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A pair of chiral fluorescent sensors for enantioselective recognition of mandelate in water

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ABSTRACT: A pair of chiral compounds **S-1** and **R-1** derived from (1S, 2S) or (1R, 2R)-1, 2-diphenylethane-1, 2-diamine were designed and synthesized, the interactions of S-1 and R-1 with mandelate were studied in H_2O (0.01 M HEPES buffer, pH=7.4) by fluorescence titration experiments. The sensors **S-1** and **R-1** were found to present enantioselective fluorescent sensing ability to mandelate. The results indicated that the sensors **S-1** and **R-1** were very promising to be used as fluorescent sensors in determining the enantiomeric composition of mandelate in H_2O.

Keywords: Enantioselective recognition, Fluorescent sensor, Mandelate.

1. Introduction

Molecular recognition is a fundamental property of various natural systems, based on the ability of a molecular receptor to form a complex preferentially with one of the enantiomers of a chiral molecule by noncovalent interaction such as hydrogen bonding, electrostatic interaction, and hydrophobic interaction [1-4]. Molecular recognition in protic solvents, especially in aqueous media, is another attractive topic since noncovalent forces derived from electrostatic interaction are weakened according to the dielectric constant of the solvent. In addition, the designed formation of hydrogen bonds between two molecules is especially difficult in protic solvent since a large number of solvent molecules can act as a hydrogen donor and/or acceptor [5-7]. Hydrogen bonding, capable of showing a high degree of complementarity and directionality, is frequently used for chiral recognition. During the past several years, there has been a growing interest in the enantioselective recognition of α-hydroxycarboxylic acid [8-13], especially using fluorescence spectroscopy, owing to the basic building blocks of many natural products, biological

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molecules and drugs. Therefore, the development of enantioselective fluorescent sensors for structurally diverse α-hydroxycarboxylic acids has become a major challenge in this area. Several fluorescent sensors, including those developed within our group, have been reported to show high enantioselectivity in the recognition of α-hydroxycarboxylic acids [14-15]. However, the enantioselective recognition of the chiral α-hydroxycarboxylic acid in aqueous media is poor. Here we report enantioselective recognition mandelate based on fluorescent quenching mechanism in water. The molecular structures of two synthesized fluorescent sensors were shown in Scheme 1.

2. Experimental

2.1 Apparatus

The reagents used were of commercial origin and were employed without further purification. Purifications by column chromatography were carried out over silica gel (230–400 mesh). Melting point was determined with a MEL-TEMP□ melting-piont apparatus (uncorrected). The IR spectra were performed on a Nicolet 670 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer. High resolution mass spectra (HRMS) were measured on a Agilent 1290LC-6540 Accurate Mass Q-TOF using electrospray ionization (ESI).Optical rotations were taken on a Perkin–Elmer Model 341 polarimeter. Fluorescence spectra were obtained with F-7000 FL Spectrophotometer. Elemental analyses were performed with the Vario Elemental CHSN-O microanalyzer. The anions were used as their tetrabutylammonium salts. All other commercially available reagents were used without further purification.

2.2 Synthesis

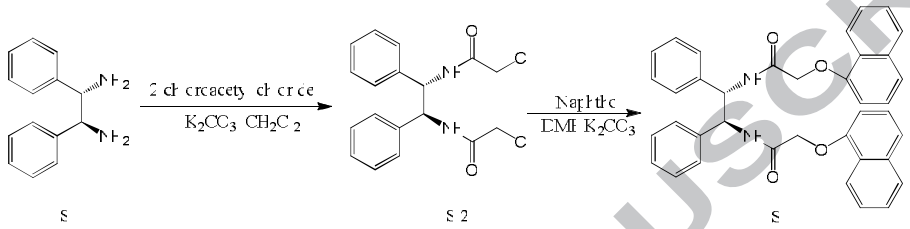
Synthesis of S-2: (1S, 2S)-1, 2-diphenylethane-1, 2-diamine (1.0 g, 4.7 mmol) was dissolved in 30 mL of dried chloroform and cooled in the ice bath. 1.4 g (10 mmol) anhydrous K_2CO_3 was placed in the solution as the base. 2-Chloroacetyl chloride (1.6 g, 14.1 mmol) was dropwisely added to the mixture within 30 min. The mixture was

then stirred at room temperature for 3 h. After filtration, the filtrate was collected and washed with 20 mL 10% HCl, saturated $NaHCO_3$ and water respectively. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was then purified by column chromatography on silica gel using $CHCl_3$/MeOH (50:1) as eluent to obtain pure products a as a solid (1.20 g, 70%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.48 (s, 2H, CONH), 7.21 (br.s, 6H, Ph-H), 7.11 (br.s, 4H, Ph-H), 5.31 (d, 2H, J = 3.6 Hz, chiral-H), 4.07 (m, 4H, CH_2Cl). Elemental analysis calcd (%) for $C_{18}H_{18}Cl_2N_2O_2$: C 59.19, H 4.97, N 7.67, Found: C 58.96, H 5.02, N 7.63. The preparation procedure of compound R-2 was the same as that of S-2 by starting with (1R, 2R)-1, 2-diphenylethane-1, 2-diamine.

Synthesis of S-1. The synthesis procedure of compound S-1: 0.18 g（0.5 mmol）compound S-2 and 0.28 g（2.0 mmol）anhydrous K_2CO_3 were dissolved in 6 mL dry DMF firstly, then a solution of 0.15 g（1.1 mmol）α-naphthol dissolved in 4 mL dry DMF was added dropwisely to the mixture. After that, the solution was stirred at 60 □ for 8 h, monitoring with TLC. When completed, the mixture was poured into ice-water, adjusted to weak acid by using 10% dilute HCl, extracted by using CH_2Cl_2 respectively. The organic phase was washed with saturated $NaHCO_3$ (3×30 mL), water (2×50 mL) before drying it with anhydrous Na_2SO_4. After removing the solvent by rotary evaporation, the crude product was purified by silica column chromatography using CH_2Cl_2/MeOH (50:1) as eluent to get 0.22 g product as a white powder. Yield: 76.4%, m.p. 217-219 □. ^1H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.25 (s, 1H), 8.23 (s, 1H), 7.83 (d, J = 5.6 Hz, 2H), 7.64 (d, J = 4.8 Hz, 2H), 7.56 (d, J = 5.6 Hz, 2H), 7.53 (d, J =6.0Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.19-7.13(m, 6H), 7.04-7.01(m, 4H), 6.67 (d, J = 7.6 Hz, 2H), 5.39 (s, 1H), 5.37 (s, 1H), 4.54 (s, 2H), 4.44 (s, 2H); ^{13}C NMR ($CDCl_3$) δ: 168.74, 152.87, 137.80, 134.57, 128.67, 128.13, 127.73, 127.53, 126.81, 125.87, 125.64, 125.18, 121.86, 121.65, 105.51, 67.51, 58.37. HRMS m/z: 580.2362, found (calculated for $C_{38}H_{32}N_2O_4$, $[M+H]^+$ requires 581.2439，$[M+Na]^+$ requires 603.2259). IR: NH(3313.89 cm^{-1}), C=O

(1668.22 cm^{-1}), Ar (1649.87 cm^{-1}, 1597.66 cm^{-1}, 1580.01 cm^{-1}, 1528.03 cm^{-1}), -O- (1231.13 cm^{-1}, 1106.06 cm^{-1}). Specific rotation, $[\alpha]_D^{20}$ = -101.09 (c=0.13, $CHCl_3$).

Synthesis of R-1. The compound was prepared using a procedure analogous to that described previously for **S-1**. Yield: 74.7%, m.p. 218-220 ℃. HRMS m/z: 580.2362, found (calculated for $C_{38}H_{32}N_2O_4$, $[M+H]^+$ requires 581.2437, $[M+Na]^+$ requires 603.2260). Specific rotation $[\alpha]_D^{20}$ = +99.31(c=0.13，$CHCl_3$).



Scheme 1. Synthetic Route for the compound **S-1**

2.3 Binding Experiments

General procedure for the fluorescent measurement: All solutions were prepared by volumetric syringes, pipettes, and volumetric flasks. A DMSO stock solution of the sensor (0.1 M) was freshly prepared before each measurement. The tetrabutylammonium salts were prepared by adding 1 equiv. of tetrabutylammonium hydroxide in methanol to a solution of the corresponding carboxylic acid in methanol. The resulting syrup was dried under high vacuum for 24 h, analyzed by NMR spectroscopy, and stored in a desiccator, then the stock solutions of the salts were prepared in HEPES-buffered H_2O (0.01 M, pH=7.4). The test solutions were prepared by adding different volumes of anion solution to a series of test tubes and then the same amount of stock solution of the sensor was added to each of the test tubes and diluted to 3.0 mL with HEPES-buffered H_2O. After being shaken for several minutes, the test solutions were analyzed immediately.

3. Results and discussion

3.1 Design and synthesis of the new chiral sensors

The chiral fluorescence sensor **S-1** was efficiently synthesized using (1S, 2S)-1, 2-diphenyl-ethane-1, 2-diamine. The preparation procedure of compound **R-1** was the

same as that of **S-1** by starting with (1R, 2R)-1, 2-diphenyl-ethane-1, 2-diamine (Scheme 1). The structures of these compounds were characterized by IR, HRMS, ^{1}H NMR and ^{13}C NMR spectra. Compounds **S-1** and **R-1** containing oxygen atoms adjacent to the naphthyl rings, as we have shown earlier, interaction of these oxygen atoms with hydroxyl of α-hydroxycarboxylic acids could turn off the fluorescence of the naphthalenes by enhancing the fluorescence quenching of the photoinduced-electron-transfer (PET)[16-17] of the oxygen lone pair electrons. The multiple chiral functional groups of the sensor also provided efficient binding sites for functional organic molecules.

3.2 Fluorescence spectra study

Because there was almost no change observed on the UV–vis spectra of sensors upon addition of the anions (see Fig.s1), the interaction between sensor and anion was only evaluated by fluorescent spectra. Fluorescent spectra were recorded from a solution of **S-1** in the presence of various enantiomers α-hydroxylcarboxylic acid anions, such as *D*- or *L*-mandelate (Man), phenylactic acid, methoxymandelic acid and alanine anion (as tetrabutylammonium) in H_2O (including 0.3%DMSO, 0.01 M HEPES-HCl buffer, pH=7.4) (by means of titration fluorimetry).

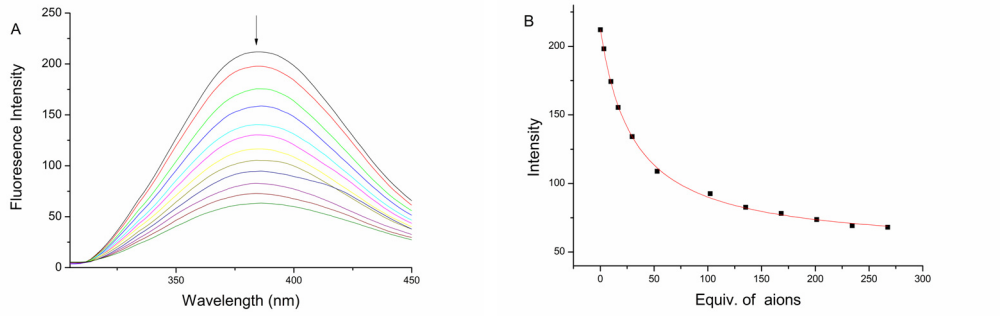


Fig. 1 (A): Fluorescent spectra of sensor S-1 (4.0×10-5 M) with D-alanine anion in buffered H2O (including 0.3%DMSO, 0.01 M HEPES buffer, pH=7.4). Equivalents of anion: 0→267. λ_{ex}=245 nm (EX: 5; EM: 5). (B): changes in the fluorescence intensity of S-1 at 388 nm upon addition of D-alanine anion. The line shown is a line-fitted curve. The correlation coefficient (R) of the non-linear curve fitting is 0.9996.

First we studied on using the sensors for the fluorescent recognition of alanine

anion. The primary amine group in amino acid could quench the fluorescence of the fluorophores. The fluorescence measurements were conducted in buffered water solutions with the addition of a small amount of DMSO in order to increase the solubility of **S-1**. The fluorescence emission of **S-1** (λ_{ex} = 245 nm; λ_{em} = 388 nm) decreased gradually with the addition of *D*-alanine anion (Fig.1). Similar phenomena were found when *L*-alanine anion was added into the solution of **S-1** (see Fig.s2), which indicated complex between the sensor **S-1** and *L*- or *D*-alanine.

TABLE 1. Association constants (*Kass*) of sensor **S-1** and **R-1** with *D*- or *L*-α-carboxylic acid anions in water.

Entry	Host	Guest	$Kass[M^{-1}]^{[a,b]}$	$K_{(d)}/K_{(l)}$	R
1	S-1	D-alanine	$(3.31\pm0.11)\times10^3$		0.9996
2	S-1	L-alanine	$(2.61\pm0.18)\times10^3$	1.27	0.998
3	S-1	D-Man	$(4.85\pm0.23)\times10^3$		0.9991
4	S-1	L-Man	$(1.31\pm0.09)\times10^3$	3.7	0.9989
5	S-1	D-phenylactic	$(3.00\pm0.24)\times10^3$		0.9978
6	S-1	L-phenylactic	$(1.49\pm0.16)\times10^3$	2.01	0.9974
7	S-1	D-methoxyphenylacetic	$(7.71\pm0.60)\times10^2$		0.999
8	S-1	L-methoxyphenylacetic	$(1.19\pm0.10)\times10^3$	0.65	0.9991
9	R-1	D-alanine	$(3.92\pm0.29)\times10^3$		0.9976
10	R-1	L-alanine	$(3.43\pm0.23)\times10^3$	1.14	0.998
11	R-1	D-Man	$(1.30\pm0.15)\times10^3$		0.9976
12	R-1	L-Man	$(4.96\pm0.36)\times10^3$	0.26	0.9979
13	R-1	D-phenylactic	$(1.58\pm0.12)\times10^3$		0.9984
14	R-1	L-phenylactic	$(2.96\pm0.16)\times10^3$	0.53	0.9989
15	R-1	D-Methoxyphenylacetic	$(7.87\pm0.46)\times10^2$		0.9996
16	R-1	L-methoxyphenylacetic	$(1.13\pm0.12)\times10^3$	0.7	0.9973

[a]The data were calculated from results of fluorescence titrations in a aqueous solution (including 0.3%DMSO, 0.01 M HEPES buffer, pH 7.4).

[b]All error values were obtained from nonlinear curve fitting.

On the basis of the change of fluorescent intensity associated with the stepwise addition of guest anions, the complex association constants (K_a) compiled in Table 1, were calculated by nonlinear least-squares curve fitting using the following equation from the Origin 7.5 software package [18]. Where *I* represents the fluorescence

intensity, C_H and C_G were the host and guest concentrations, and C_0 was the initial concentration of the sensor.

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

The fitting (R>0.99) of the titration data points shown in Figures (Fig.1, Fig.s2) demonstrated that **S-1** formed 1:1 complexes with alanine anion. The K_a of **S-1** with *D*- and *L*-alanine anion were $(3.92\pm0.29)\times10^3$ M^{-1} and $(3.43\pm0.23)\times10^3$ M^{-1}, respectively. Similar phenomena were observed when *D*- or *L*-alanine anion was added into a solution of **R-1**(see Fig.s3, Fig.s4). Their fluorescent responses were indicative of poor enantioselectivity (Table 1). We believed that the hydrogen in primary amine of alanine anion participated in the formation of hydrogen bond with oxygen of the sensor which resulted the recognition.

Then we studied the enantioselectivity of **S-1** with *D*- or *L*-Man. Upon addition of *D*- or *L*-Man anions, different fluorescent-quenching degrees of **S-1** were observed. Fig. 2 showed the different fluorescence intensity changes when the same equivalent of *D*- or *L*-Man anion was added to the sensor **S-1**. The quenching efficiency was 43% when 19.8 equiv. of *D*-Man anion was added to the solution of **S-1**, while the quenching efficiency was only 30% when 19.8 equiv. of *L*-Man anion was added. The quenching efficiencies ($\Delta I_D/\Delta I_L$ = 3.12) indicated that the sensor **S-1** had a good enantioselective recognition ability between the *D*- and *L*-Man anions. The quenching efficiency of *D*-Man anion was much higher than the *L*-Man anion.

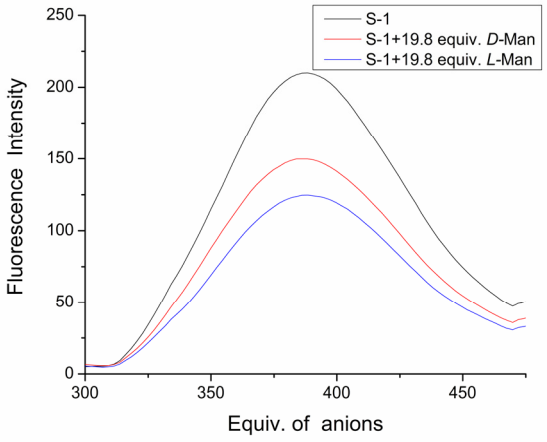


Fig.2 Fluorescent spectra of sensor S-1with 19.8 equiv of *D*- and *L*-Man anions in H_2O (including 0.3%DMSO, 0.01 M HEPES buffer, pH 7.4)

Fig. 3(A) and 4(A) showed the fluorescence emission spectra of a mixture of **S-1** and different concentrations of the *D*- or *L*-Man anion in H_2O, respectively. The Fig. 3(B) and 4(B) illustrated the fluorescence intensity changes of receptor **S-1** upon addition of *D*- and *L*-Man anions, which gave $K_{a(D)}/K_{a(L)}$ 3.70 for Man. We also prepared **R-1**, the enantiomer of **S-1**, and studied its interaction with Man anion, which showed the opposite enantioselectivity, that was, the enantiomer of *L*-Man quenched the fluorescence of **R-1** more efficiently than the *D*-Man (Fig.s5, Fig.s6). The results of fluorescence titrations experiments indicated that the expected mirror image responses for the enantiomers of Man anions. We believed the sensors both **S-1** and **R-1** had excellent enantioselective recognition ability due to their good preorganized structures, which can be easily combined the sensors with Man anions through hydrogen bonds. Moreover, we demonstrated the formation of a 1:1 inclusion complex between sensor **S-1** or **R-1** and Man by ESI-MS studies. When Man were added to the sensor **S-1** or **R-1**, the ESI-MS results provided strong evidence for the formation of the 1:1 complex of the sensor **S-1** or **R-1** and Man acid anion (Fig.s7, Fig.s8). The results suggested that the **S-1** and **R-1** formed a 1:1 complex with *D*- or *L*-Man.

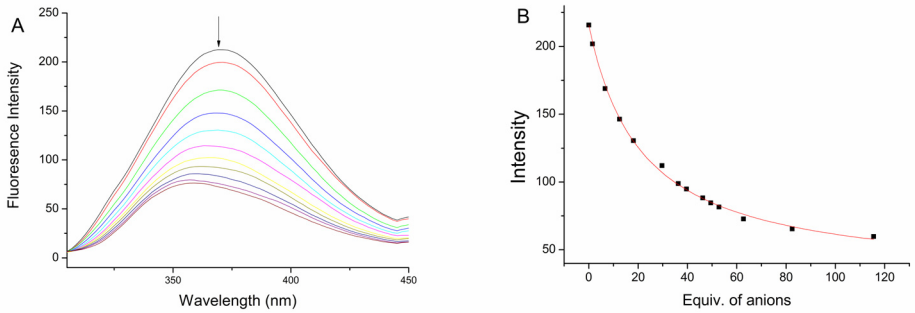


Fig. 3 (A) Fluorescence spectra of sensor **S-1** (4.0×10^{-5} mol L^{-1}) with *D*-Man in H_2O (including 0.3%DMSO, 0.01 M HEPES buffer, pH 7.4). The anion equivalents are: 0→115. λ_{ex}= 245nm. (B)The fluorescence intensity changes in the **S-1** at 388 nm upon addition of *D*-Man. The line shown is a line-fitted curve. The correlation coefficient (*R*) of the nonlinear curve fitting is 0.9991.

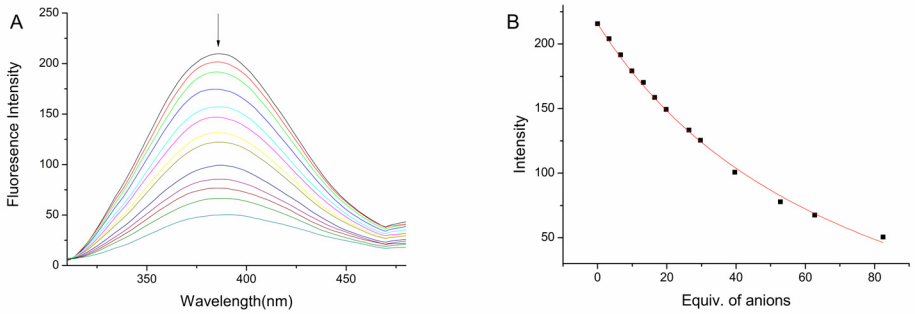


Fig. 4 (A) Fluorescence spectra of sensor **S-1** (4.0×10^{-5} mol L^{-1}) with *L*-Man in H_2O (including 0.3%DMSO, 0.01 M HEPES buffer, pH 7.4). The Man equivalents are: 0→82. λ_{ex} = 245nm. (B)The fluorescence intensity changes in the **S-1** at 388 nm upon addition of D-Man. The line shown is a line-fitted curve. The correlation coefficient (*R*) of the nonlinear curve fitting is 0.9989.

To study the effect on the structure of the guests, the binding properties of phenylactic acid anion and methoxyphenylacetic acid anion towards **S-1** and **R-1** were also studied using the same fluorescent titration method (Fig.s9-Fig.s16). As shown in Table 1, the sensors **S-1** and **R-1** showed more enantiomeric recognition abilities towards the enantiomers of Man than phenylactic acid anions. The possible reason was that the guest phenylactic acid anions had a more methene group on their stereogenic centre moiety. This demonstrated that the steric hindrance around the stereogenic centers in the ligand played an important role on the degree of enantiomeric recognition. It was also observed that the stability constants of the complexes of **S-1** and **R-1** with methoxyphenylacetic acid anions were smaller than what with Man, which could be attributed to the complex of the chiral sensors **S-1** and **R-1** with Man possibly occurs through interaction of the oxygen atoms in the sensors S-1 and R-1 with the hydroxyl of Man. So the steric hindrance around the stereogenic centers and the hydroxyl of the guests may also play important roles in enantioselectivity recognition in the tested cases.

The large fluorescence decreasing could be attributed to the photoinduced electron transfer (PET) mechanism. In the absence of anions, PET between the naphthyl unit and the oxygen substituents might result in quenched fluorescence. In the presence of guest anions, the fluorescence quenching of sensor **S-1** most likely arose from the

change of the free energy (ΔG_{PET}) of the electron transfer between the excited fluorophore and the sensor [19-23]. Therefore, fluorescence quenching was observed. The phenomenon of fluorescence intensity decreasing upon the addition of guest anion was similar to the anion-induced fluorescence quenched reported previously.

4. Conclusion

We have demonstrated that the easily accessible chiral fluorescence sensor **S-1** and **R-1** exhibited excellent enantioselective fluorescent recognition abilities toward Man anions and formed 1:1 complexes. It was clear that the nature of the receptor, good structural preorganization, multiple hydrogen-bonding interactions and the complementary stereogenic center interactions induced might be responsible for the enantiomeric recognition of Man anion. To our knowledge, it is the first good enantioselective fluorescent sensor for mandelic acid anion in water. Sensors **S-1** and **R-1** are promising in their use as fluorescence sensors for Man anions in water.

Acknowledgments

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Supplementary data

The ^{1}H and ^{13}C NMR spectra of **R-1** and **S-1**, the fluorometric titration experiment, ESI-MS studies with this article can be found, in the online version, at http://

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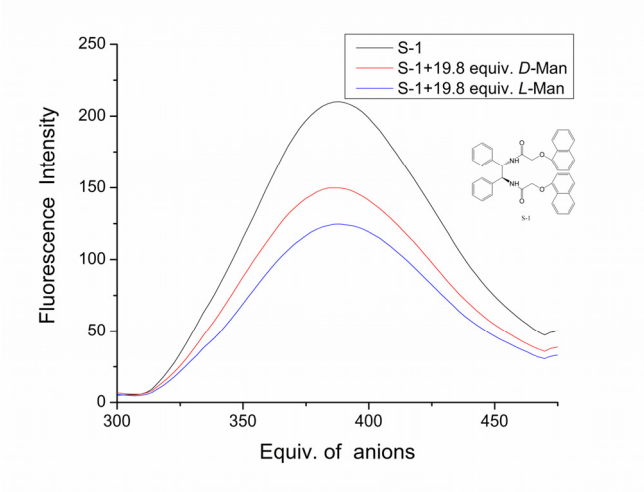
Highlights

The developed a pair of chiral fluorescent sensors selectively enantioselective detects mandelate in water.

In the binding with mandelate, the large fluorescence decrease can be attributed to the PET mechanism.

The chemosensors exhibited selectively enantioselective for mandelate in water (0.01 M HEPES, buffer, pH=7.4).

Graphical abstract



The sensors **S-1** and **R-1** were found to present enantioselective fluorescent sensing ability to mandelate in H_2O.