Assembly and Characterization of Novel Hydrogen-Bond-Induced Nanoscale Rods

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A class of bis-urea compounds with perylene bisimide was synthesized and characterized successfully. ^{1}H NMR and fluorescence spectra confirmed that strong hydrogen-bonding interactions between neighboring urea groups were formed. Interestingly, the photocurrent measurement showed that the self-assembled films of bis-urea compounds could produce steady and rapid anodic photocurrent responses. The TEM images indicated that well-defined nanoscale rods with uniform diameter distribution could be fabricated by self-assembly of hydrogen-bonding interactions and $\pi-\pi$ stacking interactions of perylene rings.

Introduction

There is growing interest in supramolecular chemistry in attempts to construct organic molecules into well-defined functional aggregates.[1] Well-defined nanosized aggregates should be very useful for the development of novel functional materials and nanoelectronic devices. In particular, hydrogen bonding is a very useful means of constructing the supramolecular system and has been used for the design of various molecular aggregates.[2] Meanwhile, energy- and electron-transfer processes have also been investigated in the assembled supramolecular systems through the interaction of hydrogen bonds.[3] 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 unites.[4] The urea functionality has been utilized to create highly organized hydrogen-bonded molecular assemblies.[5] A class of compounds that is particularly well suited for the spatial organization of functional entities is bis-urea compounds.[6] Bis-urea compounds with the thiophene moiety self-assembled into ribbons and fibers through multiple hydrogen bonds with neighboring molecules have been synthesized.[7] A class of bis-urea macrocycles that self-assembled into columnar nanotubes via urea−urea hydrogen bonding was re-

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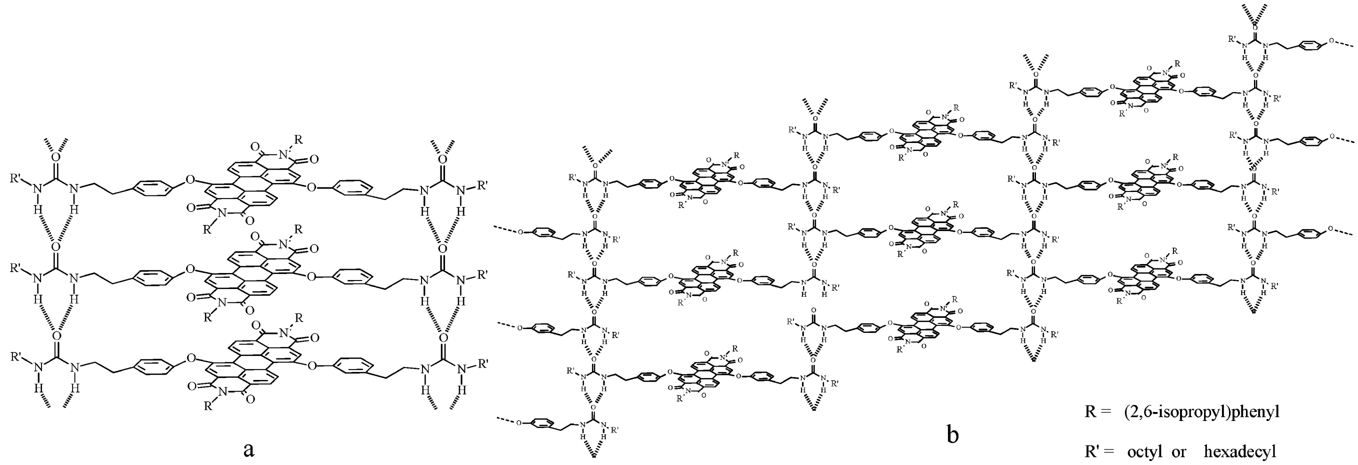

FIGURE 1. Possible superstructure arrangements of **7** through hydrogen-bonding and $\pi-\pi$ stacking interactions.

ported.[8] Perylene bisimides have been extensively studied as organic semiconductors, in electronic and optical application such as field-effect transistors,[9] fluorescent solar collectors,[10] electrophotographic devices,[11] photovoltaic devices,[12] dye lasers,[13] and molecular switches.[14] They have outstanding chemical, thermal, and photochemical stability.[15] Recently, we discussed the photocurrent generation of the self-assemblies of [60]fullerene derivative with perylene bisimide and perylene derivative with perylene bisimide through hydrogen-bonding interactions.[16] Here, we report a class of bis-urea compounds with perylene bisimides that self-assembly into nanoscale rodlike superstructures through 3-centered intermolecular hydrogen-bonding interactions of urea−urea groups and $\pi-\pi$ stacking interactions of perylene rings (Figure 1) and study their photocurrent responses. We hope that the supramolecular systems can demonstrate the energy and electron transfer and can provide effective conversion from photons to electrons.

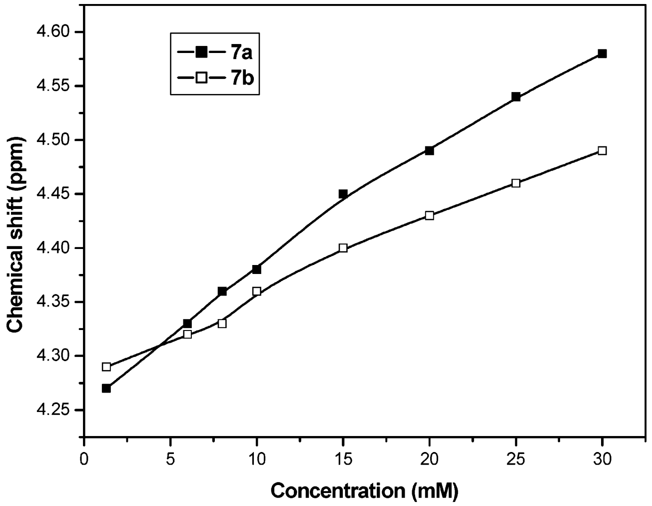

FIGURE 2. ^{1}H NMR shifts of the urea N−H protons of **7a** and **7b** as a function of concentration in $CDCl_3$ solution at room temperature.

Results and Discussion

The bis-urea compounds with perylene bisimide were synthesized in four steps from 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride **1**, as shown in Scheme 1. Briefly, compound **1** was converted to the corresponding perylene bisimide **4** using 2,6-diisopropylaniline. Subsequently, compound **5** was prepared by the nucleophilic substitution of the two bromine atoms using *N*-(*tert*-butoxycarbonyl)tyramine **3**. Compound **6** was obtained by removing the protective units of amino groups. Finally, the bis-urea compounds **7a** and **7b** were synthesized by the reaction of corresponding isocyanates and amino-groups of compound **6**, respectively. In contrast to the reported bis-urea thiophenes,[7a] the solubility of compounds **7a** and **7b** is rather good in organic solvents such as chloroform or ethyl acetate at room temperature.

We studied the formation of hydrogen bonds of bis-urea compounds in $CDCl_3$ by a ^{1}H NMR titration experiment. As shown in Figure 2, an increase of the concentration

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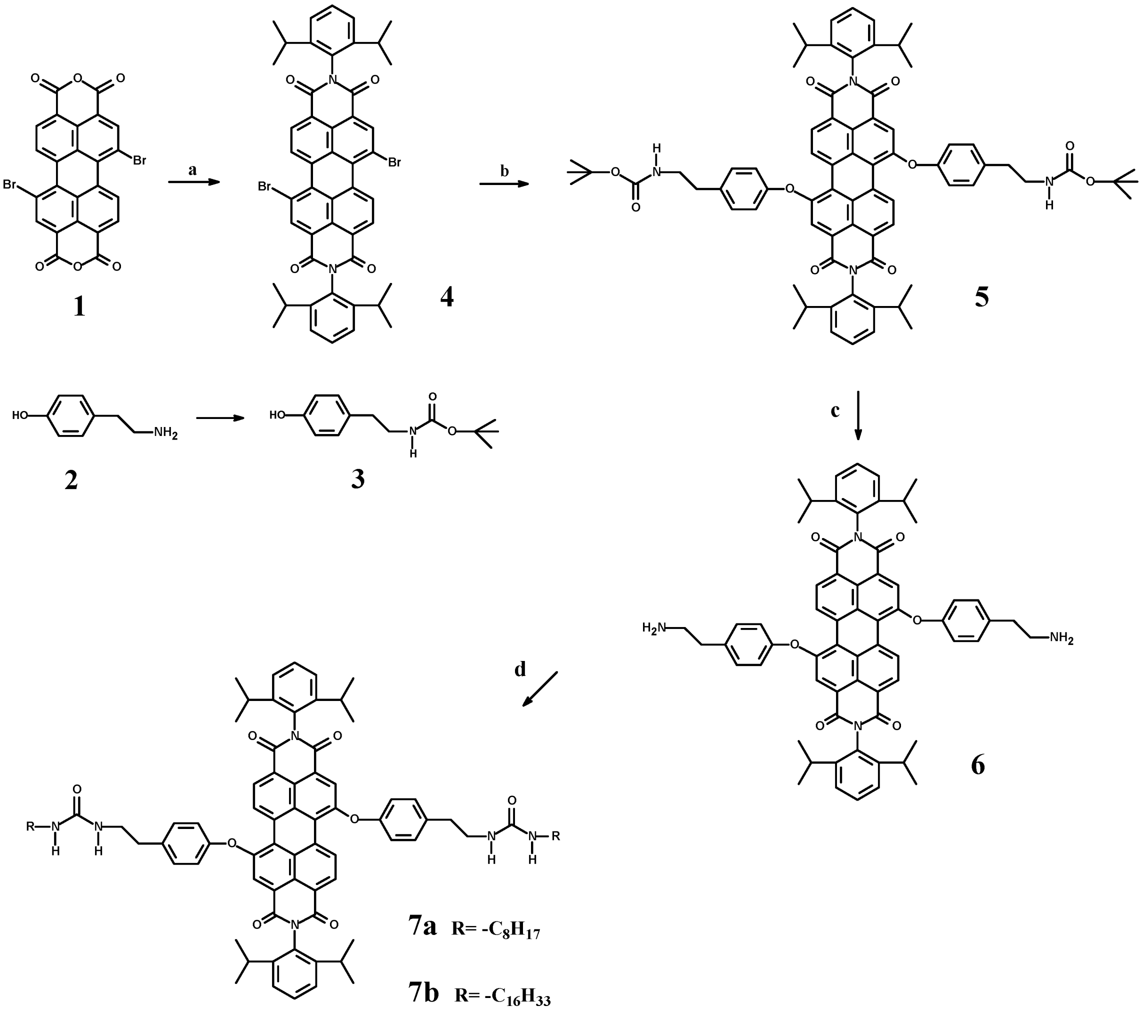
SCHEME 1. Synthesis of Bis-Urea Compounds with Perylene Bisimides[a]



[a] (a) 2,6-Diisopropylaniline, propionic acid, nitrogen, reflux, 26 h, 44%. (b) Compound **3**, anhydrous K_2CO_3, 18-crown-6, toluene, nitrogen, reflux, 2 h, 75%. (c) CF_3COOH, CH_2Cl_2 (anhydrous), at room temperature, 2 h, 95%. (d) **7a**: octyl isocyanate, CH_2Cl_2 (anhydrous), at room temperature, 6 h, 99%. **7b**: hexadecyl isocyanate, CH_2Cl_2 (anhydrous), at room temperature, 12 h, 79%.

of bis-urea compounds in $CDCl_3$ resulted in a clear downfield shift of the spectral position of the urea N−H protons since the electron densities of the protons involved in hydrogen bonds were decreased and consequently their NMR signals were shifted to lower magnetic fields. When the concentration of **7a** increased from 1.3 to 30 mM, the chemical shift for the urea N−H protons changed from 4.27 parts per million (ppm) to 4.58 ppm. While the concentration of **7b** increased from 1.3 to 30 mM, the chemical shift for the urea N−H protons changed from 4.29 to 4.49 ppm. These results indicated that strong 3-centered intermolecular hydrogen bonds between neighboring urea−urea groups were formed. Moreover, hydrogen-bonding interactions between the urea groups of **7a** were stronger than those of **7b** since the chemical shift for the urea N−H protons of **7a** was bigger than that of **7b**. This indicated that the length of the alkyl chains connected with the urea groups could affect the interactions of hydrogen bonds between urea groups.[17]

The formation of hydrogen bonds of bis-urea compounds in chloroform was further studied by means of infrared spectroscopy since the N−H stretch and the amide-II band of the urea groups generally show clear shifts upon the formation of hydrogen bonds. When **7a** was dissolved in chloroform at the concentration of 5×10^{-5} M, this solution showed two absorptions at 3457 (N−H) and 1522 (amide-II) cm^{-1}, which were characteristic for the presence of non-hydrogen-bonded urea groups[18] (Table 1). The peak in the amide-I region of urea groups was not precisely determined because the absorption band of amide-I overlapped that of the C=O stretch region of the diimide units. As shown in Table 1, increasing the concentration of **7a** from 5×10^{-5} M to 2.7×10^{-3} M caused a shift of the N−H stretch absorption toward a shorter wavenumber and a shift of the amide-II band toward a higher wavenumber. These concentration-dependent spectral changes clearly indicated the formation of intermolecular hydrogen bonds between urea groups. Similar changes were observed in the

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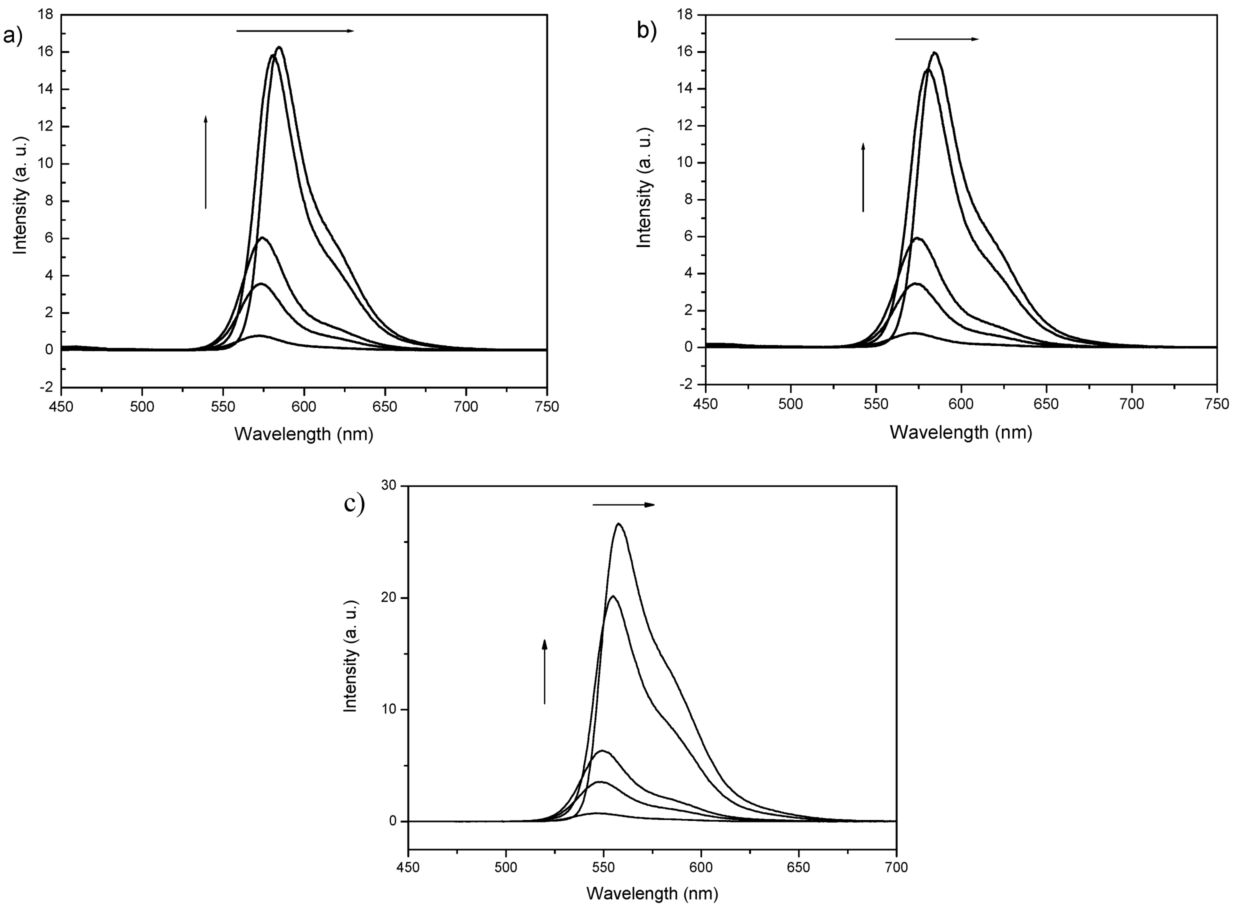

FIGURE 3. (a) Fluorescence emission spectra of (a) **7a**, (b) **7b**, and (c) **4** in $CHCl_3$ at different concentrations. (Arrows indicate increasing concentrations from 10^{-6} to 10^{-4} mol L^{-1}, respectively; $\lambda_{em} = 420$ nm).

TABLE 1. Infrared Spectroscopy of 7a and 7b in Chloroform

compound	concn [10^{-4} M]	NH stretch [ν cm^{-1}]	amide-II [ν cm^{-1}]
7a	0.5	3457	1522
	1	3455	1522
	5	3447	1526
	10	3446	1527
	27	3444	1541
7b	1	3459	1527
	5	3456	1527
	10	3449	1532
	27	3447	1535

infrared spectra of **7b** in chloroform, and spectral shifts were smaller than those of **7a**. This indicated that hydrogen-bonding interactions between urea groups of **7b** were weaker than those of **7a**, consistent with the results of ^{1}H NMR titration experiments.

Little attention has been paid to the study of the fluorescence of bis-urea compounds.[19] We also studied the fluorescence spectra of **7a** and **7b** in chloroform at different concentrations. As shown in Figure 3a, while the concentration of **7a** increased from 10^{-6} to 10^{-4} M, not only was the intensity of its fluorescence strengthened but also its fluorescence was red-shifted by 12 nm from 572 to 584 nm. To investigate the interactions of hydrogen-bonding resulting in the red-shifting of the fluorescence of **7**, compound **4** not containing hydrogen-bonded groups was utilized as a comparative object. Figure 3c showed that the fluorescence of compound **4** was red-shifted by 10 nm from 547 to 557 nm with the increasing concentration from 10^{-6} to 10^{-4} M. The red-shifting of the fluorescence of compound **4** was mainly caused by molecular collision at increased concentrations. These results indicated that the red-shifting of the fluorescence of **7** upon the increasing concentration might be produced as a result of corporate interactions of both molecular collision and hydrogen bonding.[20] A similar phenomenon was observed in the fluorescence spectrum of **7b** in chloroform (Figure 3b).

We first study the photoinduced electron-transfer property of the self-assembled **7** on the basis of the hydrogen-bond-induced nanostructure system. The anodic photocurrent responses of 0.2 and 0.06 μA cm^{-2} at 100 mW cm^{-2} white light irradiation were produced (Figure 4) as the irradiations of the **7a** and **7b** films were switched on and off, respectively. The responses to on/off cycling were prompt and reproducible; five cycles are shown in Figure 4. The photocurrent stabilities in two systems were good in the monitored time. The introduction of a perylene unit in the urea compound led to the occurrence of efficient charge-transport pathways,

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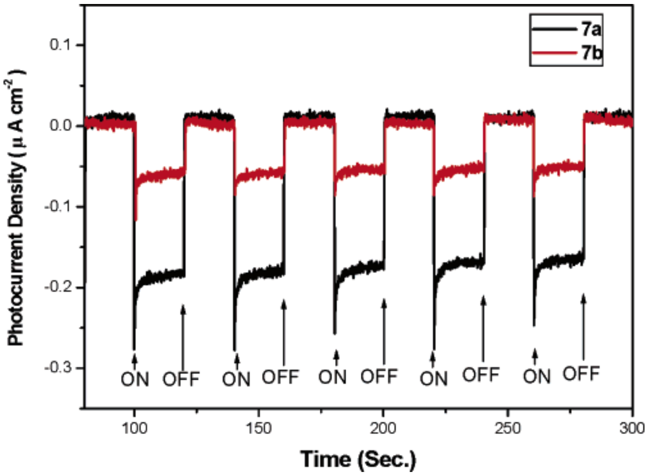

FIGURE 4. Time dependence of the photocurrent responses of the self-assembled **7a** and **7b** films upon irradiation by 100 mW cm^{-2} white light in 0.5 M KCl solution.

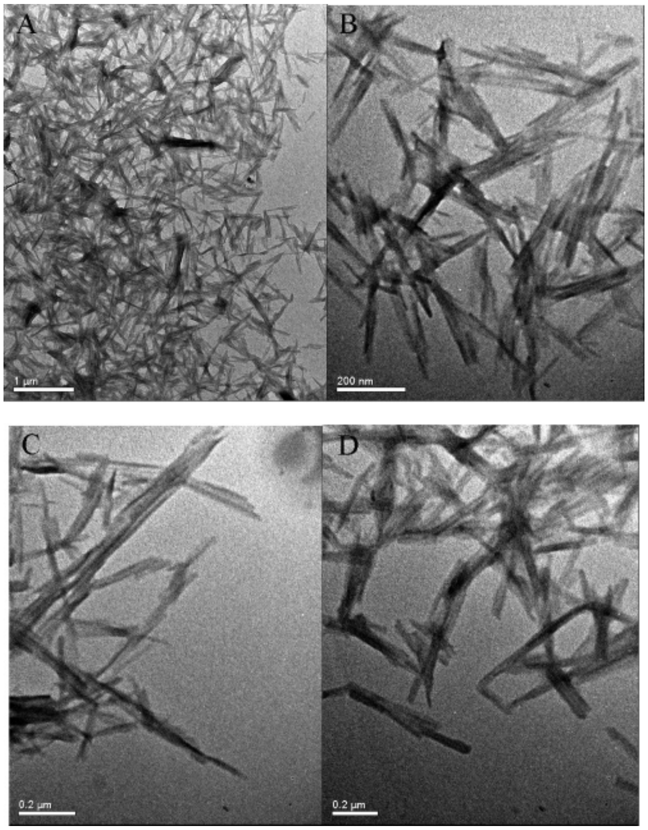

FIGURE 5. (A) Transmission electron micrograph (TEM) images of self-assembled **7a** in *p*-xylene. (B−D) High magnification of TEM image.

similar to the introduction of the thiophene unit.[7a] It can be seen that the photocurrent response of **7a** was stronger than that of **7b** at the same experimental condition. This indicated that hydrogen-bonding interactions between the urea groups of **7a** were stronger than those of **7b**, consistent with the results of ^{1}H NMR titration experiments.

Figure 5 showed the transmission electron micrograph (TEM) images of self-assembled **7a** in *p*-xylene. From the electron micrograph in Figure 5 it is clear that self-assembled **7a** in *p*-xylene can form large quantity of rodlike nanostructures with diameters in the range of 30−80 nm, while their lengths were extended to several micrometers. Because of the hydrogen-bonding interactions of the bis-urea groups of compound **7a**, self-assembled aggregates tend to form hydrogen-bonded chains. Moreover, the $\pi-\pi$ stacking interactions of perylene rings and the interactions of alkyl chains can also facilitate aggregates to form one-dimensional rodlike supramolecular structures. However, similar rodlike nanostructures were not observed in the electron micrograph of **7b** in *p*-xylene. This indicated that because hydrogen-bonding interactions between the urea groups of **7b** were weaker than those of **7a**, **7b** could not self-assembly into rodlike nanostructures as **7a** did through 3-centered intermolecular hydrogen bonding interactions of urea−urea groups. The results also suggested that the length of the alkyl chains connected with the urea groups could affect the interactions of hydrogen bonds between urea groups.

Conclusions

In conclusion, two bis-urea compounds with perylene bisimide were synthesized and characterized successfully. ^{1}H NMR and fluorescence spectra confirmed the existence of strong hydrogen-bonding interactions between neighboring urea groups. The TEM images indicated that well-defined nanoscale rods could be fabricated by self-assembly due to hydrogen-bonding interactions and $\pi-\pi$ stacking interactions of perylene rings. Interestingly, the photocurrent measurement showed that the self-assembled films of bis-urea compounds could produce steady and rapid anodic photocurrent responses. Therefore, these perylene bisimides modified with bis-urea units, with the capability for self-assembly through hydrogen-bonding interactions, are promising candidates for inclusion in photoelectric devices based on organic semiconducting layers.

Experimental Section

1,7-Dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride **1** and *N*-(*tert*-butoxycarbonyl)tyramine **3** were prepared according to literature procedures.[21,22]

***N,N′*-Bis[(2,6-diisopropyl)phenyl]-1,7-dibromoperylene-3,4,9,10-tetracarboxylic Acid Bisimide (4).** 2,6-Diisopropylaniline (2.832 g, 16 mmol) was added to a suspension of 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride **1** (2.2 g, 4 mmol) in propionic acid (40 mL), and the mixture was refluxed under a nitrogen atmosphere for 26 h. Unreacted starting material was removed by filtering the hot mixture. The product precipitated from the cooled filtrate was collected by filtration, washed with methanol, and dried in a vacuum at 100 °C to give **4** as a red solid (1.53 g, 44%): ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ 9.57 (d, 2H, J = 7.8 Hz), 9.02 (s, 2H), 8.80 (d, 2H, J = 7.8 Hz), 7.52 (t, 2H, J = 7.8 Hz), 7.37 (d, 4H, J = 7.8 Hz), 2.74 (m, 4H), 1.19 (d, 24H); UV−vis (CHCl$_3$) λ_{max} 533 nm, 497 nm, 467 nm, 396 nm; fluorescence (CHCl$_3$) λ_{max} 555 nm; FT-IR (KBr), ν [cm^{-1}] 1711 (C═O), 1673 (C═O); MS (MALDI-TOF) 866.8 (M$^-$). Elemental analysis calcd (%) for

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$C_{48}H_{40}N_2O_4Br_2$ (866.1): C, 66.37; H, 4.64; N, 3.22. Found: C, 66.08; H, 4.81; N, 3.01.

***N,N′*-Bis[(2,6-diisopropyl)phenyl]-1,7-bis{[4-(2-*N*-*tert*-butoxycarbonyl)-aminoethyl]phenoxy}perylene-3,4,9,10-tetracarboxylic Acid Bisimide (5).** A mixture of *N*-(*tert*-butoxycarbonyl)tyramine **3** (71 mg, 0.3 mmol), anhydrous potassium carbonate (83 mg, 0.6 mmol), and 18-crown-6 (316 mg, 1.2 mmol) was stirred in toluene (30 mL) at room temperature. Then compound **4** (80 mg, 0.09 mmol) was added. The reaction mixture was refluxed under nitrogen with stirring for 2 h. After cooling to room temperature, the solvent was removed by reduced pressure, and the crude product was obtained. Purification was accomplished by column chromatography on silica with CH_2Cl_2/CH_3OH (20/1, v/v) to give **5** (79.7 mg, 75%): ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 9.64 (d, 2H, $J = 9.0$ Hz), 8.76 (d, 2H, $J = 9.0$ Hz), 8.43 (s, 2H), 7.47 (t, 2H, $J = 7.2$ Hz), 7.33 (d, 4H, $J = 7.2$ Hz), 7.12 (d, 4H, $J = 7.2$ Hz), 6.77 (d, 4H, $J = 7.2$ Hz), 4.60 (s, 2H), 3.35 (m, 4H), 2.82 (t, 4H, $J = 7.2$ Hz), 2.70 (m, 4H), 1.43 (s, 18H), 1.15 (d, 24H); UV−vis ($CHCl_3$) λ_{max} 548 nm, 515 nm, 403 nm; fluorescence ($CHCl_3$) λ_{max} 580 nm; FT-IR (KBr), ν [cm^{-1}] 3385 (N−H), 1707 (C═O), 1668 (C═O); MS (MALDI-TOF) 1182.4 (M^-). Elemental analysis calcd (%) for $C_{74}H_{76}N_4O_{10}$ (1180.6): C, 75.23; H, 6.48; N, 4.74. Found: C, 74.40; H, 6.77; N, 4.35.

***N,N′*-Bis[(2,6-diisopropyl)phenyl]-1,7-bis[4-(2-aminoethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic Acid Bisimide (6).** In a 50-mL flask, compound **5** (70.8 mg, 0.06 mmol) was dissolved in dichloromethane (20 mL). Then CF_3COOH (1 mL) was carefully added under stirring. The reaction mixture was stirred for 2 h. The solvent was removed under reduced pressure, and the residue was redissolved in CH_2Cl_2. The resulting solution was treated with 100 mL of 5% aqueous sodium carbonate. The organic phase was collected, washed with water, and dried over anhydrous sodium sulfate. The product was obtained after the solvent was removed in a vacuum: yield 55.7 mg (95%); ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 9.66 (d, 2H, $J = 7.8$ Hz), 8.77 (d, 2H, $J = 7.8$ Hz), 8.44 (s, 2H), 7.48 (t, 2H, $J = 7.8$ Hz), 7.34 (m, 8H), 7.13 (d, 4H, $J = 7.8$ Hz), 3.01 (s, 4H), 2.75 (t, 4H, $J = 7.8$ Hz), 2.70 (m, 4H), 1.16 (d, 24H); UV−vis ($CHCl_3$) λ_{max} 549 nm, 515 nm, 401 nm; fluorescence ($CHCl_3$) λ_{max} 582 nm; FT-IR (KBr), ν [cm^{-1}] 3423 (N−H), 1707 (C═O), 1668 (C═O); MS (MALDI-TOF) 981.0 (M^-). Elemental analysis calcd (%) for $C_{64}H_{60}N_4O_6$ (980.5): C, 78.34; H, 6.16; N, 5.71. Found: C, 77.87; H, 6.29; N, 5.13.

***N,N′*-Bis[(2,6-diisopropyl)phenyl]-1,7-bis[4-(2-(3-octylureido)ethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic Acid Bisimide (7a).** Octyl isocyanate (23 mg, 0.15 mmol) was added to a solution of compound **6** (49 mg, 0.05 mmol) in anhydrous dichloromethane (20 mL). The resulting mixture was stirred for 6 h at room temperature. The solvent was removed by reduced pressure and the crude product was obtained. Purification was accomplished by column chromatography on silica with CH_2Cl_2/CH_3OH (20/1, v/v) to give **7a** (64 mg, 99%): ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 9.65 (d, 2H, $J = 7.8$ Hz), 8.72 (d, 2H, $J = 7.8$ Hz), 8.39 (s, 2H), 7.47 (t, 2H, $J = 7.8$ Hz), 7.35 (m, 8H), 7.13 (d, 4H, $J = 7.8$ Hz), 4.33 (br, 4H), 3.48 (t, 4H, $J = 6.5$ Hz), 3.11 (m, 4H), 2.86 (t, 4H, $J = 6.5$ Hz), 2.73 (m, 4H), 1.46 (s, 6H), 1.26 (m, 24H), 1.14 (d, 24H); UV−vis ($CHCl_3$) λ_{max} 550 nm, 518 nm, 403 nm; fluorescence ($CHCl_3$) λ_{max} 584 nm; FT-IR (KBr), ν [cm^{-1}] 3365 (N−H), 1707 (C═O), 1668 (C═O); MS (MALDI-TOF) 1292.2 (M^-). Elemental analysis calcd (%) for $C_{82}H_{94}N_6O_8$ (1290.7): C, 76.25; H, 7.34; N, 6.51. Found: C, 76.16; H, 7.84; N, 6.23.

***N,N′*-Bis[(2,6-diisopropyl)phenyl]-1,7-bis[4-(2-(3-hexadecyl-ureido)ethyl)phenoxy]perylene-3,4,9,10-tetracarboxylic Acid Bisimide (7b).** Hexadecyl isocyanate (40 mg, 0.15 mmol) was added to a solution of compound **6** (49 mg, 0.05 mmol) in anhydrous dichloromethane (20 mL). The resulting mixture was stirred for 6 h at room temperature. The solvent was removed by reduced pressure, and the crude product was obtained. Purification was accomplished by column chromatography on silica with CH_2Cl_2/CH_3OH (20/1, v/v) to give **7b** (59.8 mg, 79%): ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 9.68 (d, 2H, $J = 7.8$ Hz), 8.79 (d, 2H, $J = 7.8$ Hz), 8.42 (s, 2H), 7.49 (t, 2H, $J = 7.8$ Hz), 7.37 (m, 8H), 7.16 (d, 4H, $J = 7.8$ Hz), 4.31 (br, 4H), 3.51 (t, 4H, $J = 4.5$ Hz), 3.14 (m, 4H), 2.89 (t, 4H, $J = 4.5$ Hz), 2.74 (m, 4H), 1.47 (s, 6H), 1.29 (m, 56H), 1.18 (m, 24H); UV−vis ($CHCl_3$) λ_{max} 550 nm, 518 nm, 403 nm; fluorescence ($CHCl_3$) λ_{max} 584 nm; FT-IR (KBr), ν [cm^{-1}] 3362 (N−H), 1707 (C═O), 1669 (C═O); MS (MALDI-TOF) 1515.9 (M^-). Elemental analysis calcd (%) for $C_{98}H_{126}N_6O_8$ (1515.0): C, 77.64; H, 8.38; N, 5.54. Found: C, 76.88; H, 8.94; N, 5.36.

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Supporting Information Available: General experimental methods, mass spectra for compounds **4−7,** and partial ^1H NMR spectra for compound **7a** at different concentrations in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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