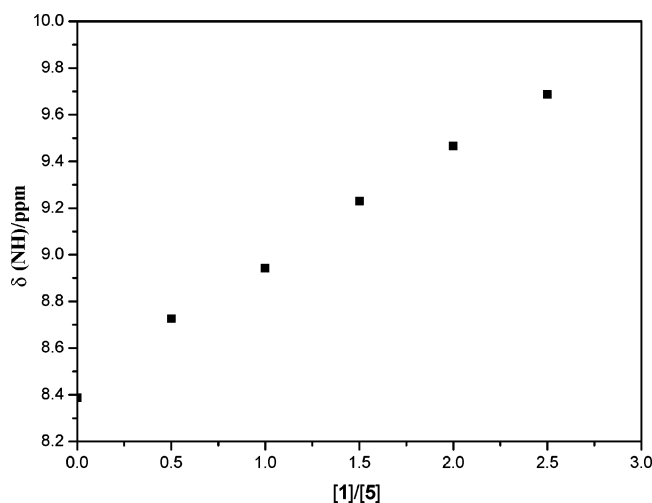


Figure 2. ^1H NMR binding isotherm for **5** with **1** in CDCl_3 at room temperature. The concentration of **5** was kept constant at 1×10^{-5} M.

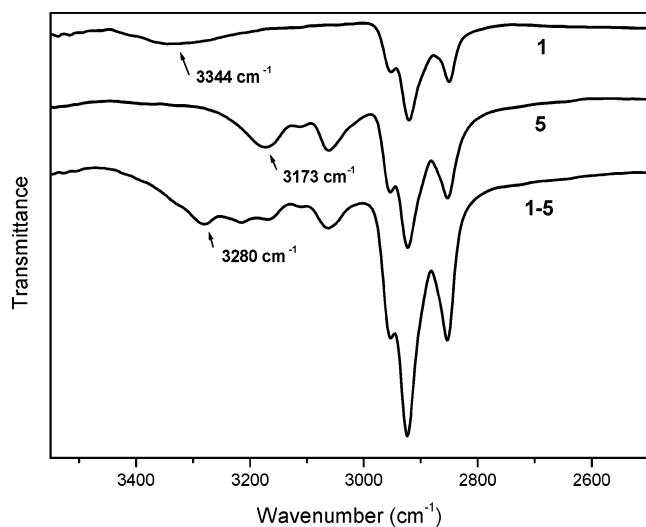


Figure 3. Partial FT-IR spectra of **1**, **5**, and **1·5** ($[\text{1}]:[\text{5}] = 2:1$ stoichiometry) in CH_2Cl_2 .

photocurrent response is shown in Figure 6, as the irradiation of the film was switched on and off. Importantly, the response of on/off cycling is prompt and reproducible; four cycles are

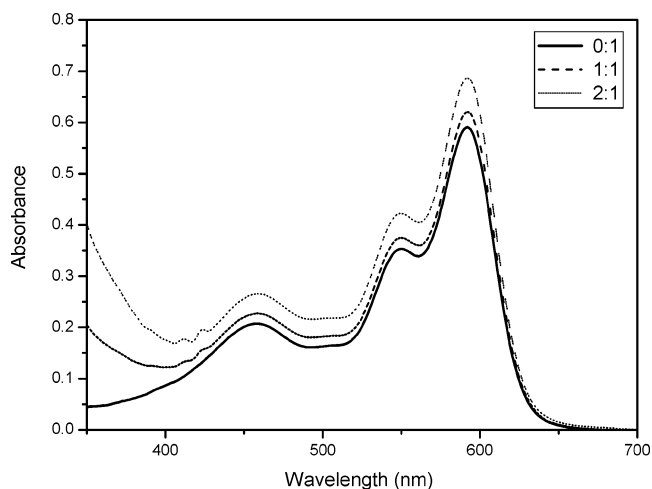


Figure 4. Changes in the UV-vis absorbance of **5** (the concentration of **5** was kept constant at 1×10^{-5} mol/L) upon addition of **1** in CHCl_3 at different ratios ($[\text{1}]:[\text{5}] = 1:1$ or $2:1$ stoichiometry).

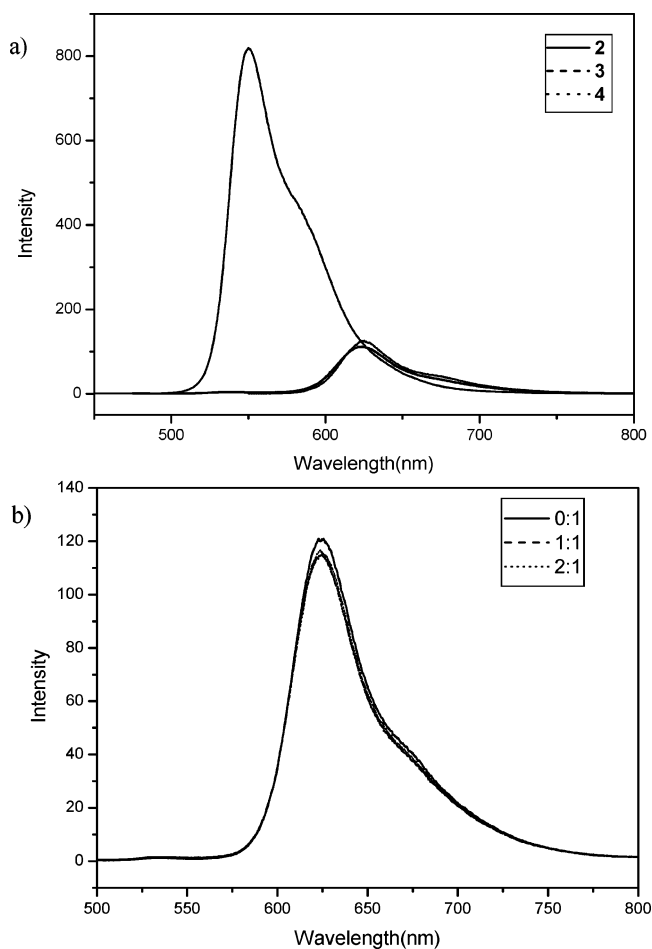


Figure 5. (a) Fluorescence spectra of compounds **3–5** at 1×10^{-5} mol/L in CHCl_3 ($\lambda_{\text{em}} = 467$ nm). (b) Fluorescence titration experiment of **5** (the concentration of **5** was kept constant at 1×10^{-5} mol/L) upon addition of **1** in CHCl_3 ($\lambda_{\text{em}} = 467$ nm) at different ratios ($[\text{1}]:[\text{5}] = 1:1$ or $2:1$ stoichiometry).

measured in the spectrum. The photocurrent stability is rather good in the system during the monitored time.

After evaporation of a dichloromethane solution of the hydrogen-bonded three-dimensional complex **1·5** on a carbon-coated copper grid, the superstructure of **1·5** could be observed in the transmission electron microscopy (TEM) image. Figure 7 shows the self-assembled balls and the size distribution

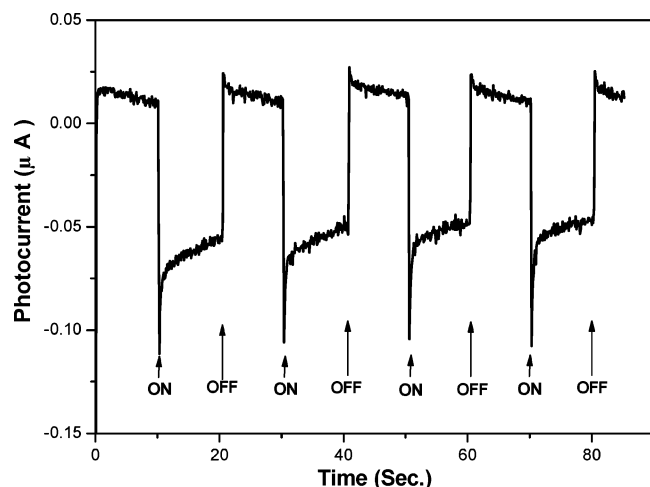


Figure 6. Time dependence of the photocurrent response of the self-assembly film. ([1]:[5] = 2:1 stoichiometry)

histogram of the assemblies of **1** and **5**. The diameters of the balls are in the range of 30–80 nm. As the image shows, the **1**·**5** system consists of spherical particles having a mean diameter of 50 nm. It is likely that this is driven by phase transitions in the drying process and would depend on the solvent, substrate, and environment. The similar ball-like superstructures of self-assemblies of organofullerene containing a 2,6-diacylaminopyridine unit with a uracil derivative through three-point hydrogen bonding in chloroform were also observed in our previous

research.^{7a} However, the ball-like superstructures of the **1**·**5** system in dichloromethane look more uniform. And the Würthner group reported the supramolecular strands of perylene bisimide–melamine assemblies which self-organized hierarchically by means of orthogonal noncovalent interactions as given with triple hydrogen bonding and π – π interactions in methylcyclohexane.³ On the basis of this information, we presume that the formation of the superstructures of the ball-like assemblies of **1**·**5** results from intermolecular hydrogen bonding and π – π interactions between **1** and **5**.

Conclusions

In conclusion, a novel hydrogen-bonded supramolecular system of a [60]fullerene derivative with perylene bisimide was synthesized and characterized. ¹H NMR spectra confirmed the existence of strong hydrogen-bonding interaction between the [60]fullerene derivative and perylene bisimide. The ball-like superstructure could be of importance for future studies on three-dimensional nanomaterials applied in the field of photoelectric devices.

Experimental Section

Materials and Measurements. Most of the chemical reagents were purchased from Acros or Aldrich Corp. and were utilized as received unless indicated otherwise. 1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride (**2**) was supplied by BASF. All solvents were purified using standard

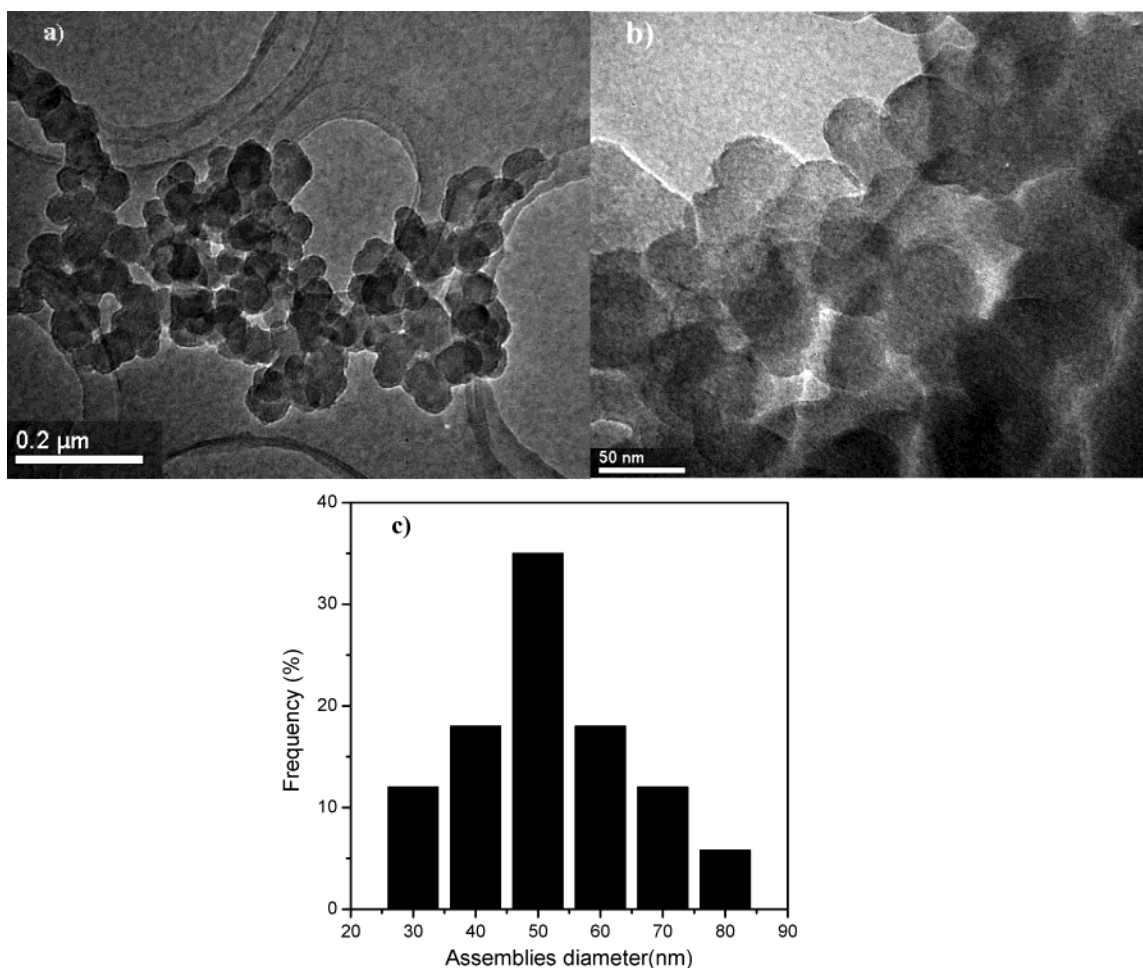


Figure 7. (a) Transmission electron micrograph of assemblies that was obtained by evaporation of a 1×10^{-5} mol/L dichloromethane solution of the **1**·**5** complex (2:1 stoichiometry) on a carbon-coated copper grid. (b) High magnification of the TEM image. (c) Size distribution histogram of the assemblies.

procedures. Column chromatography was performed on silica gel (mesh size 160–200 μm). UV/vis spectra were taken on a Hitachi U-3010 spectrometer, and fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer. NMR spectra were obtained on a Bruker Avance DPS-400 (400 MHz) spectrometer. FT-IR spectra were measured on a Bruker EQUINOX55 spectrometer. MALDI-TOF mass spectrometric measurements were performed on a Bruker Biflex MALDI-TOF mass spectrometer.

***N,N'*-Dioctyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic Acid Bisimide (3).** In a 100 mL single-necked flask, 1.59 g (3 mmol) of **2** was finely suspended in 50 mL of propionic acid. Then, 2.5 mL (15 mmol) of *n*-octylamine was added, and the mixture was refluxed under stirring for 24 h. After the mixture cooled to room temperature, the precipitate was filtered, washed neutral with water, and dried in a vacuum at 100 °C to give the crude product as a red solid (2.03 g, 90%). The crude product was purified by column chromatography on silica with CH_2Cl_2 to give **3** (1.69 g, 83%): ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 8.69 (s, 4H), 4.23 (t, 4H, $J = 8.2$ Hz), 1.75 (m, 4H), 1.45–1.26 (m, 20H), 0.90 (m, 6H); UV/vis (CHCl_3) λ_{max} 519, 485, 426 nm; fluorescence (CHCl_3) λ_{max} 550 nm; FT-IR (KBr) ν (cm^{-1}) 1705 (C=O), 1666 (C=O); MS (MALDI-TOF) m/z 750.6 (M^+). Anal. Calcd for $\text{C}_{40}\text{H}_{38}\text{N}_2\text{O}_4\text{Cl}_4$ (750.2): C, 63.84; H, 5.09; N, 3.72. Found: C, 64.27; H, 5.22; N, 3.49.

***N,N'*-Dioctyl-1,6,7,12-tetra[4-(octyloxy)phenoxy]perylene-3,4,9,10-tetracarboxylic Acid Bisimide (4).** Perylene bisimide **3** (752 mg, 1 mmol), 4-(*n*-octyloxy)phenol (1.11 g, 5 mmol), and K_2CO_3 (345 mg, 2.5 mmol) were stirred under argon in NMP (50 mL) at 80 °C for 24 h. After being cooled to room temperature, the reaction mixture was poured into a mixture of 10% hydrochloric acid (80 mL) and methanol (120 mL) with stirring. The precipitate was filtered, repeatedly washed with methanol/water (3:2), and dried in a vacuum at 100 °C. Purification was accomplished by dissolving the crude product in CH_2Cl_2 and precipitation by methanol followed by chromatography on SiO_2 with CH_2Cl_2 : ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 8.09 (s, 4H), 6.90 (d, 8H, $J = 9.7$ Hz), 6.81 (d, 8H, $J = 9.7$ Hz), 3.92 (t, 8H, $J = 7.3$ Hz), 2.63 (s, 4H), 2.05 (m, 8H), 1.88 (m, 4H), 1.50 (m, 12H), 1.36–1.23 (m, 48H), 0.92 (m, 18H); UV/vis (CHCl_3) λ_{max} 592, 550, 456 nm; fluorescence (CHCl_3) λ_{max} 625 nm; FT-IR (KBr) ν (cm^{-1}) 1697 (C=O), 1661 (C=O); MS (MALDI-TOF) m/z 1494.9 (M^+). Anal. Calcd for $\text{C}_{96}\text{H}_{122}\text{N}_2\text{O}_{12}$ (1494.9): C, 77.07; H, 8.22; N, 1.87. Found: C, 76.86; H, 8.00; N, 2.05.

1,6,7,12-Tetra[4-(octyloxy)phenoxy]perylene-3,4,9,10-tetracarboxylic Acid Bisimide (5). To a suspension of **4** (310 mg, 0.2 mmol) in 50 mL of 2-propanol were added 10 mL of water and 11 g (200 mmol) of KOH. The reaction mixture was refluxed with vigorous stirring under argon for 42 h. During the course of the reaction, the color changed from red to green. After being cooled to room temperature, the resulting reaction mixture was poured into 100 mL of 10% hydrochloric acid under stirring. A precipitate appeared and was filtered, washed neutral with water, and dried in a vacuum at 100 °C to give a red solid (232 mg, 87%). The red solid was not purified and was suspended in 40 mL of propionic acid. Then, ammonium acetate (4 g, 52 mmol) was added, and the mixture was refluxed under stirring for 24 h. After being cooled to room temperature, the reaction mixture was diluted with water and left to stand

overnight. The precipitate was filtered, washed neutral with water, and dried in a vacuum at 100 °C to give a dark solid (197 mg, 86%). The solid was purified by column chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{EtAc}$, 40:1) to give perylene bisimide **5**: ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 8.39 (s, 2H), 8.09 (s, 4H), 6.89 (d, 8H, $J = 8$ Hz), 6.82 (d, 8H, $J = 8$ Hz), 3.93 (t, 8H, $J = 7.2$ Hz), 1.83–1.75 (m, 8H), 1.56 (s, 8H), 1.37–1.31 (m, 32H), 0.90 (m, 12H); UV/vis (CHCl_3) λ_{max} 592, 550, 458 nm; fluorescence (CHCl_3) λ_{max} 623 nm; FT-IR (KBr) ν (cm^{-1}) 3186 (N–H), 1699 (C=O), 1677 (C=O); MS (MALDI-TOF) m/z 1270.9 (M^+). Anal. Calcd for $\text{C}_{80}\text{H}_{90}\text{N}_2\text{O}_{12}$ (1270.7): C, 75.56; H, 7.13; N, 2.20. Found: C, 75.65; H, 7.30; N, 2.14.

Acknowledgment. This work was supported by the Major State Basic Research Development Program and the National Natural Science Foundation of China (Grants 20151002, 50372070, and 90101025).

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