Selective Sensing of Fumarate Over Maleate by Benzimidazolium – Based Fluororeceptors

Kumaresh Ghosh[*a], Indrajit Saha[a], Roland Fröhlich[b] and Amarendra Patra[c]

[a]*Department of Chemistry, University of Kalyani, Kalyani, Nadia-741235, India*

[b]*Organisch-Chemisches Institut, Universität Münster, Corrensstraβe 40, D-48149, Münster, Germany*

[c]*Department of Chemistry, University College of Science, 92 A. P. C. Road, Kolkata 700 009, India*

Abstract: A new benzimidazolium – based chiral fluororeceptor **1** has been designed and synthesized. The open cleft of **1** is found to recognize fumarate selectively over maleate in CH_3CN by exhibiting greater change in emission. In comparison, the achiral receptor **2**, under similar condition, shows poor selectivity in the recognition of fumarate over maleate. Interaction studies were performed by ^1H NMR, fluorescence and UV-vis spectroscopic methods.

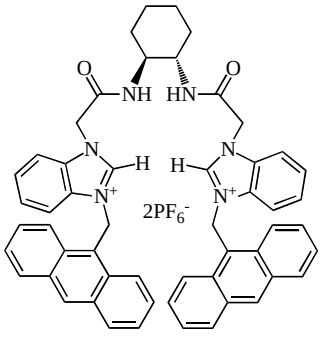
Keywords: Selective recognition of fumarate, florescence sensing, benzimidazolium- based receptors, anthracene probe.

1. INTRODUCTION

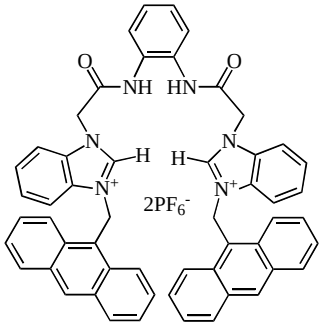
The development of fluororeceptors capable of selective sensing of anionic species has aroused great interest in supramolecular chemistry [1-3]. Fluororeceptors are attractive due to the simplicity and high detection limit of fluorescence. In last few decades a large number of fluorescent receptors have been reported in the literature for sensing of anions [4]. Among the anions, dicarboxylates are important targets because of their biological importance [5]. Selective recognition of dicarboxylates by colorimetrically [6,7] and fluorometrically [8-11] is, therefore, an important topic of research. Considerable efforts along this direction have been made in the literature. In relation to this, the diastereoselective recognition of dicarboxylates, such as maleate and fumarate is important because of their biological relevance. In fact, whereas fumarate is generated in the Krebs cycle, maleate is a well-known inhibitor of this cycle and its implication in different kidney diseases has been widely described [12,13]. Therefore, the selective detection of either maleate or fumarate is challenging, and to the best of our knowledge, only few examples are known [6]. Costero *et al*. [14] reported the synthesis of chiral cyclohexyl-based thiourea receptors for selective recognition of maleate from fumarate. Kim and co-workers used Zn (II) cyclams that behaved differently with maleate and fumarate in respect to coordination behavior [15]. Similarly, Yen *et al.* introduced anthraquinone - based thiourea group containing chromogenic receptors for colorimetric distinction of isomeric dicarboxylates [16]. Gold nanoparticles, functionalized with carboxylate binding units, were also found to be effective for the discrimination of maleate from fumarate [17]. With this information we were interested to design and synthesize easy-to-make simple fluororeceptor for diastereoselective recognition between maleate and fumarate and accordingly, we report here the design and synthesis of **1** toward selective recognition of fumarate over maleate anion. The receptor **1** shows selective binding of fumarate in CH_3CN by exhibiting a significant change in emission of anthracene. The selectivity towards fumarate over maleate was also investigated with the achiral analogue **2** [18]. In the design, amide and benzimidazolium protons have been taken into account for complexing carboxylate motif involving both conventional N-H---O and unconventional polar C^+-H---O hydrogen bonds. The complex is further stabilized by charge - charge interaction.

2. RESULTS AND DISCUSSION

The synthesis of receptor 1 was accomplished according to the Scheme **1**. The reaction of *trans*-1(S),2(S)-cyclohexanediamine



1

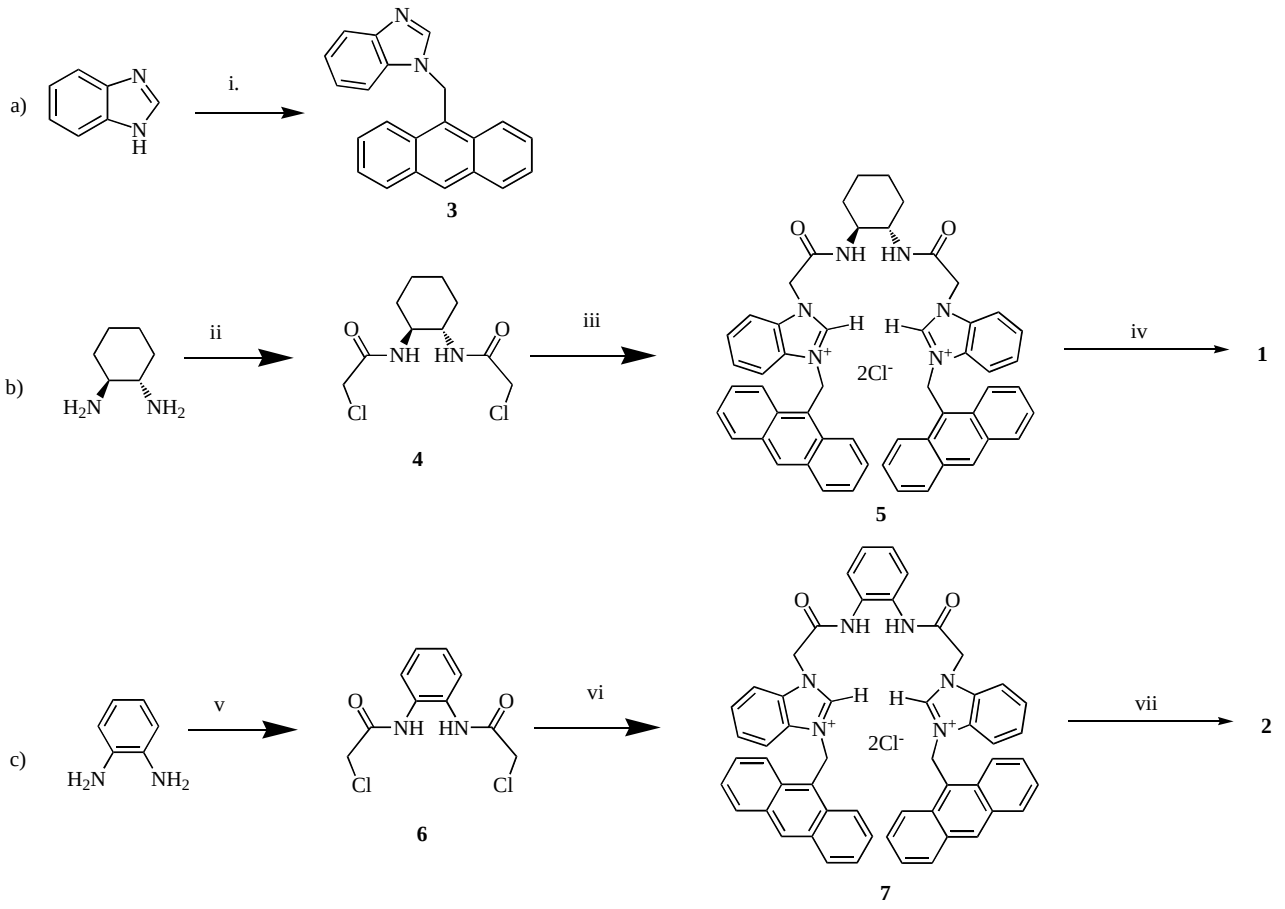


2

with chloroacetyl chloride in dry CH_2Cl_2 gave diamide 4 in 94% yield. On refluxing **4** in CH_3CN with compound **3**, which was obtained according to Scheme **1a** by the reaction of benzimidazole with 9-chloromethylanthracene in the presence of NaH in dry THF, afforded dichloride salt **5**. The subsequent anion exchange of dichloride salt **5** using NH_4PF_6 gave the desired receptor **1** in appreciable yield. In the similar way, compound **2** was synthesized

*Address correspondence to this author at the Department of Chemistry, University of Kalyani, Kalyani, Nadia-741235, India; Tel: +91-33-25828750; Fax: +91-33-25828282; E-mail: ghosh_k2003@yahoo.co.in

1570-193X/11 $58.00+.00



Scheme 1. i. NaH, dry THF, 9-chloromethylanthracene, reflux, 10 h; ii. chloroacetyl chloride, Et_3N, dry CH_2Cl_2, 1h; iii. **3** in dry CH_3CN, reflux, 5 days; iv. NH_4PF_6, DMF-water, stirring for ½ h; v. chloroacetyl chloride, Et_3N, dry CH_2Cl_2, 1 h; vi. **3** in dry CH_3CN, reflux, 5 days, 55% yield; vii. NH_4PF_6, DMF–water, stirring for ½ h.

(Scheme **1c**) [18]. All the compounds were thoroughly characterized by the usual spectroscopic techniques.

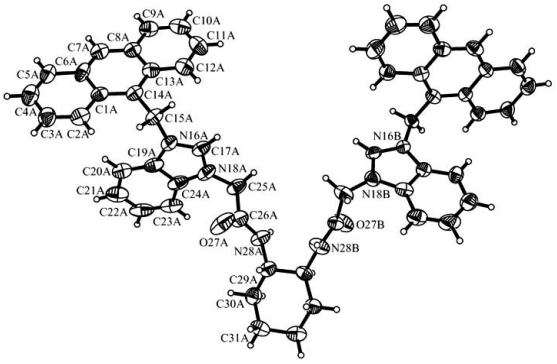


Fig. (1). ORTEP plot of **1**.

The structure of **1** was further confirmed by X-ray analysis of single crystals (Fig. **1**) [19,20], obtained from slow evaporation of the mixture solvent $CHCl_3$ and MeOH ($CHCl_3$:MeOH = 4:1). It is evident from Fig. (**1**) that in solid state, two amides are not perfectly in one plane. Amide hydrogen of one arm is little away from the other one. In addition, the benzimidazolium cation moiety comes close to the anthracene π-surface and shows cation – π interaction as evident from the packing plot in Fig. (**2**). Such cation – π interactions contribute to assemble the molecules in *zig-zag* polymeric fashion in the solid state.

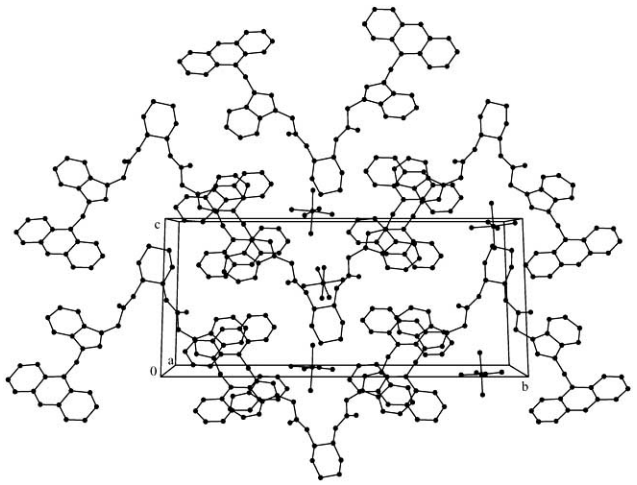


Fig. (2). Packing plot of **1**.

The sensing ability of the receptor **1** for maleate and fumarate anions was monitored by fluorescence in CH_3CN. The anions were added as terabutylammonium salts to the CH_3CN solutions of the receptor **1** (c = 3.54 x 10^{-5} M). Receptor **1** (c = 3.54 x 10^{-5} M) on excitation at 370 nm in CH_3CN displayed structured emission centered at 418 nm. Upon complexation of maleate and fumarate, the emission of anthracene in **1** was quenched to the different extents.

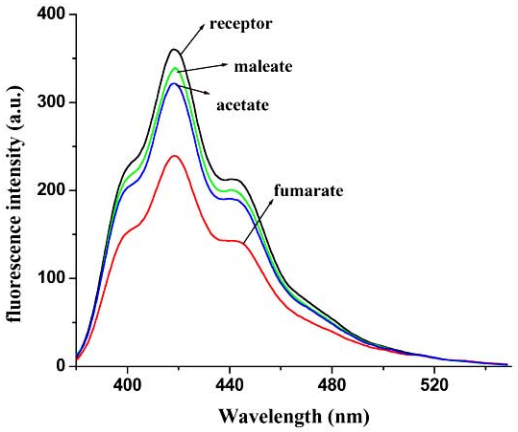


Fig. (3). Change in fluorescence intensity of **1** at 419 nm (λ_{Ex} = 370 nm) in the presence of 2 equivalent amounts of anions.

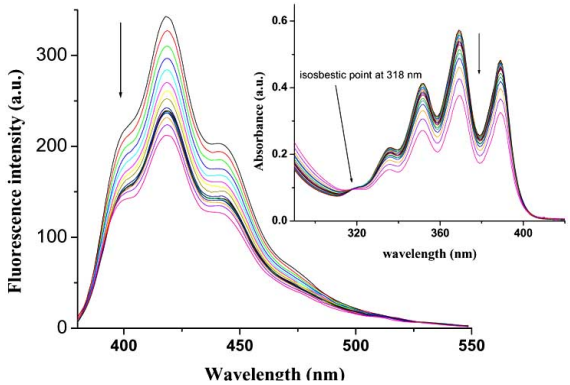


Fig. (4). Change in emission spectra of **1** (c = 3.54 x 10^{-5} M) upon addition of fumarate (as tetrabutylammonium salt) in CH_3CN; Inset: Change in absorption spectra of **1** (c = 3.54 x 10^{-5} M) upon addition of fumarate.

Fig. (**3**), in this regard, represents the change in emission intensity of **1** in the presence of 2 equivalent amounts of a particular anion. Interestingly, while the emission intensity of **1** is significantly reduced in the presence of fumarate, the emission is hardly perturbed in the presence of maleate. The results were compared with acetate; upon addition of which the change in emission of **1** was similar to that of maleate. Fig. (**4**) shows the titration spectra of **1** upon progressive addition of fumarate. The quenching of emission of **1** in the titration experiments was realized from the Stern-Volmer plot in Fig. (**5**). The non-linear nature of the curves in Fig. (**5**) revealed that during interaction both static and dynamic quenching processes have the contribution toward the overall quenching of emission. Importantly, the greater quenching of emission of **1** in the presence of fumarate clearly distinguishes it from maleate.

The complexation induced quenching of emission of **1** is believed to be due to the activation of photo-induced electron transfer (PET) that occurs between the binding site and the excited state of anthracene. The complexation of anions enhances the electron density into the binding site of **1** and possibly encourages the electron transfer to the excited state of anthracene.

The stoichiometry of the complexes in the binding event was 1:1 as confirmed from the sharp break of the titration curves at [G]/[H] = 1 (Fig. **6**). The linear nature of the curve for maleate in Fig. (**6**) also intimated 1:1 stoichiometry. The stoichiometry was further confirmed by fluorescence Job plots [21].

The open cleft of **1** also showed measurable interaction with fumarate and maleate in the ground state. During titration with fumarate (see inset of Fig. **4**) and maleate (Fig. **7**), the intensity of

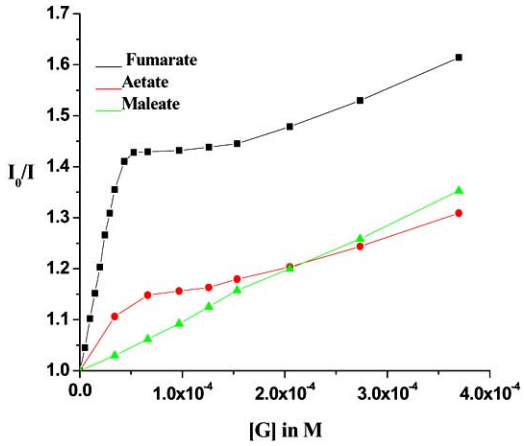


Fig. (5). Stern-Volmer plot of **1** at 419 nm (λ_{ex} = 370 nm).

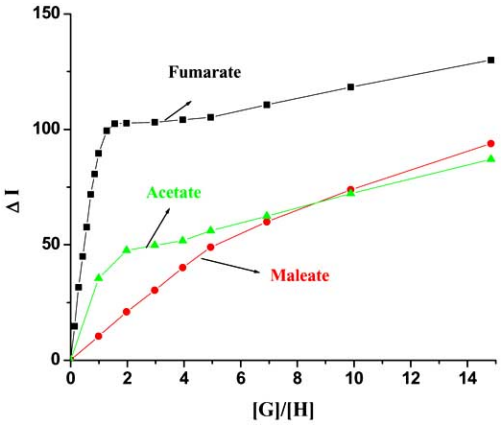


Fig. (6). Fluorescence titration curves ([Guest]/[Host] vs change in emission) of **1** (measured at 419 nm).

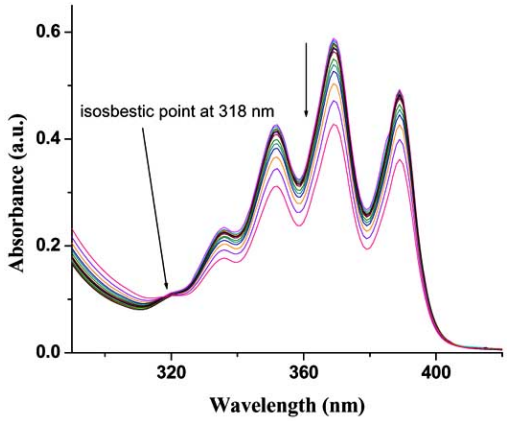


Fig. (7). Change in absorption spectra of **1** (c = 3.54 x 10^{-5} M) upon addition of maleate.

absorption peak for anthracene decreased and a clear isosbestic point in each case was noticed suggesting the formation of new complexes that remain in equilibrium with the free receptor in solution. Receptor **1** showed a marginally higher change in absorbance upon titration with fumarate. The stoichiometry of the complexes in the ground state was also 1:1, confirmed from the UV Job plots (Fig. **8**). In relation to the results of **1**, the sensing properties of achiral receptor **2** were also investigated under similar experimental conditions. Here also a distinction between maleate and fumarate was noted when fluorescence titration of **2** was carried out in

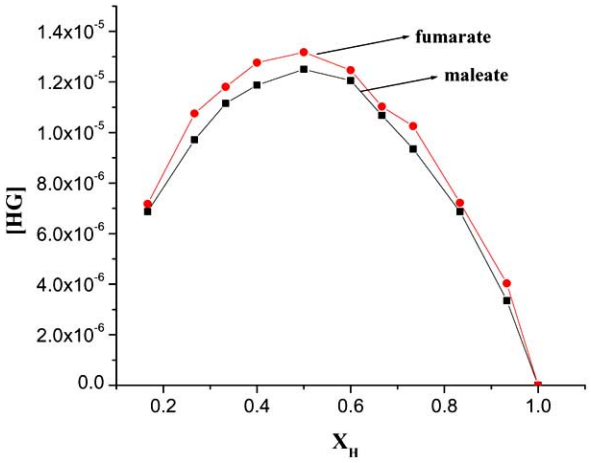


Fig. (8). UV Job plots for **1** with fumarate and maleate.

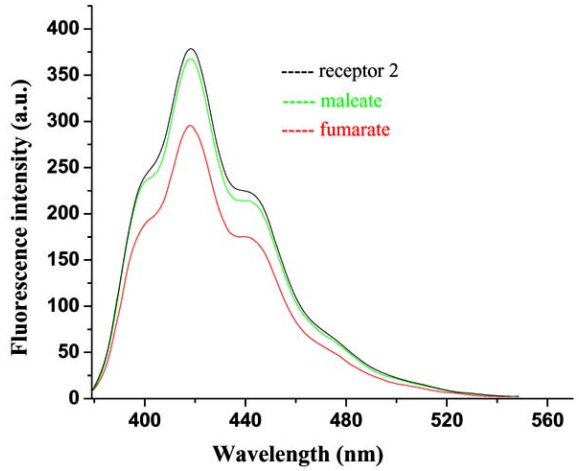


Fig. (9). Change in fluorescence intensity of **2** (3.46 x 10^{-5} M) at 419 nm (λ_{Ex} = 370 nm) in the presence of 2 equivalent amounts of maleate and fumarate.

CH_3CN. Fig. (**9**) represents the change in emission intensity of **2** in the presence of 2 equivalent amounts of a particular anion. Like **1**, the emission of anthracene in **2** was quenched in the presence of fumarate although less in magnitude. The stoichiometry of the complexes of **2** with both maleate and fumarate was also 1:1 like **1**.

In order to establish the binding modes of **1** and **2** with maleate and fumarate, NOESY experiments on the 1:1 complexes of **1** and **2** with fumarate and maleate were performed. No characteristic correlation of the protons of fumarate (appeared at 6.30 ppm) with the protons of receptor **1** was noticed (Fig. **10a**). But on contrary, a weak NOE effect between protons of maleate (appeared at 6.02 ppm) with the amide protons (appeared at 7.92 ppm) of the receptor **1** was observed (Fig. **10b**). Furthermore, while the amide protons of **1** underwent a greater downfield chemical shift ($\Delta\delta$ = 0.75) in the presence of equivalent amount of fumarate, maleate anions interacted weakly giving a small downfield shift of the amide protons (0.12 ppm). During the interaction, the benzimidazolium protons (C^+-H) of **1** were found non-interacting except for the case of fumarate, which shifted the benzimidazolium proton to the downfield direction only by 0.02 ppm. These findings enable us to suggest the different binding modes for maleate and fumarate as shown in Fig. (**10**).

In a similar way, NOESY experiments on the 1:1 complexes of **2** with maleate and fumarate were performed. Interestingly, here also only correlation between maleate and benzimidazolium ring protons was noticed (Fig. **11**). Based on this, binding modes for **2** with maleate and fumarate are suggested. All the NOESY experiments were performed in CD_3CN containing few drops of d_6-DMSO. During the experiment, precipitation appeared in the solution. Due to this reason we were unable to determine the binding constant values for **1** and **2** in the NMR concentration range. To get an insight about the binding strength, we determined the binding constant values by fluorescence method (Table **1**) [22]. As can be seen from Table **1**, the receptor **1** shows a greater affinity for fumarate over maleate. Similar trend was observed with **2**. Only the difference between **1** and **2** lies with the efficiency in the binding process.

Table 1. Binding Constants Values[a] by Fluorescence Method

Anions[b]	Receptor 1	Receptor 2
Fumarate	7.31 x 10^5	2.94 x 10^4
Maleate	1.20 x 10^3	5.51 x 10^2

[a.] Error < 30%; [b.]Tetrabutylammonium salts were used.

Chiral analogue **1** is more efficient binder of fumarate than **2** and to our opinion, structural effect of the *trans*-1,2-diaminocyclohexane contributes to this aspect. Fig. (**12**), for example, represents the binding constant curve for **1** with fumarate.

3. CONCLUSION

In conclusion, we have demonstrated that the benzimidazolium – based open cleft of **1** can differentiate the geometrical isomers, such as fumarate, from its *cis*-isomer maleate. Performance of the receptors is dependant on the diamine motif on which the cleft is built in. The achiral cleft **2** is thus less efficient in attaining greater selectivity for fumarate over maleate. We believe that the discrimination between maleate and fumarate into the binding sites of **1** and **2** is attributed to their different modes of binding, which regulate the photophysical properties either efficiently or weakly. Further work along this direction is underway in our laboratory.

4. EXPERIMENTAL

Synthesis of 1-(anthracen-9-ylmethyl)benzimidazole 3

To a solution of benzimidazole (0.300 g, 2.54mmol) in dry THF (15 mL), NaH (0.14g) was added and refluxed for 1 h under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and 9-chloromethylanthracene (0.700 g, 3.09 mmol) in THF (15 mL) was added. Reflux was further continued for 10 h and then THF was removed, water was added and extracted with $CHCl_3$ (3 x 30 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated on rotary evaporator. Purification of the crude mass by silica gel column chromatography using 20% ethyl acetate in pet ether yielded compound **3** (0.500g, yield 64%). ^{1}HNMR in $CDCl_3$ (400 MHz) δ 8.61 (s, 2H), 8.10 (d, 4H, *J* = 8 Hz), 7.82 (d, 1H, *J* = 8 Hz), 7.71 (d, 1H, *J* = 8 Hz), 7.51 (m, 4H), 7.42 (t, 1H, *J* = 8 Hz), 7.35(t, 1H, *J* = 8 Hz), 6.19 (s, 2H); *m/z* (ES^+): 308.9 $[M]^+$.

Synthesis of *N*, *N*'- bis (2-chloroacetyl)-(1S, 2S)-diaminocyclohexane 4

To a stirred solution of *trans*-1 (S), 2(S)-1,2-cyclohexanediamine (0.200g, 1.75 mmol) in dry CH_2Cl_2 (10 mL) chloroacetyl chloride (0.31 mL, 3.85 mmol) was added followed by addition of Et_3N (0.54 mL, 3.85 mmol). The reaction mixture was stirred for 1 h at room temperature and then solvent was evaporated under reduced pressure. The reaction mixture was neutralized with $NaHCO_3$ solution and extracted with $CHCl_3$ (20 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated on rotary evaporator. Purification of the crude mixture by silica gel column chromatography using 2% methanol in chloroform gave the compound **4** in 94% yield (0.400g); mp 214 °C; ^{1}HNMR (400

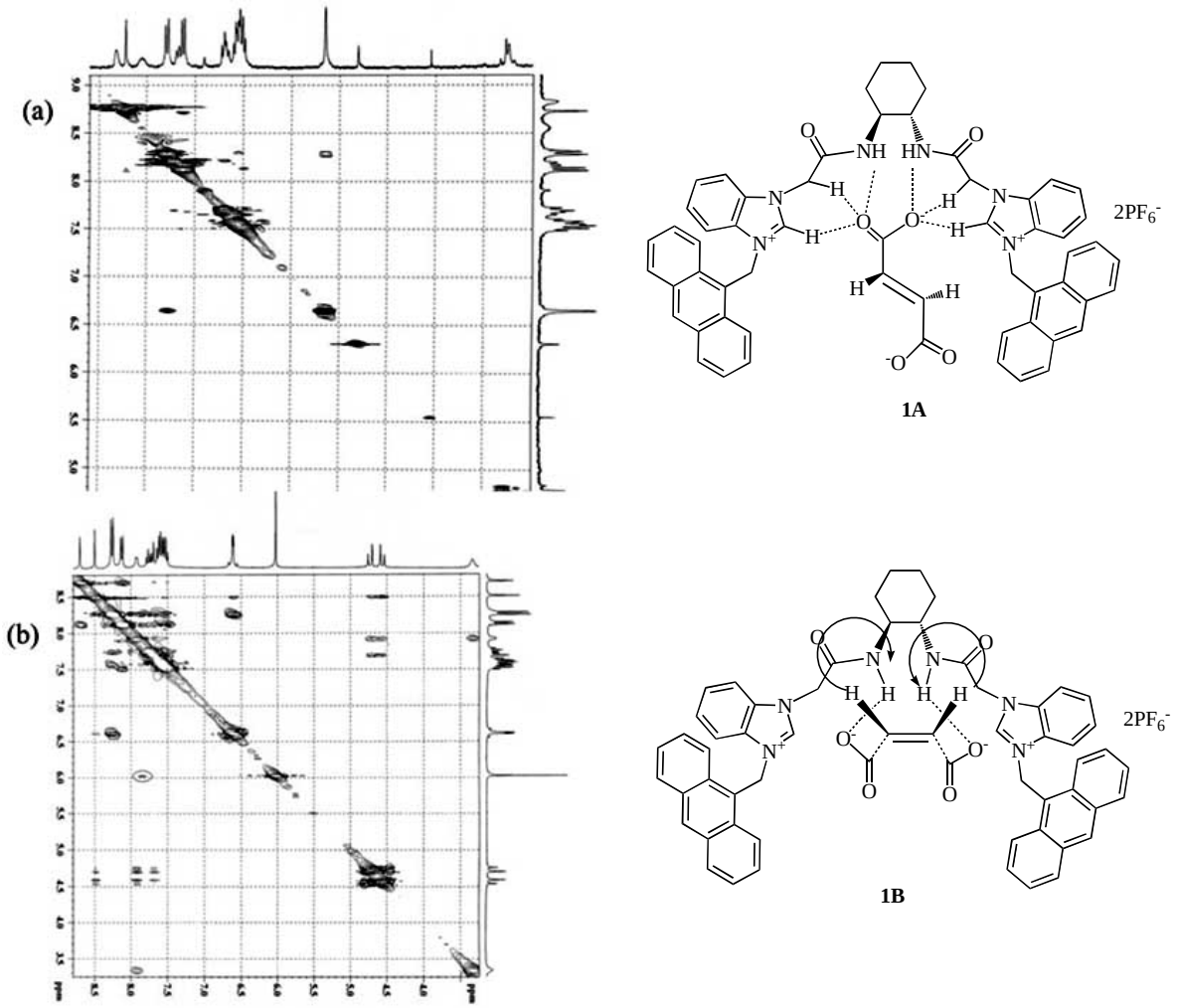


Fig. (10). NOESY experiments on the 1:1 complexes of **1** (c = 2.17 x 10^{-3} M) with (**a**) fumarate and (**b**) maleate and the different binding modes.

MHz, $CDCl_3$) δ 6.77 (s, 2H, NH), 3.98 (s, 4H), 3.74 (m, 2H), 2.07 (m, 2H), 1.78 (m, 2H), 1.33 (m, 4H); FTIR (KBr) 3269, 3085, 2945, 2858, 1651, 1560 cm^{-1}.

Synthesis of Receptor 1

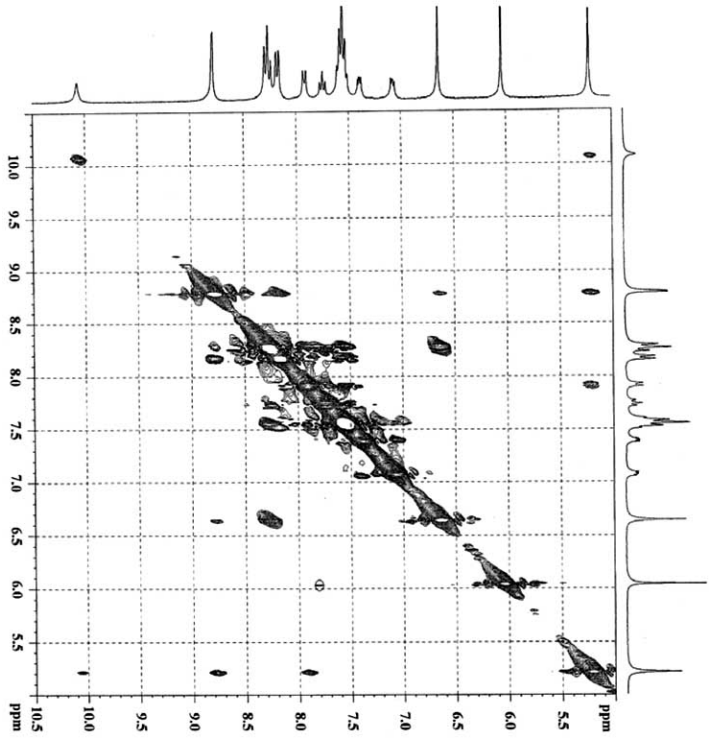
To a solution of **4** (0.06 g, 0.27 mmol) in CH_3CN (10 mL), compound **3** (0.207 g, 0.674 mmol) in CH_3CN (10 mL) was added. The reaction mixture was refluxed with stirring for 5 days under nitrogen atmosphere. On cooling the reaction mixture, precipitate appeared. The precipitate was filtered and washed with CH_3CN for several times to give pure dichloride salt **5** (0.150 g, 56%). The pure dichloride salt **5** (0.100 g, 0.11 mmol) was dissolved in 2 mL hot DMF and NH_4PF_6 (0.056 g, 0.34 mmol) was added in one portion. After stirring the reaction mixture for 20 min. water was added to precipitate the compound. Repeated washing of the precipitate with water and ether afforded the desired salt **1** in 86% yield (0.105 g); mp 190 ºC; ^{1}HNMR (400 MHz, d_6-DMSO) δ 8.83 (s, 2H), 8.74 (s, 2H), 8.41-8.35 (m, 6H), 8.24-8.19 (m, 6H), 7.94 (t, 2H, J = 8 Hz), 7.70-7.56 (m, 12H), 6.77(s, 4H), 4.88 (d, 2H, J = 16 Hz), 4.72 (d, 2H, J = 16 Hz), 3.32 (br t, 2H), 1.62 (m, 2H), 1.55 (m, 2H), 1.13 (m, 4H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 163.8, 141.6, 131.7, 131.3, 131.1, 130.9, 130.5, 129.4, 127.9, 127.0, 126.7, 125.6, 123.2, 121.6, 114.3, 113.3, 51.7, 48.2, 43.3, 30.9, 23.6; HRMS (TOF MS ES$^+$) $C_{54}H_{48}N_6O_2.2PF_6$ requires 1102.3122 for $(M + 2PF_6)^+$ and 957.3475 for $(M + PF_6)^+$, Found 957.3824 for $(M\text{-}PF_6)^+$; $[\alpha]^{25}$ = - 0.018 (0.019 M, CH_3OH); $C_{54}H_{48}N_6O_2.2PF_6$: calcd. C 58.81, H 4.39, N 7.62; found C 58.77, H 4.36, N 7.56.

Synthesis of Compound 6

To a stirred solution of *o*-phenylenediamine (1 g, 5.62 mmol) in dry CH_2Cl_2 (30 mL) chloroacetyl chloride (1.07 mL, 13.48 mmol) was added followed by addition of Et_3N (1.87 mL, 13.48 mmol). After stirring the reaction mixture for 1 h at room temperature, solvent was evaporated under reduced pressure. The reaction mixture was neutralized with $NaHCO_3$ solution and extracted with $CHCl_3$ (30 mL x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated on rotary evaporator. Purification of the mixture by silica gel column chromatography using 3% methanol in chloroform yielded compound **6** in 91% yield (2.2 g): mp 191 ^{0}C; ^{1}HNMR (400 MHz, $CDCl_3$ containing two drops of DMSO-d_6) δ 9.40 (s, 2H, amide NH), 7.53 – 7.50 (m, 2H), 7.28 – 7.24 (m, 2H), 4.20 (s, 4H); FTIR (KBr) 3253, 3195, 1674, 1655 cm^{-1}.

Synthesis of Receptor 2

To a stirred solution of **6** (0.07 g, 0.27 mmol) in CH_3CN, compound **3** (0.333 g, 1.08 mmol) in CH_3CN (10 mL) was added. The reaction mixture was refluxed with stirring for 5 days under nitrogen atmosphere. After completion the reaction mixture was cooled to room temperature and filtered. The precipitate was washed with CH_3CN for several times to give pure dichloride salt **7** (0.130 g, yield 55%). The dichloride salt **7** (0.100 g, 0.11 mmol) was dissolved in 2 mL hot DMF and NH_4PF_6 (0.056 g, 0.34 mmol) was added to it in one portion. After stirring the reaction mixture for 20



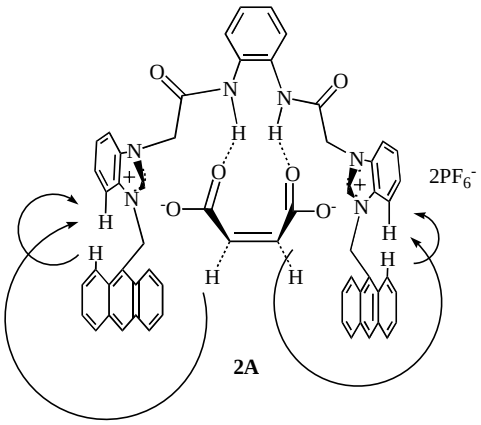


Fig. (11). NOESY experiment on the 1:1 complexes of **2** (c = 2.19 x 10^{-3} M) with maleate and suggested binding mode.

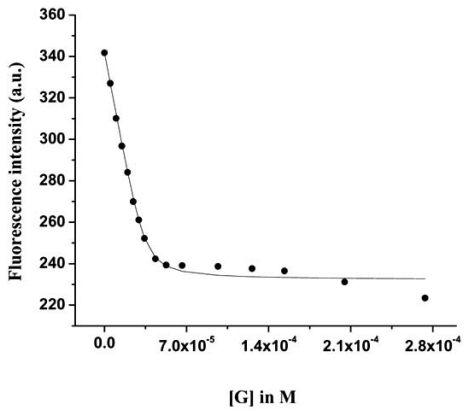


Fig. (12). Binding constant curve for **1** with fumarate.

min. water was added. The precipitate was filtered and washed with water to give **2** (0.100, yield 80%); mp 150 °C (decomposition and turns black); ^{1}H NMR (400 MHz, d_6-DMSO) δ 10.9 (br s, 2H, -NH-), 8.98 (s, 2H), 8.90 (s, 2H), 8.38 – 8.35 (m, 4H), 8.24 (d, 4H, J = 8 Hz), 7.95 – 7.89 (m, 2H), 7.77 – 7.69 (m, 4H), 7.63 – 7.54 (m, 10H), 7.38 (t, 2H, J = 8 Hz), 7.02 (br t, 2H), 6.79 (s, 4H), 5.26 (s, 4H); ^{13}C NMR (100 MHz, d_6-DMSO) δ 163.3, 141.9, 131.8, 131.1, 131.0, 130.8, 130.4, 129.3, 127.8, 126.8, 126.6, 125.5, 125.0, 124.7, 124.0, 123.7, 121.6, 114.1, 113.4, 48.7, 43.3; FTIR (KBr) 3379, 1700, 1623, 1565, 1542, 1487, 1458, 1449 cm^{-1}; HRMS (TOF MS ES$^+$) $C_{54}H_{42}N_6O_2.2PF_6$ requires 951.3006 for $(M\text{-}PF_6)^+$ and 806.3358 for $(M\text{-}2PF_6)^+$; found 951.3009 for $(M\text{-}PF_6)^+$ and 806.3309 for $(M\text{-}2PF_6)^+$, respectively; $C_{54}H_{42}N_6O_2.2PF_6$: calcd. C 59.13, H 3.86, N 7.66; found C 59.02, H 3.78, N 7.59.

General Procedure of Fluorescence Titration

Stock solutions of the receptors were prepared in CH_3CN and 2.5 ml of the individual receptor solution was taken in the cuvette. The solution was irradiated at the excitation wavelength 370 nm (for both **1** and **2**). Upon addition of anions, the change in fluorescence emission of the receptor was noticed. The corresponding emission values during titration were noted and used for the determination of binding constant values. The change of fluorescence emission in the presence of different amounts of guest anions was used to have the Stern-Volmer plot.

ACKNOWLEDGEMENTS

We thank CSIR, Government of India for financial support. I.S. thanks CSIR, New Delhi, India for a fellowship. We also thank DST, Government of India for providing facilities in the department under FIST program.

REFERENCES

[1] Martinez-Manez, R.; Sancenon, F. Fluorogenic and chromogenic chemosensors and reagents for anions. *Chem. Rev.*, **2003**, *13*, 4419-4476.

[2] Bianchi, E.; Bowman – James, K.; Garcia-Espana, E. *Supramolecular Chemistry of Anions*. Wiley – VCH: New York, **1997**.

[3] Beer, P. D.; Gale, P. A. Anion recognition and sensing: the state of the art and future perspectives. *Angew. Chem. Int. Ed.*, **2001**, *40*, 486-516.

[4] de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. Signaling recognition events with fluorescent sensors and switches. *Chem. Rev.*, **1997**, *97*, 1515-1566.

[5] Voet, D.; Voet, J. G. *Biochemistry*, 2nd ed.; Wiley: New York, **1995**.

[6] Yen, Y. –P.; Ho, K. –W. Development of colorimetric receptors for selective discrimination between isomeric dicarboxylate anions. *Tetrahedron Lett.*, **2006**, *47*, 7357-7361.

[7] Yen, Y. –P.; Ho, K. -W. Synthesis of colorimetric receptors for dicarboxylate anions: a unique color change for malonate. *Tetrahedron Lett.*, **2006**, *47*, 1193-1196.

[8] Mei, M.; Wu, S. Fluorescent sensor for α,ω-dicarboxylate anions. *New. J. Chem.*, **2001**, *25*, 471-475.

[9] Liu, S. -Y.; He, Y. -B.; Chan, W. H.; Lee, A. W. M. Cholic acid-based high sensitivity fluorescent sensor for α,ω-dicarboxylate: an intramolecular excimer emission quenched by complexation. *Tetrahedron*, **2006**, *62*, 11687-11696.

[10] Plush, S. E.; Gunnlaugsson, T. Luminescent sensing of dicarboxylates in water by a bismacrocyclic dinuclear Eu(III) conjugate. *Org. Lett.*, **2007**, *9*, 1919-1922.

[11] Ghosh, K.; Masanta, G.; Chattopadhyay, A. P. Triphenylamine-based pyridine N-oxide and pyridinium salts for size-selective recognition of carboxylates. *Eur. J. Org. Chem.*, **2009**, *26*, 4515.

[12] Stepinski, J.; Pawlowska, D.; Angielski, S. Effect of lithium on renal gluconeogenesis. *Acta Biochim. Pol.*, **1984**, *31*, 229-240.

[13] Eiamong, S.; Spohn, M.; Kurtzman, N. A.; Sabatini, S. Insights into the biochemical mechanism of maleic acid-induced Fanconi syndrome. *Kidney Int.,* **1995**, *48*, 1542-1548.

[14] Costero, A. M.; Colera, M.; Gavina, P.; Gil, S. Fluorescent sensing of maleate versus fumarate by a neutral cyclohexane based thiourea receptor. *Chem. Commun*., **2006**, 761-763.

[15] Kim, J. C.; Lough, A. J.; Park, H.; Kang, Y. C. Molecular interactions of zinc(II) cyclams toward maleate and fumarate anions. *Inorg. Chem. Commun.,* **2006**, *9*, 514-517.

[16] Tseng, Y. -P.; Tu, G. -M.; Lin, C. -H.; Chang, C. T.; Lin, C. Y.; Yen, Y. -P. Synthesis of colorimetric sensors for isomeric dicarboxylate anions: selective discrimination between maleate and fumarate. *Org. Biomol. Chem.,* **2007**, *5*, 3592-3598.

[17] Youk, K. -S.; Kim, K. M.; Chatterjee, A.; Ahn, K. H. Selective recognition of fumarate from maleate with a gold nanoparticle-based colorimetric sensing system. *Tetrahedron Lett*., **2008**, *49*, 3652-3655.

[18] Ghosh, K.; Saha, I.; Patra, A. Design and synthesis of an ortho-phenylenediamine-based open cleft: a selective fluorescent chemosensor for dihydrogen phosphate. *Tetrahedron Lett.,* **2009**, *50*, 2392-2397 and references cited therein.

[19] X-ray crystal structure analysis for **1**: formula $C_{54}H_{48}N_6O_2$*2 PF_6, M = 1102.92, light brown crystal 0.40 x 0.10 x 0.10 mm, a = 8.9329(5), b = 25.8166(11), c = 11.1240(5) Å, β = 103.248(3)°, V = 2497.1(2) Å^3, ρ_{calc} = 1.467 g cm^{-3}, μ= 1.623 mm^{-1}, empirical absorption correction ($0.563 \leq T \leq 0.855$), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ= 1.54178 Å, T = 223 K, ω and φ scans, 18129 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 7812 independent (R_{int} = 0.055) and 6473 observed reflections [$I \geq 2\,\sigma(I)$], 415 refined parameters, R = 0.089, wR^2 = 0.266, max. (min.) residual electron density 0.25 (-0.27) e Å^{-3}, one of the anions is heavily disordered, refined with thermal and geometrical restraints, hydrogen atoms calculated and refined as riding atoms. CCDC 762958 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

[20] Data sets were collected with Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W.: Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol.*, **1997**, *276*, 307-326), absorption correction Denzo (Otwinowski, Z., Borek, D., Majewski, W., Minor, W.: Multiparametric scaling of diffraction intensities. *Acta Cryst.,* **2003**, *A59*, 228-234), structure solution SHELXS-97 (Sheldrick, G.M.: Phase annealing in *SHELX*-90: direct methods for larger structures. *Acta Cryst.,* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (Sheldrick, G.M. Universität Göttingen, 1997), graphics XP (BrukerAXS, 2000).

[21] Job, P. Formation and stability of inorganic complexes in solution. *Ann. Chim.,* **1928**, *9*, 113-203.

[22] For determination of binding constant values working formula used $I = I_0 + (I_{lim} - I_0)/2C_H\{C_H + C_G + 1/K_a - [(C_H + C_G + 1/K_a)^2 - 4C_HC_G]^{1/2}\}$. (a) Valeur, B.; Pouget, J.; Bourson, J.; Kaschke, M.; Eensting, N. P.: Tuning of photoinduced energy transfer in a bichromophoric coumarin supermolecule by cation binding. *J. Phys. Chem.,* **1992**, *96*, 6545-6549; (b) Bourson, J.; Pouget, J.; Valeur, B. Ion-responsive fluorescent compounds. 4. Effect of cation binding on the photophysical properties of a coumarin linked to monoaza- and diaza-crown ethers. *J. Phys. Chem*., **1993**, *97*, 4552-4557.

Received: March 01, 2010 Revised: March 30, 2010 Accepted: May 03, 2010