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Enantioselective Fluorescent Recognition of Amino Alcohol Based on Calix[4]arenes Bearing Diphenylethylenediamine Units

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Two novel chiral fluorescence calix[4]arenes functionalized at the lower rim with diphenylethylenediamine and thiourea units were synthesized and examined for their enantioselective recognition abilities by the fluorescence and ^{1}H NMR spectra in DMSO. The results indicate that 1 and 2 both formed a 1:1 complex with amino alcohol and exhibit good enantioselective fluorescent responses for phenylglycinol (receptor 1 $K_L/K_D = 4.85$, $\Delta\Delta G_0 = -3.90\,kJ\,mol^{-1}$).

Keywords: Chiral calix[4]arenes; Enantioselective recognition; Fluorescence; Amino alcohol

INTRODUCTION

Molecular recognition, and in particular chiral recognition, is a fundamental characteristic of biochemical systems. The study of synthetic model systems could contribute to the understanding of these processes and offer new perspectives for the development of pharmaceuticals, enantiomer-selective sensors, catalysts, selectors and other molecular devices [1–3]. Some chiral artificial receptors with specific structures have exhibited excellent enantioselective recognition abilities to the chiral enantiomers [4–6]. Among all the detection methods, fluorescent chemosensors for enantiomers have appeared to particularly attractive due to their simplicity, high sensitivity, and high detection limits for trace chemicals detection [7,8].

Chiral amino alcohols are useful as intermediates for making a variety of biologically active molecules [9,10] and also as ligands for stereoselective catalysts [11–13]. Kubo *et al.* prepared colored indophenol-derived calixcrowns allowing "naked-eye" detection of enantiomeric composition of chiral amine samples. Chirality was introduced by coupling 1,1′-binaphthyl units to the crown ether moieties. The complexations of amines, associated always with proton transfer from the host to the guest, induced dramatic color change [14,15]. Recently a novel class of chiral binaphthyl dendrimers was presented by Lin Pu and co-workers. The fluorescence of these dendrimers can be enantioselectively quenched by chiral amino alcohol [16–18].

Calixarenes are an important class of macrocyclic compounds and ideal platforms for the development of specific functional receptors for ions [19], anions [20,21] or neutral guests [22]. Diphenylethylenediamine is a useful chiral ligand and could be used to build the chiral stationary phases or other chiral receptors, which exhibit good chiral recognition abilities toward several racemic compounds [23,24]. Urea, thiourea and amide groups are good H-bonding donors, thiourea bonding units have especially strong hydrogen binding abilities, which are used widely to design and synthesize artificial receptors for anions or neutral molecules [25,26]. Although many enantioselective receptors for chiral amino alcohol have been synthesized and shown their application in chiral recognition [27–32], reports focusing their interests on the design of neutral molecular receptors based on calixarenes are still limited [33–35].

Herein, we report two novel fluorescent chemosensors (**1**, **2**) based on calix[4]arene bearing diphenylethylenediamine and thiourea units, which exhibit obvious fluorescence enhancement when

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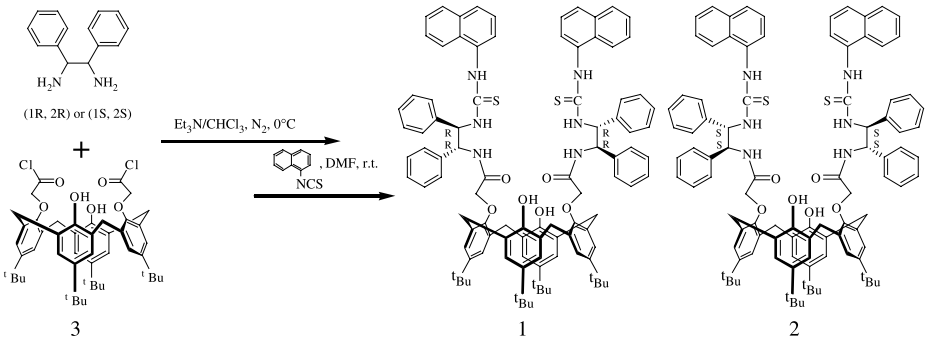

SCHEME 1 The synthesis of receptors **1** and **2**.

interact with two kind of amino alcohol. The chiral recognition study indicates that receptor **1** have good enantioselective fluorescent recognition toward the enantiomers of phenylglycinol.

RESULTS AND DISCUSSION

Synthesis

The synthesis of chiral calix[4]arene derivatives **1** and **2** is outlined in Scheme 1. The chiral fluorescence receptors (**1** and **2**) were efficiently synthesized by the reaction of compound **3** and (1R,2R) or (1S,2S)-diphenylethylenediamine to gain the intermediate, then reacted with 1-naphtylisothiocyanate to give target molecules **1** and **2**, which were well soluble in common organic solvents, such as $CHCl_3$, CH_3OH, CH_3COCH_3, DMSO and DMF. The structures of **1** and **2** were characterized by IR, ESI-MS, ^1H NMR, ^{13}C NMR spectra and elemental analysis.

The stereogenic centers of receptors **1** and **2** disturb the planar symmetry of the parent rings, which results in more aromatic carbon signals appearing in the ^{13}C NMR spectra of receptors **1** and **2**. This pattern is similar to that which has been observed in other chiral calix[4]arenes [36–38]. The ^1H NMR spectra of **1** and **2** show two sets of doublets for the bridging methylene protons and two sets of singlets for the *tert*-butyl group. This indicates that the two receptors are in the cone conformation in $CHCl_3$. The ^1H NMR spectra of **1** and **2** also exhibit one set of doublets for the $ArOCH_2$ protons. This splitting pattern may relate to the introduction of the chiral moieties in the molecules, as seen in other chiral calix[4]arenes [36–38]. Because of some differences in structure speculated from the ^1H NMR spectra that maybe induced by the weak distortion of calixarenes framework (see Supporting Information Part 1), we presumed that receptors **1** and **2** were not the complete enantiomorph, which would result in the inconsistent phenomena observed in the fluorescence titration and ^1H NMR study.

Fluorescence Spectra Study

The fluorescence spectra were recorded from the solution of **1** or **2** in the absence and presence of two kinds of amino alcohol such as phenylglycinol and phenylalaninol.

When a DMSO solution of receptor **1** was excited at 345 nm, it exhibited one emission maxima at 426 nm, which could be attributed to the intramolecular excimer formed by the two naphthalenes of the receptor **1** (Fig. 1) [39–41], while the emission of the monomer of naphthalene was covered by the strong emission of excimer [39–41]. Upon the addition of L-phenylglycinol, the fluorescence intensity of **1** at 460 nm showed obvious enhancement of about 420% with 300 equiv. of L-phenylglycinol (Fig. 1). While

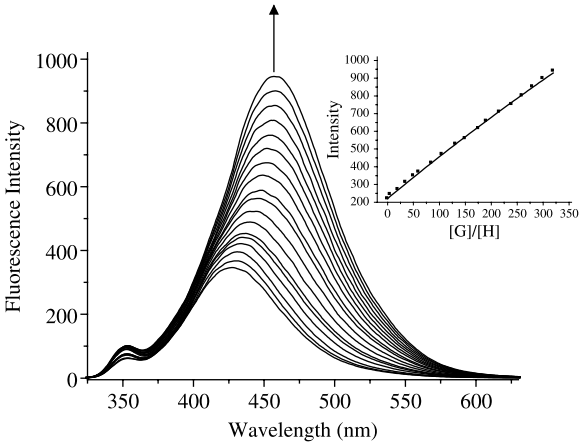

FIGURE 1 Fluorescence spectra of receptor **1** (5.0×10^{-5} mol L^{-1}) with L-phenylglycinol in DMSO. The equivalents of guest are: 0, 5.0, 15.0, 30.0, 50.0, 60.0, 85.0, 100.0, 130.0, 150.0, 180.0, 200.0, 220.0, 240.0, 260.0, 280.0, 300.0 and 320.0. $\lambda_{ex} = 345$ nm. Inset: changes of fluorescence intensity of **1** at 460 nm upon addition of L-phenylglycinol. The line is fitting curve. The correlation coefficient (R) of non-linear curve fitting is 0.9920.

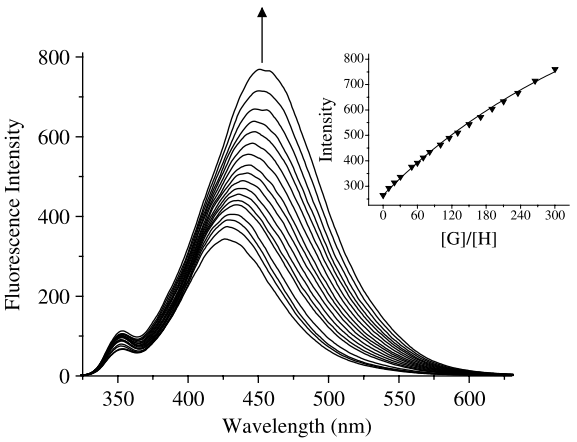

FIGURE 2 Fluorescence spectra of receptor **1** (5.0×10^{-5} mol L^{-1}) with D-phenylglycinol in DMSO. The equivalents of guest are: 0, 10.0, 20.0, 30.0, 50.0, 60.0, 70.0, 80.0, 100.0, 115.0, 130.0, 150.0, 170.0, 190.0, 210.0, 235.0, 265.0 and 300.0. $\lambda_{ex} = 345$ nm. Inset: changes of fluorescence intensity of **1** at 452 nm upon addition of D-phenylglycinol. The line is fitting curve. The correlation coefficient (R) of non-linear curve fitting is 0.9957.

the fluorescence intensity of **1** at 452 nm showed an enhancement of about 290% upon the addition of 300 equiv. of D-phenylglycinol (Fig. 2). The emission spectrum produced obviously red-shifted from 426 nm to 460 nm or 452 nm, respectively, which is an important indicator that there is an excimer formation. In the structure of **1**, two naphthalene rings were in close proximity, an intramolecular excimer was formed through the interaction of one naphthalene in the excited state with the other naphthalene in the ground state. When the phenylglycinol was added, the π−π stacking between the aromatic ring of phenylglycinol and the naphthalene of receptor promoted energy transfer from the excited fluorophore to the one in the ground state, and the enhancement of fluorescence were observed [42,43].

The satisfactory result (the correlation coefficient is over 0.99) of non-linear curve fitting confirmed that **1** and L- or D-phenylglycinol formed a 1:1 complex (see the top right plot of Figs. 1 and 2). For the complex of 1:1 stoichiometry, an association constant K_{ass} can be calculated by using the following equation in Origin 7.0 [43–49]:

$$I = I_0 + \frac{I_{lim} - I_0}{2C_0}\left\{C_H + C_G + 1/K_{ass}. - \left[(C_H + C_G + 1/K_{ass})^2 - 4C_H C_G\right]^{1/2}\right\}$$

Where I represents the fluorescence intensity, and C_H and C_G are the corresponding concentrations of host and guest. C_0 is the initial concentration of host. The association constants (K_{ass}) and correlation coefficients (R) obtained by a non-linear least-squares analysis of I versus C_H and C_G are listed in Table I.

The association constant of **1** with L-phenylglycinol is 29.1 M^{-1}, while it is 6.0 M^{-1} for D-phenylglycinol, which demonstrated **1** has a good enantioselective recognition ability for the enantiomers of phenylglycinol.

Similar phenomena was found when receptor **2** interacted with L- or D-phenylglycinol (see Supporting Information). The fluorescence intensity of **2** showed obvious enhancement of about 295% (at 455 nm) with 1100 equiv. of L-phenylglycinol. While the fluorescence intensity of **2** showed stronger enhancement of about 365% (at 456 nm) upon the addition of 1100 equiv. of D-phenylglycinol. The emission spectrum produced also obviously red-shifted from 428 nm to 455 nm or 456 nm, respectively. The association constant of **2** with L-phenylglycinol is 4.0 M^{-1}, while it is 7.8 M^{-1} for D-phenylglycinol. As shown in Fig. 4, the fluorescence responses of **1** toward L- or D-phenylglycinol is opposite to that of **2** toward the enantiomers of phenylglycinol, which demonstrated that the observed fluorescence difference of chiral calix[4]arene receptors **1** and **2** with the enantiomers of phenylglycinol is due to enantioselective recognition.

Compared with phenylglycinol, receptors **1** and **2** both exhibited slow fluorescent enhancement when L- or D-phenylalaninol was added into the solutions. Figure 3 shows the fluorescence change of **2** with the

TABLE I Association constants (K_{ass}), the correlation coefficients (R), enantioselectivities K_D/K_L for **1**, **2**, the Gibbs free energy changes ($-\Delta G_0$) and $\Delta\Delta G_0$ calculated from ΔG_0 for the complexation of receptors **1** and **2** with L/D-amino alcohol guests in DMSO at 25°C

Enry	Host	Guest	**K** (dm^3 mol^{-1})†	R	$\mathbf{K_L/K_D}$	$-\Delta G_0$(kJ mol^{-1})	$\Delta\Delta G_0$ (kJ mol^{-1})
1	**1**	L-phenylglycinol	29.1 ± 2.8	0.9920	4.85	8.36	−3.90
2	**1**	D-phenylglycinol	6.0 ± 1.6	0.9957		4.46	
3	**1**	L-phenylalaninol	21.0 ± 2.7	0.9922	1.44	7.54	−0.89
4	**1**	D-phenylalaninol	14.6 ± 1.5	0.9950		6.65	
5	**2**	L-phenylglycinol	4.0 ± 0.5	0.9994	0.51	3.45	1.63
6	**2**	D-phenylglycinol	7.8 ± 0.4	0.9980		5.08	
7	**2**	L-phenylalaninol	13.9 ± 2.0	0.9931	0.83	6.52	0.46
8	**2**	D-phenylalaninol	16.7 ± 2.3	0.9915		6.98	

† The data were calculated from fluorescence titrations in DMSO. All error values were obtained by the results of nonlinear curve fitting.

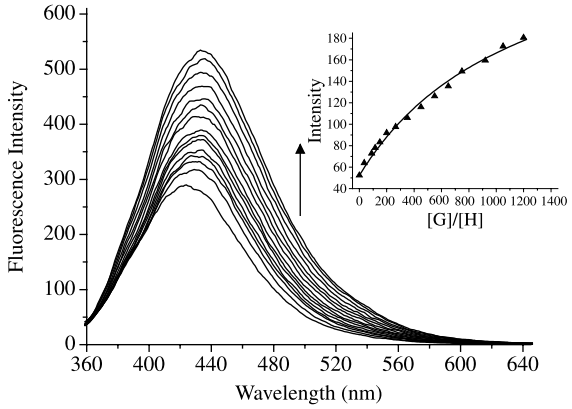

FIGURE 3 Fluorescence spectra of receptor **2** (5.0×10^{-5} mol L^{-1}) with D-phenylalaninol in DMSO. The equivalents of guest are: 0, 35, 90, 115, 150, 200, 265, 350, 450, 550, 650, 750, 920, 1050 and 1200. $\lambda_{ex} = 344$ nm. Inset; changes of fluorescence intensity of **2** at 500 nm upon addition of D-phenylalaninol. The line is fitting curve. The correlation coefficient (R) of non-linear curve fitting is 0.9915.

addition of D-phenylglycinol, only 190% (at 433 nm) enhancement was observed when 1200 equiv. of guest was added and the emission spectrum only produced a weak red-shift from 428 nm to 433 nm. Similar phenomena was observed when receptor **1** interacted with L- or D-phenylalaninol (see Supporting Information Part 2), which is probably due to the aromatic ring of phenylalaninol failing to form effective $\pi-\pi$ stacking with the naphthalene of the receptors to promote the energy transfer between the two fluorophores.

Figure 4 shows the fluorescence intensity change of receptor **1** or **2** in the presence of L- or D-phenylglycinol and phenylalaninol. Clear differences in the fluorescence responses indicate receptor **1** has good enantioselective recognition ability toward the enantiomers of phenylglycinol.

From the ^{1}H NMR spectra study, we found that the hydrogen bonding between host and guest was rather weak. Therefore, we presume that the emission enhancement of fluorescence might not be attributed to inhibition of the PET quenching mechanism, in which the interaction happened mainly through the hydrogen bonding between the neutral amino alcohol and the protons of thiourea attached to the naphthalene groups [50–52]. Many examples of anion-induced excimer formation in which anion coordination favors the proximity between the two fluorophores have been reported [53–55]. In this system, however, we could just conclude that the $\pi-\pi$ stacking between the aromatic ring of phenylglycinol and the naphthalene of receptors was the crucial point for the enhancement of fluorescence, because it is hard to presume that the neutral amino alcohol has sufficient ability to let the two naphthalene get closer considering the weak hydrogen bonding and steric hindrance caused by the aromatic rings of the host. The rather small association constants calculated from the fluorescence titration also confirmed our conclusion (see Table I).

In order to clarify the interaction mode, three kinds of anions were chosen as the guests to detect the fluorescent response when the hosts interacted with anions. Alpha-phenylglycine anion and mandelate, having a similar structure to phenylglycinol, could be used to compare the effect caused by the static and hydrogen bonding interaction between host and guest. The fluorescence intensity of **1** exhibited mild enhancement about 140% upon the addition of 280 equiv. of L-phenylglycine anion (Fig. 5). The emission spectrum produced a weak red-shift from 428 nm to 438 nm. The association constant of **1** with L-phenylglycine anion is 650.5 M^{-1}, which is much larger than that with L-phenylglycinol. Similar phenomena were observed when receptor **1** or **2** interacted with L-mandelate. When the anion was added into the solution of the receptor, an anion-receptor complex was formed through the static and hydrogen bonding interaction between the electron-sufficient anion and the protons of thiourea attached to the naphthalene groups. The cooperation effect

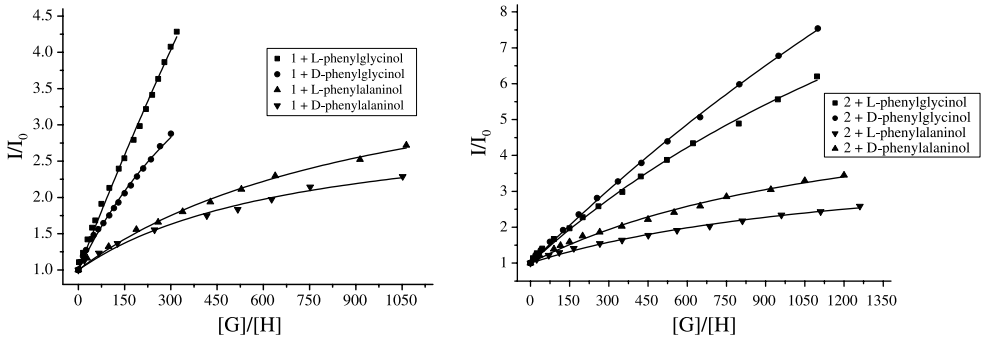

FIGURE 4 Fluorescence intensity change of receptor **1** (left) or **2** (right) (5.0×10^{-5} mol L^{-1}) with L- or D-phenylglycinol, L- or D-phenylalaninol in DMSO, the line is fitting curve.

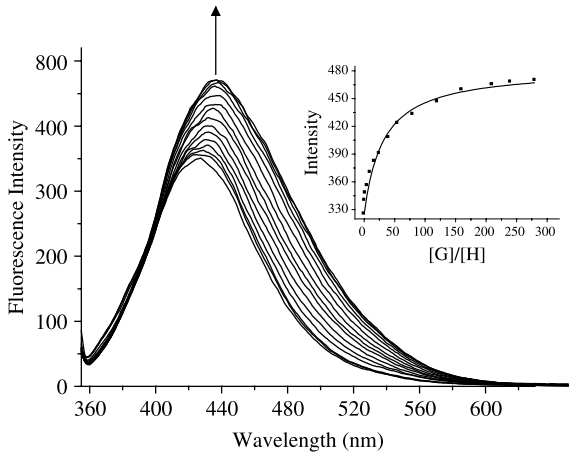

FIGURE 5 Fluorescence spectra of receptor **1** (5.0×10^{-5} mol L^{-1}) with L-phenylglycine anion in DMSO. The equivalents of anion are: 0, 1, 2, 5, 10, 18, 25, 40, 55, 80, 120, 160, 210, 240 and 280. $\lambda_{ex} = 345$ nm. Inset; changes of fluorescence intensity of **1** at 438 nm upon addition of L-phenylglycine anion. The line is fitting curve. The correlation coefficient (R) of non-linear curve fitting is 0.9922.

of the two hydrogen donating side arms in binding anions made the two branches get closer to induce spatial proximity between the two naphthalene groups in the presence of anions [43,53–55]. So the enhancement of the emission of **1** at 438 nm is due to the formation of a new conjugative system by excimer. However, because of the spatial hindrance caused by the aromatic rings and naphthalene groups, the interaction between the receptor and the anion by hydrogen bonding were still very weak, the small association constants proved our prediction, which indicated that the anion would not favor the proximity of the two naphthalene groups, so the anion-induced excimer formation is weak and caused a limited enhancement of fluorescent emission [43,53–55]. Tartrate is a kind of dicarboxylic acid anion that has not got the aromatic ring, which could be used to compare the π–π stacking effect. Limited enhancement of fluorescence was observed when **1** interacted with L-tartrate; the mechanism is similar to phenylglycine anion (see Supporting Information Part 3). Such obvious difference in the fluorescent response also proves that the π–π stacking is the most important in the fluorescence response upon complexation between the host and amino alcohol [56–59].

^{1}H NMR Study

The continuous variation methods were used to determine the stoichiometric ratios of receptors **1** or **2** with enantiomers of phenylglycinol [60,61]. The ^{1}H NMR spectra of **1**, **2** and L- or D-phenylglycinol in a variety of ratios in DMSO-d_6 at a constant total concentration of 4.0×10^{-3} M were taken. It was found that the methene proton (*CH) signal of phenylglycinol at δ 3.818 underwent a downfield shift gradually when treated with two receptors. The Job plots of Δδ vs the mole fraction $C_G/(C_H + C_G)$ of L- or D-phenylglycinol in the mixture was listed in the Supporting Information Part 4 [60,61]. The result illustrates that receptor **1** (or **2**)-L (or D)-phenylglycinol complex concentration approached the maximum when the mole fraction of guest was about 0.5, which indicates that the receptors **1**, **2** both form a 1:1 complex with the L- or D-phenylglycinol, respectively [62,63].

When L- or D-phenylglycinol was added into the equimolar amounts of solution of receptor **1** in DMSO-d_6, the *CH proton of guest showed a downfield shift from δ 3.818 ppm to 4.028 ppm or 3.965 ppm, respectively; while the OH proton also had a downfield shift from 4.748 ppm to 5.102 ppm or 4.980 ppm for L- or D-enantiomers. When treated with equimolar amounts of receptor **2** in DMSO-d_6, the *CH proton of L- or D-phenylglycinol had a downfield shift from δ 3.818 ppm to 3.884 ppm or 3.904 ppm, respectively; while the OH proton also had a downfield shift from 4.748 ppm to 4.890 ppm or 4.905 ppm for L- or D-enantiomers. The protons of amide and thiourea nearly have no change in chemical shift when the neutral guest was added into the solution of receptor **1** or **2** in DMSO-d_6, which indicated that the hydrogen bonding interaction were rather weak. Considering the above results, we presume that the interaction between host and guest mainly happened through the π–π stacking between the aromatic ring of phenylglycinol and the naphthalene of the receptors [56–59].

CONCLUSION

Two chiral fluorescence calix[4]arene containing diphenylethylenediamine and thiourea units were synthesized. The different fluorescent responses and the results of the ^{1}H NMR study confirm that both **1** and **2** exhibit a different enantioselective recognition ability toward phenylglycinol, and formed a 1:1 complex between host and guest. The complementary structure between host and guest, the good preorganization property of host and cooperative act by π–π stacking in the complexation may result in the good enantioselective recognition of receptors for the enantiomers of phenylglycinol.

EXPERIMENTAL

Materials and Methods

Melting point was determined with a Reichert 7905 melting-point apparatus (uncorrected). Optical rotations were taken on a PerkinElmer Model 341 polarimeter. IR spectra were obtained on a Nicolet

670 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury VX-300 M Hz spectrometer. ^{13}C NMR spectra were recorded on a Varian Inova unity−600 M Hz spectrometer. Mass spectra were recorded on a Finnigan LCQ advantage mass spectrometer. Elemental analysis was determined with a Carlo-Erba 1106 instrument. Fluorescence spectra were obtained on a Shimadzu RF−5301 spectrometer. The UV−vis spectra were performed with a TU-1901 spectrophotometer. $CHCl_3$ was washed with water and dried with $CaCl_2$. DMF and Et_3N were dried and distilled from CaH_2 and KOH respectively. All other commercially available reagents were used without further purification. The anions were used as their tetrabutylammonium salts. Compound **3** was synthesized according to the method reported in the literature [64]. (1*R*,2*R*)-Diphenylethylenediamine or (1*S*,2*S*)-diphenylethylenediamine were purchased from the Acros corporation.

Synthesis

General Procedure for the Synthesis of 1 and 2

To a solution in ice brine bath of (1*R*,2*R*)-Diphenylethylenediamine or (1*S*,2*S*)-diphenylethylenediamine (0.21 g, 1.0 mmol) and triethylamine (2.0 mmol) in dry $CHCl_3$ (10 ml), **3** (0.40 g, 0.5 mmol) in dry $CHCl_3$ (50 ml) was added dropwise for 12 h under nitrogen atmosphere. After addition, the reaction mixture was stirred at 0°C overnight and then stirred for 5 h at room temperature. The solvent was evaporated under reduced pressure to gain the viridescent crude products; then the crude products and 1-naphthylisothiocyanate (0.185 g, 1 mmol) were stirred in dry DMF (20 ml) at room temperature for 24 h. The solvent was removed under reduced pressure; the residue was dissolved in the 50 ml $CHCl_3$ and then washed with brine twice. The organic layer was collected and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on Silica gel (eluant: $CHCl_3/CH_3CH_2OH$ = 200:1 (v/v)).

*5,11,17,23-Tetra-4-*tert*-butyl-25,27-bis(1-naphthythioureido-(1R,2R)-1,2-diphen-ylethyl-aminocarbonylmethoxy)-26,28-dihydroxycalix[4]arene (1)*

Pure product **1** (0.20 g) was obtained as yellow powder in 26.3% yield; **1** was decomposed at 220°C. $[\alpha]_D^{20} = +36.06°$ ($c = 0.05$, $CHCl_3$); IR (KBr, cm^{-1}) ν: 3383, 3057, 2960, 2867, 1698, 1599, 1526, 1483, 1388, 1363, 1298, 1241, 1200, 1123, 1034, 872, 773, 699, 603, 559; ^{1}H NMR ($CDCl_3$) δ(ppm): 1.15 (s, 18H, Bu^t), 1.30 (s, 18H, Bu^t), 3.40 (d, $J = 12.9$ Hz, 2H, $ArCH_2Ar$), 3.54 (d, $J = 14.1$ Hz, 2H, $ArCH_2Ar$), 3.93 (d, $J = 14.1$ Hz, 2H, $ArCH_2Ar$), 4.31 (d, $J = 12.6$ Hz, 2H, $ArCH_2Ar$), 4.39 (d, $J = 14.4$ Hz, 2H, OCH_2CO), 4.51 (d, $J = 14.7$ Hz, 2H, OCH_2CO), 5.97 (d, $J = 10.5$ Hz, 2H, C*HCH), 6.82 (d, $J = 6.0$ Hz, 2H, CHC*H), 7.01 (s, 4H, ArH-calix), 7.06 (s, 4H, ArH-calix), 7.12−7.25 (m, 16H, ArH), 7.32−7.36 (m, 4H, ArH-DPDEA, 4H, H-naph), 7.50−7.65 (m, 6H, NH-naph), 7.71−7.73 (m, 4H, NH-naph), 7.85−7.94 (m, 4H, NHCSNH, D_2O, exchangeable), 8.22 (s, 2H, ArOH), 8.67 (d, $J = 10.8$ Hz, 2H, CONHC); ^{13}C NMR ($CDCl_3$): δ (ppm) 31.3, 31.7, 31.9, 32.8, 34.2, 34.5, 57.4, 64.3, 74.4, 122.6, 125.4, 125.5, 125.9, 126.0, 126.3, 126.6, 127.1, 127.3, 127.5, 127.8, 127.9, 128.0, 128.5, 128.6, 128.8, 128.9, 129.2, 129.3, 130.0, 132.0, 133.2, 135.0, 139.2, 143.3, 147.4, 149.0, 150.0, 167.2; ESI-MS m/z: 1524(M^+, 100). Elemental analysis calc. (%) for $C_{98}H_{102}N_6O_6S_2$: C, 77.23; H, 6.75; N, 5.51; found: C, 77.15; H, 6.81; N, 5.48.

*5,11,17,23-Tetra-4-*tert*-butyl-25,27-bis(1-naphthylthioureido-(1S,2S)-1,2-diphen-ylethyl-aminocarbonylmethoxy)-26,28-dihydroxycalix[4]arene (2)*

Pure product (0.28 g) was obtained as yellow powder in 27.8% yield; **2** was decomposed at 220°C. $[\alpha]_D^{20} = 52.79°$ ($c = 0.05$, $CHCl_3$); IR (KBr, cm^{-1})ν: 3381, 3056, 2959, 2866, 1699, 1598, 1515, 1483, 1450, 1360, 1299, 1263, 1241, 1200, 1123, 1094, 1037, 873, 798, 774, 700, 605, 558, 519; ^{1}H NMR ($CDCl_3$) δ(ppm): 1.14 (s, 18H, Bu^t), 1.29 (s, 18H, Bu^t), 3.39 (d, $J = 12.6$ Hz, 2H, $ArCH_2Ar$), 3.53 (d, $J = 14.4$ Hz, 2H, $ArCH_2Ar$), 3.91 (d, $J = 13.8$ Hz, 2H, $ArCH_2Ar$), 4.30 (d, $J = 12.3$ Hz, 2H, $ArCH_2Ar$), 4.36 (d, $J = 14.7$ Hz, 2H, OCH_2CO), 4.48 (d, $J = 14.7$ Hz, 2H, OCH_2CO), 5.97 (d, $J = 11.1$ Hz, 2H, C*HCH), 6.80 (d, $J = 7.2$ Hz, 2H, CHC*H), 7.00 (s, 4H, ArH-calix), 7.05 (s, 4H, ArH-calix), 7.12 (s, 4H, ArH), 7.16 (s, 4H, ArH), 7.31 (s, 4H, ArH), 7.34 (s, 4H, ArH), 7.47−7.52 (m, 4H, ArH-DPDEA, 12H, H-naph), 7.69−7.71 (m, 2H, NH-naph), 7.78−7.93 (m, 4H, NHCSNH, D_2O, exchangeable), 8.23 (s, 2H, ArOH), 8.66 (d, $J = 10.8$ Hz, 2H, CONHC); ^{13}C NMR ($CDCl_3$): δ (ppm) 31.1, 31.3, 31.9, 32.8, 34.2, 34.5, 57.3, 64.3, 74.3, 122.1, 122.6, 125.4, 125.5, 125.9, 126.0, 126.1, 126.3, 126.6, 127.1, 127.3, 127.5, 127.8, 127.9, 128.0, 128.5, 128.6, 128.7, 128.9, 129.2, 129.3, 130.2, 130.4, 131.9, 133.2, 134.3, 134.4, 134.7, 134.9, 135.0, 137.6, 139.1, 143.3, 147.4, 149.0, 150.0, 167.2; ESI-MS m/z: 1524(M^+, 100). Elemental analysis calc. (%) for $C_{98}H_{102}N_6O_6S_2$: C, 77.23; H, 6.75; N, 5.51; found: C, 77.13; H, 6.79; N, 5.49.

Fluorescence Spectra Measurement

The host compounds **1** and **2** were prepared as stock solution in DMSO for 5×10^{-4} mol/L. Amino alcohol guests were prepared to approximate 0.175 mol/L and 0.875 mol/L of stock solution in DMSO. The work solutions were prepared by adding

different volumes of guest solution to a series of test tubes, then, the same amount of stock solution of host compound was added into each test tube followed by dilution to 3.5 ml by DMSO. After being shaken for several minutes, the work solution could be measured immediately.

Job Plot

The solutions (4.0×10^{-3} M) of host **1**, **2**, L- or D-phenylglycinol in DMSO-d_6 were freshly prepared. The host and guest were added to NMR tubes in ratios of 1:9, 2:8, ... to 9:1, respectively. The resulting mixed solutions were allowed to stand at room temperature for 4 h before the ^{1}H NMR measurements.

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