

Synthesis and enantiomeric recognition studies of optically active 5,5-dioxophenothiazine bis(urea) and bis(thiourea) derivatives

Dávid Pál,^a Ildikó Móczár,^a Attila Kormos,^a Péter Baranyai,^b

Péter Huszthy^{a,*}

^a *Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, PO Box 91, H-1521 Budapest, Hungary*

^b *“Lendület” Supramolecular Chemistry Research Group, Institute of Organic Chemistry, Research Centre of Natural Sciences, Hungarian Academy of Sciences, PO Box 286, H-1519 Budapest, Hungary*

* *Corresponding author. Tel.: +36 1 463 1071; fax: +36 1 463 3297; e-mail: huszthy@mail.bme.hu*

Abstract

Novel optically active 5,5-dioxophenothiazine bis(urea) and bis(thiourea) derivatives were synthesized and their enantiomeric recognition abilities toward the enantiomers of tetrabutylammonium salts of α -hydroxy and *N*-protected α -amino acids were examined in acetonitrile using fluorescence spectroscopy.

1. Introduction

Enantiomeric recognition as a special case of molecular recognition is a widespread and vital phenomenon in Nature. A great number of biologically important molecules are chiral, and many biological processes are based on enantioselective reactions. Since one of the enantiomers of a biologically active chiral compound may have different toxicological and pharmacological properties than the other, the determination of the enantiomeric composition of chiral organic compounds has great significance in drug discovery, food industry and pesticide chemistry.

Carboxyl group is a very common functional group in amino acids, enzymes, metabolic intermediates and several physiologically active molecules. Therefore, the synthesis and studies of sensor and selector molecules, which are able to distinguish between the enantiomers of chiral

carboxylic acids, are of great interest. The enantiomers of chiral carboxylic acids can be differentiated in their neutral forms,^{1,2} and in most cases as their deprotonated forms by enantioselective anion receptors.^{2–24} The enantiomeric recognition of chiral carboxylic acids as carboxylates is advantageous, because carboxylic acids exist in their dissociated forms under physiological conditions.^{13,21}

The most frequently used chiral motifs in anion receptors are amino acid, BINOL, steroid and monosaccharide units,^{2–14,19–22} but among others 1-arylethyl^{24–29} moieties have also been applied as sources of chirality. These sensor molecules often contain urea and thiourea units as receptor parts, which have good hydrogen bond donating ability therefore high affinity toward anions.² Some chiral anion sensors possessing two urea or thiourea moieties have a fluorescent signalling unit, which provide a sensitive tool for the examination of their anion recognition ability by the use of fluorescence spectroscopy.^{2,24,29–38}

Neutral anion sensors, which bind anions *via* hydrogen bonds for example with their amide, urea or thiourea moieties,³⁹ can also contain a heterocyclic unit having a slightly acidic NH group such as pyrrole,⁴⁰ indole or carbazole⁴¹ and in a few cases, acridone^{24,42–44} or 5,5-dioxophenothiazine.^{45–47} In our research group, achiral bis(amide),⁴⁵ bis(urea),⁴⁶ bis(thiourea)⁴⁶ and chiral bis(thiourea)⁴⁷ type 5,5-dioxophenothiazine-based sensor molecules (**1–5**, Fig. 1) were synthesized, and their anion recognition properties were studied by UV–vis spectroscopy.

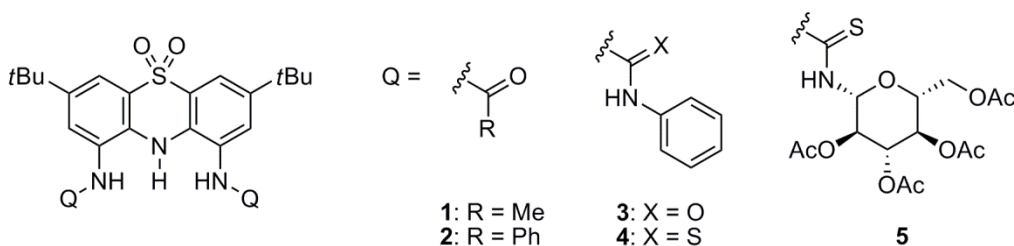


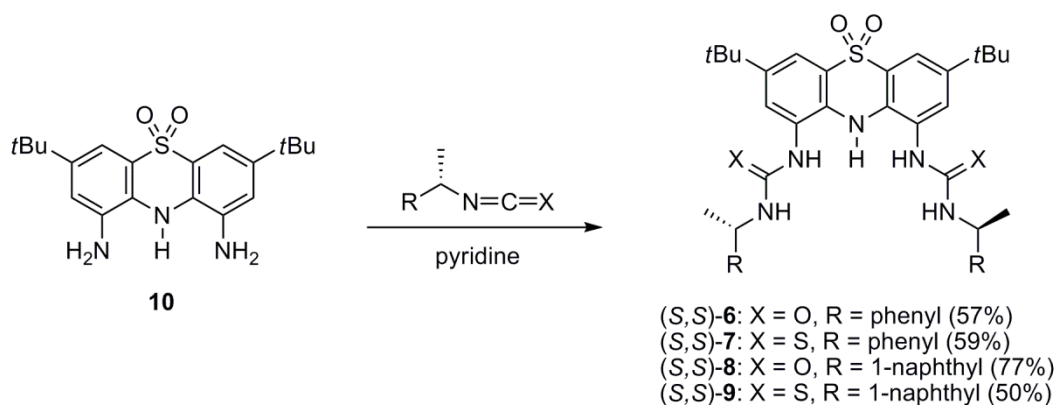
Figure 1. Reported 5,5-dioxophenothiazine-based anion sensors.

In this paper, we report the synthesis of novel 5,5-dioxophenothiazine bis(urea) and bis(thiourea) derivatives containing (*S*)-1-arylethyl units [(*S,S*)-**6**–(*S,S*)-**9**, Scheme 1] as well as the UV–vis and fluorescence studies on their complexation properties and enantiomeric recognition abilities toward the enantiomers of different optically active tetrabutylammonium carboxylates in acetonitrile.

2. Results and discussion

2.1. Synthesis

The synthesis of new 5,5-dioxophenothiazine bis(urea) and bis(thiourea) derivatives containing (*S,S*)-1-arylethyl units [(*S,S*)-**6**–(*S,S*)-**9**] was carried out as outlined in Scheme 1. Diamine **10**⁴⁵ was reacted with the appropriate commercially available optically active isocyanate and isothiocyanate in pyridine to give bis(urea) and bis(thiourea) derivatives (*S,S*)-**6**–(*S,S*)-**9**.



Scheme 1. Synthesis of receptors (*S,S*)-**6**–(*S,S*)-**9**.

2.2. Enantiomeric recognition studies

The complexation properties and enantiomeric recognition abilities of receptors (*S,S*)-**8** and (*S,S*)-**9** toward the enantiomers of tetrabutylammonium salts of mandelic acid (Man), *tert*-butoxycarbonyl-protected phenylglycine (Boc-Phg), *tert*-butoxycarbonyl-protected phenylalanine (Boc-Phe) and *tert*-butoxycarbonyl-protected alanine (Boc-Ala) were studied in acetonitrile by UV-vis and fluorescence spectroscopies (Fig. 2).

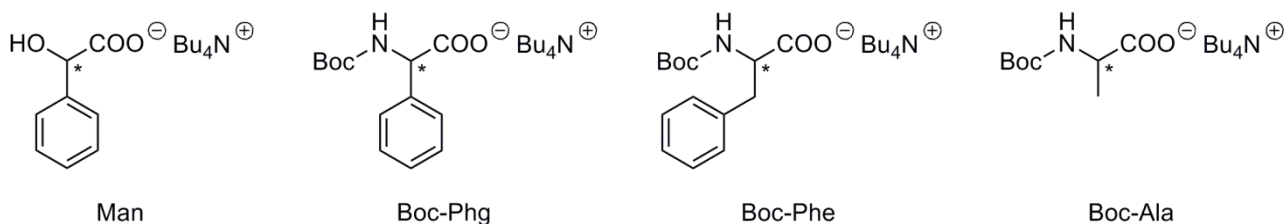


Figure 2. Optically active tetrabutylammonium carboxylates used in the enantiomeric recognition studies.

Since basic anions often cause the deprotonation of neutral anion sensors, we recorded the UV-vis spectra of the deprotonated forms of receptors *(S,S)*-**8** and *(S,S)*-**9** using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base (Fig. 3).

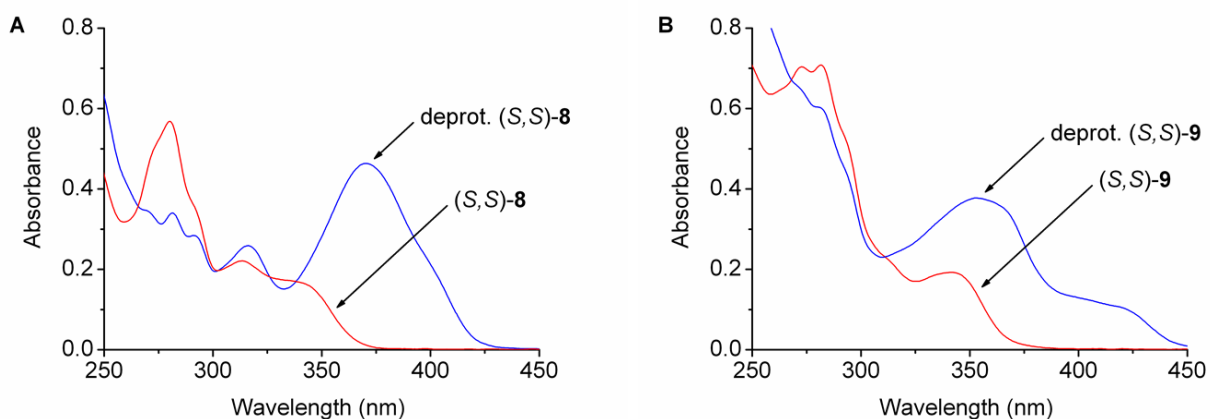


Figure 3. Absorption spectra of *(S,S)*-**8**, *(S,S)*-**9** and their deprotonated forms (20 μ M) (A and B) in MeCN.

Upon addition of carboxylate anions to receptors *(S,S)*-**8** and *(S,S)*-**9**, the absorption spectra showed changes due to complexation, and no spectral changes characteristic to deprotonation could be observed (Fig. 4).

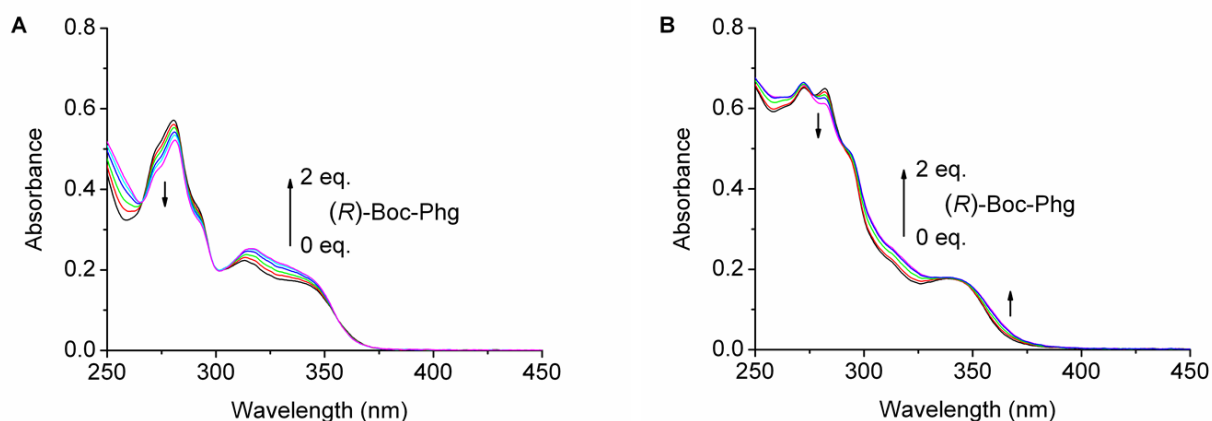


Figure 4. Series of absorption spectra upon titration of *(S,S)*-**8** (20 μ M) with *(R)*-Boc-Phg (0, 0.2, 0.4, 0.7, 1, 2 equiv) (A) and *(S,S)*-**9** (20 μ M) with *(R)*-Boc-Phg (0, 0.2, 0.5, 1, 2 equiv) (B) in MeCN.

However, the complex formations with the chiral carboxylates were almost quantitative at the applied concentration of the sensor molecules (20 μM), and manifested in slight spectral changes in the case of thiourea receptor (*S,S*)-**9** (Fig. 4). Because of these, it was more advantageous to follow the complexation processes by fluorescence spectroscopy using significantly lower concentrations of the sensor molecules (5, 3 or 2 μM), which also provided larger spectral changes in the case of thiourea derivative (*S,S*)-**9** (see later).

The fluorescence emission spectra of the neutral and deprotonated forms of receptors (*S,S*)-**8** and (*S,S*)-**9** were taken (Fig. 5), and the fluorescence quantum yields of these species were also determined (Table 1). Both neutral sensor molecules have low fluorescence quantum yields, and comparing them, a considerably lower value can be observed in the case of thiourea derivative (*S,S*)-**9**. The latter can be attributed to the quenching effect of the sulphur atoms in the molecule, probably due to a photoinduced electron transfer (PET) process.^{24,48–50} In both cases, the deprotonation significantly decreases the fluorescence quantum yields.

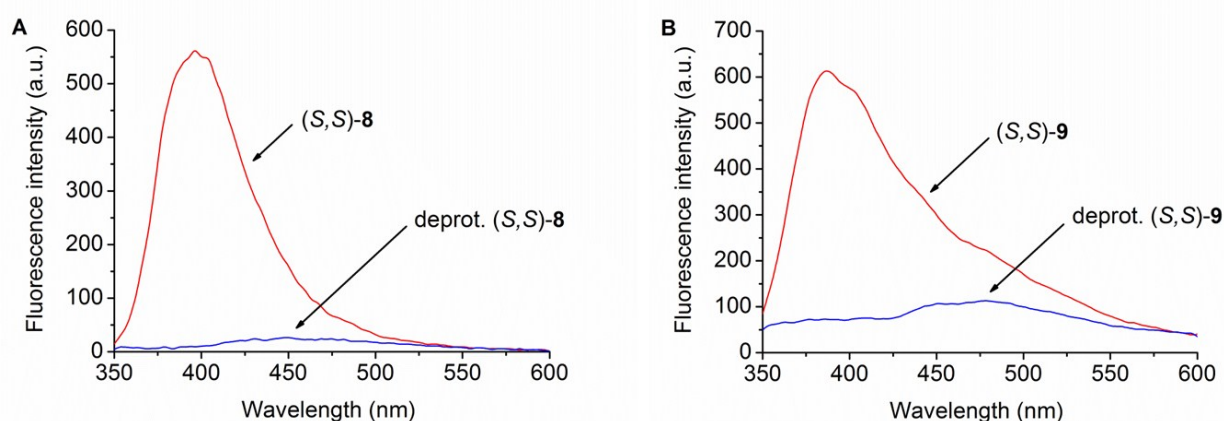


Figure 5. Fluorescence emission spectra of (*S,S*)-**8**, (*S,S*)-**9** and their deprotonated forms (20 μM) (A and B) in MeCN, $\lambda_{\text{ex}} = 310 \text{ nm}$.

Table 1

Fluorescence quantum yields of (*S,S*)-**8**, (*S,S*)-**9** and their deprotonated forms in MeCN, $\lambda_{\text{ex}} = 325 \text{ nm}$.

	Φ_f	
	neutral form	deprotonated form
(<i>S,S</i>)- 8	0.032	0.0037
(<i>S,S</i>)- 9	0.0053	0.0013

The fluorescence emission spectra of receptors (*S,S*)-**8** and (*S,S*)-**9** showed 17–32% increases and 33–45% decreases, respectively, at their maxima upon addition of the carboxylates (Fig. 6 and 7), which could be fitted satisfactorily (considering the residual analysis⁵¹ also) by assuming 1:1 complex formation, and the stability constants were calculated (Table 2).

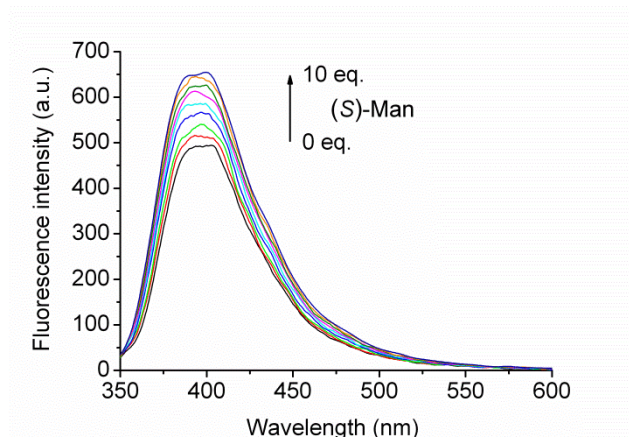


Figure 6. Series of fluorescence emission spectra upon titration of (*S,S*)-**8** (5 μ M) with (*S*)-Man (0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.4, 4, 10 equiv) in MeCN, $\lambda_{\text{ex}} = 320$ nm.

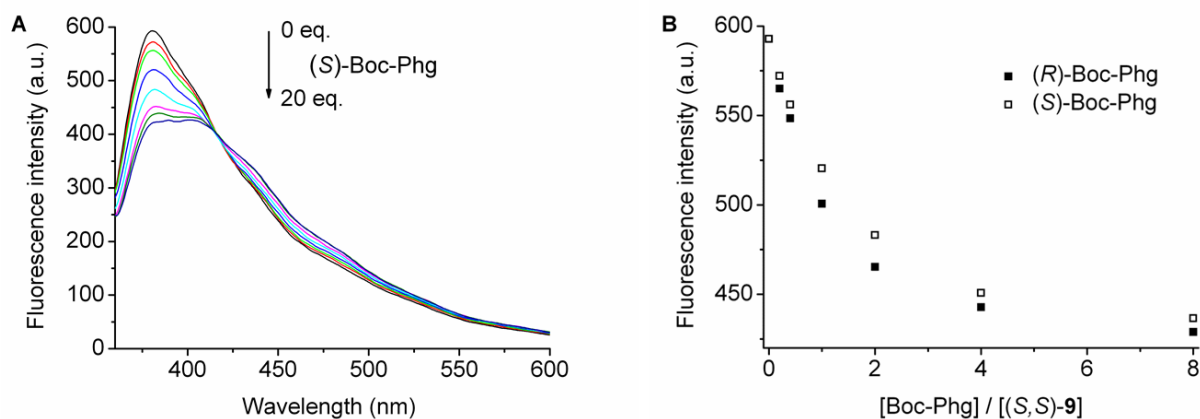


Figure 7. Series of fluorescence emission spectra upon titration of (*S,S*)-**9** (5 μ M) with (*S*)-Boc-Phg (0, 0.2, 0.4, 1, 2, 4, 8, 20 equiv) in MeCN, $\lambda_{\text{ex}} = 340$ nm (A). Titration curves with (*R*)-Boc-Phg and (*S*)-Boc-Phg (0–8 equiv) at 381 nm (B).

Table 2

Stability constants for complexes of (*S,S*)-**8** and (*S,S*)-**9** with the enantiomers of optically active tetrabutylammonium carboxylates and the degrees of enantiomeric recognition in MeCN

	<i>(S,S)</i> - 8		<i>(S,S)</i> - 9	
	log <i>K</i>	Δ log <i>K</i>	log <i>K</i>	Δ log <i>K</i>
(<i>R</i>)-Man	5.50	0.09	5.16	-0.11
(<i>S</i>)-Man	5.41		5.27	
(<i>R</i>)-Boc-Phg	5.79	0.03	5.71	0.24
(<i>S</i>)-Boc-Phg	5.76		5.47	
(<i>R</i>)-Boc-Phe	5.87	-0.07	6.09	0.12
(<i>S</i>)-Boc-Phe	5.94		5.97	
(<i>R</i>)-Boc-Ala	5.94	0.12	6.01	0.10
(<i>S</i>)-Boc-Ala	5.82		5.91	

In most cases, receptors (*S,S*)-**8** and (*S,S*)-**9** showed slight or no enantiomeric recognition abilities toward the enantiomers of chiral carboxylates (Table 2). However, in the case of thiourea receptor (*S,S*)-**9** and the enantiomers of Boc-Phg, moderate selectivity could be observed, which was the highest among the others. These results suggest that the enantiomeric differentiation is based on very subtle effects.¹⁹ One of these effects is the type of the receptor units (urea or thiourea) in the anion sensors, which significantly influenced the recognition ability toward the enantiomers of Boc-Phg. The structure of the guest molecules also affected the enantioselectivity: the presence of a hydroxyl group (in Man) instead of the protected amino group (in Boc-Phg) and the presence of a benzyl (aralkyl) group (in Boc-Phe) or a methyl (alkyl) group (in Boc-Ala) instead of the phenyl group (in Boc-Phg) decreased the recognition ability of receptor (*S,S*)-**9**. This preference of receptor (*S,S*)-**9** is similar to that of the reported bis(thiourea) derivative **5** containing glucopyranosyl groups, in which case the highest enantioselectivity was also observed toward (*R*)-Boc-Phg over its (*S*)-isomer (Δ log *K* = 0.22) among the same chiral carboxylates.⁴⁷ Another trend can be observed: the stability constants of complexes with the enantiomers of Man are lower than those with the enantiomers of amino acid derivatives (Boc-Phg, Boc-Phe, Boc-Ala) in the cases of 5,5-dioxophenothiazine-based anion sensors **5**, (*S,S*)-**8** and (*S,S*)-**9**.

The complexation properties of receptors (*S,S*)-**6** and (*S,S*)-**7** toward the chiral carboxylates were also examined. Sensor molecules (*S,S*)-**6** and (*S,S*)-**7** showed similar, but considerably smaller absorption and fluorescence spectral changes compared to those of receptors (*S,S*)-**8** and (*S,S*)-**9**. These slight changes did not allow the accurate determination of the stability constants of

complexes, therefore, the enantiomeric recognition abilities of receptors (*S,S*)-**6** and (*S,S*)-**7** could not be evaluated.

3. Conclusion

We synthesized four 5,5-dioxophenothiazine derivatives as potential enantioselective anion sensors, and their absorption and fluorescence behaviour in the presence of the enantiomers of tetrabutylammonium salts of α -hydroxy and *N*-protected α -amino acids were studied. Receptors (*S,S*)-**6** and (*S,S*)-**7** containing phenyl groups at their stereogenic centres gave considerably small absorption and fluorescence spectral changes upon addition of the carboxylates, which did not allow the accurate determination of the stability constants of these complexes. However, derivatives (*S,S*)-**8** and (*S,S*)-**9** containing 1-naphthyl groups at their stereogenic centres showed larger spectral changes in the presence of the chiral carboxylates, and the enantiomeric recognition abilities were evaluated based on the fluorescence spectral changes. The highest enantioselectivity, which is a moderate one, could be observed in the case of receptor (*S,S*)-**9** and the enantiomers of Boc-Phg.

4. Experimental

4.1. General

Starting materials were purchased from Sigma–Aldrich Corporation unless otherwise noted. (*S*)-1-(1-Naphthyl)ethyl isothiocyanate was obtained from Alfa Aesar. Silica gel 60 F₂₅₄ (Merck) plates were used for TLC. Silica gel 60 F₂₅₄ (Merck) plates (1 mm) were used for PLC. Silica gel 60 (70–230 mesh, Merck) was used for column chromatography. Ratios of solvents for the eluents are given in volumes (mL/mL). Solvents were dried and purified according to well established methods.⁵² Evaporations were carried out under reduced pressure.

Melting points were taken on a Boetius micro-melting point apparatus and are uncorrected. Optical rotations were taken on a Perkin–Elmer 241 polarimeter, which was calibrated by measuring the optical rotations of both enantiomers of menthol. IR spectra were recorded on a Bruker Alpha-T FT-IR spectrometer. ¹H (500 MHz) NMR spectra were obtained on a Bruker DRX-500 Avance spectrometer. ¹H (300 MHz) and ¹³C (75.5 MHz) NMR spectra were obtained on a Bruker 300 Avance spectrometer. The signals of NH protons in the ¹H NMR spectra were helped to identify by shaking the NMR samples with D₂O. Mass spectra were recorded on an Agilent-6120 Single Quadrupole LC/MS instrument using ESI method. Elemental analyses were performed in the

Microanalytical Laboratory of the Department of Organic Chemistry, Institute for Chemistry, L. Eötvös University, Budapest, Hungary.

UV–vis spectra were taken on a Unicam UV4-100 spectrophotometer. Quartz cuvettes with path length of 1 cm were used. Fluorescence spectra were recorded on a Perkin–Elmer LS 50B luminescent spectrometer. Emission spectra were corrected by the spectrometer software. Quartz cuvettes with path length of 1 cm were used. Fluorescence quantum yields were determined relative to quinine sulfate ($\Phi_f = 0.53$ in 0.1 M H₂SO₄).³⁸ Stability constants of the complexes were determined by global nonlinear regression analysis using SPECFIT/32TM software.

The enantiomers of mandelic acid and Boc-protected amino acids were purchased from Sigma–Aldrich Corporation. The tetrabutylammonium salts of the anions were prepared by adding 1 equiv of carboxylic acid to 1 equiv of Bu₄NOH dissolved in MeOH. After evaporating MeOH, the salts were dried under reduced pressure over P₂O₅. During the fluorescence titrations, the concentrations of the solutions of receptors (*S,S*)-**6**–(*S,S*)-**9** were 2, 3 and 5 μ M, and the concentrations of the titrant solutions of chiral carboxylates were 0.2, 0.5, 1 and 10 mM.

4.2. General procedure for the synthesis of receptors (*S,S*)-**6**–(*S,S*)-**9**

To a stirred solution of diamine **10**⁴⁵ (200 mg, 0.535 mmol) in pyridine (3 mL) was added the solution of the appropriate (*S*)-1-arylethyl isocyanate (1.12 mmol, R = phenyl: 165 mg, R = 1-naphthyl: 222 mg) or (*S*)-1-arylethyl isothiocyanate (1.61 mmol, R = phenyl: 262 mg, R = 1-naphthyl: 342 mg) in pyridine (2 mL) under Ar at rt. The mixture was stirred at rt for 1 h (X = O) or 2 days (X = S) (see Scheme 1). After the reaction was completed, the reaction mixture was poured into a water–ice mixture, and acidified to pH 2 using concentrated hydrochloric acid. The precipitate was filtered off, washed with water, and the crude product was purified as described below for each compound.

4.2.1. 1,1'-(3,7-Di-*tert*-butyl-5,5-dioxo-5,10-dihydro-5 λ ⁶-phenothiazine-1,9-diyl)bis{3-[(1*S*)-1-phenylethyl]urea} [(*S,S*)-6**].** The crude product was triturated with ethanol to give receptor (*S,S*)-**6** (203 mg, 57%) as off-white crystals. Mp: 216–217°C; *R*_f: 0.46 (silica gel TLC, MeOH–CH₂Cl₂ 1:20); $[\alpha]_D^{27} = +65.2$, $[\alpha]_{578}^{27} = +69.5$, $[\alpha]_{546}^{27} = +81.3$, $[\alpha]_{436}^{27} = +154$ (*c* 1.00, DMF); IR (KBr) ν_{\max} 3372, 3085, 3063, 3030, 2965, 2907, 2871, 1665, 1609, 1547, 1495, 1453, 1365, 1240, 1137, 901, 875, 760, 701, 600, 547 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆) δ 1.30 (s, 18H), 1.39 (d, *J* = 6 Hz, 6H), 4.82–4.97 (m, 2H), 7.18–7.47 (m, 10H + 2H, NH), 7.51 (s, 2H), 7.98 (s, 2H), 9.08 (br s, 2H,

NH), 9.20 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $\text{DMSO-}d_6$) δ 23.55, 30.86, 34.36, 49.08, 111.68, 121.34, 123.88, 125.73, 126.61, 127.64, 128.27, 128.40, 144.25, 145.09, 154.80; MS calcd for $\text{C}_{38}\text{H}_{45}\text{N}_5\text{O}_4\text{S}$: 667.3, found $(\text{M}+\text{H})^+$: 668.3; Anal. calcd for $\text{C}_{38}\text{H}_{45}\text{N}_5\text{O}_4\text{S}$: C 68.34, H 6.79, N 10.49, S 4.80, found: C 68.11, H 6.91, N 10.24, S 4.53.

4.2.2. 1,1'-(3,7-Di-*tert*-butyl-5,5-dioxo-5,10-dihydro-5 λ^6 -phenothiazine-1,9-diyl)bis{3-[(1*S*)-1-phenylethyl]thiourea} [(*S,S*)-7]. The crude product was purified by preparative layer chromatography using 1:20 MeOH– CH_2Cl_2 as an eluent to give receptor (*S,S*)-7 (220 mg, 59%) as yellow crystals. Mp: 155–156°C; R_f : 0.85 (silica gel TLC, MeOH– CH_2Cl_2 1:20); $[\alpha]_D^{32} = +34.3$, $[\alpha]_{578}^{32} = +35.7$, $[\alpha]_{546}^{32} = +42.2$, $[\alpha]_{436}^{32} = +105$ (c 0.67, CH_2Cl_2); IR (KBr) ν_{max} 3346, 3085, 3062, 3030, 2965, 2870, 1606, 1494, 1454, 1366, 1286, 1139, 1095, 1024, 901, 884, 756, 700, 552 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.31 (s, 18H), 1.55 (d, $J = 7$ Hz, 6H), 5.48–5.62 (m, 2H), 6.04–6.32 (br s, 2H, NH), 7.10–7.39 (m, 12H), 8.02 (s, 2H), 8.76 (br s, 1H, NH), 10.07 (br s, 2H, NH); ^{13}C NMR (75.5 MHz, CDCl_3) δ 22.53, 31.29, 35.13, 54.72, 119.26, 123.07, 123.49, 126.49, 127.60, 128.81, 129.90, 132.10, 142.76, 146.16, 180.25; MS calcd for $\text{C}_{38}\text{H}_{45}\text{N}_5\text{O}_2\text{S}_3$: 699.3, found $(\text{M}+\text{H})^+$: 700.3; Anal. calcd for $\text{C}_{38}\text{H}_{45}\text{N}_5\text{O}_2\text{S}_3$: C 65.20, H 6.48, N 10.00, S 13.74, found: C 64.95, H 6.19, N 9.76, S 13.49.

4.2.3. 1,1'-(3,7-Di-*tert*-butyl-5,5-dioxo-5,10-dihydro-5 λ^6 -phenothiazine-1,9-diyl)bis{3-[(1*S*)-1-(naphthalen-1-yl)ethyl]urea} [(*S,S*)-8]. The crude product was triturated with ethanol to give receptor (*S,S*)-8 (318 mg, 77%) as off-white crystals. Mp: 184–187°C; R_f : 0.68 (silica gel TLC, *i*PrOH–hexane 1:5); $[\alpha]_D^{31} = +38.9$, $[\alpha]_{578}^{32} = +40.6$, $[\alpha]_{546}^{32} = +46.6$, $[\alpha]_{436}^{32} = +96.5$ (c 1.04, DMF); IR (KBr) ν_{max} 3369, 3063, 3051, 3012, 2964, 2905, 2870, 1667, 1609, 1544, 1494, 1450, 1396, 1365, 1286, 1239, 1138, 1056, 900, 875, 799, 778, 728, 598, 549 cm^{-1} ; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 1.28 (s, 18H), 1.54 (d, $J = 7$ Hz, 6H), 5.66–5.75 (m, 2H), 7.14 (d, $J = 8$ Hz, 2H, NH), 7.45–7.56 (m, 6H), 7.58 (d, $J = 2$ Hz, 2H), 7.66 (d, $J = 7$ Hz, 2H), 7.69 (d, $J = 2$ Hz, 2H), 7.81 (d, $J = 8$ Hz, 2H), 7.92 (d, $J = 8$ Hz, 2H), 8.15 (d, $J = 8$ Hz, 2H), 8.60 (s, 2H, NH), 9.72 (s, 1H, NH); ^{13}C NMR (75.5 MHz, $\text{DMSO-}d_6$) δ 22.33, 30.85, 34.33, 45.25, 112.93, 121.38, 122.16, 123.10, 125.02, 125.46, 125.60, 126.19, 127.31, 127.52, 128.67, 129.77, 130.19, 133.44, 140.34, 144.21, 155.33; MS calcd for $\text{C}_{46}\text{H}_{49}\text{N}_5\text{O}_4\text{S}$: 767.4, found $(\text{M}+\text{H})^+$: 768.4; Anal. calcd for $\text{C}_{46}\text{H}_{49}\text{N}_5\text{O}_4\text{S}\cdot\text{H}_2\text{O}$: C 70.29, H 6.54, N 8.91, S 4.08, found: C 70.03, H 6.67, N 8.69, S 4.29.

4.2.4. 1,1'-(3,7-Di-*tert*-butyl-5,5-dioxo-5,10-dihydro-5 λ ⁶-phenothiazine-1,9-diyl)bis{3-[(1*S*)-1-(naphthalen-1-yl)ethyl]thiourea} [(*S,S*)-9]. The crude product was purified by column chromatography on silica gel using 1:15 iPrOH–hexane as an eluent to give receptor (*S,S*)-9 (214 mg, 50%) as yellow crystals. Mp: 167–170°C; R_f : 0.42 (silica gel TLC, iPrOH–hexane 1:7); $[\alpha]_D^{29} = +116$, $[\alpha]_{578}^{29} = +121$, $[\alpha]_{546}^{29} = +142$, $[\alpha]_{436}^{29} = +297$ (c 0.71, CH₂Cl₂); IR (KBr) ν_{\max} 3346, 3098, 3050, 3014, 2963, 2906, 2869, 1605, 1494, 1467, 1366, 1286, 1240, 1138, 900, 884, 798, 777, 734, 648, 556 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.04 (s, 18H), 1.77 (d, $J = 6$ Hz, 6H), 6.04–6.52 (m, 2H + 2H, NH), 7.15–7.35 (m, 4H), 7.43–7.61 (m, 6H), 7.72 (d, $J = 8$ Hz, 2H), 7.85 (d, $J = 8$ Hz, 2H), 7.90 (s, 2H), 8.20 (d, $J = 8$ Hz, 2H), 8.64 (br s, 1H, NH), 9.88 (br s, 2H, NH); ¹³C NMR (75.5 MHz, CDCl₃) δ 21.49, 30.99, 34.83, 51.33, 119.12, 122.98, 123.31, 123.41, 125.54, 125.64, 126.10, 127.02, 128.52, 129.17, 129.76, 131.00, 132.08, 134.16, 138.07, 146.24, 180.20; MS calcd for C₄₆H₄₉N₅O₂S₃: 799.3, found (M+H)⁺: 800.3; Anal. calcd for C₄₆H₄₉N₅O₂S₃: C 69.05, H 6.17, N 8.75, S 12.02, found: C 68.94, H 5.92, N 8.49, S 11.85.

Acknowledgements

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