Anion specificity induced conformational changes in cresol-based tripodal podands controlled by weak interactions: structural and Hirshfeld surface analysis[†]

Sandeep Kumar Dey, Avijit Pramanik and Gopal Das*

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N-bridged tripodal receptors have shown a distinct behaviour on their assembly and binding ability towards complexation with inorganic and organic anions. All supramolecular complexes have been structurally authenticated using X-ray diffraction with a detailed analysis of the Hirshfeld surfaces facilitating an understanding of the type and nature of intermolecular interactions present in the complexes and extended structures. The *p*-substituted podand (L_1) crystallized in the symmetric rhombohedral *R3c* space group to form hemicarcerand in the solid state *via* intermolecular C–H··· π interactions. Protonation of L_{1-3} in presence of inorganic anions results in conformational locking of tripodal cavity by N–H···O_{ether} trifurcated hydrogen bond formation (1–4) due to the *endo*-orientation of the apical proton (5–7) and thereby, results into conformational opening of the tripodal arms *via* the formation of N–H···O_{anion} and π ··· π interactions with the anion. This study also establishes bilayer assembly formation in inorganic anion complexes (2–4) guided primarily by interligand C–H··· π interactions and multiple C–H···anion hydrogen bonds. NMR studies further establish the different orientations of flexible tripodal arms in presence of organic and inorganic counter anions in solution.

Introduction

The use of anionic templates for the synthesis of superstructures has become an attractive strategy in recent years.¹ Anions have shown to be very versatile templates for the synthesis of a wide range of organic and metal-organic molecules and supramolecular assemblies.^{1,2} Template-induced association of molecular species represents one of the main approaches in the control of supramolecular assembly formation.² The challenges encountered in the use of anion templating can be attributed to the properties of anions, such as low charge to radius ratio, various geometries, high solvation energies, and pH-dependent charge.³ Hydrogen bonds formed by anions are weaker and more difficult to control as compared to metal cation coordinative bonds. Although numerous synthetic molecular capsules have been achieved, the challenges still exist to control the assembly and disassembly processes when a guest acts as a template. When anions are an integral part of supramolecular aggregates, it is expected that if the templating anion is changed with other anions it might collapse or re-orient the assembly. Therefore, by varying the geometry of the anions involved in a self-assembly process, it should in principle be possible to re-orient or rupture the self-assembled architectures. Template-directed processes

that are anion specific can lead us to the challenging development of new selective systems with industrial, ecological, and biomedical applications.⁴ Systems that show great oxoanions selectivity are of special interest in the area of nuclear and toxic waste management.⁵

Most hydrogen bonding anion receptors utilize N-H---anion or O-H…anion hydrogen bond and C-H…anion hydrogen bonds are rarely utilized for anion binding even though C-H··· anion hydrogen bonds play an important role in nature and thus, are drawing increasing attention among researchers.⁶ Although not typically considered to be significant donors, there is increasing evidence that C-H groups can participate in hydrogen bonding and lead to enhanced anion-binding affinity. This evidence comes in the form of direct observation of close contacts in crystallographic structures,7 anion-induced chemical shifts of C-H protons in NMR spectra⁸ and theoretical calculations.⁹ The binding ability of tripodal receptors for anions varies with the attached functionality to the tripodal unit, since functional groups modify the hydrogen-bonding capability. Whereas the coordination chemistry of anionic guests within pre-organized macrocyclic systems are relatively straightforward to understand but the binding processes of flexible podand receptors remain more elusive.

In this study we have chosen cresol based tripodal podands L_{1-3} (Scheme 1a) to investigate the various possible structural topologies of supramolecular complexes formed between protonated podands and different inorganic and organic anions. The tertiary bridgehead nitrogen of the podands is more susceptible to undergo protonation and the hydrogen of the protonated nitrogen could either become *exo-* or *endo*-oriented with respect to tripodal side arms, depending upon the nature of the anion. Thus, counter anion(s) could play an

Department of Chemistry, Indian Institute of Technology Guwahati, Assam, 781 03, India. E-mail: gdas@iitg.ernet.in; Fax: +91-361-258-2349; Tel: +91-361-258-2313

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amine (L_{1-3}); (b) schematic representation depicting the conformational locking of tripodal cavity in acyclic podands (middle) *via* trifurcated N–H···O_{ether} hydrogen bond formation in the presence of templating inorganic anion (left) and conformational opening of the tripodal arms due to the formation of N–H··· O_{anion} and $\pi \cdots \pi$ interactions with the planar organic anion (right).

important role in assembling and controlling the structural topologies of the podands in the solid state. Herein we report a solid-state study of some supramolecular complexes assembled by an anion-templated reaction of flexible ligands L_{1-3} with inorganic anions of spherical (Br⁻) and tetrahedral geometry (ClO₄⁻) as well as planar organic anions (picrate and pyromellitate). In the proof-of-concept experiments described here, we demonstrate the formation of inorganic anion (bromide and perchlorate) assisted conformational locking of flexible tripodal molecules by the formation of intramolecular N-H.Oether trifurcated hydrogen bonds and conformational opening in presence of organic anions by intermolecular N-H···Oanion hydrogen bond formation resulting into flat and extended orientation of the flexible tripodal arms (Scheme 1b). The tripodal assembly is highly anion specific, and the occurrence of the perchlorate complexes of L_{1-3} in systems with equivalent concentrations of competing anions has also been explored.

We also report a detailed analysis of the various interactions using Hirshfeld surfaces.¹⁰ Hirshfeld surfaces are very informative in mapping out the interactions between molecules within the molecular crystal in a visual manner allowing for a rapid understanding of the nature of such interactions, even for complex supramolecular systems.¹¹ The related two-dimensional fingerprint plots give a quantitative analysis of the nature and type of interaction, which is of particular importance in structures that contain the same or structurally similar molecules.¹²

Experimental

Materials and methods

All reagents and solvents were obtained from commercial sources and used as received. NMR spectra 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. The IR spectra were recorded on a Perkin Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000–450 cm⁻¹. Elemental analyses were carried out on a Perkin-Elmer 2400 automatic carbon, hydrogen and nitrogen analyzer. Hirshfeld surfaces and fingerprint plots were produced with CrystalExplorer¹³ with bond lengths to hydrogen atoms set to standard values.¹⁴

Synthesis and characterization

The acyclic tripodal receptor L_{1-3} have been synthesized by modification of our recent literature procedure.15 To a solution of cresol (5 g, 46 mmol) in ethanol (30 mL) was added crushed NaOH (2.27 g, 55 mmol), and the solution was stirred at room temperature for 1 h. To the resulting suspension, tris(2-chloroethyl)amine hydrochloride (3.71 g, 15 mmol) was added at once, and the mixture was stirred for another 1 h at room temperature. For completion of the reaction, the mixture was refluxed for 8 h followed by removal of the solvents under reduced pressure and addition of 20 mL of cold water. The expected product was extracted from this mixture, with 3×20 mL of CHCl₃. The organic layer was washed several times with water and dried over anhydrous Na₂SO₄ and solvents were removed under reduced pressure. The crude product was purified by column chromatography using ethyl acetate and hexane (1:9) as eluent. The purity of the compounds was monitored by TLC.

All supramolecular complexes 1–7 were isolated as white or yellow solids upon addition of a methanolic solution of 1.1 equiv of the corresponding acids to the respective ligand solution, L_{1-3} in methanol (50 mg in 20 mL MeOH). After a constant stirring for about an hour a solid precipitate was formed which was then filtered, washed with ether and dried under vacuum. Colourless/ yellow crystals suitable for single-crystal X-ray analysis were grown by slow evaporation of CH₃OH–CH₃CN binary solution mixture of the solids at room temperature within 1–2 weeks. All complexes have been characterized by ¹H-NMR and FT-IR spectroscopy (ESI).[†]

L₁. White crystalline solid; yield: 78%; mp: 65 °C; ¹H-NMR (400 MHz, CDCl₃): $\delta = 2.29$ (s, 9 H, CH₃), 3.12–3.15 (t, 6 H, NCH₂), 4.06–4.09 (t, 6 H, OCH₂), 6.79–6.81 (d, 6 H, ArH), 7.06–7.08 (d, 6 H, ArH); ¹³C-NMR (100 MHz, CDCl₃): $\delta = 20.64$ (×3 C, CH₃), 54.59 (×3 C, NCH₂), 66.98 (×3 C, OCH₂), 114.58 (×3 C, Ar), 130.04 (×6 C, Ar), 156.81 (×6 C, Ar). Anal. calcd (%) for C₂₇H₃₃NO₃: C 77.29, H 7.93, N 3.34%. Found: C 78.21, H 6.24, N 2.85%.

L₂. Brown viscous liquid; yield: 66%; ¹H-NMR (400 MHz, CDCl₃): $\delta = 2.33$ (s, 9 H, CH₃), 3.17–3.20 (t, 6 H, NCH₂), 4.11–4.14 (t, 6 H, OCH₂), 6.71–6.79 (m, 9 H, ArH), 7.15–7.18 (t, 3 H, ArH); ¹³C-NMR (100 MHz, CDCl₃): $\delta = 21.45$ (×3 C, CH₃), 54.29 (×3 C, NCH₂), 66.26 (×3 C, OCH₂), 111.36 (×3 C, Ar), 115.42 (×3 C, Ar), 121.63 (×3 C, Ar), 129.17 (×3 C, Ar), 139.35 (×3 C, Ar), 158.65 (×3 C, Ar). Anal. calcd (%) for C₂₇H₃₃NO₃: C 77.29, H 7.93, N 3.34%. Found: C 78.93, H 5.79, N 2.67%.

L₃. Brown viscous liquid; yield: 73%; ¹H-NMR (400 MHz, CDCl₃): $\delta = 2.31$ (s, 9 H, CH₃), 3.28–3.31 (t, 6 H, NCH₂), 4.17–4.20 (t, 6 H, OCH₂), 6.87–6.96 (m, 9 H, ArH), 7.20–7.22 (d, 3 H, ArH); ¹³C-NMR (100 MHz, CDCl₃): $\delta = 16.67$ (×3 C, CH₃), 54.96 (×3 C, NCH₂), 63.06 (×3 C, OCH₂), 110.91 (×3 C, Ar), 122.04 (×3 C, Ar), 126.93 (×3 C, Ar), 127.46 (×3 C, Ar), 131.33 (×3 C, Ar), 155.59 (×3 C, Ar). Anal. calcd (%) for C₂₇H₃₃NO₃: C 77.29, H 7.93, N 3.34%. Found: C 78.55, H 5.98, N 2.59%.

X-Ray crystallography[‡]

The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo-K α radiation ($\lambda = 0.71073$ Å) at 298(2) K, with increasing ω (width of 0.3° per frame) at a scan speed of 6 s per frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP¹⁶ software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.¹⁷ Structures were solved by direct methods using SHELXS-97 and were refined by full-matrix least squares on F^2 using SHELXL-97 in Sheldrick's program package.¹⁸ In all the six compounds, non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to all carbon atoms were geometrically fixed while the hydrogen of protonated amino nitrogen of the salts and lattice water molecules were located from the difference Fourier map, and the positional and temperature factors are refined isotropically. Structural illustrations have been generated using ORTEP-319 and MERCURY 1.3²⁰ for Windows.

Results and discussion

Crystal structure studies

Structural information obtained from single-crystal X-ray analysis of podand L_1 and anion complexes (1–7) of L_{1-3} can

‡ Crystal data for L₁: FW = $C_{27}H_{33}NO_3$, M = 419.54, CCDC = 766465, T = 298(2) K, rhombohedral, space group R3c, a = 20.4711(17), b =20.4711(17), c = 9.5827(14) Å, V = 3477.8(7) Å³, Z = 6, $\mu = 0.077$ mm⁻¹, 1907 unique reflections, 1278 observed ($R_{int} = 0.1102$), R(F) =0.0547 ($I > 2\sigma(I)$, w $R(F^2) = 0.1295$ (all data). 1: FW = C₂₇H₃₄ClNO₇, M = 520.00, CCDC = 766466, T = 298(2) K, rhombohedral, space group R3c, a = 12.58630(10), b = 12.58630(10), c = 28.7108(5) Å, V =3938.87(8) Å³, Z = 6, $\mu = 0.191 \text{ mm}^{-1}$, 2175 unique reflections, 1675 observed ($R_{\text{int}} = 0.0631$), R(F) = 0.0326 ($I > 2\sigma(\hat{I})$, $wR(F^2) = 0.0906$ (all data). 2: FW = $C_{27}H_{34}CINO_7$, M = 520.00, CCDC = 766468, T =298(2) K, triclinic, space group $P\overline{1}$, a = 13.5714(2), b = 14.9166(2), c =15.3649(3) Å, $\alpha = 93.2570(11)^{\circ}$, $\beta = 96.0490(10)^{\circ}$, $\gamma = 116.2500(11)^{\circ}$, V = 2755.43(8) Å³, Z = 4, $\mu = 0.181$ mm⁻¹, 13 120 unique reflections, 12 127 observed ($R_{int} = 0.0209$), R(F) = 0.0654 ($I > 2\sigma(I)$, $wR(F^2) =$ 0.2320 (all data). 3: FW = $C_{27}H_{34}CINO_7$, M = 520.00, CCDC = 766467, T = 298(2) K, triclinic, space group $P\bar{1}$, a = 10.5293(2), b =10.7210(1), c = 13.2388(2) Å, $\alpha = 98.5670(12)^{\circ}$, $\beta = 109.2240(10)^{\circ}$, $\gamma =$ 97.0280(11)°, V = 1371.66(4) Å³, Z = 2, $\mu = 0.183$ mm⁻¹, 6551 unique reflections, 6070 observed ($R_{int} = 0.0205$), R(F) = 0.0795 ($I > 2\sigma(I)$, $wR(F^2) = 0.2108$ (all data). 4: FW = $C_{27}H_{38}BrNO_5$, M = 536.48, CCDC = 766469, T = 298(2) K, monoclinic, space group C2/c, a =43.2178(12), b = 7.6050(2), c = 17.6312(4) Å, $\hat{\beta} = 105.385(3)^{\circ}$, V =5587.2(3) Å³, Z = 8, $\mu = 1.506$ mm⁻¹, 6964 unique reflections, 6598 observed ($R_{int} = 0.0938$), R(F) = 0.0352 ($I > 2\sigma(I)$, w $R(F^2) = 0.1094$ (all data). 5: FW = $C_{33}H_{36}N_4O_{10}$, M = 648.61, CCDC = 766470, T =298(2) K, triclinic, space group $P\overline{1}$, a = 10.0888(3), b = 12.3654(4), c =13.7716(4) Å, $\alpha = 81.260(2)^{\circ}$, $\beta = 76.965(2)^{\circ}$, $\gamma = 83.641(1)^{\circ}$, V =1649.10(9) Å³, Z = 2, $\mu = 0.097$ mm⁻¹, 7968 unique reflections, 7776 observed ($R_{int} = 0.0643$), R(F) = 0.0529 ($I > 2\sigma(I)$, $wR(F^2) = 0.1646$ (all data). **6**: FW = $C_{33}H_{36}N_4O_{10}$, M = 648.66, CCDC = 766471, T =298(2) K, monoclinic, space group $P2_1/n$, a = 9.890(2), b = 28.388(6), c = 28.388(6)11.602(3) Å, $\beta = 92.896(9)^{\circ}$, V = 3253.2(12) Å³, Z = 4, $\mu = 0.099$ mm⁻¹. 8066 unique reflections, 7814 observed ($R_{int} = 0.1158$), R(F) = 0.0551 (I > 0.0551 $2\sigma(I)$, w $R(F^2) = 0.1537$ (all data). 7: FW = C₃₇H₃₉NO₁₁, M = 673.69, 3602.5(6) Å³, Z = 4, $\mu = 0.091$ mm⁻¹, 7600 unique reflections, 7498 observed ($R_{int} = 0.1090$), R(F) = 0.0615 ($I > 2\sigma(I)$, w $R(F^2) = 0.1611$ (all data).

provide insight into the anion templated supramolecular assembly formation and proper binding topology of anions with the cationic tripodal podand receptors. The neutral p-cresol based tripodal podand L1 crystallizes in the highly symmetric rhombohedral space group R3c with C_{3v} axis of symmetry passing through the bridgehead N-atom (Fig. 1a). The torsion involving N_{amino} -C-C-O_{ether} with an ideal value of 89.70(3)° $(\sim 90^{\circ})$ implies that the tripodal arms are oriented neither in a folded nor in an open conformation with an average distance of 5.037 Å between the identical ethereal oxygen atoms.^{15,21} The crystal packing diagram of the podand molecule shows that the structure is stabilized by weak intermolecular C-H \cdots π interactions forming hemicarcerand through self-assembly in the solid state. Each tripodal unit is surrounded by six other molecules occupying a chair conformation with a distance measuring 13.43 Å between the apical nitrogen atoms of two adjacent tripodal units (ESI).[†] Each arm of the tripodal unit is linked with its neighbouring unit by aromatic C–H \cdots π interactions involving the hydrogen H5 and electron- π cloud of the phenyl rings (C5... Cg = 3.648 Å) generating a highly symmetrical 2D sheet like network (Fig. 1b). Overall non-covalent interactions resulted in the formation of a honeycomb like structure when viewed along crystallographic c-axis (ESI).[†]

In all anion complexes, independently of the geometry and nature of the anion, the L_{1-3} :anion stoichiometry is 1:1.



Fig. 1 (a) Crystal structure of C_3 -symmetrical tripodal podand L_1 showing the C_{3v} axis of symmetry passing through the bridgehead N-atom Thermal ellipsoids are scaled to the 30% probability level. (b) Symmetrical crystal packing in L_1 along *c*-axis showing hexagonal arrangement of tripodal units around each ligand, occupying a cyclohexane conformation formed as a result of C–H··· π interactions (blue dotted lines).

Crystallographic studies reveal that the bridgehead amino group of L_{1-3} is protonated in presence of different organic and inorganic acids and participate in different modes of intramolecular hydrogen bonding as hydrogen-bond donors depending upon the nature of the counter anions. Upon protonation of L_1 with $HClO_4$ in methanol we isolated complex 1, $[HL_1^+ \cdot ClO_4^-]$ where the hydrogen of the protonated apical nitrogen is endo-oriented with respect to the tripodal arms and crystallizes in rhombohedral space group R3c retaining the C_{3v} symmetry similar to L₁. The endo-oriented hydrogen of the apical nitrogen is involved in intramolecular trifurcated N-H···O hydrogen bonding with the three identical ethereal oxygen atoms (N1…O1 = 2.781(2) Å) dropping the size of the flexible tripodal cavity when compared to L_1 (Fig. 2a) and thereby, locks up the cavity well known for cation binding and anionic guest encapsulation.²² As a consequence of trifurcated hydrogen bond formation, the tripodal arms are now oriented in a folded conformation which is reflected in the torsional value of $\sim 63.30(2)^{\circ}$ for each arm



Fig. 2 (a) Crystal structure of C₃-symmetrical supramolecular complex 1 depicting the formation of trifurcated N–H···O_{ether} hydrogen bonds (green dotted lines). Thermal ellipsoids are scaled to the 30% probability level. (b) Highly symmetrical crystal packing motif in 1 showing hexagonal arrangement of tripodal cations around each unit generated as a result of interligand C–H··· π and C–H···O interactions along crystal-lographic *c*-axis.

involving atoms Namino-C-C-Oether and the distance between the identical ethereal oxygen reduces to 3.667 Å. Similar to L₁, each tripodal cation is surrounded by six other units occupying a chair conformation but with a distance measuring 12.01 Å between the apical nitrogen atoms of two adjacent tripodal cations involved in the cyclohexane class of chair conformation (ESI).† A considerable decrease of 1.42 Å in the cyclohexane ring size is possibly, due to the immediate outcome of conformational locking of the podand cavity which allows a closer approach of tripodal units in the crystals of 1. The protonated podand does not have any kind of supramolecular interactions with the perchlorate ion in the solid-state. However, each arm of a cationic tripodal unit is linked with two neighbouring units by aliphatic C–H··· π interaction (C1···Cg = 3.981 Å) and C–H···O hydrogen bond formed between a methyl hydrogen with an ethereal oxygen (C9...O1 = 3.467(2) Å). Expansion of 1 through hydrogen bonds leads to a highly symmetrical 3D organic solid (Fig. 2b).

Similar modes of conformational adaptability have been observed for complexes 2 $[HL_2^+ \cdot ClO_4^-]$ and 3 $[HL_3^+ \cdot ClO_4^-]$ obtained upon protonation of podands L2 and L3 with HClO4. Both 2 and 3 crystallize in the lower symmetry triclinic space group $P\bar{1}$. The *endo*-oriented hydrogen forms trifurcated hydrogen bonds to the ethereal oxygen atoms with an average hydrogen bond distance (N1···Oether) of 2.730 Å and 2.808 Å in complexes 2 and 3, respectively. The gradual increase in the trifurcated N-H···O hydrogen bond distances in complexes 1-3 is apparently due to the increased steric hindrance provided by the methyl group at meta and ortho positions in podands L_2 and L_3 , respectively. Unlike 1, perchlorate oxygen atoms in complexes 2 and 3 are engaged in multiple aliphatic C-H···O hydrogen bond formation with various methylene hydrogen atoms presented from the neighbouring tripodal cations. In addition, complex 2 also demonstrates the formation of aryl C-H...O hydrogen bonds with perchlorate anion. Complex 2 has two crystallographically independent molecules in the asymmetric unit. The binding of perchlorate by surrounding HL₂⁺ units clearly reveal that both the symmetrically non-equivalent ClO₄⁻ ions involving chlorine atoms Cl(1) and Cl(2) are C-H...O hydrogen bonded with four tripodal cations each but with six-point and four-point attachments, respectively. Perchlorate oxygen O7 acts as trifurcated hydrogen bond acceptor by forming C-H...O hydrogen bonds with aryl and aliphatic hydrogen H7, H17 and H38A of three different cations whereas O10 behaves as bifurcated hydrogen bond acceptor by interacting with aliphatic protons H11A and H28A of two symmetrically non-equivalent cations. The six-point contacts on perchlorate anion involving chlorine Cl(1) is finally satisfied by the interaction between aliphatic hydrogen H37B with the perchlorate oxygen O9. A close up view of the binding modes of $Cl(1)O_4^-$ anion by four cationic L₂ units along with the relevant contact distances is depicted in Fig. 3a. The binding of $Cl(2)O_4^-$ anion by four encircling cations clearly reveals that the perchlorate oxygen atoms O11 and O14 are involved in bifurcated C-H···O hydrogen bond formation with an aliphatic and an aromatic proton each whereas O12 and O13 are devoid any hydrogen bond contacts. C-H protons H19A and H52 from two neighbouring cations are making contacts with perchlorate oxygen O11 while O14 is engaged in C-H···O interactions with protons H2A and H35 presented from the other



Fig. 3 (a) Close-up view of the C–H hydrogen bonding contacts on $Cl(1)O_4^-$ anion in **2** (green dotted lines) with four encircling L_2H^+ units (For clarity, the symmetry independent units have been shown in different colours and binding of $Cl(2)O_4^-$ is provided in the ESI).[†] (b) Crystal packing of complex **2** as viewed down the *a*-axis showing the hydrophobic bilayer assembly formation of cationic ligand moieties (blue transparent arrows) diagonally along *bc*-plane with the perchlorate anions entrapped between the adjacent ligand arrays in a zigzag fashion forming hydrophilic anion chain (pink transparent shades). (c) Close-up view of the C–H hydrogen bonding contacts on ClO_4^- anion in **3** (green dotted lines) with two neighbouring L_3H^+ units. (d) Crystal packing motif of complex **3** as viewed down the *a*-axis showing the hydrophobic bilayer assembly formation of cationic ligand moieties along *b*-axis with the perchlorate anions being entrapped between the adjacent bilayers.

two encircling cations (ESI).[†] However, in complex 3 each perchlorate ion is involved in a four-point C-H hydrogen bonding contacts with two neighbouring cations through an average hydrogen bond distance of 3.375 Å (Fig. 3c). Aliphatic protons H10A and H10B from two tripodal cations interact with perchlorate oxygen O6 while O5 and O7 make contacts with H10B and H2A respectively, revealing that the perchlorate oxygen O6 behaves as bifurcated hydrogen bond acceptor and methylene hydrogen H10B acts as a bifurcated hydrogen bond donor (Table 2). Complexes 2 and 3 are further stabilized through the network of interligand C-H··· π hydrogen bonds formed between the methylene CH₂ protons and phenyl rings of protonated podand. The details of the hydrogen bond interactions are provided in Table 1. The overall non-covalent interactions result in the formation of hydrophobic bilayer assembly of ligand moieties both in complexes 2 and 3 when viewed down the crystallographic a-axis with the anions being situated in the available space between the bilayers in a zigzag fashion stitching the adjacent cationic arrays by C-H···O hydrogen bonds (Fig. 3b and 3d).

In our effort to validate the effect of spherical halide anions, we prepared the bromide and chloride complexes of L_1 by treating a methanolic solution of L_1 with HBr and HCl, respectively. The bromide complex $[HL_1^+ Br^-] \cdot 2H_2O$ (4) crystallizes in the lower symmetry monoclinic space group C2/c. The hydrogen of the protonated nitrogen is *endo*-oriented similar to perchlorate complex 1 but interestingly, the C_{3v} symmetry of the podand is lost upon bromide complexation (unlike 1) possibly due to the presence of two lattice water molecules. However, we

were unsuccessful in obtaining the single crystals of chloride complex of L_1 suitable for XRD analysis. As compared to 1, the endo-oriented hydrogen forms somewhat weak trifurcated N- $H \cdots O$ hydrogen bonds to the ethereal oxygen atoms with an average distance of 2.758(3) A in complex 4. An average torsional (N_{amino}-C-C-O_{ether}) value of ~60.14(3)° implies that the tripodal arms are all oriented in a folded conformation with an average distance of 3.569 Å between the ethereal oxygen. The binding of bromide clearly demonstrates that each anion is involved in a six-point attachment provided by three encircling L_1H^+ units and lattice water molecules O4 and O5 (Fig. 4a). The methylene protons H10B, H20A and H19B from each tripodal cation is C-H hydrogen bonded to Br⁻ with an average hydrogen bonding distance of 3.823 A. Hexa-coordination to Br⁻ is finally satisfied by the hydrogen bonded lattice water molecules (O4… O5 = 2.870(4) Å), where one O4 and two O5 molecules make contacts with each bromide anion via O-H...Br interactions through an average hydrogen bonding distance of 3.375 Å. The tripodal cations are interlinked among themselves via aromatic C-H··· π interactions involving the phenyl ring (C3g) bonded to the ethereal oxygen O3 and aryl hydrogen H7 and H14 presented from two neighbouring units $(C7 \cdots C3g = 3.655 \text{ Å}; C14 \cdots C3g =$ 3.922 Å). The crystal packing diagram viewed down the *c*-axis (Fig. 4b) clearly reveals that the podand molecules beautifully pack in a bilayer assembly forming a hydrophobic chain of ligand moieties and the bromide ions are entrapped between the adjacent bilayers in association with the lattice water molecules generating a hydrophilic chain parallel along the b-axis.

$\begin{array}{c} \hline D - H \cdots A \\ [HL_1^+] \cdot [ClO_4^-] (1) \end{array}$	$d(H\cdots A)/Å$	$d(\mathbf{D}\cdots\mathbf{A})/\mathbf{\mathring{A}}$	∠(DHA)/°
N1–H···O1 C9–H9···O1 C1–H1B···Cg	2.31(1) 2.70(1) 3.04	2.781(2) 3.467(2) 3.981	114(2) 127(2) 165
$\frac{\text{[HL}_2^+] \cdot [\text{ClO}_4^-] (2)}{[\text{HL}_2^+] \cdot [\text{ClO}_4^-] (2)}$	5.04	5.901	105
	2 26(2)	2 747(2)	121(2)
N1–H···O2	2.20(3)	2.747(3)	121(2) 117(2)
N1–H···O3	2.27(2)	2.718(3)	117(2)
N2-H-O4	2.26(2)	2.749(3)	117(2)
N2–H···O5	2.20(3)	2.684(4)	117(2)
N2–H···O6	2.33(2)	2.778(3)	114(2)
C7–H7···O7	2.65(3)	3.550(5)	162(2)
$C17-H17\cdots O7$	2.59(3)	3.479(4)	159(2)
C38-H38A0/	2.60(2)	3.408(4)	140(2) 112(2)
$C_{28} H_{28} M_{10} O_{10}$	2.03(3) 2.47(3)	3.138(3) 3.283(4)	113(2) 140(2)
C37–H37B…O9	2.47(3) 2.57(3)	3,263(4) 3,448(5)	140(2) 150(2)
C19–H19A…O11	2.47(3)	3.274(5)	139(2)
С52-Н52…О11	2.62(4)	3.548(6)	176(3)
C2-H2A…O14	2.44(2)	3.310(3)	148(2)
C35–H35…O14	2.64(3)	3.572(4)	173(2)
C19–H19B····C3g	3.07	3.856	138
C28–H28B····C4g	2.77	3.696	158
C20–H20B…C6g	3.63	3.699	131
$[\text{HL}_{3}^{+}] \cdot [\text{ClO}_{4}^{-}] (3)$			
N1–H…O1	2.44(2)	2.856(3)	110(2)
N1–H···O2	2.35(3)	2.768(4)	110(2)
N1–H···O3	2.31(3)	2.800(3)	116(2)
C2–H2A···O7	2.68(7)	3.434(8)	134(3)
$C10-H10A\cdots O6$	2.55(5)	3.411(6)	146(3)
$C10 - H10B \dots O5$	2.02(3) 2.46(6)	3.440(3) 3.216(7)	141(3) 134(3)
$C1_H1B\cdots C1_g$	2.40(0)	3.210(7)	134(3)
C11–H11B···C3g	3.27	3.967	129
$[\mathrm{HL}_{1}^{+}] \cdot [\mathrm{Br}^{-}] \cdot 2\mathrm{H}_{2}\mathrm{O} \ (4$	ł)		
N1–H…O1	2.23(2)	2.755(3)	116(2)
N1–H···O2	2.28(3)	2.793(3)	115(2)
N1–H···O3	2.25(2)	2.728(3)	112(2)
C10-H10B····Br1	2.96(3)	3.816(3)	147(2)
C19–H19B…Br1	3.04(4)	3.815(4)	137(2)
C20–H20A…Brl	3.04(4)	3.839(3)	139(2)
$O4-H2O\cdots$ Brl	2.51(2)	3.396(3)	170(3)
$O_5 = H_3 O_{12} Br_1$	2.43(2) 2.51(2)	3.322(3)	1/1(3) 171(3)
03-114005	2.31(3) 1.97(3)	2,870(4)	176(3)
C11–H11A…O4	2.66(3)	3414(4)	134(2)
C7–H7···C3g	2.92	3.655	136
C14–H14····C3g	3.46	3.922	113
$[HL_1^+] \cdot [Picrate] (5)$			
N1–H···O4	1.81(3)	2.713(3)	172(3)
C2–H2A····O4	2.65(2)	3.394(3)	133(1)
CII-HIIA····O4	2.61(2)	3.386(4)	136(2)
C13-H13····O5	2.53(3)	3.455(5)	171(2)
C1 H1A Of	2.37(3)	3.247(4)	148(1)
$C_1 = H_1 A \cdots O_0$	2.00(3)	3.203(4)	120(1) 100(1)
C5-H507	2.07(3)	3.001(4)	100(1) 148(2)
C19–H19B…O7	2.32(2) 2.71(2)	3 476(3)	135(1)
C26–H26····O9	2.55(2)	3.435(3)	157(1)
C22–H22····C3g	3.53	4.179	128
C2g···Cg(anion)		3.839	
Cg(anion)…Cg(anion)	3.450	

 Table 1
 Relevent hydrogen bond parameters in Anion complexes 1–7

$[HL_{3}^{+}] \cdot [Picrate] (6)$			
N1–H····O4	1.80(2)	2.684(3)	150(2)
N1–H···O5	2.39(2)	3.072(3)	127(2)
C2–H2A····O4	2.42(2)	3.205(3)	137(2)
C19–H19A…O5	2.61(2)	3.244(3)	122(1)
C13–H13…O7	2.68(3)	3.397(4)	133(2)
C18–H18B…O7	2.53(3)	3.418(4)	153(2)
C2–H2B···O8	2.70(2)	3.310(3)	121(2)
C19–H19A…O9	2.58(2)	3.029(3)	108(1)
C15–H15…O10	2.46(2)	3.267(5)	144(3)
C1–H1B···C1g	3.29	4.197	154
C10–H10A····C2g	3.25	3.810	118
C3g…Cg(anion)		3.937	
$[HL_1^+] \cdot [Pyromellitate]$	(7)		
N1–H····O7	1.87(3)	2.783(3)	149(2)
C5–H5…O7	2.70(2)	3.594(4)	160(3)
C18-H18A…O10	2.55(3)	3.460(5)	156(2)
C19–H19A…O4	2.29(2)	3.210(4)	157(2)
C1–H1B···O8	2.46(2)	3.334(4)	149(2)
O6–H6···O4	2.67(2)	3.208(3)	124(2)
O6–H6…O5	1.71(2)	2.530(3)	176(2)
O9–H9…O10	2.71(2)	2.576(3)	071(2)
C16–H16···C3g	3.30	4.137	150
C2g···Cg(anion)		3.931	



Fig. 4 (a) Close-up view of bromide binding depicting the C–H and O– H hydrogen-bonding interactions on bromide (green dotted lines) with three cationic receptor units and lattice water molecules. (b) Crystal packing structure of complex **4** as viewed down the *c*-axis showing the hydrophobic bilayer assembly formation of cationic ligand moieties along *b*-axis and hydrophilic chain of anions between the adjacent bilayers.

It is worth to be mentioned that in spite of our repeated efforts, we were unable to crystallize the podands L_{1-3} in presence of other oxoacids which finally directed us to carry out the competitive crystallization experiments in presence of various competing anions to examine the selectivity of HL_{1-3}^+ for perchlorate in methanol (ESI).† All the above mentioned complexes are stabilized by various weak as well as strong directional hydrogen bonds, which induce rigidity in the formed cationic podands and thus, serve as the foundation for selective crystallization of desired salts. Guided by this principle, the selectivity of HL1-3+ for perchlorate in an experiment of competitive crystallization has been accomplished.23 High yields of perchlorate complexes of L1-3 were found even in the presence of equivalent concentrations of competitive anions. The ligands expressed high affinity for perchlorate vs. AcO⁻, BO₃³⁻, CO₃²⁻, NO_3^- , PO_4^{3-} , SO_4^{2-} and BF_4^- and the formation of L: perchlorate is observed in above 75% yield (ESI, Table S1).† However, comparatively poorer affinity was observed for perchlorate in the presence of halides.

At this juncture we were interested to find out the role of organic anions as a templating anion in the system that affects the orientation of HL_{1-3}^+ and we prepared complexes 5 $[HL_1^+ \cdot Picrate]$ and 6 $[HL_3^+ \cdot Picrate]$, which crystallize in triclinic $P\bar{1}$ and monoclinic $P2_1/n$ space groups, respectively. Singlecrystal X-ray analysis of 5 and 6 revealed the formation of noncapsular infinite hydrogen bonded network of the cationic units with picrate anion. In both the complexes, the tripodal arms are all oriented in three different directions with the hydrogen of the protonated amine being exo-oriented and forms intermolecular N-H...O hydrogen bond with the phenolate oxygen O4 of picrate anion. Exo-orientation of the apical hydrogen and lack of intramolecular noncovalent interactions between the tripodal arms is perhaps responsible for the flat and extended orientations of the podands in both the complexes. Interactions of picrate with the surrounding tripodal units, making various hydrogen bonds clearly represent that each picrate anion interacts with five and six tripodal cations in complexes 5 and 6, respectively, where one or both the oxygen from each nitro group are engaged in multiple weak C-H···O interactions with different aliphatic and aromatic hydrogen of the encircling cations (Table 1). The phenolate oxygen O4 is C-H hydrogen bonded to the aliphatic

Fig. 5 Ball and stick representation of crystal structures of **5** (a) and **6** (b) depicting the open conformation of the tripodal unit and the relevant H-bond contacts on picrate oxygen atoms (green dotted lines) with the *exo*-oriented bridgehead N–H and C–H protons.

protons H2A and H11A (C2...O4 = 3.394(3) Å; C11...O4 = 3.386(4) Å) whereas nitro oxygen atoms O5 and O10 is in interaction with C-H protons H13 and H19A (C13...O5 = 3.455(5) Å; C19...O10 = 3.247(4) Å), respectively, from the same tripodal cation forming the electrostatic N-H...O4 hydrogen bond in 5 (N1...O4 = 2.713(3) Å) as depicted in Fig. 5a. The nitro oxygen O9 is involved in aromatic C-H···O interaction with the arvl hydrogen H26 whereas both O6 and O7 acts as bifurcated hydrogen bond acceptor by interacting with C-H protons H1A, H2A and H5, H19B, respectively, resulting overall in nine C-H hydrogen bonding contacts on picrate anion (Table 1). However in complex 6, O4 is C-H hydrogen bonded to the aliphatic proton H2A and nitro oxygen O5 is in interaction with the methylene hydrogen H19A from the same tripodal cation forming the bifurcated N-H···O hydrogen bonds to O4 and O5 (N1...O4 = 2.684(3) Å; N1...O5 = 3.072(3) Å; C2... O4 = 3.205(3) Å; $C19 \cdots O5 = 3.244(3)$ Å) as depicted in Fig. 5b. Furthermore, O8, O9 and O10 of picrate are making C-H···O contacts with hydrogen atoms H2B, H19A and H15, respectively, while O7 is in interaction with C-H protons H13 and H18B resulting in seven C-H hydrogen bonding contacts on picrate anion. The details of the hydrogen bonding interactions are presented in Table 1. The crystal packing motif of complex 5 as viewed down the *c*-axis, clearly shows that the tripodal cations are arranged in a face to face fashion diagonally along the abplane with one of the phenyl rings (C2g) bonded to the ethereal oxygen O2 is involved in intermolecular $\pi \cdots \pi$ stacking interaction with the dimeric picrate anion through an interaction strength of 3.839 A along the *a*-axis (ESI).[†] However, the crystal packing of complex 6 reveals that the phenyl ring C3g is in $\pi \cdots \pi$ interaction with two picrate anions situated on either side of the ring C3g through an interaction strength of 3.937 A along the caxis (ESI).†

To examine the conformational adaptability of the podands in presence of other organic anions, we prepared the PMA (pyromellitic acid) complex of L_1 , [HL₁⁺·pyromellitate] (7) which crystallizes in monoclinic space group $P2_1/c$. Single crystal analysis reveals similar kind of conformational behaviour of HL_{1}^{+} unit as observed in complexes 5 and 6, with the tripodal arms being devoid of any intramolecular interactions are in an extended conformation and the exo-oriented hydrogen is N-H… O hydrogen bonded with the carboxylate oxygen O7 of PMA $(N1 \cdots O7 = 2.783(3) \text{ Å})$ as depicted in Fig. 6a. Interactions of PMA with the surrounding tripodal units, making various hydrogen bonds clearly represent that each PMA anion interacts with four encircling cations in complex 7 where one of the oxygen from each carboxylate groups are engaged in weak C-H···O interactions with different aliphatic and aromatic hydrogen of the encircling cations (Table 1). Carboxylate oxygen atoms O4, O7, O8 and O10 are making C-H...O contacts with alkyl hydrogen H19A, H5, H1B and H18A, respectively, from four different tripodal cations with an average hydrogen bond distance of 3.399 Å. Similar to the picrate complexes, 7 retains the intermolecular aromatic $\pi \cdots \pi$ stacking between one of the phenyl rings C2g of tripodal cation and electron π -cloud of pyromellitate anion with an interaction strength of 3.931 Å. PMA units are interlinked among themselves forming a 2D hydrogen bonded sheet having R44 pattern hydrogen bonded rings along *ab* plane of the crystal (Fig. 6b).²⁴





Fig. 6 (a) Ball and stick representation of the crystal structure of 7 depicting the open conformation of the tripodal unit with relevant H-bond interactions. (b) 2D hydrogen bonded sheet structure of pyromellitate anions along the *ab*-plane in complex **7**.

Hirshfeld surface analysis

The weak interactions involved in the conformational changes of tripodal podands in presence of different anions can also be visualised by the Hirshfeld surfaces, which is a useful tool to describe the surface characteristics of molecules.¹⁰ Hirshfeld surfaces offer a novel way of visualizing intermolecular interactions by colour-coding short or long contacts, the colour intensity indicating the relative strength of the interactions. Two-dimensional fingerprint plots complement these surfaces, quantitatively summarizing the nature and type of intermolecular contacts experienced by the molecules in the crystal. The



Fig. 7 Hirshfeld surface analysis of the tripodal molecule L_1 . (a) d_{norm} surface. (b) Two-dimensional fingerprint plots with the C-H $\cdots \pi$ interactions highlighted in colour.

two-dimensional fingerprint plots can also be broken down to give the relative contribution to the Hirshfeld surface area from each type of interactions present, quoted as the "contact contribution".²⁵

Fig. 7(a) displays the Hirshfeld surface mapped with d_{norm} for L_1 which highlights the interligand $C-H\cdots\pi$ close contacts between the tripodal molecules as bright red spots. Two red spots on the surface of each side arm correspond to the identical $C-H\cdots\pi$ interactions formed between the aryl proton H5 and a phenyl ring of the adjacent podand molecule. The bright red spot near the edge of the surface of each arm corresponds to the C5–H5 donor hydrogen atom whereas the spot at the centre of each identical side arm corresponds to the π acceptor ring. The corresponding fingerprint plot for the L_1 Hirshfeld surface is shown in Fig. 7(b) with the characteristic "wings" in the upper left and lower right of the plot that represent the C–H… π close contacts, with total contact contribution of 27.7% (Table 2).

Fig. 8(a) displays the Hirshfeld surfaces mapped with d_{norm} for the tripodal segments in supramolecular complexes of perchlorate anion (1–3) and picrate anion (5 and 6). The d_{norm} surfaces highlight the interligand C-H··· π close contacts and C-H···O interactions between the oxygen of perchlorate/picrate anions and C-H donors of the tripodal unit as red spots. In complex 1, where there is no involvement of the C-H donors in making interaction with the perchlorate oxygen atoms, the bright red spots on the upper half of the surface correspond to the methylene C-H··· π donor H1B hydrogen atom whereas the bright spots in the middle of the surface can be assigned for the π acceptor ring of the tripodal side arms. Although C9-H9...Oether contact is present towards the lower part of the Hirshfeld surface, the area is displayed as faint red to white, meaning contacts around the van der Waals separation. In perchlorate complexes 2 and 3, the d_{norm} Hirshfeld surfaces for tripodal segments primarily highlight the various C-H···O_{anion} and C-H··· π interactions as bright red to faint red spots on the outer walls of the tripodal surface, which is in contrast to complex 1, have only methylene C-H··· π and methyl C-H···O_{ether} interactions, among others. In complex 2, the bright red spots present in the upper half of Hirshfeld surfaces for the tripodal segments correspond mostly to methylene C-H...Oanion interactions except for those marked with stars, which represent C-H $\cdots\pi$ interactions. Whereas, the spots towards the edge of the lower half of the surfaces mostly correspond to C-H $\cdots\pi$ interactions and the rest represent aromatic C-H...Oanion contacts. In complex 3, the spots towards the upper half of the Hirshfeld surface of the tripodal segment symbolize participation of the methylene CH2 protons in C-H···Oanion close contacts as depicted in Table 1. Whereas, the two faint red spots towards the lower half (marked with stars) of the surface represent aliphatic C–H··· π interactions. The bright spot at the extreme right of the

Table 2 Summary of the various contact contributions to the tripodal Hirshfeld surface area in L_1 and anion complexes $1\!-\!7$

	L_1	1	2	3	4	5	6	7
H…C	27.7	19.3	17.1	17.1	20.5	20.3	17.9	22.3
H…O	9.0	24.8	23.0	18.9	16.6	23.2	21.8	19.1
$C \cdots C$	0.0	0.0	0.8	1.2	0.1	1.6	4.8	2.2
$H \cdots H$	62.1	55.6	57.5	61.9	56.6	53.3	52.0	54.5

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surface correspond to the H···H interaction between identical methyl proton H27A. The corresponding fingerprint plots of the tripodal Hirshfeld surfaces in complexes 1-3 are shown in Fig. 8(b) and 8(c) for the C–H··· π and C–H···O close contacts, respectively, highlighted in colour. The contact contributions for the Hirshfeld surface areas are 19.3, 17.1, and 17.1% for the C- $H\cdots\pi$ close contacts and 24.8, 23.0, and 18.9% for the C-H···O close contacts in complexes 1-3, respectively (Table 2). The fingerprint plots for the C-H··· π close contacts display the characteristic "wings" in the upper left and lower right of the plot and show pseudosymmetry on either side of the diagonal where $d_{\rm e} = d_{\rm i}$. A noteworthy feature of the tripodal fingerprint plots of perchlorate complexes 1-3 is the substantial change in the characteristic H···C and H···O contact contributions with the variation in the position of the methyl substituents in L_{1-3} . To compensate for the decrease in C-H··· π and C-H···O close contacts, the percentage of H...H close contacts increases, and this effect is more clearly seen in complex 3 due to the steric hindrance within the tripodal unit offered by the methyl substituent at ortho-position of the terminal phenyl ring and thus, the $H \cdots H$ short contacts become more apparent (Table 2).

In picrate complexes of L_1 and L_3 (5 and 6), the bright red spot at the centre of the Hirshfeld surfaces mapped with d_{norm} (Fig. 8a) correspond to the apical N–H···O_{anion} interactions with the phenolate oxygen of picrate anion. Due to the *endo*-orientation of the hydrogen of the protonated apical nitrogen, similar type of interaction is absent in the perchlorate complexes of L_{1-3} and subsequently, no bright red spots could be observed on the Hirshfeld surfaces near the apical nitrogen of the tripodal segment. The faint red spots subsequent to the bright spot correspond to methylene C-H···Oanion contacts both in complexes 5 and 6. Whereas, spots towards the edge of the surface correspond mostly to the aromatic C-H...Oanion interactions. Spots that has been marked with a star represent C-H... π interactions. The fingerprint plots of the tripodal Hirshfeld surfaces in complexes 5 and 6 are shown in Fig. 8(b) and 8(c) for the C-H··· π and C-H···O close contacts respectively, highlighted in colour. The contact contributions for the Hirshfeld surface areas are 20.3 and 17.9% for the C–H $\cdots\pi$ close contacts and 23.2 and 21.8% for the CH…O close contacts in complexes 5 and 6, respectively (Table 2). Similar to the perchlorate complexes, the fingerprint plots for the C–H $\cdots\pi$ close contacts display the characteristic "wings" in the upper left and lower right of the plot and show pseudosymmetry on either side of the diagonal where $d_e = d_i$. Whereas, unlike the perchlorate complexes, the considerable decrease in the H…C and H…O contact contributions is compensated by an increase in the C…C close contacts instead of the $H \cdots H$ close contacts (Table 2). The fingerprint plots for $H \cdots O$ close contacts show a sharp spike at $d_i = 0.996$ Å and de = 1.297 Å in complex 5 and at $d_i = 0.881$ Å and $d_e = 1.207$ Å in complex 6, which is associated with the apical N-H \cdots O_{anion} close contact between the hydrogen of the apical nitrogen and phenolate oxygen of picrate anion.

Fig. 9 displays the Hirshfeld surfaces mapped with d_{norm} for the tripodal segments in bromide and pyromellitate complexes of L₁ (4 and 7) together with the corresponding fingerprint plots for the C-H… π and C-H…O close contacts. In bromide complex 4, two bright spots on the upper half of the Hirshfeld surface



Fig. 8 Hirshfeld surface analysis of the tripodal segments in complexes 1, 2, 3, 5 and 6. (a) d_{norm} surface: spots representing C–H··· π interactions have been marked with stars. (b) Two-dimensional fingerprint plots with the C–H··· π interactions highlighted in colour. (c) Two-dimensional fingerprint plots with the C–H··· π interactions highlighted in colour.



Fig. 9 Hirshfeld surface analysis of the tripodal segments in complexes **4** and **7**. (a) d_{norm} surface. (b) Two-dimensional fingerprint plots with the C-H··· π interactions highlighted in color. (c) Two-dimensional fingerprint plots with the C-H···O interactions highlighted in colour.

correspond to the methylene C–H···Br close contacts (Table 1). The bright spot towards the upper edge represent the C10– H10B···Br interaction whereas the spot towards the left (upper half) stand for C10–H20A···Br interaction. The spots at the extreme right and left of the lower half of the Hirshfeld surface represent the C14–H14··· π (C3g) interaction for the donor and the acceptor respectively. The brighter spot at the centre of the lower half correspond to the C7–H7··· π (C3g) interaction for the donor atom. Finally, the bright spot at the edge of the lower half correspond to the repulsive H···H interaction between H9C and H27B. The contact contributions for the Hirshfeld surface areas are 6.1 and 20.5% for C–H···Br and C–H··· π close contacts, respectively. Although, there is interaction between the methylene proton H11A and O4 (lattice water), the area is displayed as blue with a contact contribution of 16.6%.

In pyromellitate complex 7, the bright red spot at the middle of the Hirshfeld surface correspond to the apical N–H···O_{anion} close contact with the pyromellitate oxygen atom O7. The next brighter spot just below to the above mentioned spot represent the methylene C1–H1B···O8 interaction. The faint red spot at the edge of upper part of the Hirshfeld surface correspond to the methyl C18–H18A···O10 contact whereas the faint spot at the extreme left (lower half) stand for the C5–H5···O7 interaction. The spot at the centre of the upper half of the surface can be designated to the C16–H16··· π (C3g) close contact. The contact contributions for the Hirshfeld surface areas are 22.3 and 19.1% for C–H··· π and C–H···O close contacts respectively. Similar to the picrate complexes, the fingerprint plot for H···O close contacts shows a spike at $d_i = 0.981$ Å and $d_e = 1.287$ Å, which is associated with the apical N–H···O_{anion} close contact between the hydrogen of the apical nitrogen with one of the pyromellitate oxygen atoms.

Rationalization of C-H hydrogen bond formation

In continuation of our efforts to investigate the anion directed self assembly of various substituted tripodal molecules^{24,26} we discovered that, the cresol based tripodal ether ligands upon protonation in presence of inorganic anions results into conformational locking of the tripodal cavity via trifurcated N-H···O hydrogen bond formation due to the endo orientation of the protonated bridgehead N-H proton. However when organic anions are used as template, the podand molecules are forced to adopt a flat and extended orientation of their arms due to intermolecular face to face interaction involved between one of the phenyl rings of ligand arms and electron π -cloud of the planar organic anion. In addition, the hydrogen of the protonated apical nitrogen is exo-oriented by forming electrostatic N-H…anion hydrogen bond with the organic anion. The existence of $\pi \cdots \pi$ stacking interactions between a phenyl ring of tripodal arms and aromatic π -cloud of planar organic anion is probably responsible for exo-orientation of the hydrogen of protonated bridgehead nitrogen together with other weak supramolecular interactions with the anions. The sharp spikes present in the two dimensional fingerprint plots are the characteristic for the supramolecular complexes of organic anions which represent apical N–H \cdots O_{anion} close contact and is absent in the complexes having inorganic anions. Structural analysis of anion complexes 2-7 reveals the formation of multiple weak aliphatic and aromatic C-H...anion contacts with the neighbouring tripodal cations. The unusual and variable coordination modes in bromide and perchlorate complexes (2-4) suggests that the interactions with the C-H donors are too weak to impose a definite coordination structure around the anions, and instead the CH groups on the flexible arms of the podand embrace the anion so as to match its size and shape to provide a favourable electrostatic environment around it. Calculations on C₆H₆-anion complexes have shown that the aryl C-H donors are effective anion binding groups, compared to aliphatic C-H donors.²⁷ The strength of an aryl C-H donor group can in theory, be adjusted through the addition of different functional groups on the arene ring.²⁸ However, protonation at the bridgehead nitrogen render the methylene C-H hydrogen bond donors sufficiently acidic for their active participation in C-H···O interactions as observed in all complexes. Though charge neutralisation in the crystals and conventional hydrogen bonds are the main driving forces in the formation of supramolecular complexes,29 yet the weak CH hydrogen bonds provide added stabilization to the complexes and thus, satisfy the geometrical necessity of the LH⁺ units by providing a favourable electrostatic environment around the anions. Moreover, interligand C-H \cdots π interactions provide further stabilization to the supramolecular complexes having inorganic counter anions (1-4) resulting into the bilayer assembly formation of ligand moieties in the solid state which has not been observed in the organic anion complexes (5-7). Detailed structural investigation clearly demonstrates that the self-alignment, flexibility and orientation of the ligand units, depending upon the dimensionality and nature of the anions play a crucial role in making various molecular interactions possible in

complexation of various anions. NMR spectroscopy has been used to evaluate and correlate structural and conformational properties of anion receptors to their pre-organization and conformational changes for interaction with diverse range of anions.³⁰ The excellent solubility of the perchlorate and picrate complexes in CHCl₃ (4 and 7 are insoluble in CHCl₃) allowed us to perform ¹H NMR experiment in CDCl₃. A comparison of the proton δ values of complexes 1 and 5 with L_1 showed significant downfield shift of the aliphatic CH_2 protons and slight upfield shift of aromatic CH protons whereas the signal for the CH₃ protons remains almost same. Considerable downfield shift of the aliphatic CH₂ protons indicate the influence of protonation at the apical nitrogen on the neighbouring methylene protons. However, interestingly, the resonance for the endo-oriented hydrogen of the protonated apical nitrogen in complex 1 occurs at $\delta = 3.462$ ppm and in complex 5 where the hydrogen of the protonated bridgehead nitrogen is exo-oriented show resonance at $\delta = 3.045$ ppm (Fig. 10). The occurrence of the bridgehead N-H proton resonances at considerably different δ values ($\Delta \delta = 0.417$ ppm) with notable differences in the CH proton resonances further accounts for the different orientations of the tripodal side arms in presence of inorganic and organic counter anions in solution. However, in DMSO- d_6 the resonances for the apical N–H proton could not be observed.



Fig. 10 Comparison of the partial ¹H NMR spectra (in CDCl₃) of complexes 1 and 5 with L₁ demonstrating the occurrence of apical N–H proton resonances at different δ values ($\Delta \delta = 0.417$ ppm) with notable differences in the CH proton resonances.

Conclusions

We have structurally authenticated for the conformational changes in cresol-based tripodal molecules, based on anion specificity and undertaken a detailed analysis of their Hirshfeld surfaces to gain a greater understanding of the various interactions involved in the crystal packing for assembled arrays containing different anions. To conclude, the present findings provide evidence for inorganic anion assisted conformational locking of acyclic tripodal podands L_{1-3} by the formation of intramolecular trifurcated N-H···O hydrogen bonds whereas protonation in presence of organic anions force the podand molecules to become conformationally open via intermolecular N–H···anion hydrogen bond formation and $\pi \cdots \pi$ interaction. This is an example of a system in which a simple and flexible molecule adapts its conformation to respond to the demands of the specific anion. This conformational movement could prove to be significant in the field of anion sensing and signal transduction. We have also shown the solid state evidence for the active participation of both aliphatic and aryl C-H donors in interaction with different anions, exhibiting aliphatic C-H... anion hydrogen bond strengths comparable to those of aryl C-H…anion hydrogen bond. Therefore, due to the interesting structural and binding properties, the tripodal podand molecules can provide an excellent case of understanding C-H…anion hydrogen bonding in its protonated form. Furthermore, the architecture of the podand molecule could serve as a model for building novel, highly selective receptors for perchlorate which is indicated by the impressive selectivity for the anion, even in highly competitive environment. We are currently investigating the conformational adaptability of similar class of ligands possessing amide and urea or thiourea functionalities in the presence of anions of different dimensionality.

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Notes and references

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