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Synthesis and chiral recognition of novel chiral fluorescence receptors bearing 9-anthryl moieties

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Abstract—Two chiral fluorescence receptors **1** and **2** have been synthesized, and their structures characterized by IR, ^{1}H NMR, MS spectra and elemental analysis. The chiral recognition of the receptors was studied by ^{1}H NMR and fluorescence spectra. The results demonstrate that the receptors and tetrabutylammonium mandelate formed a 1:1 complex. Two receptors exhibit good chiral recognition abilities towards the enantiomers of tetrabutylammonium mandelate.

1. Introduction

Molecular recognition of guests by synthetic hosts have attracted considerable attention in organic, biological and medicinal chemistry. The development of chiral artificial receptors, which have the properties of chiral recognition and chiral catalysis is especially important,[1] because these are fundamental characteristics of biochemical systems and could contribute to the development of pharmaceuticals, enantioselective sensors and enzyme models.

In the synthesis of chiral receptors, amino acids or peptides can be employed as chiral sources in building the desired molecules because of their accessibility[2] and biological relevance. A great number of artificial chiral receptors have been synthesized and studied, which contain the chiral macrocyclic and acyclic polyamines,[3] chiral calixarenes,[4] and chiral cyclodextrin derivatives.[5] However, few examples have been reported dealing with the synthesis and chiral recognition studies of chiral fluorescence receptors.[4a] Herein, we report the synthesis of two new chiral fluorescence receptors **1** and **2** containing both an amino acid unit and 9-anthryl groups, and their enantioselective recognition ability for D- and L-tetrabutylammonium mandelate by ^{1}H NMR and fluorescence spectroscopy. The synthetic route to the receptors is shown in Scheme 1.

2. Results and discussion

2.1. Synthesis

Chiral fluorescence receptors **1** and **2** were efficiently synthesized by the reaction of intermediates **4** or **6** and 9-anthraldehyde, and subsequent reduction by $NaBH_4$ (Scheme 1). To avoid a cyclic product, intermediates **4** and **6** were prepared with good yields by the reaction of **3** or **5** and excess ethylenediamine. The ^{1}H NMR spectra exhibited all the expected signals with the desired integral values and support the molecular structures. The structures of these compounds were characterized by IR, MS, ^{1}H NMR spectra and elemental analysis.

2.2. Fluorescence spectra

The fluorescence spectra were recorded from a solution of receptors **1** or **2** in DMSO in the absence and presence of D- or L-mandelate. Figures 1 and 2 show the fluorescence spectra of a mixture of receptor **1** (1.4×10^{-5} mol L^{-1}) with different concentrations of D- or L-mandelate anion in DMSO. By gradually increasing the concentration of the D- or L-mandelate, the fluorescence emission intensities of receptor **1** at 418 and 441 nm (λ_{ex} = 370 nm) gradually increased, which indicates complexation happened between receptor **1** and

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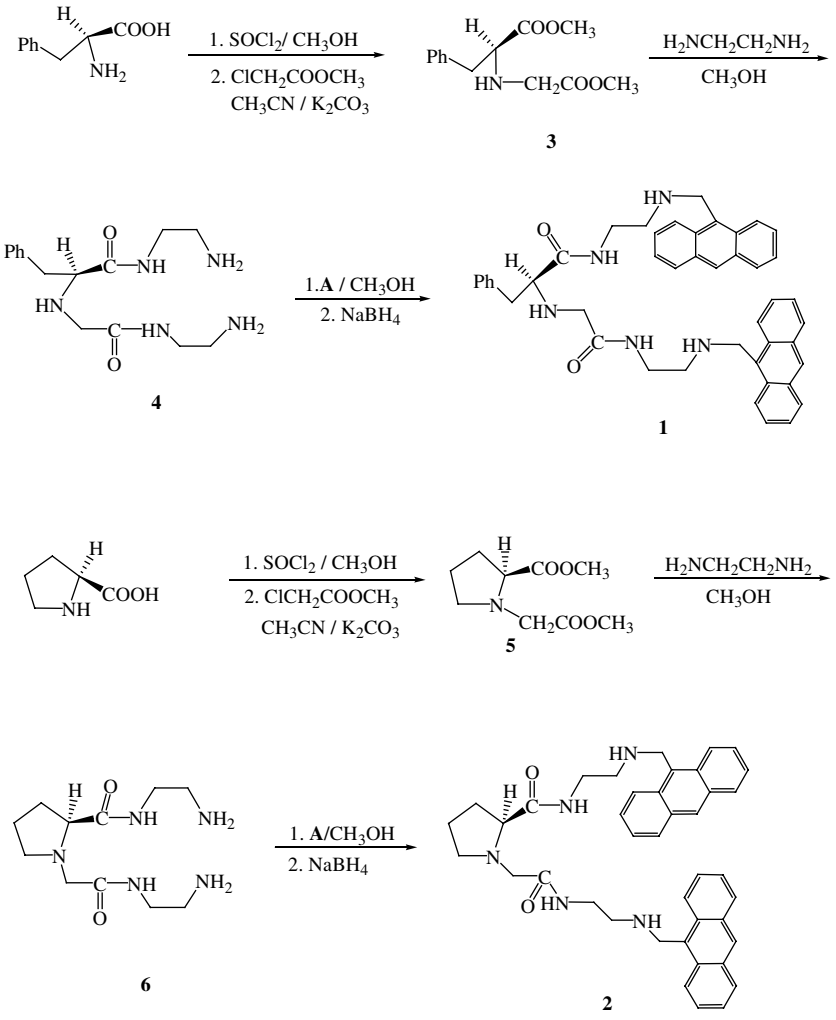

Scheme 1. The synthesis of receptors.

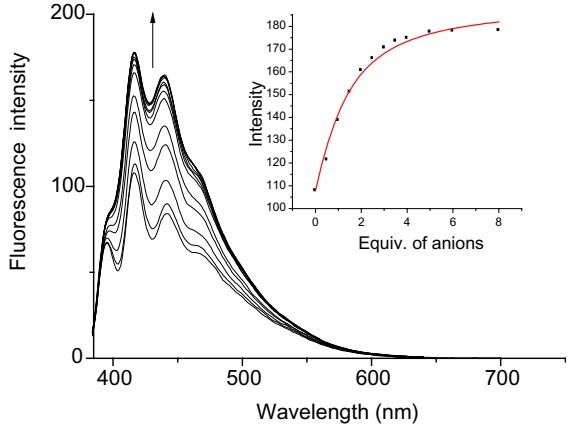

Figure 1. Fluorescence spectra of receptor **1** (1.4×10^{-5} mol L^{-1}) with D-mandelate anion in DMSO. The equivalents of anion are: 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.5, 5.0, 6.0 and 8.0. λ_{ex} = 370 nm. Inset: changes of fluorescence intensity of **1** at 418 nm upon addition of D-mandelate anion. The line is curve fitting. The correlation coefficient (R) of non-linear curve fitting is 0.9936.

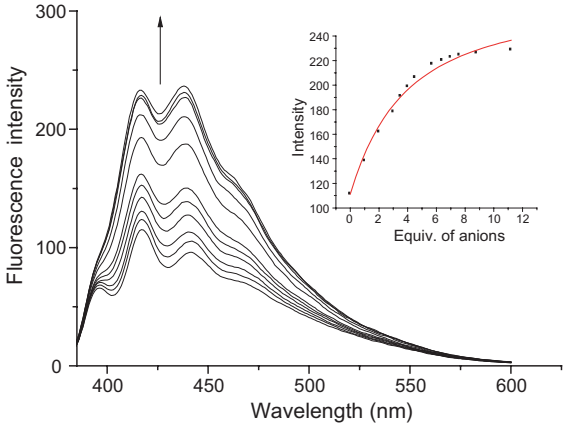

Figure 2. Fluorescence spectra of receptor **1** (1.4×10^{-5} mol L^{-1}) with L-mandelate anion in DMSO. The equivalents of anion are: 0.0, 1.0, 2.0, 3.0, 3.5, 4.0, 4.5, 5.5, 6.5, 7.0, 7.5, 8.5 and 11.0. λ_{ex} = 370 nm. Inset: changes of fluorescence intensity of **1** at 418 nm upon addition of L-mandelate. The line is curve fitting. The correlation coefficient (R) of non-linear curve fitting is 0.9929.

D- or L-mandelate. The phenomenon of fluorescence intensity increasing upon addition of a guest anion is similar to the anion-induced fluorescence enhancement already reported.[6] In the absence of an anion, the

photoinduced electron-transfer (PET) process between the anthracene group and the weak electron-withdrawing amide substituents might result in decreased fluorescence intensity. Upon the addition of anions, the interaction of an anion with a receptor unit could diminish the PET progress to induce fluorescence retrieval. Therefore anion-induced fluorescence enhancement was observed.[7] The satisfactory result (the correlation coefficient is over 0.99) of non-linear curve fitting (fluorescence intensity at 418 nm vs equivalents of mandelate anion) confirmed that receptor **1** and D- or L-mandelate anion formed a 1:1 complex (see the top right plot of Figs. 1 and 2).[8] For a complex of 1:1 stoichiometry, an association constant K_{ass} can be calculated by using the following equation:[8,9]

$$X = X_0 + (X_{lim} - X_0)/2C_0\{C_H + C_G + 1/K_{ass} - [(C_H + C_G + 1/K_{ass})^2 - 4C_HC_G]^{1/2}\},$$

where X represents the fluorescence intensity, and C_H and C_G are the corresponding concentrations of host and anion guest. The association constants (K_{ass}) and correlation coefficients (R) obtained by a non-linear least-squares analysis of X versus C_H and C_G are listed in Table 1.

Figures 3 and 4 show the changes in the fluorescence spectra of receptor **2** at a concentration of 1.8×10^{-5} mol L^{-1} or 3.6×10^{-5} mol L^{-1} in DMSO upon addition of D- or L-mandelate. When D- or L-mandelate anions were introduced to the solution of **2**, the fluorescence emission intensities of receptor **2** at 417 and 441 nm (λ_{ex} = 371 nm) also increased. The result of a non-linear curve fitting (at 441 nm) indicates that a 1:1 complex was formed between receptor **2** with D- or L-mandelate anion (see the top right plot of Figs. 3 and 4).[8] The association constants (K_{ass}) and correlation coefficients (R) obtained by a non-linear least-squares analysis of X versus C_H and C_G are also listed in Table 1.

The data in Table 1 illustrate that the two receptors can bind D- or L-mandelate anions in the same order: D-mandelate anion, L-mandelate anion and receptor **2** have more selectivity for recognition of the D-mandelate anion. This may be due to the relatively greater rigidity of the structure of receptor **2**, which results in a more selective recognition.

2.3. ^{1}H NMR study

^{1}H NMR experiments were undertaken to assess the chiral recognition properties between receptor and D- or L-tetrabutylammonium mandelate because it can directly provide structural and dynamic information.[10] Studies on the chiral recognition were carried out on a 300 MHz NMR spectrometer using compounds **1** and **2** as chiral solvating agents.

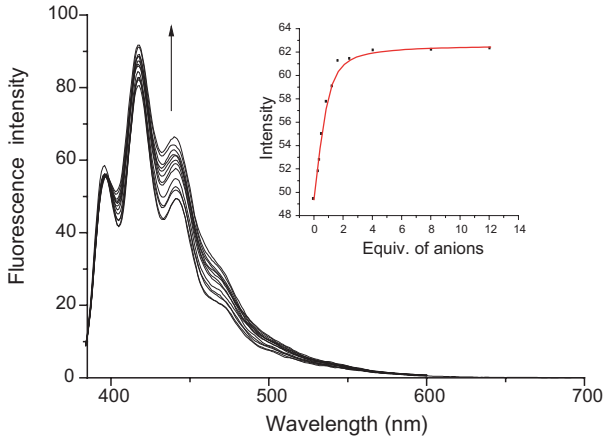

Figure 3. Fluorescence spectra of receptor **2** (1.8×10^{-5} mol L^{-1}) with D-mandelate in DMSO. The equivalents of anion are: 0, 0.32, 0.4, 0.56, 0.88, 1.28, 1.68, 2.48, 4.08, 8.08 and 12.08. λ_{ex} = 371 nm. Inset: changes of fluorescence intensity of **2** at 441 nm upon addition of D-mandelate anion. The line is curve fitting. The correlation coefficient (R) of non-linear curve fitting is 0.9938.

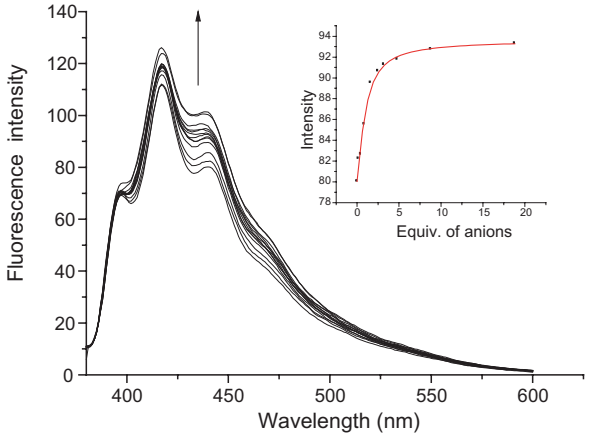

Figure 4. Fluorescence spectra of receptor **2** (3.6×10^{-5} mol L^{-1}) with L-mandelate in DMSO. The equivalents of anion are: 0, 0.16, 0.46, 0.87, 1.2, 1.6, 2.5, 3.2, 4.8, 8.8 and 18.8. λ_{ex} = 370 nm. Inset: changes of fluorescence intensity of **2** at 441 nm upon addition of L-mandelate anion. The line is curve fitting. The correlation coefficient (R) of non-linear curve fitting is 0.9963.

Table 1. Association constants (K_{ass}) and correlation coefficients (R) of **1** and **2** with D- or L-mandelate in DMSO

Anion[a]	Receptor **1**		Receptor **2**	
	K_{ass} (M^{-1})	R	K_{ass} (M^{-1})	R
D-Mandelate	$(8.35 \pm 0.36) \times 10^4$	0.9936	$(3.64 \pm 0.12) \times 10^5$	0.9938
L-Mandelate	$(2.08 \pm 0.06) \times 10^4$	0.9929	$(4.06 \pm 0.06) \times 10^4$	0.9963

[a] Anions were used as their tetrabutylammonium salts.

Tetrabutylammonium mandelate was chosen as the probe. Figure 5A shows the ^{1}H NMR spectrum of racemic mandelate in $CDCl_3$; only one singlet (δ 5.20 ppm) for the CH proton resonance of racemic mandelate was observed in the absence of the host. The ^{1}H NMR spectra of receptor **1** (2×10^{-3} M) and its complex with equimolar amounts (2×10^{-3} M) of D-, L- or racemic mandelate are shown in Figure 5. Two singlet resonances (δ 4.83 and 4.88 ppm) due to the CH proton of racemic mandelate were observed in the presence of receptor **1** (Fig. 5C), with their intensity ratio being about 1:1 and with the separation between the two peaks being 15 Hz. This indicates that the interactions of receptor **1** with the D- and L-forms of mandelate are different, resulting in two singlet resonances for the racemic CH proton. The CH proton singlets of D- and L-mandelate were shifted upfield by about 0.37 and 0.32 ppm in the presence of receptor **1** (Fig. 5D and E), respectively. The larger upfield shift of the CH proton towards the D-enantiomer reveals that the receptor **1** has a stronger chiral recognition ability than with the L-enantiomer.

The ^{1}H NMR spectra of the receptor **2** and its complex with equimolar amounts of D-, L- or racemic mandelate are shown in Figure 6. Addition of receptor **2** to racemic mandelate in $CDCl_3$ caused remarkable upfield shifts (δ 4.68 and 4.77 ppm) of the CH proton of mandelate (Fig. 6B). The methine signal has clearly split into two peaks ($\Delta\Delta\delta$ 27 Hz). The interaction of receptor **2** with the D-enantiomer shows that the CH proton has a larger upfield shift ($\Delta\delta$ 0.52 ppm, Fig. 6C) than the CH proton of the L-enantiomer ($\Delta\delta$ 0.43 ppm, Fig. 6D). It is similar to receptor **1** in the recognition ability for the enantiomers, while receptors **1** and **2** have a strong interaction to D-mandelate. Receptor **2** revealed the highly enantioselective recognition for the enantiomers of the mandelate.

The ^{1}H NMR spectra of receptors **1** and **2** show dramatic changes in the presence of a guest. Upon the addition of an equimolar amount of D-mandelate to a solution of receptor **1**, the peaks of the anthracene fragments are shifted downfield to 8.91 ppm and broadened; one characteristic peak of amide (N*H*) is shifted upfield

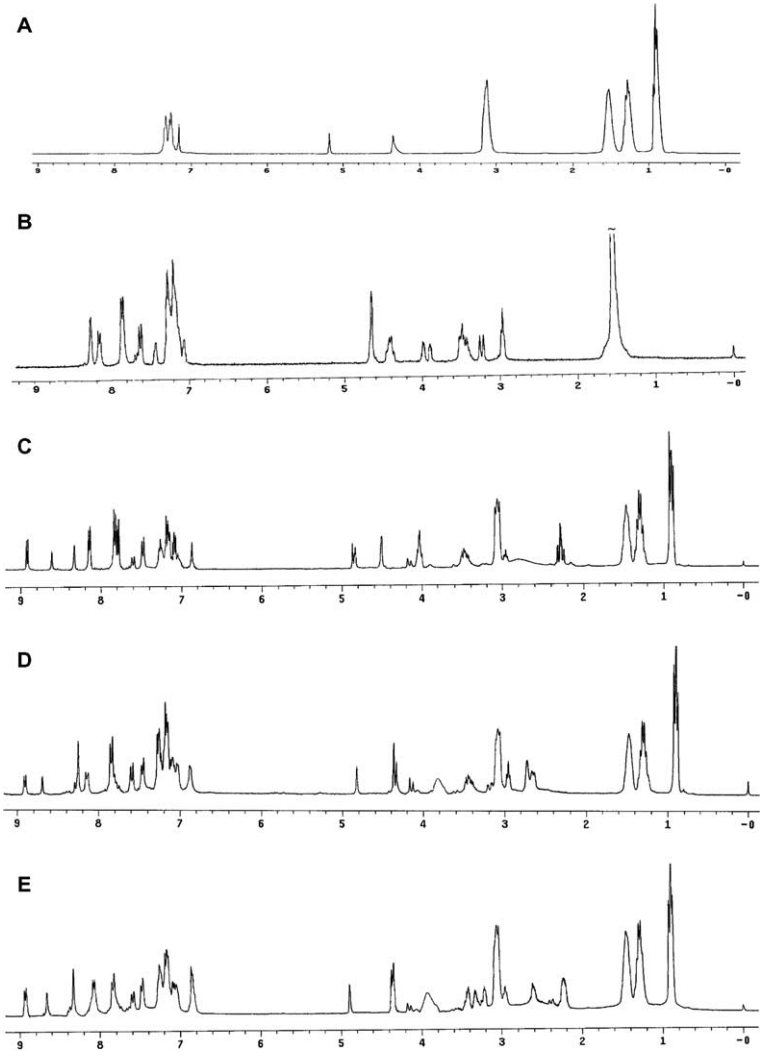

Figure 5. ^{1}H NMR spectra of **1** and its guest complex at 25 °C ([**1**] = [guest] = 2.0×10^{-3} M) in $CDCl_3$ at 300 MHz. (A) Racemic tetrabutylammonium mandelate; (B) receptor **1**; (C) receptor **1** + racemic tetrabutylammonium mandelate; (D) receptor **1** + D-tetrabutylammonium mandelate; (E) receptor **1** + L-tetrabutylammonium mandelate.

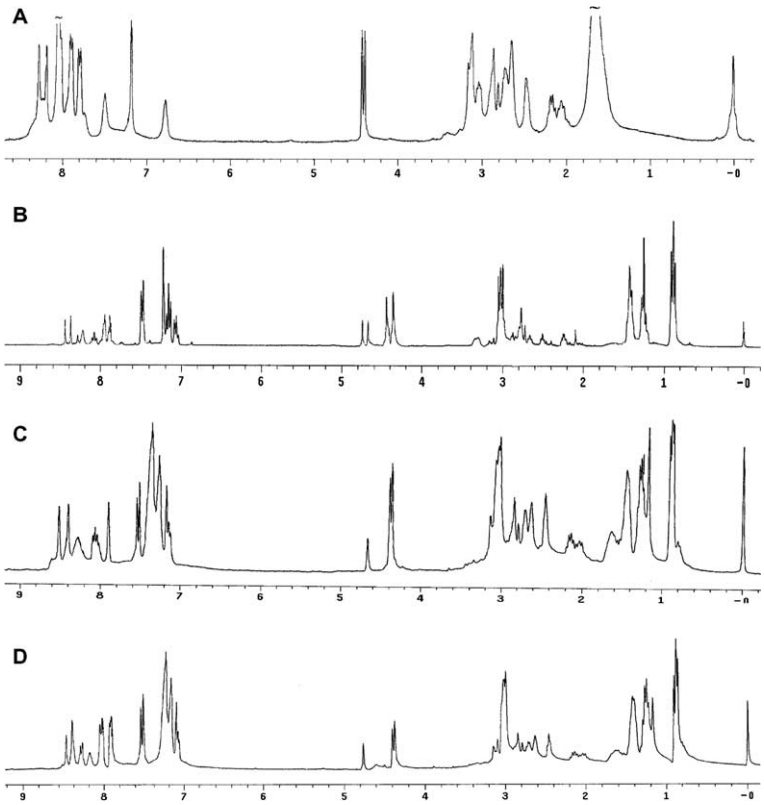

Figure 6. ^{1}H NMR spectra of **2** and its guest complex ([**2**] = [guest] = 2.0×10^{-3} M) at 25 °C in $CDCl_3$ at 300 MHz. (A) Receptor **2**; (B) receptor **2** + racemic tetrabutylammonium mandelate; (C) receptor **2** + D-tetrabutylammonium mandelate; (D) receptor **2** + L-tetrabutylammonium mandelate.

from 7.05 to 6.86 ppm ($\Delta\delta$ 0.19 ppm), while the other amide (N*H*) peak disappeared. Upon addition of an equimolar amount of L-mandelate to a solution of **1**, the peaks of the anthracene fragments also shifted downfield and broadened; one amide (N*H*) peak shifted upfield from 7.05 to 6.82 ppm ($\Delta\delta$ 0.23 ppm), while the other amide (N*H*) peak disappeared.

The ^{1}H NMR spectra in the interactions of receptor **2** and D- or L-mandelates show that the peaks of the anthracene fragments are shifted downfield and broadened, but one amide (N*H*) proton signal at 6.77 ppm disappeared, while the other amide (N*H*) peak at 7.49 ppm was shifted downfield to 8.28 ppm for the D-form and 8.20 ppm for L-form.

The above results illustrate that the enantioselective recognition of the receptors for D- or L-mandelates is through multiple hydrogen bonding interactions[11] and the π–π interaction between anthryl-ring of the host and phenyl-ring of the guest.[12] Receptors **1** and **2** exhibit good enantioselectivity for D-mandelate, and receptor **2** has better selective recognition because the structure of receptor **2** has a relatively large rigidity than receptor **1**.

3. Conclusion

In summary, two chiral fluorescence receptors **1** and **2** have been synthesized. The enantioselective recognition of the receptors was studied by ^{1}H NMR and fluorescence spectra. Receptors **1** and **2** exhibit different chiral recognition abilities towards the enantiomers of D- and L-tetrabutylammonium mandelate, and formed a 1:1 complex between the host and guest; receptor **2** has a better chiral recognition ability than receptor **1**. The receptor steric effect, structural rigidity, hydrogen bond and π–π stacking between the aromatic groups may be responsible for the enantiomeric recognition of mandelates.

4. Experimental

4.1. Materials and methods

Acetonitrile was dried and distilled from CaH_2; ethylenediamine and thionyl chloride were distilled before use. All other commercially available regents were used without further purification. The anions were used as their tetrabutylammonium salts. Melting points were measured on a Reichert 7905 melting point apparatus (uncorrected). The IR spectra were performed on a Nicolet 670 FT-IR spectrophotometer. Mass spectra were recorded on a ZAB-HF-3F mass spectrometer. Elemental analyses were determined by Perkin–Elmer 204B elemental autoanalyzer. ^{1}H NMR spectra were recorded on a Varian Mercury VX-300 MHz spectrometer. Fluorescence spectra were obtained on a Shimadzu RF-5301 spectrometer. 9-Anthraldehyde was prepared according to the literature method.[3c,13]

4.2. Syntheses

Intermediates **4** *and* **6**: a solution of **3** or **5** (1 mmol) in methanol (30 mL) was added dropwise to the stirred solution of ethylenediamine (0.6 g, 10 mmol) in methanol (10 mL). The mixture was stirred for 48 h under N_2 protection at room temperature. The solvent and excess amine were removed under reduced pressure and the residue dried in vacuo to give product **4** or **6** as a mildly hygroscopic solid.

Compound **4**: yield 95%; IR (cm^{-1}): 3448, 3287, 1674, 1542, 1441, 687; ^1H NMR ($CDCl_3$): δ 7.39 (br, 1H, CONH), 7.25–7.19 (m, 5H, ArH), 6.93 (br, 1H, CONH), 3.41 (dd, $J = 4.2$, 9.0 Hz, 1H, C**H*CH_2), 3.26–3.13 (m, 5H, N*H*CH_2CO, PhCH_2), 3.07–2.89 (m, 4H, 2CONHCH_2), 2.74–2.61 (m, 8H, 2CH_2CH_2NH_2).

Compound **6**: yield 90%; IR (cm^{-1}): 3452, 3293, 1667, 1539, 1445; ^1H NMR ($CDCl_3$): δ 7.74 (br, 1H, CONH), 7.35 (br, 1H, CONH), 3.35–3.08 (m, 7H, 2CONHCH_2, NCH_2CO, Pro-NC**H*), 2.83–2.80 (m, 4H, 2CH_2NH_2), 2.79 (br, 4H, 2NH_2, D_2O, exchangeable), 2.64–2.40 (m, 2H, Pro-N-CH_2), 1.95–1.80 (m, 4H, Pro-CH_2CH_2).

Receptors **1** *and* **2**: a mixture of **4** or **6** (1 mmol) and 9-anthraldehyde (2.2 mmol) in CH_3OH (10 mL) was stirred for 24 h at room temperature, after which $NaBH_4$ (0.2 g) was poured into the solution. The mixture was stirred for 24 h under N_2 protection at ambience temperature. Then the mixture was heated to 50 °C and stirred for 2 h. The solvent was removed under reduced pressure and the residue washed with water. The crude product was purified by column chromatography on silica gel using $CHCl_3/CH_3OH$ (50:1) as eluant to obtain pure product **1** or **2**, respectively.

Compound **1**: yield: 79%; mp: 222–224 °C; $[\alpha]_D^{20} = -8.6$ (*c* 0.05, $CHCl_3$); IR (KBr/cm^{-1}): 3292, 3050, 2926,1661, 1599, 1499, 734; ^1H NMR ($CDCl_3$): δ 8.26 (s, 2H, anthryl), 8.15 (d, $J = 8.4$ Hz, 2H, anthryl), 7.85 (d, $J = 8.4$ Hz, 4H, anthryl), 7.62 (d, $J = 8.4$ Hz, 2H, anthryl), 7.43 (br, 1H, CONH), 7.31–7.10 (m, 13H, anthryl and phenyl), 7.05 (br, 1H, CONH), 4.65 (s, 4H, anthryl–CH_2), 4.50–4.37 (m, 2H, –N*H*C*H*CO–), 3.95 (dd, $J = 4.5$ Hz, 2H, NHCH_2CO), 3.52–3.32 (m, 6H, PhCH_2, 2CONHCH_2), 3.26 (br, 1H, CH_2N*H*CH_2), 3.21 (br, 1H, CH_2N*H*CH_2), 2.98 (t, $J = 7.5$ Hz, 4H, 2CH_2CH_2NH); FAB-MS *m/z* (%): 688 (M^++1, 24). Elemental analysis calcd (%) for $C_{45}H_{45}N_5O_2$: C, 78.56; H, 6.61; N, 10.18; found: C, 78.32; H, 6.73; N, 10.15.

Compound **2**: yield: 64%; mp: 196–198 °C; $[\alpha]_D^{20} = -5.7$ (*c* 0.05, $CHCl_3$), IR (KBr/cm^{-1}): 3414, 3050, 2923,1649, 1525, 1448, 732; ^1H NMR ($CDCl_3$): δ 8.28 (s, 2H, anthryl), 8.20 (s, 2H, anthryl), 8.12–7.96 (m, 6H, anthryl), 7.90 (d, $J = 8.1$ Hz, 4H, anthryl), 7.80 (d, $J = 8.1$ Hz, 4H, anthryl), 7.49 (br, 1H, CONH), 6.77 (br, 1H, CONH), 4.41(s, 2H, anthracene–CH_2), 4.38 (s, 2H, anthracene–CH_2), 3.22–2.57 (m, 13H, 2CH_2CH_2, NCH_2CO, Pro-ring NCH_2 and C*H*), 2.46 (s, 2H, 2ArCH_2N*H*, D_2O exchangeable), 2.30–2.10 (m, 2H, Pro-ring CH_2), 2.10–1.95 (m, 2H, Pro-ring CH_2); FAB-MS *m/z* (%): 638 (M^++1, 10). Elemental analysis calcd (%) for $C_{41}H_{43}N_5O_2$: C, 77.19; H, 6.81; N, 10.98; found: C, 77.08; H, 6.95; N, 10.87.

Acknowledgements

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