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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 18 (2007) 1769–1774

Enantioselective fluorescent sensor for dibenzoyl tartrate anion based on chiral binaphthyl derivatives bearing an amino acid unit

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Received 17 April 2007; accepted 20 June 2007
Available online 30 August 2007

Abstract—The fluorescent photoinduced electron transfer (PET) chemosensors **1**–**3** based on (*S*)-1,1′-bi-2-naphthol were designed for their recognition of dibenzoyl tartrate anions. The binding properties for hydroxy acid anions were examined by the fluorescence and ^{1}H NMR spectra. The results indicated that receptor **1** exhibit excellent enantioselectivity toward the enantiomers of dibenzoyl tartrate anion.

1. Introduction

Chirality is a fundamental property of Nature.[1] Natural living systems are mostly composed of chiral biological molecules, which exist only in one of the enantiomeric forms, and functions for a certain living process. As is well known to all, the living systems may metabolize drug enantiomers in separate pathways to produce different pharmacological activities, but only the matched drug isomer may contribute to treatment of disease. Although chiral biomolecules in our body can recognize the matched drug isomer to some degree, it is still not enough.[2]

Nowadays, as one of the most fundamental and significant process in natural systems, enantioselective recognition is receiving increasing focus from researchers.[3] However, enantioselective recognition still remains a major challenge for host–guest chemists.[4]

Using fluorescence in chiral recognition has the advantages of real time response, high sensitivity, and many modes of detection.[5] A proper host requires a compatible configuration with the guest. The binaphthyl unit was especially eye-catching for its stable chiral configuration and tunable dihedral angle between the two naphthalene rings. As a result, binaphthol and its derivatives have been extensively used in chiral recognition and asymmetric catalysis.[6]

Tartaric acid is a common natural product present in wines and other grape-derived beverages. It is suitable for complexation by a synthetic sensor since it is relatively small and possesses 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.[7]

In order to find facile, easily synthesized, highly sensitive and highly enantioselective fluorescent sensors, the optically active (*S*)-1,1′-bi-2-naphthyl framework was employed in our target chiral molecules in addition to an amino acid moiety. Herein, we report a fluorescent chemosensor, which exhibits excellent enantioselective recognition for the enantiomers of tartrate anion.

2. Results and discussion

2.1. Synthesis

As a naturally occurring chiral source, amino acids generally exhibit biologically activity. Furthermore, they can be easily modified at the amino and carboxylic groups, which can also act as binding sites to form coordinate bonds with chiral molecules, so they were often used in the design and synthesis of artificial chiral receptors.[8]

We chose several familiar amino acids (e.g., alanine, phenylalanine and tryptophan) as chiral building blocks and introduced them into the (*S*)-1,1′-binaphthyl framework

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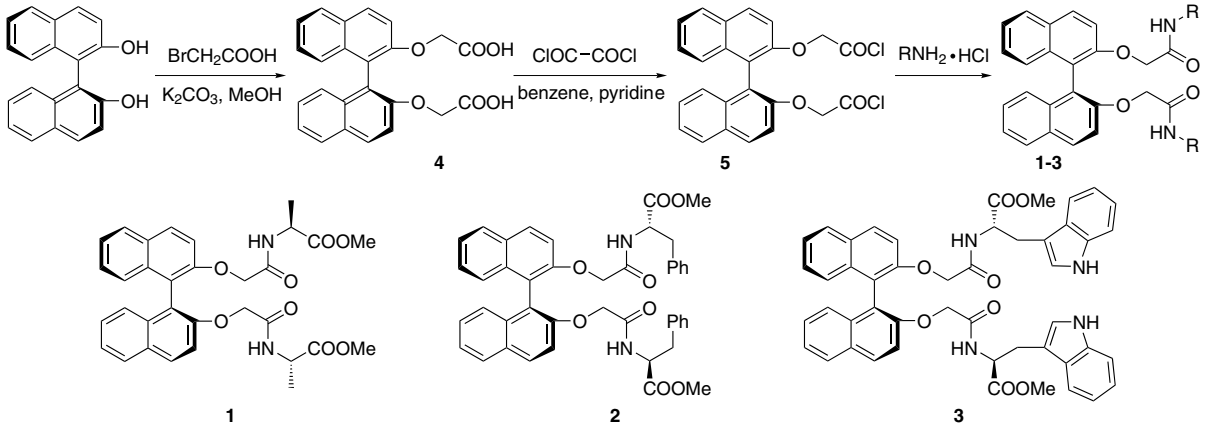
doi:10.1016/j.tetasy.2007.06.027



Scheme 1. The synthesis of receptors **1**–**3**.

to construct the fluorescent receptors **1**–**3** (Scheme 1). Compound **5** was synthesized according to a literature procedure.[9] All of the compounds were characterized by IR, MS, ^{1}H NMR, ^{13}C NMR and elemental analysis. They were all obtained in high yield and were easily soluble in common organic solvents such as $CHCl_3$, EtOH, and DMSO.

2.2. Fluorescence spectra

The properties of the chiral recognition of receptors **1**–**3** were investigated for D- and L-hydroxy acid anions (D- and L-dibenzoyl tartrate, D- and L-malate). The fluorescence spectra were recorded from a solution of receptors **1**–**3** (5×10^{-5} mol/L) in DMSO in the absence or presence of hydroxy acid anions; in each case the counter cations were tetrabutylammonium. Because there was almost no change observed on the UV–vis spectra of receptors upon addition of D- or L-hydroxy acid anions, the interaction between host and hydroxyl acid anion was only evaluated by fluorescent spectra.

Figure 1 shows the fluorescence emission spectra of the interaction between receptor **1** and D-malate anion in DMSO. The fluorescence emission of receptor **1** (5×10^{-5} mol/L) at 371 nm was slightly quenched by about 1.2% upon the addition of 20 equiv of D-malate anion. When the fluorescence intensity quenched to 616, it needed about 500 equiv of D-malate anion. A similar change in the fluorescence spectra was found when L-malate anion was added. Receptors **2** and **3** also gave the same change when they interacted with D- or L-malate anions.

Figure 2a and 2b shows the fluorescence emission spectra of **1** with different concentrations of D- or L-dibenzoyl tartrate anions in DMSO. Gradually increasing the concentration of the D-enantiomer caused the fluorescence emission intensities of **1** (5×10^{-5} mol/L) at 371 nm ($\lambda_{ex}=338$ nm) to decrease remarkably (Fig. 2a). The quenching efficiency was 56.0% with 20 equiv of D-dibenzoyl tartrate anion, when 99 equiv of D-dibenzoyl tartrate anion was added, the fluorescence emission intensity was almost quenched off. This indicated that receptor **1**

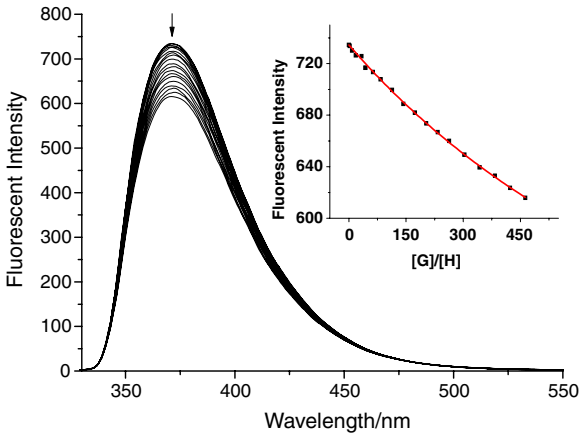


Figure 1. Fluorescence spectra of **1** (5×10^{-5} mol/L, DMSO) upon the addition of various amounts of D-malate in DMSO, $\lambda_{ex}=338$ nm, equivalent of Bu_4N^+ (D-malate): 0→463. The non-linear fitting curve of change in fluorescence intensity at 371 nm with respect to the amount of Bu_4N^+ (D-malate) is shown in the inset.

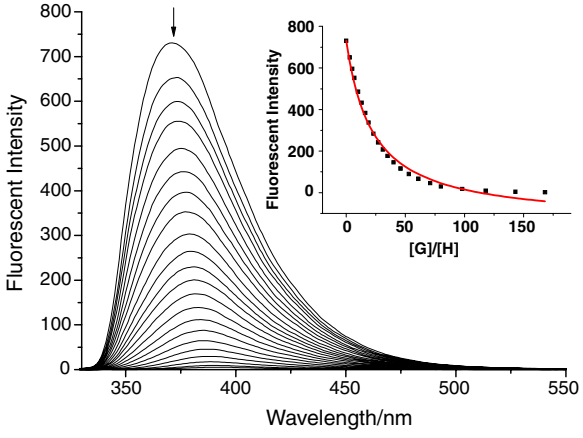


Figure 2a. Fluorescence spectra of **1** (5×10^{-5} mol/L, DMSO) upon the addition of various amounts of D-dibenzoyl tartrate in DMSO, $\lambda_{ex}=338$ nm, equivalent of Bu_4N^+ (D-dibenzoyl tartrate): 0 → 168. The non-linear fitting curve of change in fluorescence intensity at 371 nm with respect to amount of Bu_4N^+ (D-dibenzoyl tartrate) is shown in the inset.

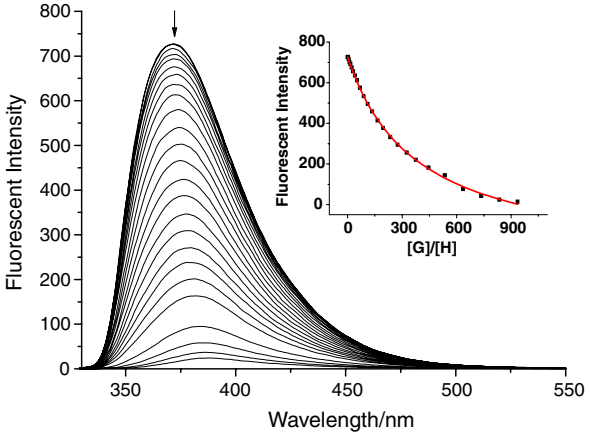


Figure 2b. Fluorescence spectra of **1** (5×10^{-5} mol/L, DMSO) upon the addition of various amounts of L-dibenzoyl tartrate in DMSO, $\lambda_{ex} = 338$ nm, equivalent of Bu_4N^+ (L-dibenzoyl tartrate): 0→935. The non-linear fitting curve of change in fluorescence intensity at 371 nm with respect to the amount of Bu_4N^+ (L-dibenzoyl tartrate) is shown in the inset.

exhibited a good interaction with D-dibenzoyl tartrate anion.

Upon the addition of L-dibenzoyl tartrate anion, however, the quenching efficiency was only 7.1% with 20 equiv of L-dibenzoyl tartrate anion. When the fluorescence emission intensity was nearly quenched off it required 935 equiv of the L-enantiomer (Fig. 2b). The different quenching efficiencies ($\Delta I_D/\Delta I_L \approx 7.9$) indicated excellent enantioselective recognition ability of receptor **1** between D- and L-dibenzoyl tartrate anions. Such a large difference in fluorescence quenching implies that receptor **1** can be used as a sensitive enantioselective fluorescent sensor for dibenzoyl tartrate anions.

Similar fluorescence emission spectra changes were observed when D- or L-dibenzoyl tartrate anions were added into hosts **2** and **3**. Due to the similar structure of **1**–**3**, the fluorescent variations of **1**–**3** showed the same trend. Since there were no changes in the UV–vis spectra of receptors when treated with D- or L-dibenzoyl tartrate anions, a PET process might be responsible for the fluorescent quenching.[10]

In the presence of guest anions, the fluorescence quenching of receptors **1**–**3** most likely arose from the change of the free energy (ΔG_{PET}) of the electron transfer between the excited fluorophore and the receptor.[11] When the guest anions interacted with receptors **1**–**3**, the reductive potential of the amide group increased along with the ratio of the electron transfer from the HOMO orbit of receptors to the excited binaphthyl group, which in turn led to a more facile intramolecular PET process (Fig. 3).[12]

Assuming the complex stoichiometry was 1:1, the association constant (K_{ass}) can be calculated with the following equation:[13]

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

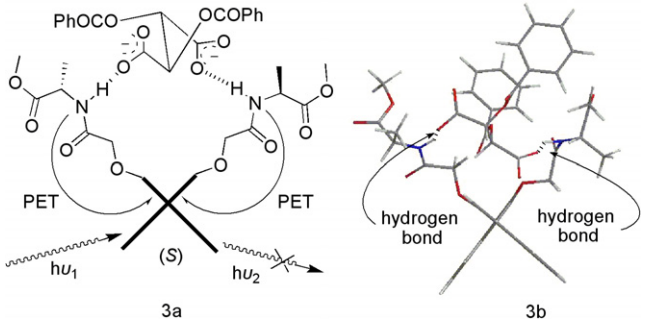


Figure 3. (a) Schematic representation showing the proposed structure for its complex between **1** and D-dibenzoyl tartrate anion. Dotted lines indicate hydrogen bonds. (b) Energy-minimized structure of the complex formed from **1** and D-dibenzoyl tartrate anion.

where X represents the fluorescence intensity, and c_H and c_G represent the corresponding concentration of host and guest. The non-linear curve fitting results of the fluorescence intensity (at 371 nm) of the interaction between **1**–**3** and D-, L-dibenzoyl tartrate anions are shown in Table 1. The correlation coefficients of the non-linear curve fitting were all large ($R > 0.99$), which indicated that the 1:1 complex between **1**–**3** and the dibenzoyl tartrate anions has been formed.[14] The data in Table 1 illustrate that the association constants (K_{ass}) of **1**–**3** with D-dibenzoyl tartrate anion were much higher than those of **1**–**3** with L-dibenzoyl tartrate anion, which is probably due to the more complementary structure of D-dibenzoyl tartrate anion with receptors **1**–**3**.

Receptor **1** gave the highest enantioselectivities $K_{ass(D)}/K_{ass(L)} = 17.35$, which is in sharp contrast with the lower enantioselectivity of **2** and **3** toward the enantiomers of dibenzoyl tartrate anion. These indicated that the smaller spatial hindrance of **1** resulted in the high enantioselectivity.

When receptors interacted with malate anions, all the receptors only gave faint fluorescence quenching and a small association constant, which means that receptors have no recognition ability.

2.3. ^{1}H NMR study

In order to understand the structural and dynamic information of the chiral recognition properties when receptor **1** interacted with dibenzoyl tartrate anions, ^{1}H NMR experiments were undertaken.[15] The study was carried out on a 300 MHz NMR spectrometer in DMSO-d_6 at

Table 1. Association constants (K_{ass}) and correlation coefficients (R) of **1**–**3** with dibenzoyl tartrate anions in DMSO

Host	D-Dibenzoyl tartrate[a]		L-Dibenzoyl tartrate[a]	
	K_{ass}	R	K_{ass}	R
1	$(9.18 \pm 0.55^b) \times 10^2$	0.9957	52.90 ± 1.20^b	0.9997
2	$(3.93 \pm 0.21^b) \times 10^2$	0.9977	$(1.23 \pm 0.07^b) \times 10^2$	0.9977
3	$(3.81 \pm 0.21^b) \times 10^2$	0.9974	91.74 ± 3.59^b	0.9989

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

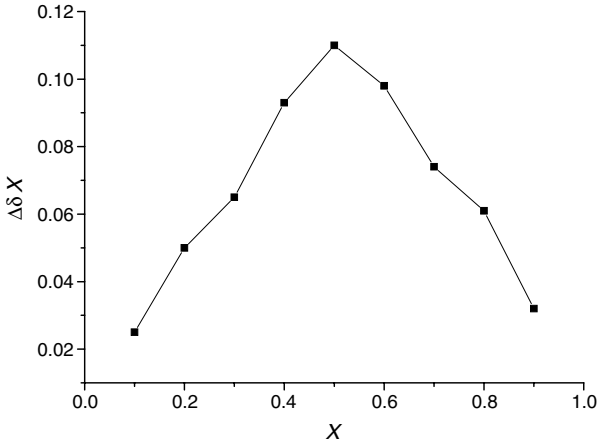


Figure 4. Job plot of **1** with D-dibenzoyl tartrate anion (X = mole fraction of the D-dibenzoyl tartrate anion, $\Delta\delta$ = chemical shift change of the CH proton of the anion). The total concentration of the host and guest is 8.0×10^{-3} mol/L in DMSO-d_6.

room temperature using receptor **1** as a chiral solvating agent.

Figure 4 is a Job plot of $\Delta\delta X$ versus the mole fraction (X) of D-dibenzoyl tartrate anion in the mixture.[16] A maximum at $X = 0.5$ was observed. This indicates that receptor **1** can form a 1:1 complex with the dibenzoyl tartrate anion under the conditions.

The ^{1}H NMR spectra of receptor **1** (4×10^{-3} mol/L) and its complex with equimolar amounts of racemic, D- or L-dibenzoyl tartrate anions (4×10^{-3} mol/L) in DMSO-d_6 are shown in Figure 5. It was observed that the CH proton signal of racemic dibenzoyl tartrate was only one singlet (δ 5.26 ppm, Fig. 5A), but when treated with equimolar amounts of receptor **1**, it was cleaved into two singlets (δ 5.24 and 5.35 ppm, $\Delta\Delta\delta = 0.11$ ppm, Fig. 5c). The NH signals of the host (at 7.88 ppm) experienced a slightly downfield shift and exhibited some reduction. The interaction of **1** with D-dibenzoyl tartrate anion showed that the CH proton signal shifted downfield by $\Delta\delta = 0.09$ ppm, the NH signal of the host (at 7.88 ppm) shifted downfield by $\Delta\delta = 0.01$ ppm with some reduction (Fig. 5d). When receptor **1** was interacted with L-dibenzoyl tartrate anion, the CH proton signal only shifted upfield for 0.02 ppm. The NH signal also showed some downfield shift (from δ 5.26 to 5.24 ppm, $\Delta\delta = -0.02$ ppm) and exhibited some reduction (Fig. 5E). The different shifts of the CH proton of D- and L-enantiomers revealed the good enantioselective recognition ability of receptor **1**. At the same time, the peaks of the amide (NH) at 7.88 ppm were all shifted to a certain degree with some reduction. This indicated that the interaction between the receptors and dibenzoyl tartrate anions was through multiple hydrogen bonding.[17]

3. Conclusion

Three optically active (*S*)-1,1′-bi-2-naphthol-based receptors **1**–**3** were synthesized. The enantioselective recognition of these receptors was studied by the fluorescence spectra and ^{1}H NMR. Receptors **1**–**3** formed a 1:1 complex between host and guest, while **1** has an excellent enantioselective recognition ability in comparison with other receptors. It is clear that the good preorganization property and small spatial hindrance of the host, and the cooperative action by multiple hydrogen bonding in the complex may result in the highly enantioselective recognition of the enantiomers of dibenzoyl tartrate anion.

4. Experimental

4.1. Materials and methods

$CHCl_3$, MeOH, Et_3N and K_2CO_3 were purified before use according to the standard procedure. All other commercially available reagents were used without further purification. Melting points were determined with a Reichert 7905 melting-point apparatus and are uncorrected. Optical rotations were taken on a Perkin–Elmer Model 341 polarime-

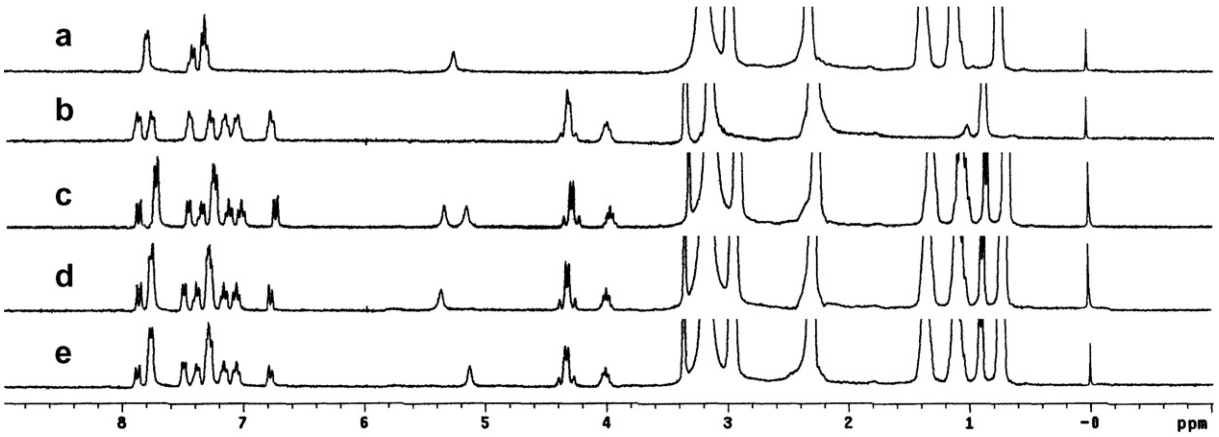


Figure 5. ^{1}H NMR spectra of **1** and its guest complex at 25 °C ([**1**] = [guest] = 4.0×10^{-3} mol/L) in DMSO-d_6 at 300 MHz: (a) racemic dibenzoyl tartrate anion (b) receptor **1** (c) receptor **1** + racemic dibenzoyl tartrate anion (d) receptor **1** + D-dibenzoyl tartrate anion and (e) receptor **1** + L-dibenzoyl tartrate anion.

ter. 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 DMSO-*d*. 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. Syntheses of compound 4. (*S*)-1,1′-bi-2-naphthol (2.00 g, 6.99 mmol), 10.10 g (72.65 mmol) of bromoacetic acid and 17.40 g (0.13 mol) of anhydrous potassium carbonate were suspended in 140 mL anhydrous methanol. The mixture was heated at reflux for 6 h and evaporated to dryness. Distilled water (60 mL) was added and the pH was adjusted to 1 with HCl (3 mol/L), the solution was then extracted with 3×50 mL $CHCl_3$. The combined organic phases were washed with distilled water (3×20 mL) and dried over anhydrous Na_2SO_4 for 5 h. After filtration, the solvent was evaporated to dryness to give a white solid 2.90 g, yield: 99.6%. mp: 94–96 °C. IR (film, cm^{-1}): *v* 3058, 2926, 1731, 1216, 751. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.97 (d, $J = 9.0$ Hz, 2H, Ar–H), 7.88 (d, $J = 8.1$ Hz, 2H, Ar–H), 7.10–7.40 (m, 8H, Ar–H), 4.57 (q, $J = 16.8$ Hz, 4H, OCH_2).

4.2.2. General procedure for the synthesis of 1–3. Compound **5** (0.74 g, 2.3 mmol) in 30 mL anhydrous $CHCl_3$ was added dropwise into a mixture of amino acid methyl ester hydrochloride (4.66 mmol) with Et_3N (1.0 mL) in anhydrous $CHCl_3$ (50 mL) under an ice-bath. After the addition, the mixture was stirred at room temperature for 24 h, and then washed successively with 10% HBr, saturated sodium bicarbonate solution, and brine. The organic layer was dried over anhydrous Na_2SO_4, and the solvent evaporated under reduced pressure. The residue was purified on a column of silica gel (eluent: $CHCl_3$/EtOH 100:1) to give the pure products **1**–**3** as a white solid.

Compound **1**: yield: 72.9%; mp: 192–193 °C; $[\alpha]_D^{20} = -77.0$ (*c* 0.05, $CHCl_3$); IR (film, cm^{-1}): *v* 3403, 3059, 2947, 1737, 1684, 1529, 1268, 1234, 750. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 7.88 (d, $J = 9.6$ Hz, 2H, CONH), 7.78 (d, $J = 8.1$ Hz, 2H, Ar–H), 7.46 (d, $J = 8.1$ Hz, 2H, Ar–H) 7.28 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.16 (t, $J = 8.1$ Hz, 2H, Ar–H), 7.06 (t, $J = 8.1$ Hz, 2H, Ar–H), 6.79 (d, $J = 8.1$ Hz, 2H, Ar–H), 4.34 (q, 4H, $J = 14.7$ Hz, OCH_2), 3.92–4.03 (m, 2H, C**H**CH_3), 3.36 (s, 6H, OCH_3), 0.90 (d, 6H, $J = 7.2$ Hz, CHC**H**$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.6, 163.2, 147.8, 128.9, 125.8, 125.2, 123.8, 122.9, 120.6, 120.1, 114.8, 109.8, 63.5, 47.8, 42.5, 12.7. ESI-MS *m*/*z* (%): 595 (M^++Na, 100); Elemental analysis calcd (%) for $C_{32}H_{32}N_2O_8$: C, 67.12; H, 5.63; N, 4.89; Found: C, 67.34; H, 5.80; N, 4.76.

Compound **2:** yield: 66.7%; mp: 170–172 °C; $[\alpha]_D^{20} = -37.6$ (*c* 0.05, $CHCl_3$); IR (film, cm^{-1}): *v* 3400, 3028, 2951, 1744, 1683, 1509, 1272, 1215, 751. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.00 (d, $J = 8.7$ Hz, 2H, CONH), 7.93 (d, $J = 8.1$ Hz, 2H, Ar–H), 7.03–7.44 (m, 16H, phenyl–H, Ar–H), 6.75 (d, $J = 6.6$ Hz, 2H, phenyl–H), 6.17 (d, $J = 8.1$ Hz, 2H, Ar–H), 4.57-4.64 (m, 2H, C**H**CH_2), 4.32 (q, 4H, $J = 15.3$ Hz, OCH_2), 3.57 (s, 6H, $COOCH_3$), 2.84 (q, 2H, $J = 6$ Hz, CHC**H**$_2$), 2.39 (q, 2H, $J = 9$ Hz, CHC**H**$_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 171.3, 168.3, 152.6, 136.0, 133.8, 130.6, 130.0, 129.4, 129.1, 129.0, 128.7, 128.5, 127.7, 127.2, 125.3, 124.9, 119.6, 114.4, 68.2, 52.9, 52.5, 37.8. ESI-MS *m*/*z* (%): 723 (M^+-1, 100); Elemental analysis calcd (%) for $C_{44}H_{40}N_2O_8$: C, 72.91; H, 5.56; N, 3.86. Found: C, 73.06; H, 5.84; N, 3.75.

Compound **3**: yield: 71.3%; mp: 119–121 °C; $[\alpha]_D^{20} = +24.4$ (*c* 0.05, $CHCl_3$); IR (film, cm^{-1}): *v* 3423, 3348, 3257, 3207, 3057, 1780, 1248, 1214, 1192, 1070, 1044, 827, 750. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.00 (s, 2H, Ind NH), 7.88 (d, $J = 8.1$ Hz, 2H, CONH), 7.80 (d, $J = 9.0$ Hz, 2H, Ar–H), 6.98–7.43 (m, 16H, Ar–H, Ind–H), 6.38 (s, 2H, Ind–H), 6.33 (d, 2H, $J = 8.1$ Hz, Ar–H) 4.67–4.74 (m, 2H, C**H**CH_2), 4.16 (q, 4H, $J = 15.3$ Hz, OCH_2), 3.56 (s, 6H, CH_3), 3.11 (q, 2H, $J = 4.5$ Hz, CHC**H**$_2$), 2.79 (q, 2H, $J = 7.5$ Hz, CHC**H**$_2$). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 171.8, 168.6, 152.8, 136.3, 133.7, 130.4, 130.0, 128.5, 127.4, 127.3, 125.5, 124.8, 122.6, 122.4, 119.8, 119.7, 118.6, 115.2, 111.7, 109.8, 68.6, 52.6, 52.0, 27.5. ESI-MS *m*/*z* (%): 802 (M^+, 100); Elemental analysis calcd (%) for $C_{48}H_{42}N_4O_8$: C, 71.81; H, 5.27; N, 6.98. Found: C, 71.95; H, 5.50; N, 6.86.

4.3. Tetrabutylammonium salts

All tetrabutylammonium salts were prepared by adding 2 equiv of tetrabutylammonium hydroxide in methanol to a solution of the corresponding amino acids (1 equiv) in methanol. The mixture was stirred at room temperature for 4 h and then evaporated to dryness under reduced pressure. The resulting syrup was dried at high vacuum 24 h, characterized by NMR and stored in a desiccator.

4.4. Binding studies

The studies on the binding properties of **1**–**3** were carried out in DMSO. The fluorescence titration was performed with a series of 5×10^{-5} mol/L solutions of receptor **1**–**3** containing different amounts of chiral anions (the excited wavelength was 338 or 339 nm, the excitation and emission slit width were $\lambda_{ex} = 1.5$ nm, $\lambda_{em} = 3$ nm, while it was $\lambda_{ex} = \lambda_{em} = 3$ nm for receptor **3**). ^{1}H NMR studies were recorded as adding equivalent dibenzoyl tartrate anions into receptors (4×10^{-3} mol/L). Association constants were calculated by means of a non-linear least-square curve fitting with Origin 7.0 (Origin-Lab Corporation).

Acknowledgment

We thank the National Natural Science Foundation for financial support (Grant No. 20572080).

References

1. (a) Jennings, K.; Diamond, D. *Analyst* **2001**, *126*, 1063–1067; (b) Yadav, G. D.; Sivakumar, P. *Bio. Eng. J.* **2004**, *19*, 101–107; (c) Schmidtchen, F. P. *Top. Curr. Chem.* **2005**, *255*, 1–29; (d) Nagai, K.; Maeda, K.; Takeyama, Y.; Sakajiri, K.; Yashima, E. *Macromolecules* **2005**, *38*, 5444–5451.
2. (a) Choi, M. S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 150–158; (b) Neelakandan, P. P.; Hariharan, M.; Ramaiah, D. *J. Am. Chem. Soc.* **2006**, *128*, 11334–11335; (c) Chen, H. G.; Wang, H. L.; Liu, J. W.; Wang, F. S.; Ma, J. T. *J. Mol. Catal. A: Chem.* **2007**, *269*, 125–132.
3. (a) Alfonso, I.; Rebolledo, F.; Gotor, V. *Chem. Eur. J.* **2000**, *6*, 3331–3338; (b) Kobayashi, Y.; Maeda, J.; Saigo, K. *Tetrahedron: Asymmetry* **2006**, *17*, 1617–1621; (c) Su, Z.; Borho, N.; Xu, Y. J. *J. Am. Chem. Soc.* **2006**, *128*, 17126–17131.
4. (a) Hartely, J. H.; James, T. D.; Ward, C. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3155–3160; (b) Borovkov, V. V.; Inoue, Y. *Org. Lett.* **2006**, *8*, 2337–2340; (c) Rodriguez-Docampo, Z.; Pascu, S. I.; Kubik, S.; Otto, S. *J. Am. Chem. Soc.* **2006**, *128*, 11206–11210.
5. (a) Li, Z. B.; Lin, J.; Pu, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1690–1693; (b) Kimaru, I. W.; Xu, Y. F.; McCarroll, M. E. *Anal. Chem.* **2006**, *78*, 8485–8490; (c) Trupp, S.; Schweitzer, A.; Mohr, G. J. *Org. Biomol. Chem.* **2006**, *4*, 2965–2968.
6. (a) Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–897; (b) Wang, Q.; Chen, X.; Tao, L.; Wang, L.; Xiao, D.; Yu, X. Q.; Pu, L. *J. Org. Chem.* **2007**, *72*, 97–101; (c) Matsumoto, M.; Maeda, H.; Hoshiya, N.; Watanabe, N.; Ijuin, H. K. *Tetrahedron Lett.* **2007**, *48*, 491–496.
7. (a) Zhao, J. Z.; Davidson, M. G.; Mahon, M. F.; Ciok-Köhn, G. K.; James, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 16179–16186; (b) Karakucuk, A.; Durmaz, M.; Sirit, A.; Yilmaza, M.; Demirb, A. S. *Tetrahedron: Asymmetry* **2006**, *17*, 1963–1968.
8. (a) Kuroda, Y.; Kato, Y. *J. Am. Chem. Soc.* **1995**, *117*, 10950–10958; (b) Bhattacharyya, T.; Nilsson, U. J. *Tetrahedron Lett.* **2001**, *42*, 2873–2875; (c) Narumi, F.; Hattori, T.; Matsumura, N.; Onodera, T.; Katagiri, H.; Kabuto, C.; Kameyama, H.; Miyano, S. *Tetrahedron* **2004**, *60*, 7827–7833.
9. Lehn, J. M.; Simon, J.; Moradour, A. *Helv. Chim. Acta* **1978**, *61*, 2407–2418.
10. (a) Gunnlaugsson, T.; Bichell, B.; Nolan, C. *Tetrahedron* **2004**, *60*, 5799–5806; (b) Wong, K. T.; Chen, H. F.; Fang, F. C. *Org. Lett.* **2006**, *8*, 3501–3504.
11. (a) Amendola, V.; Fabbrizzi, L.; Mangano, C.; Pallavicini, P. *Acc. Chem. Res.* **2001**, *34*, 488–493; (b) Gunnlaugsson, T.; Davis, A. P.; O'Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449–2452.
12. (a) Martinez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419–4476; (b) Kang, J.; Kima, H. S.; Jang, D. O. *Tetrahedron Lett.* **2005**, *46*, 6079–6082.
13. Valeur, B.; Pouget, J.; Bourson, J. J. *Phys. Chem.* **1992**, *96*, 6545–6549.
14. Collins, E. M.; Mckervey, M. A.; Madigan, E.; Moran, M. B.; Owens, M.; Ferguaon, G.; Harris, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, *2*, 3137–3142.
15. (a) Zheng, Y. S.; Zhang, C. *Org. Lett.* **2004**, *6*, 1189–1192; (b) Nakazawa, J.; Mizuki, M.; Shimazaki, Y.; Tani, F.; Naruta, Y. *Org. Lett.* **2006**, *8*, 4275–4278; (c) Mazik, M.; Cavga, H. *J. Org. Chem.* **2007**, *72*, 831–838.
16. Blanda, M. T.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **1989**, *54*, 4626–4636.
17. (a) Lee, J. Y.; Cho, E. J.; Mukamel, S.; Nam, K. C. *J. Org. Chem.* **2004**, *69*, 943–950; (b) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445–3448; (c) Chou, H. C.; Hsu, C. H.; Cheng, Y. M.; Cheng, C. C.; Liu, H. W.; Pu, S. C.; Chou, P. T. *J. Am. Chem. Soc.* **2004**, *126*, 1650–1651; (d) Ema, T.; Tanida, D.; Sakai, T. *Org. Lett.* **2006**, *8*, 3773–3775.