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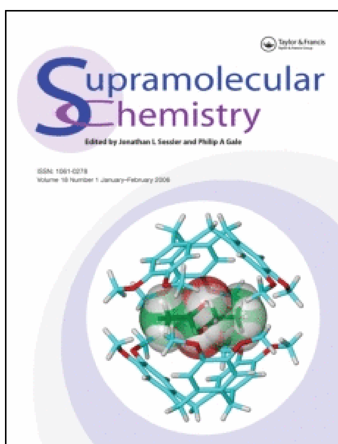

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Highly selective fluorescent recognition of amino alcohol based on chiral calix[4]arenes bearing L-tryptophan unit

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Four two-armed chiral calix[4]arenes (**1a**–**1d**) functionalised at the lower ring with amino acid units have been synthesised and the structures of these compounds were characterised by IR, MS, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis. Their molecular recognition abilities towards amino alcohol were examined by fluorescence titration experiment in three kinds of solution. The results indicated that these receptors exhibited excellent fluorescent response to phenylglycinol and could distinguish phenylglycinol from phenylalaninol rapidly through the obvious difference in the fluorescent response. Solvent comparative experiments also indicated that acetonitrile was the best solvent to detect these phenomena.

Keywords: calix[4]arene; molecular recognition; fluorescence; amino alcohol

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Introduction

Fluorescence molecular sensors for detection of ions or molecules have attracted considerable interest because of their high sensitivity and potential applications in analytical, biological and clinical biochemical environments (*1*–*3*). Chiral amino alcohols are useful as intermediates for making a variety of biologically active molecules (*4*, *5*) and also as ligands for stereoselective catalysts (*6*–*8*). Recently, much research effort has been devoted to the synthesis of chiral chromogenic/fluorogenic supramolecular hosts capable of distinguishing between the enantiomers of chiral amino alcohol guest molecules (*9*–*12*). Among these chemical sensors, calixarenes have been found to be an excellent platform for the design of receptor sites for the specific recognition of guests (*13*–*15*). Diamond reported a propranolol amide derivative of *p*-allycalix[4] arenes, which can discriminate between the enantiomers of phenylalaninol through the quenching of the fluorescence emission in methanol; while the (*S*)-dinaphthylprolinol calix[4]arene derivative can discriminate between the enantiomers of phenylglycinol (*16*, *17*). Then the (*R*)- and (*S*)-enantiomers of a binaphthyl-appended calix[4]crown-6 ether with two 2,4-dinitrophenylazo chromophore units were reported and exhibited two-step process for the enantioselective recognition of phenylglycinol (*18*). Herein, we report four two-armed chiral calix[4]arenes derivatives bearing L-tryptophan units, which exhibit high-sensitive fluorescence response to phenylglycinol and can discriminate phenylglycinol from phenylalaninol quickly through the obvious difference in the fluorescence titration, they also have good enantioselective recognition abilities towards phenylglycinol. Solvent comparative experiments indicate that acetonenitrile is the most proper solvent for the fluorescence detection to determine the concentration of guests and carry out the process of molecular recognition.

Results and discussion

Synthesis

These four two-armed chiral calix[4]arenes derivatives (**1a**–**1d**) were synthesised as outlined in Scheme 1. The two-armed diamino calix[4]arenes compounds **2a**–**d** were synthesised according to the method reported in the literature (*19*) and reacted with N-Boc-protected L-tryptophan in chloroform to obtain the target compounds **1a**, **1b**, **1c** and **1d** in 38, 23, 28 and 29% yields, respectively. They were easily soluble in common organic solvent such as $CHCl_3$, CH_3CN, DMSO and DMF. The structures of these compounds were characterised by IR, MS, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis.

Fluorescence spectra study

The fluorescence spectra were recorded from the solution of **1a**–**1d** in the absence and presence of two kinds of amino alcohol such as phenylglycinol and phenylalaninol. First we chose CH_3CN as the solvent to investigate the fluorescence response. Figure 1 shows the fluorescence emission of receptor **1d** ($5.0 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$)

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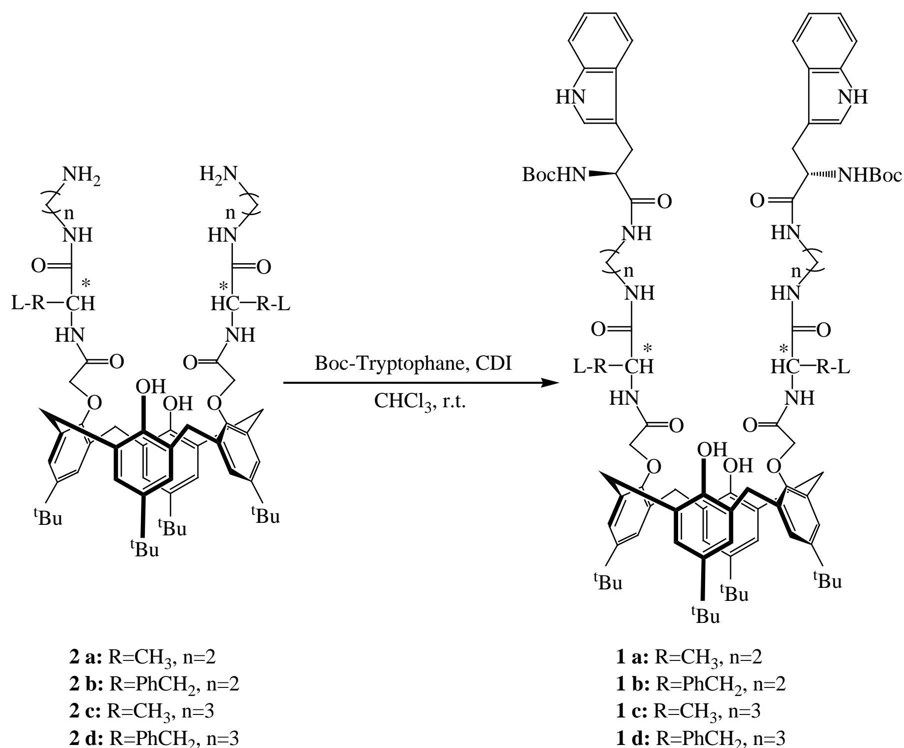

Scheme 1. The synthesis of compounds **1a** ~ **1d**.

with different concentrations of (*R*)-phenylglycinol in CH_3CN. When the solution of receptor **1d** in CH_3CN was excited at 368 nm, it exhibited one weak emission, which could be attributed to the intramolecular excimer formed by the two indole rings of the receptor **1d** (*20*, *21*). The fluorescence emission of **1d** ($\lambda_{ex} = 368$ nm) rapidly increased along with the addition of (*R*)-phenylglycinol, while the fluorescent intensity of **1d** at 456 nm showed enhancement about 800% with the 6.0 equiv. of guest. Compared with (*R*)-phenylglycinol, (*R*)-phenylalaninol could not induce such obvious fluorescence enhancement as shown in the Figure 2, and the intensity of **1d** at 450 nm just increased about 35% with the same equiv. of guest. The fluorescence emission could enhance gradually with more guests, and then the intensity

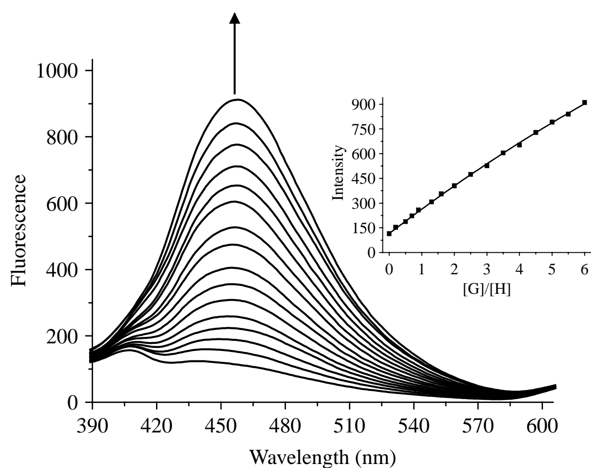

Figure 1. Fluorescence spectra of receptor **1d** (5.0×10^{-5} mol l^{-1}) with (*R*)-phenylglycinol in CH_3CN. The equivalents of guest are: 0, 0.2, 0.5, 0.7, 0.9, 1.3, 1.6, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0. $\lambda_{ex} = 368$ nm. Inset: changes of fluorescence intensity of **1d** at 456 nm upon addition of (*R*)-phenylglycinol. The line is fitting curve. The correlation coefficient (*R*) of non-linear curve fitting is 0.9993.

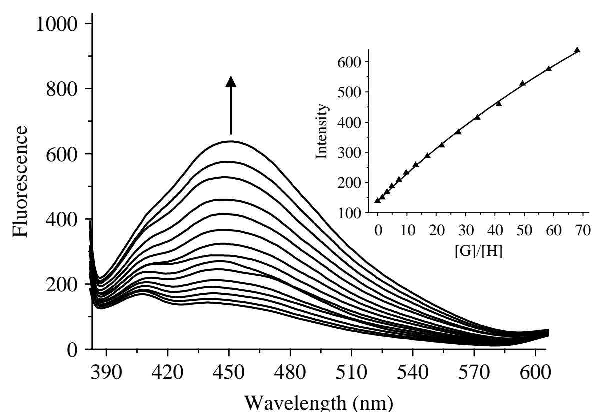

Figure 2. Fluorescence spectra of receptor **1d** (5.0×10^{-5} mol l^{-1}) with (*R*)-phenylalaninol in CH_3CN. The equivalents of guest are: 0, 1.5, 3.0, 6.0, 7.5, 10.0, 12.5, 17.0, 22.0, 27.5, 35.0, 40.0, 50.0, 60.0 and 70.0. $\lambda_{ex} = 368$ nm. Inset: changes of fluorescence intensity of **1d** at 450 nm upon addition of (*R*)-phenylalaninol. The line is fitting curve. The correlation coefficient (*R*) of non-linear curve fitting is 0.9980.

Table 1. Association constants (K_{ass}) and enantioselectivities K_R/K_S of receptors **1a** ~ **1d** with R/S-amino alcohol guests in CH_3CN or $CHCl_3$ at 25°C.[a]

	Receptor **1a**		Receptor **1b**		Receptor **1c**		Receptor **1d**	
Guest	*K*ass (dm^3 mol^{-1})[b]	K_R/K_S	*K*ass (dm^3 mol^{-1})[b]	K_R/K_S	*K*ass (dm^3 mol^{-1})[b]	K_R/K_S	*K*ass (dm^3 mol^{-1})[b]	K_R/K_S
In CH_3CN								
(*R*)-**3**	88.5 ± 10.6	2.54	110.8 ± 10.6	0.77	145.7 ± 12.3	0.44	564.5 ± 51.5	2.00
(*S*)-**3**	34.9 ± 3.9		144.1 ± 14.5		331.2 ± 28.7		281.8 ± 23.4	
(*R*)-**4**	10.3 ± 1.5	1.98	18.6 ± 4.2	0.94	51.3 ± 9.8	0.41	91.2 ± 13.7	0.81
(*S*)-**4**	5.2 ± 0.8		19.7 ± 3.8		124.0 ± 13.5		112.0 ± 9.8	
In $CHCl_3$								
(*R*)-**3**	15.6 ± 2.4	2.44	16.8 ± 2.6	1.18	24.7 ± 3.5	0.17	223.4 ± 35.2	2.73
(*S*)-**3**	6.4 ± 1.3		14.2 ± 2.0		141.3 ± 12.6		81.9 ± 10.5	
(*R*)-**4**	5.7 ± 1.1	2.28	11.7 ± 1.9	1.43	27.3 ± 3.8	0.76	48.3 ± 6.3	1.63
(*S*)-**4**	2.5 ± 0.6		8.2 ± 1.2		35.6 ± 4.6		29.7 ± 2.9	

[a]The association constants of receptors **1a–1d** with R/S-amino alcohol in DMSO were too small to be reliable. [b]The values were calculated from the change of the fluorescence spectra.

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could reach 415% upon the addition of 60.0 equiv. of (*R*)-phenylalaninol.

The satisfactory result (the correlation coefficient is over 0.99) of non-linear curve fitting confirmed that receptor **1d** and (*R*)-phenylglycinol formed 1:1 complex (*22–25*) (see the top right plot of Figure 1). For the complex of 1:1 stoichiometry, an association constant K_{ass} can be calculated by using the following equation in origin 7.0: (*22–25*):

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

where I represents the fluorescence intensity, and C_H and C_G are the corresponding concentrations of host and guest, respectively. 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 1. The association constant of **1d** with (*R*)-phenylglycinol was $564.5\,M^{-1}$, while that of **1d** with (*R*)-phenylalaninol was $91.2\,M^{-1}$, which demonstrated that **1d** has a good recognition ability between phenylglycinol and phenylalaninol.

In the structure of **1d**, two indole rings were in close proximity, and an intramolecular excimer was formed through the interaction of one indole in the excited state with the other indole in the ground state. When the phenylglycinol was added, the π–π stacking between the aromatic ring of phenylglycinol and the indole rings of receptor promoted energy transfer from the excited fluorophore to the other one in the ground state, and the enhancement of fluorescence was observed (*1–3*, *22*, *23*). In order to confirm this presumption, we chose (*R*)-2-amino-1-propanol that has no phenyl ring as the guest to investigate the fluorescence response under the same condition. The fluorescence emission of **1d** nearly had no change with 100 equiv. of guests (see Supporting Information part 2), which illustrated that the fluorescent enhancements rely heavily on the π–π stacking effect (*26–28*). Phenylalaninol could not induce such obvious fluorescence enhancement probably because the aromatic ring of phenylalaninol was incapable of forming effective π–π stacking with the indole rings of receptors to promote the energy transfer between the two fluorophore. In order to investigate these phenomena deeply, we also chose some anions such as mandelate, phenylglycine anion and malate as the guests to observe the changes of fluorescence emission. With the addition of large amount of mandelate or phenylglycine anion, the fluorescence emission of receptor **1d** nearly had no change, while the malate could just induce the enhancement of fluorescence about 250% with 50 equiv. of guest. It is indicated that the anion could not favour the proximity of the two indole rings obviously, so the anion-induced excimer formation was still weak and the limited enhancement of fluorescent emission was caused (*29–31*). Such obvious differences in the fluorescent response also prove that the π–π stacking is the most important factor in the fluorescence response upon complexation between the host and amino alcohol (Figure 3).

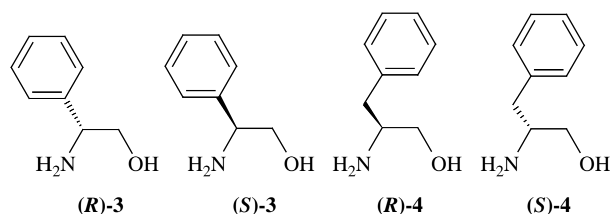

Figure 3. Structures of **3** and **4**.

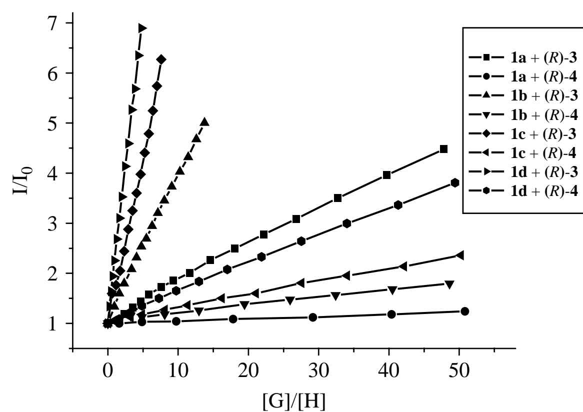

Figure 4. Fluorescence intensity change of receptors **1a–1d** (5.0×10^{-5} mol l^{-1}) with (*R*)-phenylglycinol or (*R*)-phenyl alaninol in CH_3CN.

Similar phenomena have also been observed when receptors **1a–1c** interacted with phenylglycinol or phenylalaninol in CH_3CN as shown in Figure 4. All these receptors exhibited obvious fluorescent enhancement with the addition of (*R*)-phenylglycinol, while exhibiting rather weak response to (*R*)-phenylalaninol. Moreover, interestingly we found that receptors **1c** or **1d** exhibited better fluorescent response compared with **1a** or **1b**, which may be because the receptor **1c** or **1d** has a much more flexible structure than **1a** or **1b**. And the flexible structures could enable the two indole rings to approach closer to promote the energy transfer process more easily (*21*).

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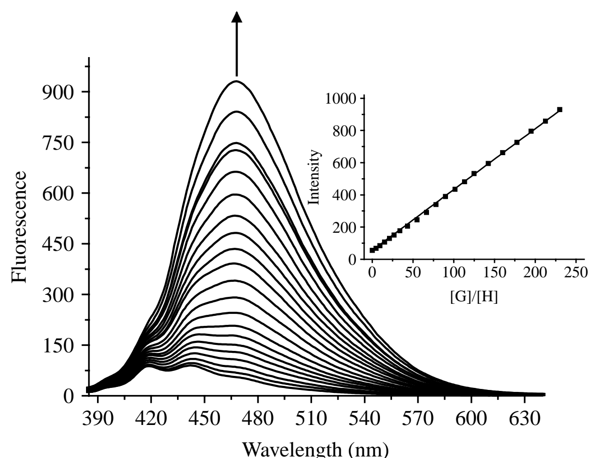

Figure 5. Fluorescence spectra of receptor **1d** (5.0×10^{-5} mol l^{-1}) with (*R*)-phenylglycinol in DMSO. The equivalents of guest are: 0, 5, 10, 15, 20, 25, 35, 45, 55, 65, 80, 90, 100, 115, 125, 140, 160, 180, 195, 215 and 230. $\lambda_{ex} = 371$ nm. Inset: changes of fluorescence intensity of **1d** at 468 nm upon addition of (*R*)-phenylglycinol. The line is fitting curve. The correlation coefficient (*R*) of non-linear curve fitting is 0.9990.

Solvent has an important effect on the fluorescence detection (*22*). In order to investigate the solvent effect; we chose DMSO and $CHCl_3$ as the solvent against CH_3CN to obtain the differences of fluorescent response. Figure 5 shows the fluorescence emission change of **1d** upon the addition of (*R*)-phenylglycinol in DMSO. In comparison with the obvious and rapid fluorescence enhancement shown in Figure 1, we found this process to take place much more slowly, and 65 equiv. of phenylglycinol could just induce 520% enhancement, while the association constant between the host and guest was rather small and unreliable.

A mixed solvent (containing 80% DMSO and 20% CH_3CN) was also used to detect whether the fluorescence emission was switched on with the addition of CH_3CN to DMSO solution (as shown in Supporting Information Part 3 figures S3.10–S3.13). In the mixed solvent, the fluorescence emission change is much quicker compared with that in the pure DMSO, while it is slower than that in the pure CH_3CN. We presume that the CH_3CN will largely promote the fluorescence enhancement; these phenomena are being further researched.

Although receptor **1d** did not exhibit sensitive fluorescence response to (*R*)-phenylglycinol in DMSO, it still exhibited good molecular recognition ability towards phenylglycinol and phenylalaninol as shown in the Figure 6. Based on these phenomena, we could use these receptors as chemical sensors in practice. The CH_3CN solution of receptors could be prepared accurately to detect low concentration of amino alcohol guests and distinguish phenylglycinol from phenylalaninol rapidly. When we need to detect the high concentration of guests, the DMSO solution of receptors can be used as the substitute.

$CHCl_3$ is the most common solvent in organic synthesis. The fluorescence changes of receptors **1a** ~ **1d**

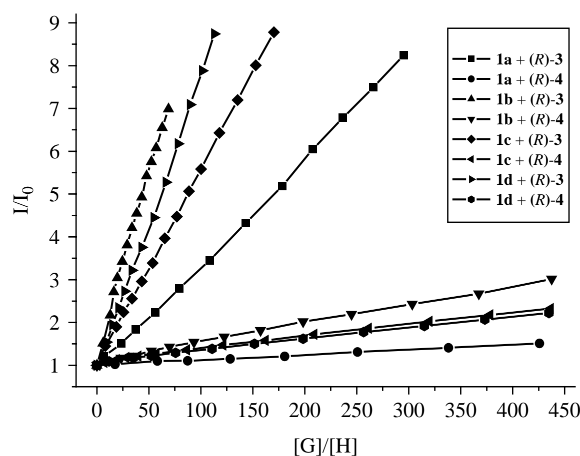

Figure 6. Fluorescence intensity change of receptors **1a–1d** (5.0×10^{-5} mol l^{-1}) with (*R*)-phenylglycinol or (*R*)-phenyl alaninol in DMSO.

with the addition of phenylglycinol or phenylalaninol were also investigated. Compared with the highly selective recognition abilities in CH_3CN or DMSO, these four receptors just exhibited sensitive fluorescence response to the guests in $CHCl_3$, but the chemical recognition abilities were reduced. The fluorescence emission of receptors **1c** or **1d** even could cause obvious enhancement with a small amount of (*R*)-phenylalaninol (Figure 7). Therefore, $CHCl_3$ is not the proper solvent to detect the amino alcohol through fluorescence titration for these receptors. Consistent phenomena that receptors **1a–1d** all have much more obvious fluorescence enhancement with the addition of (*S*)-phenylglycinol than with that of (*S*)-phenylalaninol have been found in these three solvents (see Supporting Information part 4).

Because of the asymmetry structures and multi-chiral centres of these receptors, the enantioselective recognition abilities towards phenylglycinol or phenylalaninol were also studied by fluorescence titration. From the data listed in the Table 1, receptors **1a–1d** just have common enantioselective recognition abilities in CH_3CN, while receptors **1c** and **1d** have better chiral recognition abilities towards enantiomers of phenylglycinol in $CHCl_3$ as shown in Figure 8. The association constant of **1c** with (*R*)-phenylglycinol was $24.7\,M^{-1}$, while that of **1c** with (S)-enantiomers was $141.3\,M^{-1}$, yielding an S/R selectivity ($Kass_{(S)}/Kass_{(R)} = 5.72$) for phenylglycinol. The receptors good preorganised structures provided by the calix[4]arene units and the chiral centre of L-tryptophan may be responsible for the enantioselective recognition process (*16–18*, *20*, *21*).

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Conclusion

Summing up, four fluorescence chemical sensors based on two-armed chiral calix[4]arenes bearing *l*-tryptophan units have been synthesised and they exhibited excellent selective fluorescent recognition abilities towards phenylglycinol and phenylalaninol. Solvent comparative experiments demonstrated that CH_3CN was the most proper solvent to detect the concentration of amino alcohol and carry out the chemical recognition process. Although these receptors just exhibited common enantiomers recognition abilities towards amino alcohol guests, their highly selective fluorescence response to phenylglycinol and phenylalaninol will promote them to be used as good chemical sensors in the near future.

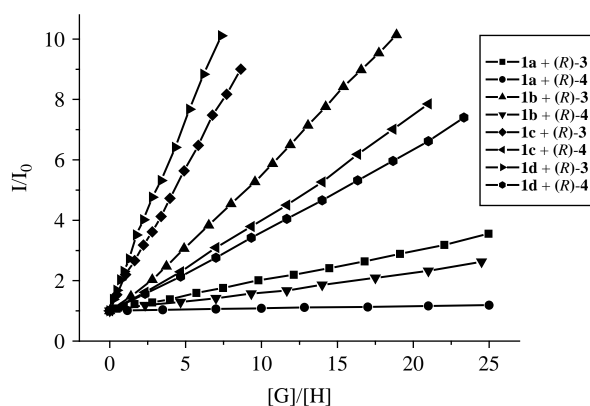

Figure 7. Fluorescence intensity change of receptors **1a–1d** ($5.0 \times 10^{-5}\,mol\,l^{-1}$) with (*R*)-phenylglycinol or (*R*)-phenylalaninol in $CHCl_3$.

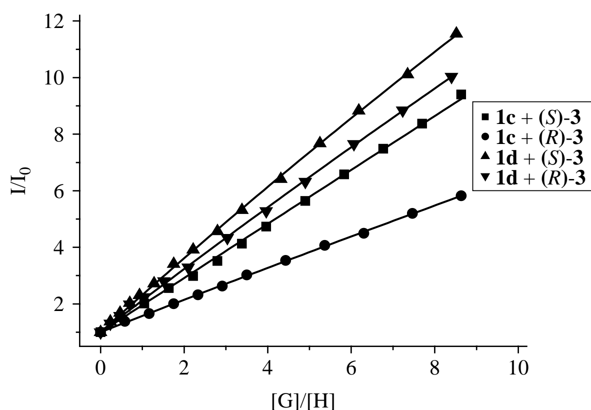

Figure 8. Fluorescence intensity change of receptors **1c** or **1d** ($5.0 \times 10^{-5}\,mol\,l^{-1}$) with (*R*) or (*S*)-phenylglycinol in $CHCl_3$. The line is fitting curve.

Experimental

Material 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. ^1H NMR spectra were recorded in $CDCl_3$, on a Varian Mercury VX-300 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian Inova unity–600 MHz 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. $CHCl_3$ was washed with water and dried from $CaCl_2$. Compounds **2a–2d** were synthesised according to the method reported in the literature (*19*).

Synthesis

*General procedure for the synthesis of chiral calix[4]arene derivatives **1a–d**:*

To a stirred and ice cooled solution of N-Boc-protected tryptophan (0.61 g, 2.0 mmol) in anhydrous chloroform

(40 ml) was added CDI (0.36 g, 2.2 mmol), and the mixture was stirred for 2 h. And then **2a** ~ **d** (1.0 mol) in the $CHCl_3$ 80 ml was added to the complex solution. The mixture was stirred 48 h under Ar protection at room temperature and then increased to 55 for 5 h. The reaction solution was washed with brine, then the organic solution 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 yielding white powder. These four compounds gave spectroscopic data in agreement with the structures indicated. (see Supporting Information part 1)

Compound 1a: (eluant: $CHCl_3/CH_3CH_2OH$ = 30:1 (V/V)). Pure product was obtained as white powder (0.60 g, 38%). m.p. 147–149°C; $(\alpha)_D^{20} = +25.64°$ (*c* 0.015, $CHCl_3$); IR (KBr/cm^{-1}) ν: 3421, 2963, 1660, 1541, 1484, 1384, 1364, 1245, 1168, 1047, 743; ^1H NMR ($CDCl_3$): δ(ppm) 1.24(s, 18H, Bu^t), 1.44(s, 6H, CCH_3), 1.57(s, 18H, Bu^t), 1.71(s, 18H, Bu^t), 3.05–3.16(m, 4H, Indole-CH_2, 4H, NCH_2C), 3.43–3.53(m, 4H, $ArCH_2Ar$), 3.72–3.75(m, 4H, NCH_2C), 4.19–4.26(m, 4H, $ArCH_2$-Ar), 4.30(d, $J = 15.3$ Hz, 2H, OCH_2CO), 4.56–4.58(m, 2H, NC*HCO), 4.87(d, $J = 15$ Hz, 2H, OCH_2CO), 5.36–5.39(m, 2H, NC*HCO-Indole), 6.43(s, 2H, NH-Boc), 6.99–7.08(m, 8H, ArH, 2H, Indole), 7.16–7.23(m, 4H, Indole), 7.30(d, $J = 8.1$ Hz, 2H, Indole), 7.45(d, $J = 7.8$ Hz, 2H, Indole-NH), 7.59(d, $J = 8.1$ Hz, 2H, Indole), 8.30(s, 2H, ArOH), 9.40(d, $J = 6.3$ Hz, 2H, CONH), 9.65(s, 2H, CONHC), 10.13(s, 2H, CONH-Indole); ^{13}C NMR ($CDCl_3$): δ(ppm) 17.1, 18.5, 28.3, 30.9, 31.5, 32.3, 32.5, 33.9, 34.1, 38.8, 39.3, 40.8, 48.9, 49.1, 55.2, 74.8, 80.0, 111.4, 118.7, 119.3, 119.6, 121.9, 122.2, 123.6, 125.2, 125.5, 125.7, 126.0, 126.5, 126.6, 126.9, 127.5, 132.2, 136.2, 143.0, 148.3, 149.2, 149.9, 150.1, 155.6, 169.3, 172.9, 173.0; ESI-MS m/z (%): 1586.8 ($(M + Na)^+$, 100); elemental analysis calcd. (%) for $C_{90}H_{118}N_{10}O_{14}$: C, 69.12; H, 7.60; N, 8.96. Found: C, 69.02; H, 7.63; N, 8.89.

Compound 1b: (eluant: $CHCl_3/CH_3CH_2OH$ = 50:1 (V/V)). Pure product was obtained as white powder (0.40 g, 23%). m.p. 110–112°C; $(\alpha)_D^{20} = -2.78°$ (*c* 0.05, $CHCl_3$); IR (KBr/cm^{-1}) ν: 3414, 2965, 1660, 1541, 1384, 1365, 1248, 1168, 1047, 743; ^1H NMR ($CDCl_3$): δ(ppm) 1.10(s, 18H, Bu^t), 1.29(s, 18H, Bu^t), 1.32(s, 18H, Bu^t), 2.77–2.90(m, 4H, CCH_2N), 3.03–3.16(m, 4H, Indole-CH_2, 4H, $ArCH_2$), 3.23(d, $J = 12.0$ Hz, 4H, $ArCH_2Ar$), 3.70–3.74(m, 4H, NCH_2C), 4.09(d, $J = 12.3$ Hz, 4H, $ArCH_2Ar$), 4.18(d, $J = 15.0$ Hz, 2H, OCH_2CO), 4.92–4.64(m, 2H, NC*HCO), 5.06(d, $J = 15.3$ Hz, 2H, OCH_2CO), 5.50–5.53(m, 2H, NC*HCO-Indole), 6.73(s, 2H, NH-Boc), 6.94(s, 8H, ArH), 7.03–7.18(m, 18H, ArH), 7.30(d, $J = 8.1$ Hz, 2H, indole), 7.63(d, $J = 8.1$ Hz, 2H, indole-NH), 8.15(s, 2H, ArOH), 8.69(d, $J = 8.1$ Hz, 2H, CONHC), 9.65(s, 2H, CONH-indole), 9.76(d, $J = 9$ Hz, 2H, CONH); ^{13}C NMR ($CDCl_3$): δ(ppm) 28.6, 29.2, 31.1, 31.8, 32.4, 34.0, 34.2, 37.6, 38.2, 41.2, 54.2, 56.2, 75.0, 80.5, 111.1, 111.9, 119.2, 120.1, 122.7, 123.1, 125.0, 126.4, 126.6, 127.0, 127.5, 128.3, 128.5, 128.8, 129.1, 132.3, 132.6, 136.2, 136.9, 143.1, 148.3, 149.3, 150.3, 155.7, 169.3, 171.5, 172.1; ESI-MS m/z (%): 1738.2 ($(M + Na)^+$, 100); elemental analysis calcd. (%) for $C_{102}H_{126}N_{10}O_{14}$: C, 71.39; H, 7.40; N, 8.16. Found: C, 71.25; H, 7.44; N, 8.09.

Compound 1c: (eluant: $CHCl_3/CH_3CH_2OH$ = 20:1 (V/V)). Pure product was obtained as white powder (0.44 g, 28%). m.p. 119–121°C; $(\alpha)_D^{20} = -27.68°$ (*c* 0.05, $CHCl_3$); IR (KBr/cm^{-1}) ν: 3326, 2963, 1660, 1529, 1488, 1456, 1366, 1303, 1249, 1167, 1050, 743; ^1H NMR ($CDCl_3$): δ(ppm) 1.10(s, 18H, Bu^t), 1.27(s, 18H, Bu^t), 1.40(s, 18H, Bu^t), 1.44(d, $J = 7.2$ Hz, 6H, CCH_3), 2.97–3.03(m, 4H, CCH_2N), 3.23(d, $J = 5.1$ Hz, 4H, indole-CH_2), 3.36(d, $J = 12.6$ Hz, 2H, $ArCH_2Ar$), 3.46(d, $J = 13.2$ Hz, 2H, $ArCH_2Ar$), 3.69–3.73(m, 8H, $CONCH_2CH_2$), 4.17–4.27(m, 4H, $ArCH_2Ar$), 4.30(d, $J = 14.7$ Hz, 2H, OCH_2CO), 4.55–4.59(m, 2H, NC*HCO), 4.87(d, $J = 14.4$ Hz, 2H, OCH_2CO), 5.43–5.46(m, 2H, NC*HCO-indole), 6.95(s, 2H, ArH), 6.97(s, 2H, ArH), 7.05–7.07(m, 8H, indole, 2H, ArH), 7.08(s, 2H, ArH), 7.11(d, $J = 8.1$ Hz, 2H, indole), 7.33(d, $J = 7.5$ Hz, 2H, indole-NH), 7.64(s, 2H, CONHC), 7.66(s, 2H, NH-Boc), 7.98(s, 2H, ArOH), 8.85(s, 2H, CONH-indole), 9.61(d, $J = 6.9$ Hz, 2H, CONH); ^{13}C NMR ($CDCl_3$): δ(ppm) 17.4, 28.6, 29.3, 31.3, 31.6, 31.7, 32.3, 33.1, 34.2, 34.3, 34.5, 36.1, 38.5, 50.2, 55.7, 56.8, 67.3, 75.4, 80.7, 111.3, 111.7, 118.9, 1119.4, 119.7, 119.9, 122.3, 122.6, 123.2, 123.7, 126.2, 127.1, 127.3, 127.6, 127.7, 128.4, 136.0, 136.4. 144.1, 144.4, 147.1, 148.0, 148.3, 149.0, 149.3, 156.0, 169.2, 171.8, 172.8, 173.0; ESI-MS m/z (%): 1591.6 ($M^+ - 1$, 100); elemental analysis calcd. (%) for $C_{92}H_{122}N_{10}O_{14}$: C, 69.41; H, 7.72; N, 8.80. Found: C, 69.38; H, 7.75; N, 8.78.

Compound 1d: (eluant: $CHCl_3/CH_3CH_2OH$ = 50:1 (V/V)). Pure product was obtained as white powder (0.50 g, 29%). m.p. 123–125°C; $(\alpha)_D^{20} = -25.00°$ (*c* 0.05, $CHCl_3$); IR (KBr/cm^{-1}) ν: 3313, 2963, 1659, 1541, 1484, 1365, 1238, 1169, 1047, 742; ^1H NMR ($CDCl_3$): δ(ppm) 1.04(s, 18H, Bu^t), 1.29(s, 18H, Bu^t), 1.57(s, 18H, Bu^t), 2.77–2.97(m, 8H, CCH_2CH_2N), 3.08–3.16(m, 4H, indole-CH_2, 4H, $ArCH_2$), 3.25–3.32(m, 4H, NCH_2C), 3.52(d, $J = 13.5$ Hz, 4H, $ArCH_2Ar$), 4.00(d, $J = 12.8$ Hz, 4H, $ArCH_2Ar$), 4.11(d, $J = 15.3$ Hz, 2H, OCH_2CO), 4.95–5.00(m, 2H, NC*HCO), 5.23(d, $J = 15.0$ Hz, 2H, OCH_2CO), 5.36–5.39(m, 2H, NC*HCO-Indole), 6.33(s, 2H, NH-Boc), 6.84(s, 2H, ArH), 6.86(s, 2H, ArH), 6.94(s, 2H, ArH), 6.98(s, 2H, ArH), 7.00–7.04(m, 10H, ArH), 7.11–7.14(m, 10H, indole), 7.20(d, $J = 8.1$ Hz, 2H, CONHC), 7.50(d, $J = 7.5$ Hz, 2H, indole-NH),

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7.70(s, 2H, ArOH), 9.51(d, $J = 8.4$ Hz, 2H, CONH), 9.65(s, 2H, CONH-indole); ^{13}C NMR ($CDCl_3$): δ(ppm) 27.0, 27.6, 28.6, 29.3, 31.2, 31.8, 32.6, 32.8, 34.1, 34.3, 38.0, 38.4, 53.8, 56.8, 75.2, 80.6, 111.2, 111.7, 119.4, 119.9, 122.5, 123.2, 125.1, 125.7, 126.6, 126.7, 126.9, 127.0, 127.3, 128.1, 128.5, 128.9, 132.7, 132.8, 136.0, 137.1, 143.1, 148.2, 149.3, 150.6, 156.0, 169.8, 171.3, 171.8; ESI-MS m/z (%): 1743.5 ($M^+ - 1$, 100); elemental analysis calcd. (%) for $C_{104}H_{130}N_{10}O_{14}$: C, 71.62; H, 7.51; N, 8.03. Found: C, 71.58; H, 7.61; N, 7.98.

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Supporting information

The NMR spectra of **1a–1d**, additional fluorescence titration graphs of **1a–1d** with amino alcohol guests in CH_3CN, DMSO or $CHCl_3$, and the fluorescence intensity change graphs of receptors **1a–1d** with (*S*)-phenylglycinol and (*S*)-phenylalaninol in CH_3CN, DMSO or $CHCl_3$ are available in PDF format.

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