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Enantioselective recognition by optically active chiral fluorescence sensors bearing amino acid units

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Abstract—Chiral fluorescence receptors **1** and **2** were synthesized and their structures characterized by IR, ^{1}H NMR, ^{13}C NMR, MS spectra, and elemental analysis. The chiral recognition abilities of **1** and **2** were studied by ^{1}H NMR and fluorescence spectra. The results demonstrate that receptors **1** and **2** with bis(tetrabutylammonium) dibenzoyl tartrate formed a 1:1 complex. Receptor **2** exhibits an excellent enantioselective recognition ability toward the enantiomers of bis(tetrabutylammonium) dibenzoyl tartrate.

1. Introduction

The development of molecule-based enantioselective fluorescence receptors is receiving growing research attention because such receptors can potentially provide a real time technique to determine the enantiomeric composition of chiral molecules.[1] For the molecular designs of chemosensors, that is, how to achieve the specific recognition of a certain molecule and how to transduce the recognition event into a signal are crucial points. Fluorescent molecular sensors for the detection of ions or molecules have attracted considerable interest because of their high sensitivity and potential applications in analytical, biological, and clinical biochemical environments.[2] Only a few samples containing indole groups for recognition have been reported.[3] Amide groups are good H-bonding donors, which are used widely to design and synthesize artificial receptors for anions.[4] We have previously utilized an amide as a binding site for the chiral anions, such as mandelate and amino acid derivatives.[4f,5] Tartaric acid is a common natural product present in wines and other grape-derived beverages. The structure of tartaric acid makes it quite attractive for complexation by a synthetic sensor since it is relatively small, while still possessing several functional groups for binding interaction. As a result many hydrogen-bonding receptors for the binding of neutral tartaric acid and its derivatives have been reported.[6] Herein, we report the design and synthesis of two new chiral fluorescence receptors **1** and **2**, which have two stereogenic centers in close proximity to the binding site of the receptors. Amongst the many amino acids, we chose tryptophan because it can provide indole, which is a good fluorophore group, and has a chiral binding site. The fluorescence receptors **1** and **2** bearing a tryptophan were synthesized (Scheme 1) and their enantioselective recognitions for D- and L-bis(tetrabutylammonium) dibenzoyl tartrate were studied by ^{1}H NMR and fluorescence spectra. The results reveal that receptor **2** has an excellent enantioselective recognition for the enantiomers of dibenzoyl tartrate.

2. Results and discussion

2.1. Synthesis

The chiral fluorescence receptors **1** and **2** were efficiently synthesized by the reaction of 2,7-bis(aminoethylenecarbamoylmethoxy)naphthalene **4a** or 2,7-bis(aminopropylenecarbamoylmethoxy)naphthalene **4b** with *N*-Boc-L-tryptophan **3**. Receptors **1** and **2** are easily soluble in common organic solvents such as $CHCl_3$, CH_3OH, DMSO, and DMF. The structures of these compounds were characterized by IR, MS, ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis.

2.2. Fluorescence spectra

The properties of the chiral recognition of receptors **1** and **2** were investigated for D- or L- bis(tetrabutylammonium) dibenzoyl tartrate. The fluorescence spectra were

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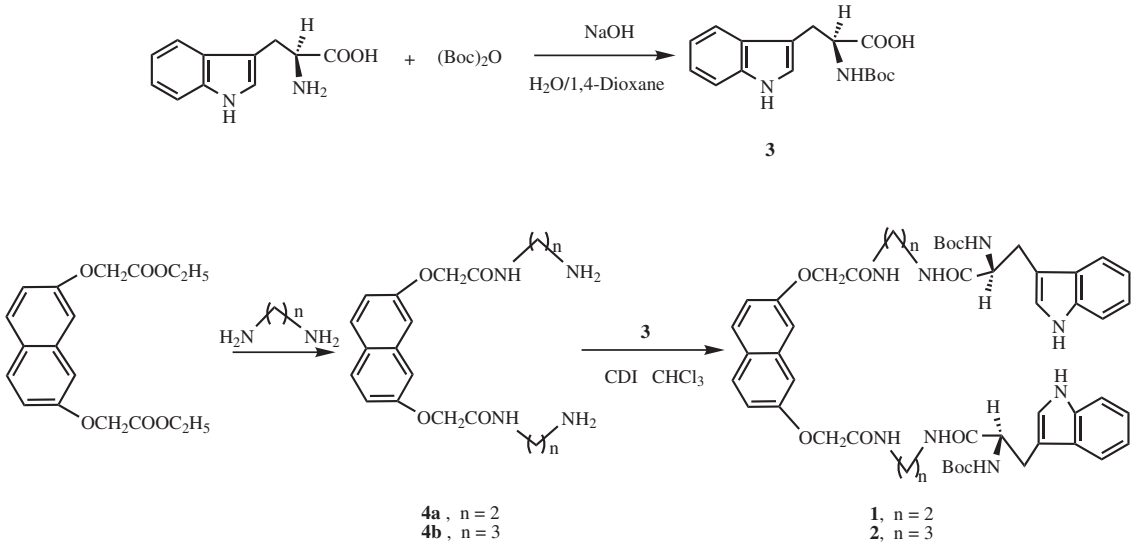

Scheme 1. The synthesis of receptors **1** and **2**.

recorded from a solution of receptors **1** or **2** in DMSO in the absence and presence of D- or L-dibenzoyl tartrate anion. Figures 1 and 2 showed the fluorescence spectra of a mixture of receptor **2** (2.60×10^{-5} mol L^{-1}) with different concentrations of D- or L-dibenzoyl tartrate in DMSO. With a gradual increase in the concentration of D- or L-dibenzoyl tartrate, the fluorescence emission intensities of **2** at 411 and 436 nm ($\lambda_{ex} = 359$ nm) gradually increased, which indicates complexation between receptor **2** and D- or L-dibenzoyl tartrate.

The phenomenon of fluorescence intensity increasing upon the addition of a guest anion is similar to the anion-induced fluorescence enhancement reported previously.[7] In the absence of an anion, the photoinduced electron-transfer (PET) process between the indole group and weak electron-withdrawing amide substituents might result in decreased fluorescence intensity. Upon the addition of anions, the interaction of an anion with a receptor unit could diminish the PET progress to induce the fluorescence retrieval. Therefore anion-induced fluorescence enhancement was observed.[4f,8] The satisfactory result (the correlation coefficient is over 0.99) of a non-linear curve fitting (fluorescence intensity at 436 nm vs equivalent of dibenzoyl tartrate) confirmed that **2** and D-dibenzoyl tartrate formed a 1:1 complex (see the top right corner plot of Fig. 1).[9] For the complex of a 1:1 stoichiometry, an association constant K_{ass} can be calculated by using the following equation:[9,10]

$$X = X_0 + (X_{lim} - X_0)/2C_0\{C_H + C_G + 1/K_{ass} - [(C_H + C_G + 1/K_{ass})^2 - 4C_H C_G]^{1/2}\}$$

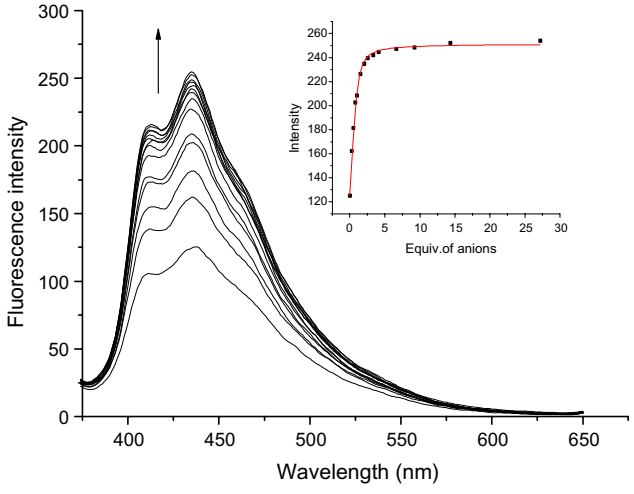

Figure 1. Fluorescence spectra of receptor **2** (2.60×10^{-5} mol L^{-1}) with D-dibenzoyl tartrate anion in DMSO. The equivalents of anion are 0, 0.26, 0.51, 0.77, 1.03, 1.54, 2.05, 2.56, 3.33, 4.10, 6.67, 9.23, 14.36, and 27.18. $\lambda_{ex} = 359$ nm. Inset: changes of fluorescence intensity of **2** at 436 nm upon addition of D-dibenzoyl tartrate anion. The line is a fitting curve. The correlation coefficient (R) of the non-linear curve fitting is 0.9982.

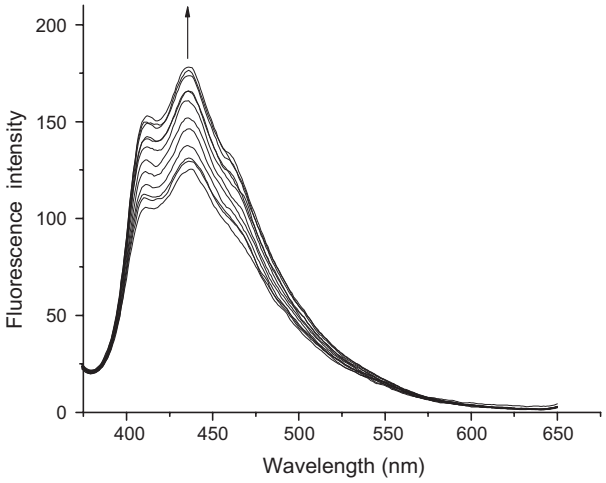

Figure 2. Fluorescence spectra of sensor **2** (2.60×10^{-5} mol L^{-1}) with L-dibenzoyl tartrate anion in DMSO. The equivalents of anion are 0, 0.51, 1.03, 1.54, 2.56, 3.59, 4.62, 6.15, 8.78, 11.28, 16.42, and 26.67. $\lambda_{ex} = 359$ nm.

Table 1. Association constants (K_{ass}) and correlation coefficients (R) of **1** and **2** with D- or L-dibenzoyl tartrate anions in DMSO

Anion[a]	Compound **1**		Compound **2**	
	K_{ass} (M^{-1})	R	K_{ass} (M^{-1})	R
D-Dibenzoyl tartrate	$(7.93 \pm 0.04^{c}) \times 10^4$	0.9953	$(2.61 \pm 0.05^{c}) \times 10^5$	0.9982
L-Dibenzoyl tartrate	$(1.28 \pm 0.02^{c}) \times 10^4$	0.9918	[b]	

[a] Anions were used as their bis(tetrabutylammonium) salts.
[b] The association constants are too small to calculate.
[c] All error values were obtained by the results of non-linear curve fitting.

where X represents the fluorescence intensity, and C_H and C_G are the corresponding concentrations of host and anion guest. The association constants (K_{ass}) and correlation coefficients (R) obtained by a non-linear least-square analysis of X versus C_H and C_G are listed in Table 1.

Similar phenomena were observed when D- or L-dibenzoyl tartrate was added into a solution (2.60×10^{-5} mol L^{-1}) of the receptor **1**. The emission spectra of **1** appeared at 438 nm when it was excited at 361 nm. Enantioselective fluorescence responses were observed, which gave $K_{ass(D)}/K_{ass(L)} \approx 6.2$ for dibenzoyl tartrate anions. The association constants (K_{ass}) and correlation coefficients (R) obtained by a non-linear least-squares analysis of X versus C_H and C_G are also listed in Table 1.

The data in Table 1 illustrate that the two receptors have the enantioselective recognition to D- or L-dibenzoyl tartrate anions. The association constants of **1** and **2** with D-dibenzoyl tartrate anion are much higher than that of **1** and **2** with L-dibenzoyl tartrate anion, which is probably due to D-dibenzoyl tartrate anion having a more complementary structure with receptors **1** and **2**. The results in Table 1 reveal that receptor **2** has a highly enantioselective recognition ability to the enantiomers of dibenzoyl tartrate. The selectivity of receptor **1** was less in the recognition process maybe because the two linking arms of receptor **1** cannot approach each other due the hindrance of the bulky groups (naphthylene, Boc, and indole) and the shorter chain. Receptor **2** has a highly enantioselective recognition ability due to receptor **2** having a good preorganized structure, which can be easily formed through hydrogen bonds between the two longer linking arms.

2.3. ^{1}H NMR study

^{1}H NMR experiments were undertaken to assess the chiral recognition properties between receptors and D- or L-dibenzoyl tartrates because it can provide structural and dynamic information.[11] Studies on the chiral recognition were carried out on a 300 MHz NMR spectrometer using compounds **1** and **2** as chiral solvating agents.

Bis(tetrabutylammonium) dibenzoyl tartrate was chosen as the probe. Figure 3A shows the ^{1}H NMR spectrum of racemic dibenzoyl tartrate in $CDCl_3$, with only one singlet (δ 5.82 ppm) for the CH proton resonance of racemic dibenzoyl tartrate was observed in the absence of host. The ^{1}H NMR spectra of the receptor **2** (2.0×10^{-3} M) and its complex with equimolar amounts (2.0×10^{-3} M) of D-, L-, or racemic dibenzoyl tartrate are shown in Figure 3. Two singlet resonances (δ 6.16 and 6.12 ppm) are due to the CH proton of racemic dibenzoyl tartrate in the presence of **2** (Fig. 3C), and their intensity ratio is about 1:1, the separation between the two peaks is 12 Hz. This indicates that the interactions of **2** with D- and L-forms of dibenzoyl tartrate are different, resulting in two singlet resonances for the racemic CH proton. The CH proton singles of D- and L-dibenzoyl tartrate were shifted downfield about 0.34 and 0.30 ppm in the presence of **2** (Fig. 3D and 3E), respectively. The different downfield shift of the CH proton of the L- and D-enantiomers reveals that receptor **2** has a good enantioselective recognition ability.

The ^{1}H NMR spectra of receptor **1** and its complex with equimolar amounts of D-, L-, or racemic dibenzoyl tartrate are shown in Figure 4. The addition of racemic dibenzoyl tartrate in $CDCl_3$ also caused downfield shifts (δ 6.02 and 5.98 ppm) of the CH proton of dibenzoyl tartrate (Fig. 4B). The interaction of **1** with the D-enantiomer shows that the CH proton has a larger downfield shift ($\Delta\delta$ 0.20 ppm, Fig. 4C) that than of the CH proton of L-enantiomer ($\Delta\delta$ 0.16 ppm, Fig. 4D). This is similar to receptor **2** in the recognition ability for the enantiomers, **1** and **2** have a strong recognition interaction to D-dibenzoyl tartrate. Receptor **2** revealed the highly enantioselective recognition for the enantiomers of dibenzoyl tartrate.

The ^{1}H NMR spectra of receptors **1** and **2** also show dramatic changes in the presence of a guest. Upon the addition of an equimolar amount of D-dibenzoyl tartrate to the solution of **2**, the peak of the indole NH was downfield shifted from 8.45 to 8.56 ppm, one characteristic peak of amide (N*H*) at 6.19 ppm disappeared. Upon the addition of an equimolar amount of L-dibenzoyl tartrate to the solution of **2**, the indole NH peak was downfield shifted from 8.45 to 8.54 ppm, while the characteristic peak of the amide (NH) at 6.19 ppm of **2** was slightly downfield shifted to 6.24 ppm. The above results of ^{1}H NMR of the interaction of **2** and guest indicated that the interaction between **2** and D-dibenzoyl tartrate was stronger than that of **2** with L-enantiomers. Upon the addition of an equimolar amount of D-dibenzoyl tartrate to a solution of **1**, the indole NH peak is downfield shifted to 8.61 ppm, causing one characteristic peak of amide (N*H*) at 6.33 ppm to disappear. Upon the addition of the equimolar amount of L-dibenzoyl tartrate to the solution of **1**, the peak of indole NH is downfield shifted to 8.63 ppm.

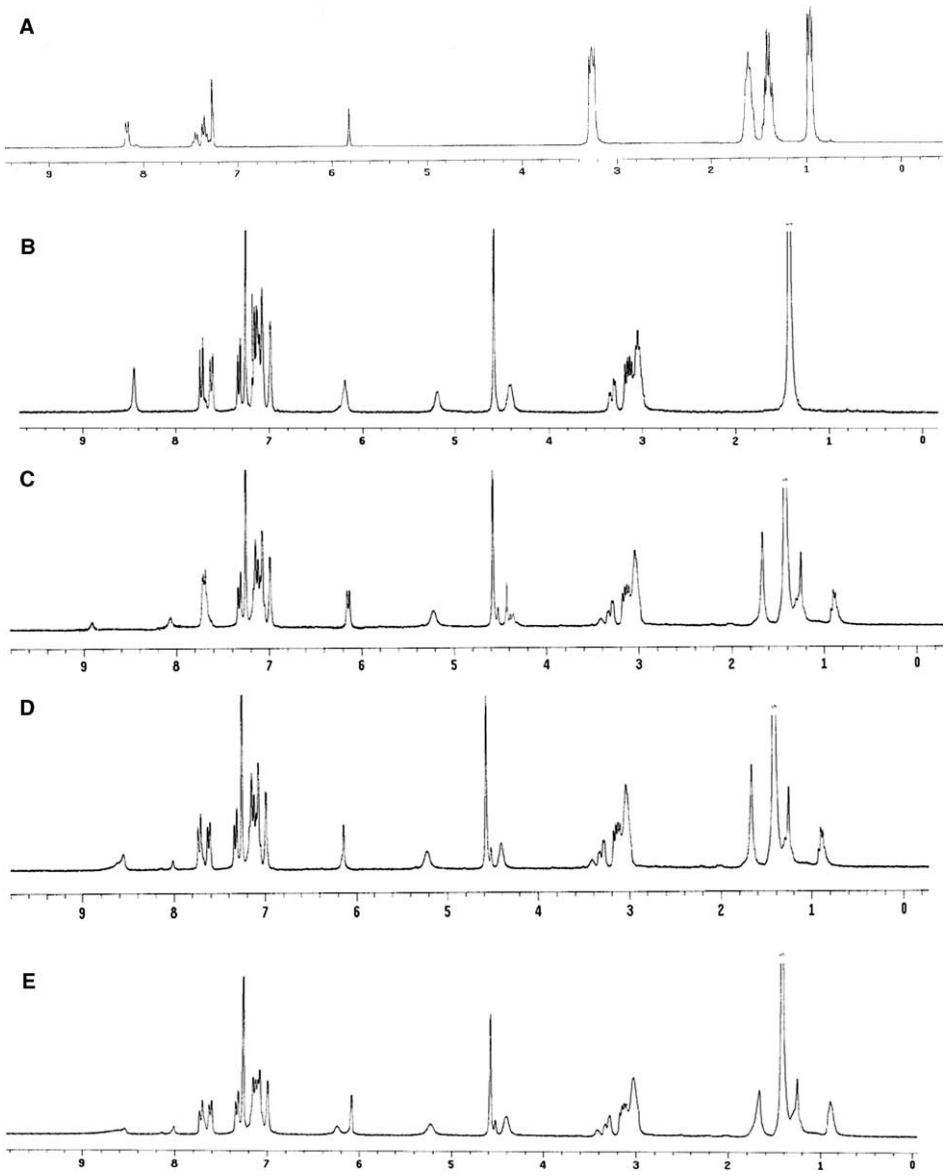

Figure 3. ^{1}H NMR spectra of **2** and its guest complex at 25 °C ([**2**] = [guest] = 2.0×10^{-3} M) in $CDCl_3$ at 300 MHz: (A) racemic dibenzoyl tartrate; (B) receptor **2**; (C) receptor **2** + racemic dibenzoyl tartrate; (D) receptor **2** + D-dibenzoyl tartrate; (E) receptor **2** + L-dibenzoyl tartrate.

Except for the steric recognition, the above results illustrate that the enantioselective recognition of the receptors for D- or L-dibenzoyl tartrate is through multiple hydrogen bonding interactions.[4f,12] Receptors **1** and **2** exhibit good recognition ability for D-dibenzoyl tartrate, and **2** reveals an excellent enantioselective recognition for the enantiomers of dibenzoyl tartrate.

3. Conclusion

Two chiral fluorescence receptors **1** and **2** containing amide units and L-tryptophan were synthesized. The enantioselective recognition of receptors was studied by ^{1}H NMR and fluorescence spectra. Receptors **1** and **2** exhibit different chiral recognition abilities toward the enantiomers of D- and L-bis(tetrabutylammonium) dibenzoyl tartrate, and formed a 1:1 complex between host and guest, while **2** has an excellent enantioselective recognition ability in comparison with **1**. The complementary structure between host and guest, the good preorganization property of host and the cooperative act by multiple hydrogen bondings in the complexation may result in the high enantioselective recognition of receptor **2** for the enantiomers of dibenzoyl tartrate anion.

4. Experimental

4.1. Materials and methods

Ethylenediamine and propylenediamine were distilled before use. Chloroform was dried and distilled from $CaCl_2$. All other commercially available reagents were used without further purification. The anions were used as their bis(tetrabutylammonium) salts. Melting

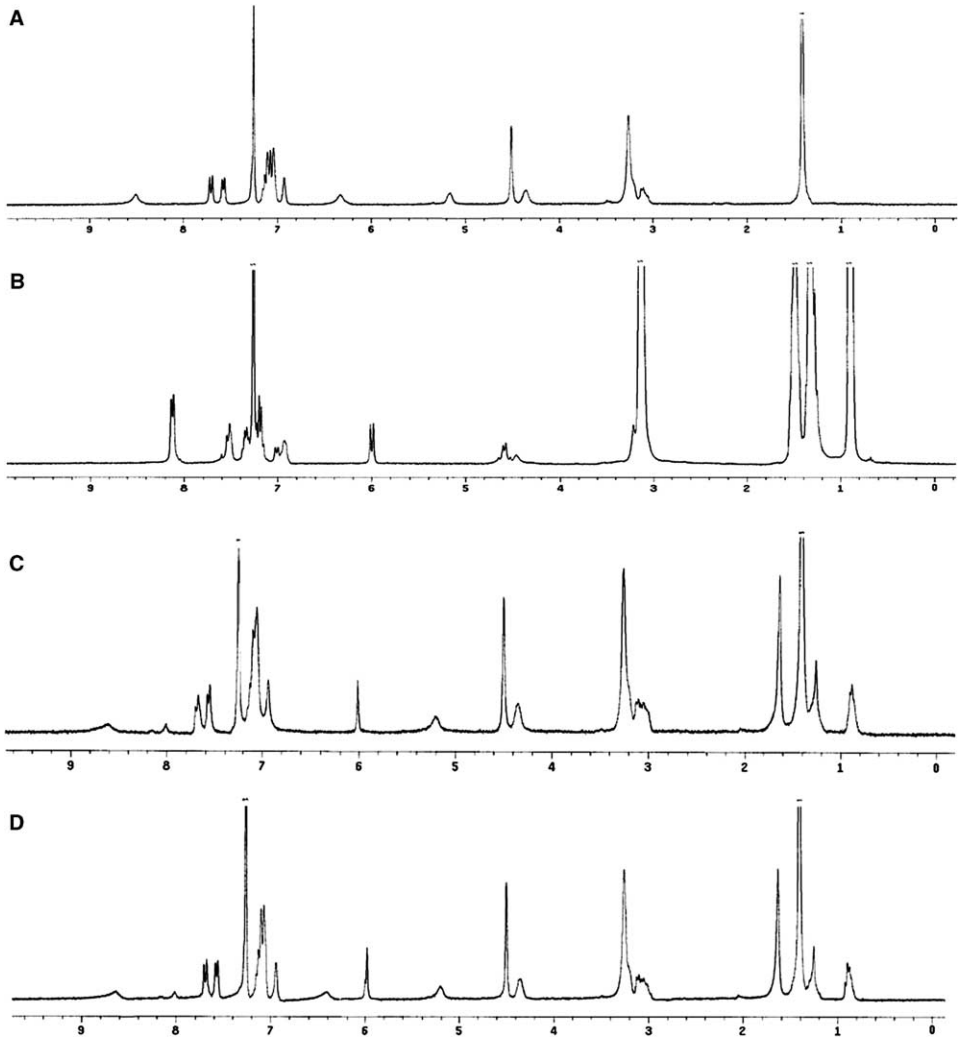

Figure 4. ^{1}H NMR spectra of **1** and its guest complex ([**1**] = [guest] = 2.0×10^{-3} M) at 25 °C in $CDCl_3$ at 300 MHz: (A) receptor **1**; (B) receptor **1**+racemic dibenzoyl tartrate; (C) receptor **1**+D-dibenzoyl tartrate; (D) receptor **1**+L-dibenzoyl tartrate.

points were measured on Reichert 7905 melting-point apparatus (uncorrected). The IR spectra were performed on a Nicolet 670 FT-IR spectrophotometer. Mass spectra were recorded on a Finnigan LCQ advantage mass spectrometer. Elemental analyses were determined by Perkin–Elmer 204B elemental autoanalyzer. ^{1}H NMR spectra were recorded on a Varian Mercury VX-300 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian Inova unity-600 MHz spectrometer. Fluorescence spectra were obtained on a Shimadzu RF–5301 spectrometer. Optical rotations were taken on a Perkin–Elmer Model 341 polarimeter. 2,7-Bis(aminoethylenecarbamoyl-methoxy)naphthalene **4a** was prepared according to the literature method.[4g]

4.2. Syntheses

4.2.1. Syntheses of *N*-Boc-L-tryptophan. $(Boc)_2O$ (2.10 g, 12 mmol) and 1 M NaOH (10 mL) were added to a solution of L-tryptophan (2.0 g, 10 mmol) in water–dioxane 1:1 (40 mL). The mixture was stirred for 24 h at room temperature, then the pH was adjusted to 2.4 by adding aqueous HCl, and the product extracted with EtOAc (2×30 mL). The solvent was evaporated to give *N*-Boc-L-tryptophan (2.71 g, 89%) as a white solid. Mp: 136–138 °C; ^{1}H NMR ($CDCl_3$): 8.13 (br, 1H, Ind-NH), 7.61 (d, 1H, $J = 7.6$ Hz, Ind-7-H), 7.37 (d, 1H, $J = 8.1$ Hz, Ind-4-H), 7.15–7.11 (m, 2H, Ind-5,6-H), 7.03 (s, 1H, Ind-2-H), 5.06 (br, 1H, N*H*Boc), 4.68–4.64 (m, 1H, C*H), 3.37–3.31 (m, 2H, CH_2) 1.43 (s, 9H, CH_3).

4.2.2. Syntheses of 2,7-bis(3-aminopropylenecarbamoyl-methoxy)naphthalene 4b. A mixture of 2,7-bis(ethoxy-carbonylmethyloxy)naphthalene (1.66 g, 5 mmol), excess 1,3-propylenediamine (2.5 mL) in dry $CHCl_3$ (20 mL), and anhydrous EtOH (20 mL) was stirred for 24 h at room temperature. After evaporation of the solvent and the residual 1,3-propylenediamine under reduced pressure, a light yellow powder (1.85 g, 95%) was obtained. Mp 146–148 °C. IR (KBr): 3351, 2936, 2867, 1655, 1629, 1548, 1516, 1256, 1212, 1170, 1049, 841, 598, 469 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.72 (s, 2H, naph-1,8-H), 7.74 (br, 2H, *CONH*), 7.07–7.02 (m, 4H,

naph-3,4,5,6-H), 4.59 (s, 4H, OCH_2), 3.46–3.42 (m, 4H, CH_2NH), 2.83–2.76 (m, 4H, $CH_2CH_2CH_2$), 1.71–1.49 (m, 8H, CH_2NH_2).

4.2.3. Syntheses of compounds 1 and 2. To a stirred and ice cooled solution of *N*-Boc-L-tryptophan (0.30 g, 1.25 mmol) in anhydrous chloroform (10 mL) was added 1,1′-carbonyldiimidazole (CDI) (0.24 g, 1.5 mmol), and the mixture was stirred for 2 h. Then a solution of either 2,7-bis(aminoethylenecarbamoylmethoxy)naphthalene **4a** (0.18 g, 0.5 mmol) or 2,7-bis(3-aminopropylenecarbamoylmethoxy)naphthalene **4b** (0.20 g, 0.5 mmol) in anhydrous chloroform (10 mL) was added dropwise to the stirred mixture. The mixture was stirred for 48 h under Ar at room temperature. The mixture was washed successively with 1 M HCl (3×20 mL), saturated Na_2CO_3 (3×20 mL), saturated NaCl (3×20 mL), and then dried over anhydrous Na_2SO_4. Solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using $CHCl_3/CH_3OH$ (50/1) as eluant to obtain pure products **1** and **2**, respectively.

Compound **1**: Yield: 76%; Mp: 124–126 °C; $[\alpha]_D^{20} = -16.8$ (*c* 0.05, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (br, 2H, Ind-N*H*), 7.71 (d, 2H, $J = 9.6$ Hz, naph-3,6-H), 7.57 (d, 2H, $J = 7.8$ Hz, Ind-7-H), 7.16–7.04 (m, 12H, Ind-2,4,5,6-H, naph-1,4,5,8-H), 6.93 (s, 2H, CONH), 6.33 (br, 2H, CONH), 5.16 (br, 2H, NHBoc), 4.50 (s, 4H, OCH_2), 4.35 (br, 2H, C*H), 3.26 (s, 8H, NCH_2CH_2N), 3.18–3.03 (m, 4H, CH_2–Ind), 1.41 (s, 18H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 28.5, 36.7, 40.0, 55.7, 67.3, 77.1, 107.3, 110.6, 111.5, 116.7, 119.0, 120.0, 122.4, 123.4, 127.6, 129.9, 135.7, 136.4, 156.2, 161.3, 169.5; IR (KBr/cm^{-1}): 3415, 2925, 1655, 1515, 1436, 1385, 1165, 1057, 746; ESI-MS *m*/*z* (%): 955 ((M+Na)$^+$,100); Elemental analysis calcd (%) for $C_{50}H_{60}N_8O_{10}$: C 64.36, H 6.48, N 12.01; found C 64.11, H 6.39, N 11.92.

Compound **2**: Yield: 87%; Mp: 136–138 °C; $[\alpha]_D^{20} = -10.4$ (*c* 0.05, $CHCl_3$), ^{1}H NMR ($CDCl_3$): δ 8.45 (br, 2H, Ind-N*H*), 7.75 (d, 2H, $J = 9.3$ Hz, naph-3,6-H), 7.62 (d, 2H, $J = 8.1$ Hz, Ind-7-H), 7.32 (d, 2H, $J = 8.1$ Hz, Ind-4-H), 7.16–7.08 (m, 10H, Ind-2,5,6-H, naph-1,4,5,8-H), 6.99 (s, 2H, CONH), 6.19 (br, 2H, CONH), 5.20 (br, 2H, NHBoc), 4.58 (s, 4H, OCH_2), 4.40 (br, 2H, C*H), 3.36–3.29 (m, 4H, NCH_2), 3.18–3.03 (m, 12H, CH_2–Ind, $NCH_2CH_2CH_2N$), 1.41 (s, 18H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 28.7, 29.7, 35.7, 36.2, 55.9, 67.6, 80.4, 107.3, 111.5, 116.7, 119.1, 119.8, 122.3, 123.5, 125.5, 127.7, 129.9, 135.6, 136.4, 155.6, 156.2, 168.7, 172.5; IR (KBr/cm^{-1}): 3411, 2926, 1661, 1539, 1436, 1367, 1210, 1164, 1057, 746; ESI-MS *m*/*z* (%): 983 ((M+Na)$^+$, 100); Elemental analysis calcd (%) for $C_{52}H_{64}N_8O_{10}$: C 64.98, H 6.71, N 16.65; found C 64.62, H 6.65, N 16.52.

4.3. Tetrabutylammonium salts

All tetrabutylammonium salts were prepared by adding 2 equiv of tetrabutylammonium hydroxide in methanol to a solution of the corresponding dibenzoyl tartaric acid (1 equiv) in methanol. The mixture was stirred at room temperature for 2 h and evaporated to dryness under reduced pressure. The resulting syrup was dried at high vacuum and 50 °C for 24 h, checked by NMR and stored in a desiccator.

4.4. Binding studies

The studies on the binding properties of **1** and **2** were carried out in $CHCl_3$ or DMSO. The fluorescence titration was performed with a series of 2.60×10^{-5} M solutions of receptor **1** or **2** containing different amounts of chiral anions (the excited wavelength was 359 or 361 nm, the excitation and emission slit width were 5 nm). Association constants were calculated by means of a non-linear least-square curve fitting method with Origin 7.0 (Origin-Lab Corporation). ^{1}H NMR studies were recorded as adding equivalent racemic, D- or L-dibenzoyl tartrate anions into receptors (2.0×10^{-3} M).

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