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Multiple hydrogen-bond-induced supramolecular nanostructure from a pincer-like molecule and a [60]fullerene derivative

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Abstract—A new supramolecular self-assembled system between a perylene bisimide bearing diaminopyridine-substituted isophthalamide groups (**PP**) and a [60]fullerene containing barbituric acid moiety (**C$_{60}$bar**) through a complementary six-point hydrogen-bonding interaction was constructed. The formation of hydrogen bonding was confirmed by ^{1}H NMR spectra studies in CDCl$_3$. Fluorescence quenching experiments indicated that the fluorescence of **PP** was greatly quenched by the hydrogen-bonded **C$_{60}$bar** ($K_{sv}=2.71\times10^4$ M^{-1}). A steady and rapid cathodic 0.15 μA cm^{-2} photocurrent response of the **PP/C$_{60}$bar** film deposited onto an ITO electrode was produced under the irradiation of 20 mW cm^{-2} white light, indicating the presence of photo-induced electron transfer between **PP** and **C$_{60}$bar**. TEM images showed that spherical particles were fabricated by the self-assembly of **PP** and **C$_{60}$bar** through hydrogen-bonding interaction.

1. Introduction

The [60]fullerene molecule has unique and attractive electronic, optical, and mechanical properties owing to its chemical properties and uniform, spherical, and nanoscale physical structure.[1] In order to develop fullerene-containing supramolecular assemblies and advanced materials,[2] [60]fullerene has been incorporated into multi-component molecular systems such as porphyrins,[3] rotaxanes,[4] and catenanes.[5] The encouraging properties of these [60]fullerene hybrids have attracted much more interests in the construction of even more complex two- and three-dimensional systems. And the self-assembly of [60]fullerene-based molecules has been found to be an efficient way to construct nanoscale aggregates with specific properties.[6]

π-Conjugated perylene bis-imides represent one of the most thoroughly studied classes of organic semiconductors with a variety of different structures,[7] with possible applications such as fluorescent solar collectors,[8] photovoltaic devices,[9] dye lasers,[10] and molecular switches.[11] These dyes have outstanding chemical, thermal, and photochemical stability, which offers great opportunities for preparing new materials.

Hydrogen bonds are among the most useful interactions to encourage the self-assembly of molecules into well-defined aggregates and to order an ensemble of molecules spontaneously into larger and more complex structure.[12] The strength and selectivity of hydrogen bonds can be improved by introducing arrays of donor (D) and acceptor (A) sites. Arrays of two and three hydrogen bonds have already been studied, and the self-complementary quadruple hydrogen bonds (DDAA) derived from diaminotriazines or diaminopyrimidines have also been studied for their high dimerization constants.[13] The self-assembly between cyanuric or barbituric acid wedge (ADA–ADA array) and a corresponding diaminopyridine-substituted isophthalamide receptor (DAD–DAD array) provided six-point hydrogen bonds, which made them attractive for molecular recognition studies, supramolecular polymer, and self-assembly of multi-chromophores.[14]

In our previous work based on the hydrogen-bonded supramolecular systems of [60]fullerene, we reported the self-assembly of 2,6-di(acylamino)pyridine-substituted [60]fullerene derivative with 1-dodecyluracil,[15a,b] perylene bisimide derivative[15c] and PPV derivative[15d] by three-point hydrogen-bonding interactions. These molecules tended to form stable nanoscale aggregates. Their energy and electron-transfer processes were investigated. Bassani et al. reported the facile synthesis of a fullerene-barbituric acid from C$_{60}$ and 5-bromobarbituric acid by a modified

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Keywords: Hydrogen bond; Fullerene; Supramolecular.

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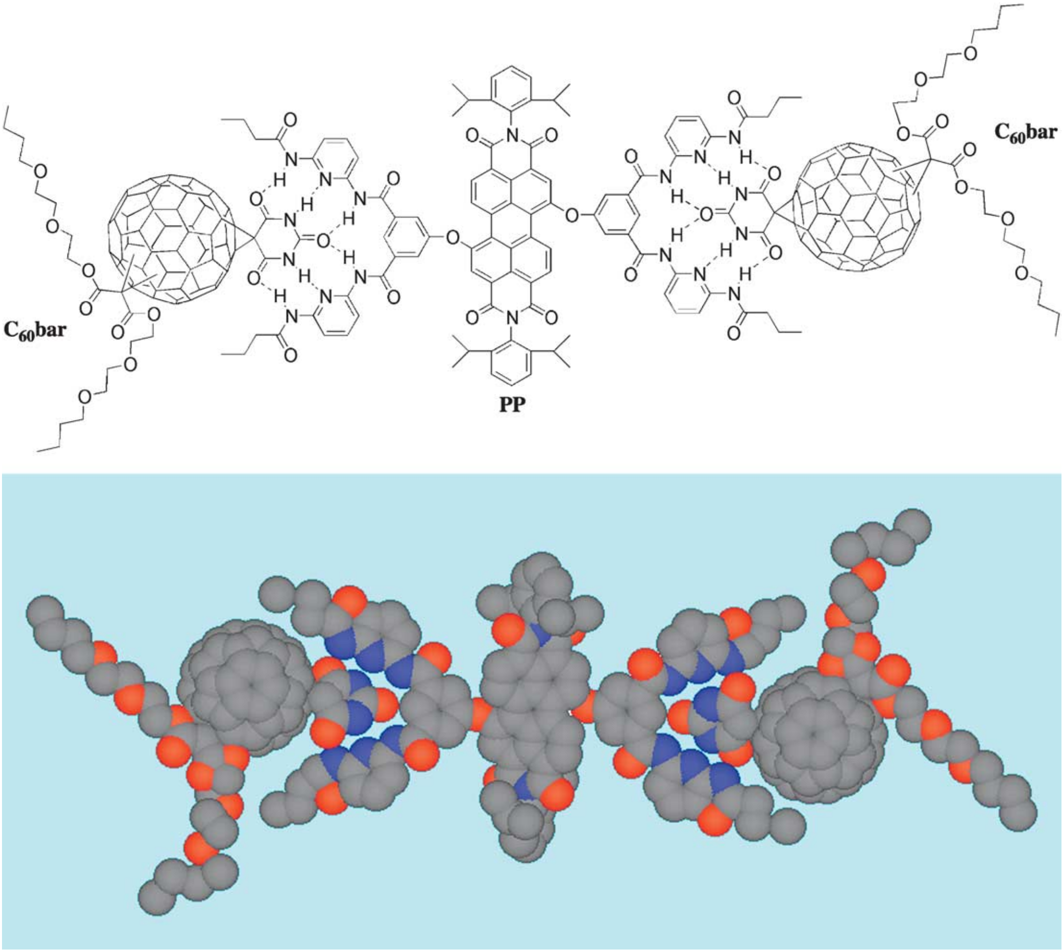


Scheme 1. Supramolecular system of hydrogen-bonded self-assembly of **PP/C_{60}bar** with a 3D model.

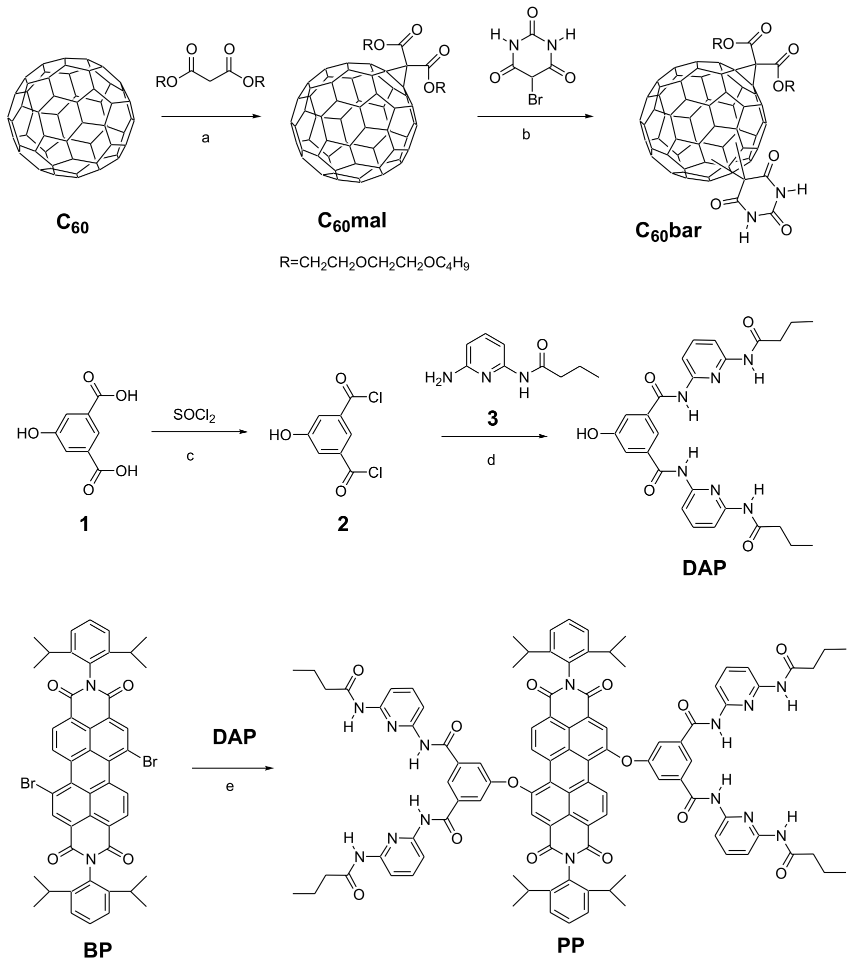
Bingel reaction.[16] This reaction introduced six hydrogen-bonding sites of a barbituric acid into [60]fullerene in one step. These sites were non-self-complementary, and their spatial arrangement made the fullerene-barbituric acid well suitable for the construction of fullerene-containing architectures. Although the structure of this fullerene-barbituric acid was novel, the poor solubility of this compound limited its application in supramolecular chemistry studies. In this paper, we introduced barbituric acid into [60]fullerene-di[2-(2-butoxy-ethoxy)-ethyl] malonate (**C_{60}mal**) to form a novel fullerene derivative (**C_{60}bar**) with excellent solubility in organic solvents. We also synthesized a perylene bisimide (**PP**) with two diaminopyridine-substituted isophthalamide groups for the formation of a pincer-like structure in order to increase hydrogen-bonding interaction. Because the association constant between the barbituric acid ring and the diaminopyridine-substituted isophthalamide receptors was in the range of 10^4–10^5 M^{-1},[14] the supromolecular assembly of **C_{60}bar** and **PP** exhibited strong interaction and formed uniform aggregates. (Scheme 1)

2. Results and discussion

The synthesis of **PP** and **C_{60}bar** was sketched in Scheme 1. **C_{60}mal** was synthesized from C_{60} and di[2-(2-butoxy-ethoxy)-ethyl] malonate by Bingel reaction using CBr_4 and DBU in toluene.[17] **C_{60}bar** was synthesized from **C_{60}mal** and 5-bromobarbituric acid according to the literature method.[16] The crude product was worked up on silica gel using a mixture of toluene/MeOH (v/v, 10:1) as the eluent, and the second band was collected to give **C_{60}bar**. The **C_{60}bar** had excellent solubility in toluene and $CHCl_3$, owing to the introduction of di[2-(2-butoxy-ethoxy)-ethyl] malonate into the fullerene-barbituric acid structure, therefore, greatly facilitated its application Scheme 2.

The cyclopropanation of C_{60} with two addends afforded mixed bisadducts, where *e* and *trans*-3 isomers were the main products.[18] In this work, the barbituric acid ring was introduced into C_{60} as the second addend. The product **C_{60}bar** contained position isomers. However, here we try to use **C_{60}bar** as a building block for the construction of supramolecular assemblies, the *trans*-3 and *e* isomers could form same supramolecular structure with diaminopyridine-substituted isophthalamide group by hydrogen-bonding interaction.

MALDI-TOF MS spectra of **C_{60}bar** showed three peaks, 1237.3 (M^+), 1110.4 (M^+ − barbituric acid ring) and 720.1 (M^+ − barbituric acid ring-bis[2-(2-butoxy-ethoxy)-ethyl] malonate). ^1H NMR spectra showed two broad peaks at δ 9.3 and 11.1, which were assigned to the resonance of the



Scheme 2. Synthesis of **C$_{60}$bar** and **PP**. (a) CBr_4, DBU, toluene, rt, 2 h, 44%; (b) DBU, toluene/DMSO (v/v, 95:5), rt, 7 h, 12%; (c) THF, reflux, 4 h; (d) pyridine, THF, 0–10 °C, 7 h, 56%; (e) K_2CO_3, 18-crown-6, toluene, 80 °C, 4 h, 88%.

imidic protons of barbituric acid ring. Because **C$_{60}$bar** was an isomeric mixture, the signals of imidic protons appeared at different positions and are rather broad.

N,*N*′-di(6-butyrylamino-pyridin-2-yl)-5-hydroxy-isophthalamide (**DAP**) was synthesized from *N*-butyryl-2,6-diaminopyridine, 5-hydroxy-benzene-1,3-dicarbonyl chloride and pyridine in anhydrous THF. 1,7-dibromo-*N*,*N*′-di(2,6-diisopropyl-phenyl)perylenediimine (**BP**) was synthesized according to a known method.[19] **PP** was obtained by the nucleophilic reaction of **BF**, **DAP** and K_2CO_3 in anhydrous toluene in the presence of 18-crown-6.[20]

The formation of hydrogen-bonded self-assembly of **C$_{60}$bar** and **PP** was demonstrated by ^1H NMR spectroscopic studies. Titration experiment in $CDCl_3$ between the diaminopyridine-substituted isophthalamide group and complementary barbiturate substrate led to the characteristic changes in the ^1H NMR spectra of the two components, which confirmed the formation of hydrogen-bonded self-assembly.[14] The ^1H NMR spectra changes of **C$_{60}$bar** with increasing **PP** concentration were recorded. Figure 1A showed the partial ^1H NMR spectra of **C$_{60}$bar** (12 mmol/L) and **C$_{60}$bar**+**PP** (12 and 6 mmol/L). Two broad peaks at δ 9.3 and 11.1 were observed, which were assigned to the resonance of the imidic protons of the barbituric ring of **C$_{60}$bar**. When **C$_{60}$bar** was mixed with 0.5 equiv **PP** (stoichiometric ratio), significant downfield shifts were observed for the resonance of the imidic protons of **C$_{60}$bar** (from δ 9.3 and 11.1 to 13.2). These shifts showed that strong hydrogen bonding took place between **C$_{60}$bar** and **PP**.

The ^1H NMR spectra changes of **PP** with increasing the concentration of **C$_{60}$bar** were also recorded in $CDCl_3$. The concentration of **PP** was kept constant (6 mmol/L), and the concentration of **C$_{60}$bar** was increased gradually (from 0 to 12 mmol/L). As shown in Figure 1B, the signals at δ 8.5 and 7.8, assigned for the two amidic protons of the diaminopyridine-substituted isophthalamide unit, were observed before the addition of **C$_{60}$bar**. When the concentration of **C$_{60}$bar** was increased, the signals for the two amidic protons became broad and shifted to lower magnetic fields. When the concentration of **C$_{60}$bar** was increased to 12 mmol/L, the signals for the two amidic protons shifted downfield to δ 9.8 and 8.8, respectively. And the 2-proton of the isophthalic acid group, which positioned close to the 2-CO of the barbiturate ring, also shifted downfield by 0.25 ppm from δ 8.20 to 8.45. All the spectra changes of the **C$_{60}$bar** and **PP** in the titration experiment showed the formation of multiple hydrogen-bonding interaction between **PP** and **C$_{60}$bar**.

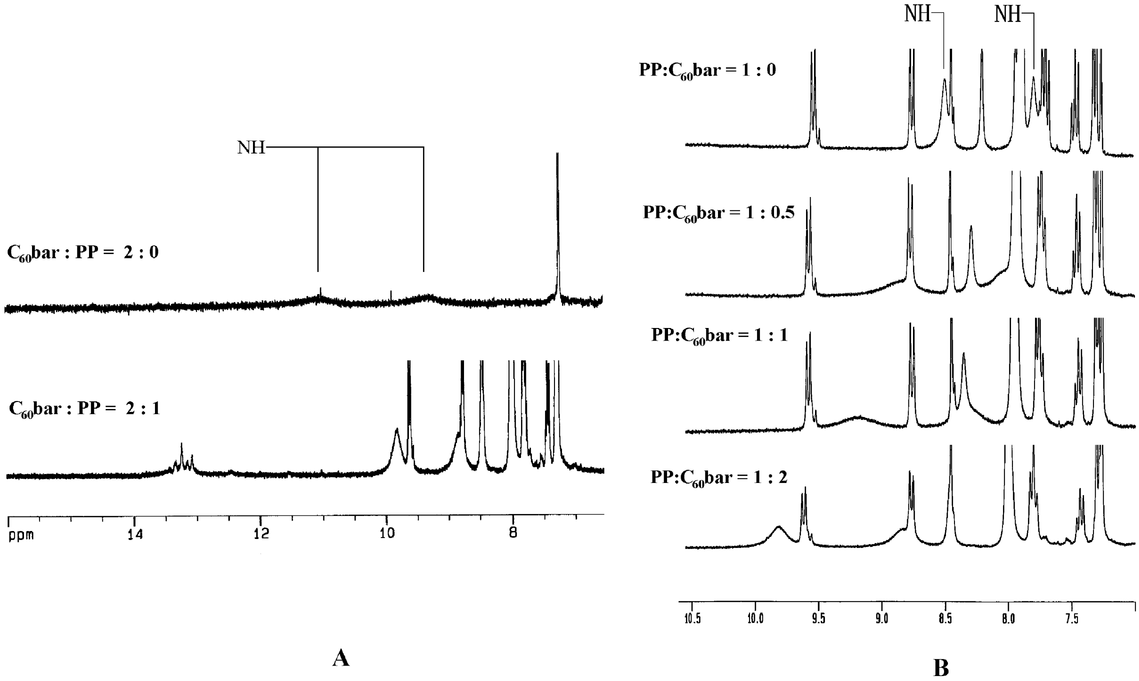


Figure 1. Partial ^{1}H NMR spectra of **PP/C$_{60}$bar** supramolecular system in CDCl$_3$ at rt. (A) the concentration of **C$_{60}$bar** was kept constant (12 mmol/L), and the concentration of **PP** was 0 and 6 mmol/L, respectively; (B) the concentration of **PP** was kept constant (6 mmol/L), and the concentration of **C$_{60}$bar** was increased gradually (from 0 to 12 mmol/L).

The fluorescence quenching experiment of **PP** by **C$_{60}$bar** was carried out in chloroform. The concentration of **PP** was kept constant at 1×10^{-5} mol/L and the concentration of **C$_{60}$bar** was increased gradually. Because of the competition absorptions of **C$_{60}$bar** at the excitation and emission wavelength of **PP**, the fluorescence intensities were calibrated according to the literature method.[21] The dependence of the fluorescence intensity of **PP** on the concentration of **C$_{60}$bar** follows the Stern–Volmer equation. [Eq. 1],[22] in which F_0 is the fluorescence intensity of **PP** without the addition of **C$_{60}$bar**, F is the calibrated fluorescence intensity of **PP** upon the addition of **C$_{60}$bar**, K_{sv} is the quenching constant, and $[Q]$ is the concentration of **C$_{60}$bar**.

$$\frac{F_0}{F} = 1 + K_{sv}[Q] \qquad 1$$

As shown in Figure 2A, **PP** showed a strong emission band at 561 nm and a shoulder band at 600 nm with the excitation wavelength at 490 nm. The fluorescence of **PP** was strongly quenched with the addition of **C$_{60}$bar**. The Stern–Volmer constant (K_{sv}) is 2.71×10^4 M^{-1}.

For comparison, the fluorescence quenching experiment of **PP** by **C$_{60}$mal**, which would not form hydrogen bonds with **PP** was also performed. Figure 2B showed the fluorescence spectra of **PP** (1×10^{-5} M, solid line) and **PP+C$_{60}$mal** (1×10^{-5} and 2×10^{-5} M, dash line). We found the

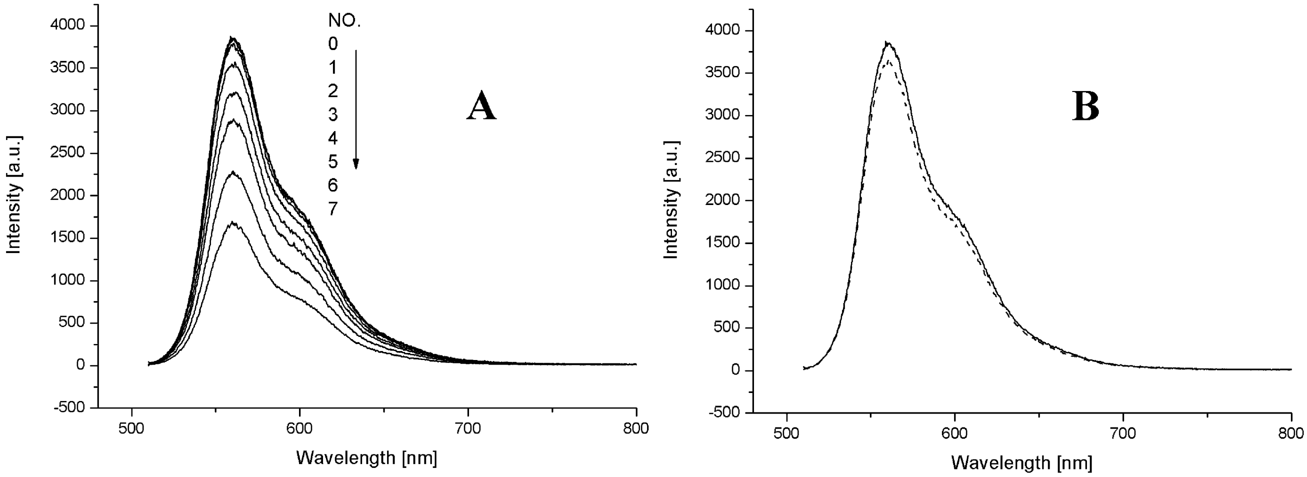


Figure 2. (A) The fluorescence spectra of **PP** ([**PP**] = 1×10^{-5} M) in chloroform with increasing concentration of **C$_{60}$bar**: 0.0 (0), 1×10^{-6} M (1), 2×10^{-6} M (2), 4×10^{-6} M (3), 8×10^{-6} M (4), 1.2×10^{-5} M (5), 2×10^{-5} M (6), 4×10^{-5} M (7); (B) The fluorescence spectra of **PP** (1×10^{-5} M, solid line) and a mixture of **PP+C$_{60}$mal** (1×10^{-5} M and 2×10^{-5} M, dash line) in chloroform. Excitation wavelength was 490 nm.

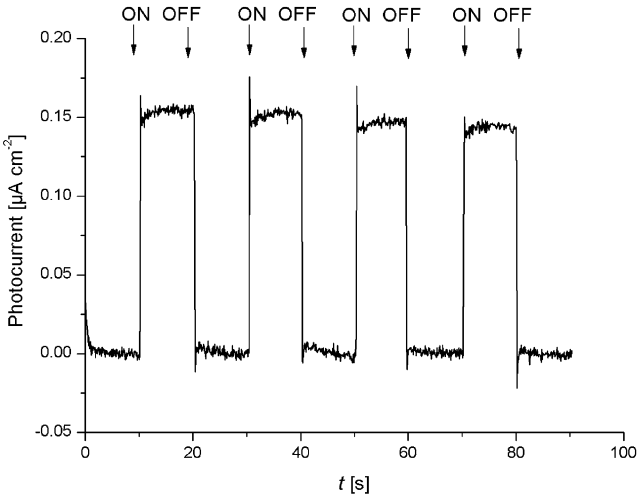


Figure 3. Photocurrent generation of the **PP/C$_{60}$bar** supramolecular assembly film upon the irradiation of white light (20 mW/cm^2) in 0.5 M KCl solution without bias voltage.

fluorescence of **PP** was almost unchanged upon the addition of 2 equiv **C$_{60}$mal**. Consider the competition absorptions of **C$_{60}$mal** at the excitation and emission wavelength of **PP**, we might conclude that the fluorescence of **PP** was not affected with the addition of **C$_{60}$mal**. This suggested that the hydrogen-bonding interaction between **PP** and **C$_{60}$bar** played an important role in the fluorescence quenching. These results indicated that there existed intermolecular charge transfer between the supramolecular system of **PP** and **C$_{60}$bar** by hydrogen-bonding interaction.

A conventional three-electrode cell was used to measure the photoelectrochemical properties of the self-assembled **PP/C$_{60}$bar** film.[23] The photocurrent generation of **PP/C$_{60}$bar** film deposited onto an ITO electrode was measured at 20 mW cm^{-2} white light irradiation. When the irradiation was switched on and off, a steady and rapid cathodic 0.15 µA cm^{-2} photocurrent response of the **PP/C$_{60}$bar** film was produced. Four cycles of the photocurrent generation were shown in Figure 3, which showed that the response to on–off cycling was prompt and reproducible. The photocurrent stability in the system was rather good during the monitored time.

Our group has reported the self-assembly of [60]fullerene containing 2,6-di(acylamino) pyridine unit with 1-dodecyluracil and perylene bis-imides derivative. These hydrogen-bonded supramolecular systems formed spherical nanoaggregates observed by SEM and TEM.[15a,b,c] Some hydrogen-bonded supramolecular system containing perylene derivatives were also reported to form well-defined

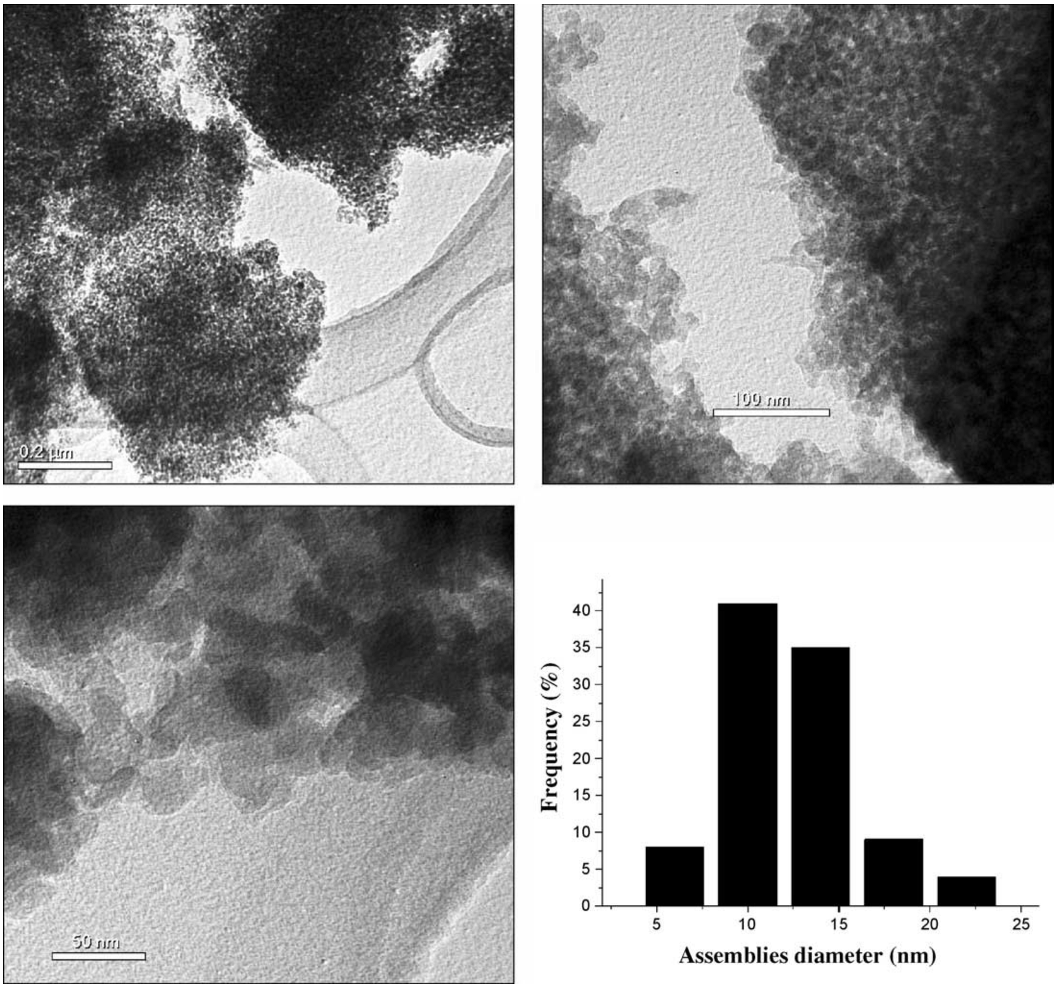


Figure 4. Transmission electron micrograph and size distribution histogram of assemblies resulting from evaporation of 10^{-5} M **PP/C$_{60}$bar** in CHCl$_3$.

nano-fibrous structures.[24] Consider the self-assembly behavior of **PP** with **C_{60}bar**, we can assume that certain three-dimensional supramolecular structures stabilized by the intermolecular hydrogen bonding through barbituric acid groups and diaminopyridine-substituted isophthalamide moieties was formed. Figure 4 showed the transmission electron micrographs (TEM) of **C_{60}bar/PP** self-assembled on a carbon-coated copper grid after evaporation of $CHCl_3$ solvent and the corresponding size distribution histogram. Spherical particles could be observed and the diameters of these particles were in the range of 5–25 nm with a mean diameter of 12 nm. [60]Fullerene derivatives had high aggregation tendency because of the strong π–π stacking of the carbon cage,[25] and the perylene ring also showed strong intermolecular π–π stacking,[24] which led to the formation of spherical particle aggregates of the hydrogen-bonded **PP/C_{60}bar** supramolecular structure.

3. Conclusions

In conclusion, a novel pincer-like molecule **PP** was synthesized and the supramolecular system between **PP** and **C_{60}bar** through a six-point hydrogen-bonding interaction was fabricated. ^{1}H NMR and fluorescence measurements indicated that strong hydrogen-bonding interaction took place between **PP** and **C_{60}bar**. The photocurrent generated by the self-assembled film was measured, and a cathodic photocurrent response of 0.15 $\mu A\ cm^{-2}$ at 20 $mW\ cm^{-2}$ white light irradiation was obtained. TEM images of **PP/C_{60}bar** aggregates showed spherical particles having a mean diameter of 12 nm. These bichromophoric assemblies could be of importance for potential applications in photovoltaic and nanoscale devices.

4. Experimental

4.1. General

Reagents were purchased from Acros or Aldrich Corporation and were utilized as received unless indicated otherwise. All solvents were purified using standard procedures.

UV–vis and fluorescence spectra were measured on a Hitachi U-3010 and Hitachi F-4500 spectrometer, respectively. IR spectra were recorded as KBr pellets on a Perkin-Elmer System 2000 spectrometer. 300 MHz ^{1}H NMR spectra were recorded on a Bruker dm×300 spectrometers. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF. Transmission electron micrographs (TEM) were collected on a JEOL JEM 2010 instrument.

The photocurrent generation measurement was carried out using a platinum wire as a counter electrode and the saturated calomel electrode as a reference electrode. A solution of 0.5 M KCl was selected as the supporting electrolyte in the measurements. The ITO plates were cleaned by repeated sonication in isopropyl alcohol and in deionized water. The dry ITO plates were immersed into a chloroform solution of **PP/C_{60}bar** (1×10^{-3} mol/L, molar ratio of **PP** and **C_{60}bar** is 1:2) for 30 min and dried in N_2 stream.

4.1.1. Synthesis of DAP. *N*-butyryl-2,6-diaminopyridine (600 mg, 3.35 mmol) and freshly distilled pyridine (323 μL, 4 mmol) were dissolved in anhydrous THF (30 mL). The reaction mixture was cooled to 0–10 °C with ice water bath. After degassing for 10 min, 5-hydroxy-benzene-1,3-dicarbonyl chloride (360 mg, 1.65 mmol) dissolved in 10 mL anhydrous THF was added dropwise over 1 h. After stirring for 6 h at rt, 20 mL water was added and the reaction mixture was stirred for additional 20 min. THF was then removed under reduced pressure and the resulting precipitate was filtered, washed several times with water, dried at rt, and purified by column chromatography using $CHCl_3$/MeOH (v/v, 100:1) as the eluent to give **DAP** as a white powder. Yield: 463 mg, 56%; IR (KBr): 3370, 3280, 2965, 2875, 1672, 1586, 1516, 1450, 1295, 1242, 1156, 1084, 801 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 10.30 (s, 2H), 10.15 (s, 1H), 10.05 (s, 2H), 7.97 (s, 1H), 7.81–7.72 (m, 6H), 7.49 (s, 2H), 2.36 (t, $J=7.2$ Hz, 4H), 1.62–1.55 (m, 4H), 0.88 (t, $J=7.2$ Hz, 6H) ppm MS: *m/z* (EI, 70 eV) 504 [M^+]. Anal. Calcd for $C_{26}H_{28}N_6O_5$: C, 61.89; H, 5.59; N, 16.66; Found C, 61.64; H, 5.65; N, 16.59%.

4.1.2. Synthesis of PP. BP (104 mg, 0.12 mmol), **DAP** (140 mg, 0.278 mmol), K_2CO_3 (100 mg, 0.73 mmol) and 18-crown-6 (50 mg, 0.19 mmol) were dissolved in anhydrous toluene (20 mL). The reaction mixture was degassed for 10 min and then heated to 80 °C. After stirring for 4 h, nearly all the **BP** was consumed (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by column chromatograph on silica gel using CH_2Cl_2/MeOH (v/v, 100:1) as the eluent to give **PP** as a red solid. Yield: 181 mg, 88%. UV–vis ($CHCl_3$): $\lambda_{max}(\varepsilon)=302$ (70220), 389 (8610), 491 (36600), 525 nm (55510 $mol^{-1}\ dm^3\ cm^{-1}$); fluorescence ($CHCl_3$): $\lambda_{max}=561$ nm; IR (KBr): 3305, 3067, 2965, 2931, 1704, 1667, 1588, 1511, 1448, 1404, 1338, 1306, 1247, 1156, 1078, 961, 902, 799, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 9.53 (d, $J=8.4$ Hz, 2H), 8.75 (d, $J=8.4$ Hz, 2H), 8.52 (br s, 4H), 8.44 (s, 2H), 8.21 (s, 2H), 7.93–7.87 (m, 12H), 7.81 (br s, 2H), 7.69 (t, $J=8.1$ Hz, 4H), 7.46 (t, $J=7.8$ Hz, 2H), 7.30 (d, $J=7.5$ Hz, 4H), 2.77–2.72 (m, 4H), 2.29 (t, $J=7.2$ Hz, 8H), 1.75–1.67 (m, 8H), 1.15–1.11 (m, 24H), 0.97 (t, $J=7.2$ Hz, 12H) ppm; MALDI-TOF MS: Calcd for $C_{100}H_{94}N_{14}O_{14}$ (M^+), $m/z=1714.7$; found 1714.8.

4.1.3. Synthesis of C_{60}mal. C_{60} (250 mg, 0.35 mmol) and CBr_4 (166 mg, 0.5) were dissolved in anhydrous toluene (150 mL) with vigorous stirring. After degassing for 15 min, di[2-(2-butoxy-ethoxy)-ethyl] malonate (196 mg, 0.5 mmol) and DBU (150 μL, 1 mmol) were added and the mixture color changed gradually from purple to dark red. After stirring for 2 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography using toluene/ethyl acetate (v/v, 10:1) as the eluent to give **C_{60}mal** as a brown solid. Yield: 170 mg, 43.8%; IR (KBr): 2954, 2927, 2864, 1746, 1429, 1378, 1232, 1113, 1031, 706, 527 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.65 (t, $J=4.8$ Hz, 4H), 3.88 (t, $J=4.8$ Hz, 4H), 3.68 (t, $J=4.8$ Hz, 4H), 3.57 (t, $J=4.8$ Hz, 4H), 3.45 (t, $J=6.8$ Hz, 4H), 1.58–1.53 (m, 4H), 1.39–1.33 (m, 4H), 0.91 (t, $J=7.2$ Hz, 6H) ppm; MALDI-TOF MS: Calcd for $C_{79}H_{34}O_8$ (M^+), $m/z=$ 1110.2; found 1110.1.

4.1.4. Synthesis of C_{60}bar. **C_{60}mal** (111 mg, 0.1 mmol) and 5-bromobarbituric acid (21 mg, 0.1 mmol) were dissolved in toluene/DMSO (v/v, 95:5, 150 mL) with vigorous stirring. After degassing for 15 min, DBU (20 μL, 0.2 mmol) was added. After stirring at rt for 2 h, the reaction mixture was washed with water (60×3 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$/MeOH (v/v, 10:1) as the eluent to give **C_{60}bar** as a brown solid. Yield: 17 mg, 12%; IR (KBr): 3173, 2955, 2925, 2857, 1744, 1663, 1541, 1457, 1377, 1245, 1114, 1031, 880, 766 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.1 (br), 9.3 (br), 4.6–4.5 (br, 4H), 3.7–3.4 (br, 16H), 1.5–0.8 (br, 14H) ppm^{-1}. MALDI-TOF MS: Calcd for $C_{83}H_{36}O_{11}$ (M^+), $m/z=1236.23$; found 1237.3 ($M^+ + H$), 1110.4 ($M^+ -$ barbituric acid), 720.1 ($M^+ -$ barbituric acid ring-bis[2-(2-butoxy-ethoxy)-ethyl] malonates).

4.2. Supporting information available

^1H NMR and MS spectra of **PP**, **C_{60}mal** and **C_{60}bar**.

Acknowledgements

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