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Neutral Acyclic Anion Receptor with Thiadiazole Spacer: Halide Binding Study and Halide-Directed Self-Assembly in the Solid State

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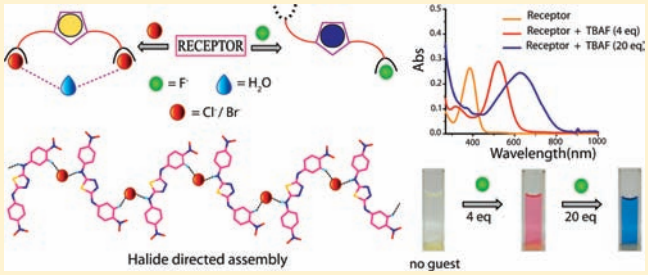
Supporting Information

ABSTRACT: A halide binding study of a newly synthesized neutral acyclic receptor $\mathbf{LH_2}$ with a thiadiazole spacer has been methodically performed both in solution and in the solid state. Crystal structure analysis of the halide complexes elucidate the fact that fluoride forms an unusual 1:1 hyrogen-bonded complex with monodeprotonated receptor, whereas in the case of other congeners, such as chloride and bromide, the receptor binds two halide anions along with formation of a halide-bridged 1D polymeric chain network by participation of N−H···X^- and aromatic C−H···X^- hydrogen-bonding (where X = Cl and Br) interactions. The presence of a rigid thiadiazole spacer presumably opens up enough space for capturing two halide anions by a single receptor molecule, where the coordinated −NH protons are pointed in the same direction with respect to the spacer and eventually favor formation of halide (Cl^- and Br^-) induced polymeric architecture, although no obvious chloride- or bromide-directed polymeric assembly is found in solution. A significant red shift of 243 nm in the absorption spectra of $\mathbf{LH_2}$ was solely observed in the presence of excess fluoride anion, which enables $\mathbf{LH_2}$ as an efficient colorimetric sensor for optical detection of fluoride anion (yellow to blue). Furthermore, spectroscopic titration experiments with increasing equivalents of fluoride anion suggest formation of a H-bonded complex with subsequent stepwise deprotonation of two N−H groups, which can be visually monitored by a change in color from yellow to blue via pink.



INTRODUCTION

The field of anion coordination chemistry continues to expand with new synthetic molecules capable of recognizing anions which are not only within the interest of supramolecular chemistry but also have immense environmental and biomedical significance.[1,2] Various types of neutral synthetic receptors have been developed that employ hydrogen bonds offered by specific binding sites as in amides,[3] urea/thiourea,[4] pyrroles,[5] and indole[6] to bind anions with size and shape selectivity and are well explored in various media. However, design and synthesis of new class of neutral anionic receptor always remains a challenge for the researcher due to the high directionality of H-bond donors required to obtain a stable receptor−anion complex. As a consequence of this interest, considerable efforts have been devoted to development of new H-bonding receptors, capable of selective recognition of a specific anion from a mixture of anions. Recently, Hay and co-workers have shown their active interest toward the design of computer-aided sophisticated receptors for targeted anions of varying geometry.[7]

As compared to metal-directed coordination polymers, anion-directed assembly of coordination polymers has also attracted considerable attention motivated by their potential applications in recognition, separation, guest inclusion, and catalysis.[8] Indeed, several approaches have been fruitfully made to pursue anion-assisted variety of architectures by strengthening hydrogen bonding through electrostatic interaction with protonated ligands[9] or utilizing the metal−ligand interaction to assist formation of networks.[10] Moreover, anion-directed metal-free self-assembled coordination polymer formation in a neutral system is rarely highlighted in the literature.[11] In this context, the structure of the receptor requires a tailored design to ensure that the anion-binding sites of the receptor should be well separated by a rigid spacer. The spacer favors formation of an anion-assisted self-assembled architecture by adapting suitable receptor−anion hydrogen-bonding interactions.

In our continuing effort toward design and synthesis of new anion receptors,[12] herein we report the synthesis and characterization of an anion receptor $\mathbf{LH_2}$ with a thiadiazole spacer and its detailed halide binding studies both in solid and in the solution state. This receptor selectively recognizes fluoride among the other halides, which is manifested by a visual color change. Except iodide, the receptor also forms significant H-bonded complexes with other halides. Crystal structure analysis of the chloride and bromide complexes reveals that the receptor $\mathbf{LH_2}$ binds two halides along with formation of a halide-bridged 1D chain polymeric network structure through participation of N−H···X^- and aromatic C−H···X^- H-bonding interactions (where X = Cl and Br). However, no obvious chloride- or bromide-directed polymeric assembly is found in solution. Therefore, such structural

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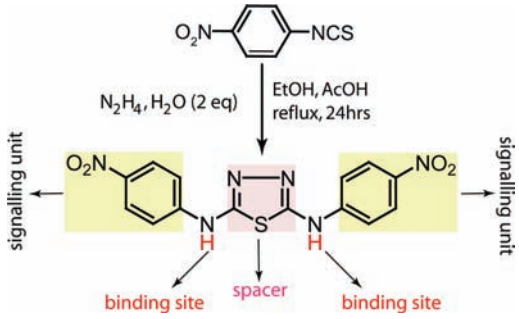
features are worthwhile only in the solid state, while in the case of the fluoride complex the receptor is present in its monodeprotonated form with a hydrogen-bonded fluoride anion.

RESULTS AND DISCUSSION

The receptor $\mathbf{LH_2}$ was synthesized with satisfactory yield by refluxing the 1:2 mixture of 4-nitrophenylisothiocyanate and hydrazine hydrate in the presence of acetic acid (catalytic amount) in EtOH for 24 h (Scheme 1). Receptor $\mathbf{LH_2}$ is fully

Scheme 1. Synthesis of the Receptor $\mathbf{LH_2}$



characterized by NMR, ESI-MS, UV−vis, and IR spectroscopies. The receptor $\mathbf{LH_2}$ consists of two acidic N−H protons which are separated by a rigid thiadiazole spacer. The 4-nitro phenyl rings help to increase the acidity of N−H protons and also act as a chromophoric signaling unit during the receptor−halide interaction process.

X-ray Crystal Structure Analysis of Receptor Halide Complexes. Light orange block-shaped crystals of chloride complex $[LH_2(Cl)_2(n\text{-}Bu_4N)_2]\cdot H_2O$ suitable for single-crystal X-ray diffraction analysis were obtained after 20 days of slow evaporation of an acetonitrile solution of the receptor $\mathbf{LH_2}$ in the presence of excess $[n\text{-}Bu_4N]Cl$ with an isolated yield of about 48%. The complex crystallized into the orthorhombic space group $Pna2_1$ with $Z = 4$ (Table 1). Structural elucidation of the complex reveals that the receptor is involved in a 1:2 binding stoichiometry of host to guest where each chloride anion is bound to a single receptor molecule by a moderate N−H···Cl^- interaction together with the hydrogen-bonding participation from adjacent TBA countercations and the lattice water molecule. The hydrogen-bonding interactions of chloride anions with the receptor and adjacent tetrabutylammonium groups are shown in Figure 1 along with the atom numbering scheme. The water molecule behaves as a hydrogen-bonded bridge between two coordinated anions forming a $[Cl_2H_2O]^{2-}$ triangle with a Cl^-−O−Cl^- angle of 114.9(1)° and Cl^-−Cl^- separation distance of 5.643(2) Å (Figure 1 inset). The presence of a rigid thiadiazole spacer between the two acidic NH protons of $\mathbf{LH_2}$ resists the convergent hydrogen bonding to a single chloride anion, whereas convergent hydrogen bonds to an acceptor species are quite common for urea/thiourea-based anion receptors.[4] Both the N−H protons of the receptor are directed in the same direction and participate in hydrogen-bonding interactions with two different chloride anions. The donor−acceptor distances (N···Cl^-) fall in the range 3.10−3.14 Å, which corresponds to formation of moderate hydrogen bonds, mainly electrostatic in nature.[13] Structural analysis of the complex reveals that Cl^- (1) is stabilized by four hydrogen bonds involving one −NH proton (N2H), one −OH proton

Table 1. Crystal Parameters and Refinement Data

compound	chloride complex	bromide complex	fluoride complex
formula	$C_{46}H_{84}Cl_2N_8O_5S$	$C_{46}H_{84}Br_2N_8O_5S$	$C_{46}H_{81}FN_8O_4S$
fw	932.18	1021.08	861.26
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	*Pna*2(1)	*Pna*2(1)	*Pnma*
a (Å)	31.492(3)	31.372(7)	40.264(7)
b (Å)	8.0970(7)	8.1971(19)	12.8688(18)
c (Å)	21.497(2)	21.581(5)	9.7766(16)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00
V (Å)	5481.5(8)	5550.0(2)	5065.7(14)
Z	4	4	4
T (K)	298(2)	298(2)	298(2)
μ (cm^{-1})	0.204	1.545	0.115
d_{calcd} (g cm^{-3})	1.130	1.222	1.131
cryst dimens (mm^3)	0.38 × 0.31 × 0.29	0.39 × 0.31 × 0.27	0.42 × 0.34 × 0.29
no. of reflns collected	4827	4604	4598
no. of unique reflns	4780	4548	4549
no. of params	583	585	314
R1; wR2 ($I > 2\sigma(I)$)	0.0533, 0.1082	0.0459, 0.1072	0.0667, 0.2491
R(int)	0.0633	0.0857	0.1882
GOF (F^2)	0.997	0.992	1.099
CCDC NO.	835051	835050	801324

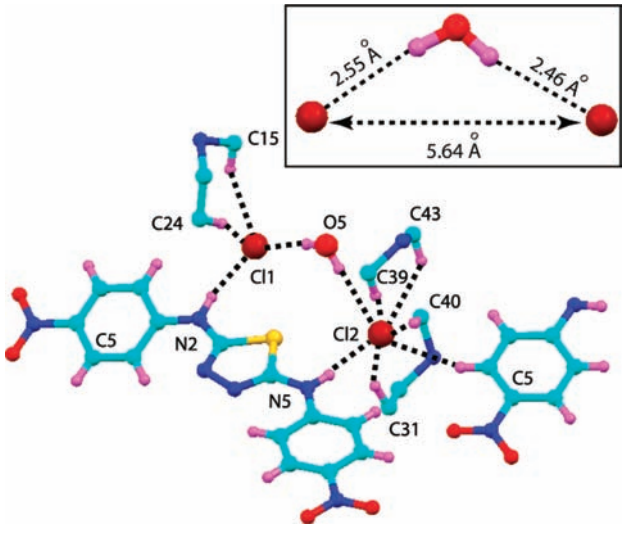


Figure 1. Hydrogen-bonding interactions of chloride anions with receptor ($\mathbf{LH_2}$) and tetrabutylammonium groups. Only the interacting parts of the tetrabutylammonium unit have been shown for clarity. (Inset) Magnified view of the water chloride hydrogen-bonding interactions. Dashed lines indicate the hydrogen-bonding interactions.

(O5H, lattice water), and two aliphatic−CH protons (C15H and C24H) from a nearby tetrabutylammonium unit (Tables 2 and 3). On the other hand, Cl^- (2) is stabilized by participation of seven hydrogen bonds involving one −NH proton (N5H), one aryl −CH proton (C5H), one −OH proton (O5H, lattice water), and four aliphatic −CH protons from two neighboring tetrabutylammonium units donating two C−H···Cl^- hydrogen bonds each. One of the nitro phenyl rings is slightly twisted out of the plane relative to the central thiadiazole ring, where the

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Table 2. N−H···Anion and O−H···Anion Hydrogen-Bonding Interactions in Receptor−Halide Complexes

donor group	D···A [Å]	H···A [Å]	D−H···A [deg]	acceptor atom
N(2)−H(2N)	2.300(9)	1.442(5)	177.0(5)	F1
N(2)−H(2N)	3.076(4)	2.216(4)	168.0(4)	Cl1
N(2)−H(2N)	3.113(4)	2.258(6)	173.3(5)	Cl2
O(5)−H(5O)	3.320(5)	2.465(6)	172.8(5)	Cl1
O(5)−H(6O)	3.374(6)	2.537(7)	167.6(9)	Cl2
N(2)−H(2N)	3.193(8)	2.300(8)	173.0(6)	Br1
N(2)−H(2N)	3.255(7)	2.300(8)	166.6(4)	Br2
O(5)−H(5O)	3.404(7)	2.568(7)	165.2(6)	Br1
O(5)−H(6O)	3.464(6)	2.645(4)	162.0(5)	Br2

Table 3. C−H···Anion Hydrogen-Bonding Interactions in Receptor−Halide Complexes

donor group	D···A [Å]	H···A [Å]	D−H···A [deg]	acceptor atom
C(2)−H(2)	3.250(1)	2.668(5)	121.4(7)	F1
C(15)−H(15A)	3.061(5)	2.178(3)	150.6(3)	F1
C(23)−H(23B)	3.254(5)	2.434(4)	142.1(3)	F1
C(5)−H(5)	3.664(6)	2.810(1)	153.3(3)	Cl2
C(39)−H(39A)	3.616(6)	2.717(1)	154.4(4)	Cl2
C(43)−H(43A)	3.689(6)	2.917(1)	137.2(4)	Cl2
C(31)−H(31A)	3.743(6)	2.787(1)	168.9(4)	Cl2
C(40)−H(40B)	3.612(9)	2.771(1)	145.6(7)	Cl2
C(15)−H(15A)	3.825(7)	2.913(1)	157.0(4)	Cl1
C(24)−H(24B)	3.802(7)	2.905(1)	154.4(4)	Cl1
C(5)−H(5)	3.673(8)	2.814(9)	154.0(4)	Br2
C(39)−H(39A)	3.670(7)	2.774(9)	153.8(5)	Br2
C(43)−H(43A)	3.800(8)	3.006(9)	140.0(5)	Br2
C(31)−H(31A)	3.844(8)	2.878(8)	172.8(5)	Br2
C(40)−H(40B)	3.640(1)	2.812(9)	144.1(9)	Br2
C(15)−H(15A)	3.873(8)	2.963(8)	156.6(5)	Br1
C(24)−H(24B)	3.899(9)	3.011(9)	152.8(6)	Br1

angle between the planes of the two rings is 25.08°. Additionally, one of the ortho aryl hydrogens (C5H) with respect to the nitro group of the twisted phenyl ring forms a significant C−H···Cl^- hydrogen-bonding interaction with the neighboring Cl^- (2) anion. This C−H···Cl^- interaction leads to formation of an anion-bridged 1D polymeric chain network in association with the moderate N−H···Cl^- (2) H bond along with a weak intermolecular C−H···O (nitro) interaction (Figure 2). The chloride Cl^- (2) anions in this polymeric chain extension are alternately arranged in a zigzag array with a distance of 11.49(2) Å and Cl^-−Cl^-−Cl^- angle of 149.20(2)°. The other chloride anion Cl^- (1) is not involved in this polymeric array.

Single crystals suitable for X-ray diffraction analysis of the bromide complex were obtained as $[\mathbf{LH_2}(Br)_2(n\text{-}Bu_4N)_2]\cdot H_2O$ with a fair yield (42%) by slow evaporation of an acetonitrile solution of the receptor $\mathbf{LH_2}$ in the presence of a large excess of $[n\text{-}Bu_4N]Br$. The complex crystallized into the orthorhombic space group $Pna2_1$ with $Z = 4$ (Table 1). Interestingly, X-ray crystal structure analysis of the bromide complex reveals that the receptor $\mathbf{LH_2}$ interacts with bromide anions in exactly the same fashion as that of chloride anions (Supporting Information, Figure S6). Hydrogen-bond distances of the bromide complex are slightly greater than those of the chloride complex (Tables 2 and 3). This is due to the larger ionic radii and lower basicity of the bromide ion compared to chloride. Similar to the chloride complex, here also the bromide-bridged 1D chain polymeric network structure is observed.

The crystal structure of the fluoride complex revealed some interesting features of the complex. Dark violet block-shaped single crystals of the fluoride complex were grown from acetonitrile as $[LH(F)(n\text{-}Bu_4N)_2]$ with a satisfactory yield of about 55% upon slow evaporation of a mixture of $\mathbf{LH_2}$ and 5 equiv of $[n\text{-}Bu_4N]F$. The fluoride complex crystallizes in the orthorhombic system with a *Pnma* space group with $Z = 4$ (Table 1). In contradiction to the chloride and bromide complexes, fluoride forms an unusual 1:1 host−guest complex with monodeprotonated receptor. A structural study of the complex reveals that fluoride anion is stabilized by six hydrogen bonds involving one −NH proton (N2H), one aryl −CH proton (C2H) of the monodeprotonated receptor, and four aliphatic−CH protons from the acidic $-CH_2$ group, adjacent to the bridgehead nitrogen of two different tetrabutylammonium cations present in close proximity with fluoride anion. The presence of two tetrabutylammonium cations and a hydrogen-bonded fluoride in the crystal lattice of the fluoride complex supports the fact that the receptor present is in its monodeprotonated form. The significantly small N···F^- distance of 2.300(9) Å suggests that the deprotonated receptor forms comparatively a much stronger hydrogen bond with fluoride as compared to chloride and bromide in their respective complexes, where the receptors are in the neutral form. The mode of hydrogen-bonding interactions of the fluoride anion with monodeprotonated receptor and tetrabutylammonium groups is shown in Figure 3a, and the corresponding parameters are given in Tables 2 and 3. Comparative bond distance analysis of the complexes again confirms that in the fluoride complex the receptor exists in its monodeprotonated form (Supporting Information, Table S2.).

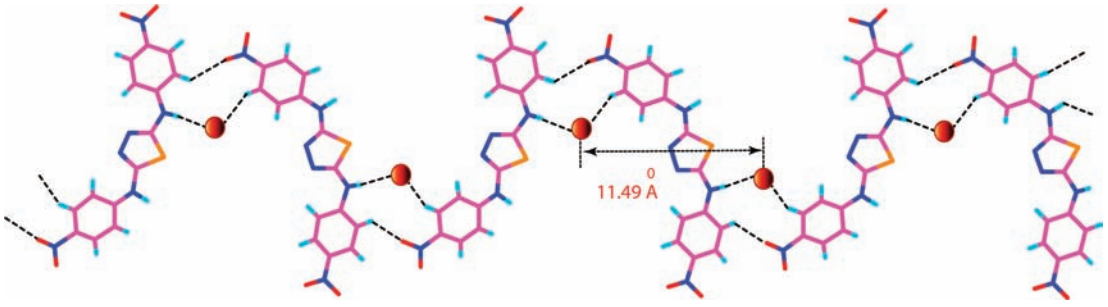

Figure 2. Formation of a chloride Cl^- (2) directed network obtained by self-assembly (view along the *b* axis). Countercations $[n\text{-}Bu_4N^+]$ and solvent molecules and the other chloride anion (Cl^- (1)) are omitted for clarity. Hydrogen bonds have been drawn as dashed lines.

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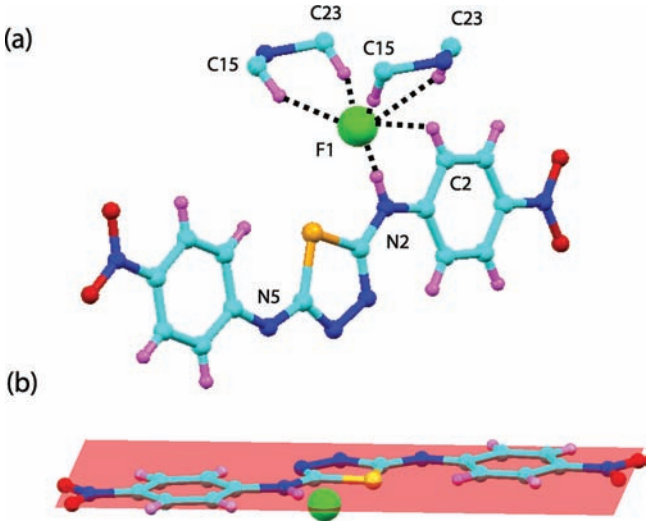

Figure 3. (a) Hydrogen-bonding interactions of fluoride anion with monodeprotonated receptor ($\mathbf{LH}^-$) and two tetrabutylammonium groups. Only the interacting parts of the tetrabutylammonium units have been shown for clarity. Dashed lines indicate the hydrogen-bonding interactions. (b) Crystal structure of the fluoride complex showing the presence of F^- anion in the same molecular plane.

It is interesting to observe that in the fluoride complex the monodeprotonated receptor is present in its anti conformation with respect to the thiadiazole spacer. This conformation is due to minimizing the repulsion between two negatively charged species (fluoride anion and N5 atom of monodeprotonated receptor), while in the bromide and chloride complexes the receptor $\mathbf{LH_2}$ is present in its syn conformation. Furthermore, it is important to mention here that while interacting with the fluoride ion the monodeprotonated receptor ($\mathbf{LH}^-$) adopts an exactly planar geometry (Figure 3b) which eventually favors formation of an aromatic C−H···F^- interaction involving the aryl proton C2H of the adjacent nitro phenyl ring due to its directionality acquired because of the planarity, whereas such type of hydrogen-bonding interactions have not been observed in the chloride and bromide complexes. Close inspection of the crystal structure elucidates that the fluoride anion is getting sandwiched between two cationic tetrabutylammonium units by four aliphatic C−H···F^- interactions with an average donor to acceptor distance 3.15 Å (Supporting Information, Figure S8). Formation of a 1:1 complex between fluoride and monodepronated receptor could be justified due to the higher basicity of the fluoride ion. The approaches of more than two fluoride anions to the receptor $\mathbf{LH_2}$ initiate the deprotonation process, and thereby, we found in the fluoride complex the receptor present in its monodeprotonated form with a hydrogen-bonded fluoride anion.

The overall crystal structure analyses of the receptor−halide complexes reveal that 1:2 chloride and bromide complexes form a halide-bridged 1D polymeric chain network by participation of N−H···X^- and aromatic C−H···X^- hydrogen-bonding (where X = Cl and Br) interactions. Most likely the rigid thiadiazole spacer opens up enough space to confine two halide anions by a single receptor molecule which eventually favors formation of halide (Cl^- and Br^-) induces 1D polymeric chain, whereas no such fluoride-induced polymeric architecture is observed in the fluoride complex. Presumably the fluoride induces formation of a 1:1 complex between monodeprotonated receptor, and the fluoride anion prevents construction of any fluoride-induced polymeric assembly in the solid state. Significantly, in all three halide complexes the aliphatic CH protons of the tetrabutylammonium countercations actively participate in the hydrogen-bonding interactions with halides. This type of hydrogen-bonding interaction between anions and nonaromatic CH groups as hydrogen-bond donors is very rare in the literature,[14] and the C−H···anion interactions involving organic cations have also attracted considerable attention because of their biological and chemical importance.[15]

Halide Binding Study by UV−Vis Spectroscopy. The halide binding properties of $\mathbf{LH_2}$ have been investigated in solution by qualitative as well as quantitative UV−vis spectroscopic experiments in CH_3CN. The absorption spectroscopic study reveals that the receptor is capable of selectively detecting fluoride ion by a visible color change from yellow to blue even in the presence of other halides like Cl^-, Br^-, and I^- (Supporting Information, Figure S11). Free receptor shows an absorption maximum at 385 nm in CH_3CN. However, addition of excess fluoride ion (50 equiv as TBA salt) shows the disappearance of the peak at 385 nm with concomitant emergence of a new peak at 628 nm (Figure 4a).

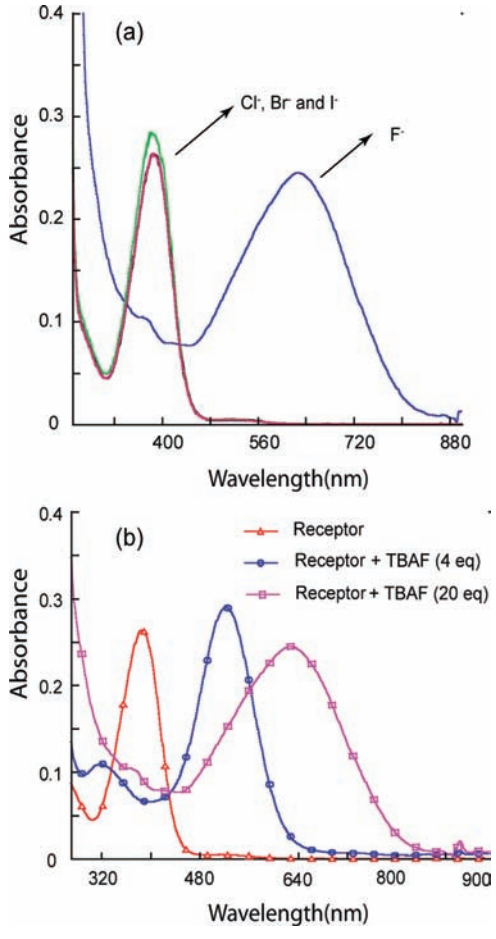

Figure 4. (a) Changes in the UV−vis spectra of $\mathbf{LH_2}$ in CH_3CN upon addition of tetrabutylammonium salts of different halides (50 equiv). (b) Changes of UV−vis specctra of $\mathbf{LH_2}$ (4.6×10^{-6} M) in CH_3CN upon addition of different equivalents of $[n\text{-}Bu_4N]F$ solution at 298 K.

A significant red shift of 243 nm is fairly comparable to the report by Zhao et al.,[16a] although the highest value of a fluoride-induced red shift has recently been reported by Ghosh et al.[16b] To evaluate the fluoride binding, quantitative UV−vis titration

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of $\mathbf{LH_2}$ is carried out with increasing equivalents of F^-. The titration experiment (Figures 4b and 5) reveals that a fluoride-induced color change of the receptor occurs in a ratiometric fashion. Initially, at lower concentration of F ions, the light yellow solution of $\mathbf{LH_2}$ turned pink at 4 equiv of F^- addition and then turned blue at higher F^- equivalents (~20 equiv) (Figure 6). This significant change in the UV–vis spectrum of receptor $\mathbf{LH_2}$ upon quantitative addition of fluoride anion suggests that the interaction between the fluoride and $\mathbf{LH_2}$ takes place in three well-defined steps, similar to the sequence previously reported.[16a,17] In particular, upon gradual addition of standard fluoride solution (1×10^{-3} M) to the solution of $\mathbf{LH_2}$ (4.6×10^{-6} M) the UV–vis absorption at 385 nm decreases and a new peak at 522 nm appears with two distinct isosbestic points at 426 and 335 nm up to 4 equiv of fluoride addition (Figure 5a). We assume this spectral change is due to the combination of both receptor–fluoride H-bonded complex formation and fluoride-induced monodeprotonation of the receptor.[18] Moreover, further addition of fluoride decreases the intensity of the band centered at 522 nm with the emergence of a new band at 628 nm with a sharp isosbestic point at 562 nm (Figure 5b). This process is initiated when the fluoride concentration is more than 4 equiv and reaches its saturation after addition of 20 equiv of fluoride. Further generation of a new peak in the red-shifted region (628 nm) indicates the fluoride-induced double deprotonation of the receptor in solution.[17a]

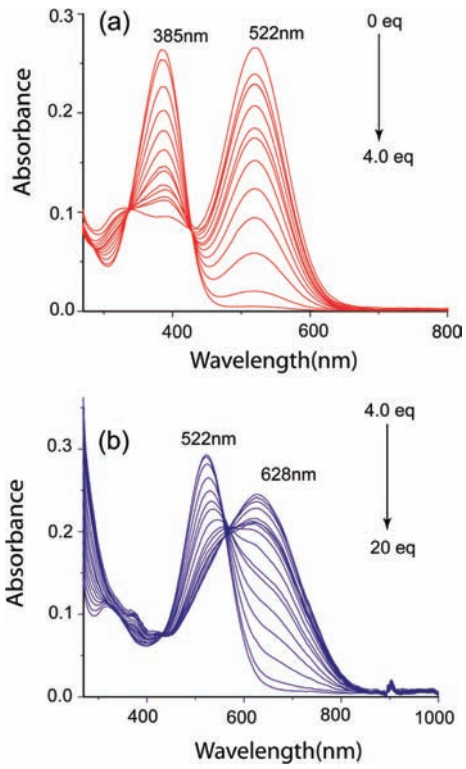

Figure 5. Family of spectra taken over the course of the titration of a 4.6×10^{-6} M solution of $\mathbf{LH_2}$ upon incremental addition of $[n\text{-Bu}_4\text{N}]\text{F}$ in CH_3CN at 298 K: (a) from 0 to 4 equiv of [*n*-Bu4N]F; (b) from 4 to 20 equiv of $[n\text{-Bu}_4\text{N}]\text{F}$.

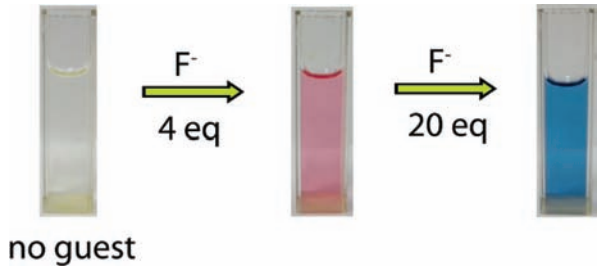

Figure 6. Stepwise color change observed for the receptor $\mathbf{LH_2}$ ($\sim 10^{-5}$) upon addition of different equivalents of standard $[n\text{-Bu}_4\text{N}]$F solution.

The presence of the absorption band at 522 nm in the UV–vis spectrum of isolated single crystals of the fluoride complex supports our assumption that during titration the fluoride-induced new band at 522 nm is a combination of both receptor–fluoride H-bonded complex formation and fluoride-induced monodeprotonation of the receptor (Supporting Information, Figures S10 and S16), whereas the fluoride-induced stepwise double deprotonation of the receptor $\mathbf{LH_2}$ was confirmed by titrating the receptor with standard $[n\text{-Bu}_4\text{N}]$OH (Supporting Information, Figure S17). The titration spectra display consecutive development of bands at 522 (associated to monodeprotonation) and 628 nm (associated to double deprotonation) after addition of 1 and 5 equiv of standard $[n\text{-Bu}_4\text{N}]$OH solution respectively.

As the spectral changes due to formation of the H-bonded complex and the first deprotonation occur in the same concentration range of added F^-, the individual steps cannot be analyzed in solution. Therefore, the apparent binding constant of fluoride binding to $\mathbf{LH_2}$ is calculated on the basis of the change in absorbance at 522 nm and considering a 1:1 binding isotherm; a value of log K_{app} = 3.75 (error 10%) is determined. The apparent binding constant K_{app} is a combined binding constant for both the hydrogen-bonded complex and the first deprotonation steps. Moreover, the significantly high fluoride-induced red shift (243 nm) of the receptor is due to its planarity and conjugation, which help complete delocalization of the negative charge(s) of the deprotonated receptor. The fluoride-induced complex UV–vis spectral behavior of the receptor $\mathbf{LH_2}$ also supports the unusual formation of a 1:1 fluoride complex with monodeprotonated receptor ($\mathbf{LH^-}$) in the solid state.

Halide Binding Study by ^{1}H NMR Spectroscopy. The binding properties of the receptor $\mathbf{LH_2}$ with halides in solution are investigated by ^{1}H NMR experiments in d_6-DMSO in the presence of various halides as their $[n\text{-Bu}_4\text{N}]$X salts (where X = F, Cl, Br, and I) at room temperature. Figure 7 shows the chemical shift changes found by addition of different halides to the receptor $\mathbf{LH_2}$ in d_6-DMSO. The most substantial changes are observed for the –NH protons, indicating that the –NH protons of receptor $\mathbf{LH_2}$ provides suitable sites of interaction between the receptor and the halides.

^{1}H NMR titration of receptor $\mathbf{LH_2}$ with $[n\text{-Bu}_4\text{N}]$F shows that upon gradual addition of standard F^- solution a small but important change in the chemical shift of the aryl –CH protons $\Delta\delta$ = 0.08 is observed, indicating fluoride induced a change in the electronic environment of the –CH protons. In addition, a significant disappearance of the –NH proton is observed. The disappearance of the –NH proton is noticed even after the first addition (0.25 equivalents) of fluoride ion (Supporting Information, Figure S17). This is due to the binding induced broadening of the –NH signals rather than deprotonation, which is supported by the absence of a characteristic HF_2^- peak

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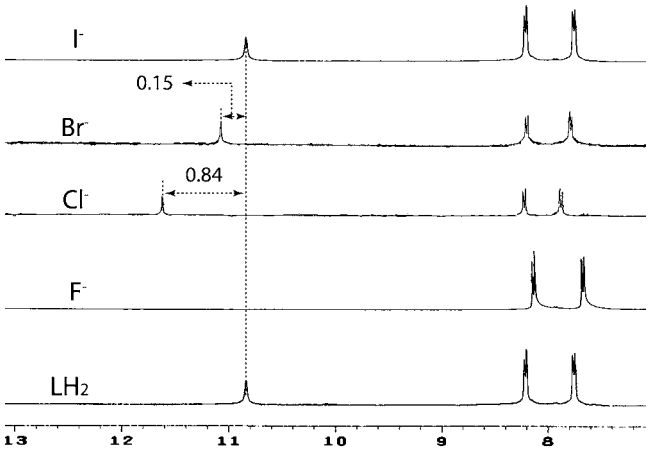

Figure 7. ^{1}H NMR spectra (400 MHz, d_6-DMSO, 298 K) of $\mathbf{LH_2}$ and change of NH resonance upon addition of F^-, Cl^-, Br^-, and I^- as their tetrabutylammonium salts.

at ~16.0 ppm.[16a] Moreover, after addition of 4 equiv of F^-, the appearance of broad HF_2^- signals at 16.1 ppm suggests deprotonation of the N−H protons of the receptor $\mathbf{LH_2}$ (Supporting Information, Figure S19). These results from ^{1}H NMR titration experiments preclude determination of a suitable binding constant with fluoride, whereas significant downfield shifts of the N−H proton $\Delta\delta$ = 0.84 for Cl^- and $\Delta\delta$ = 0.15 in the case of Br^- are observed. There is no notable change in the chemical shift of the NH protons with I^-, indicating the hydrogen-bonding interactions between receptor and the iodide anion are energetically unfavorable. Subsequently, ^{1}H NMR titrations were carried out with Cl^- and Br^- in d_6-DMSO at 298 K. The ^{1}H NMR titration spectra of the receptor $\mathbf{LH_2}$ in the presence of increasing amounts of [n-Bu_4N]Cl are shown in Figure 8, whereas the titration spectra with [n-Bu_4N]Br are

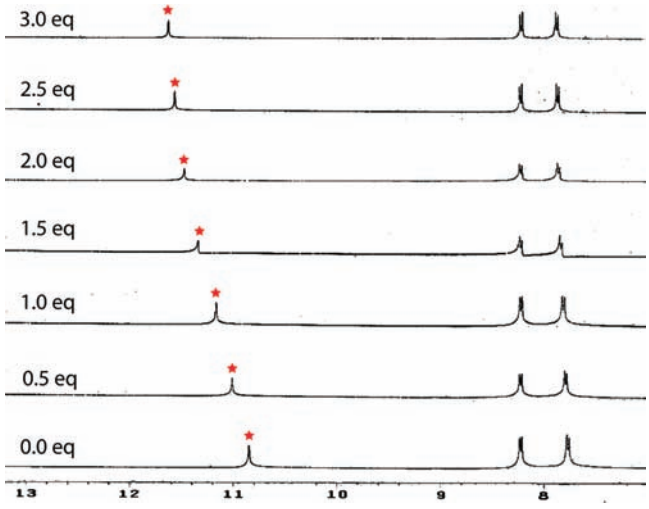

Figure 8. Stack plot of the ^{1}H NMR spectra of receptor $\mathbf{LH_2}$ in the presence of increasing amounts of [n-Bu_4N]Cl recorded in d_6-DMSO at 298 K.

given in the Supporting Information (Figure S22). The binding stoichiometry between the receptor $\mathbf{LH_2}$ and both anions is determined by Job plot experiments (Figure 9). The maximum changes in the chemical shift during the titrations are obtained when the mole fraction of both anions has reached about 0.67,

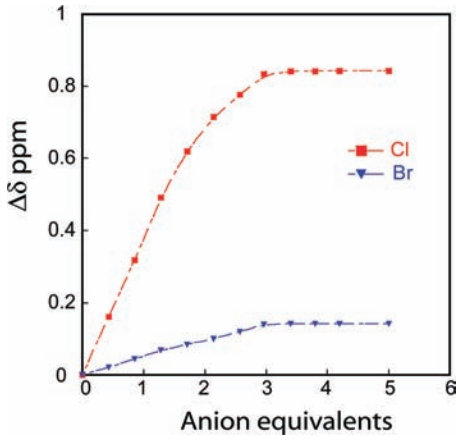

Figure 9. Plot of the change in the chemical shift of the −NH proton of $\mathbf{LH_2}$ with increasing amounts of [n-Bu_4N]X in d_6-DMSO at 298 K (where X = Cl and Br).

which suggests a host−guest binding in a 1:2 stoichiometry (Supporting Information, Figure S24 and S25). The cumulative binding constant for Cl^- ion (log β = 3.92) is higher than that of Br^- (log β = 2.87), indicating that the receptor preferentially binds chloride more than bromide. This is due to the higher basicity and smaller ionic radii of chloride compare to bromide anion. Detailed ^{1}H NMR titration experiments showed that the affinity order of different halides toward $\mathbf{LH_2}$ is $Cl^- > Br^- > I^-$. We kept the fluoride anion out of the halide binding affinity order of the receptor $\mathbf{LH_2}$ because the spectroscopic results demonstrate that apart from receptor−fluoride hydrogen-bonded complex formation the fluoride anion also deprotonates the receptor in the same concentration range (4 equiv). Therefore, it is difficult to get a real binding constant for fluoride from this experiment.

CONCLUSION

We systematically investigated the halide binding of a newly synthesized anion receptor with a thiadiazole spacer $\mathbf{LH_2}$ both in solution and in the solid state. The experimental results corroborate that except iodide the receptor forms a hydrogen-bonding complex with the other halides. Detailed crystal structure analysis of the halide complexes ascertains that the fluoride forms a 1:1 hydrogen-bonded complex with mono-deprotonated receptor ($\mathbf{LH^-}$), while in the case of the other halides (Cl^- and Br^-) the receptor $\mathbf{LH_2}$ binds two halides along with formation of a halide-bridged 1D zigzag chain polymeric network structure by participation of N−H···X^- and aromatic C−H···X^- hydrogen-bonding interactions (where X = Cl and Br), although no chloride- or bromide-directed polymeric assembly are found in solution. Therefore, such structural features are worthwhile only in the solid state. Moreover, the presence of a thiadiazole spacer in the receptor significantly affects the hydrogen-bonding nature between the receptor and the halides, which in turn helps to form an anion-induced 1D polymeric structure. This finding could motivate the development of anion-directed coordination polymers.

EXPERIMENTAL SECTION

Materials and Methods. All reagents and tetrabutylammonium salts were obtained from commercial sources and used as received. Solvents were distilled freshly following standard procedures.

Instruments. IR spectra were recorded on a Perkin-Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range

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4000−400 cm^{-1}. UV−vis spectra were recorded with a Perkin-Elmer Lambda-25 UV−visible spectrophotometer. NMR spectra were recorded on a Varian FT-400 MHz instrument. Chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) as a reference. ESI-MS spectra were recorded in a WATERS LC-MS/MS system, Q-Tof Premier in the Central Instrument Facility (CIF) of IIT Guwahati.

Synthesis of LH_2. The receptor LH_2 was synthesized by refluxing the 1:2 mixture of 4-nitrophenylisothiocyanate and hydrazine hydrate in the presence of acetic acid (catalytic amount) in EtOH for 24 h. The precipitate was filtered and washed with 15 mL of ethanol five times. An orange solid was obtained after drying the precipitate in a vacuum (yield 62%).^{1}H NMR (d_6-DMSO) δ (ppm): 10.852(s, H−N), 8.216 (J = 8 Hz d, 4H), and 7.760 (J = 8 Hz, d, 4H). ^{13}C NMR (d_6-DMSO) δ (ppm): 116.63, 125.604, 140.544, 146.668, and 156.064. ESI mass spectrometry: calcd for 359.06. [M + H^+]; found 359.06 [M + H^+].

X-ray Crystallography. Intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (λ) 0.71073 (Å) at 298 K, with increasing ω (width of 0.3° per frame) at a scan speed of 5 s/frame. The SMART software was used for data acquisition. Data integration and reduction were performed with SAINT and XPREP software.[19] Multiscan empirical absorption corrections were applied to the data using the program SADABS.[20] Structures were solved by direct methods using SHELXS-97[21a] and refined with full-matrix least-squares on F^2 using the SHELXL-97[21b] program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to all carbon atoms were geometrically fixed, while the hydrogen atoms connected to the nitrogen atom were located from the difference Fourier maps, and the positional and temperature factors were refined isotropically. Structural illustrations have been drawn with ORTEP-3[22a] and MERCURY[22b] Windows.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, NMR, IR, LC-MS, UV−vis, and optical micrograph images of crystals, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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