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Self-Assembly and Characterization of Hydrogen-Bond-Induced Nanostructure Aggregation

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*A supramolecular system of a perylene derivative containing bis(2,6-diacylaminopyridine) units and a perylene bisimide bound through three hydrogen-bonds was synthesized and characterized. ^{1}H NMR spectra confirmed the existence of hydrogen-bonding interactions between the perylene derivative (**3**) and the perylene bisimide (**7**). The photocurrent generation of the self-assem-bled **3·7** film was measured, and a cathodic photocurrent response was obtained. SEM images indicated that well-defined long fibers could be fabricated by self-assembly, by exploiting the hydrogen bonding interactions and π-π stacking interactions of perylene rings.*

Introduction

Design and self-assembly of organic molecules to form functional superstructures is a main goal of supramolecular chemistry. Control of hydrogen bonding, because of its directionality and specificity, has attracted much attention in the design of various molecular assemblies.[1] Well-defined nanosized aggregates should be very useful for the development of novel functional materials and nanoelectronic devices. Hydrogen-bonding assemblies are the most promising avenue to fabrication of molecular arrays and shapes for efficient intermolecular energy and electron transfer between donor and acceptor units.[2, 3] Perylene bisimides are a class of organic semiconductors with a variety of different structures[4–7] and possible applications such as optical switching,[8] photovoltaic devices,[9] and dye lasers.[10] They have excellent chemical, thermal, and photochemical stability. Perylene bisimides are potential candidates for electron-accepting materials in organic photovoltaic solar cells.[11] Examples of self-assembly of perylene bisimides with chiral oligo(p-phenylenevinylene) and melamine derivatives by three-point hydrogen-bonding interactions have been reported,[2b, 12, 13] and these hydrogen-bonded systems have been shown to form well-defined supramolecular structures.

Mesoscopic order can be achieved by applying the principles of supramolecular chemistry.[14] We would like to develop a complementary strategy for the fabrication of a novel supramolecular system which would form a well-defined structure through self-assembly of molecules that are structurally different from previously reported ones.[15] In this construction process, the typical organic molecules are self-assembled into a nanostructure by mutual recognition properties. Previously, we have shown that a well-defined superstructure of ball-like assemblies of a [60]fullerene derivative and a perylene bisimide can be obtained by exploiting hydrogen-bonding interactions.[16] Herein, we discuss the self-assembly and characterization of the perylene derivative, **3**, and perylene bisimide, **7**, to

form a supramolecular system in which the three amino functionalities of compound **3** positioned on the assembly interact with compound **7** via an amino-carboxylic acid interaction (Scheme 1). More interestingly, the chemical system can form long 1D fibers, as observed in scanning electron micrographs. Only a few examples have been reported of the use of hydrogen-bonding motifs to organize π-conjugated systems and form nanometer-sized fibers.[14] Here, we describe a supramolecular system that exhibits energy and electron transfer and that effectively converts photons into electrons. In fact, the supramolecular system was shown to produce a photocurrent response when illuminated by a 500 W halogen light source.

Results and Discussion

N,N′-dioctyl-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide (**BF**) was synthesized according to a known method.[17] The nucleophile, *N*-(6-dodecanoylamino-pyridin-2-yl)-4-hydroxy-benzamide, (**2**), was synthesized by acylation of 2-amino-6-lauroylamino-pyridine with 4-methoxybenzoyl chloride, followed by demethylation with BBr$_3$. Compound **3** (see Scheme 2) was obtained by the nucleophilic reaction of **BF**, **2**, and K$_2$CO$_3$ in 1,4-dioxane in the presence of 18-crown-6. Long

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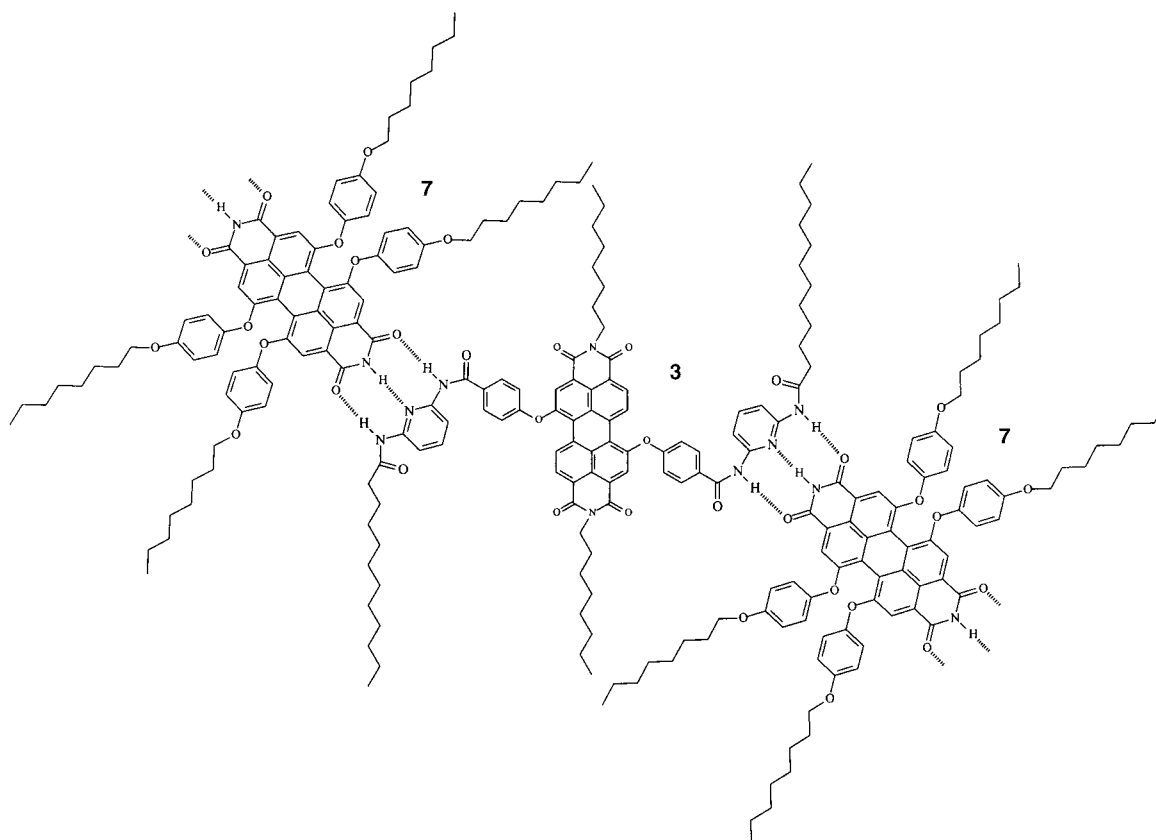
Scheme 1. *Superstructure of the self-assembly of the perylene derivative **3** with the perylene bisimide **7** by hydrogen bonding.*
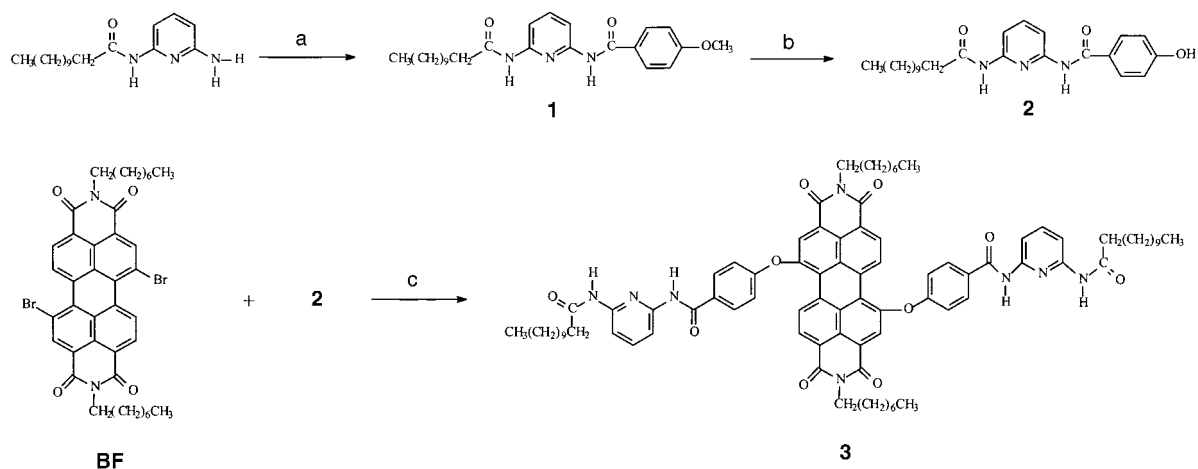
Scheme 2. *Synthesis of **3**. a) 4-methoxybenzoyl chloride, tetrahydrofuran (THF), rt, 2 h. b) BBr₃, CH₂Cl₂, rt, 48 h. c) K₂CO₃, dioxane, 18-crown-6, reflux, 4 h.*

alkyl chains were introduced to increase the solubility of **3** in organic solvents. The synthesis of the perylene bisimide (**7**) is sketched in Scheme 3. Briefly, 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid dianhydride, (**4**) was converted into the corresponding *n*-octyl bisimide, (**5**), using *n*-octylamine. Subsequently, compound **6** was prepared by the nucleophilic substitution of the four chlorine atoms using 4-(*n*-octyloxy)phenol. Perylene bisimide (**7**) was synthesized by cleavage of **6** and reaction with ammonium acetate, according to known methods.[18]

The self-assembly of **3** and **7** via hydrogen bonding was demonstrated by nuclear magnetic resonance (NMR) spectroscopic studies. Upon complexation of **7** by **3**, the signal due to the imide protons' of **7** underwent a downfield shift in the ^{1}H NMR titration experiment because 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 **7** with **3** was investigated by ^{1}H NMR spectroscopic titration carried out in Cl₂CD₂CD₂Cl₂. For the ^{1}H NMR studies, the concentration of **7** was kept constant, and
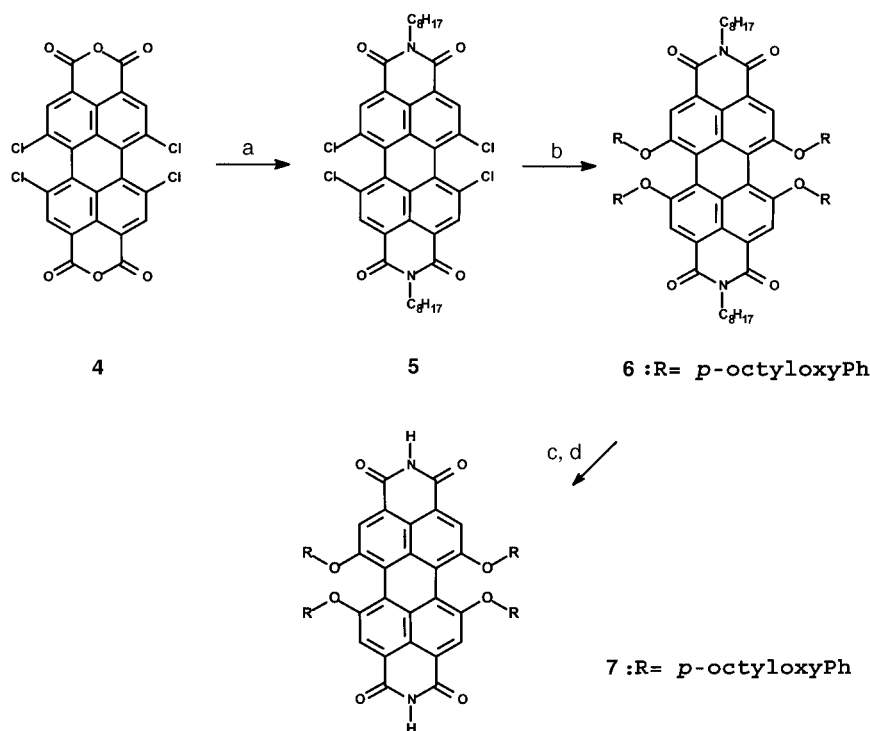
Scheme 3. Synthesis of perylene bisimide **7**. a) n-Octylamine, propionic acid, reflux, 24 h. b) 4-(n-octyloxy)phenol, K$_2$CO$_3$, N-methyl-2-pyrrolidinone (NMP), reflux, argon, 24 h. c) KOH, 2-propanol/water, reflux, argon, 42 h. d) Ammonium acetate, propionic acid, reflux, 24 h.

to 8.48, 8.53, and 8.63 ppm, respectively. These results show that hydrogen-bonding interactions took place between **3** and **7**.

In UV/Vis titration experiments, the concentration of **7** was kept constant upon addition of **3** in Cl$_2$CH$_2$CH$_2$Cl$_2$ at different ratios. As shown in Figure 2, the absorption spectra of the mixture of **3** and **7** exhibited distinct changes with increasing concentration of **3**. The absorption of pure **3** showed three peaks at 535, 500, and 395 nm. The absorption of pure **7** showed three peaks at 598, 554, and 462 nm, in Cl$_2$CH$_2$CH$_2$Cl$_2$. When the concentration of **7** was kept constant while increasing the concentration of **3**, the absorption intensities of the complex **3·7** at 535, 500, and 395 nm increased, but the absorption intensity of the complex **3·7** at 598 nm de-

the change in the chemical shift was followed as a function of increasing concentration of **3**. The NMR titration experiments revealed a downfield shift of the signal arising from the amidic protons because of complexation of **3** (Figure 1). The signal at $\delta = 8.34$ ppm was assigned to the N–H protons of **7**. When **7**
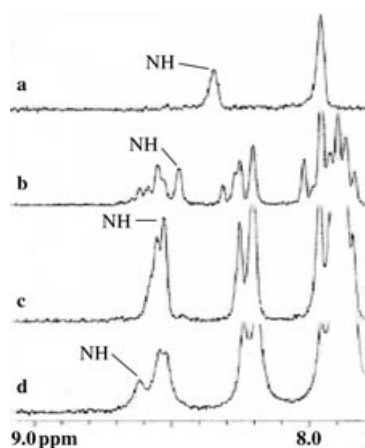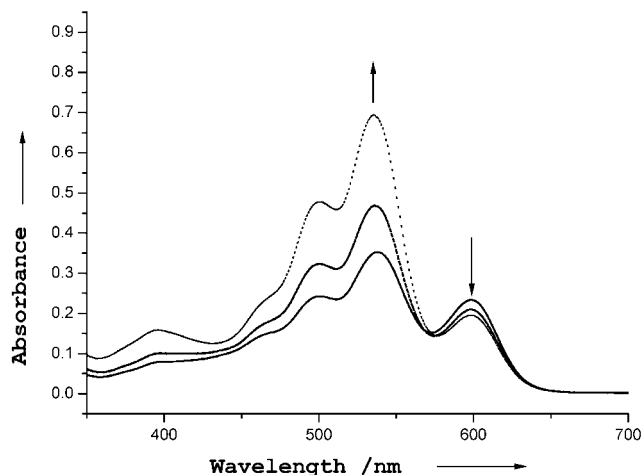

Figure 1. Partial ^{1}H NMR spectra of **3·7** at different concentration ratios in Cl$_2$CD$_2$CD$_2$Cl$_2$ at room temperature. The concentration of **7** was kept constant at 2×10^{-3} M. a) Pure **7**; b) [3]/[7] = 1:1; c) [3]/[7] = 2:1; d) [3]/[7] = 3:1.

Figure 2. UV/Vis absorption spectra in Cl$_2$CH$_2$CH$_2$Cl$_2$ for a stoichiometry mixture of **7** (the concentration of **7** was kept constant at 5×10^{-6} mol L^{-1}) and **3** at different ratios ([7]/[3] = 1:1, 1:2, 1:3). Arrows indicate changes upon increasing concentration of **3**.

creased. These spectral changes were mainly caused by hydrogen bonds from the amine NH protons of **3** to the imide oxygen atoms of **7**.[3a]

Figure 3 shows the fluorescence spectra for a solution of the **3·7** complex in Cl$_2$CH$_2$CH$_2$Cl$_2$ at different ratios. The peak of the fluorescence spectrum of the pure perylene derivative **3** in 1,1,2,2-tetrachloroethane was at 568 nm. The pure perylene bisimide **7** showed weak fluorescence at 628 nm because the
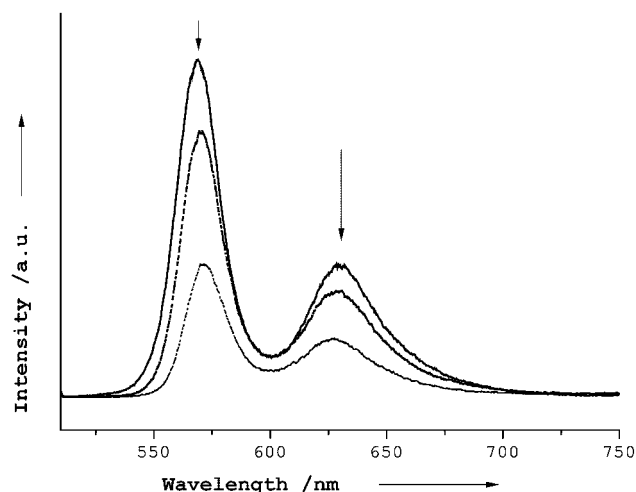
(2×10^{-3} M) was blended with 1, 2, and 3 equivalents of **3**, respectively, in Cl$_2$CD$_2$CD$_2$Cl$_2$, the chemical shift for the proton resonance of the amidic protons of **7** changed from 8.34 ppm

Figure 3. Fluorescence spectra in $Cl_2CH_2CH_2Cl_2$ for a stoichiometric mixture of **7** (the concentration of **7** was kept constant at 1×10^{-4} mol L^{-1}) and **3** at different ratios ([**7**]/[**3**] = 1:1, 1:2, 1:3). Arrows indicate changes upon increasing concentration of **3**. ($\lambda_{ex} = 510$ nm)

Figure 4. Time dependence of the photocurrent response of the self-assembled **3·7** film upon the irradiation of 32 mW cm^{-2} white light in 0.5 M KCl solution. ([**3**]/[**7**] = 1:2 in CHCl$_3$)

p-octyloxy group of **7** leads to strong fluorescence quenching.[2a, 16] It was observed that while the concentration of **7** was kept constant, the fluorescence of the **3·7** complex showed obvious quenching with increased concentration of **3**. The fluorescent quenching at 568 nm was mainly caused by the concentration quenching of **3**; however, the fluorescent quenching at 628 nm was mainly caused by hydrogen-bonding interactions. These results indicate there was intramolecule and intermolecule charge transfer between the octyloxy group and the perylene bisimide moiety as well as between the perylene bisimide and the 2,6-bis(acylamino)pyridine group in these systems.

To investigate photoinduced electron-transfer process of the self-assembled **3·7** system, photocurrent measurements were performed using a voltammetric analyzer with a 500 W halogen lamp as the light source. A conventional three-electrode cell was used to measure the photo-electrochemical properties of the self-assembled **3·7** system. A platinum wire was used as a counter electrode and a saturated calomel electrode was used as a reference electrode. A solution of 0.5 M KCl was selected as the supporting electrolyte in measurement. Indium-tin-oxide (ITO) glass modified with a self-assembled **3·7** film was used as the working electrode. A cathodic photocurrent response of 0.08 µA cm^{-2} at 32 mW cm^{-2} white light irradiation was produced (Figure 4) as the irradiation of the film was switched on and off. The response to on/off cycling was prompt and reproducible. Four cycles are shown in Figure 4. The photocurrent stability in this system was good in the monitored time.

After evaporation of a CHCl$_3$ or $Cl_2CH_2CH_2Cl_2$ solution of the **3·7** complex on a quartz plate, the superstructure of **3·7** aggregates could be observed with a scanning electron microscope (SEM). The SEM images (Figure 5a, b) show that **3·7** aggregates in CHCl$_3$ can form a large quantity of fibrous nanostructures with diameters in the range of 40–70 nm and lengths of several micrometers. Figure 5c displays a nanofiber of **3·7** aggre-
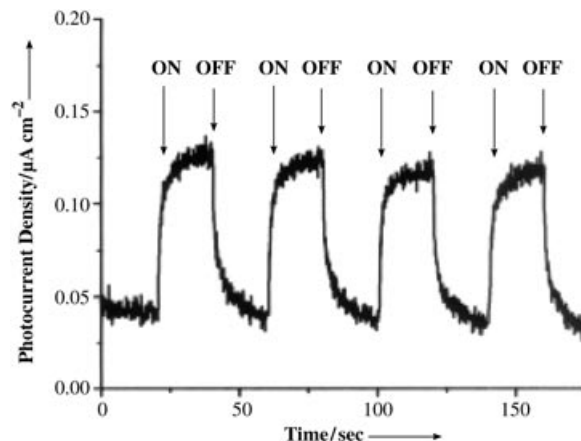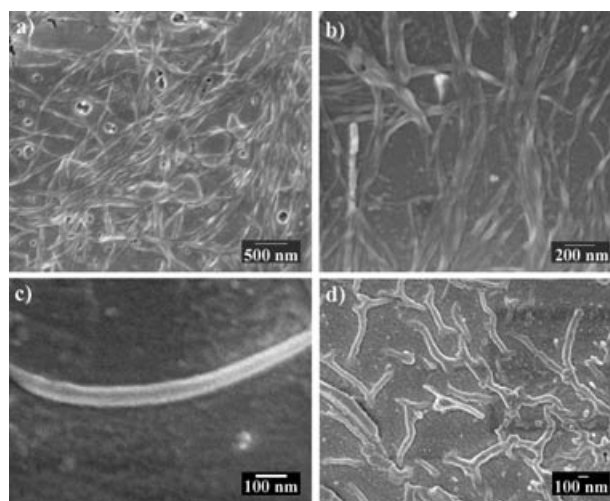

Figure 5. a) SEM image of **3·7** in CHCl$_3$ to show the large quantity of nanofibers; b) Magnified SEM images of the fibrous nanostructures of **3·7** in CHCl$_3$; c) SEM image of **3·7** in $Cl_2CH_2CH_2Cl_2$ to show a nanofiber; d) SEM image of **3·7** in $Cl_2CH_2CH_2Cl_2$ to show the large quantity of nanofibers. ([**3**]/[**7**] = 1:2).

gates in $Cl_2CH_2CH_2Cl_2$ with a 60 nm diameter. The nanofibers of **3·7** aggregates in $Cl_2CH_2CH_2Cl_2$ differed from those in CHCl$_3$ in appearance (Figure 5d). As shown in Figure 5d, the fibers in $Cl_2CH_2CH_2Cl_2$ have shorter lengths (several hundred nanometers) and larger diameters (50–100 nm) than those in CHCl$_3$. Figure 5c shows that the surfaces of the nanofibers are clean and smooth. These results indicate that solvents can affect the appearance of self-assembled **3·7** aggregates. Because of the hydrogen-bonding interaction between the 2,6-diacylaminopyridine groups of **3** and the imide groups of **7**, **3·7** aggregates tend to form hydrogen-bonded chains. Moreover, the π–π stacking interactions of perylene rings and the interactions of alkyl chains can also cause **3·7** aggregates to form 1D supramolecular structures.

Conclusions

In conclusion, a supramolecular system bound by three hydrogen-bonding interactions was synthesized and characterized. ^{1}H NMR spectra confirmed the existence of hydrogen-bonding interactions between the perylene derivative **3** and the perylene bisimide **7**. The photocurrent generated by the self-assembled **3·7** film was measured, and a cathodic photocurrent response of $0.08\ \mu A\,cm^{-2}$ at $32\ mW\,cm^{-2}$ white light irradiation was obtained. SEM images indicated that well defined long fibers could be fabricated by a self-assembly process that exploits the hydrogen bonding and $\pi-\pi$ stacking interactions of perylene rings. The nanofibrous superstructure could be of importance for future studies on 1D nanomaterials in the field of photoelectric devices.

Experimental Section

Materials and measurements: Most chemical reagents were purchased from Acros or Aldrich Corporation and were used as received unless indicated otherwise. 2-Amino-6-lauroylaminopyridine[17] and **BF** were synthesized according to ref. [19]. Compound **4** was supplied by BASF. All solvents were purified using standard procedures. Column chromatography was performed on silica gel (mesh size 160–200 μm). UV/Vis spectra were recorded on a Hitachi U-3010 spectrometer, and fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer. ^{1}H 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 Bruker Biflex MALDI-TOF. Scanning electron micrographs were recorded on a JSM 6700F NT instrument. The photocurrent measurements were carried out on a model 600 voltammetric analyzer (CH Instruments, USA) with a 500 W halogen lamp as the light source. Unmodified ITO glass substrates were cleaned in an ultrasonicator bath of isopropyl alcohol, then deionized water, prior to use.

N-(6-Dodecanoylamino-pyridin-2-yl)-4-methoxy-benzamide (**1**): A solution of 4-methoxybenzoyl chloride (2.1 g, 12 mmol) in anhydrous THF (10 mL) was slowly added to a solution of 2-amino-6-lauroylaminopyridine (2.9 g, 10 mmol) and triethylamine (2 g, 20 mmol) in anhydrous THF (100 mL) at 10°C. The mixture was stirred for 2 h. Then water (5 mL) was added, and the mixture was stirred for 10 min. THF was removed under reduced pressure, and CH_2Cl_2 (100 mL) was added to the residue. This solution was washed with water and brine (containing 5% NaOH). After the solution was dried (Na_2SO_4), and the solvent was evaporated, the crude product was obtained. Recrystallization from ethanol yielded the pure compound **1** (3.52 g, 82.8%); ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 8.21$ (s, 1 H), 8.06 (d, ^3J(H,H) = 8 Hz, 1 H), 7.93–7.88 (m, 3 H), 7.77 (t, ^3J(H,H) = 8 Hz, 1 H), 7.61 (s, 1 H), 7.69 (d, ^3J(H,H) = 8 Hz, 2 H), 3.89 (s, 3 H), 2.40 (t, ^3J(H,H) = 7.2 Hz, 2 H), 1.75–1.26 (m, 18 H), 0.88 (t, ^3J(H,H) = 6 Hz, 3 H); FTIR (KBr): $\tilde{\nu} = 3333, 2919, 2850, 1675, 1649, 1585, 1503, 1465, 1309, 1247, 1177, 1029, 842, 802, 603\ cm^{-1}$; MS (70 eV): m/z (42%): 425 [M$^+$].

N-(6-Dodecanoylamino-pyridin-2-yl)-4-hydroxy-benzamide (**2**): A solution of BBr$_3$ (3 g, 12 mmol) in dried CH_2Cl_2 (10 mL) was slowly added, with stirring under nitrogen, to a solution of **1** (425 mg, 1 mmol) in dried CH_2Cl_2 (40 mL) at −78°C. After the addition of BBr$_3$, the mixture was warmed to room temperature and stirred for

48 h. The reactant solution was slowly added to ice water (100 g) containing NaHCO$_3$ (5.1 g, 60 mmol), and the mixture was stirred for 30 min. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (100 mL) and EtOAc (100 mL). The organic layers were combined and dried (Na_2SO_4). Removal of the solvent under reduced pressure and purification of the residue by column chromatography (silica gel; petroleum ether/EtOAc, 2:1) yielded compound **2** as a white powder (310 mg, 75.4%); ^{1}H NMR (400 MHz, [d$_6$]DMSO, 25°C): $\delta = 7.85$ (d, ^3J(H,H) = 8 Hz, 2 H), 7.77–7.73 (m, 3 H), 6.83 (d, ^3J(H,H) = 8 Hz, 2 H), 2.36 (t, ^3J(H,H) = 7.3 Hz, 2 H), 1.55–1.22 (m, 18 H), 0.83 (t, ^3J(H,H) = 6.4 Hz, 3 H); FTIR (KBr): $\tilde{\nu} = 3334, 2921, 2852, 1673, 1651, 1608, 1587, 1528, 1502, 1450, 1307, 1244, 1174, 846, 797, 614\ cm^{-1}$; MS(70 eV): m/z(90%): 411 [M$^+$].

Compound **3**: A solution of **BF** (77 mg, 0.1 mmol), **2** (98 mg, 0.12 mmol), K$_2$CO$_3$ (50 mg, 0.36 mmol), and 18-crown-6 (26 mg, 0.1 mmol) in anhydrous 1,4-dioxane (20 mL) was refluxed for 4 h under nitrogen. After the total consumption of the **BF** (monitored by TLC), the solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel; CH_2Cl_2/EtOAc, 10:1) to give **3** as a violet powder (82 mg, 57.2%). ^{1}H NMR (400 MHz, Cl$_2$CD$_2$CD$_2$Cl$_2$, 25°C): $\delta = 9.46$ (d, ^3J(H,H) = 8.4 Hz, 2 H), 8.65 (t, ^3J(H,H) = 8.8 Hz, 2 H), 8.33 (d, ^2J(H,H) = 14.4 Hz, 2 H), 8.27 (s, 2 H), 8.03–7.95 (m, 10 H), 7.79 (t, ^3J(H,H) = 8.0 Hz, 2 H), 7.65 (s, 2 H), 7.28 (d, ^3J(H,H) = 8.0 Hz, 2 H), 4.12 (m, 4 H), 2.39 (t, ^3J(H,H) = 7.6 Hz, 4 H), 1.71–0.85 (m, 72 H); UV/Vis (CHCl$_3$): $\lambda_{max} = 527, 494, 394, 301$ nm; fluorescence (CHCl$_3$): $\lambda_{max} = 560$ nm; FTIR (KBr): $\tilde{\nu} = 3424, 3321, 2925, 2854, 1698, 1660, 1592, 1493, 1449, 1338, 1219, 1169, 1107, 1014, 805\ cm^{-1}$; MS (MALDI-TOF): calcd for C$_{88}$H$_{104}$N$_8$O$_{10}$ 1433.8; found 1433.2.

Compound **5**: In a 100 mL single-necked flask, **4** (1.59 g, 3 mmol) was finely suspended in propionic acid (50 mL). Then, *n*-octylamine (2.5 mL, 15 mmol) 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 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 **5** (1.69 g, 83%). ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 8.69$ (s, 4 H), 4.23 (t, ^3J(H,H) = 8.2 Hz, 4 H), 1.75 (m, 4 H), 1.45–1.26 (m, 20 H), 0.90 (m, 6 H); UV/Vis (CHCl$_3$): $\lambda_{max} = 519, 485, 426$ nm; fluorescence (CHCl$_3$): $\lambda_{max} = 550$ nm; FTIR (KBr): $\tilde{\nu} = 1705$ (C=O), 1666 cm^{-1}(C=O); MS (MALDI-TOF): 750.6 [M$^-$]; calcd for C$_{40}$H$_{38}$N$_2$O$_4$Cl$_4$ (750.2): C 63.84, H 5.09, N 3.72; found: C 64.27, H 5.22, N 3.49.

Compound **6**: A mixture of **5** (752 mg, 1 mmol), 4-(*n*-octyloxy)phenol (1.11 g, 5 mmol), and K$_2$CO$_3$ (345 mg, 2.5 mmol) was stirred under argon in NMP (50 mL) at 80°C for 24 h. After cooling to room temperature, the reaction mixture was poured into a mixture of 10% hydrochloric acid (80 mL) and methanol (120 mL) while stirring. The precipitate was filtered, repeatedly washed with methanol/water (3:2), and dried in vacuum at 100°C. The compound was purified by dissolving the crude product in CH_2Cl_2, and precipitated by addition of methanol, followed by chromatography on SiO$_2$ with CH_2Cl_2: ^{1}H NMR (400 MHz, CDCl$_3$, 25°C): $\delta = 8.09$ (s, 4 H), 6.90 (d, ^3J(H,H) = 9.7 Hz, 8 H), 6.81 (d, ^3J(H,H) = 9.7 Hz, 8 H), 3.92 (t, ^3J(H,H) = 7.3 Hz, 8 H), 2.63 (s, 4 H), 2.05 (m, 8 H), 1.88 (m, 4 H), 1.50 (m, 12 H), 1.36–1.23 (m, 48 H), 0.92 (m, 18 H); UV/Vis (CHCl$_3$): $\lambda_{max} = 592, 550, 456$ nm; fluorescence (CHCl$_3$): $\lambda_{max} = 625$ nm; FTIR (KBr): $\tilde{\nu} = 1697$ (C=O), 1661 cm^{-1}(C=O); MS (MALDI-TOF): 1494.9 [M$^+$]; calcd for C$_{96}$H$_{122}$N$_2$O$_{12}$ (1494.9): C 77.07, H 8.22, N 1.87; found: C 76.86, H 8.00, N 2.05.

Compound **7**: Water (10 mL) and KOH (11 g, 200 mmol) were added to a suspension of **6** (310 mg, 0.2 mmol) in 2-propanol (50 mL). The reaction mixture was heated to reflux with vigorous stirring under argon for 42 h. During the course of the reaction, the color changed from red to green. Once it had cooled to room temperature, the resulting reaction mixture was poured into 10% hydrochloric acid (100 mL) under stirring, and a precipitate appeared. The precipitate was filtered, washed neutral with water, and dried in vacuum at 100 °C to give a red solid (232 mg, 87%). The red solid was not purified, but it was suspended in propionic acid (40 mL). Then, ammonium acetate (4 g, 52 mmol) was added, and the mixture was refluxed while stirring for 24 h. After it cooled to room temperature, the reaction mixture was diluted with water and allowed to stand overnight. The precipitate was filtered, washed to neutral pH with water, and dried in vacuum at 100 °C to give a dark solid (197 mg, 86%). The solid was purified by column chromatography on silica (CH_2Cl_2/EtOAc, 40:1) to give **7**. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.39$ (s, 2H), 8.09 (s, 4H), 6.89 (d, $^3J(H,H) = 8$ Hz, 8H), 6.82 (d, $^3J(H,H) = 8$ Hz, 8H), 3.93 (t, $^3J(H,H) = 7.2$ Hz, 8H), 1.83–1.75 (m, 8H), 1.56 (s, 8H), 1.37–1.31 (m, 32H), 0.90 (m, 12H); UV/Vis ($CHCl_3$): $\lambda_{max} = 592$, 550, 458 nm; fluorescence ($CHCl_3$): $\lambda_{max} = 623$ nm; FTIR (KBr): $\tilde{v} = 3186$ (N–H), 1699 (C=O), 1677 cm^{-1} (C=O); MS (MALDI-TOF): 1270.9 [M$^+$]; calcd for $C_{80}H_{90}N_2O_{12}$ (1270.7): C 75.56, H 7.13, N 2.20; found: C 75.65, H 7.30, N 2.14.

Acknowledgements

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