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BINOL-Based Chiral Receptors as Fluorescent and Colorimetric Chemosensors for Amino Acids†

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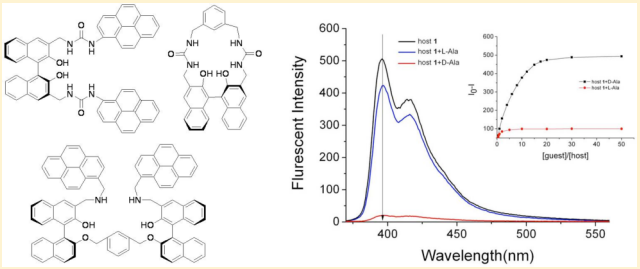
Supporting Information

ABSTRACT: Three representative BINOL derivatives were examined for their chiral recognitions with D- and L-*t*-Boc-amino acid anions: an open system 1, which bears two urea groups and two pyrene groups; a closed ring system 2, which bears two urea groups with a closed ring system; and a dimeric system 3, which bears two benzylic amine groups and two pyrene groups. Dimeric system 3 displayed a $\Delta I_D/\Delta I_L$ of 12.95 for *t*-Boc-alanine.



Since the enantiomeric recognition of chiral compounds was pioneered by Cram et al. in the early 1970s,[1] investigations on highly sensitive and selective enantioselective recognition of chiral organic molecules have received increasing attention. Various techniques have been applied to detect these species, such as NMR, UV/vis, and fluorescence spectroscopy. Fluorescent and colorimetric sensors allow for the real time and space detection of analytes.[2] Accordingly, fluorescence and colorimetric changes have been actively adopted for chiral recognition.[3] Chiral fluorescence and colorimetric sensors can be used for rapid determination of the enantiometric composition of chiral compounds with high sensitivity and high-throughput screening (HTS) determination.[4]

Since Irie et al. reported the fluorescence quenching of 1,1′-binaphthyl by the enantiomers of *N*,*N*-dimethyl-α-phenethyl-amine in 1978,[5] the binaphyl unit has become especially popular for its stable chiral configuration and tunable dihedral angle between the two naphthalene rings.[6] Pu et al. reported pioneering works in this area.[7] For example, a recently reported BINOL derivative showed a high chiral selectivity with I_R/I_S of 11.2 for (*R*)- or (*S*)-phenyllactic acid in benzene (DME, 0.4% v/v).[7d] Another BIONOL derivative was reported by the same group to show enantioselective fluorescent responses for *N*-carbobenzyloxy-serine (*N*-Cbz-serine) with $\Delta I_D/\Delta I_L$ as 12.5.[7e] However, in these cases, benzene was used as a solvent or major solvent.

In this study, we synthesized three representative BINOL derivatives as chiral and fluorescent hosts for the recognition of amino acids: an open system **1**, which bears two urea groups and two pyrene groups; a closed ring system **2**, which bears two urea groups with a closed ring system; and a dimeric system **3**, which bears two benzylic amine groups and two pyrene groups. Multiple hydrogen-bonding interactions between these hosts and carboxylate group of amino acid induced interesting fluorescence and UV absorption changes. For example, chiral host **1** displayed enanthioselective fluorescence responses ($\Delta I_D/\Delta I_L$) of 6.1 for *t*-Boc-alanine. Closed system **2** and a dimeric system **3** showed a $\Delta A_D/\Delta A_L$ value of 4.43 and $\Delta I_D/\Delta I_L$ of 12.95 for *t*-Boc-alanine, respectively.

For the synthesis, 3,3-bis(aminomethyl)-2,2′-dimethoxy-1,1′-binaphthalene (**4**) was first prepared according to a reported procedure.[8] Intermediate **4** was then reacted with 1-pyrene isocyanate and *m*-xylelene diisocyanate to afford **1-a** and **2-a** in 78% and 92% yields, respectively. After demethylation of **1-a** and **2-a** using BBr_3, the desired fluorescent receptors **1** and **2** were prepared in over 82% yield (Scheme 1). For fluorescent receptor **3**, **3-a** was synthesized according to reported procedures,[6] and after sodium borohydride reduction, **3** was obtained in 90% yield (Scheme 1). The ^{1}H NMR and ^{13}C NMR spectra of **1**-**3** are explained in the Supporting Information (Figures S1−S10).

Compounds **1**−**3** were examined for chiral recognition with tetrabutylammonium salts of D- and L-*t*-Boc-amino acid anions, such as alanine (Ala), phenylalanine (Phe), leucine (Leu), and serine (Ser). The fluorescence spectra were recorded from a solution of receptors **1**−**3** (10 μM) in DMSO in the absence or presence of amino acid anions.

Figure 1 explains the fluorescence titrations of receptor **1** with different concentrations of D- and L-*t*-Boc-alanine in DMSO. Gradually increasing the concentration of the D-

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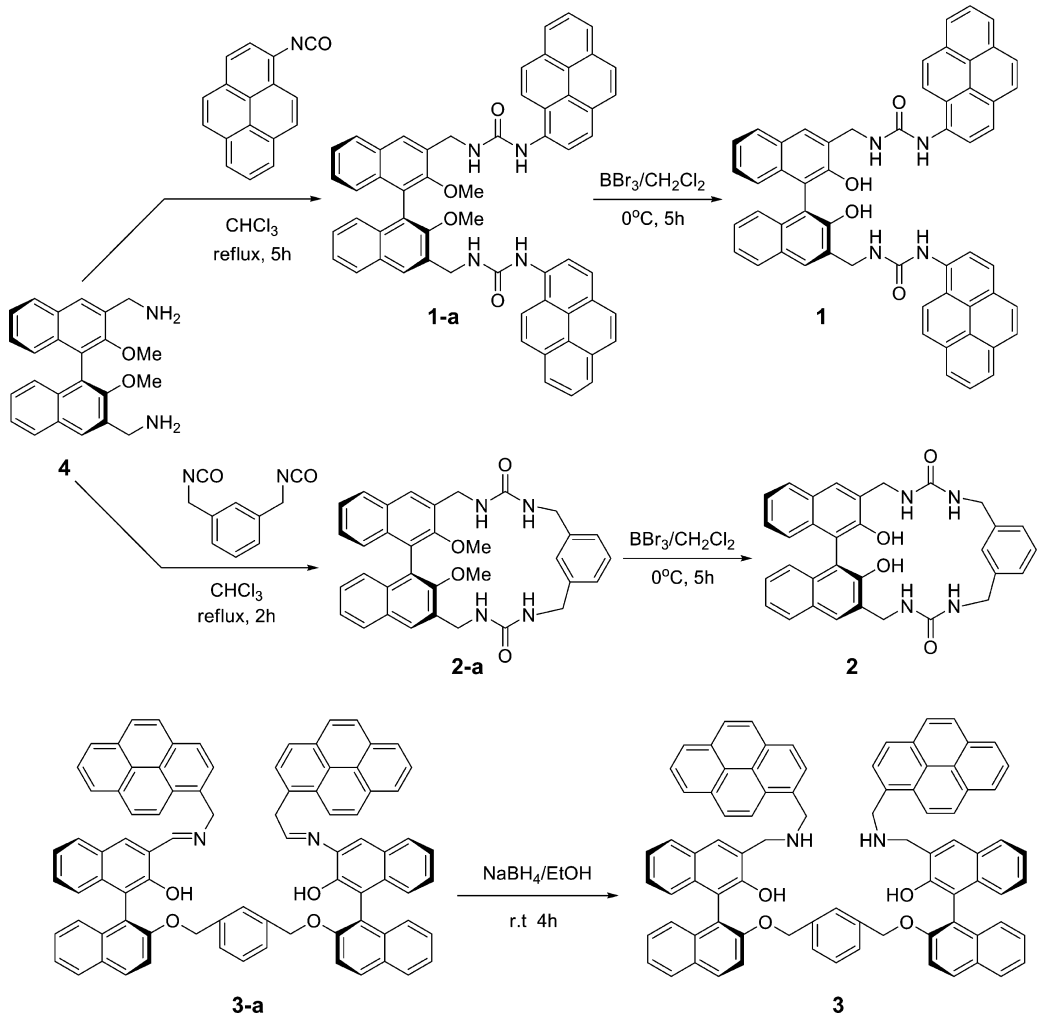
Scheme 1. Synthesis of Chiral Receptors 1−3



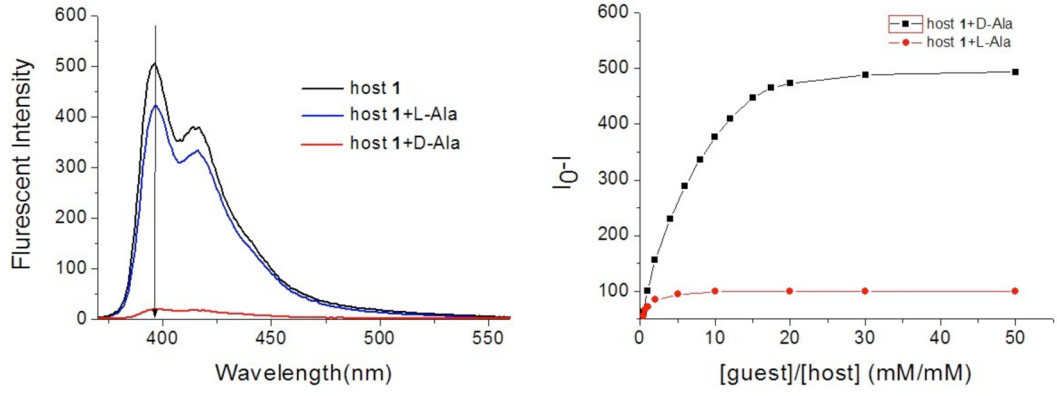


Figure 1. (a) Fluorescence spectra of host **1** (1.0×10^{-5} M) with D-*t*-Boc-Ala and L-*t*-Boc-Ala (5.0×10^{-4} M). (b) Fluorescence emission change of host **1** (1.0×10^{-5} M) with various concentrations of D-*t*-Boc-Ala and L-*t*-Boc-Ala at 390 nm. (Solvent: DMSO, λ_{ex} = 344 nm.)

enantiomer caused the fluorescence emission intensities of **1** (10 μM) at 390 nm (λ_{ex} = 344 nm) to decrease remarkably (Figure 1a). The quenching efficiency was over 90% with D-*t*-Boc-alanine. In contrast, the quenching efficiency with L-*t*-Boc-alanine was less than 20%, which can also be expressed as a $\Delta I_D/\Delta I_L$ of 6.1 [$\Delta I_D = I_D - I_0$ and $\Delta I_L = I_L - I_0$]. The $\Delta I_D/\Delta I_L$ values of fluorescence sensor **1**−**3** with different kinds of tetrabutyl ammonium salts of D- and L-*t*-Boc-amino acid anions were summarized in Table 1. The fluorescence quenching can be attributed to the photoinduced electron-transfer (PET) process[3g,9] from urea nitrogen to pyrene moiety due to the strong hydrogen-bonding interaction. Such a large difference in fluorescence quenching implies that receptor **1** can be used as a sensitive enantioselective fluorescent sensor for alanine anions.

Chiral host **2** displayed distinct UV absorption changes, as shown in Figure 2. Figure 2 explains the UV absorption titrations of chemosensor **2** (20 μM) with D-*t*-Boc-alanine (Figure 2a) and L-*t*-Boc-alanine (Figure 2b) in DMSO. There

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Table 1. Enantioselective Fluorescence or UV Absorption Responses of Hosts 1−3 with *t*-Boc-Protected Ala, Phe, Leu, and Ser

	host **1**	host **2**		host **3**
guest	$\Delta I_D/\Delta I_L$	$\Delta A_D/\Delta A_L$	$\Delta I_D/\Delta I_L$	$\Delta I_D/\Delta I_L$
t-Boc-D-Ala	6.10	4.43	1.96	12.95
t-Boc-L-Ala				
t-Boc-D-Phe	1.39	1.69	1.04	2.19
t-Boc-L-Phe				
t-Boc-D-Leu	1.06	1.70	1.06	1.73
t-Boc-L-Leu				
t-Boc-D-Ser	1.02	1.42	1.10	1.05
t-Boc-L-Ser				

were three notable changes in the UV absorption: an enhancement at 258 nm, a decrease at 342 nm, and another enhancement at 370 nm. D-*t*-Boc-alanine induced large UV absorption changes at these wavelengths, whereas there were relatively smaller changes upon the addition of L-*t*-Boc-alanine. Based on absorption changes at 370 nm, $\Delta A_D/\Delta A_L$ [$\Delta A_D = A_D - A_0$ and $\Delta A_L = A_L - A_0$] was calculated as 4.43. Similar absorbance variations of compounds **2** with tetrabutyl ammonium salts of D- and L-*t*-Boc-amino acid anions are shown in the Supporting Information (Figures S11−S14).

Compound **1** showed only monomeric emission, even though it contains two pyrene groups, whereas dimeric system **3** showed both monomeric emission at 400 nm and excimer emission at 475 nm. For dimeric system **3**, D-*t*-Boc-alanine induced fluorescence quenching effects for both monomer and excimer emission, whereas almost no significant change was observed with L-*t*-Boc-alanine for both monomer emission and excimer emission (Figure 3). $\Delta I_D/\Delta I_L$ as large as 12.95 was observed for *t*-Boc-alanine. A similar fluorescent quench of sensor **1**−**3** with tetrabutylammonium salts of D- and L-*t*-Boc-amino acid anions is shown in the Supporting Information (Figures S15−S26).

According to the linear Benesi−Hildebrand expression, the measured emission $[1/(F - F_0)]$ at 344 nm varied as a function of amino acids in a linear relationship ($R \cong 0.9995$), indicating ~1:1 stoichiometry between the amino acids and hosts. The 1:1 stoichiometry was further confirmed by the Job plot (Figure S27, Supporting Information). The association constants of **1**−**3** with *t*-Boc amino acids are described in Table S1 (Supporting Information). In general, host **1** displayed a larger K_a value with D-amino acid derivatives than with L-isomers. For example, the association constants of **1** with D- and L-*t*-Boc-alanine were calculated as 16600 and 5530 M^{-1}, respectively, and K_D/K_L was found to be 3.00 (Table S1, Supporting Information). The details of fluorescent titration spectra of **1**−**3** upon addition of tetrabutylammonium salts of D- and L-*t*-Boc-amino acid anions are shown in the Supporting Information (Figures S28−S39). The details of UV titration spectra of **2** upon addition of tetrabutylammonium salts of D- and L-*t*-Boc-amino acid anions are shown in the Supporting Information (Figures S40−S43).

The ^{1}H NMR spectra of receptor **1** (0.5 mM) and its complex with D- and L-*t*-Boc-alanine (tetrabutylammonium salt) in DMSO-d_6 were obtained. Even though the exact binding mode cannot be easily predicted, we could confirm that D-*t*-Boc-alanine generally induces larger chemical shifts than L-isomer. As shown in Figure 4, two N-H proton signals of receptor **1** appear at7.355 ppm and 9.312 ppm (Ha and Ha′). However, when treated with *t*-Boc-alanine, the N-H protons displayed downfield shifts. Upon addition of chiral guest (1.5 equiv), D-alanine induced a larger downfield shift (δ 7.355 to 7.534 ppm) of N−H peak (Ha) in host **1** than L-alanine (δ 7.355 to 7.524 ppm). The other N−H peak (Ha′) also displayed large downfield shifts ($\Delta\delta$ = 0.154 for D-alanine, $\Delta\delta$ = 0.139 for L-alanine) when 1.5 equiv of D- and L-alanine was added to host **1**. When 0.5 equiv of L-alanine was added, the O-H proton signal of host **1** was observed as a singlet at 9.072 ppm (Figure 4, L-ala 0.5 equiv) but when treated with the same amount of D-alanine, the O-H proton signal almost disappeared with severe broadness (Figure 4, D-Ala 0.5 equiv).

In conclusion, we have synthesized three representative BINOL receptors for anion recognition. An open system **1** bears two urea groups and two pyrene groups in addition to the two BINOL phenols. A closed ring system **2** bears a relatively more rigid and cyclic binding pocket, which is composed of two urea groups and two BINOL phenol groups. Dimeric system **3** contains two benzylic amine groups and two pyrene groups. Compounds **1**−**3** were examined for chiral recognitions with tetrabutyl ammonium salts of D- and L-*t*-Boc-amino acid anions, such as alanine (Ala), phenylalanine (Phe) leucine (Leu), and serine (Ser). Chiral host **1** displayed enanthioselective fluorescence responses ($\Delta I_D/\Delta I_L$) of 6.1 for D-*t*-Boc-alanine and L-*t*-Boc-alanine. Closed system **2** showed unique absorption changes with these amino acids. Dimeric system **3** displayed a $\Delta I_D/\Delta I_L$ of 12.95 for *t*-Boc-alanine.

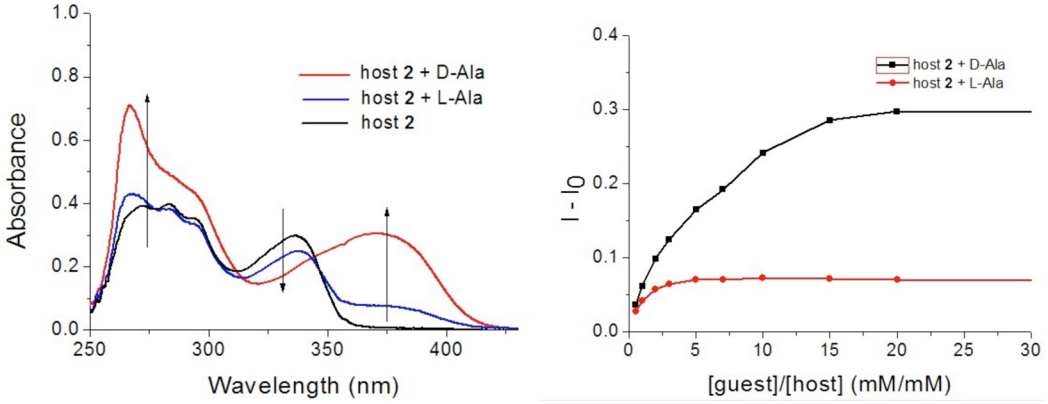

Figure 2. Absorbance spectra of host **2** (1.0×10^{-5} M) with D-*t*-Boc-Ala and L-*t*-Boc-Ala (3.0×10^{-4} M) in DMSO. (b) Absorbance change of host **2** (1.0×10^{-5} M) with various concentrations of D-*t*-Boc-Ala and L-*t*-Boc-Ala at 370 nm.

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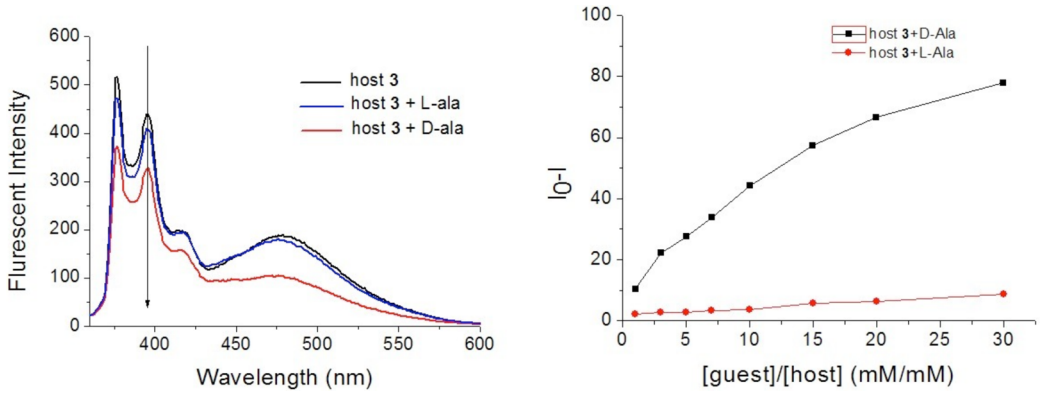

Figure 3. Fluorescence spectra of host **3** (1.0×10^{-5} M) with D-*t*-Boc-Ala and L-*t*-Boc-Ala (3.0×10^{-4} M). (b) Fluorescence emission change of host **3** (1.0×10^{-5} M) with various concentrations of D-*t*-Boc-Ala and L-*t*-Boc-Ala at 478 nm. (Solvent: DMSO, λ_{ex} = 344 nm.)

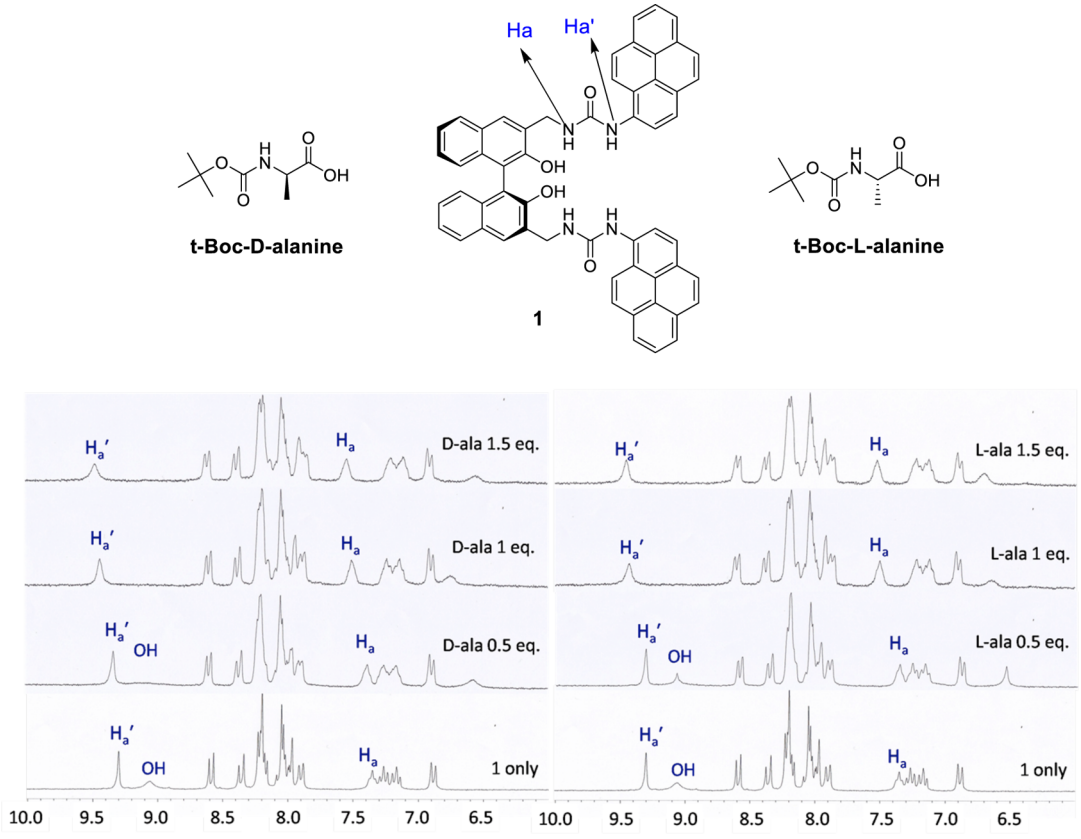

Figure 4. Partial ^{1}H NMR (250 MHz) spectra of **1** upon the addition of D- and L-*t*-Boc-Ala (tetrabutylammonium salt) in DMSO-d_6.

EXPERIMENTAL SECTION

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel (230−400 mesh).^{1}H NMR and ^{13}C NMR spectra were recorded using 250 MHz NMR. Chemical shifts were expressed in ppm and coupling constants (*J*) in Hz. HRMS data was obtained either by mass spectra (FAB) with a magnetic sector−electric sector double-focusing mass analyzer or ESI (electrospray ionization) with ion-trap analyzer.

Compound 1-a. 3,3-Bis(aminomethyl)-2,2′-dimethoxy-1,1′-binaphthalene **4** (450 mg, 1.2 mmol) and 1-pyrene isocyanate (639 mg, 2.64 mmol) were taken in chloroform (30 mL) and refluxed for 5 h. The precipitate formed was filtered, washed with chloroform several times, and dried to afford the product **1-a**: yield 800 mg (78%); mp 220−225 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 3.42 (s, 6H), 4.72 (d, *J* = 5.04 Hz, 4H), 7.02 (d, *J* = 8.43 Hz, 2H), 7.29 (d, *J* = 9.37 Hz, 4H), 7.27 (t, *J* = 7.59 Hz, 2H), 7.70 (t, *J* = 5.30 Hz, 2H), 7.71−8.01 (m, 8H), 8.16−8.22 (m, 10H), 8.33 (s, 2H), 8.56 (d, *J* = 4.17 Hz, 2H), 8.72 (d, *J* = 8.5 Hz, 2H), 9.55 (s, 2H); ^{13}C NMR 60.3, 79.1, 119.5, 120.5, 121.2, 124.2, 124.6, 124.8, 125.1, 125.4, 126.0, 126.3, 126.6, 127.4, 127.9, 130.2, 130.7, 131.1, 133.0, 133.3, 133.9, 154.5, 155.8; HRMS (FAB) obsd *m*/*z* = 859.3283 $(M + H)^+$, calcd for $C_{58}H_{43}O_4N_4$ = 859.3284.

Compound 1. The dipyrene compound (250 mg, 0.29 mmol) was taken in methylene chloride under ice-cooled conditions, and BBr_3 (0.07 mL, 0.73 mmol) was added slowly over a period of 15 min. The reaction was allowed to stir for further 2 h at room temperature. The solvent was evaporated, and the product formed was washed with CH_2Cl_2 several times to yield the desired product **1**: yield 200 mg (83%); mp 220−230 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 4.64 (d, *J* = 4.68 Hz, 4H), 6.89 (d, *J* = 8.25 Hz, 2H), 7.24 (t, *J* = 6.87 Hz, 2H), 7.34 (t, *J* = 6.04 Hz, 2H), 7.46 (t, *J* = 6.97 Hz, 2H), 7.90 (d, *J* = 7.83 Hz, 2H), 7.91−8.05 (m, 8H), 8.16−8.23 (m, 8H), 8.36 (d, *J* = 9.38 Hz,

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2H), 8.59 (d, J = 8.47 Hz, 2H), 9.12 (s, 2H), 9.30 (s, 2H); ^{13}C NMR (DMSO-d_6, ppm) δ 115.3, 119.9, 120.9, 124.2, 124.3, 124.5,124.8, 125.3, 126.3, 126.7, 127.3, 127.7, 128.2, 129.3, 130.6, 131.1, 133.5, 133.6, 151.9, 156.5; HRMS (FAB) obsd m/z = 831.2972 $(M + H)^+$, calcd for $C_{56}H_{39}O_4N_4$ = 831.2971.

Compound 2-a. 3,3′-Bis(aminomethyl)-2,2′-dimethoxy-1,1′-binaphthalene (**4**) (500 mg, 1.34 mmol) and *m*-xylene diisocyanate (0.25 mL, 1.61 mmol) were taken in $CHCl_3$ (25 mL) and refluxed for 2 h. The precipitate formed was filtered, washed with $CHCl_3$ several times, and dried to afford the product **2-a**: yield 680 mg (92%); mp 245−255 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 3.20 (s, 6H), 4.05 (d, J = 3.44 Hz, 4H), 4.37 (d, J = 4.68 Hz, 4H), 6.44−6.69 (m, 4H), 6.91 (d, J = 8.15 Hz, 4H), 7.17−7.37 (m, 10H), 7.96 (s, 4H); ^{13}C NMR (DMSO-d_6, ppm) δ 43.03, 60.1, 79.1, 123.9, 124.9, 125.3, 125.8, 125.9, 127.1, 127.7, 128.2, 129.9, 132.7, 133.9, 140.9, 154.1, 158.1; HRMS (ESI) obsd m/z = 561.2502 $(M + H)^+$, calcd for $C_{34}H_{33}N_4O_4$ = 561.2501.

Compound 2. The cyclic compound (250 mg, 0.44 mmol) was taken in CH_2Cl_2 under ice-cooled conditions, and BBr_3 (0.11 mL, 1.10 mmol) was added slowly over a period of 15 min. The reaction was allowed to stir for a further 5 h at room temperature. The solvent was evaporated, and the product form was washed with CH_2Cl_2 several times to yield the desired product **2**: yield 200 mg (82.2%); mp >250 °C dec; ^{1}H NMR (DMSO-d_6, ppm) δ 3.97 (d, J = 5.30 Hz, 4H), 3.99 (s, 4H), 6.81 (d, J = 8.22 Hz, 6H), 7.09−7.35 (m, 10H), 7.77 (s, 4H), 8.05 (d, J = 13.18 Hz, 1H), 9.54 (s, 1H); ^{13}C NMR (DMSO-d_6, ppm) δ 115.7, 117.6, 117.7, 121.1, 122.7, 124.1, 125.6, 127.6, 128.1, 128.6, 129.5, 133.4, 140.2, 140.3, 151.8, 156.0, 156.1; HRMS (FAB) obsd m/z= 533.2189 $(M + H)^+$, calcd for $C_{32}H_{29}N_4O_4$ = 533.2188.

Compound 3. The BINOL Schiff base **3-a**[6] (0.5 g, 0.432 mmol) was taken in a cosolvent of THF and ethanol, $NaBH_4$ (0.048 g, 1.27 mmol) was added, and the mixture was stirred at room temperature for 4 h. The resulting mixture was quenched and extracted with CH_2Cl_2 to obtain the desired product **3**: yield 450 mg (90%); mp 125−135 °C; ^{1}H NMR (DMSO-d_6, ppm) δ 3.79 (dd, J = 26.78, 4H), 4.61 (s, 4H), 6.32 (s, 1H), 6.45 (s, 3H), 6.98−7.38 (m, 20H), 7.54−7.78 (m, 22H), 7.89 (d, J = 5.71, 2H); ^{13}C NMR (DMSO-d_6, ppm) δ 14.4, 21.5, 22.9, 29.9, 30.2, 30.5, 32.1, 33.7, 34.4, 49.9, 52.7, 71.1, 76.8, 77.3, 77.8, 116.4, 117.0, 124.7, 124.8, 125.2, 125.3, 127.4, 128.3, 128.8, 130.7, 130.8, 131.2, 131.5, 134.3, 137.4, 151.7, 154.2, 154.4,161.8; HRMS (FAB) obsd m/z = 1161.4626 $(M + H)^+$, calcd for $C_{84}H_{61}O_4N_2$ = 1161.4631.

■ ASSOCIATED CONTENT

Supporting Information

Fluorescent spectra, UV spectra, and ^{1}H and ^{13}C NMR spectra of compounds are described. The material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

†This paper is dedicated to Professor Teruaki Mukaiyama in celebration of the 40th anniversary of the Mukaiyama aldol reaction.

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