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Fluoride Selectivity Induced Transformation of Charged Anion Complexes into Unimolecular Capsule of a π-Acidic Triamide Receptor Stabilized by Strong N−H···F⁻ and C−H···F⁻ Hydrogen Bonds

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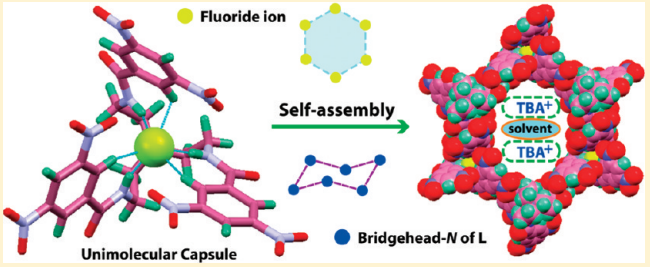
Supporting Information

ABSTRACT: The structural aspects of binding of anions such as halides (chloride, **1**, and bromide, **2**) and oxyanions (perchlorate, **3**, and hydrogen sulfate, **4**) with the protonated tris(amide) receptor **L** were carried out in detail. In all of these complexes, the hydrogen of protonated *bridgehead* nitrogen of the ligand is endo-oriented, forming a strong N−H···O hydrogen bond with an amide oxygen of a tripodal side arm, and binding of anions is primarily governed by N−H···anion and C−H···anion interactions involving multiple receptor cations. Furthermore, transformation of the charged complexes into a unimolecular capsule of **L** has also been accomplished in the presence of excess fluoride ion in dimethyl sulfoxide (DMSO) solution. Crystallographic analysis of fluoride complex [TBA(**L**·F)]2DMSO·4H_2O (**5**; TBA = tetrabutylammonium) shows that F^- is fully encapsulated within the tripodal cleft governed by six strong hydrogen bonds from the amide -NH and aryl -CH protons of the π-acidic receptor. ^{1}H NMR titration experiments further provide evidence for the formation of the F^- encapsulated receptor capsule from the charged complexes.



1. INTRODUCTION

The field of anion receptor chemistry continues to expand its horizon with new synthetic hosts capable of recognizing anions with environmental and biomedical relevance.[1] The observations in natural systems have inspired researchers to develop numerous neutral receptors that employ hydrogen bonds offered by specific binding sites from amide,[2] urea/thiourea,[3] pyrrole[4] and indole[5] functionalities for the recognition and binding of anionic guests on suitable frameworks. In contrast, cationic hosts with guanidinium[6] and polyammonium[7] functionalities ensure an adequate electrostatic attraction reinforced by H-bond contacts with the coordinated anions, and the selectivity can be attributed to the charge and basicity factors, rather than true selectivity of the host for anions. Anions generally have very high solvation energies that must be compensated by the host for effective anion recognition.[8] Tripodal scaffolds offer a flexible and structurally preorganized cavity, which has previously been explored in the area of anion coordination chemistry and anion induced formation of capsular assemblies.[9] One of the most fascinating features of molecular capsules is their ability to create a distinct microenvironment that isolates the encapsulated guest from the bulk of the solvent media and, thereby, leads to phenomena such as molecular sorting when formation is possible for different capsules present in the same solution.[10]

Furthermore, when anions are an integral part of supramolecular aggregates, it is expected that if the templating anion is exchanged with other anions; it should in principle be possible to reorient or rupture the self-assembled architectures. Although numerous synthetic molecular capsules have been achieved, the challenges still exist to control the capsular assembly formation in the presence of a guest anion that acts as a template in the process. Template-induced association of molecular species represents one of the main approaches in the control of supramolecular assembly formation.[11] Template-directed processes that are anion specific can lead us to the challenging development of new selective systems with industrial, ecological, and biomedical applications.[12] Acyclic podand receptors with multiarmed functionality have been shown to be effective systems for binding of a variety of anions; however, their uses as selective anion encapsulating hosts involving equal and strong participation from both -NH and -CH protons are rarely known. Although not typically considered to be significant donors, there is increasing evidence that -CH groups can actively take part in H-bonding and lead to enhanced anion-binding affinity.[13] Anion receptors in nature often involve amide linkages in association with -OH and -CH groups as hydrogen bond donors,[14] and therefore, amide-based receptors with polarized -CH donors are important from the perspective of anion binding study.

In our recent communication, we have shown that the dinitrophenyl-functionalized tris(amide) receptor **L** (Scheme 1)

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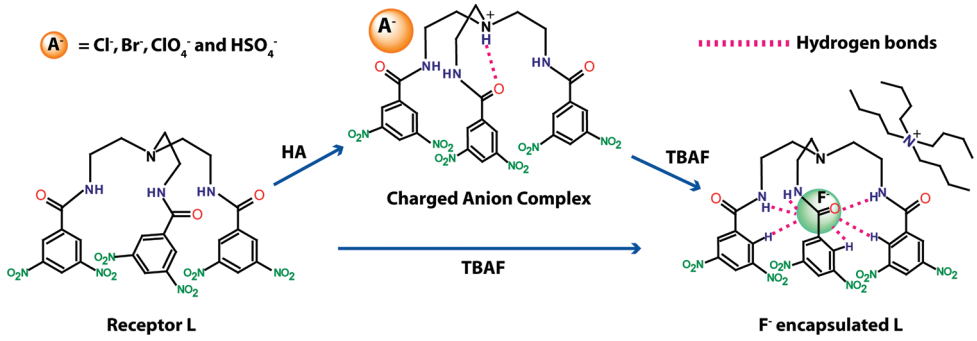
Scheme 1. Schematic Representation Depicting the Formation of F^- Encapsulated Unimolecular Capsule of L from Charged Anion Complexes in the Presence of Excess Tetrabutylammonium Fluoride ((TBA)F)



behaves as a selective chemosensor for fluoride ion by encapsulation within the tripodal scaffold in polar aprotic solvents exhibiting solvatochromism and solvatomorphism.[15] Herein, we structurally demonstrate the anion binding properties of receptor **L** in its protonated form with different anions such as Cl^-, Br^-, ClO_4^-, and HSO_4^- in complexes **1**−**4**, respectively. Anion binding by protonated **L** is attributable entirely to the N−H···anion and C−H···anion interactions that presented a means of participating in the reexamination of the role of C−H hydrogen bonding. Furthermore, in the proof-of-concept experiments described here, the high selectivity of **L** toward recognition of F^- has been employed in the transformation of charged complexes (**1**−**4**) into unimolecular capsules of **L**, wherein F^- is encapsulated within the tripodal scaffold governed by six strong hydrogen bonds from the polarized -NH and -CH functions as evident in the crystal structure of F^- encapsulated complex **5**. The transformation phenomenon and strong participation of -NH and -CH protons in the F^- binding event has been manifested in solution state as well.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. All reagents and solvents were obtained from commercial sources and used as received without further purification. Tris(2-aminoethyl)amine (tren) and 3,5-dinitrobenzoyl chloride were purchased from Sigma-Aldrich and used as received. Triethylamine, 37% hydrochloric acid, 49% hydrobromic acid, 70% perchloric acid, and concentrated sulfuric acid were purchased from Merck and used as received. NMR spectra were recorded on a Varian FT-400 MHz instrument, and chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) or residual solvent peak as a reference. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with KBr disks in the range of 450−4000 cm^{-1}. Thermal analysis was performed by using an SDTA 851 e TGA thermal analyzer (Mettler Toledo) with a heating rate of 5 °C/min in a N_2 atmosphere.

2.2. Syntheses and Characterization. Tripodal receptor **L** was synthesized following our recent report where reaction of tren with 3,5-dinitrobenzoyl chloride in a 1:3 molar ratio at room temperature yielded **L** in high yield. Tren (0.292 g, 2 mmol) was dissolved in 30 mL of dry chloroform ($CHCl_3$) in a 100 mL round bottomed flask, and 0.708 g (7.0 mmol) of dry triethylamine (Et_3N) was added to the reaction mixture. Then, 1.380 g of 3,5-dinitrobenzoyl chloride (6 mmol) was added in portions to the reaction mixture over a period of 1 h with constant stirring at room temperature. After the addition was complete, a pale brown precipitate formed and the reaction mixture was allowed to stir at room temperature overnight. The precipitate formed was then filtered through a filter paper and washed several times with (3 × 50 mL) of water, two times with (2 × 10 mL) of methanol, and finally with diethyl ether. Yield of **L**: 75%; mp 252 °C. ^{1}H NMR (DMSO-d_6, 400 MHz; ppm): δ 2.84 (s, 6H, NCH_2), 3.48 (d, 6H, CONH−CH_2), 8.88 (d, 3H, *p*-ArCH), 8.91 (s, 6H, *o*-ArCH), 9.15 (s, 3H, amide−NH). ^{13}C NMR (100 MHz, DMSO-d_6; ppm): δ 45.73 (×3C, -NCH_2), 53.08 (×3C, CONH−CH_2), 120.58 (×3C, ArH), 127.35 (×6C, ArH), 137.06 (×3C, ArH), 148.01 (×6C, ArH), 162.20 (×3C, C═O).

Synthesis of Complex [HL·Cl], ***1***. Complex **1** was obtained by adding 0.4 mL of 37% hydrochloric acid (HCl) to 5 mL of dimethyl sulfoxide (DMSO) solution of **L** (364 mg, 0.5 mmol). After the addition of acid, the solution was stirred at room temperature for 30 min and filtered in a test tube. The filtrate was allowed to evaporate at room temperature, which yielded colorless crystals suitable for X-ray crystallography analysis within 6−7 days. Yield of **1**: 68% based on **L**. ^{1}H NMR (DMSO-d_6, 400 MHz; ppm): δ 3.61 (s, 6H, NCH_2), 3.82 (s, 6H, CONH−CH_2), 8.91 (d, 3H, *p*-ArCH), 8.94 (d, 6H, *o*-ArCH), 9.66 (s, 3H, amide−NH), 10.57 (s, 1H, apical-NH). ^{13}C NMR (DMSO-d_6, 100 MHz; ppm): δ 38.88, 52.00, 120.96, 127.44, 136.28, 147.98, 163.26.

Synthesis of Complex [HL·Br]H_2O, ***2***. Complex **2** was obtained by adding 0.3 mL of 49% hydrobromic acid (HBr) to 5 mL of dimethyl sulfoxide solution of **L** (364 mg, 0.5 mmol). After the addition of acid, the solution was stirred at room temperature, then filtered, and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography analysis were obtained after 6−7 days. Yield of **2**: 62% based on **L**. ^{1}H NMR (DMSO-d_6, 400 MHz; ppm): δ 3.64 (s, 6H, NCH_2), 3.82 (s, 6H, CONH−CH_2), 8.90 (s, 6H, *o*-ArCH), 8.92 (s, 3H, *p*-ArCH), 9.57 (s, 3H, amide−NH), 9.62 (s, 1H, apical-NH). ^{13}C NMR (DMSO-d_6, 100 MHz; ppm): δ 37.14, 51.69, 121.66, 128.14, 136.98, 148.67, 163.96.

Synthesis of Complex [HL·ClO_4]H_2O·DMSO, ***3***. Complex **3** was obtained by adding 0.2 mL of 70% perchloric acid ($HClO_4$) to 5 mL of dimethyl sulfoxide solution of **L** (364 mg, 0.5 mmol). After stirring for about 30 min, the solution was filtered and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography analysis were obtained within 10−12 days. Yield of **3**: 66% based on **L**. ^{1}H NMR (DMSO-d_6, 400 MHz; ppm): δ 3.64 (s, 6H, -NCH_2), 3.82 (s, 6H, CONH−CH_2), 8.84 (s, 6H, *o*-ArCH), 8.91 (s, 3H, *p*-ArCH), 9.51 (s, 3H, amide−NH), 9.36 (s, 1H, apical-NH). ^{13}C NMR (DMSO-d_6, 100 MHz; ppm): δ 34.79, 52.59, 121.03, 127.39, 136.26, 148.03, 163.53.

Synthesis of Complex [HL·HSO_4]DMSO, ***4***. Complex **4** was obtained by adding 0.2 mL of concentrated sulfuric acid (H_2SO_4) to 5 mL of dimethyl sulfoxide solution of **L** (364 mg, 0.5 mmol). After stirring for about 30 min, the solution was filtered and kept for crystallization at room temperature. Colorless crystals suitable for X-ray crystallography analysis were obtained after 10−15 days. Yield of **4**: 56% based on **L**.

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Table 1. Crystallographic Parameters and Refinement Details of Complexes 1−5

parameters	1	2	3	4	5
formula	$C_{27}H_{25}ClN_{10}O_{15}$	$C_{54}H_{52}Br_2N_{20}O_{32}$	$C_{29}H_{33}ClN_{10}O_{22}S$	$C_{29}H_{31}N_{10}O_{21}S_2$	$C_{47}H_{72}FN_{11}O_{21}S_2$
CCDC	827 379	827 380	827 381	827 382	835 049
FW	765.02	1652.96	1201.21	919.78	1210.30
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	Cc	$P\bar{1}$
a/Å	12.3254(4)	15.1066(6)	11.2376(9)	22.249(2)	9.8296(6)
b/Å	13.5063(5)	20.5781(8)	11.5873(10)	11.9035(11)	19.1561(13)
c/Å	20.0938(7)	22.9600(8)	16.4312(12)	15.5067(13)	19.1973(13)
α/deg	93.146(3)	90.00	100.305(4)	90.00	61.201(3)
β/deg	95.493(2)	102.365(2)	106.260(4)	112.327(5)	83.109(4)
γ/deg	92.688(2)	90.00	94.657(5)	90.00	89.652(4)
V/Å^3	3320.1(2)	6971.9(5)	2001.2(3)	3799.0(6)	3139.3(4)
Z	4	4	2	4	2
D_c/(g cm^{-3})	1.531	1.575	1.562	1.608	1.280
μ (Mo K$_\alpha$)/mm^{-1}	0.203	1.267	0.247	0.242	0.166
T/K	298(2)	298(2)	298(2)	298(2)	298(2)
θ_{max}.	28.530	28.36	28.39	28.28	24.92
total reflecns	30 898	90 986	25 763	22 691	40 060
independent reflecns	16 876	17 344	9 585	4 706	10 638
obsd reflecns	13 623	14 087	6 198	3 954	9 471
params	987	1 013	594	576	748
R_1, $I > 2\sigma(I)$	0.0565	0.0555	0.0919	0.0605	0.0914
R_{w2} (all data)	0.1584	0.1666	0.2428	0.1578	0.1859
GOF (F^2)	0.951	0.901	0.919	0.998	1.011

^{1}H NMR (DMSO-d_6, 400 MHz; ppm): δ 3.63 (s, 6H, NCH$_2$), 3.82 (s, 6H, CONH−CH$_2$), 8.88 (s, 6H, *o*-ArCH), 8.90 (s, 3H, *p*-ArCH), 9.58 (s, 3H, amide−NH), 9.82 (s, 1H, apical-NH). ^{13}C NMR (DMSO-d_6, 100 MHz; ppm): δ 34.45, 51.91, 120.77, 127.28, 136.18, 147.82, 163.15.

Synthesis of Complex [TBA(L·F)]2DMSO·4H$_2$O, ***5***. Complex **5** was obtained by adding an excess (5 equiv) of tetrabutylammonium fluoride (1.0 M solution in tetrahydrofuran (THF)) solution either to a 3 mL of DMSO solution of **1** (382 mg, 0.5 mmol) or a 3 mL of DMSO solution of **4** (413 mg, 0.5 mmol). After the addition of F$^-$ ions, the solution was stirred at room temperature and filtered in a test tube for crystallization. Slow evaporation of the filtrate at room temperature yielded yellow colored crystals suitable for X-ray crystallography analysis within 2−3 weeks, in both cases. It should be noted that, during the process of crystallization, the solution mixtures do not evaporate completely and the mother liquor that remained contains the excess (TBA)F as well as a complex equilibrium of other salts. It is worth mentioning that, crystallization of complex **5** can also be accomplished from a solution mixture of **L** and excess (TBA)F in DMSO and can be confirmed by FT-IR, thermogravimetric (TGA), and ^{1}H NMR analyses of the isolated crystals; mp 198 °C. ^{1}H NMR (DMSO-d_6, 400 MHz; ppm): δ 0.91 (t, 12H, TBA−CH$_3$), 1.30 (q, 8H, TBA−CH$_2$), 1.57 (t, 8H, TBA−CH$_2$), 2.60 (s, 6H, -NCH$_2$), 3.16 (t, 8H, TBA−N$^+$CH$_2$), 3.19 (s, 6H, CONH−CH$_2$), 8.79 (s, 3H, *p*-ArCH), 9.64 (s, 6H, *o*-ArCH), 12.69 (s, 3H, amide−NH). ^{13}C NMR (DMSO-d_6, 100 MHz; ppm): δ 13.76, 19.51, 23.40, 38.55, 53.89, 57.91, 120.63, 127.97, 137.65, 148.23, 162.57.

2.3. X-ray Crystallography. In each case, a crystal of suitable size was selected from the mother liquor and immersed in silicone oil, and it was mounted on the tip of a glass fiber and cemented using epoxy resin. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube, with Mo Kα radiation (λ = 0.710 73 Å) at 298(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 5 s/frame. The crystal-to-detector distance was about 51 mm. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP[16] software. Multiscan empirical absorption corrections were applied to the data using the program SADABS.[17] Structures were solved by direct methods using SHELXS-97[18] and refined with full-matrix least-squares on F^2 using SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms attached to all carbon atoms were geometrically fixed and the positional and temperature factors are refined isotropically. Hydrogen atoms attached with the amide nitrogen atoms were located from electron Fourier map and refined isotropically. However, H-atoms attached to the lattice water molecules in complex **5** could not be located by Fourier map due to disorder. Usually, temperature factors of H-atoms attached to carbon atoms are refined by restraints −1.2 or −1.5 U_{iso} (C), although the isotropic free refinement is also acceptable. Structural illustrations have been drawn with MERCURY 2.3[20] for Windows. Parameters for data collection and crystallographic refinement of complexes **1**−**5** are summarized in Table 1.

3. RESULTS AND DISCUSSION

For a receptor to bind with the anionic guests, it should in principle possess preorganized anion binding elements decorated on the suitable platform/framework. Receptor **L** possesses a preorganized tripodal cleft with amide functionality suitable for anion recognition/encapsulation. In addition, functionalization of **L** with π-acidic dinitrophenyl moiety as aryl terminals significantly enhances the binding ability of the receptor toward anionic guests. It has been well established that the electron-withdrawing substituents on the benzene ring assist the active participation of the aryl -CH protons toward anion binding via

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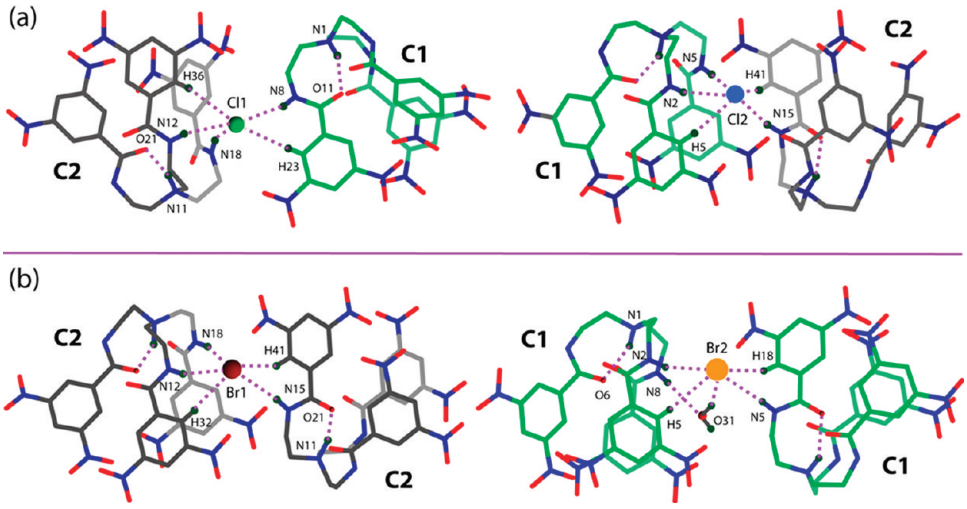

Figure 1. (a) Structural representation depicting the H-bonding contacts on Cl^- ions with two symmetry-independent receptor cations in complex **1**, and (b) structural representation showing the H-bonding interactions of Br^- with two symmetry identical receptor cations in complex **2**. H-bonds have been shown with blue dotted lines.

C−H···anion interactions. Moreover, protonation at the apical nitrogen could considerably enhance the acidity of the methylene -CH_2 protons and, thereby, could possibly form moderate to weak C−H···anion hydrogen bonds perhaps of similar strength to aryl C−H···anion hydrogen bond. Thus, the attached electron-withdrawing nitro substituents on the aryl terminals and protonation at the bridgehead nitrogen in the ligand architecture can presumably play a variable role in changing the binding nature of **L** toward anions in its protonated and neutral structure.

3.1. Anion Binding with Protonated Receptor $[HL]^+$. Structural information obtained from single-crystal X-ray analysis of anion complexes **1**−**4** can provide insight into the proper binding topology of halides and oxyanions with the protonated receptor molecule and anion templated supramolecular assembly formation. We have attempted to isolate the protonated salt of **L** with anions of various geometries under identical crystallization conditions in DMSO. However, we were able to isolate only four complexes (**1**−**4**) as single crystals suitable for X-ray crystallography analysis. Structural analyses revealed that complexation of anions is primarily governed by N−H···anion and C−H···anion interactions involving multiple receptor cations. In all four complexes, the tripodal cavity of **L** is closed by strong intramolecular N−H···O hydrogen bonding of the endo-oriented apical N−H proton with one of the amide oxygens of the receptor side arms. In addition, the complexes are further stabilized by multiple weak intermolecular C−H···O hydrogen bonds, which induce rigidity in the formed cationic podand and serve as the foundation for crystallization of the desired complexes. In supramolecular chemistry, the existence of more than one molecular conformer in the same crystal structure has been described by the term *conformational isomorphism*, as exhibited by the halide complexes **1** and **2**. According to Desiraju, structures which contain more than one molecule in the crystallographic asymmetric unit ($Z' > 1$) are a useful tool for close inspection of the reaction coordinates of a supramolecular reaction and their occurrence enlightens concepts such as kinetic and thermodynamic crystal stability as they are considered to be consequences of interrupted crystallization.[21] A five-point coordination mostly via amide N−H···X and aryl C−H···X (X = Cl^- and Br^-) interactions is responsible for the binding of halides with two adjacent receptor cations of identical or different symmetry outside the tripodal cavity, whereas binding of oxoanions is primarily governed by N−H···O and C−H···O interactions in association with a C−H···O contact from the lattice DMSO molecule. The detailed structural analyses of these complexes are described as follows.

Binding of Cl^- to $[HL]^+$ in Complex ***1***. Complex **1** $[(HL)\cdot Cl]$ crystallizes in triclinic space group $P\bar{1}$, and the asymmetric unit contains two symmetry-independent receptor cations ($Z' = 2$) and two chloride anions. The two conformers of $[HL]^+$ (conformers **C1** and **C2**) differ considerably in their torsion angles involving the amide functionality of each tripodal side arm (Table S2 in the Supporting Information). The endo-oriented proton of the apical amine is in strong intramolecular N−H···O hydrogen bonding with one of the amide oxygens of the receptor cation in both conformers **C1** and **C2** (N1···O11 = 2.718(2), ∠N1−H···O11 = 151(2)°; N11···O21 = 2.774(4); ∠N11−H···O21 = 156(2)°). Binding of Cl^- with adjacent receptor cations clearly reveals that both of the chloride ions $Cl^-(1)$ and $Cl^-(2)$ are in interaction with two receptor cations of dissimilar conformations with a five-point attachment each via three N−H···Cl^- and two C−H···Cl^- interactions having an average donor-to-acceptor H-bond distance of 3.268 (N···Cl^-) and 3.589 Å (C···Cl^-), respectively. It is evident from Figure 1a, that the amide hydrogen H8N and aryl proton H23 of conformer **C1** are involved in coordination with $Cl^-(1)$, whereas the hydrogen H2N, H5N, and H5 are in interaction with $Cl^-(2)$. In a similar fashion, the amide hydrogens H12N, H18N and aryl proton H36 of the other conformer **C2** provides a three-point coordination to $Cl^-(1)$ while H15N and H41 make interactions with $Cl^-(2)$ completing the five-point attachment on chloride anions. The details of these H-bonding interactions are provided in Table 2. The packing diagram of complex **1** as viewed down the crystallographic *b*-axis shows the bilayer assembly formation of the cationic receptor moieties along the *a*-axis with chloride being entrapped between the adjacent bilayers (Supporting Information). The receptor moieties are further organized via several intermolecular C−H···O_{nitro} interactions between the alkyl/aryl hydrogen of tripodal side arms with oxygen

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Table 2. Characteristic Hydrogen Bonds with Anions Observed in Complexes 1−4

charged complex	D−H···A	d(H···A)/Å	d(D···A)/Å	∠D−H···A/deg
complex **1**	N8−H8N···Cl1	2.53(3)	3.228(2)	154(2)
	N12−H12N···Cl1	2.66(3)	3.389(2)	155(2)
	N18−H18N···Cl1	2.28(3)	3.136(2)	153(2)
	C23−H23···Cl1	2.75(7)	3.673(3)	168(2)
	C36−H36···Cl1	2.79(7)	3.671(3)	157(2)
	N2−H2N···Cl2	2.64(3)	3.408(3)	162(2)
	N5−H5N···Cl2	2.42(4)	3.197(3)	158(3)
	N15−H15N···Cl2	2.43(3)	3.252(2)	170(2)
	C5−H5···Cl2	2.70(7)	3.630(3)	173(2)
	C41−H41···Cl2	2.87(7)	3.384(3)	115(2)
complex **2**	N12−H12N···Br1	2.69(4)	3.375(4)	155(4)
	N15−H15N···Br1	2.95(3)	3.663(4)	178(3)
	N18−H18N···Br1	2.65(3)	3.463(4)	165(3)
	C32−H32···Br1	2.80(4)	3.734(4)	173(3)
	C41−H41···Br1	2.98(5)	3.386(4)	108(2)
	N2−H2N···Br2	2.48(4)	3.335(4)	165(4)
	N5−H5N···Br2	2.72(4)	3.437(4)	167(4)
	C5−H5···Br2	2.90(6)	3.807(4)	164(3)
	C18−H18···Br2	2.98(5)	3.449(4)	112(3)
	O31−H2O···Br2	2.42(2)	3.314(8)	172(2)
	N8−H8N···O31	2.01(4)	2.952(7)	171(4)
complex **3**	N2−H2N···O17	2.54(5)	3.122(1)	125(4)
	N2−H2N···O18	2.38(5)	3.183(1)	153(4)
	C5−H5···O18	2.48(9)	3.340(1)	154(3)
	C1−H1B···O17	2.69(1)	3.495(1)	140(3)
	C2−H2A···O17	2.69(7)	3.354(9)	126(3)
	C28−H28A···O16	2.63(2)	3.450(2)	144(7)
complex **4**	N2−H2N···O16	2.59(6)	3.264(9)	155(6)
	N2−H2N···O18	2.43(6)	3.077(9)	149(6)
	N5−H5N···O17	1.86(5)	2.732(7)	156(4)
	C1−H1B···O18	2.48(6)	3.318(8)	143(3)
	C9−H9···O16	2.64(8)	2.990(1)	103(3)
	C23−H23···O16	2.49(6)	3.361(7)	155(3)
	C28−H28C···O17	2.51(5)	3.391(1)	151(5)

atoms from each nitro group (Table S1 in the Supporting Information).

Binding of Br^- to $[HL]^+$ in Complex ***2***. Complex **2** $[(HL)\cdot Br]H_2O$, crystallizes in monoclinic space group $P2_1/c$, and the asymmetric unit contains two symmetry-independent receptor cations ($Z' = 2$) and two bromide anions with two lattice water molecules (O31 and O32) as the solvent of crystallization. Identical to complex **1**, intramolecular N−H···O hydrogen bonding involving the endo-oriented apical proton and one of the amide oxygen is also prevalent in both of the conformers of complex **2** (N1···O6 = 2.903(4), ∠N1−H···O6 = 152(4)°; N11···O21 = 2.868(4), ∠N11−H···O21 = 147(3)°), and the conformers **C1** and **C2** of receptor cation differ appreciably in their torsions involving each tripodal side arm (Table S2 in the Supporting Information). Binding of bromide with adjacent receptor cations clearly shows that bromide ions $Br^-(1)$ and $Br^-(2)$ are in interaction with two receptor units of identical symmetry with a five-point attachment each (Figure 1b). The amide hydrogens H12N, H18N and aryl proton H32 from one of the receptor cations with conformation **C2** provides a three-point coordination to $Br^-(1)$ whereas hydrogens H15N and H41 of another receptor cation with identical conformation provides the other two contacts on $Br^-(1)$. However, in the case of $Br^-(2)$, two adjacent receptor cations of conformation **C1** provide a four-point contact via one N−H···Br^- and one C−H···Br^- interactions each, while the fifth coordination contact is provided by a lattice water molecule (O31) which is in strong H-bond interaction with the amide hydrogen H8N. The details of these H-bonding interactions are provided in Table 2. The lattice diagram viewed normal to the *ab*-plane shows the hexagonal channels formed by intermolecular C−H···O_{nitro} interactions among conformers **C1** are filled with Br^- ions in association with the lattice water molecules from one end to the other end of the crystals (Supporting Information).

Binding of ClO_4^- to $[HL]^+$ in Complex ***3***. Complex **3** $[(HL)\cdot ClO_4]H_2O\cdot DMSO$ crystallizes in triclinic space group $P\bar{1}$ with one disordered DMSO and a water molecule as the solvent of crystallization. The solid-state structure of complex **3** shows intramolecular N−H···O hydrogen bonding between the apical proton H1N with the amide oxygen O1 (N1···O1 = 2.742(5),

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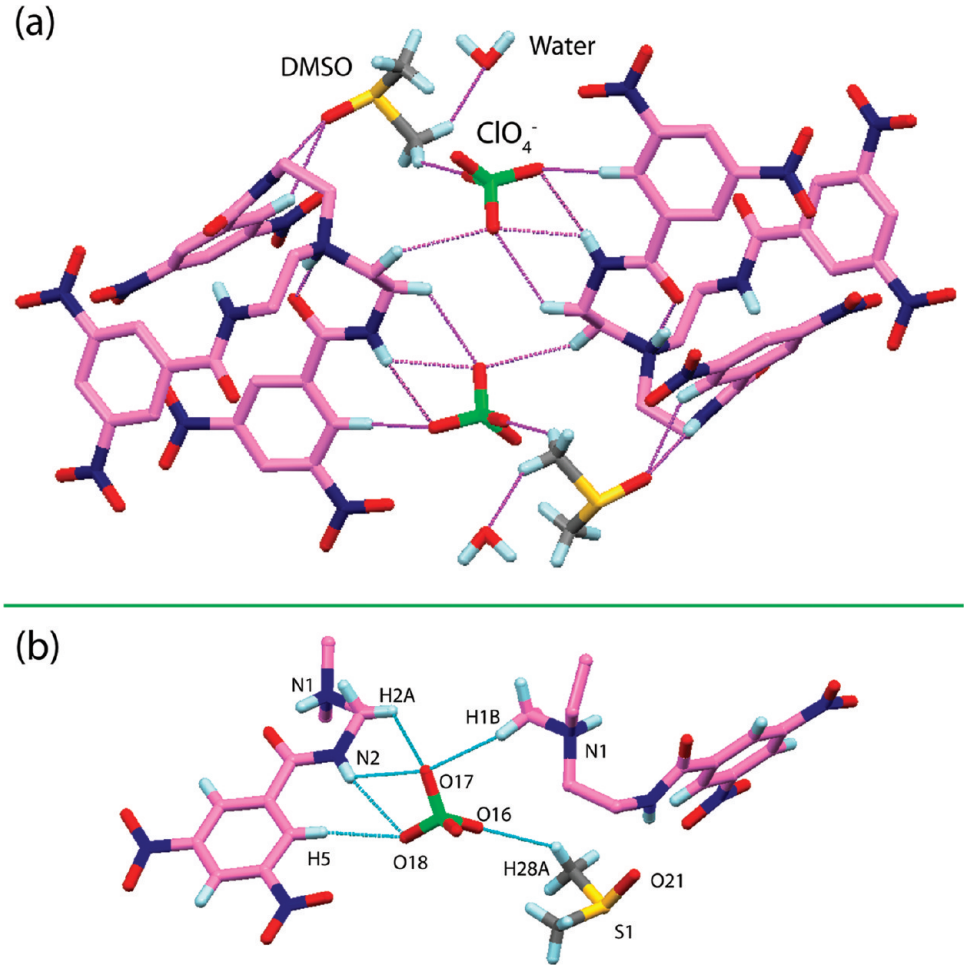

Figure 2. (a) Structural representation depicts the H-bonding interactions of ClO_4^- anion and lattice DMSO with two protonated receptor units in complex **3**, and (b) coordination environment of ClO_4^- showing the formation of six H-bonds with two receptor cations and lattice DMSO molecule.

∠N1−H···O1 = 168(3)°) and between amide hydrogen H5N with O11 (N5···O11 = 2.984(4), ∠N5−H···O11 = 167(4)°) of the other receptor arm restricting the size of the tripodal cavity toward encapsulation of perchlorate ion. The magnified view of the H-bonding interactions on ClO_4^- (Figure 2) clearly shows that each perchlorate anion is involved in a six-point coordination provided by two adjacent receptor cations and lattice DMSO. Perchlorate oxygen O17 is engaged in a trifurcated H-bonding contact with the amide hydrogen H2N and two methylene protons H2A and H1B from the two coordinating receptor units, whereas O18 is in bifurcated interaction with the same amide hydrogen H2N and aryl proton H5 of a receptor cation. The hexacoordination on ClO_4^- is finally satisfied by the weak C−H···O interaction between O16 and methyl hydrogen H28A of lattice DMSO. The details of these H-bonding interactions are provided in Table 2. The complex is further stabilized by several moderate to weak H-bonds formed between the lattice DMSO with the receptor cation and lattice water molecule (Table S1 in the Supporting Information).

Binding of HSO_4^- to $[HL]^+$ in Complex ***4***. Complex **4** [(**HL**)·HSO_4]DMSO crystallizes in monoclinic non-centrosymmetric space group *Cc* with one disordered DMSO molecule as the solvent of crystallization. Due to disorder, it was not possible to locate the hydrogen for the monovalent sulfate anion, in order to unambiguously determine the degree of protonation and charge upon the anion. However, structural elucidation reveals the 1:1 stoichiometric salt formation confirming the hydrogen sulfate complex of **L**. Similar to the halide complexes, there exists intramolecular H-bonding between the apical proton H1N and amide oxygen O6 of a receptor side arm (N1···O6 = 2.816(5), ∠N1−H···O6 = 154(4)°). The H-bonding contacts on HSO_4^- (Figure 3) clearly demonstrate that each bisulfate anion is involved in a seven-point attachment via N−H···O and C−H···O interactions provided by three adjacent receptor cations and lattice DMSO. In nature, a seven-coordinate sulfate structure was observed in a sulfate binding protein, where three of four oxygen atoms were linked with two hydrogen bonds. However in **4**, sulfate oxygen O16 behaves as a trifurcated H-bond acceptor by making interactions with the amide hydrogen H2N and two aryl protons H9 and H23 from two coordinating receptor units whereas O18 is involved in bifurcated interaction with the amide hydrogen H2N and methylene proton H1B of the same receptor cation. Finally, O17 interacts with the amide hydrogen H5N of a third coordinating receptor cation and methyl hydrogen H28C of lattice DMSO, completing the seventh coordination contacts on HSO_4^-. The details of these H-bonding interactions are provided in Table 2.

3.2. Binding of F^- within Unimolecular Capsule of L in Complex 5. The fluoride encapsulated neutral complex

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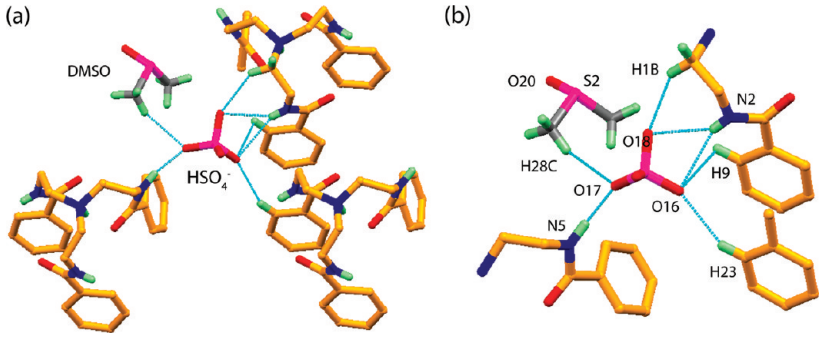

Figure 3. (a) Structural representation shows the H-bonding interactions of HSO_4^- with three protonated receptor units in complex **4**, and (b) Cclose-up view of the coordination environment of HSO_4^- showing the formation of seven H-bonds with three receptor cations and lattice DMSO molecule.

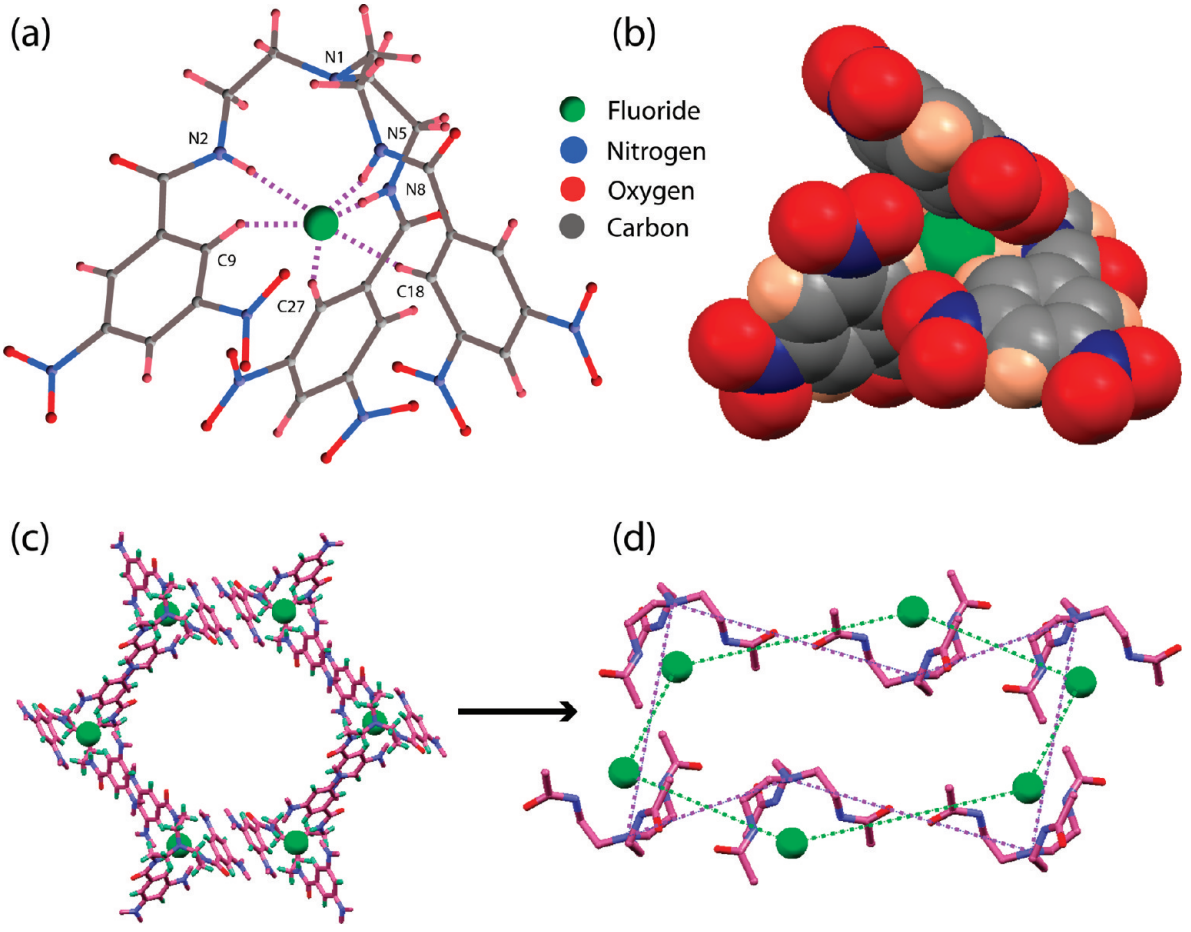

Figure 4. (a) Crystal structure of **5** showing encapsulation of F^- within the tripodal cleft of **L** where blue dotted lines represent D−H···F^- interactions (D = donor atoms, N or C), (b) spacefill representation depicting the formation of a F^- encapsulated receptor capsule in **5**, (c) self-assembly of the unimolecular capsule into hexagonal channels when viewed down the *a*-axis, and (d) cyclohexane type of chair conformation adopted by the F^- encapsulated receptor units in the crystal of **5** (dinitrophenyl rings are omitted from the receptor skeleton for clarity of presentation).

$[TBA(\mathbf{L}\cdot F)]\cdot 2DMSO\cdot 4H_2O$, **5**, crystallizes in triclinic space group $P\bar{1}$ with two disordered DMSO and four water molecules in the crystal lattice. To gain a better insight into the nature of the solvents included in the crystal lattice, we have carried out the TGA of the crystals that shows a weight loss of 15.72% (−1.51 mg) for the solvent molecules close to the calculated value of 16.19% (Supporting Information). Structural analysis of complex **5** shows that the fluoride anion is completely encapsulated within the tripodal cavity governed by six intramolecular hydrogen bonds from the amide -NH and three aryl -CH protons of the π-acidic receptor (Figure 4a,b). The encapsulated F^- ion is hydrogen-bonded to the amide protons with an average N···F^- distance of 2.708 Å, whereas the coordinating *o*-CH protons interact with an average C···F^- distance of 2.993 Å, demonstrating the strong binding of F^- with **L** in the solid state (Table 3). Furthermore, the encapsulated F^- interacts with one of the π-acidic ringS (C3g) of **L** via weak $F^-\cdots\pi$ interactions with a contact distance of 4.039 Å. A correlation of the D−H···F^-

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angle vs DH···F^- distance shows that all contacts are in the strong hydrogen bonding interaction region with $d_{H\cdots F^-} \leq 2.35$ Å and $d_{D\cdots F^-} \leq 3.02$ Å (Table 3). The active participation of the aryl -CH protons toward F^- binding is primarily due to the presence of electron-withdrawing nitro functions in the aryl terminals of the receptor which render these protons considerably acidic toward forming strong C−H···F^- hydrogen bonds. Additionally, each arm of the F^- encapsulated receptor unit is in interaction with the identical arm of an adjacent unit via intermolecular C−H···O-(nitro) hydrogen bonds involving the *p*-CH proton and one of the nitro oxygen atoms of neighboring receptor molecules (Figure 5a). A schematic diagram depicting the participation of aryl -CH protons toward F^- binding event and H-bonded synthon formation has been shown in Figure 5b. Expansion through hydrogen bonds resulted in hexagonal arrangement of F^- encapsulated **L** units with opposite orientation in a cyclohexane type of

Table 3. Characteristic Hydrogen Bonds with F^- in Unimolecular Capsule 5

D−H···F	*d*(H···F)/Å	*d*(D···F)/Å	∠D−H···F/deg
N2−H···F1	1.85(2)	2.703(5)	170(3)
N5−H···F1	1.85(3)	2.696(5)	167(2)
N8−H···F1	1.90(2)	2.726(3)	158(3)
C5−H5···F1	2.12(2)	3.027(5)	163(3)
C14−H14···F1	2.13(3)	3.025(5)	160(2)
C23−H23···F1	2.35(2)	2.929(4)	120(3)

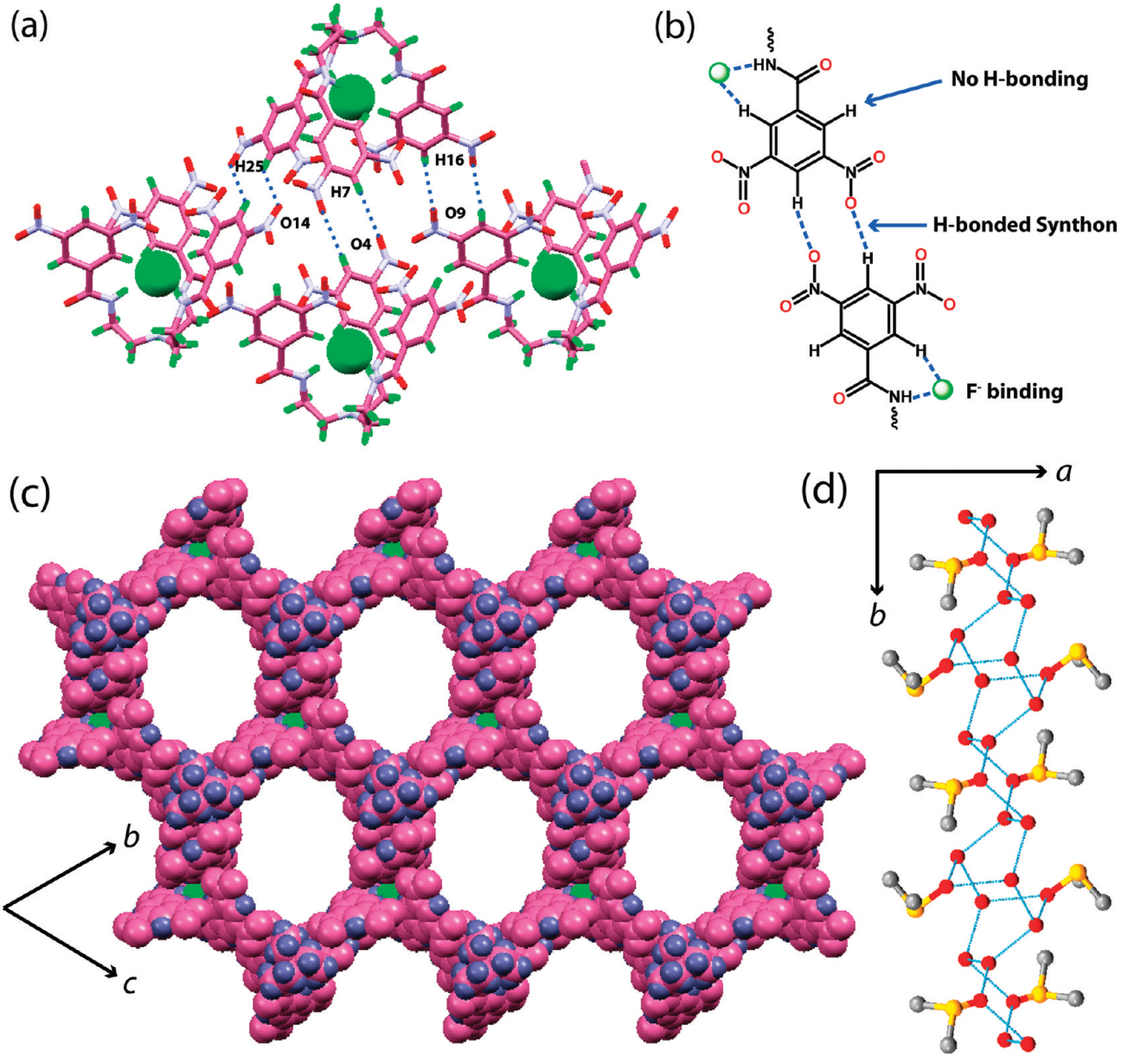

Figure 5. (a) Structural representation showing the H-bonded synthon formation between the identical arms of adjacent receptor units involving the *p*-aryl CH proton and nitro oxygen atoms in **5**, (b) schematic representation depicting the involvement of the aryl CH protons toward F^- (green) binding and H-bonded synthon formation in **5**, (c) honeycomb-like structure formed as a result of intermolecular short interactions between the F^- bound receptor units (TBA cations and solvent molecules are omitted for clarity), and (d) structural representation showing the H-bond formation between lattice solvent molecules along crystallographic *b*-axis.

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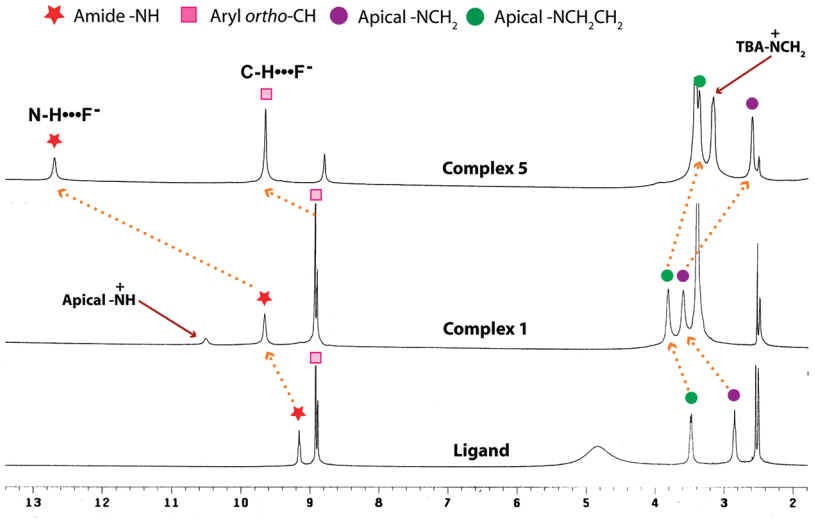

Figure 6. Comparison of the partial ^{1}H NMR spectra of free **L** and complexes **1** and **5a** in DMSO-d_6 at 298 K. The shift of the proton resonances have been shown with orange dotted lines and identical color codes.

chair conformation, whereas the corresponding F^- ions occupy the vertices of a hexagon as depicted in Figure 4c,d, respectively. The packing diagram of the complex as viewed down the crystallographic *a*-axis shows formation of a honeycomb-like structure from the extended ligand architecture (Figure 5c), entrapping the tetrabutylammonium countercations and lattice solvents in the crystal voids (Supporting Information). The tetrabutylammonium cations are held within the hexagonal voids diagonally along the *bc*-plane involving four C−H···O and one C−H···π interactions (Table S1) that presumably provide additional stability to the capsular assembly formation whereas the H-bonded lattice solvents (Figure 5d) are sandwiched between the tetrabutylammonium cations within the voids that run from one end to the other end of the crystal along the *a*-axis (Supporting Information).

3.3. ^{1}H NMR Study. The free receptor molecule (**L**) shows the amide -NH resonance at δ 9.15 ppm whereas the aromatic -CH protons resonate at 8.91 (s, *o*-CH) and 8.88 (s, *p*-CH) ppm when recorded in DMSO-d_6 at 298 K. Appreciable downfield shift of the aliphatic -CH_2 protons ($\Delta\delta$ (ppm; N−CH_2): 0.77 in **1**, 0.80 in **2**, 0.81 in **3**, and 0.79 in **4** wrt **L**) in the ^{1}H NMR spectra of the charged complexes **1**−**4** indicate the influence of protonation at the apical nitrogen on the neighboring methylene protons. Furthermore, observable downfield shift of the amide -NH protons ($\Delta\delta$ (ppm): 0.51 in **1**, 0.42 in **2**, 0.37 in **3**, and 0.43 in **4** wrt **L**) indicate the active interactions of anions with the amide functions as established in the solid state (Supporting Information). However, no notable changes in chemical shift values of the aryl -CH resonances are observed, suggesting weak interactions of anions with the aryl -CH protons of the receptor cation in solution. In contrast, the ^{1}H NMR spectra of the isolated crystals of **5** show a significant downfield shift of the amide -NH and aryl *o*-CH resonances with high $\Delta\delta$ values of ∼3.54 and ∼0.73 ppm, respectively, indicative of a strong solution state binding of F^- with **L** via amide N−H···F^- and *o*-C−H···F^- interactions as observed in the solid state (Figure 6), whereas only a slight upfield shift ($\Delta\delta$ = 0.09 ppm) of the aryl *p*-CH protons were observed which could be the result of *p*-C−H···O(nitro) H-bonded synthon formation in solution as well.

To further explore the mechanistic details involved in the transformation of charged complexes into the unimolecular capsule of **L** in the presence of excess fluoride ion, we have performed ^{1}H NMR titration of complexes **1** and **4** with aliquots of standard (TBA)F solution in DMSO-d_6 at 298 K. It has been observed that, upon addition of 1 equiv of F^- to a solution of **1** or **4**, the aliphatic -CH_2 proton signals undergo a considerable upfield shift with $\Delta\delta$ (N−CH_2) 0.85 and 0.87 ppm for **1** and **4**, respectively, and noticeable upfield shift of the amide -NH signal has also been observed which indeed indicates the formation of the charge neutral receptor **L** in solution assisted by F^- ions (Supporting Information). In addition, the signal for the proton at the apical nitrogen (protonated) which resonates at 10.52 and 9.80 ppm in **1** and **4**, respectively, disappears upon addition of F^-, further confirming the occurrence of the neutral form of **L**. With a second equivalent of F^- addition, the amide -NH signal disappears whereas the signal for aryl *o*-CH proton gets broadened and experiences a slight downfield shift, which could be due to binding-induced broadening of signals upon recognition of F^-. Further addition of F^- ions (up to 5 equiv) results in gradual and appreciable downfield shift of *o*-CH proton resonance ($\Delta\delta$ = 0.68 ppm in the case of **1** and $\Delta\delta$ = 0.70 ppm in the case of **4**) with reappearance of the -NH signal at 4 equiv of F^- ($\Delta\delta$ = 2.95 ppm in the case of **1** and $\Delta\delta$ = 2.84 ppm in the case of **4**), indicative of a structural alteration of the receptor unit in complexes **1** and **4** in the presence of excess F^-, which could influence both the -NH and -CH protons for its encapsulation in solution as well (Supporting Information).

4. CONCLUSION

In summary, we have shown the structural insights of coordination of halides and oxyanions (tetrahedral) with the protonated form of the π-acidic tris(amide) receptor (**L**), and transformation of these charged complexes into a unimolecular capsule of **L** has been accomplished in the presence of excess fluoride ion. ^{1}H NMR titration experiments reveal that fluoride ion encourages deprotonation of the apical nitrogen in complexes **1** and **4** with 1 equiv of (TBA)F, followed by formation of the capsular assembly with excess addition of fluoride, which is in

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agreement with the results observed in the crystal structure of **5**. Structural elucidation of the charged complexes clearly demonstrates that the anion binding occurs mostly via N−H···anion and C−H···anion interactions involving multiple receptor cations wherein the tripodal cavity gets locked by intramolecular N−H···O(amide) hydrogen bonding between the endo-oriented apical N−H proton and an amide oxygen of the receptor side arms. Crystallographic analysis of fluoride encapsulated complex **5** shows that the fluoride anion is fully encapsulated within the tripodal cleft governed by six strong hydrogen bonds from the amide -NH and aryl *o*-CH protons of the π-acidic receptor whereas the *p*-CH protons are involved in H-bonded synthon formation with a nitro oxygen atom of adjacent **L** units. Detailed structural investigation of the complexes clearly demonstrates that the self-alignment, flexibility, and pseudocavity of the tripodal ligand play a crucial role in making a variety of molecular interactions possible with anions of different sizes and geometry in its protonated and neutral forms. Thus, receptor **L** provides an excellent case of understanding the anion coordination chemistry employing N−H···anion and C−H···anion hydrogen bonds.

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic files in CIF format, additional crystallographic data, characterization data, and ^{1}H NMR titration spectra. This information is available free of charge via the Internet at http://pubs.acs.org/.

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