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Furo-Fused BINOL Based Crown as a Fluorescent Chiral Sensor for Enantioselective Recognition of Phenylethylamine and Ethyl Ester of Valine

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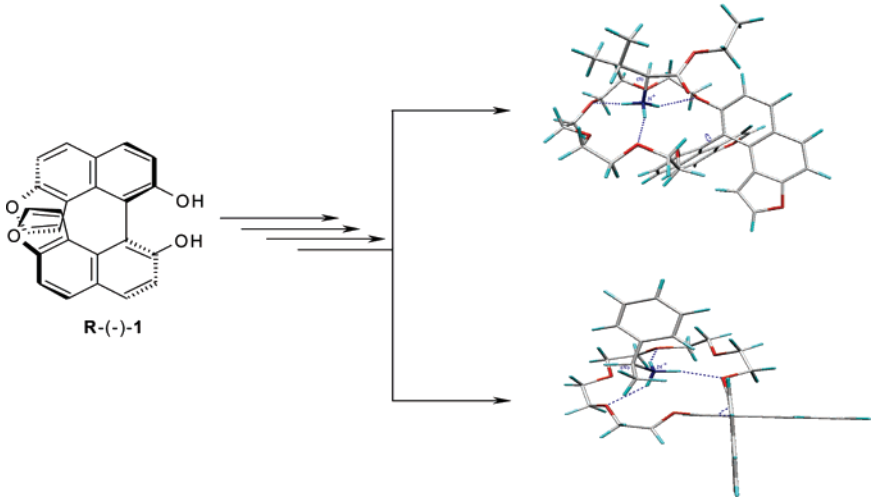

A furo-fused BINOL based chiral crown was developed as an enantioselective chiral sensor for phenylethylamine and ethyl ester of valine. Fusion of furan to BINOL has resulted in a highly stereodiscriminating backbone for the chiral crown developed. This chiral crown exhibited a flourescence enhancement difference of 2.97 times between two enantiomers of phenylethylamine and 2.55 times between two enantiomers of ethyl ester of valine. The ratio of association constants for two diastereomeric complexes of two enantiomers of phenylethylamine was found to be 11.30, and the ratio for two enantiomers of ethyl ester of valine was 7.02.

Introduction

In recent years, the development of synthetic molecular receptors with the ability to recognize, selectively, small biologically important molecules[1] has become an important research activity. Many factors that affect the extent of binding of the guest in the host cavity have been recognized, for example, for chiral ammonium guests, receptors with C_2, C_3, and D_2 symmetry,[2] and crown ethers especially with six ethylene-oxy units, which exhibited better enantioselectivity.[3] Steric features of the host have been recognized as an important factor in high degrees of enantiomeric recognition.[4] Receptors with fluorescence signaling modes are preferred due to the

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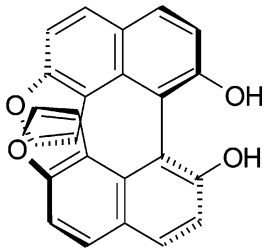


R-(-)-1

FIGURE 1. Furo-fused BINOL, (*R*)-(−)[9,9′]bi[naphtho(2,1-*b*)furanyl]-8,8′-diol.

advantages of the technique such as practical convenience, high sensitivity, low cost, and wide applicability along with multisignaling modes associated with the technique.[5]

The use of binaphthyl based chiral crowns for enantioselective recognition of chiral ammoinium salts was pioneered by Cram et al.[6] The binaphthyl backbone for the construction of a chiral crown offers some unique advantages such as inherent C_2 symmetry,[7] substantially disposed 2,2′-hydroxyls, and an availability of the conjugated π-electron system of the naphthyl moiety capable of giving suitable detectable signals for qualitative (differentiation between two enantiomers) and quantitative (signal intensity depending on enantiomer composition) estimation of the enantioselective complexation. A variety of substituents can be placed on the binaphthyl moiety to alter the electronic and steric properties of the subsequent chiral crowns, many of which have shown good promise as enantioselective sensors.[8] By modifying the BINOL scaffold, chemists can effectively tune both the steric and the electronic properties of the chiral macrocycles.

Many chiral crowns have been reported with BINOL or its derivatives as backbones, which exhibit differing degrees of enantioselectivities.[9] Recently, a furo-fused BINOL derivative was developed in our laboratory. This molecule, (*R*)-(−)[9,9′]-bi[naphtho(2,1-*b*)furanyl]-8,8′-diol (**1**) (Figure 1),[10] presented a potentially promising chiral scaffold for the construction of a suitable chiral crown host for possible enantioselective complexation with chiral ammmonium guests. Molecule **1** has many desired features such as C_2 symmetry, a sufficiently enlarged dihedral angle for better stereo-discrimination, and modified electronic properties as compared to BINOL.

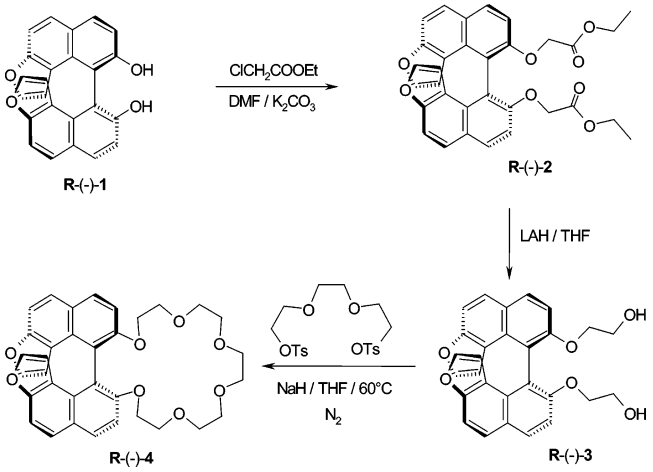
Chiral amines and amino acids are abundant in nature and are basic building blocks of biologically useful molecules. Chiral amines and amino acids also find use in many pharmaceutical preparations. The availability of a suitable chiral host for the fast and accurate determination of these classes of compounds is vital from an academic and industrial point of view. It was therefore decided to determine the efficacy of the crown (*R*)-(−)-**4** for this purpose.

Herein, we report the enantioselective binding of perchlorate salts of chiral (*S*)-(−)-phenylethylamine (**5**) and (*S*)-(+) ethyl ester of valine (**6**) with the chiral fluorescent sensor (*R*)-(−)-**4**.

Results and Discussion

Accordingly, (*R*)-(−)[9,9′]bi[naphtho(2,1-*b*)furanyl]-8,8′-diol based 20 crown 6 (**4**) was synthesized from enantiopure (*R*)-(−)[9,9′]bi[naphtho(2,1-*b*)furanyl]-8,8′-diol (**1**) (Scheme 1).

SCHEME 1. Synthesis of Chiral Furo-Fused Binol Based Crown



The enantiopurity of (*R*)-(−)-**4** was determined by the formation of a diastereomeric complex of (*R*)-(−)-**4** with an enantiopure perchlorate salt of (*S*)-(−)-**5**, and the de was found to be 94% on the basis of the ^{1}H NMR of the complex formed. The UV spectrum of (*R*)-(−)-**4** in chloroform displayed absorptions at $\lambda_{max} = 303$ nm ($\epsilon = 20\,731$). In the same solvent, this compound emitted at 367 nm when excited at 313 nm.

Figure 2 shows a proposed structure of complex (*R*)-(−)-**4** with (*S*)-(−)-**5** featured with three specific hydrogen bonds. Figure 3 shows a proposed structure of complex (*R*)-(−)-**4** with (*S*)-(+)-(**6**). The molecular modeling structure is energy-minimized with the AM1 empirical level of theory using the Gaussian 03W package.[11]

When (*R*)-(−)-**4** was treated with perchlorate salts of (*R*)-(+)-**5** or (*S*)-(−)-**5**, a large fluorescence enhancement was observed as expected. It is proposed that the lone pair of electrons on the oxygen atom attached to the 8 position of naphtho(2,1-*b*)furan in (*R*)-(−)-**4** is incorporated to quench the fluorescence of the molecule through an intramolecular photoinduced electron transfer (PIET) process[1c,12] and that hydrogen

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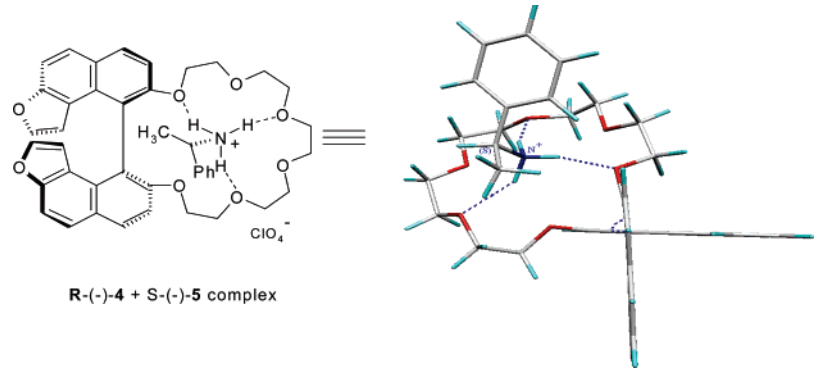

FIGURE 2. Proposed structure for complex (*R*)-(−)-4 and (*S*)-(−)-phenylethylamine (**5**).

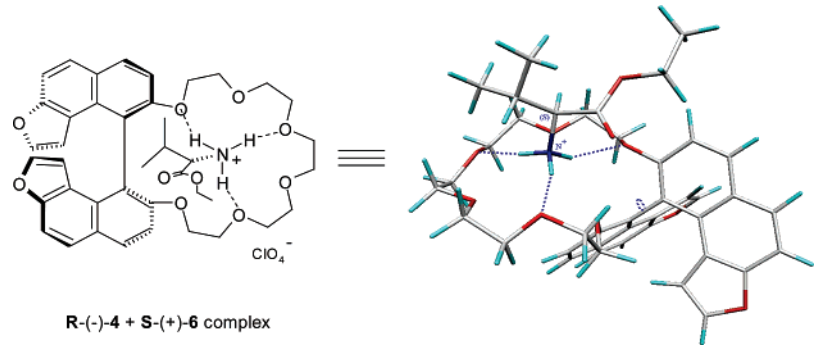

FIGURE 3. Proposed structure for complex (*R*)-(−)-4 and (*S*)-(+)-ethyl ester of valine (**6**).

bonding of the oxygen atom with the hydrogen of the quaternized nitrogen of the amine removes the intermediate quenching step, leading to an overall fluorescence enhancement. A diastereomeric interaction of (*R*)-(−)-**4** with (*R*)-(+)-**5** and (*S*)-(−)-**5** perchlorate salts of phenylethylamines and perchlorate salts of (*S*)-(+)-**6** and (*R*)-(−)-**6**, the ethyl ester of valine, was expected to exhibit a different extent of fluorescence enhancement. We observed that this fluorescence enhancement was highly enantioselective. In chloroform, the fluorescence intensity of (*R*)-(−)-**4** (1.64×10^{-6} M) was increased to 1.25 times that of the original value by (*S*)-(−)-**5** (1.64×10^{-6} M) but only to 1.08 times by (*R*)-(+)-**5** (1.64×10^{-6} M). The net fluorescence intensity increase of (*R*)-(−)-**4** by (*S*)-(−)-**5** was found to be 2.97 times than by (*R*)-(+)-**5** (i.e., the enantiomeric fluorescence difference ratio, ef: $[(I_S - I_0)/(I_R - I_0)]$, was 2.97) (Figure 4).

When perchlorate salts of (*S*)-(+)-6 and (*R*)-(−)-6 (1.37×10^{-6} M) were complexed with (*R*)-(−)-4 (1.37×10^{-6} M), the corresponding fluorescence intensities were recorded as 1.40 and 1.16, respectively. The net fluorescence intensity increase of (*R*)-(−)-4 by (*S*)-(+)-6 was found to be 2.55 times than by (*R*)-(−)-6 (i.e., the enantiomeric fluorescence difference ratio, ef: $[(I_S - I_0)/(I_R - I_0)]$, was 2.55) (Figure 5).

These remarkable differences in fluorescence enhancement make this molecule a useful practical sensor for the enantioselective recognition of chiral (*S*)-(−)-**5** and (*S*)-(+)-**6**. When (*R*)-(−)-**4** (1.64×10^{-6} M) was treated with phenylethylamine in the concentration range of 1.64×10^{-6} to 8.26×10^{-6} M, the fluorescence enhancement of the sensor followed a Benesi−Hildebrand equation.[13]

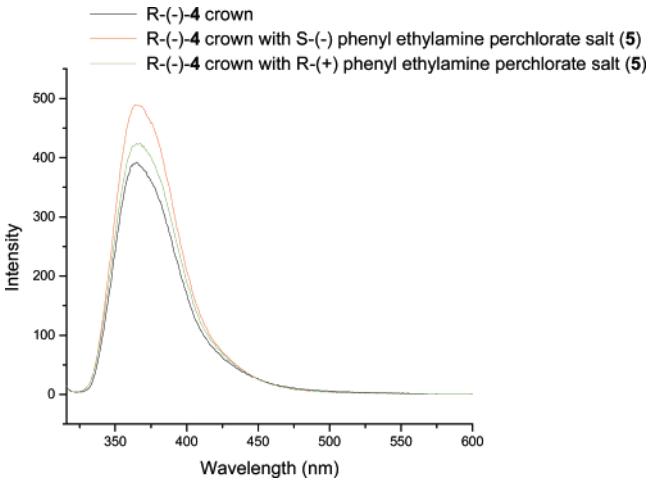

FIGURE 4. Fluorescence spectra of sensor (*R*)-(−)-**4** and (*R*)-(−)-**4** with (*R*)-(+)-**5** and (*S*)-(−)-**5** ($\lambda_{ex} = 303$ nm) at 1.64×10^{-6} M.

(*S*)-(−)-**6** was also evaluated for the same parameters in the concentration range of 1.37×10^{-6} to 6.85×10^{-6} M, and it followed the Benesi−Hildebrand equation as well.

$$\frac{I_0}{I - I_0} = \frac{b}{a - b}\left[\frac{1}{K[\mathrm{M}]} + 1\right]$$

where I_0 is the fluorescence intensity of the sensor in the absence of guest (ammonium salt); I is the fluorescence intensity of the sensor in the presence of guest; [M] is the concentration of the substrates; and K is the association constant between the sensor and the substrates. In the equation, a and b are constants. The value of $b/a - b$ can be found out by plotting $I_0/I - I_0$ against the inverse of the concentration term, M^{-1}. The intercept of

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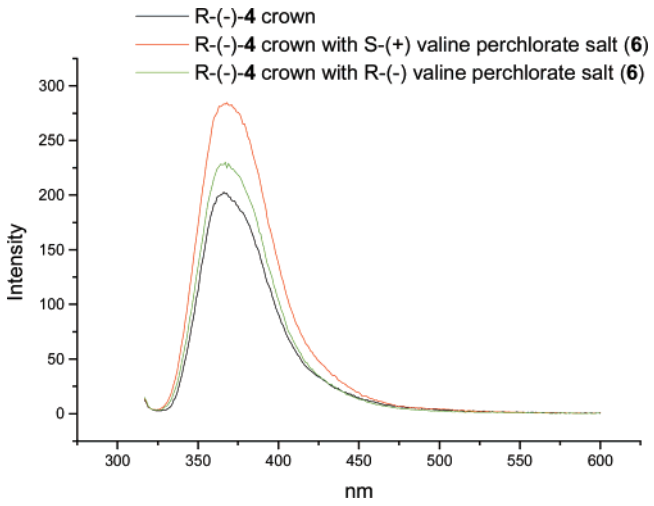

FIGURE 5. Fluorescence spectra of sensor (*R*)-(−)-**4** and (*R*)-(−)-**4** with (*R*)-(−)-**6** and (*S*)-(+)-**6** (λ_{ex} = 306 nm) at 1.37 × 10^{-6} M.

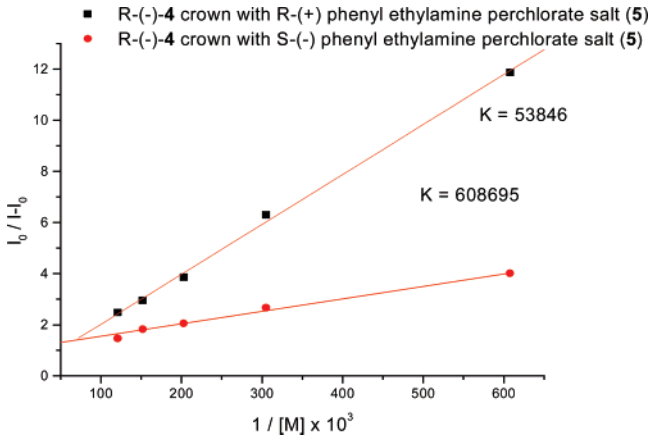

FIGURE 6. Benesi−Hildebrand plot of sensor (*R*)-(−)-**4** (1.64 × 10^{-6} to 8.26 × 10^{-6} M in chloroform) in the presence of (*R*)-(+)-**5** or (*S*)-(−)-**5** (1.64 × 10^{-6} to 8.26 × 10^{-6} M).

the graph gives $b/a - b$; I_0 and I are found out experimentally, and hence, K can then be calculated. Thus, the association constant of (*R*)-(−)-**4** + (*S*)-(−)-**5** was found to be 6.08695 × 10^5 M^{-1} and that of (*R*)-(−)-**4** + (*R*)-(+)-**5** was found to be 5.3846 × 10^4 M^{-1} (Figure 6).

This indicated that the complex (*R*)-(−)-**4** + (*S*)-(−)-**5** was more stable than the complex (*R*)-(−)-**4** + (*R*)-(+)-**5** by ca. −0.2 kcal/mol ($\Delta\Delta G$). In the case of ethyl ester of valine, the association constant of (*R*)-(−)-**4**/(*S*)-(+)-**6** was found to be 2.31481 × 10^5 M^{-1} and that of (*R*)-(−)-**4**/(*R*)-(−)-**6** was found to be 3.2967 × 10^4 M^{-1} (Figure 7). This indicated that the complex (*R*)-(−)-**4** + (*S*)-(+)-**6** was more stable than the complex (*R*)-(−)-**4** + (*R*)-(−)-**6** by ca. −1.30 kcal/mol ($\Delta\Delta G$).

The fluorescence study of (*R*)-(−)-**4** with perchlorate salts of **5** and **6** demonstrated that hydrogen bonding between the lone pair of electrons on the oxygen and the quaternized nitrogen group of phenylethylamine was important for the enantioselective fluorescence enhancement of the sensor. This is consistent with the proposed multiple hydrogen bonding structure between the sensor and the amine. The fluorescence of (*R*)-(−)-**4** in the presence of phenylethylamine with various molar ratios was studied. The study of fluorescence at different composition ratios between (*R*)-(−)-**4** and (*S*)-(−)-**5** revealed a linear relationship

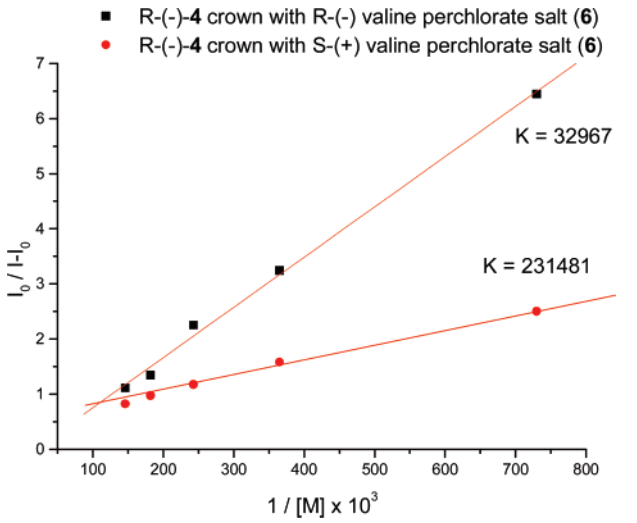

FIGURE 7. Benesi−Hildebrand plot of sensor (*R*)-(−)-**4** (1.37 × 10^{-6} M in chloroform) in the presence of (*R*)-(−)-**6** or (*S*)-(+)-**6** (1.37 × 10^{-6} to 6.85 × 10^{-6} M).

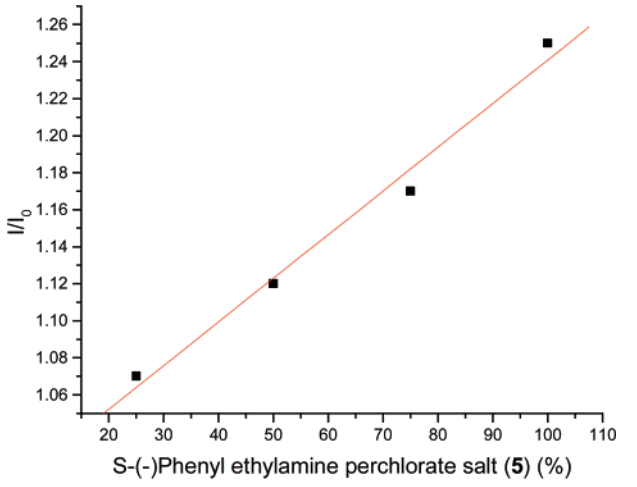

FIGURE 8. Fluorescence enhancement of sensor (*R*)-(−)-**4** (1.64 × 10^{-6} M in chloroform) vs enantiomeric composition of (*S*)-(−)-**5** (8.20 × 10^{-7} to 1.64 × 10^{-6} M in chloroform).

between I/I_0 and the percent of the *S* component of phenylethylamine (Figure 8).

A fair linear relationship was observed for the concentration versus intensity ratio. This indicated that the sensor (*R*)-(−)-**4** was useful for enantiomer composition determination of the amine (*S*)-(−)-**5**. The same was also found to be true for (*S*)-(+)-**6** (Figure 9).

Thus, the enantiomeric composition of (*S*)-(−)-**5** and (*S*)-(+)-**6** can be readily determined by measuring the fluorescence intensity of the sensor (*R*)-(−)-**4** in the presence of the chiral ammonium guest. The association constant, *K*, for (*S*)-(−)-**5** using (*R*)-(−)-**4** was calculated to be 6.08695 × 10^5 M^{-1}, and *K* for (*R*)-(+)-**5** using (*R*)-(−)-**4** was calculated to be 5.3846 × 10^4 M^{-1}. The difference between the association constants for the two diastereomeric complexes with **5** was 5.54849 × 10^5 M^{-1}, and the ratio was found to be 11.30. This difference in signal amplification caused by (*S*)-(−)-**5** and (*R*)-(+)-**5** makes (*R*)-(−)-**4** a much more sensitive fluorescent sensor for (*S*)-(−)-**5** than (*R*)-(+)-**5**. Similarly, the association constant, *K*, for (*S*)-(+)-**6** using (*R*)-(−)-**4** was calculated to be 2.31481 × 10^5

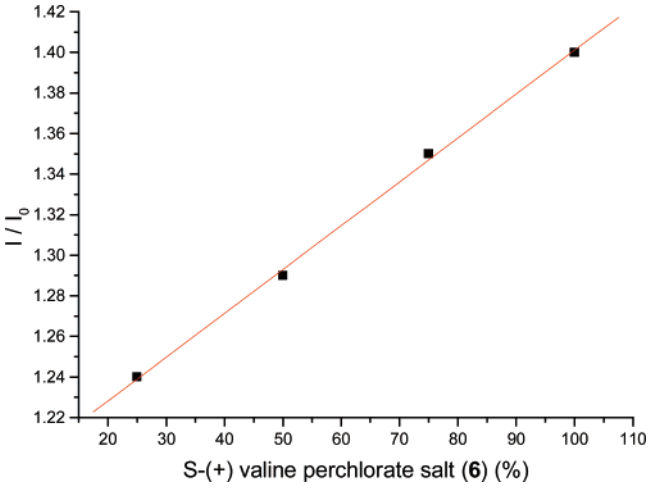

FIGURE 9. Fluorescence enhancement of sensor (*R*)-(−)-**4** (1.37×10^{-6} M in chloroform) vs enantiomeric composition of (*S*)-(+)-**6** (3.42×10^{-7} to 1.37×10^{-6} M).

M^{-1}, and *K* for (*R*)-(−)-**6** using (*R*)-(−)-**4** was calculated to be 3.2967×10^4 M^{-1}. The difference between the association constants for the two diastereomeric complexes with **6** was 1.98514×10^5 M^{-1}, and the ratio was found to be 7.02. This difference in signal amplification caused by (*S*)-(+)-**6** and (*R*)-(−)-**6** makes (*R*)-(−)-**4** a much more sensitive fluorescent sensor for (*S*)-(+)-**6** than (*R*)-(−)-**6**.

The study of the energy minimized structures obtained by use of the AM1 program revealed reasons for the experimental difference in the extent of binding in diastereomeric complexes. The reason mainly seems to be steric in nature. In both diastereomeric complexes, the attractive interaction between three hydrogen atoms of the quaternized nitrogen stabilizes the complexes. The steric repulsion between the methyl group of the phenylethylamine and the ethylene oxy units of the crown appears to be less in the *R*−*S* complex as compared to the *R*−*R* complex. In valine, the tripod binding stabilized complexes differ in spatial orientation of isopropyl group and ethyl carboxy groups. In the *R*−*S* complex, the ethyl carboxy group is apparently placed at a sterically non-hindered position, resulting in a more stable complex as compared to the *R*−*R* diastereomeric complex.

Conclusion

We conclude that to the best of our knowledge, the (*R*)-(−)-**4** sensor has exhibited the best chiral discrimination among the various BINOL based crowns reported thus far for the recognition of phenylethylamine and ethyl ester of valine. The success of this molecule ((*R*)-(−)-**4**) can be attributed to the presence of a furan ring at sterically the most crucial position of BINOL and effective coupling of furan with oxygens at the 8,8′ positions of **1**.

Experimental Section

Synthesis of (*R*)-(−)-[9,9′]Bi[naphtho[2,1-*b*]furanyl]-8,8′-diol Based Diethyl Diester (2). In a 50 mL round-bottomed flask fitted with a calcium chloride guard tube and N_2 inlet were put a mixture of (*R*)-(−)-[9,9′]bi[naphtho[2,1-*b*]furanyl]-8,8′-diol (**1**) (0.2 g, 0.55 mmol) and anhydrous K_2CO_3 (0.166 g, 1.2 mmol) in dry DMF (15 mL). To this mixture was added ethyl chloacetate (0.147 g, 1.2 mmol), and the resulting mixture was stirred for 4 h (monitored by TLC) at room temperature. On completion of the reaction, it was poured into ice-cold water (100 mL). The solid separated and was filtered through a Buchner funnel, dried, and crystallized from alcohol to give a white solid (*R*)-(−)-**2**, (0.282 g, 0.52mmol, 96%), mp 185−186 °C, $[\alpha]^{25}_{589}$ −122 ° (THF, c 1): FTIR (KBr); 3128, 2933, 1759, 1732, 1614, 1584, 1514, 1474, 1229, 1196 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$); δ 1.2 (t, 6H, $J = 6.6$ Hz), δ 4.0 (q, 4H, $J = 6.6$ Hz), δ 4.7 (dd, 4H, $J = 20$ Hz), δ 4.9 (d, 2H, $J = 2.0$ Hz), δ 7.4 (d, 2H, $J = 9.2$ Hz), δ 7.5 (d, 2H, $J = 2.0$ Hz), δ 7.6 (d, 2H, $J = 8.8$ Hz), δ 7.9 (d, 2H, $J = 9.2$ Hz), δ 8.2 (d, 2H, $J = 8.8$ Hz). ^{13}C NMR (DMSO-d_6): δ 13.9 (p), 60.4 (s), 65.9 (s), 106.9 (t), 110.8 (t), 113.0 (q), 119.9 (t), 120.6 (q), 125.8 (q), 126.4 (t), 128.4 (q), 130.5 (t), 143.6 (q), 152.7 (q), 154.4 (t), 168.7 (s). MS (70 eV) *m*/*z* (%) 538 (M+, 100). Elemental analyses for C_{32} H_{26} O_8: Calcd % C (71.37), % H (4.87). Found: % C (71.30), % H (4.85).

Synthesis of (*R*)-(−)-[9,9′]Bi[naphtho[2,1-*b*]furanyl]-8,8′-diol Based Diethanol (3). In a 50 mL round bottomed flask fitted with a calcium chloride guard tube was put diethyl ester of modified (*R*)-(−)-[9,9′]bi[naphtho[2,1-*b*]furanyl]-8,8′-diol (**2**) (0.2 g, 0.37 mmol) in dry THF (15 mL). To this was added $LiAlH_4$ (0.028 g, 0.74 mmol), and the resulting mixture was stirred for 6 h (monitored by TLC) at room temperature. After completion of the reaction, a 1 M NaOH (0.1 mL, 0.032 g, 0.8 mmol) solution was added, and the mixture was stirred until a clear solution was obtained. It was then filtered through a Buchner funnel to remove the insoluble residue. From the filtrate, THF was removed under reduced pressure to yield a solid. This solid on crystallization with alcohol gave a white solid (*R*)-(−)-**3**, (0.144 g, 0.32 mmol, 85%), mp 190 °C, $[\alpha]^{25}_{589}$ −79° (THF, c 1). FTIR (KBr); 3428, 3127, 2935, 2878, 1613, 1584, 1532, 1512, 1469, 1450, 1247 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6); δ 2.2 (s, 2H), δ 3.5−3.6 (m, 4H), δ 4.0 (m, 2H), δ 4.3 (m, 2H), δ 5.1 (d, 2H, $J = 2.0$ Hz), δ 7.2 (d, 2H, $J = 2.0$ Hz), δ 7.5 (d, 2H, $J = 8.4$ Hz), δ 7.6 (d, 2H, $J = 9.2$ Hz), δ 7.8 (d, 2H, $J = 8.4$ Hz), δ 8.1 (d, 2H, $J = 9.2$ Hz). MS (70 eV) *m*/*z* (%) 454 (M+, 100). Elemental analyses for $C_{28}H_{22}O_6$: Calcd % C (74.00), % H (4.88). Found: % C (73.95), % H (4.85).

Synthesis of (*R*)-(−)-[9,9′]Bi[naphtho[2,1-*b*]furanyl]-8,8′-diol Based 20 Crown 6 (4). In a 100 mL three-necked round bottomed flask fitted with a reflux condenser with a calcium chloride guard tube and N_2 inlet was taken sodium hydride (0.125 g, 3.3 mmol) and was washed twice with hexane (10 mL). Then, hexane was decanted, and dry THF (30 mL) was added. To the refluxing solution was added slowly in 1 h a 1:1 mixture of (*R*)-(−)-[9,9′]-bi[naphtho[2,1-*b*]furanyl]-8,8′-diol based diethanol (**3**) (0.2 g, 0.55 mmol) and triethylene ditosylate (0.202 g, 0.44 mmol) in THF (30 mL). After complete addition, the mixture was further refluxed for 4 h (monitored by TLC), and finally, the THF was concentrated under reduced pressure and the oily residue obtained was added to 100 g of ice. The solid was separated and was filtered, dried, and purified by column chromatography using petroleum ether and ethyl acetate (60:40) as eluents to afford a white solid (*R*)-(−)-**4**, (0.113 g, 0.2 mmol, 45%), mp 121 °C, $[\alpha]^{25}_{589}$ −180.6° (THF, c 1). FTIR (KBr); 3120, 2907, 2870, 1613, 1584, 1511, 1472, 1449, 1247, 1047 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$); δ 3.3−3.6 (m, 16H), δ 4.0 (m, 2H), δ 4.2 (m, 2H), δ 5.1 (d, 2H, $J = 2.0$ Hz), δ 7.1 (d, 2H, $J = 2.0$ Hz), δ 7.5 (d, 2H, $J = 8.4$ Hz), δ 7.5 (d, 2H, $J = 8.8$ Hz), δ 7.8 (d, 2H, $J = 8.4$ Hz), δ 8.1 (d, 2H, $J = 8.8$ Hz). ^{13}C NMR (DMSO-d_6): δ 69.7 (s), δ 69.9 (s), δ 70.6 (s), δ 70.7 (s), δ 70.9 (s), δ 107.4 (t), 110.9 (t), 113.7 (t), 121.3 (q), 121.5 (q), 125.6 (t), 126.7 (q), 129.0 (q), 130.3 (t), 142.8 (t), 153.4 (q), 155.4 (q). LCMS (70 eV) *m*/*z* (%) 569 (M + 1, 100), 481 (51), 393 (31). Elemental analyses for $C_{34}H_{32}O_8$: Calcd % C (71.82), % H (5.67). Found: % C (71.79), % H (5.65).

The enantiopurity of (*R*)-(−)-**4** was determined by preparing a complex of (*R*)-(−)-**4** and enantiopure (*S*)-(−)-**5**. The two diastereomeric peaks were seen at δ 4.9 and δ 5.0 for the C-1;C-1′ protons. The % de was found out to be 94%.

Supporting Information Available: IR (KBr), ^{1}H NMR, ^{13}C NMR, and LCMS (M + 1) scans of **4**. ^{1}H NMR scan and its expansion showing the % de. Details of sample preparation for fluorescence studies of **4**−**6**. Computational details for finding the energy minimized structures by using the Gaussian 03W package with the AM1 emperical force field. This material is available free of charge via the Internet at http://pubs.acs.org.

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