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Novel chiral fluorescent macrocyclic receptors: synthesis and recognition for amino acid anions

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Abstract—New chiral fluorescence macrocycles **1** and **2** containing naphthalene and amino acid units were synthesized. The binding properties for amino acid anions were examined by the fluorescence and ^{1}H NMR spectra. The results indicated good enantioselectivity of **1** toward the N-protected phenylalanine anions.

1. Introduction

Chirality is a fundamental property of most biological molecules, and chiral recognition has been widely studied because it is one of the most significant processes in living systems.[1] The development of fluorescent chiral artificial receptors with the properties of chiral recognition and optical change, has attracted increasing attention because of their high sensitivity and potential applications in pharmaceuticals, analysis, biology, and catalysts.[2] The chemical and more important biological activities of many chiral substances depend much on the stereochemistry. That is why the design, synthesis, and structural activity relationships of enantioselective receptors are still vital areas of research.[3] Much attention has been paid recently to the development of the synthesis of molecular receptors with the ability to recognize chiral molecules. Fluorescent sensors are preferred because they are well suited to meet the need for in vivo probes, such as mapping the spatial and temporal distribution of the biological analyses.[4]

Amino acids are often used as a chiral source in building the desired chiral artificial receptors because of their accessibility and biological relevance.[5] Macrocyclic structures have received much attention in the search for artificial receptors, mainly because of their higher degree of preorganization as compared to their acyclic counterparts. A great number of artificial chiral receptors have been synthesized and widely studied.[6] However, the synthesis and chiral recognition of chiral fluorescent macrocyclic receptors have seldom been reported. Herein, we report the synthesis and chiral recognition of new chiral fluorescent macrocyclic receptors **1** and **2** containing both an amino acid unit and a fluorophore of naphthalene.

2. Results and discussion

2.1. Synthesis

The synthesis of chiral fluorescent receptors **1** and **2** is outlined in Scheme 1. Compounds **5a** and **5b** were synthesized by a literature procedure.[7]

Intermediates **3**, **4**, **6a**, and **6b** were all obtained in high yield. Compounds **6a** and **6b** were treated with diacid chloride **4** to afford target molecules **1** and **2**, which were soluble in common organic solvents such as $CHCl_3$, CH_3CH_2OH, DMSO, and DMF. These compounds were characterized by IR, MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

2.2. Fluorescence spectra

The chiral recognition properties of receptors **1** and **2** were investigated for Boc-amino acid anions (D- and L-Phe anions, D- and L-Ala anions). The fluorescence spectra was recorded from a solution of receptors **1** and **2** (5×10^{-5} mol/L) in DMSO in the absence or presence of Boc-amino acid anions, in each case the counter cations were tetrabutylammonium.

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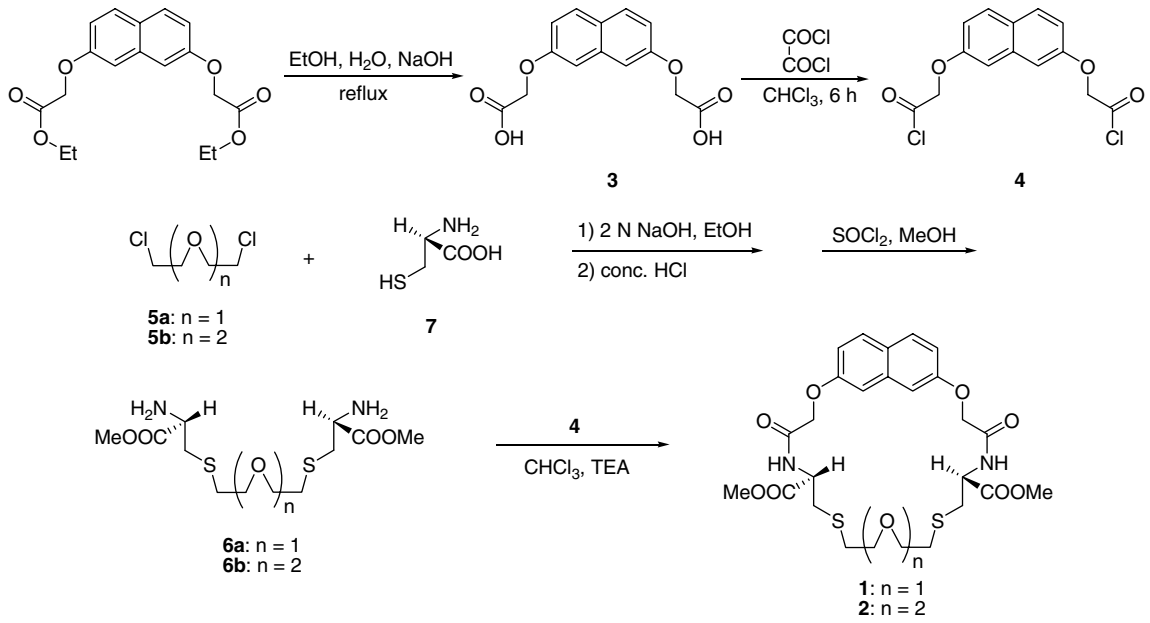

Scheme 1. The synthesis of receptors **1** and **2**.

Figures 1 and 2 show the fluorescence emission spectra of **1** with different concentrations of D- or L-Phe anions in DMSO. When gradually increasing the concentration of the anions, the fluorescence emission intensities of **1** (5×10^{-5} mol/L) at 343 nm ($\lambda_{ex} = 301$ nm) decreased. The quenching efficiency was 83% with 20 equiv of D-Phe anion while it was 34% with 20 equiv of L-Phe anion. The different quenching efficiencies ($\Delta I_D/\Delta I_L \approx 2.5$) indicated that receptor **1** has a good enantioselective recognition ability between D- and L-Phe anions. Upon addition of 20 equiv of D- or L-Ala anions to a solution of **1**, the enantioselective fluorescence response was 1.3 ($\Delta I_D/\Delta I_L$).

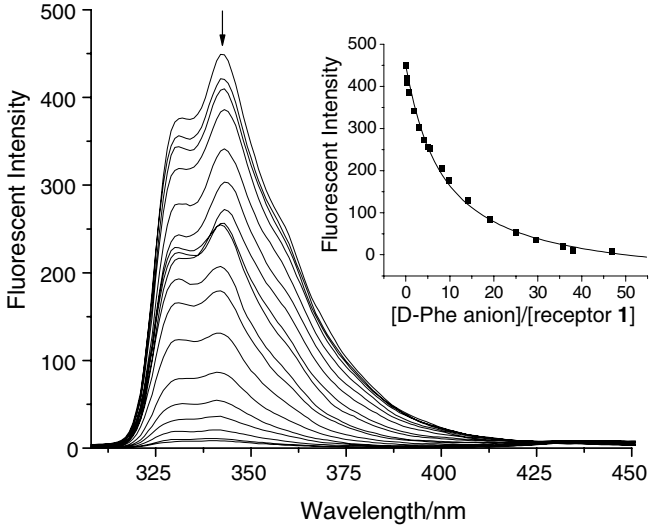

Figure 1. Fluorescence spectra of **1** (5×10^{-5} mol/L, DMSO) upon the addition of various amounts of D-Phe anion in DMSO, $\lambda_{ex} = 301$ nm, equivalent of Bu_4N^+ (N-protected phenylalanine): 0 → 46. The non-linear fitting curve of change in the fluorescence intensity at 343 nm with respect to the amount of Bu_4N^+ (N-protected phenylalanine) is shown in the inset.

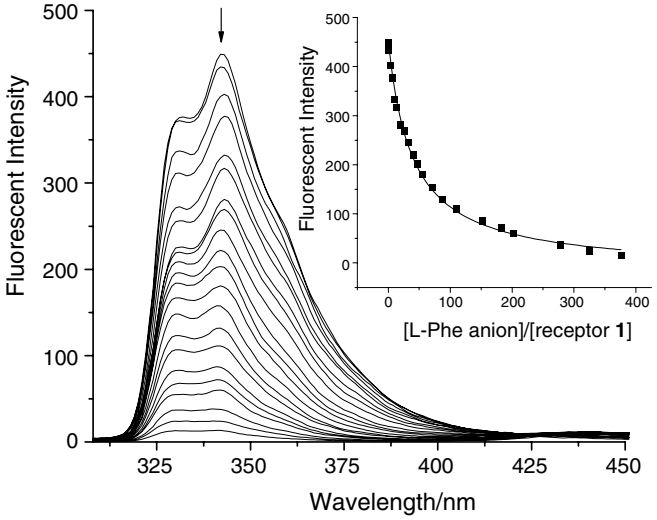

Figure 2. Fluorescence spectra of **1** (5×10^{-5} mol/L, DMSO) upon the addition of various amounts of L-Phe anion in DMSO, $\lambda_{ex} = 301$ nm, equivalent of Bu_4N^+ (N-protected phenylalanine): 0 → 325. The non-linear fitting curve of change in the fluorescence intensity at 343 nm with respect to the amount of Bu_4N^+ (N-protected phenylalanine) is shown in the inset.

When the enantiomers of Phe or Ala anions were added into a solution of **2** in DMSO, respectively, the fluorescence changes were similar. More anions were needed when the fluorescence of **2** was nearly completely quenched (Figs. 3 and 4), and the changes of quenching efficiencies were smaller, which indicated that the recognition ability for anions of **2** was weaker compared with receptor **1**.

In the presence of amino acid anions, the fluorescence quenching of receptors **1** and **2** most likely arose from the change of the free energy (ΔG_{PET}) of electron transfer between the excited fluorophore and the receptor.[8] When

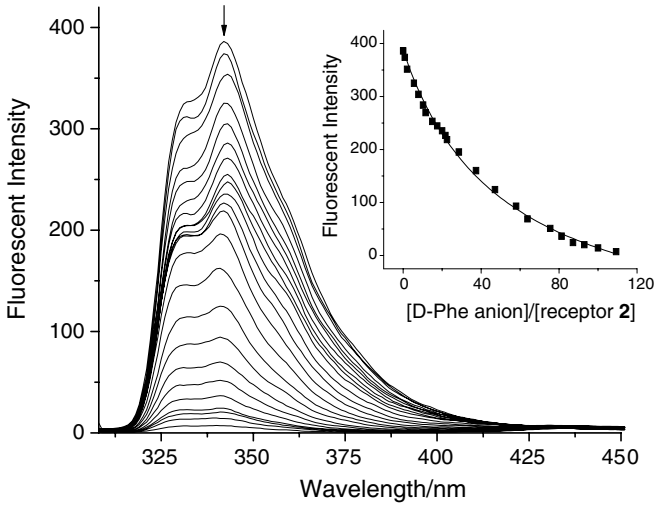

Figure 3. Fluorescence spectra of **2** (5×10^{-5} mol/L, DMSO) upon the addition of various amounts of D-Phe anions in DMSO, $\lambda_{ex} = 299$ nm, equivalent of Bu_4N^+ (N-protected phenylalanine): $0 \rightarrow 109$. The non-linear fitting curve of change in fluorescence intensity at 342 nm with respect to the amount of Bu_4N^+ (N-protected phenylalanine) is shown in the inset.

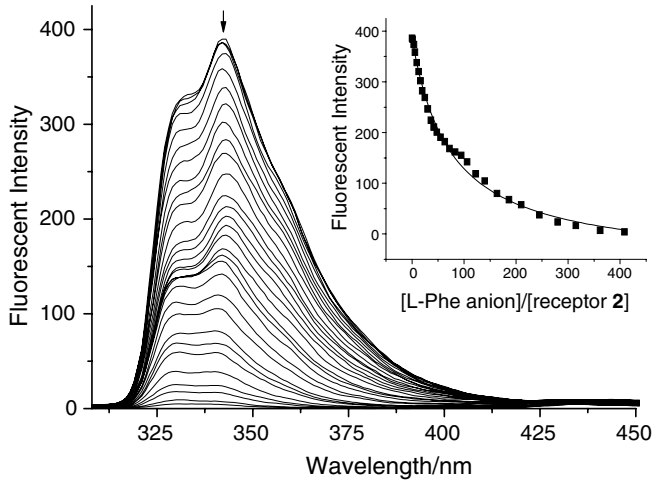

Figure 4. Fluorescence spectra of **2** (5×10^{-5} mol/L, DMSO) upon the addition of various amounts of L-Phe anions in DMSO, $\lambda_{ex} = 299$ nm, equivalent of Bu_4N^+ (N-protected phenylalanine): $0 \rightarrow 408$. The non-linear fitting curve of change in the fluorescence intensity at 342 nm with respect to the amount of Bu_4N^+ (N-protected phenylalanine) is shown in the inset.

the amino acid anion interacted with either receptor **1** or **2**, the reductive potential of the amide group increased along with the ratio of the electron transfer from the HOMO orbital of receptors to the excited naphthalene group, which in turn led to a more easy intramolecular PET (photo-induced electron transfer) process.[9]

The continuous variation methods were employed to determine the stoichiometric ratio of the receptor **1** with guests (D- and L-Phe anions). The total concentration of host and guest was constant (1.0×10^{-4} mol/L) in DMSO, with a continuously variable molar fraction of host ([H]/([H]+[G])). Figure 5 shows the Job plots of receptor **1** with

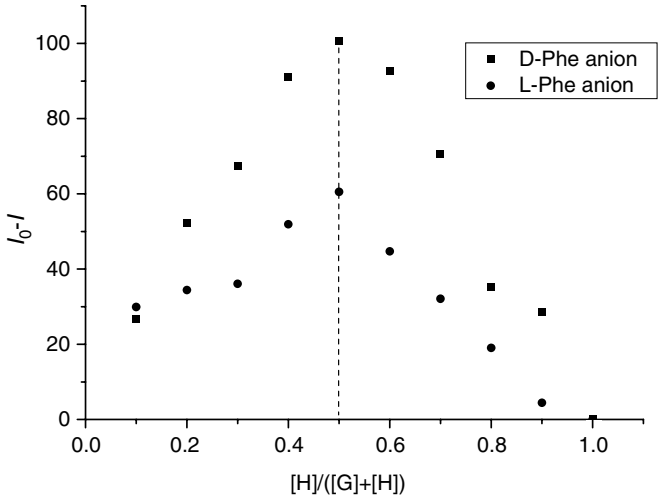

Figure 5. Job plots of **1** with D- and L-Phe anions (at 343 nm). The total concentration of the host and guest is 1.0×10^{-4} mol/L in DMSO. I_0: fluorescence intensity of **1**; I: fluorescence intensity of **1** in the presence of the guest.

D- and L-Phe anions (at 343 nm). When the molar fraction of the host was 0.50, the fluorescence intensity reached a maximum, which demonstrated that receptors **1** formed a 1:1 complex with D- and L-Phe anions, respectively.[10]

Assuming the complex stoichiometry was 1:1, the association constant (K_{ass}) can be calculated by the following equation:[11]

$$X = X_0 + (X_{lim} - X_0)/2c_0\{c_H + c_G + 1/K_{ass} - [(c_H + c_G + 1/K_{ass})^2 - 4c_H c_G]^{1/2}\} \quad (1)$$

where X represents the fluorescence intensity, c_H and c_G represent the corresponding concentration of host and guest. The non-linear curve fitting results of the fluorescence intensity (at 342 nm) of the interaction between **1** or **2** and D-, L-amino acid anions are shown in Table 1. The correlation coefficients of the non-linear curve fitting were all larger (>0.99), which indicated that the 1:1 complex between **1** or **2** and the amino acid anions has been formed.[11,12] The data in Table 1 illustrate that the two receptors exhibited good enantioselective recognition for D- or L-Phe anions. The association constants (K_{ass}) of **1** and **2** with D-Phe were much higher than those of **1** and **2** with L-Phe anion, which is probably due to the more complementary structure of the D-Phe anion with receptors **1** and **2**. Receptor **1** gave the enantioselectivity $K_{ass(D\text{-Phe})}/K_{ass(L\text{-Phe})} = 4.94$. However, the small association constant

Table 1. Association constants (K_{ass}) and correlation coefficients (R) of **1** and **2** with amino acid anions in DMSO

Anion[a]	1		2	
	K_{ass}	R	K_{ass}	R
D-Phe	$(2.55 \pm 0.17^b) \times 10^3$	0.9948	$(0.39 \pm 0.02^b) \times 10^3$	0.9966
L-Phe	$(0.52 \pm 0.02^b) \times 10^3$	0.9956	$(0.28 \pm 0.01^b) \times 10^3$	0.9948
D-Ala	47.07 ± 3.07	0.9930	48.09 ± 2.98	0.9949
D-Ala	16.23 ± 1.19	0.9924	40.21 ± 3.14	0.9977

[a] Anions were used as their tetrabutylammonium salts.
[b] All error values were obtained by the results of non-linear curve fitting.

and lower enantioselectivity of the receptors **1** and **2** to the enantiomers of the Ala anions were discovered, which indicated that the cyclic space of the receptors did not match with the structure of the Ala anion. Since the bridge chain in receptor **1** is shorter than that of receptor **2**, a larger rigidity and a good preorganization property in the cycle of receptor **1** may result in the good enantioselective recognition of receptor **1** for the enantiomers of the Phe anion.

2.3. ^{1}H NMR study

^{1}H NMR experiments were undertaken to assess the chiral recognition properties between receptor **1** and the Phe anion because it can provide structural and dynamic information.[13] The study was carried out on a 300 MHz NMR spectrometer in DMSO at room temperature using receptor **1** as a chiral solvating agent.

The ^{1}H NMR spectra of receptor **1** (4×10^{-2} mol/L) and its complex with equimolar amounts of racemic, D- or L-Phe anions (4×10^{-2} mol/L) in DMSO-d_6 are shown in Figure 6. Figure 6A shows the ^{1}H NMR spectra of racemic Phe anions, only one broad singlet (δ 3.98 ppm) is present for the CH proton resonance of racemic Phe anions. When treated with equimolar amounts of receptor **1**, the CH proton signal was cleaved into two singlets (δ 3.99 and

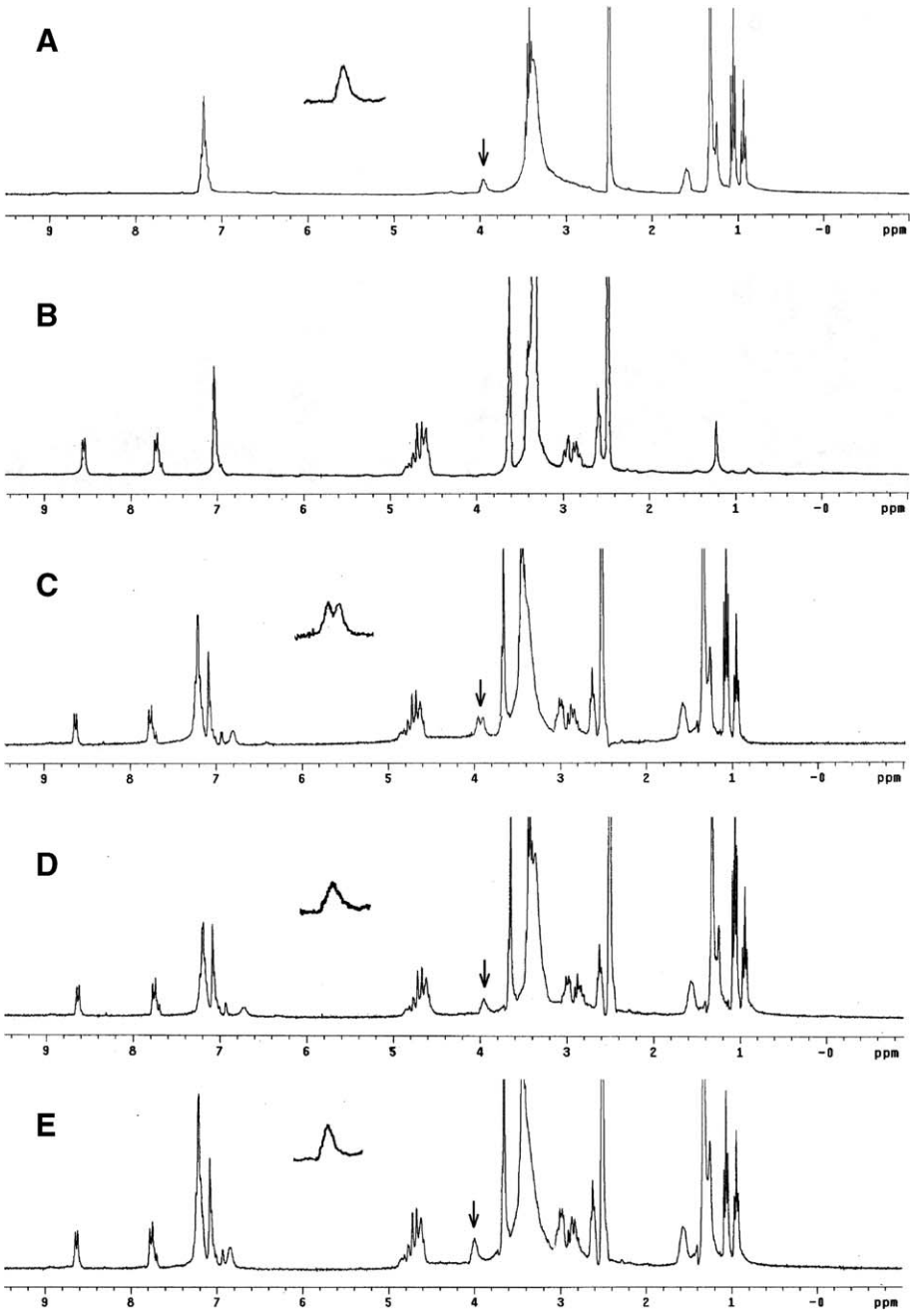

Figure 6. ^{1}H NMR spectra of **1** and its guest complex at 25 °C ([**1**] = [guest] = 4.0×10^{-2} mol/L) in DMSO-d_6 at 300 MHz: (A) racemic Phe anions; (B) receptor **1**; (C) receptor **1** + racemic Phe anions; (D) receptor **1** + D-Phe anions; (E) receptor **1** + L-Phe anions.

3.95 ppm) (Fig. 6C), and the separation between the two peaks was 12 Hz. The interaction of **1** with the D-Phe anion showed that the CH proton signal shifted upfield (Fig. 6D), but shifted downfield when interacted with the L-Phe anion (Fig. 6E), which indicated that the interactions of **1** with D- and L-Phe anion were different. The different shift of the CH proton of D- and L-enantiomers revealed the good enantioselective recognition ability of receptor **1**. At the same time, the peak of the amide (NH) at 8.58 ppm was shifted downfield to 8.64 ppm, and the proton signals of naphthalene ring were cleaved and moved upfield. This indicated that the interaction between the host and guest was also through multiple hydrogen bonding and π–π stacking of aromatic ring interactions.[14]

3. Conclusion

Two chiral fluorescence receptors **1** and **2** containing amides and L-cysteine were synthesized. The enantioselective recognition of these receptors was studied by fluorescence spectra and ^{1}H NMR spectra, the result indicated that receptors **1** and **2** can form a 1:1 complex between host and guest. The enantioselective recognition ability of receptor **1** toward the Phe anions was better in comparison to **2**. The complementary structure and π–π stacking of the aromatic rings between host and guest, the relative rigidity and the good preorganization property of the host, and the cooperative effect of multiple hydrogen bondings in the complexation may result in the good enantioselective recognition of receptor **1** for the enantiomers of the Phe anion.

4. Experimental

4.1. Materials and methods

$CHCl_3$ and Et_3N were dried and distilled from CaH_2. All other commercially available reagents were used without further purification. 2,7-Bis(ethoxycarbonyl methoxy)-naphthalene and compounds **5a** and **5b** were synthesized by a literature procedure.[7,14b] Melting points were determined with a Reichert 7905 melting-point apparatus and are uncorrected. Optical rotations were taken on a Perkin–Elmer Model 341 polarimeter. IR spectra were obtained on a Nicolet 670 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were performed on a Varian Mercury VX 300 MHz spectrometer in $CDCl_3$ and DMSO-d_6. Mass spectra were recorded on a Finnigan LCQ advantage mass spectrometer. Elemental analysis was determined with a FlashEA 1112 instrument. Fluorescence spectra were obtained on a Schimadzu RF-5301 spectrometer.

4.2. Syntheses

4.2.1. Synthesis of compound 3. 2,7-Bis(ethoxycarbonylmethoxy)naphthalene (3.32 g, 10.0 mmol) was dissolved in a mixture of 10% NaOH (100 mL) and CH_3CH_2OH (100 mL) solution and heated at reflux for 24 h. The solvents were removed and followed by the addition of water (30 mL). A white precipitate was afforded after being acidified with HCl. The precipitate was filtered and then washed with cold water to give compound **3**: 2.70 g, yield: 97.8%. Mp: 223–225 °C. ^{1}H NMR (DMSO-d_6): δ (ppm): 7.72 (d, $J = 8.7$ Hz, 2H, naph 4, 5-H), 7.12 (s, 2H, naph 1, 8-H), 6.98 (d, $J = 8.7$ Hz, 2H, naph 3, 6-H), 4.75 (s, 4H, OCH_2).

4.2.2. Synthesis of compound 4. Diacid **3** (0.55 g, 2.0 mmol) was suspended in dry $CHCl_3$ (10 mL) under an ice-bath, and DMF (two drops) was added. A solution of oxalyl chloride (2 mL, 23.3 mmol) in dry $CHCl_3$ (10 mL) was added dropwise and then stirred at room temperature for 6 h. The volatile materials were removed under reduced pressure and the residue dried under high vacuum for 3 h. Diacid chloride **4** was used without further purification.

4.2.3. General procedure for preparing 6. A solution of compound **5** (16.5 mmol) in C_2H_5OH (10 mL) was added dropwise into the mixture of L-cysteine **7** (4.0 g, 33.0 mmol), 2 M NaOH solution (25 mL), and C_2H_5OH (20 mL) under ice-bath. After addition, the mixture was stirred at room temperature for 24 h, then adjusted to pH = 9 with concd HCl, the precipitated white solid was isolated and washed with anhydrous ether, then dried under vacuum. The solid obtained was used without further purification. $SOCl_2$ (9.5 mL) was slowly added into the solution of the above solid (2.0 g) in dry CH_3OH (40 mL) under an ice-bath, after addition, the mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in water (30 mL), adjusted to pH = 9 with 2 M NaOH solution, and extracted by $CHCl_3$ (15 mL × 3). The combined extracts were dried over anhydrous Na_2SO_4. The final product **6** was afforded after being purified by column chromatography on silica gel (eluent: $CHCl_3$/CH_3OH 20:1).

4.2.3.1. Compound 6a. Yield: 54%; ^{1}H NMR ($CDCl_3$): δ (ppm): 3.74 (dd, $J = 4.8$, 4.2 Hz, 2H, CHN), 3.68 (s, 6H, OCH_3), 3.59–3.63 (m, 2H, OCH_2CH_2S), 3.55–3.59 (m, 2H, OCH_2CH_2S), 3.05 (dd, $J = 4.8$, 14.5 Hz, 2H, SCH_2CH), 2.88 (dd, $J = 4.2$, 14.5 Hz, 2H, SCH_2CH), 2.68–2.72 (m, 4H, $2SCH_2CH_2O$), 1.78 (s, 4H, $2NH_2$). Elemental analysis calcd (%) for $C_{12}H_{24}N_2O_5S_2$: C, 42.33; H, 7.12; N, 8.23. Found: C, 42.32; H, 7.41; N, 7.91.

4.2.3.2. Compound 6b. Yield: 61%; ^{1}H NMR ($CDCl_3$): δ (ppm): 3.71 (dd, $J = 4.5$, 4.8 Hz, 2H, CHN), 3.65 (s, 6H, OCH_3), 3.61–3.65 (m, 4H, OCH_2CH_2O), 3.52–3.56 (m, 2H, OCH_2CH_2S), 3.48–3.52 (m, 2H, OCH_2CH_2S), 3.02 (dd, $J = 4.5$, 14.7 Hz, 2H, SCH_2CH), 2.79 (dd, $J = 4.8$, 14.7 Hz, 2H, SCH_2CH), 2.62–2.66 (m, 4H, $2SCH_2CH_2O$), 1.75 (s, 4H, $2NH_2$). Elemental analysis calcd (%) for $C_{14}H_{28}N_2O_6S_2$: C, 43.72; H, 7.35; N, 7.29. Found: C, 43.70; H, 7.51; N, 7.12.

4.2.4. Synthesis of compounds 1 and 2. Under an argon atmosphere and ice-bath, a solution of compound **6** (2.3 mmol) in dry $CHCl_3$ (110 mL) and diacid chloride **4** (2.3 mmol) in dry $CHCl_3$ (110 mL) were simultaneously added dropwise (about 3 h) into a vigorously stirring solution of $CHCl_3$ (100 mL) and triethylamine (5.0 mmol). After addition, the mixture was stirred at room temperature for a further 12 h, and then washed with cold 2 M

H_2SO_4, saturated sodium bicarbonate solution, and water, and the organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel (eluent: $CHCl_3/CH_3CH_2OH$ 100:1) to give the pure products **1** and **2** as a white powder, respectively.

4.2.4.1. Compound 1. Yield: 46.5%; mp: 180–181 °C; $[\alpha]_D^{20} = +43.0$ (*c* 0.05, $CHCl_3$); IR (KBr): *v* 3420, 3323, 2923, 1741, 1667, 1633, 1541, 1514, 1436, 1256, 1210, 1053, 827, 470. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.62 (d, $J = 7.8$ Hz, 2H, naph 4, 5-H), 7.40 (s, 2H, NH), 6.91–7.00 (m, 4H, naph 1, 3, 6, 8-H), 4.82–4.84 (m, 2H, C*H*NH), 4.55 (s, 4H, $COCH_2$), 3.68 (s, 6H, CH_3), 3.45–3.47 (m, 4H, OCH_2CH_2), 2.97–3.01 (m, 4H, SCH_2CH_2), 2.57–2.60 (m, 4H, SCH_2CH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 171.5, 168.7, 157.0, 135.8, 129.8, 125.1, 117.0, 107.5, 70.3, 67.5, 52.7, 33.6, 31.9. ESI-MS *m*/*z* (%): 581 (M^++1, 100); Elemental analysis calcd (%) for $C_{26}H_{32}N_2O_9S_2$: C, 53.79; H, 5.52; N, 4.82. Found: C, 53.58; H, 5.61; N, 4.78.

4.2.4.2. Compound 2. Yield: 26.5%; mp: 160–161 °C; $[\alpha]_D^{20} = +57.4$ (*c* 0.05, $CHCl_3$); IR (KBr): *v* 3422, 3263, 3084, 2921, 1738, 1681, 1669, 1554, 1516, 1385, 1257, 1209, 1174, 1105, 856, 831, 555, 471; ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm): 7.72 (d, $J = 8.7$ Hz, 2H, naph-4, 5H), 7.38–7.40 (d, 2H, CONH), 7.10–7.21 (m, 4H, naph 1, 3, 6, 8-H), 4.86–4.88 (m, 2H, C*H*NH), 4.71 (s, 4H, $COCH_2$), 3.77 (s, 6H, CH_3), 3.26–3.36 (m, 8H, OCH_2CH_2S, OCH_2CH_2O), 3.01–3.06 (m, 4H, SCH_2CH_2), 2.44–2.48 (m, 4H, SCH_2CH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm): 170.9, 168.9, 156.5, 135.7, 129.8, 116.5, 108.4, 71.2, 70.0, 68.2, 53.0, 52.5, 34.1, 32.0. ESI-MS *m*/*z* (%): 625 (M^++1, 100); Elemental analysis calcd (%) for $C_{28}H_{36}N_2O_{10}S_2$: C, 53.85; H, 5.77; N, 4.49; O, 25.64; S, 10.26. Found: C, 53.96; H, 5.63; N, 4.62; O, 25.54; S, 10.34.

4.3. Tetrabutylammonium salts

All tetrabutylammonium salts were prepared by adding 1 equiv of tetrabutylammonium hydroxide in methanol to a solution of the corresponding N-protected (by Boc) amino acid derivatives (1 equiv) in methanol. The mixture was stirred at room temperature for 4 h and evaporated to dryness under reduced pressure. The resulting syrup was dried at high vacuum 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 DMSO. The fluorescence titration was performed with a series of 5×10^{-5} mol/L solutions of receptors **1** and **2** containing different amounts of chiral anions (the excited wavelength was 301 or 299 nm, the excitation and emission slit widths were 5 nm). ^{1}H NMR studies were recorded after adding equivalent racemic Phe or Ala anions into receptors (4×10^{-2} mol/L). Association constants were calculated by means of a non-linear least-square curve fitting method with Origin 7.0 (Origin-Lab Corporation).

Acknowledgments

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