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Tripodal naphthalene ether ligand: Solid-state anion recognition and fluorescence studies

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Abstract

The simple tripodal amine ligand Tris-[2-(naphthalen-1-yloxy)-ethyl]-amine (L_1) was screened for anion recognition. Four crystal structures confirmed the inorganic as well as organic anion recognition in the solid state. Solid-state structures are results of supramolecular self-assembly and 3D molecular network involves C-H···O and C-H··· π bonding in the crystal lattice. In the solid state, it forms a strong C-H···Cl and C-H···O type interactions with the anions. This anion recognition was also confirmed by steady state fluorescence spectroscopy. In complex 4, L_1 is confined between 2D hydrogen bonded sheet formed by pyromellitic acid anion. L_1 shows unusually high selectivity toward nitrate in solution resulting in both a dramatic color change and a concomitant quenching of luminescence.

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1. Introduction

Anion sensing has been of great interest in biological and environmental sciences for several decades. Various fluorescent sensors have been developed for sensitive and simple detections of anions [1]. The rapid detection of anionic species is of great significance in the environment and in physiological systems [1]. As signaling mechanisms, photoinduced electron transfer (PET) [2], intramolecular charge transfer (ICT) [3], excited-state proton transfer [4], metal to ligand charge transfer [5], excimer/exciplex formation [6] and competitive binding [7] have been reported. Although some excellent examples of compounds capable of anion recognition and sensing are reported [1]. However, these approaches have often involved the synthesis of structurally complicated hosts.

Therefore, the discovery and/or development of new simple and sensitive anion sensors are strongly desired.

We have been focusing on the discovery of new supramolecular fluorescent sensor molecules [8]. In the present paper, we report a simple and novel fluorescent anion sensor, Tris-[2-(naphthalen-1-yloxy)-ethyl]-amine (L_1). The binding of the hosts to a series of anions was investigated by fluorescence titration and ¹H NMR techniques. The anion binding properties was investigated by monitoring the changes in the fluorescence intensity of dry THF solution of L_1 at 298 K upon addition of F⁻, Cl⁻, Br⁻, NO₃⁻, ClO₄⁻, CF₃COO⁻ and Pyromellitate as their tetrabutylammonium (TBA) salt. The ligand L_1 shows a drastic change in the fluorescence intensity after anion binding.



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2. Results and discussion

2.1. Synthesis

Tris-[2-(naphthalen-1-yloxy)-ethyl]-amine (L_1) has been synthesized following literature method [9]. Synthesis of all the anionic complexes their characterization data are all given in the experimental section. IR and NMR spectral data and the results of chemical analyses are in order and in complete agreement with the molecular formulae of the compound. Crystals suitable for X-ray studies of these anionic complexes were obtained by slow crystallization from methanol:ethyl acetate (1:3) mixture at room temperature.

2.2. Crystal structure analyses

Some of our main concerns have been to ascertain the recognition of anion in the solid-state and the consequences of weak hydrogen bonding in the intermolecular network structure. Accordingly, X-ray diffraction analyses of the four anionic complexes were done and supramolecular organization in the crystals determined and pertinent structural data are provided in Table 1.

The bridgehead tertiary nitrogen of the tripodal ligand L_1 exists in monoprotonated form in presence of acid. The mono-protonated charge of the tripodal ligand is satisfied by one external counter anions. The ligand has a C_3 axis of symmetry in the solid state [9]. Space-filling model of the ligand shows the presence of a cavity of average

Table 1					
Crystallographic	data	for	1.2.3	and	4



Fig. 1. Hydrophobic pocket in L_1 .

diameter of ~5 Å (Fig. 1). However, the cavity is exclusively hydrophobic in nature. Hence, in the solid state L_1 cannot be an endo-receptor for hydrophilic anions. L_1 encapsulate these anions in between space in the solid-state.

Attempts were made to provide solid-state evidence for anion encapsulation by setting up a series of crystallization experiments of L_1 with different anion. We have shown the crystal structure analyses of the following complexes: $[HL_1^+][Br^-](1)$, $[HL_1^+][Cl^-] \cdot CH_3OH(2)$, $[HL_1^+][NO_3^-](3)$ and $[HL_1^+][Pyromellitate^-] \cdot CHCl_3(4)$. We have crystallized L_1 in presence of CF₃COO⁻ also, but structural analysis of these crystals has met with limited success. The resolution of the structure was poor [10]. CF₃COO⁻ unit is not behaved properly during refinement. However, ligand structure is properly solved.

	1	2	3	4
CCDC No.	644569	644570	644571	646021
Chemical formula	C ₃₆ H ₃₄ BrNO ₃	C ₃₈ H ₄₀ ClNO ₄	C ₃₆ H ₃₄ N ₂ O ₆	C47H40Cl3NO11
$F_{\rm w}$	608.55	610.16	590.6	901.15
Crystal system	Cubic	Triclinic	Cubic	Monoclinic
Crystal size (mm)	$0.23 \times 0.19 \times 0.11$	$0.22 \times 0.19 \times 0.16$	$0.21 \times 0.16 \times 0.12$	$0.41 \times 0.37 \times 0.31$
Space group	<i>P</i> 2(1)3	P-1	<i>P</i> 2(1)3	P2(1)/n
a (Å)	14.3769(17)	11.526(3)	14.4685(5)	13.1145(6)
$b(\mathbf{A})$	14.3769(17)	11.805(3)	14.4685(5)	24.7506(12)
c (Å)	14.3769(17)	14.313(6)	14.4685(5)	13.6777(7)
α (°)	90.00	112.108(10)	90.00	90
β (°)	90.00	108.979(10)	90.00	90.19(4)
γ (°)	90.00	96.360(7)	90.00	90
$V(\text{\AA}^3)$	2971.6(6)	1644.7(10)	3028.80(18)	4439.7(4)
Z	4	2	4	4
$d_{\rm cald} \ ({\rm mg/m}^{3})$	1.360	1.239	1.295	1.341
<i>T</i> (K)	273(2)	273(2)	273(2)	273(2)
$\mu (\mathrm{mm}^{-1})$	1.420	0.150	0.088	0.271
<i>F</i> (000)	1264	596	1248	2255
Final <i>R</i> indices $[I > 2\sigma]$				
R_1	0.0509	0.0603	0.0647	0.0556
WR_2	0.1239	0.2218	0.1658	0.1948
R indices (all data)				
R_1	0.0512	0.0901	0.948	0.726
WR_2	0.1840	0.2460	0.1942	0.2111
Goodness of fit	0.829	1.058	1.002	1.071

It appears that conformational freedom of the ligand in the crystal lattice is not so restricted thereby allowing different packing options. Thus, there is a significant degree of reciprocal intermolecular hydrogen bonding in the solid-state between molecules. Crystal structure analysis shows that L_1 acts as an exo-receptor for the anions. In the solid state, anions are present within a hydrophobic channel out side the ligand cavity. Protonated bridgehead N atom is buried inside the hydrophobic region. Moreover, the proton attached to the apical nitrogen is in endo orientation. Therefore, it cannot form $N-H\cdots X$ type hydrogen bonding. All the C-N and C-O bond lengths in these salts are longer than the corresponding free L_1 . This is because of the repulsion of the charged endo oriented N-H bond. The mean value of C-N-C bond angles in these salts are smaller than those in free L_1 (113.6(2)°), which also indicates the repulsion.

The bromide complex 1 crystallizes in a highly symmetric cubic space group with one molecule in the asymmetric unit (Fig. 2). Ligand posses C_3 axis of symmetry in the solid state. Counter anion is outside the ligand cavity, which is true for all other complexes also. The ligand moieties are organized via intermolecular $C-H\cdots\pi$ interactions (Table 2). Ligand does not have any kind of strong or weak interactions with the bromide ion in the solid-state. It forms alternate up-down 3D network of dumbbell shape boxes (Fig. 3). Each naphthalene unit is parallel to the plane of the unit cell. Bromide ion is present in a triangular channel in the lattice formed by the self-assembly of the ligand (Fig. 4).

When we replace the larger bromide ion with smaller chloride ion, the symmetry of the crystal is destroyed. Chloride complex 2 crystallizes in triclinic space group. Asymmetric unit contains one CH₃OH molecule (Fig. 5). We have observed several other differences in the solidstate structure in comparison to the bromide complex 1. The ligand moieties self-assembled via intermolecular



Fig. 2. ORTEP plot of complex1. Hydrogen atoms are omitted for clarity.

Table 2												
Hydrogen	bond	distances ((Å)	and a	ngles	(°)	in	1,	2,	3 and	4	

Complex	D–H···A	$H \cdot \cdot \cdot A (\mathring{A})$	$D \cdots A (\mathring{A})$	$\angle D - H \cdots A$ (°)
1	C2-H2A $\cdots \pi^a$	3.080	3.404	101.20
	$C4\text{-}H4\cdots\pi^a$	3.572	4.443	157.02
	C9-H9· $\cdot \cdot \pi^a$	3.498	4.267	141.66
2	C5-H5···O13	2.961	3.700	137.49
	C18-H18···O13	2.707	3.470	139.83
	C28-H28···O13	2.522	3.439	168.56
	C13-H13A···Cl1	2.731	3.529	139.92
	C13-H13B···Cl1	2.929	3.613	128.46
	C20-H20···Cl1	2.921	3.756	150.06
	C25-H25A···Cl1	2.823	3.594	137.01
	C37-H37A···Cl1	2.274	3.053	137.71
	C1-H1A $\cdots \pi^{b}$	3.420	4.166	136.30
	C4-H4 $\cdots \pi^{b}$	3.572	4.443	157.02
	C9-H9· · · π^{b}	3.498	4.267	141.66
	$C25\text{-}H25B\!\cdots\!\pi^c$	3.108	4.056	166.72
3	C6-H6· · ·O2	2.393	3.448	167.87
	C12-H12B···O2	2.547	3.380	145.50
	C11-H11B· $\cdot \cdot \pi^d$	3.227	3.461	92.39
	$C10\text{-}H10\cdots\pi^d$	3.429	4.408	155.26
4	C2-H2A···O10	2.614	3.266	124.83
	C13-H13A···O5	2.600	3.293	128.67
	C13-H13A···O7	2.572	3.432	147.85
	C25-H25A···O7	2.623	3.217	119.90
	C25-H25B···O11	2.592	3.244	124.74
	C28-H28···O4	2.468	3.377	165.91
	C32-H32···O7	2.654	3.239	121.43
	C18-H18· $\cdot \cdot \pi^{e}$	3.077	3.843	140.89

^a Centroid of ring C3–C12.

^b Centroid of ring C3–C12.

^c Centroid of ring C31–C36.

^d Centroid of ring C1–C10.

e Centroid of ring C37-C42.

C-H··· π interactions. Unlike complex 1, the ligand forms some addition weak hydrogen bond interactions. In complex 2, ligand form intermolecular C-H···O interactions with oxygen atom of solvent molecule (Table 2). Several strong C-H···Cl⁻ interactions are also present in the chloride complexes [11]. Larger Br⁻ ion does not show this kind of interaction. All the chloride ions are lined up along crystallographic *a* axis (Fig. 6). Ligands are organized as a bowl in alternated up and down manner in the solid-state. Chloride ion is situated in a rectangular channel formed by the self-assembled ligand in the crystal (Fig. 7). In the lattice, it is sandwiched between two naphthalene unit.

Crystal structure of nitrate complex **3** is similar that of the bromide complex **1**. It also crystallizes in a highly symmetric cubic space group. Asymmetric unit contains one molecule (Fig. 8). Here ligand and anion has the similar 3D arrangement like complex **1**. The packing pattern of the bromide and nitrate complex are exactly same. However, in addition to the intermolecular $C-H\cdots\pi$ interactions ligand forms intermolecular $C-H\cdots\sigma$ interactions with oxygen atom of anion (Table 2). Nitrate anion occupies the triangular hydrophobic void space in the crystal lattice, which is same as of bromide complex (Fig. 9).



Fig. 3. Packing diagram of complex 1.



Fig. 4. Bromide recognition in the solid state.

Ligand in presence of pyromellitic acid crystallizes in monoclinic space group. Asymmetric unit contains one CHCl₃ molecule (Fig. 10). Unlike CH₃OH molecule in **2**, CHCl₃ molecule does not form any type of weak interactions with the ligand or acid molecules. All the pyromellitate ions are lined up along crystallographic *c* axis (Fig. 11). Ligand and CHCl₃ molecules are arranged in in alternate up–down manner in between two hydrogen bonded sheets. Each ligand is connected to the sheet via several C–H···O interactions [10]. Geometry of the ligand does not allow two naphthalene units to come within the non-bonded distances in the solid-state. Hence, no π - π interactions are observed in the solid state within the ligand molecules. Electron deficient pyromellitic acid also does not show π - π interactions with electron rich ligand.



Fig. 5. ORTEP plot of complex 2. Hydrogen atoms are omitted for clarity.



Fig. 6. Packing diagram of complex 2.



Fig. 7. Chloride recognition in the solid state.

Pyromellitic acid unit form a 2D hydrogen bonded sheet along *ac* plane of the crystal. It forms a $R_4^4(29)$ pattern hydrogen bonded ring (Fig. 12). Another notable feature of the crystal structure of **4** is the formation of intra as



Fig. 8. ORTEP plot of complex 3. Hydrogen atoms are omitted for clarity.



Fig. 9. Nitrate recognition in the solid state.

well as intermolecularsix membered intermolecular hydrogen bonded ring.

In the case of the solution-state study by ¹H NMR, when HCl was added to the DMSO- d_6 solution of L₁, the ¹H NMR spectrum shows a shift in the position of the tren NCH₂ proton from δ 3.41 ppm to the higher δ value of 3.64 ppm. This shift indicates the influence of the protonated apical nitrogen on the neighboring proton. Similar changes observed in the solution phase with other anions also.

2.3. Absorption spectroscopy

UV-visible absorption spectra of L_1 in dry THF at 298 K shows the ${}^{1}L_a \leftarrow {}^{1}A$ transitions of the naphthalene unit in the region 250–300 nm with $\varepsilon = 1905 \text{ M}^{-1} \text{ cm}^{-1}$



Fig. 10. ORTEP plot of complex 4. Hydrogen atoms are omitted for clarity.



Fig. 11. Packing diagram of complex 4.



Fig. 12. 2D hydrogen bonded sheet structure of pyromellitic acid along *ac* plane in **4**.

and lower energy ${}^{1}L_{b} \leftarrow {}^{1}A$ transitions in the region 300– 350 nm with $\varepsilon = 932 \text{ M}^{-1} \text{ cm}^{-1}$ [8]. These transitions are found to be non-solvatochromic in nature. Changes in the UV-visible absorption spectra were monitored upon successive addition of anions to sensor \mathbf{L}_{1} . A very weak hypsochromic shift observed only when trifluoro acetic acid was added to \mathbf{L}_{1} (Fig. 13). All other sensor and inorganic anion combinations afforded almost no noticeable shift in the peak positions. These results suggest a different mode of binding of \mathbf{L}_{1} to CF₃COO⁻. During titration with pyromellitic acid we got an additional peak at 295 nm due to pyromellitic acid [10].

2.4. Fluorescence spectroscopy

The emission spectra of L_1 in dry THF at 298 K shows a locally excited (LE) broad emission of naphthalene with emission maximum at 410 nm ($\lambda_{ex} = 330$ nm) (Fig. 14). LE emission remains virtually unchanged with respect to solvent polarity. The excitation spectra monitoring λ_{max} of the emission band is identical with the absorption spectra of the free ligand in dry THF at 298 K [10]. With increasing concentration of the ligand, the total intensity of fluorescence emission decreases significantly without the appearance of any broad band in the higher wavelength region. This suggests that self-quenching takes place without formation of any excimer at higher concentration [12]. Geometry of the ligand does not allow two naphthalene chromophores to come in contact with each other, which is similar to the reported observation [8]. The concentration of the ligand was maintained at 10^{-6} M throughout the study as the emission intensity is found to be maximum at this concentration.



Fig. 13. Changes in UV–visible absorption spectra upon addition of CF_3COO^- to a THF solution of L_1 at 298 K.



Fig. 14. Emission spectrum of L_1 (1×10⁻⁶ M in dry THF) during the titration with nitric acid from 0 to 20 equivalent.

When THF solutions of acids were added gradually to THF solution of L_1 the fluorescence was quenched to varying degrees (Figs. 14 and 15). The best results were observed for additions of nitric acid to L_1 , where 97% quenching was observed after 16 equiv of anion had been added (Fig. 14 inset). Ligand L_1 exhibits high selectivity toward nitrate anion over other anions present in solution. The linear Stern–Volmer response with nitrate as quencher is consistent with well-behaved fluorescence quenching systems [13]. The absence of the red shifted band in these systems excludes the possibility of an emission from a charge transfer state involving the protonated amine/ether oxygen and the naphthalene unit [14]. To demonstrate the selectivity of L_1 toward nitrate, we have monitored the change in fluorescence quantum yields in the presence of different anions. Fig. 15 clearly shows that L_1 has a remarkably high selectivity toward nitrate anion in terms of change of fluorescence quantum yield. The dissociation constant (K_d) of 4.8 µm was calculated from this fluorescence titration [15]. The spectral characteristics of L_1 in the solid state are consistent with its solution phase behavior. In the solid state, L_1 exhibits two broad absorption bands at 275 and 320 nm. It shows a broad emission band at 415 nm.

3. Experimental

3.1. Physical measurements

The absorption spectra were recorded on a Perkin Elmer Lambda- 25 UV–Visible Spectrometer at 298 K. The fluorescence spectra were recorded on a Varian Cary-Bio spectrofluorimeter and corrected for emission. NMR spectra



Fig. 15. Schematic representation showing the change of fluorescence quantum yield ($\Phi_{\rm F}-\Phi_{\rm q}$) of \mathbf{L}_1 upon addition of the anions. $\Phi_{\rm F}$ and $\Phi_{\rm q}$ are quantum yields of \mathbf{L}_1 in absence and presence of anion, respectively. Inset: Sterni–Volmer plot for fluorescence quenching of $\mathbf{L}_1(1 \times 10^{-6} \text{ M})$ on gradual addition of nitrate ($1 \times 10^{-6} \text{ M}$) in dry THF.

were recorded on a Varian FT-400 MHz instrument. The chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) as a reference. Elemental analyses were carried out on a Perkin-Elmer 2400 automatic carbon, hydrogen and nitrogen analyzer.

3.2. X-ray structural determination

The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoK_{α} radiation $(\lambda = 0.71073 \text{ Å})$ at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP [16] software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [17]. Structures were solved by direct methods using SHEL-XS-97 and refined with full-matrix least squares on F^2 using SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 for Windows [19]. CCDC-607228, 607229 and 607230 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

3.3. General synthesis of anion complexes 1–4

 L_1 (1 mmol) was dissolved in chloroform (5 mL) followed by the slow addition of methanolic solution of tetra

butyl ammonium salt of corresponding anion (1 mmol). The resulting mixture was stirred at room temperature for 30–60 min. Precipitate (if any) was filtered and filtrate was kept at room temperature without any mechnical disturbance.

Complex 1: yellow plates, yield (88%), $C_{36}H_{34}NO_3Br$: calcd. C 71.05, H 5.63, N 2.30, found C 70.87, H 5.49, N 2.16. Complex 2: pale yellow plates, yield (92%), $C_{38}H_{40}NO_4Cl$: calcd. C 74.79, H 6.60, N 2.29, found C 74.83, H 6.68, N 2.26. Complex 3: white needles, yield (96%), $C_{36}H_{34}N_2O_6$: calcd. C 73.20, H 5.80, N 4.74, found C 73.57, H 5.87, N 4.81. Complex 4: white plates, yield (71%), $C_{47}H_{30}NO_{11}Cl_3$: calcd. C 62.64, H 4.47, N 1.55, found C 62.72, H 4.52, N 1.51.

4. Conclusion

In conclusion, a simple tripodal naphthalene ether ligand L_1 is reported as chromogenic anion sensor. It can selectively capture nitrate anion in solution. L_1 form selfassembled structures in the solid state. In the solid-state different anions are encapsulated in the channel formed by the ligand. In the solid-state they are assembled via several week non-covalent interactions. The spectral features of the ligand as well as the anionic complexes are similar in solution phase and solid state. Anions quench the fluorescence intensity of the free L_1 . Designing of supramolecular host guest fluorescence signaling systems for other type of guests is in progress in our laboratory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.08.016.

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