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Helical Assembly Induced by Hydrogen Bonding from Chiral Carboxylic Acids Based on Perylene Bisimides

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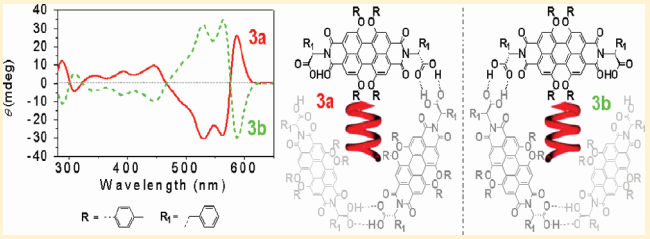
Supporting Information

ABSTRACT: The control over self-assembly behavior becomes absolutely critical because it is dependent on the orientation and morphology. The motivation is focused on borrowing the help of O—H···O hydrogen bonding interactions to realize the control in chiral self-assembly. A series of perylene bisimide (PBI) dyes **3a**—**3d** bearing chiral amino acid derivatives on the imide N atoms and four phenoxy-type substituents at the bay positions of the perylene core were synthesized. Optical properties and aggregation behavior of PBIs were investigated by absorption, fluorescence, circular dichroism (CD), and ^{1}H NMR spectroscopy. Except for the chiral ester **3c** and achiral **3d**, chiral dyes **3a** and **3b** show bisignated CD signals, indicating that the chiral carboxylic acid-functionalized PBI systems are found to be spontaneously self-assembled into supramolecular helices via intermolecular hydrogen bonding rather than $\pi-\pi$ stacking. Furthermore, the chirality-controlled helical superstructures are strongly dependent on several factors, such as solvent polarity, concentration, and temperature. The supramolecular helical chirality can be well-controlled by the chiral amino acid residues in the PBI system; that is, the assembled clockwise (plus, ***P***) or anticlockwise (minus, ***M***) helices can be induced by L- or D-isomers, respectively.



INTRODUCTION

Supramolecular helical architectures have received great interest in recent years, especially in arising from the intermolecular self-assembly with small molecular chiral building blocks.[1−8] Perylene bisimides (PBIs) exhibit a pronounced tendency to self-organization with the help of molecular stacking, metal coordination, or hydrogen bonding under conditions, even forming unique chiral supramolecular helices,[9−12] but many PBI helical assemblies are formed with the help of the intermolecular $\pi-\pi$ interactions because of their big planar structures.[13−17] To date, several PBI supramolecular architectures containing N—H···O hydrogen bonding interactions have been realized by the Würthner group.[11,16] However, little attention has been paid to the O—H···O hydrogen bonding interactions in the PBI system,[18] although the conventional hydrogen bonding in carboxylic acids is particularly strong in solutions, on surface, and in crystal with high sensitivity to various environmental factors.[19−21]

With this in mind, our motivation is focused on borrowing the help of O—H···O hydrogen bonding interactions to realize the control in chiral self-assembly. Undoubtedly, the control over their self-assembly behavior becomes absolutely critical because it is dependent on the orientation and morphology. Moreover, chirality has been utilized as a guiding element to induce self-assembly processes with the assistance of circular dichroism (CD) to assign the helical assemblies.[22,23] For this purpose, we construct the target chiral α-amino acid system based on PBI chromophore (**3a** and **3b** in Scheme 1) with the following considerations: (i) to obtain PBIs bearing the self-assembly unit of carboxylic groups, chiral α-amino acid is an obviously good choice to the building block with an easy imidation to incorporate carboxylic groups and retain the original chiral center of amino acid; (ii) to incorporate the substitute of 4-methylphenoxy to their bay-region at PBI to prevent the competitive *H*- or *J*-aggregation during the interaction process of hydrogen bonding;[11] and (iii) to attempt to realize helical arrangement via the chiral center control with two exact enantiomers of L- and D-phenylalanine. For taking insight into the effect on the intermolecular hydrogen bonding induced by carboxyl groups, we further utilized the corresponding ester **3c** as reference (Scheme 1). The apolar solvent CCl_4 and moderately polar solvent $CHCl_3$ were used in the studies, whereas MeOH was used as the breaking or blocking agent of hydrogen bond. Interestingly, the chiral carboxylic-acid-functionalized PBI systems (**3a** and **3b**) are found to self spontaneously-assemble into the supramolecular helices, which are strongly dependent on several factors, such as solvent polarity, concentration, and temperature. Moreover, the supramolecular helical chirality can be well-controlled by the chiral amino acid residues in PBI system; that is, the assembled clockwise (Plus, ***P***) or anticlockwise (Minus, ***M***) helices can be induced by L- or D- isomers, respectively.

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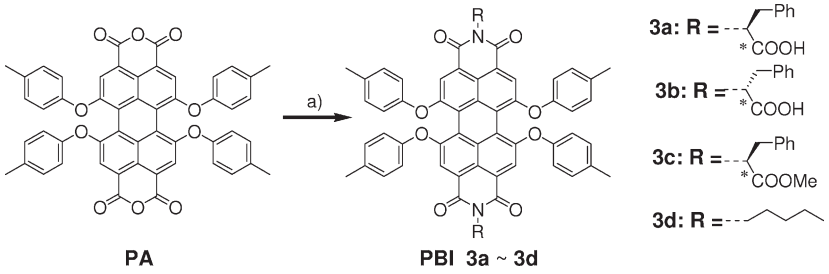
Scheme 1. Molecular Structure of Chiral Functionalized PBIs 3a−3c and the Reference 3d



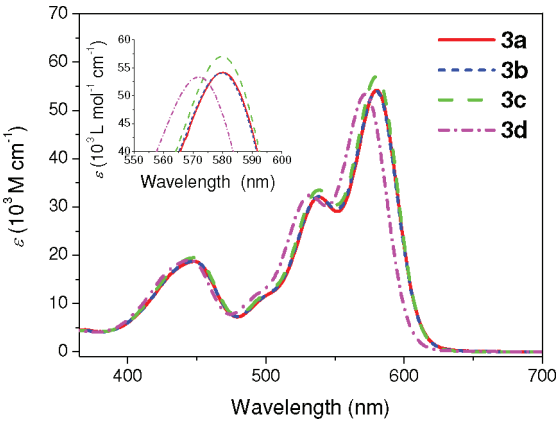


Figure 1. Absorption spectra of **3a**−**3d** in CCl_4 (1.0×10^{-5} M). Inset: expansion of the 550 to 600 nm region.

Table 1. UV/vis-Absorption Data of PBIs 3a−3d (1.0×10^{-5} M)

	in CCl_4			in MeOH−CCl_4 (5/95, v/v)		
PBI	λ_{abs} (nm)	ε_{max} (M^{-1} cm^{-1})	$A^{0\rightarrow0}/A^{0\rightarrow1}$	λ_{abs} (nm)	ε_{max} (M^{-1} cm^{-1})	$A^{0\rightarrow0}/A^{0\rightarrow1}$
3a	580	54 100	1.68	581	53 600	1.66
3b	580	54 100	1.66	581	53 500	1.67
3c	580	57 000	1.70	582	55 500	1.70
3d	572	53 400	1.65	574	53 400	1.64

RESULTS AND DISCUSSION

The PBIs **3a** and **3b** and the reference compounds **3c** and **3d** were synthesized from the commercially available starting material of 1,6,7,12-tetra-(4-methyl-phenoxy)perylene-3,4:9,10-tetracarboxylic acid dianhydride[17] (Scheme 1). Their chemical structures were fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS, as shown in the Supporting Information.

The absorption spectra of **3a**−**3c** in CCl_4 exhibit a close apparent absorption coefficients (molar extinction coefficients) and typical spectroscopic features similar to that of the tetraaryloxy-substituted PBI **3d** (Figure 1 and Table 1). As in the case of **3a**, there exist three main characteristic peaks at 449, 538, and 580 nm, arising from the typical transitions of PBI chromophore.[16] The value of 1.69 for $A^{0\rightarrow0}/A^{0\rightarrow1}$ ratios of PBI **3a** in concentration of 1.0×10^{-5} M is indicative of the mostly non-π-stacked dominance instead of *H*- or *J*-aggregations,[24−26] and

Table 2. Absorption Ratios $A^{0\rightarrow0}/A^{0\rightarrow1}$ of PBIs 3a−3d versus Concentration

	$A^{0\rightarrow0}/A^{0\rightarrow1}$ (in CCl_4 solution)				
PBI	5×10^{-6} M	1×10^{-5} M	2.5×10^{-5} M	5×10^{-5} M	1×10^{-4} M
3a	1.69	1.69	1.68	1.57	1.45
3b	1.70	1.69	1.69	1.56	1.45
3c	1.70	1.71	1.70	1.55	1.39
3d	1.65	1.65	1.62	1.47	1.31

such molecular aggregation can be ruled out in the concentration range from 5×10^{-6} to 1×10^{-4} M (Table 2). In contrast with the systems studied previously,[27] there is only a very small shift by 1 to 2 nm in the absorption peak among acids **3a**, **3b**, and ester **3c** in CCl_4 solution, even upon a small amount addition of MeOH (5 vol %, Table 1), indicative of less of a solvent polarity effect on the absorption spectra. A larger red shift by 8−10 nm is observed in the maximal absorption of acids **3a**, **3b**, and ester **3c** with respect to that of **3d** (Figure 1, inset), suggesting that the higher electronegative carboxylic or ester group can depress the electronic densities in the PBI core more than the butyl group, which is consistent with those previously reported.[28]

Unlike absorption spectra, there is an additional red shift in fluorescence peak with an increasing concentration (λ_{ex} = 538 nm). As a case illustrated in Figure 2a, the fluorescence peak of **3a** is red-shifted by 15 nm from 607 to 622 nm upon increasing the concentration from 5×10^{-6} to 1×10^{-4} M. Similarly, the fluorescence band of its corresponding ester **3c** is red-shifted by 12 nm from 607 to 619 nm with the same increment of concentration (Figure 2c). Obviously in the fluorescence band upon increasing concentration, a larger red-shifting by 3 nm for acid **3a** is observed with respect to the corresponding ester **3c**. Here the red-shifting in the fluorescence of ester **3c** is mainly caused by molecular collision at increased concentrations, whereas the red-shifting in the fluorescence of acid **3a** upon the increasing concentration might have resulted from the cooperating interactions of both molecular collision and hydrogen bonding.[29] Interestingly, such difference could be eliminated. That is, when adding 5 vol % MeOH to the CCl_4 solution, the fluorescence band of acid **3a** is blue-shifted by 4 nm from 622 to 618 nm (Figure 2a), but there is no distinct shift for the corresponding ester **3c**. The similar tendency was also observed in **3b** (Figure 2b). Additionally, the fluorescence quantum yields of **3a**−**3c** in CCl_4 were 0.64, 0.64, and 0.66, respectively, determined by comparing the integrated area of the

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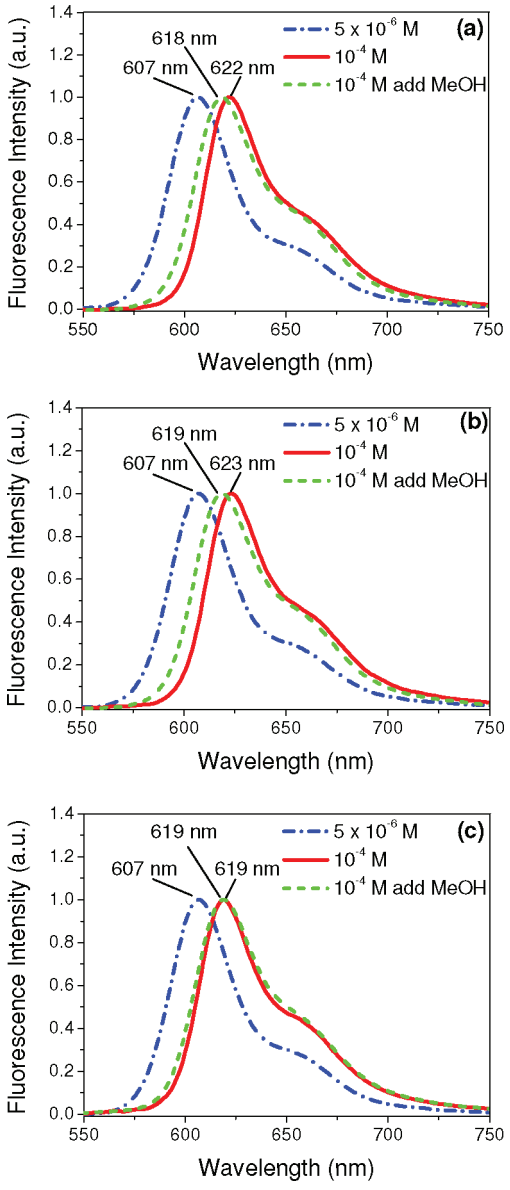

Figure 2. Normalized fluorescence emission spectra of (a) **3a**, (b) **3b**, and (c) **3c** in CCl_4 at the concentrations of 5×10^{-6} and 1×10^{-4} M (before and after the addition of 5 vol % MeOH).

corrected emission spectrum with a reference of *N*,*N*′-di(2,6-di-*n*-butyl)-1,6,7,12-tetrakis[4-*tert*-phenoxy]perylene-3,4:9,10-tetracarboxylic acid bisimides.[30] Here the very similar fluorescence quantum yields of **3a** and **3b** with **3c** further rule out the possibility of $\pi-\pi$ stacking. Accordingly from the fluorescent change, the possible intermolecular hydrogen-bonding through chiral carboxylic group in the system of **3a** and **3b** can take place upon increasing concentration in apolar solvent CCl_4, whereas MeOH can disassociate the hydrogen bonding.

Further evidence of intermolecular hydrogen bonding of PBI **3a** was gathered from ^{1}H NMR analysis in a moderately polar solvent $CDCl_3$ (Figure 3). Interestingly, the acid protons (H_a) were found to be significantly shifted downfield from 12.47 to 13.25 ppm with the concentration of **3a** increased from 1.2 to 20 mM. It is exactly in accord with the strong intermolecular hydrogen bonding between neighboring carboxylic groups, resulting

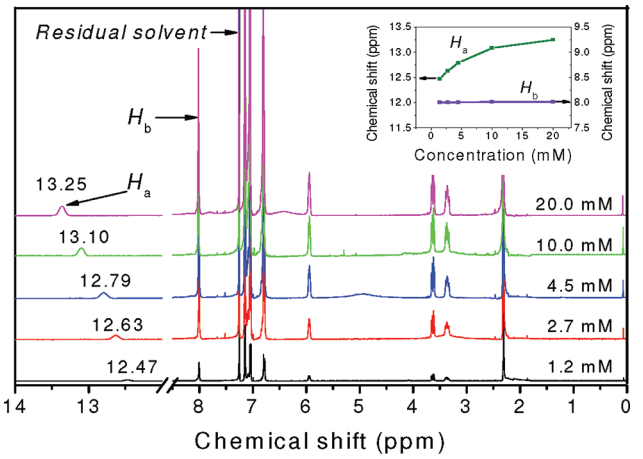

Figure 3. Concentration-dependent ^{1}H NMR spectra of **3a** in $CDCl_3$ at 25 °C. Inset: chemical shifts of −COOH protons (H_a) and protons on perylene ring (H_b) of **3a** versus concentration.

in a decrease in the electron densities of carboxylic protons and a chemical shift of NMR signal to lower magnetic field. However, no obvious shift or broadening was observed in the protons on the perylene ring (H_b) with an increase in concentration, also indicative of no *H*-aggregation of **3a** in $CDCl_3$ medium (Figure 3, inset).[31,32]

In general, the CD spectrum is the absorption difference in circularly polarized left and right light, and the signed order of bisignate CD Cotton effects (CEs) can be used to predict the relative orientation based on the exciton chirality theory.[33] As expected, the reference compound of **3d** is CD-silent because of its optically inactive normal butylamine residues (Figure 4a). Interestingly, PBIs **3a** and **3b** show two exact opposite CD signal response (Figure 4a). For instance, the positive CEs at 344, 393, 446, and 587 nm and negative CEs at 530 and 562 nm (with zero crossing at 467 and 577 nm) were observed in the CD curve for **3a** in CCl_4. Here the fairly strong bisignate CE (with zero crossing at 577 nm) as well as a strong nonbisignate CE at 530 nm and a smaller nonbisignate CE at 446 nm are corresponding to the absorption region of 480−600 nm (S_0-S_1 transition), and 380−480 nm (S_0-S_2 transition) from PBI, respectively.[34]

Moreover, in contrast with **3a** and **3b**, the corresponding ester **3c** shows a much weaker and nonbisignate CD curve at 577 nm (Figure 4a). Consequently, considering the difference in chemical structures between **3a** (containing chiral carboxylic group) and **3c** (containing chiral ester group), the enhancement in Cotton effect might have arisen from the possible assembly via the intermolecular hydrogen bonding between neighboring chiral carboxylic groups. Accordingly, MeOH is utilized as the breaking agent of the intermolecular hydrogen bonds. Surprisingly, the CD signals of **3a** and **3b** become rather decreased (Figure 4b), and the remaining weak nonbisignated band (also include **3c** in CCl_4) from 480 to 600 nm might be caused by a combinational expression of the α-carbon chirality and the axial chirality originating from the nonplanar structure of bay-substituted PBIs.[34−36]

In general, the positive bisignated CD signal (a first long-wavelength positive CE, followed by a short-wavelength negative CE) is expected that chiral excitonic couplings in PBI chromophores are assembled in close proximity with their transition dipoles and oriented in a right-handed, clockwise **P**-helical fashion.[1,36] In this view, the extraordinarily intense exciton couplet of **3a** has a positive component at 586 nm and a negative

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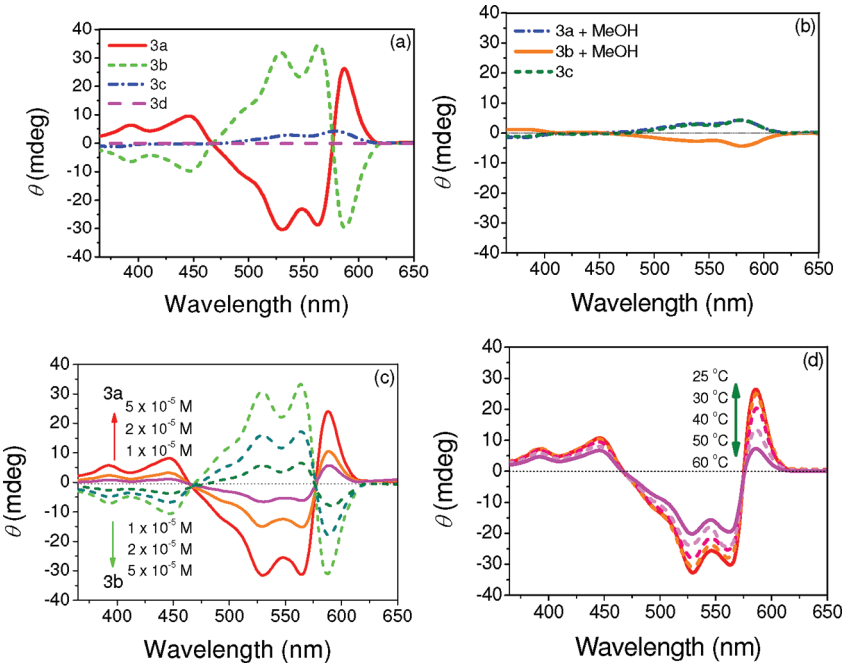

Figure 4. (a) CD spectra of **3a**−**3d** in CCl_4 (5×10^{-5} M) at 25 °C. (b) CD spectra of **3a** and **3b** in MeOH−CCl_4 (5/95, v/v) and **3c** in CCl_4 solution (5×10^{-5} M). (c) Changes in CD spectra of **3a** and **3b** in CCl_4 solution at various concentrations. (d) Changes in CD spectra of **3a** in CCl_4 solution (5×10^{-5} M) from 25 to 60 °C.

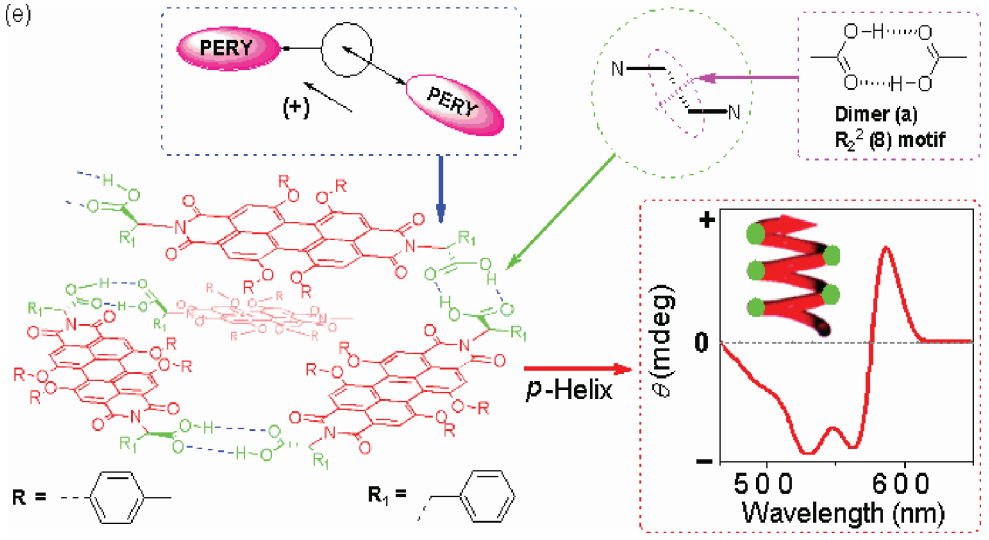

Figure 5. Proposed **P**-helical assembly of PBI **3a** via intermolecular hydrogen bonding.

component at 563 nm, attributable to the preferential formation of a ***P***-helix, and the mirror-image CD curve of **3b** (the enantiomer of **3a**) is indicative of generating an anticlockwise ***M***-helix. Accordingly, the exact opposite CD signals of **3a** and **3b** in CCl_4 show the tendency that the enantiomeric chiral amino residues can control the helical sense of the PBI assembling, resulting in a chiral bias toward homochiral assembly.

The stabilization behavior of the supramolecular helical assembly was furthered investigated with the concentration- and temperature-dependent CD spectra. As shown in Figure 4c, nearly four-fold increments in ellipticity values of both enantiomers (**3a** and **3b**) are observed with a concentration increase from 1×10^{-5} to 5×10^{-5} M, consistent with an increased degree of intermolecular hydrogen bonding to the enhancement in the hydrogen-bonding helical assemblies. Moreover, the CD intensity of **3a** becomes gradually decreased when increasing temperature from 25 to 60 °C (Figure 4d), indicating the breakdown of the hydrogen-bonding helices at high temperature. Interestingly, the thermodynamic CD behavior of **3a** is fully reversible because the hydrogen-bonding helical assembly process is dependent on temperature. That is, upon cooling the sample to room temperature, the initial CD signal can be recovered.

Accordingly, a proposed mode is shown in Figure 5 that refers to a recent calculations.[37] The exact helical assembly based on

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two exact PBI enantiomers **3a** and **3b** can be realized through the possible intermolecular hydrogen bonding between neighboring chiral carboxylic groups, most probably with a strong tendency of the carboxylic acid residue to form cyclic hydrogen bonded dimers of type $R_2^2(8)$[19] rather than the hydrogen-bonded catemers or imide···carboxlic acid hydrogen binding motif in rare cases.[38] Exactly, we envision that the helical stacking in the system of PBIs **3a** and **3b** can be modulated by intermolecular hydrogen bonding of the carboxylic acid units as well as van der Waals interaction of the four bulky bay substituents.

CONCLUSIONS

In summary, the supramolecular helices of PBIs containing chiral amino acid residues have been successfully realized in CCl_4 via hydrogen-bonding-driven self-assembly. In this way, the fluorescence from the PBI unit does not change so much, which is in contrast with the $\pi-\pi$ arrangement, resulting in serious quenching in fluorescence. By fluorescence, CD, and NMR-studies, the intermolecular hydrogen bonding can be well-developed with increasing concentration in apolar solvents but perturbed upon the addition of MeOH or increasing temperature. The use of chiral amino acid residues may provide a new strategy for the construction of chirality-confined superstructures to organic chromophores with potential application in chiral molecular recognition and guest encapsulation.

EXPERIMENTAL SECTION

General. L-Phenylalanine, L-phenylalanine methylester hydrochloride, and D-phenylalanine were purchased from Fluka. All solvents were purified using standard procedures. ^{1}H and ^{13}C NMR in $CDCl_3$ were recorded on a Bruker Avance-400 spectrometer with tetramethylsilane (TMS) as internal reference. HRMS were measured on a Waters LCT Premier XE spectrometer. Melting points were determined with a hot stage apparatus and are uncorrected. TLC analyses were performed on silica-gel plates, and flash chromatography was conducted using silica-gel column packages purchased from Qing-dao Haiyang Chemical (China).

Absorption, Emission, and Circular Dichroism Spectroscopy. UV/vis absorption spectra were obtained by using a Varian Cary 500 spectrophotometer (1 cm quartz cell) at 25 °C. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell) at 25 °C. The slit width was 5 nm for both excitation and emission. A set of absorption and fluorescence spectra for **3a**∼**3d** was recorded at different concentrations (from 5×10^{-6} to 1×10^{-4} M). CD spectra were recorded on a JASCO J-810 spectropolarimeter at 25 °C (1 cm quartz cell). The stock solution of PBIs (1×10^{-3} M) was prepared by directly dissolving PBIs in CCl_4 and then filtered with a 0.2 μm PTFE membrane filter disc to remove the insoluble particles. During the measurements of CD spectra, a few milliliters of the sample solutions were injected into a cell, followed by intense stirring for 10 s prior to the measurement and then rotated 90° around the light axis for the consecutive measurement to exclude the macroscopic anisotropic orientation. Each spectrum was collected with a scanning rate of 100 nm min^{-1}, a bandwidth of 2 nm, and a response time of 1 s. Six scans were averaged and blank-subtracted to give the spectrum. The ellipticity (θ) was expressed in millidegrees. A set of CD spectra for PBI **3a** at different temperatures (25 to 65 °C) in CCl_4 at wavelengths ranging from 300 to 650 nm was recorded.

General Procedure for PBIs 3a∼3d. A mixture of the amino acid (0.6 mmol), 1,6,7,12-tetra(4-methylphenoxy)perylene-3,4:9,10-tetracarboxylic acid dianhydride (0.12 mmol), and triethylamine (0.2 mL) in isopropanol (8 mL) were refluxed under nitrogen for 12 h. After being cooled to room temperature, the reaction mixture was diluted with 2 M HCl (80 mL). The resulting suspension was allowed to coagulate for 1 h and then filtered on a Büchner funnel. The residue was washed successively with water (3 × 50 mL) and dried in vacuo. The products as dark-red powders were purified by column chromatography on silica gel, as described below.

N,N′*-Di((*S*)-1-carboxy-1-benzyl)-1,6,7,12-tetra(4-methylphenoxy)perylene-3,4:9,10-tetracarboxylic Acid Bisimide (3a).** Purification: ethyl acetate/*n*-hexane (30:70); yield 125 mg (0.56 mmol, 94%). Dark-red powder. M_p > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 13.09 (s, 2H, −COOH), 8.02 (s, 4H, perylene-H), 7.08−7.15 (m, 10H, Ph-H), 7.05 (d, J = 8.4 Hz, 8H, Ph-H), 6.79 (d, J = 8.4 Hz, 8H, Ph-H), 5.94 (dd, J_1 = 9.2 Hz, J_2 = 5.6 Hz, 2H, −NCH***COOH), 3.63 (dd, J_1 = 14 Hz, J_2 = 5.6 Hz, 2H, PhCH*H*−), 3.36 (dd, J_1 = 14.4 Hz, J_2 = 9.2 Hz, 2H, PhC*H*H−), 2.31 (s, 12H, Ph-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 20.85, 34.78, 54.44, 119.26, 119.57, 120.24, 120.30, 121.74, 126.65, 128.43, 129.19, 130.61, 132.75, 134.47, 137.16, 152.65, 156.36, 162.84, 175.36. HRMS (TOF-ESI$^+$): calcd for $C_{70}H_{50}N_2O_{12}Na^+$ [M + Na^+], 1133.3261; found, 1133.3257.

N,N′*-Di((*R*)-1-carboxy-1-benzyl)-1,6,7,12-tetra(4-methylphenoxy)perylene-3,4:9,10-tetracarboxylic Acid Bisimide (3b).** Purification: ethyl acetate/*n*-hexane (30:70); yield 120 mg (0.55 mmol, 91%). Dark-red powder. M_p > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 13.35 (s, 2H, −COOH), 8.01 (s, 4H, perylene-H), 7.08−7.15 (m, 10H, Ph-H), 7.05 (d, J = 8.4 Hz, 8H, Ph-H), 6.79 (d, J = 8.4 Hz, 8H, Ph-H), 5.93 (dd, J_1 = 9.6 Hz, J_2 = 5.6 Hz, 2H, −NCH***COOH), 3.62 (dd, J_1 = 14 Hz, J_2 = 5.6 Hz, 2H, PhCH*H*−), 3.35 (dd, J_1 = 14.0 Hz, J_2 = 9.6 Hz, 2H, PhC*H*H−), 2.31 (s, 12H, Ph-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 20.85, 34.79, 54.46, 119.26, 119.57, 120.24, 120.30, 121.75, 126.65, 128.43, 129.19, 130.62, 132.76, 134.47, 137.17, 152.66, 156.36, 162.85, 175.36. HRMS (TOF-ESI$^+$): calcd for $C_{72}H_{54}N_2O_{12}Na^+$ [M + Na^+], 1133.3261; found, 1133.3260.

N,N′*-Di((*S*)-1-carbomethoxy-1-benzyl)-1,6,7,12-tetra(4-methylphenoxy)perylene-3,4:9,10-tetracarboxylic Acid Bisimide (3c).** Purification: dichloromethane/*n*-hexane (60:40), yield 150 mg (0.13 mmol, 33%). Dark-red needle. M_p > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.08 (s, 4H, perylene-H), 7.14−7.21 (m, 10H, Ph-H), 7.11 (d, J = 8.4 Hz, 8H, Ph-H), 6.85 (d, J = 8.4 Hz, 8H, Ph-H), 5.92−5.96 (m, 2H, −NCH***CO-OCH_3), 3.71 (s, 6H, $COOCH_3$), 3.68−3.69 (m, 2H, Ph-CH_2), 3.56−3.42 (m, 2H, Ph-CH_2), 2.36 (s, 12H, Ph-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 20.85, 35.06, 52.60, 54.61, 119.31, 119.57, 120.22, 120.36, 121.90, 126.62, 128.43, 129.22, 130.63, 132.80, 134.55, 137.39, 152.69, 156.38, 162.92, 170.01. HRMS (TOF-ESI$^+$): calcd for $C_{70}H_{50}N_2O_{12}Na^+$ [M + Na^+], 1161.3574; found, 1161.3579.

N,N′*-Dibutyl-1,6,7,12-tetra(4-methylphenoxy)perylene-3,4:9,10-tetracarboxylic Acid Bisimide (3d).**[17] Dark-red powder. M_p > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.12 (s, 4H, perylene-H), 7.08 (d, J = 8.4 Hz, 8H, Ph-H), 6.84 (d, J = 8.4 Hz, 8H, Ph-H), 4.10 (t, J = 7.2 Hz, 4H, −NCH***$_2$), 2.33 (s, 12H, Ph-CH_3), 1.60−1.68 (m, 4H, −NCH_2C***H***$_2$), 1.33−1.43 (m, 4H, −C***H***$_2CH_3$), 0.91−0.94 (t, J = 7.2 Hz, 6H, −CH_2C***H***$_3$).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.77, 20.31, 20.78, 30.14, 40.34, 119.23, 119.46, 120.11, 122.46, 130.51, 132.76, 134.28, 152.93, 156.28, 163.41.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR, ^{13}C NMR, and HRMS (TOF-ESI$^+$) spectra of compounds **3a, 3b, 3c**, and **3d** and normalized concentration-dependent absorption spectra of **3a** and **3b** in CCl_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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