Electronic Supporting Information

Structure directing roles of weak noncovalent interactions and charge-assisted hydrogen bonds in the self-assembly of solvated podands: Example of an anion-assisted dimeric water capsule

Sandeep Kumar Dey,*a Sarvesh S. Harmalkar,a Rahul K. H. O. Yadav,a Prem Lama,*b Gopal Das^c

^{a-}School of Chemical Sciences, Goa University, Taleigao Plateau, 403206 Goa, India E-mail: <u>sandeepdey@unigoa.ac.in</u> and <u>sandeepdey@outlook.com</u>

^{b-}CSIR-Indian Institute of Petroleum, Mohkampur, Dehradun, Uttarakhand 248005,

India

E-mail: prem.lama@iip.res.in

^{c-}Department of Chemistry, Indian Institute of Technology Guwahati, Assam 781039, India.

Email: gdas@iitg.ac.in

Experimental Section

Synthesis of 1,3,5-tris(4-formyl phenoxymethyl) mesitylene, 1: Podand 1 was synthesized by the reaction of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene¹ (1 equiv.) with 4-hydroxybenzaldehyde (3 equiv.) in the presence of excess potassium carbonate (6 equiv.) in acetone at room temperature. 460 mg of 4hydroxybenzaldehyde was dissolved in 20 ml of acetone in a flat-bottom flask and 1 gm of potassium carbonate was added into the solution. The solution mixture was then stirred at room temperature for about an hour and 500 mg of 1,3,5tris(bromomethyl)-2,4,6-trimethylbenzene dissolved in 20 ml of acetone was added into it followed by stirring at room temperature for about 12 hours. The solution mixture was then filtered by using Whatman filter paper to remove potassium carbonate and the filtrate was allowed to evaporate at room temperature in a 50 ml conical flask for crystallization. Single crystals suitable for X-ray diffraction analysis were obtained within 3-4 days by slow evaporation of the filtrate. The bulk crystals were collected by filtration, then washed with ethanol and dried at room temperature for characterization by NMR spectroscopy, powder XRD and thermogravimetry analysis. Isolated yield of podand 1: 550 mg (% yield 85).

¹H-NMR of **1** (400 MHz, DMSO-*d*₆) chemical shift in δ ppm: 2.36 (s, -CH₃), 2.50 (DMSO-D₆), 3.54 (HOD), 5.23 (s, -CH₂), 7.23 (d, -CH), 7.87 (d, -CH), 9.86 (s, -CHO). ¹³C-NMR of **1** (100 MHz, DMSO-d₆) chemical shift in δ ppm: 16.13 (3 x CH₃), 40.00 (DMSO-D₆), 65.83 (3 x CH₂), 115.61 (6 x CH), 130.38 (3 x CH), 131.56 (3 x CH), 132.38 (6 x CH), 139.87 (3 x CH), 164.25 (3 x CH), 191.87 (3 x CHO).

Synthesis of tris(4-aminopyridinium)-mesitylene tribromide, **2**: Podand **2** was synthesized by the reaction of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene¹ (1 equiv.) with 4-aminopyridine (3 equiv.) in acetone-acetonitrile (1:1 v/v) solvent mixture at room temperature. 500 mg of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene was dissolved in 20 ml of acetone and 355 mg of 4-aminopyridine was dissolved in 20 ml of acetonitrile in two separate beakers. The two solutions

2

were then mixed in a flat-bottom flask and allowed to stir at room temperature for about 8 hours. White precipitate formed in the reaction was then filtered, washed with acetonitrile and acetone (10 ml each), and dried at room temperature for characterization by NMR spectroscopy, powder XRD and thermogravimetry analysis. Isolated yield of podand **2**: 800 mg (% yield 94).

¹H-NMR of **2** (400 MHz, DMSO- d_6) chemical shift in δ ppm: 2.22 (s, -CH₃), 2.50 (DMSO-D₆), 3.38 (s, HOD), 5.54 (s, -CH₂), 6.85 (d, -CH), 8.04 (d, -CH), 8.17 (s, -NH).

¹³C-NMR of **2** (100 MHz, D₂O) chemical shift in δ ppm: 16.05 (3 x CH₃), 55.26 (3 x CH₂), 110.10 (6 x CH), 129.34 (3 x CH), 141.45 (6 x CH), 142.34 (3 x CH), 158.84 (3 x CH).

For crystallization, 50 mg of the compound was dissolved in 10 ml of methanol in a 25 ml conical flask. A few drops of water were added to make the solution completely homogeneous and was allowed to evaporate at room temperature when colorless crystals suitable for X-ray diffraction analysis were obtained within 3-4 days.

Synthesis of tris(4-amino-N-ethylbenzamide)amine, **3**: Podand **3** was synthesized by reduction of its nitro analogue tris(4-nitro-N-ethylbenzamide)amine), which was synthesized by modification of a reported literature procedure.² Tris(4-nitro-Nethylbenzamide)amine) was synthesized by the reaction of tris(2-aminoethyl)amine, (Tren) with 4-nitrobenzoyl chloride in 1 : 3.5 molar ratio at room temperature in dry dichloromethane. In a 100 mL flat-bottom flask, 1 mL (6.8 mmol) of tris(2aminoethyl)amine was dissolved in 30 mL of dichloromethane and 4.5 g of 4nitrobenzoyl chloride (24.3 mmol) was added in portions into the above solution with constant stirring at room temperature. The reaction mixture was allowed to stir overnight at room temperature followed by the addition of 3 ml (excess) triethylamine and stirred for another 1 hour. The precipitate obtained was then filtered, collected in a 250 ml flat bottom flask and washed with 50 ml of methanol in the presence of 1 ml of triethylamine under stirring. The pale-yellow compound obtained was finally filtered again and washed with another 50 ml of methanol over the filter paper to ensure its purity for subsequent reduction reaction. Isolated yield: 2.65 gm (% yield 65).

3

In a 250 ml flat bottom flask, 1 g of tris(4-nitro-N-ethylbenzamide)amine) was dispersed in 100 ml of ethanol and 100 mg of Pd/C and 1 ml of hydrazine hydrate was added into the flask. The reaction mixture was then refluxed overnight at about 70 °C and filtered to remove the heterogeneous Pd/C catalyst. The filtrate was then allowed to evaporate in a beaker at room temperature when colorless crystals of 3 were obtained in quantitative yield within a day or two. The crystals were collected by filtration and washed with 10 ml of ethanol to ensure its purity for spectroscopy analysis. The compound was characterized by NMR spectroscopy, powder XRD and thermogravimetry analysis. Isolated yield of podand 3: 590 mg (% yield 70).

¹H-NMR of **3** (400 MHz, DMSO-*d*₆) chemical shift in δ ppm: 2.50 (DMSO-D₆), 2.64 (t, -NCH₂), 3.30 (t, -CH₂), 3.37 (HOD), 5.56 (s, -NH₂), 6.50 (d, -CH), 7.55 (d, -CH), 7.94 (t, -NH).

¹³C-NMR of **3** (100 MHz, DMSO-d₆) chemical shift in δ ppm: 38.03 (3 x NCH₂), 40.00 (DMSO-D₆), 54.37 (3 x CH₂), 113.09 (6 x CH), 121.82 (3 x CH), 129.19 (6 x CH), 152.02 (3 x CH), 166.85 (3 x C=O).

Synthesis and crystallization of $[(3H_2)^{2+}(Br^-)_2(4H_2O)]$: 100 mg of the podand 3 was suspended in 10 ml of methanol in a 25 ml beaker and 0.5 ml of 48% hydrobromic acid was added dropwise to the suspension while stirring at room temperature. The heterogeneous solution was stirred for 15 minutes and the compound was then filtered and dried at room temperature. The isolated compound was dried and dissolved in 5 ml of distilled water and allowed to evaporate at room temperature when pale-brown crystals suitable for X-ray diffraction analysis were obtained within 6-7 days. The crystals obtained was then dried and characterized by NMR spectroscopy and thermogravimetry analysis.

¹H-NMR of $[(3H_2)^{2+}(Br^-)_2(4H_2O)]$ (400 MHz, D₂O) chemical shift in δ ppm: 3.55 (t, - NCH₂), 3.71 (t, -CH₂), 6.70 (d, -CH), 7.25 (d, -CH). Amide -NH and amine -NH₂ peaks were not observed possibly due to the fast proton exchange processes and strong hydrogen bonding with water in D₂O solution.

¹³C-NMR of $[(3H_2)^{2+}(Br^{-})_2 \cdot 4H_2O]$ (100 MHz, DMSO-D₆) chemical shift in δ ppm: 34.72 (3 x NCH₂), 52.70 (3 x CH₂), 118.24 (3 x CH), 126.99 (3 x CH), 129.52 (6 x CH), 167.29 (3 x C=O),

Synthesis and crystallization of $[(3H_4)^{4+}(Br^-)_4(H_2O\cdot CH_3OH)]$: 100 mg of the podand **3** was suspended in 5 ml of water in a 10 ml beaker and 0.5 ml of 48% HBr was added dropwise to the suspension while stirring at room temperature. The clear solution thus obtained was stirred for about 10 minutes and was allowed to evaporate at room temperature when pale-brown crystals were obtained within 6-7 days. The crystals thus obtained were recrystallized from methanol-water (1:1) mixture and the single crystal X-ray structure was elucidated at room temperature (296 K). The crystals obtained were characterized by NMR spectroscopy, powder XRD and thermogravimetry analysis.

¹H-NMR of $[(3H_4)^{4+}(Br^-)_4 H_2O]$ (400 MHz, D₂O) chemical shift in δ ppm: 3.62 (t, - NCH₂), 3.78 (t, -CH₂), 7.23 (d, -CH), 7.48 (d, -CH). Amide -NH and amine -NH₂ peaks were not observed possibly due to the fast proton exchange processes and strong hydrogen bonding with water in D₂O solution.

¹³C-NMR of $[(3H_4)^{4+}(Br^-)_4(H_2OCH_3OH)]$ (100 MHz, D₂O) chemical shift in δ ppm: 35.15 (3 x NCH₂), 54.56 (3 x CH₂), 122.71 (6 x CH), 129.45 (6 x CH), 132.54 (3 x CH), 133.97 (3 x CH), 169.92 (3 x C=O),

X-ray Crystallography: In each case, a crystal of suitable size was selected from the mother liquor and immersed in paratone oil, and it was mounted on to a fibre loop holder. Single-crystal XRD data were collected at 296 K or at 100 K with a Bruker SMART APEX-III CCD diffractometer equipped with a fine focus 1.75 kW sealed tube Mo–K α radiation (λ = 0.71073 Å). The SMART software was used for the data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software. Multi-scan empirical absorption corrections were applied to the data using the SADABS program. The structures were solved by direct methods using SHELXS, and refined with full-matrix least-squares on F² using SHELXL. All non-hydrogen atoms were refined anisotropically, hydrogen atoms attached to all carbon atoms were geometrically fixed and the positional and temperature factors were refined isotropically. The hydrogen atoms on the lattice water molecules could not be located from the electron Fourier map or geometrically fixed.

As single-crystal X-ray diffraction measurement of structures $[2 \cdot H_2O],$ $[(3H_2)^{2+}(Br^{-})_2 \cdot (4H_2O)]$ and $[(3H_4)^{4+}(Br^{-})_4 \cdot (H_2O \cdot CH_3OH)]$ were carried out at room temperature (296 K), the position of the hydrogen atoms of lattice water molecules could not the located precisely and hence, we have observed an Isolated Oxygen Atoms alert. We believe that, for room temperature determination of single-crystal Xray structures, the difficulty in locating the precise position of hydrogen atoms (bonded to oxygen) especially for lattice water molecules using Electron-Fourier map is often come across. In $[2 \cdot H_2 O]$, missing FCF Refl Between Thmin & STh/L is due to the fact that these reflections were probably affected by unexpected deviations in their intensities for symmetry equivalent measurements and omitted during initial data reduction. The short donor-acceptor distances alert in $[(3H_2)^{2+}(Br^{-})_{2}\cdot(4H_2O)]$ is due to the existence of strong hydrogen bonding interactions between the lattice water molecules and the carbonyl oxygen atom of the podand unit.

Even though we have collected the data of $[1 \cdot (CH_3)_2CO]$ at 100 K, we have observed that the lattice acetone molecule is disordered over two positions with 0.8 and 0.2 occupancy. So, in order to get the reliable thermal parameter for both the minor fraction carbon atoms (C34B and C36B), ISOR command has been used in both atoms. All non-hydrogen atoms were refined anisotropically. All the aromatic and aliphatic hydrogen atoms are fixed using the riding model and the remaining hydrogen atoms were located at the appropriate position using Fourier differences map.

Hydrogen Bonding Tables

6

D−H…A	D…A (Å)	D−H…A (Å)	D−H…A (°)
C8−H _b …O7	3.581 (5)	2.644	157
C11−H _b ····O7	3.569 (4)	2.628	161
C24-H _a …O7	3.344 (4)	2.526	139
C34–H _c …O5	3.412 (6)	2.505	154
C33-H _c …O4	3.486 (3)	2.606	149
C22-H _a …O3	3.284 (4)	2.548	132
C22-H _c …O5	3.587 (3)	2.691	153
C15-H…O6	3.538 (3)	2.659	154
C20-H…O5	3.555 (5)	2.718	147
C30-H…O1	3.392 (4)	2.701	130
C6-H…O3	3.105 (4)	2.452	125

Table S1. Selected hydrogen bond lengths (Å) and bond angles (°) of $[1 \cdot (CH_3)_2CO]$ (D = H-bond donor atom and A = H-bond acceptor atom).

Table S2. Selected hydrogen bond lengths (Å) and bond angles (°) of $[2 \cdot (H_2O)]$ (D = H-bond donor atom and A = H-bond acceptor atom).

D−H…A	D…A (Å)	D−H…A (Å)	D−H…A (°)
C27-H…O1	3.305(1)	2.613	131
C11-H…O1	3.958(1)	3.183	142
C18-H…O1	3.453(1)	2.709	137
N4−H _b …O1	3.150(1)	2.367	151
N2−H _a …Br⁻1	3.470(5)	2.637	163
N4−H _a …Br⁻1	3.381(1)	2.525	174
C16−H _b ····Br⁻1	3.829(8)	2.955	150
C22−H _b ····Br⁻1	3.889(8)	2.943	165
N6−H _a …Br⁻2	3.392(8)	2.551	166
C7−H _c …Br⁻2	3.851(6)	3.041	142
C16−H _a ····Br⁻2	3.783(8)	2.836	165
C21−H…Br⁻2	3.834(7)	2.969	155
O1…Br⁻2	3.284(9)	-	_
01…Br⁻3	3.235(9)	-	_
N2−H _b ···Br⁻3	3.645(7)	2.859	152
N6−H _b ···Br⁻3	3.475(7)	2.622	171
C14−H…Br⁻3	3.566(8)	2.700	155
C17−H…Br⁻3	3.582(1)	2.771	146

Table S3. Selected hydrogen bond lengths (Å) and bond angles (°) of $[(3H_2)^{2+}(Br)_2(4H_2O)]$.

D-H…A	D…A (Å)	D−H…A (Å)	D−H…A (°)
N1-H…O3	2.744 (5)	1.868	145
N2-H…O2	2.878 (5)	2.110	148
N4-H…O3	2.897 (5)	2.083	157
N7−H _a …O1	3.219 (6)	2.340	148
N5−H _a …Br⁻1	3.388 (5)	2.538	160
N7−H _b ···Br⁻1	3.507 (5)	2.650	162
C10−H _b ···Br⁻1	3.728 (5)	2.854	150
C19−H _a …Br⁻1	3.723 (5)	3.038	128
N3−H _a …Br⁻2	3.624 (5)	2.837	152
N6−H…Br⁻2	3.487 (5)	2.721	149
C10−H _a ···Br⁻2	3.744 (5)	2.874	150
O4W…Br⁻2	3.308 (5)	-	-
N5−H _c …O1W	2.899 (7)	2.276	127
N3−H _b ···O3W	3.202 (7)	2.366	164
N5−H _c ···O3W	3.006 (6)	2.301	136
N5−H _b ···O4W	2.782 (7)	1.920	162
C20-H _b ···O4W	3.460 (7)	2.499	170
C1−H _a …O2W	3.410 (1)	2.610	139

Table S4. Selected hydrogen bond lengths (Å) and bond angles (°) of $[(3H_4)^{4+} \cdot (Br^-)_4 \cdot (H_2O \cdot CH_3OH)].$

D-H…A	D…A (Å)	D−H…A (Å)	D−H…A (°)
N1-H…O2	2.724(5)	1.872	143
N4−H…Br⁻1	3.341(4)	2.406	168
N3−H _a …Br⁻1	3.194(4)	2.360	156
N7−H _c …Br⁻1	3.461(5)	2.833	128
N3−H _b ···Br⁻2	3.266(4)	2.423	158
N7−H _c …Br⁻2	3.348(5)	2.695	131
C1−H _b ···Br⁻2	3.789(5)	2.998	139
N5−H _a …Br⁻3	3.259(4)	2.373	173
N7−H _a …Br⁻3	3.263(4)	2.376	174
C24−H…Br⁻3	3.719(5)	3.036	131
O4−H…Br⁻3	3.278(8)	2.579	133
N2−H…Br⁻4	3.381(4)	2.563	159
N6−H…Br⁻4	3.649(5)	2.897	147
N3−H _c …Br⁻4	3.371(4)	2.483	175
N7−H _b ···Br⁻4	3.339(5)	2.452	174
N5−H _b …O1	2.820(6)	1.953	164
N5-H _c ···O3	2.853(6)	2.119	139
N5−H _c …O4	2.859(8)	2.333	117
N5−H _c …O1W	2.958(2)	2.369	123



Fig. S1. ¹H-NMR spectrum of podand **1**, [1,3,5-tris(4-formyl phenoxymethyl)mesitylene] in DMSO-D₆.



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Fig. S2. ¹³C-NMR spectrum of podand **1**, [1,3,5-tris(4-formyl phenoxymethyl)mesitylene] in DMSO-D₆.









Fig. S6. ¹³C-NMR spectrum of podand 3, tris(4-amino-N-ethylbenzamide)amine in DMSO- D_6 .

Figure S7. ¹H-NMR tetrabromide salt [$(3H_2)^{4+}(Br^-)_4 \cdot (H_2O \cdot CH_3OH)$] in D₂O.





Figure S8. ¹³C-NMR tetrabromide salt [$(3H_2)^{4+}(Br^-)_4 \cdot (H_2O \cdot CH_3OH)$] in D₂O.

Fig. S9. ¹H-NMR spectrum of dibromide salt $[(3H_2)^{2+}(Br^-)_2 \cdot (4H_2O)]$ in D₂O.



Fig. S10. ¹³C-NMR spectrum of dibromide salt $[(3H_2)^{2+}(Br^-)_2 \cdot (4H_2O)]$ in DMSO-D₆.



Fig. 11. (a) Single crystal X-ray structure of $[1 \cdot (CH_3)_2 CO]$.



Hydrogen bonding interactions of bromide ions in [2·H₂O]:

Fig. S12. Hydrogen bonding contacts of Br⁻¹ ion with four cationic podand molecules in $[2 \cdot H_2 O]$ (Refer Table S2 for hydrogen bond distances and angles).



Fig. S13. Hydrogen bonding contacts of Br-2 ion with three cationic podand molecules in $[2 \cdot H_2O]$ (Refer Table S2 for hydrogen bond distances and angles).



Fig. S14. Hydrogen bonding contacts of Br⁻³ ion with three cationic podand molecules in $[2 \cdot H_2O]$, (Refer Table S2 for hydrogen bond distances and angles).



Fig. 15. Packing diagram of $[2 \cdot H_2 O]$ as viewed down the crystallographic *b*-axis.



Hydrogen bonding interactions of bromide ions in $[(H_23)^{2+}(Br^{-})_2(4H_2O)]$:

Fig. S16. Hydrogen bonding contacts of Br⁻2 ion with three cationic podand molecules in $[(H_23)^{2+}(Br^-)_2(4H_2O)]$, (Refer Table S3 for hydrogen bond distances and angles).



Fig. S17. Hydrogen bonding contacts of Br⁻¹ ion with four cationic podand molecules in $[(H_23)^{2+}(Br^-)_2(4H_2O)]$, (Refer Table S3 for hydrogen bond distances and angles).

Hydrogen bonding interactions of bromide ions in $[(H_23)^{4+}(Br^{-})_4 \cdot (H_2O \cdot CH_3OH)]$:



Fig. S18. Hydrogen bonding contacts of Br⁻¹ ion with three cationic podand molecules in $[(H_23)^{4+}(Br^-)_4(H_2O\cdot CH_3OH)]$, (Refer Table S4 for hydrogen bond distances and angles).



Fig. S19. Hydrogen bonding contacts of Br⁻2 ion with three cationic podand molecules in $[(H_23)^{4+}(Br^-)_4(H_2O\cdot CH_3OH)]$, (Refer Table S4 for hydrogen bond distances and angles).



Fig. S20. Hydrogen bonding contacts of Br⁻3 ion with a cationic podand molecule in $[(H_23)^{4+}(Br^-)_4(H_2O\cdot CH_3OH)]$, (Refer Table S4 for hydrogen bond distances and angles).



Fig. S21. Hydrogen bonding contacts of Br⁻4 ion with two cationic podand molecules in $[(H_23)^{4+}(Br^-)_4(H_2O\cdot CH_3OH)]$, (Refer Table S4 for hydrogen bond distances and angles).

Thermogravimetry and powder X-ray diffraction analysis:



Fig. S22. Thermogravimetry curves under nitrogen atmosphere of (a) crystals of $[1 \cdot (CH_3)_2CO]$ and (b) crystals of activated $[1 \cdot (CH_3)_2CO]$. Crystals of $[1 \cdot (CH_3)_2CO]$ were activated at 60 °C for 6 hours.



Fig. S23. PXRD patterns of (a) crystals of $[1 \cdot (CH_3)_2CO]$ dried at RT, (b) crystals of activated $[1 \cdot (CH_3)_2CO]$, (c) simulated PXRD of the crystal structure of $[1 \cdot (CH_3)_2CO]$.



Fig. S24. Thermogravimetry curves under nitrogen atmosphere of (a) crystals of $[2 \cdot (H_2O)]$ and (b) crystals of activated $[2 \cdot (H_2O)]$. Crystals of $[2 \cdot (H_2O)]$ were activated at 110 °C for 6 hours.



Fig. S25. PXRD patterns of (a) crystals of $[2 \cdot (H_2O)]$ dried at RT, (b) crystals of activated $[2 \cdot (H_2O)]$, (c) simulated PXRD of the crystal structure of $[2 \cdot (H_2O)]$.



Fig. S26. Thermogravimetry curves under nitrogen atmosphere of (a) crystals of $[(H_43)^{4+}(Br^-)_4 \cdot (H_2O \cdot CH_3OH)]$ and (b) crystals of activated $[(H_43)^{4+}(Br^-)_4 \cdot (H_2O \cdot CH_3OH)]$. Crystals of $[(H_43)^{4+}(Br^-)_4 \cdot (H_2O \cdot CH_3OH)]$ were activated at 110 °C for 6 hours.



Fig. S27. PXRD patterns of (a) crystals of $[(H_43)^{4+} \cdot (Br^-)_4 \cdot (H_2O \cdot CH_3OH)]$ dried at RT, (b) crystals of activated $[(H_43)^{4+} \cdot (Br^-)_4 \cdot (H_2O \cdot CH_3OH)]$, (c) simulated PXRD of the crystal structure of $[(H_43)^{4+} \cdot (Br^-)_4 \cdot (H_2O \cdot CH_3OH)]$.



Fig. S28. Thermogravimetry curves under nitrogen atmosphere of (a) crystals of $[(H_23)^{2+}(Br^{-})_2 \cdot 4H_2O]$ and (b) crystals of activated $[(H_23)^{2+}(Br^{-})_2 \cdot 4H_2O]$. Crystals of $[(H_23)^{2+}(Br^{-})_2 \cdot 4H_2O]$ were activated at 110 °C for 6 hours.



Hirshfeld Surface (HS) analysis 2D fingerprint-plots:

Fig. S29. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of $H \cdots H$ contacts in the crystal structure of [1·(CH₃)₂CO].



Fig. S30. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of $H \cdots O$ contacts in the crystal structure of [$1 \cdot (CH_3)_2 CO$].



Fig. S31. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···C contacts in the crystal structure of $[1 \cdot (CH_3)_2 CO]$.



Fig. S32. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of C···C contacts in the crystal structure of $[1 \cdot (CH_3)_2CO]$.



Fig. S33. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of $H \cdots H$ contacts in the crystal structure of [**2**·H₂O].



Fig. S34. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of $H \cdots Br^-$ contacts in the crystal structure of [**2**·H₂O].



Fig. S35. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of $H^{...}C$ contacts in the crystal structure of [**2**·H₂O].



Fig. S36. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···O contacts in the crystal structure of [**2**·H₂O].



Fig. S37. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of C···C contacts in the crystal structure of $[2 \cdot H_2 O]$.



Fig. S38. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of $H \cdots N$ contacts in the crystal structure of [**2**·H₂O].



Fig. S39. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···H contacts in the crystal structure of $[(3H_4)^{4+} (Br^-)_4 (H_2O \cdot CH_3OH)]$.



Fig. S40. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···Br⁻ contacts in the crystal structure of $[(3H_4)^{4+} (Br^-)_4 (H_2O \cdot CH_3OH)]$.



Fig. S41. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···O contacts in the crystal structure of $[(3H_4)^{4+} \cdot (Br^-)_4 \cdot (H_2O \cdot CH_3OH)]$.



Fig. S42. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···C contacts in the crystal structure of $[(3H_4)^{4+} (Br^-)_4 (H_2O \cdot CH_3OH)]$.



Fig. S43. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···H contacts in the crystal structure of $[(3H_2)^{2+} \cdot (Br^-)_2 \cdot (4H_2O)]$.



Fig. S44. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···Br⁻ contacts in the crystal structure of $[(3H_2)^{2+} \cdot (Br^-)_2 \cdot (4H_2O)]$.



Fig. S45. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···O contacts in the crystal structure of $[(3H_2)^{2+} (Br^-)_2 (4H_2O)]$.



Fig. S46. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of H···C contacts in the crystal structure of $[(3H_2)^{2+} \cdot (Br^-)_2 \cdot (4H_2O)]$.



Fig. S47. Hirshfeld surface 2D fingerprint plot highlighting the relative contribution of C···C contacts in the crystal structure of $[(3H_2)^{2+} \cdot (Br^-)_2 \cdot (4H_2O)]$.

rystal		Atoms	Sur	face Energie	S							
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1	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot			
	1	-	6.39	HF/3-21G	-21.2	2 -8.3	-41.3	60.1	-15.4			
CE-HF	· …	HF/3-21	G electr	on densities		1.019	0.651	0.901	0.811			
-						L. ala	I. and	I. Day	1			
JE-HF		HF/3-21	G electr	on densities		1.019	0.651	0.901	0.811			
CE-B3	LYP	B3LY	P/6-310	(d,p) electron de	nsities	1.05/	0.740	0.8/1	0.618			

Fig. S48. Interaction energy (E_{-} tot) decomposition analysis of [$1 \cdot (CH_3)_2CO$] using Crystal Explorer programme at the HF/3-21G level of theory.

Crystal	Atoms	Sur	tace Energies								
Interactio R is the d Total ene four ener	n Energie istance b rgies, onl gy compo	s (kJ/m etween y report nents, s	ol) molecular centroids ted for two benchm scaled appropriately	s (mea arked / (see 1	n atomi energy i the scale	c positio models, e factor	n) in Å. are the s table bel	sum of t low)	he		
N	Symop	R	Electron Density	E_ele	E_po	E_dis	E_rep	E_tot]		
1	-	6.39	B3LYP/6-31G(d,p)	-28.	1 -4.0	-41.3	80.7	-18.8			
CE-HF CE-B3LY	. HF/3-21 P B3LY	G electr	on densities	sities	1.019	0.651	0.901	0.811			

Fig. S49. Interaction energy (E_{-} tot) decomposition analysis of [$1 \cdot (CH_3)_2CO$] using Crystal Explorer programme at the B3LYP/6-31G(d,p) level of theory.

References

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