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A Supramolecular Approach towards the Construction of Molecular Salts Using Phosphonic Acid and Pyrazole

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Section S1. Single crystal X-ray diffraction data collection, structure solution and refinement procedures:

Single crystal data were collected on performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71070 Å) at 298 K. Suitable size of crystals of all molecular salts reported in the paper was mounted on nylon CryoLoop.

In the reduction of data Lorentz and polarization corrections, empirical absorption corrections were applied.[1] Crystal structures were solved by direct method. Structure solution, refinement and data output were carried out with the SHELXTL program.[2-3] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. Structure was examined using the *ADDSYM* subroutine of *PLATON* [4] to assure that no additional symmetry could be applied to the models.

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A notable feature of the structures reported here is that molecular salts **1-3** crystallize in the non-centrosymmetric space groups $Pca2_1$ (**1**), $P2_1$ (**2**), and $Pca2_1$ (**3**). The structures were refined as twins. In salt **1**, refinement was carried out successfully with the TWIN instruction and Flack parameter[5] in a twin refinement was 0.33(10) with highest peak and deepest hole as 0.19 and -0.25 respectively surmised from Xshell[6] program. For **2**, the crystal structure was refined with the TWIN instruction and Flack parameter refined to 0.03(5) for the selected crystal with highest peak and deepest hole as 0.37 and -0.20 respectively. Some restraints, like EADP[7] was used for atoms C42, N4 and N3 on compound **2** to refine the anisotropic parameters for a better configuration on the structure. Notably, it contains multiple molecules in the crystal asymmetric unit (Z')[8] as Z' = 8. In the crystal structure, some of the tertiary butyl groups found to be disordered and probing the data reveals that there is either a static, or a dynamic disorder, with respect to the conformation of the *tert*-butyl groups[9] leading to some C-level alert. Salt **3** was solved in non-centrosymmetric space group, $Pca2_1$ but initially an attempt was also made in order to solve the same structure in centrosymmetric space group $Pbcm$ as suggested by ADDSYM[10] but latter ended up in high R values. Therefore, salt **3** was solved in non-centrosymmetric space group, $Pca2_1$ and was refined with twin and the Flack parameter was determined to be 0.35(12) with highest peak and deepest hole as 0.36 and -0.33 respectively. In

salt **5**, it was found that the solvent modeling during structure refinement was inaccessible using conventional discrete-atom models because of eminently disordered solvent molecule; consequently, the segment of partial solvent electron densities was overruled by the SQUEEZE[11] program in PLATON and the solvent molecule is tentatively designated based on TGA and SQUEEZE results. The solvent accessible void was found to be 202 $Å^3$ and the squeeze result gave ~28 electrons in its asymmetric unit which corresponds to an ethanol molecule, which was in agreement with the TGA results as well.

_Platon_squeeze_details:

According to the TGA analysis and squeeze results, the asymmetric unit of **5** may consist of one ethanol molecule its asymmetric unit. But the attempt of modeling the solvent molecule was ineffectual as it led to the number of validation alerts due to the disorder. Hence, the electron density was removed by SQUEEZE routine in PLATON to remove the solvent molecule from salt **5**. The molecular formula of salt **5** in Table S1 includes the squeezed solvent molecule (i.e. ethanol molecule).

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loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
  1  0.000 -0.032  0.000    202    56''
  2  0.000 -0.012  0.500    202    56''
```

Lastly in molecular salt **6**, the water oxygen O10, with partial occupancy, was refined isotropically with site occupation factor (s.o.f.) converged to 0.395150. Hence, it shows that salt **6** contains 0.395 (~0.4) molecules of water in its asymmetric unit. However, the addition of hydrogen on the oxygen of the water molecule was not accomplished due to disorder though the molecular formula reported in Table S1 includes the hydrogen of the water molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition Nos. CCDC 980596-980601.

Table S1: Crystallographic data for **1-6**

Parameters	1	2	3	4	5	6
Emprical formula	$C_{34}H_{46}N_8O_6P_2$	$C_{21}H_{44}N_4O_7P_2$	$C_{25}H_{41}N_8O_6P$	$C_{14}H_{23}N_4O_5P$	*$C_{15}H_{30}N_4O_8P_2$	§$C_{23}H_{34.8}N_4O_{9.4}P_3$
Formula weight	724.73	526.51	580.63	358.33	*456.37	§610.66
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pca2_1$	$P2_1$	$Pca2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/ Å	26.1677(10)	11.6984(5)	15.269(3)	10.364(3)	11.4912(9)	11.3768(9)
b/ Å	16.0917(8)	19.7930(8)	8.820(2)	16.227(4)	9.4729(7)	21.2361(15)
c/ Å	8.6296(4)	25.4741(11)	21.635(5)	11.093(3)	22.7526(18)	12.4255(9)
α/ º	90	90	90	90	90	90
β/ º	90	92.012(2)	90	102.843(12)	118.245(4)	100.766(4)
γ/ º	90	90	90	90	90	90
V / Å³	3633.8(3)	5894.8(4)	2913.6(11)	1818.9(8)	2181.8(3)	2949.1(4)
Z	4	8	4	4	4	4
$Dcalc$ (g cm⁻³)	1.325	1.186	1.324	1.309	1.389	1.375
F000	1536	2271.9	1240	760	968.0	1281.4
μ/mm⁻¹	0.175	0.189	0.148	0.182	0.247	0.258
Flack parameter	0.33(10)	0.03(5)	0.35(12)	-	-	-
θ range/ º	1.27 - 28.29	1.30 - 25.00	1.88 - 28.46	2.02 - 25.00	2.01 - 26.41	1.82 - 26.47
Reflections collected/ Independent reflections	62864/8834	65075/19847	47141/7288	22721/3197	31105/4462	35500/6042
Parameters/Restraints	463/1	1270/1	374/1	223/0	241/0	365/0
Ranges (h,k,l)	-27< h <34 -21≤ k ≤21 -11≤ l ≤11	-11< h <13 -23≤ k ≤23 -30≤ l ≤30	-20< h <20 -10≤ k ≤11 -28≤ l ≤28	-12< h <12 -19≤ k ≤19 -13≤ l ≤12	-12< h <14 -11≤ k ≤11 -28≤ l ≤27	-14< h <14 -26≤ k ≤25 -15≤ l ≤15
GOF (F^2)	1.000	0.995	0.933	1.082	1.056	0.916
$R1$; w$R2$ [I >2σ(I)]	0.0494; 0.1125	0.0485; 0.1033	0.0541; 0.1342	0.0368; 0.1236	0.0759; 0.2319	0.0581; 0.1338
$R1$; w$R2$ (all data)	0.1077; 0.1441	0.0888; 0.1211	0.0858; 0.1532	0.1719; 0.1534	0.1032; 0.2439	0.1468; 0.1821
CCDC No.	980599	980601	980598	980600	980597	980596
Temperature (K)	296(2)	296(2)	100(2)	296(2)	296(2)	296(2)

Note: The contribution of squeezed solvent molecule* (i.e. ethanol, C_2H_5OH) and hydrogen§ of the water molecule has been included in salt **5** and salt **6** respectively.

Elemental analysis and IR data:

[HPPA⁻.H₂PPA.HMBPz⁺.MBPz] (1): Elemental analysis calcd (%) for $C_{34}H_{46}N_8O_6P_2$: C, 56.35; H, 6.40; N, 15.46. Found: C, 56.26; H, 6.53; N, 15.55. IR (ν/cm⁻¹): 3406(br,m), 3134(m), 2919(m), 2862(m), 2384(w), 1697(w), 1597(m), 1447(m), 1297(s), 1139(m), 932(m), 753(m), 696(m), 560(m), 531(w).

[(HtBPA⁻)₂.H₂MBPz²⁺.EtOH] (2): Elemental analysis calcd (%) for $C_{21}H_{44}N_4O_7P_2$: C, 47.90; H, 8.42; N, 10.64. Found: C, 47.82; H, 8.59; N, 10.50. IR (ν/cm⁻¹): 3199(w), 3085(m), 2985(w), 2327(w), 1590(m), 1518(m), 1469(w), 1382(m), 1297(s), 1197(m), 996(m), 839(w), 739(m), 653(m).

[HPAA⁻.HMBPz⁺.MBPz.MeOH] (3): Elemental analysis calcd (%) for $C_{25}H_{41}N_8O_6P$: C, 51.72; H, 7.12; N, 19.30. Found: C, 51.85, H, 7.21; N, 19.42. IR (ν/cm⁻¹): 3192(w), 3078(m), 2927(w), 1726(s), 1583(m), 1518(w), 1433(m), 1290(s), 1061(s), 932(m), 867(m), 753(w), 589(m), 482(m).

[HPPRA⁻.HMBPz⁺] (4): Elemental analysis calcd (%) for $C_{14}H_{23}N_4O_5P$: C, 46.93; H, 6.47; N, 15.64. Found: C, 46.81; H, 6.39; N, 15.78. IR (ν/cm⁻¹): 3156(w), 3092(m), 2927(w), 2877(w), 2348(w), 1712(s), 1597(w), 1525(m), 1411(br,m), 1261(w), 1204(w), 1125(w), 1018(w), 932(w), 789(m), 739(s), 503(m).

[H₂EA²⁻.H₂MBPz²⁺.S] (5): Elemental analysis calcd (%) for $C_{15}H_{30}N_4O_8P_2$: C, 39.48; H, 6.63; N, 12.28. Found: C, 39.15; H, 6.85; N, 12.69. (Note: S is considered to be ethanol as per deduced by TGA analysis). IR (ν/cm⁻¹): 3385(br,w), 3034(w), 2920(s), 2350(w), 1640(w), 1590(w), 1454(m), 1268(w), 1146(br,w), 1003(w), 925(w), 811(w), 775(w), 631(w), 517(w), 453(w).

[H₃DPA⁻.(H₂DPA²⁻)₀.₅.H₂MBPz²⁺.(H₂O)₀.₄] (6): Elemental analysis calcd (%) for $C_{23}H_{34.8}N_4O_{9.4}P_3$: C, 45.24; H, 5.74; N, 9.17. Found: C, 45.69; H, 5.43; N, 9.34. IR (ν/cm⁻¹): 3399(w), 3192(w), 3134(m), 2920(w), 2355(w), 1597(m), 1511(m), 1425(m), 1368(w), 1250(m), 1268(w), 1125(w), 989(m), 939(m), 832(w), 785(w), 567(w), 482(w).

The characteristic IR absorption band in salts **1-6** with medium intensity of -N⁺–H appeared in the range of 3190-2910 cm⁻¹ and that of –O–H lies in the range of 3110-3400 cm⁻¹ corresponding to the hydrogen bonding O–H [Figure S1-S2]. Moreover, the absorption band in the range of 1297-1250, 989-925, 790-740 cm⁻¹ exemplifies the presence of P=O, P(OH) and P–C respectively in salts **1-6**.

Table S2. Various synthons involved in salts 1-6

Salts	Synthon		D–H···A	Bond length
1	Homodimer	I ($R_2^2(8)$)	O2–H2E···O4	1.73 Å
			O6–H6E···O3	1.74 Å
	Heterotrimer	IXa ($R_3^3(10)$)	N8–H8D···N1	2.03 Å
			N2–H2D···O3	1.92 Å
			O1–H1E···N7	1.71 Å
	Charge assisted Heterotrimer	IXb ($R_3^3(10)$)	N4$^+$–H4D···O5$^-$	1.68 Å
			N3–H3D···N5	2.00 Å
			N6–H6D···O4	1.94 Å
2	Charge assisted Heterotrimer	VI ($R_3^2(9)$)	N8–H8D···O6	1.81 Å
			N7$^+$–H7D···O2$^-$	1.67 Å
			O1–H1E···O6	1.81 Å
		VI ($R_3^2(9)$)	O7–H7E···O12	1.81 Å
			N14–H14D···O12	1.82 Å
			N13$^+$–H13D···O8$^-$	1.69 Å
		VI ($R_3^2(9)$)	O21–H21E···O22	1.75 Å
			N4–H4D···O22	1.86 Å
			N3$^+$–H3D···O20$^-$	1.65 Å
		VI ($R_3^2(9)$)	O15–H15E···O17	1.73 Å
			N9$^+$–H9D···O14$^-$	1.67 Å
			N10–H10D···O17	1.88 Å
	Charge assisted Heterotetramer	VIII ($R_4^3(11)$)	O26–H26E···O9	1.90 Å
			N6–H6D···O9	1.80 Å
			N5$^+$–H5D···O5$^-$	1.69 Å
			O4–H4E···O26	1.85 Å
		VIII ($R_4^3(11)$)	O28–H28E···O3	1.93 Å

			N16–H16D···O3	1.81 Å
			N15$^+$–H15D···O11$^-$	1.69 Å
			O10–H10E···O28	1.83 Å
		VIII (R$^3_4$(11))	O25–H25E···O13	1.93 Å
			O24–H24E···O25	1.83 Å
			N1$^+$–H1D···O23$^-$	1.64 Å
			N2–H2D···O13	1.82 Å
		VIII (R$^3_4$(11))	O27–H27E···O19	1.85 Å
			N12–H12D···O19	1.79 Å
			N11$^+$–H11D···O18$^-$	1.64 Å
			O16–H16E···O27	1.75 Å
3	Heterotrimer	IX a (R$^3_3$(10))	N5–H5D···N4	2.06 Å
			O1–H1E···N6	1.81 Å
			N3–H3D···O2	1.89 Å
	Charge assisted Heterotrimer	VII (R$^2_3$(8))	N8$^+$–H8D···O3$^-$	1.86 Å
			N1–H1D···N7	1.83 Å
			N2$^+$–H2D··· O3$^-$	1.74 Å
	Catemer	II	O4–H4Z···O6	1.77 Å
			O6–H6···O2	1.84 Å
4	Homodimer	I (R$^2_2$(8))	O1–H1E···O2	1.79 Å
	Discrete synthon	III D(2)	O5–H5Z···O3$^-$	1.80 Å
	Discrete synthon	IV D(2)	N1$^+$–H1D···O3$^-$	1.77 Å
	Discrete synthon	V D(2)	N2–H2D···N4	1.90 Å
5	Charge assisted Heterotrimer	VI (R$^2_3$(9))	N2$^+$–H2D···O4$^-$	1.72 Å
			N1–H1D···O2	1.84 Å
			O5–H5E···O2	1.73 Å
		VI (R$^2_3$(9))	N4$^+$–H4D···O1$^-$	1.72 Å
			N3–H3D···O6	1.91 Å

			O3–H3E···O6	1.81 Å
	Discrete synthon	**X D(2)**	O7–H7Z···O6	1.95 Å
	Catemer	**XI**	O5–H5E···O2	1.73 Å
			O3–H3E···O6	1.81 Å
6	**Charge assisted Heterotrimer**	**VI (R^2_3(9))**	$N2^+$–H2D···$O7^-$	1.78 Å
			N1–H1D···O1	1.74 Å
			O2–H2E···$O7^-$	1.79 Å
	Charge assisted Heterotrimer	**VI (R^2_3(9))**	N3–H3D···O9	1.78 Å
			$N4^+$–H4D···$O6^-$	1.79 Å
			O8–H8E···$O6^-$	1.78 Å
	Charge assisted Heterotetramer	**XII (R^4_4(12))**	O2–H2E···$O7^-$	1.79 Å
			O5–H5E···O9	1.75 Å
			O5···O10	2.81 Å
			O3···O10	2.78 Å
	Charge assisted Heterotetramer	**XIII (R^4_4(16))**	O8–H8E···$O6^-$	1.78 Å
			O5–H5E···O9	1.75 Å

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9 **Table S3**. **Non-covalent interactions and angles for 1-6 (Å and º):**

D-H···A	d(D-H)	d(H-A)	d(D-A)	<(DHA)>	Symmetery codes
1					
O2–H2E···O4	0.81	1.73	2.54(3)	170	x-1/2,-y+1,+z+1
O6–H6E···O3	0.81	1.74	2.56(3)	175	x+1/2,-y+1,+z-1
O1–H1E···N7	0.82	1.71	2.51(4)	165	x,+y-1,+z+1
N4$^+$–H4D···O5$^-$	0.86	1.68	2.52(4)	164	-
N2–H2D···O3	0.86	1.92	2.77(3)	169	x,+y,+z-1
N6–H6D···O4	0.86	1.94	2.78(4)	165	-
N3–H3D···N5	0.86	2.03	2.88(3)	168	-
N8–H8D···N1	0.86	2.09	2.92(3)	162	x,+y+1,+z
2					
N1$^+$–H1D···O23$^-$	0.86	1.64	2.49(6)	168	-x+2,+y+1/2,-z+1
N2–H2D···O13	0.85	1.82	2.63(4)	156	x+1,+y,+z
N3$^+$–H3D···O20$^-$	0.86	1.67	2.51(5)	164	-x+1,+y+1/2,-z+1
N4–H4D···O22	0.86	1.93	2.72(6)	152	-x+1,+y+1/2,-z+1
N5$^+$–H5D···O5$^-$	0.85	1.69	2.51(5)	159	-
N6–H6D···O9	0.85	1.80	2.60(4)	153	-
N7$^+$–H7D···O2$^-$	0.85	1.68	2.53(4)	169	x-1,+y,+z
N8–H8D···O6	0.86	1.84	2.68(5)	163	x-1,+y,+z
N9$^+$–H9D···O14$^-$	0.85	1.67	2.52(5)	167	x+1,+y,+z
N10–H10D···O17	0.85	1.95	2.74(6)	151	x+1,+y,+z
N11$^+$–11D···O18$^-$	0.85	1.64	2.50(5)	177	-
N12–H12D···O19	0.86	1.82	2.65(4)	160	-x+1,+y-1/2,-z+1
N13$^+$–H13D···O8$^-$	0.86	1.69	2.53(4)	166	-
N14–H14D···O12	0.86	1.84	2.68(5)	162	-
N15$^+$–H15D···O11$^-$	0.85	1.65	2.52(5)	160	x-1,+y,+z

N16–H16D···O3	0.86	1.81	2.61(4)	152	x-1,+y-1,+z
O25–H25E···O13	0.82	1.93	2.74(5)	166	-
O24–H24E···O25	0.82	1.85	2.65(4)	166	-x+1,+y-1/2,-z+1
O26–H26E···O9	0.82	1.90	2.72(5)	179	-
O4–H4E···O26	0.81	1.85	2.66(4)	169	-
O28–H28E···O3	0.82	1.93	2.73(4)	164	-
O10–H10E···O28	0.81	1.83	2.64(4)	168	x,+y-1,+z
O27–H27E···O19	0.82	1.90	2.67(5)	155	-x+1,+y+1/2,-z+1
O16–H16E···O27	0.82	1.79	2.57(4)	156	x,+y-1,+z
O1–H1E···O6	0.82	1.85	2.63(3)	158	-
O7–H7E···O12	0.82	1.82	2.63(3)	167	-
O15–H15E···O17	0.82	1.77	2.57(4)	167	-
O21–H21E···O22	0.82	1.81	2.57(4)	153	-
C25–H25A···N12	0.95	2.64	3.48(7)	147	-x+1,+y+1/2,-z+1
C70–H70A···O10	0.95	2.50	3.45(6)	169	-
C60–H60B···O11	0.97	2.63	3.55(5)	158	-
C38–H38A···O5	0.96	2.62	3.50(5)	149	-
C44–H44B···O8	0.95	2.41	3.35(4)	169	-
C19–H19B···O17	0.96	2.71	3.49(7)	139	-
3					
N5–H5D···N4	0.86	2.07	2.92(4)	168	-
N3–H3D···O2	0.86	1.89	2.74(3)	166	-
N1–H1D···N7	0.86	1.87	2.69(4)	160	x+1,+y,+z
O1–H1E···N6	0.81	1.85	2.63(3)	157	-
N8–H8D···O3$^-$	0.86	1.86	2.72(4)	148	-x+1/2,+y,+z-1/2
N2$^+$–H2D···O3$^-$	0.86	1.78	2.60(4)	157	-x+1/2+1,+y,+z-1/2
O6–H6C···O2	0.81	1.84	2.63(3)	161	-

O4–H4Z⋯O6	0.82	1.77	2.57(4)	161	x,+y+1,+z
4					
N1$^+$–H1D⋯O3$^-$	0.85	1.77	2.63(8)	174	x,-y+1/2,+z-1/2
N2–H2D⋯N4	0.86	1.93	2.76(8)	162	-x,+y-1/2,-z+1/2
N3–H3D⋯O2	0.86	1.98	2.79(5)	158	x,+y+1,+z
O5–H5Z⋯O3$^-$	0.82	1.80	2.59(7)	163	x,-y+1/2,+z-1/2
O1–H1E⋯O2	0.82	1.79	2.61(9)	173	-x+1,-y,-z+1
C9–H9B⋯O4	0.97	2.67	3.64(5)	178	-x,-y+1,-z+1
C8–H8C⋯O4	0.96	2.41	3.35(12)	163	-x,-y+1,-z+1
5					
N2$^+$–H2D⋯O4$^-$	0.85	1.72	2.55(7)	161	-x,+y+1/2,-z+1/2
N1–H1D⋯O2	0.86	1.88	2.70(9)	156	x-1,+y+1,+z
O3–H3E⋯O6	0.82	1.81	2.63(5)	161	-x+1,+y+1/2,-z+1/2
O7–H7Z⋯O6	0.82	2.02	2.77(5)	151	-x+1,+y+1/2,-z+1/2
N3–H3D⋯O6	0.86	1.94	2.77(8)	172	-x+1,-y+1,-z+1
N4$^+$–H4D⋯O1$^-$	0.86	1.74	2.58(7)	165	x,-y+1/2+1,+z+1/2
O5–H5E⋯O2	0.82	1.73	2.54(4)	168	-x+1,+y+1/2,-z+1/2
C8–H8A⋯O4	0.96	2.43	3.35(7)	157	x,+y+1,+z
C9–H9B⋯O5	0.96	2.49	3.39(11)	155	-x+1,-y+1,-z+1
C1–H1B⋯ O5	0.96	2.61	3.43(7)	143	-x+1,+y-1/2,-z+1/2
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O2–H2E⋯O7$^-$	0.81	1.79	2.59(4)	166	-
N1–H1D⋯O1	0.86	1.78	2.60(4)	156	-
N2$^+$–H2D⋯O7$^-$	0.86	1.78	2.64(7)	154	-
N4$^+$–H4D⋯O6$^-$	0.86	1.79	2.61(6)	160	-x+2,+y-1/2,-z+3/2
N3–H3D⋯O9	0.86	1.78	2.63(6)	167	x+1,+y,+z
O8–H8E⋯O6$^-$	0.82	1.78	2.57(3)	161	-x+1,+y-1/2,-z+3/2

O3–H3E···O4	0.81	1.63	2.42(4)	163	x-1,+y,+z
O5–H5E···O9	0.82	1.75	2.54(5)	162	x+1,-y+1/2,+z+1/2
C18–H18B···O1	0.97	2.61	3.55(5)	164	-x+1,-y,-z+2
C17–H17B···O8	0.96	2.41	3.33(5)	159	-x+1,-y,-z+2
C8–H8B···O10	0.97	2.67	3.39(11)	131	x,-y+1/2,+z+1/2
C9–H9B···O4	0.96	2.60	3.57(5)	150	x-1,-y+1/2,+z-1/2
C13–H13B···O8	0.96	2.67	3.57(7)	157	-
C23–H23B···O3	0.96	2.65	3.40(6)	135	-x+1,-y,-z+2
O10–O3	-	-	2.78(12)	-	-
O5–O10	-	-	2.81(11)	-	-

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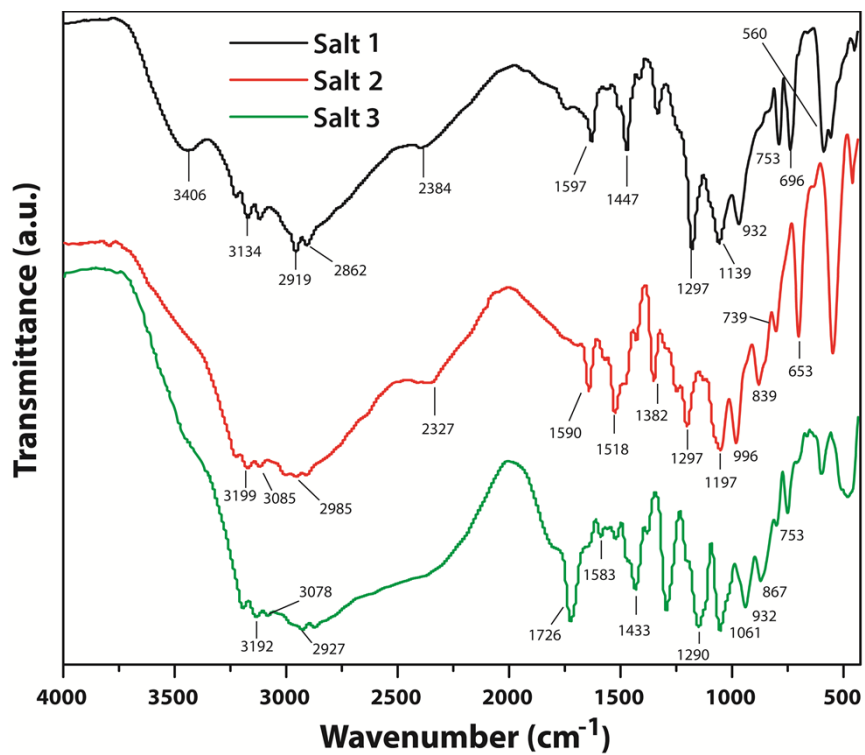
Figure S1. Infra-red spectra of salts **1-3**

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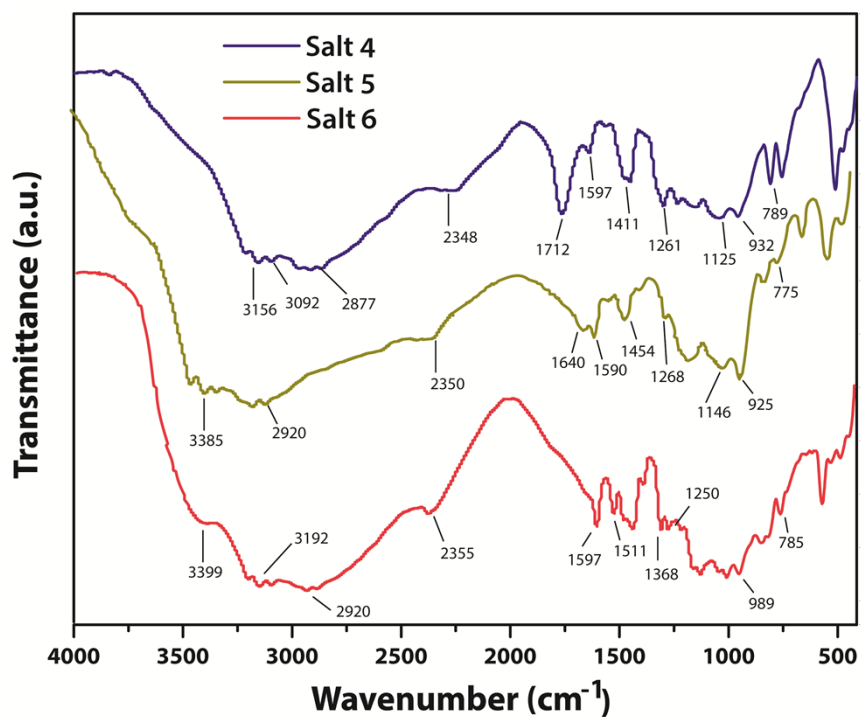
Figure S2. Infra-red spectra of salts **4-6**
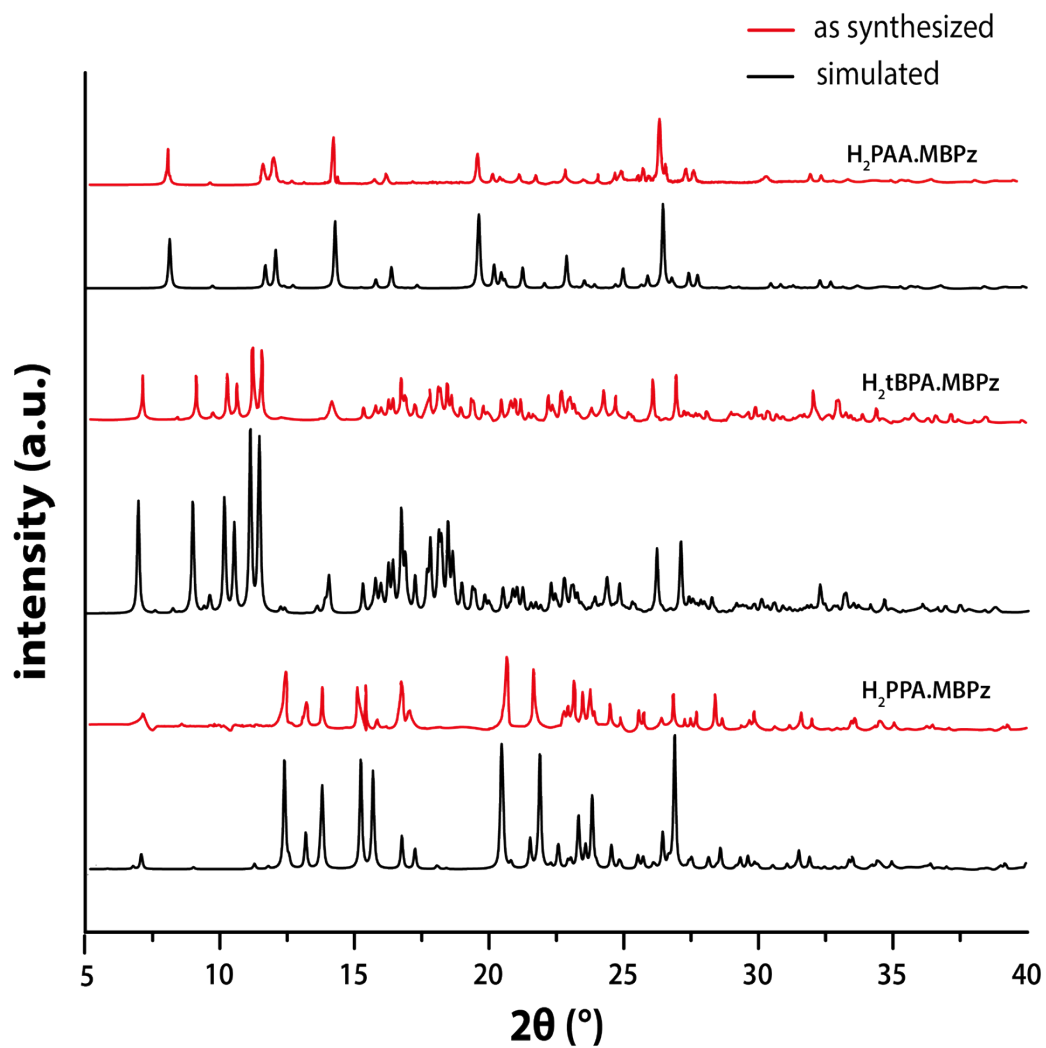
Figure S3. Comparison of as-synthesized PXRD pattern of salts **1-3** with simulated one
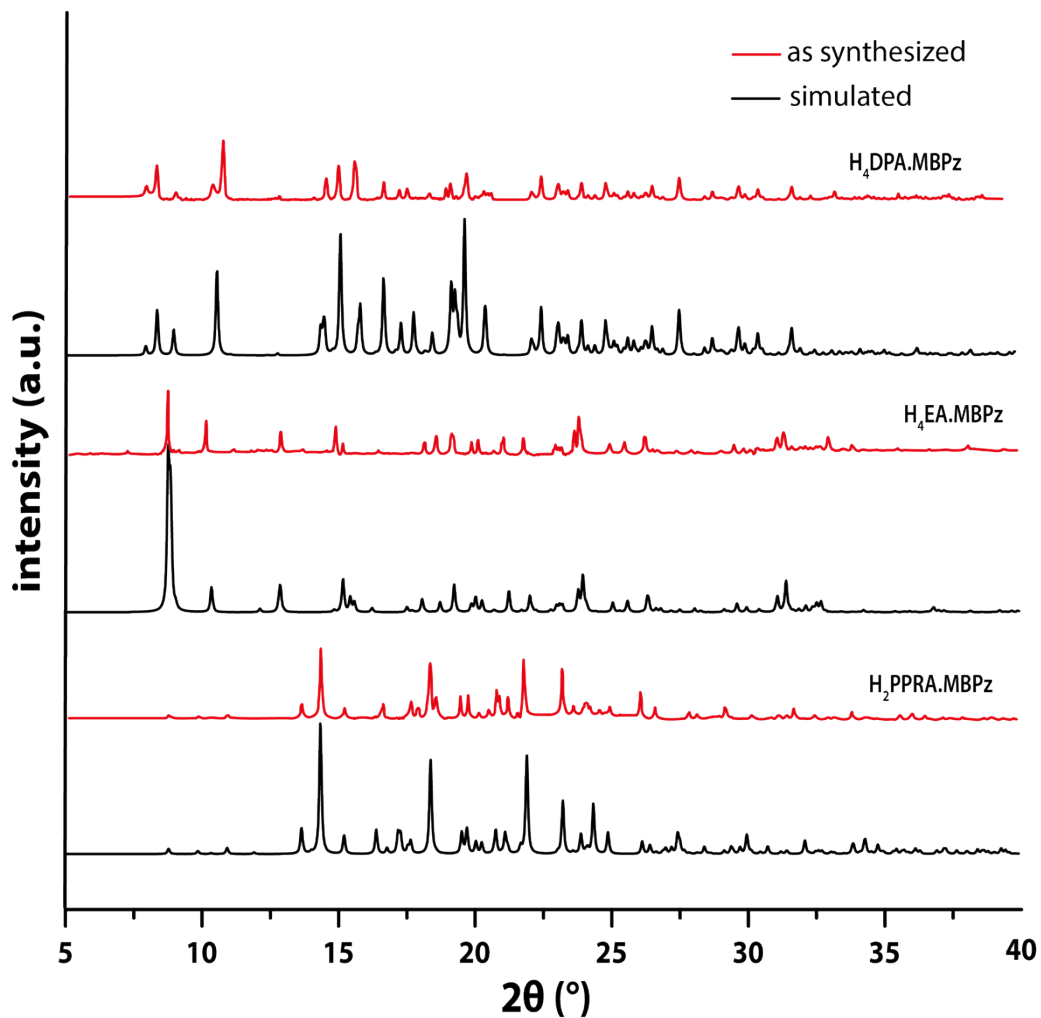
Figure S4. Comparison of as-synthesized PXRD pattern of salts **4-6** with simulated one
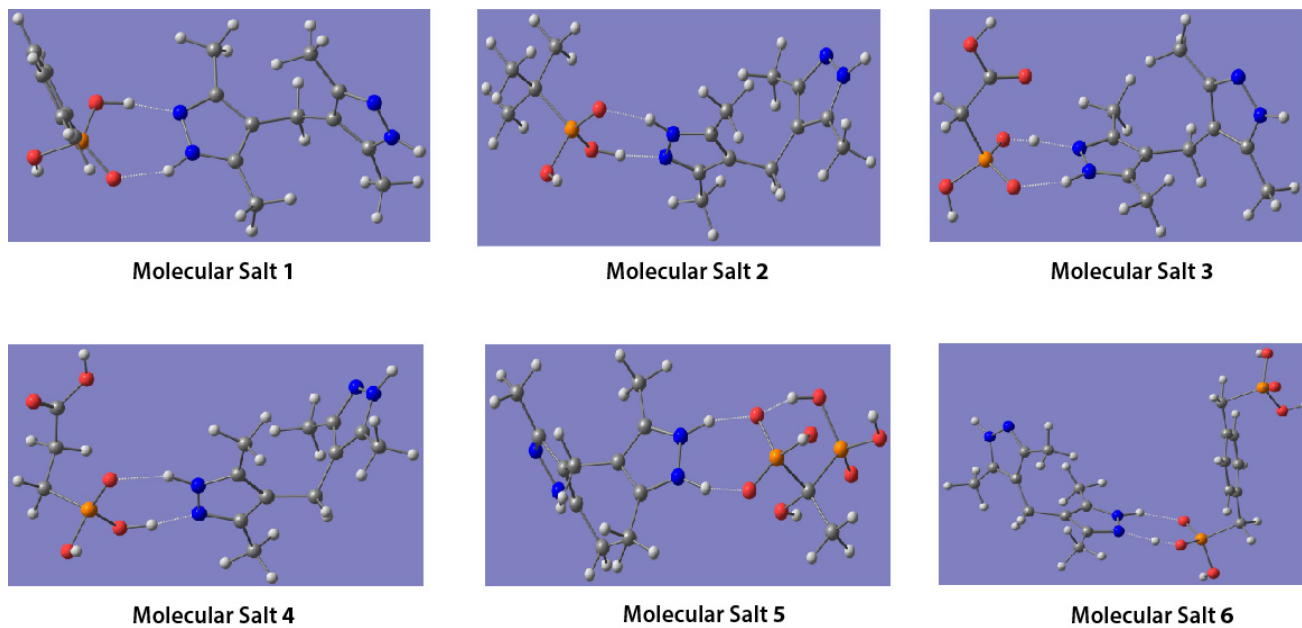
Figure S5. Optimized geometries of salts **1- 6** deduced from Gaussian program
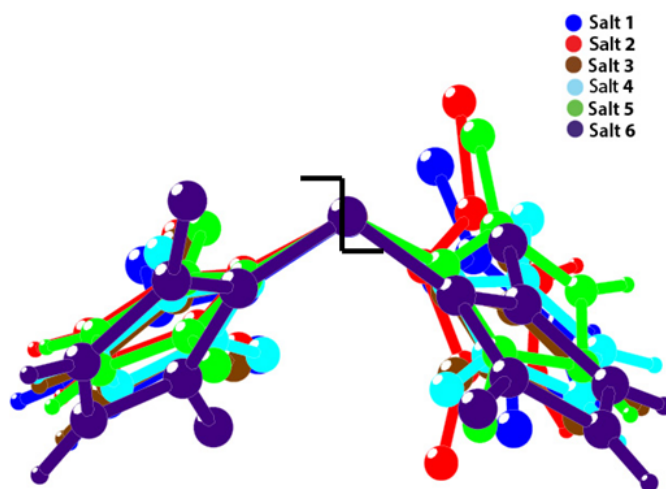
Figure S6. Conformations of MBPz in salts **1- 6**

Table S4: Trend of Torsion angle in MBPz in salts **1-6** (°)

Salt	Torsion angle in MBPz (°)
Salt **1**	76.88(0.38)
Salt **2**	63.02(0.49)/120.69(0.42)
Salt **3**	74.19(0.37)
Salt **4**	69.92(0.30)
Salt **5**	77.93(0.83)
Salt **6**	60.11(0.49)

*Note: (s.u. following Cruickshank, Internat. Tables, II, 1959, p.331)

Table S5: Trend of hydrogen bond interaction energy in salts **1-6** (Kcal/mol)

Salt No.	Salt	Hydrogen bond interaction energy (Kcal/mol)
1.	$[HPPA^-.H_2PPA.HMBPz^+.MBPz]$	-21.96
2.	$[(HtBPA^-)_2.H_2MBPz^{2+}.EtOH]$	-22.59
3.	$[HPAA^-.HMBPz^+.MBPz.MeOH]$	-21.34
4.	$[HPPRA^-.HMBPz^+]$	-21.96
5.	$[H_2EA^{2-}.H_2MBPz^{2+}.S]$	-20.08
6.	$[H_3DPA^-.(H_2DPA^{2-})_{0.5}.H_2MBPz^{2+}.(H_2O)_{0.4}]$	-27.80

Table S6: Trend of hydrogen bond interaction energy in synthons (Kcal/mol)

Synthon	Description, R^a_d (n)	Hydrogen bond interaction energy (Kcal/mol)
I	Dimer of phosphonic acid, $R_2^2(8)$	-27.17
VI	Two phosphonic groups and one pyrazole, $R^2_3(9)$	-40.79
VII	Two pyrazoles and one phosphonic group, $R^2_3(8)$	-30.67
IXa	Two pyrazoles and one phosphonic group, $R^3_3(10)$	-36.41
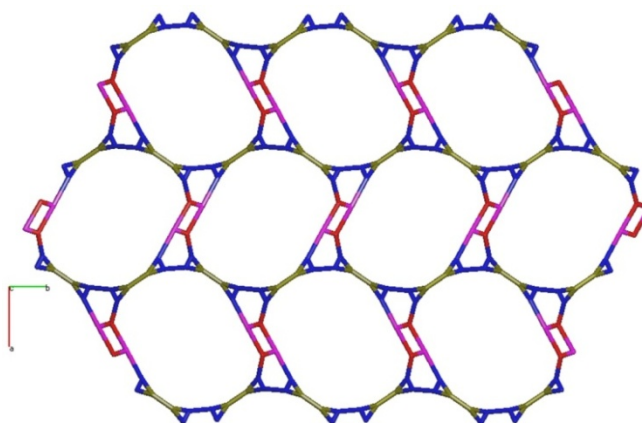
Figure S7: Simplified representation of 2D layer; produced by TOPOS of **1**
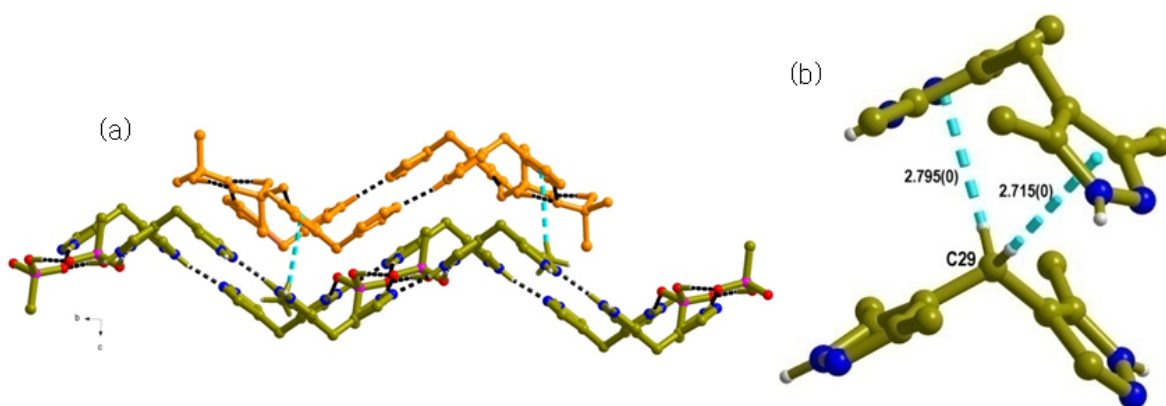
Figure S8: (a) Side view of 2D sheets in *bc*-plane; (b) Representation of C−H···π interaction in salt **1**

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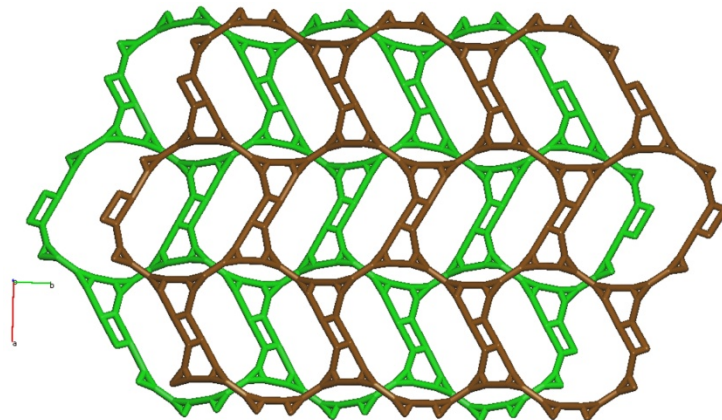
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2   **Figure S9:** Packing of adjacent layers by TOPOS (top view) in salt **1**
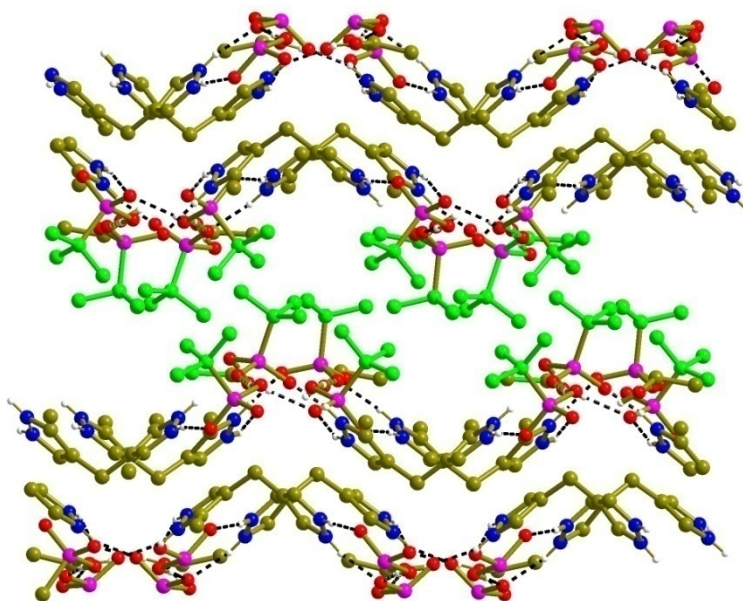

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4   **Figure S10**: Stacking of the adjacent layer of 2D sheets with tertiary butyl group in between the
5   stacked layers along *b*-axis (tertiary butyl groups are shown in green color) in salt **2**
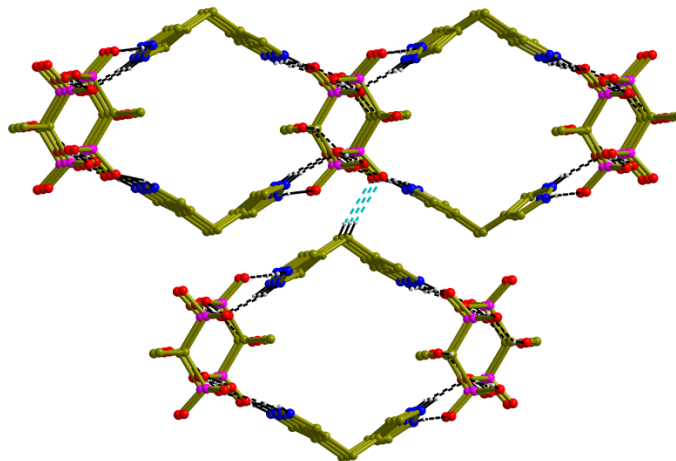
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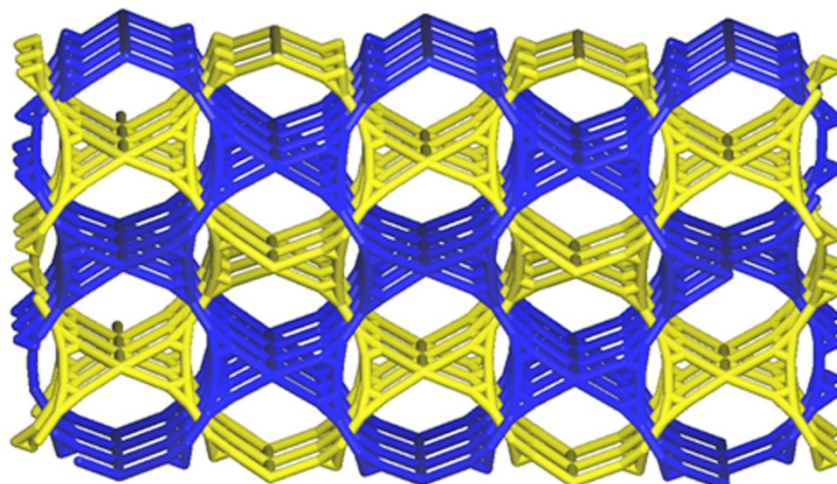
Figure S11: Simplified representation of entanglement of two networks due to slipped packing of adjacent layers, the two networks are shown in blue and yellow color (top view) produced by TOPOS in salt **3**

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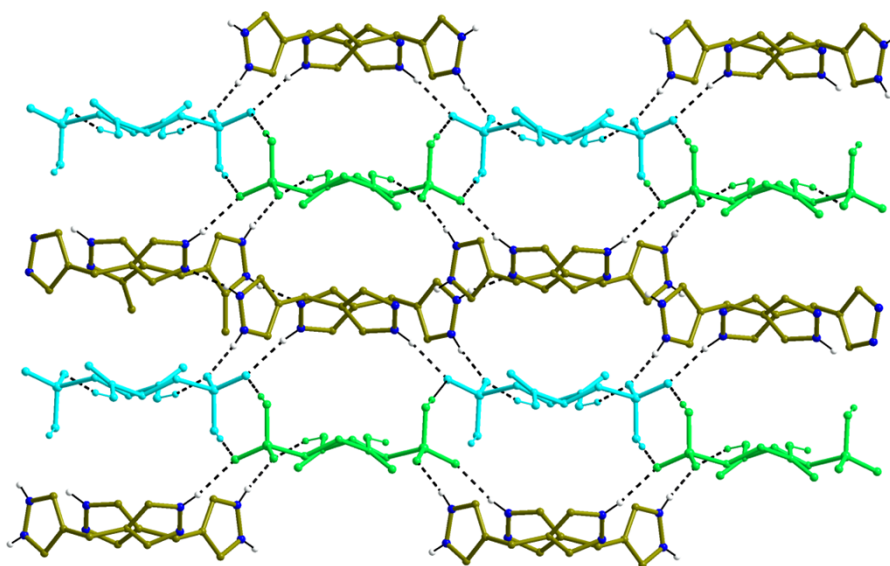
Figure S12: View of 3D supramolecular hydrogen bonded network representing troughs (in green) and crests (in blue) in salt **4**
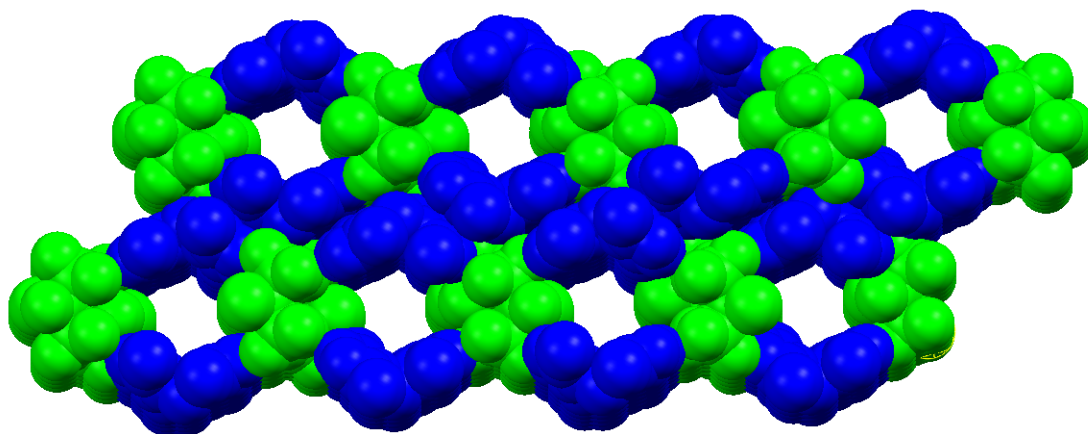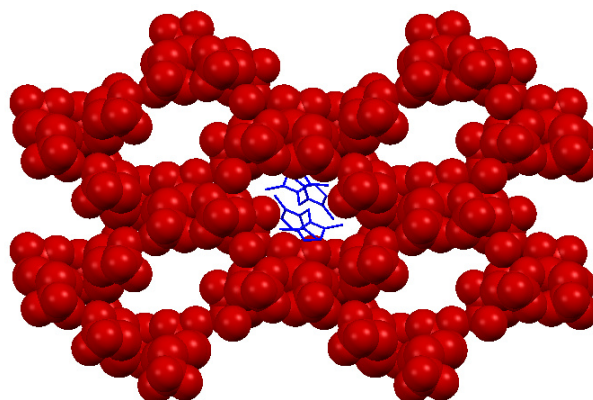
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Figure S13: Representation of C−H⋯π Interaction, responsible for extension of 2D to 3D network in salt 5
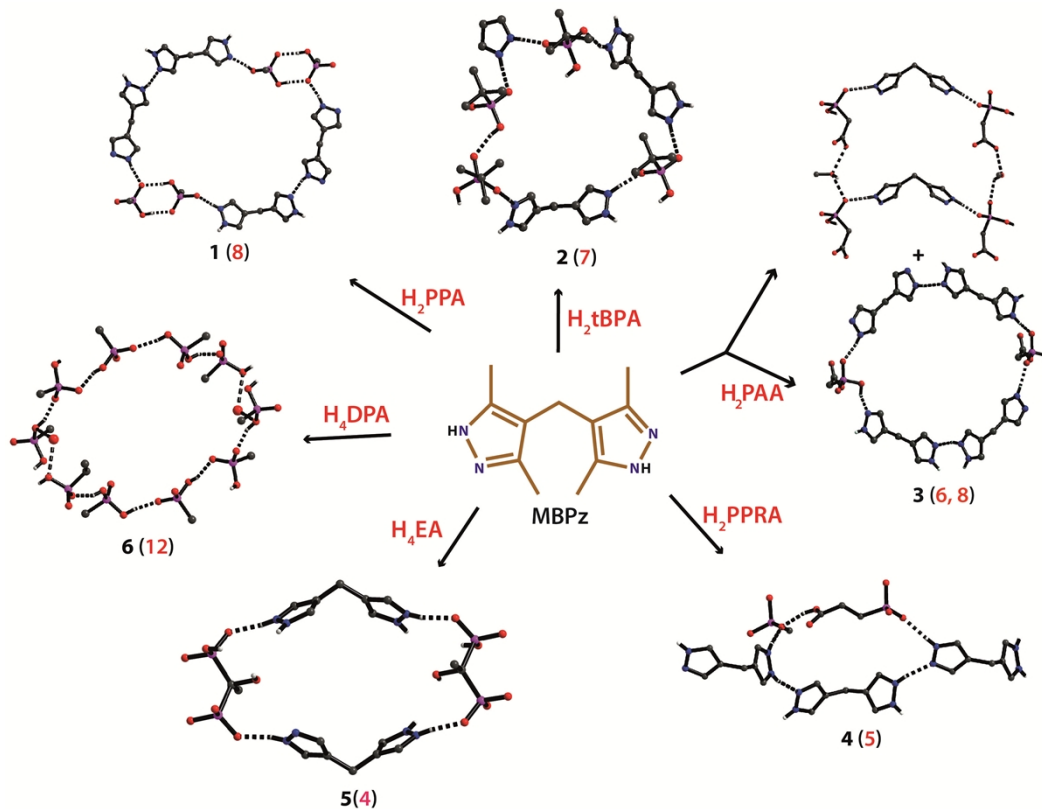

Figure S14: View of 2D supramolecular hydrogen bonded network in salt 5

Figure S15: View of 2D supramolecular hydrogen bonded network in salt 6

Scheme S1: Illustration of structural unit (hydrogen bonded ring) formed in salts **1-6**. Note: the number in bracket represents the number of molecules involved in the ring

References:

1. G. M. Sheldrick, SADABS, 1996**,** University of Göttingen. Göttingen, Germany.

2. G. M. Sheldrick, *Acta Cryst.*, 1990, **A46**, 467-473.

3. G. M. Sheldrick, SHELXTL-NT 2000 version 6.12, reference manual, University of Göttingen, Göttingen, Germany.

4. A. L. Spek, "PLATON, *A Multipurpose Crystallographic Tool*", **2005**, Utrecht University, Utrecht, The Netherlands.

5. H. D. Flack, *Acta Cryst.*, 1983, **A39**, 876-881.

6. Bruker, 2010. *APEX2*, *SAINT*, *SADABS* and *XSHELL*. *Bruker AXS Inc.*, Madison, Wisconsin, USA.

7. G. M. Sheldrick, SHELXL-93, "A Program for the Refinement of Crystal Structures".

8. (a) J. W. Steed, *CrystEngComm*, 2003, **5**, 169-179; (b) K. M. Anderson, A. E. Goeta and J. W. Steed, *Cryst. Growth Des.*, 2008, **8**, 2517-2524; (c) K. M. Anderson and J. W. Steed, *CrystEngComm*, 2007, **9**, 328-330.

9. F. Aguilar-Parrilla, H.-H. Limbach, C. Foces-Foces, F.H. Cano, N. Jagerovic and J. Elguero, *J. Org. Chem.*, 1995, **60**, 1965-1970.

10. *Gemini, v1.02, Autoindexing program for twinned crystals*, Bruker AXS, Inc., Madison, WI, 2000.

11. A. L. Spek, "PLATON/SQUEEZE—an effective tool for taking the contribution of disordered solvent into account in crystal structure refinement", 2004, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.