Supplementary Material (ESI) for CrystEngComm

Supporting Information

Exceptions to the rule: new hydrogen bonded networks from an old reliable

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General Information

All reagents were obtained from Aldrich (Milwaukee, WI) or Alfa Aesar (Ward Hill, MA) and used without further purification unless otherwise stated. Single crystal X-ray diffraction data was obtained on an APEX II or a SMART APEX II diffractometer at 100 K unless otherwise stated. Powder x-ray diffraction (PXRD) was obtained on a Rigaku Ultima-IV diffractometer under ambient conditions. Melting points were determined on a Thermo-Scientific Mel-Temp apparatus, while Infra-red spectra were collected using a Thermo Nicolet Avatar 380 FT-IR.

Note: PXRD data is not reported for hexane-1,6-diammonium•$(HPzDCA)_2$, compound **7**, as sufficient quantities of a pure phase could not be obtained.

Compound **1**: *o*-ethoxyanilinium•HPzDCA

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 3:2 EtOH-H_2O mixture. To this solution was then added 54.9 mg (52.2 µl, 0.40 mmol) of *o*-ethoxyanilne. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of *o*-ethoxyanilinium•HPzDCA (65.0 mg, 56% yield), mp 218-220 ˚C.

Compound **2**: *o*-ethylanilinium•HPzDCA•H_2O

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of MeOH. To this solution was then added 48.5 mg (49.3 µl, 0.40 mmol) of *o*-ethylaniline. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of *o*-ethylanilinium•HPzDCA•H_2O (36.8 mg, 33 % yield), mp 207-209 ˚C.

Compound **3**: 2,6-diethylanilinium•HPzDCA •H_2O

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 3:2 MeOH-H_2O mixture. To this solution was then added 59.7 mg (66.0 µl, 0.40 mmol) of 2,6-diethylaniline. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of 2,6-diethylanilinium•HPzDCA •H_2O (73.5 mg, 60 % yield), mp 253-255 ˚C.

Compound **4**: 2-Isopropylanilinium•HPzDCA

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a MeOH. To this solution was then added 54.1 mg

(56 µl, 0.40 mmol) of 2-isopropylaniline. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of 2-Isopropylanilinium•HPzDCA (56.3 mg, 47 % yield), mp 173-175 ˚C.

Compound **5**: 1,4-bis(2-hydroxyethyl)piperazinium•$(HPzDCA)_2$

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 4:1 MeOH-H_2O mixture. To this solution was then added 70.0 mg (0.40 mmol) of 1,4-bis(2-hydroxyethanol)piperazine. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of 1,4-bis(2-hydroxyethyl)piperazinium•HPzDCA (96.7 mg, 73 % yield), mp 250-252 ˚C.

Compound **6**: $TMEDAH_2$•$(HPzDCA)_2$

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of MeOH. To this solution was then added 46.5 mg (60.0 µl, 0.40 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of $TMEDAH_2$•HPzDCA (74.1 mg, 68 % yield), mp 284-286 ˚C.

Compound **7**: Hexane-1,6-diamonium•$(HPzDCA)_2$

A 20 ml scintillation vial was charged with 70.0 mg (0.40 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate, which was dissolved in 5.0 ml of a 3:2 MeOH-H_2O mixture. To this solution was then added 46.5 mg (52.2 µl, 0.40 mmol) of 1,6-diaminohexane. The mixture was filtered and the filtrate was allowed to slowly evaporate to yield colorless single crystals of hexane-1,6-diammonium•$(HPzDCA)_2$ (8.74 mg, 8 % yield), mp 134-136 ˚C.

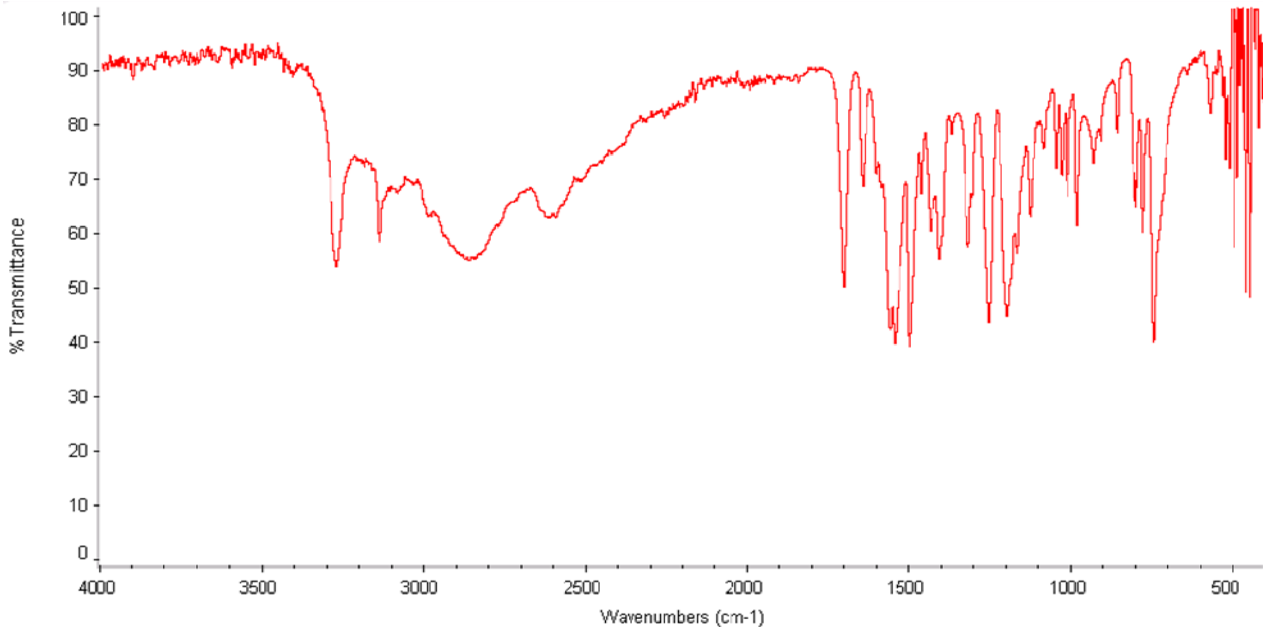

Figure S1. Infra-Red spectrum of *o*-ethoxyanilinium•HPzDCA

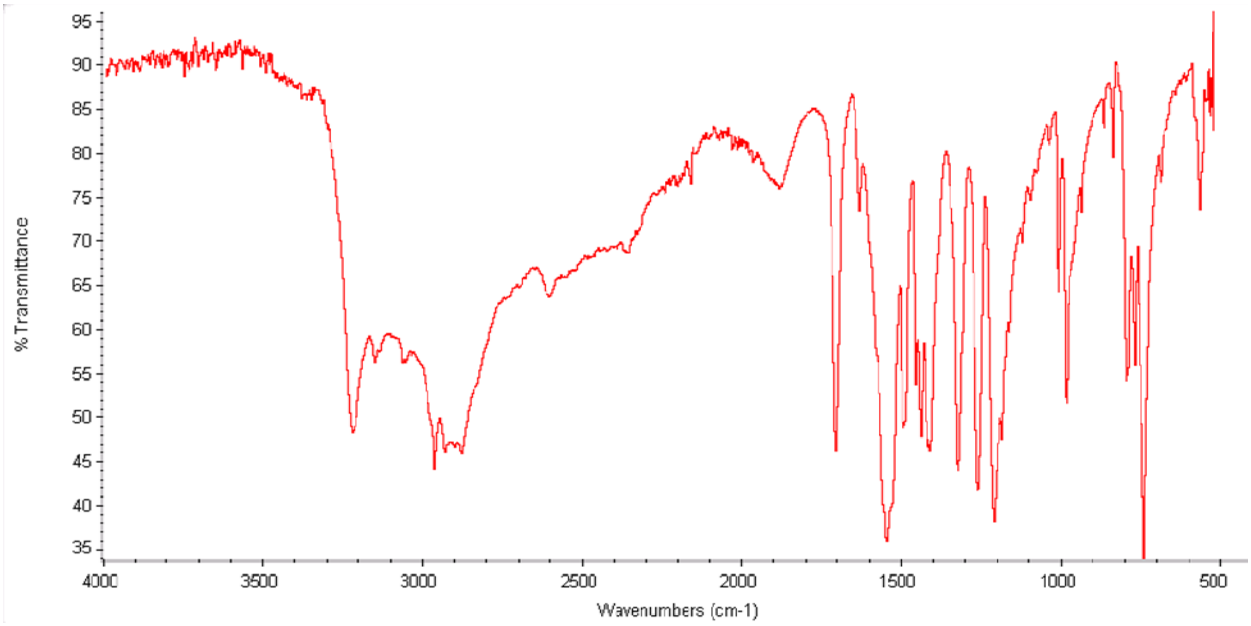

Figure S2. Infra-Red spectrum of *o*-ethylanilinium•HPzDCA•H_2O

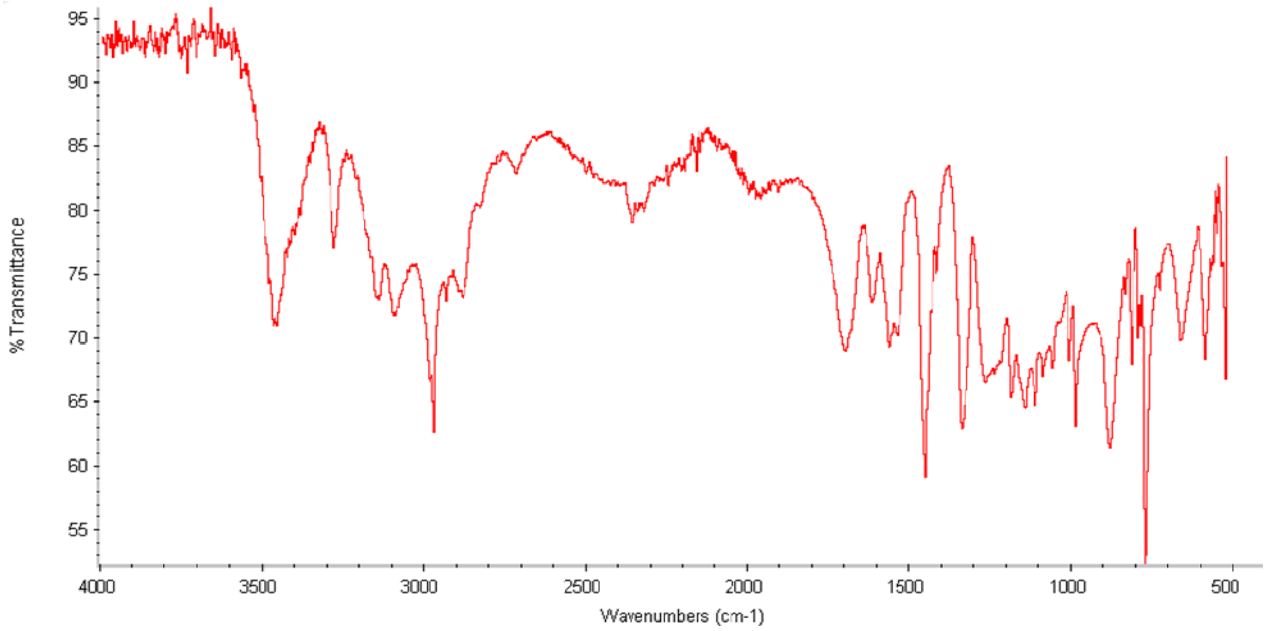

Figure S3. Infra-Red spectrum of 2,6-diethylanilinium•HPzDCA•H_2O

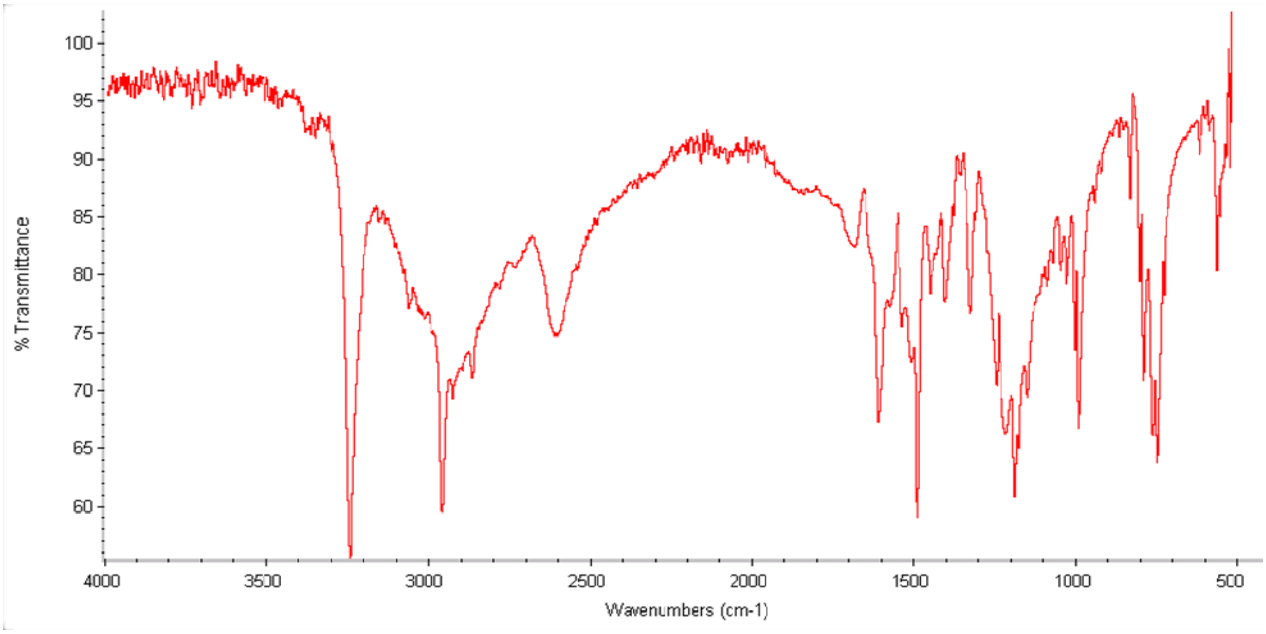

Figure S4. Infra-Red spectrum of 2-isopropylanilinium•HPzDCA

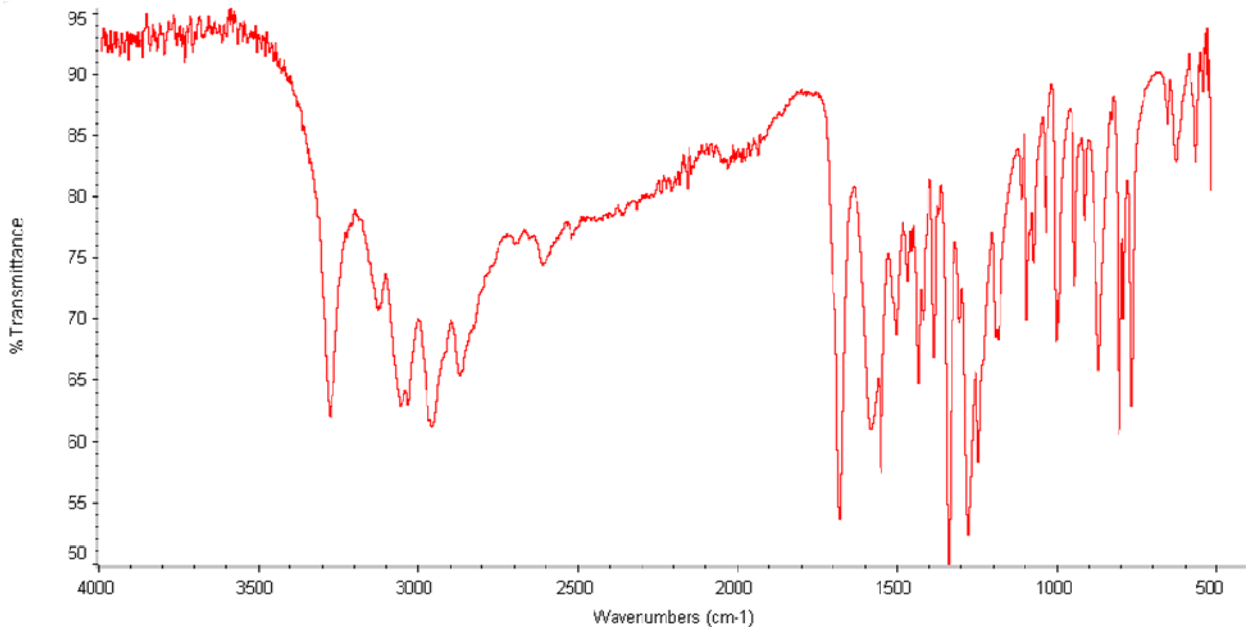

Figure S5. Infra-Red spectrum of 1,4-bis(2-hydroxyethylpiperazinium)•$(HPzDCA)_2$

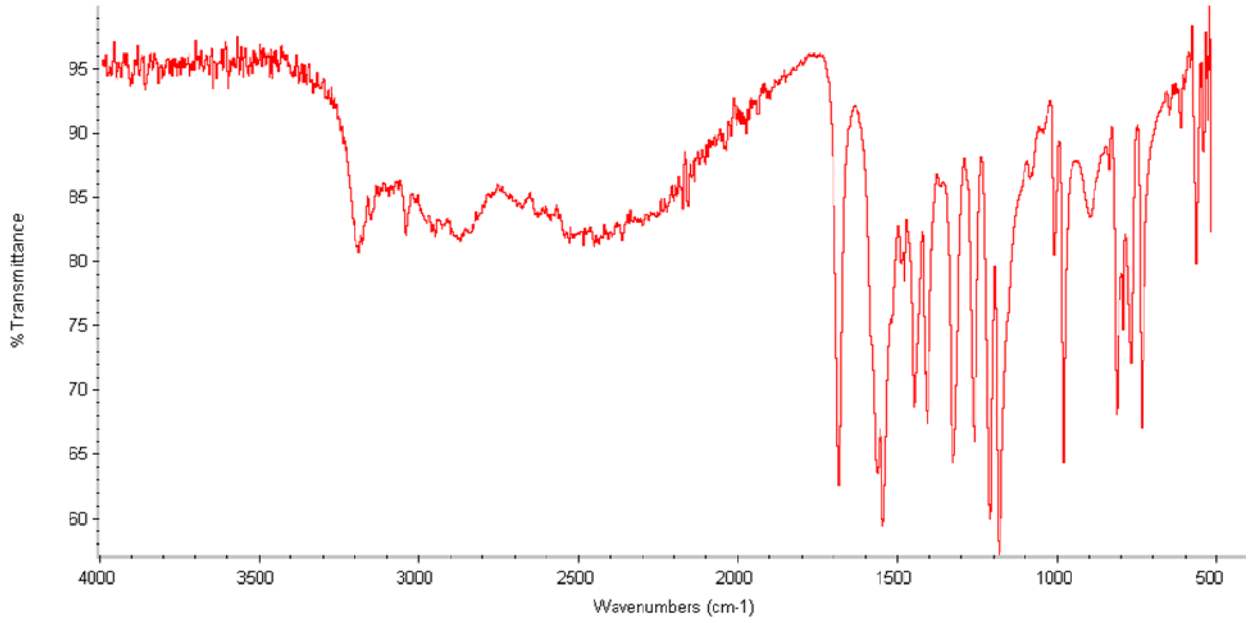

Figure S6. Infra-Red spectrum of $TMEDAH_2$•$(HPzDCA)_2$

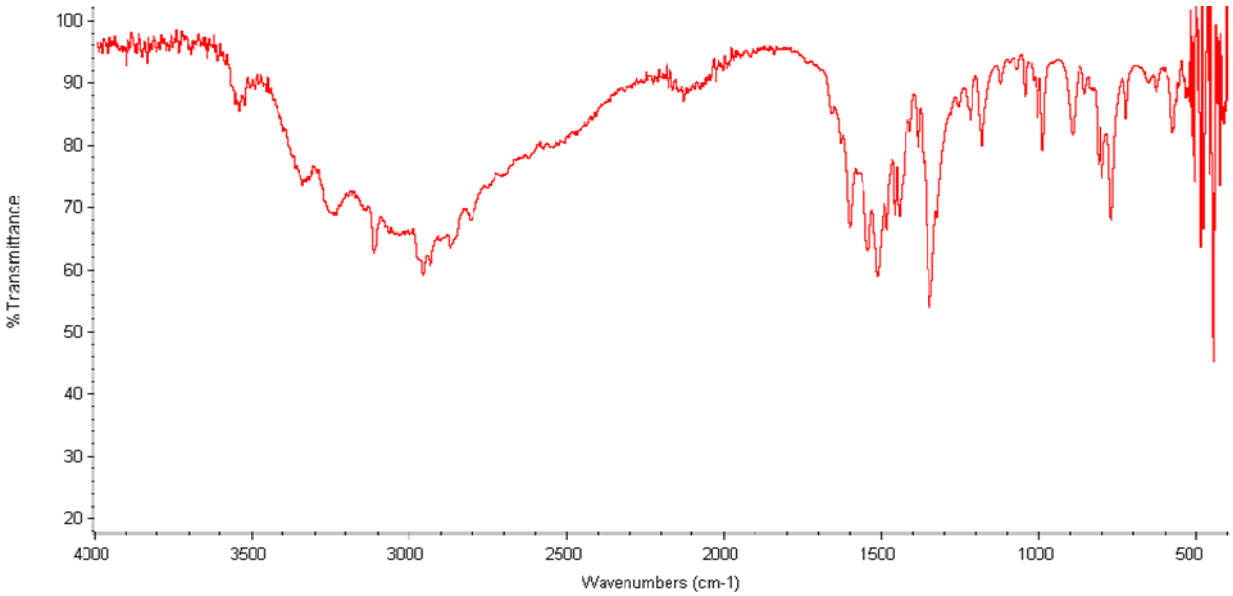

Figure S7. Infra-Red spectrum of hexane-1,6-diaminonium•$(HPzDCA)_2$

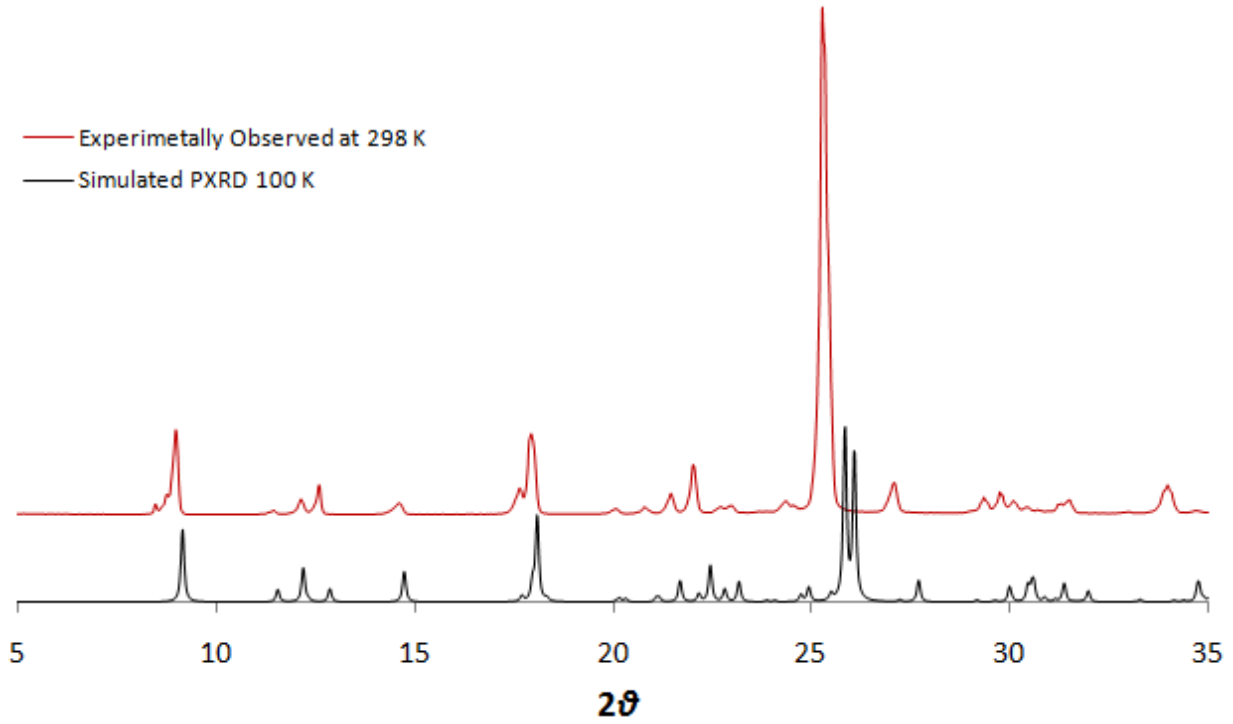

Figure S8. PXRD of *o*-ethoxyanilinium•HPzDCA

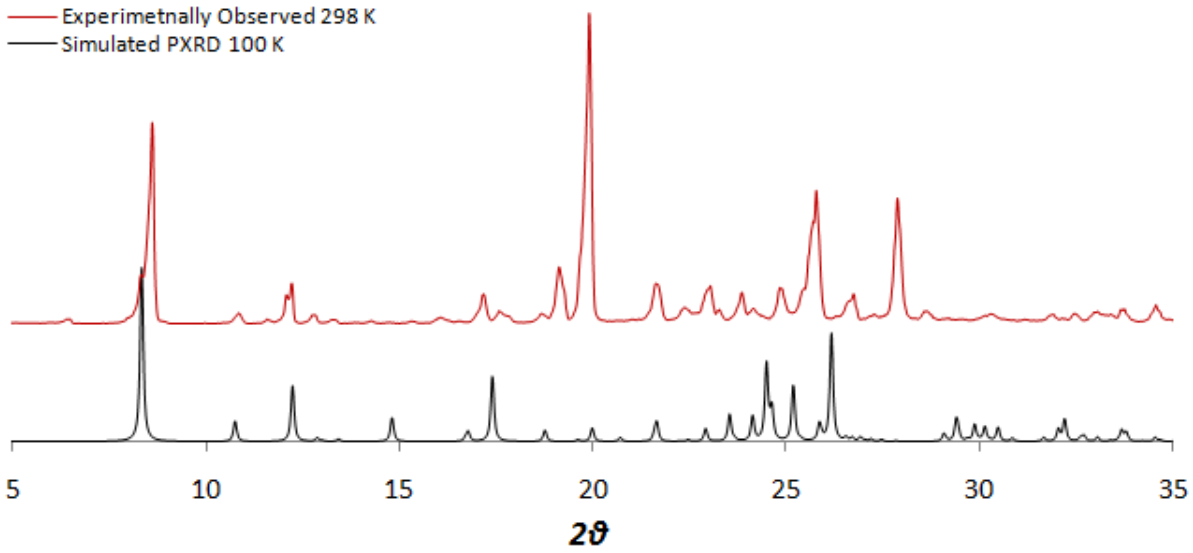

Figure S9. PXRD of *o*-ethylanilinium•HPzDCA•H_2O

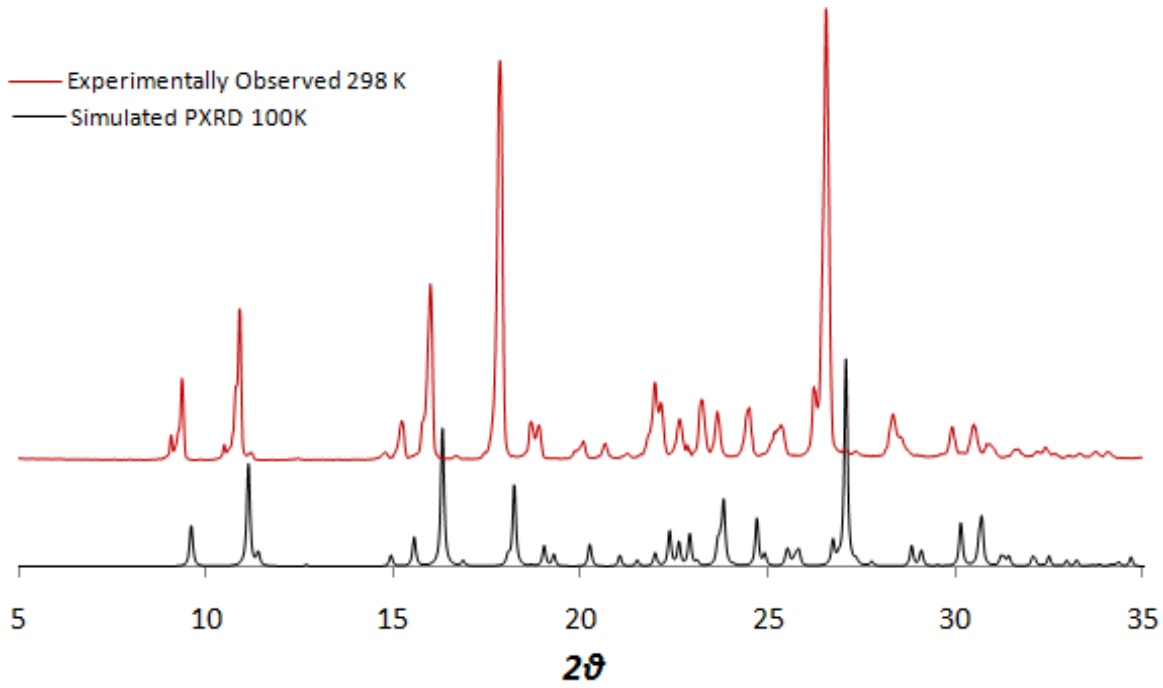

Figure S10. PXRD of 2,6-diethylanilinium•HPzDCA•H_2O

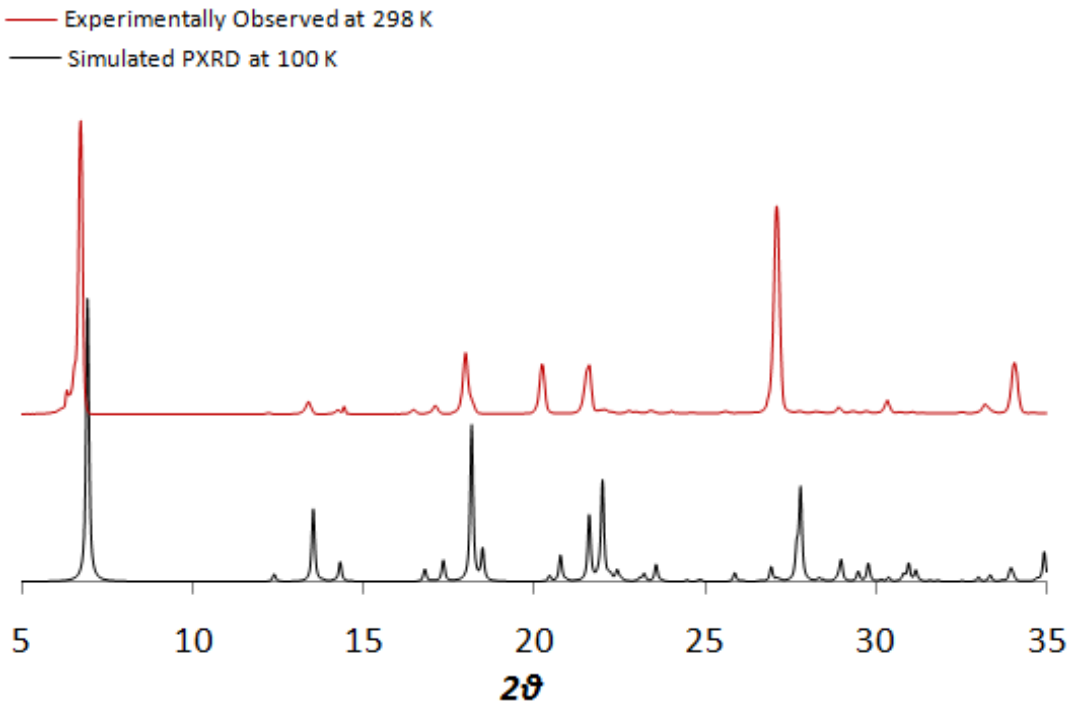

Figure S11. PXRD of 2-isopropylanilinium•HPzDCA

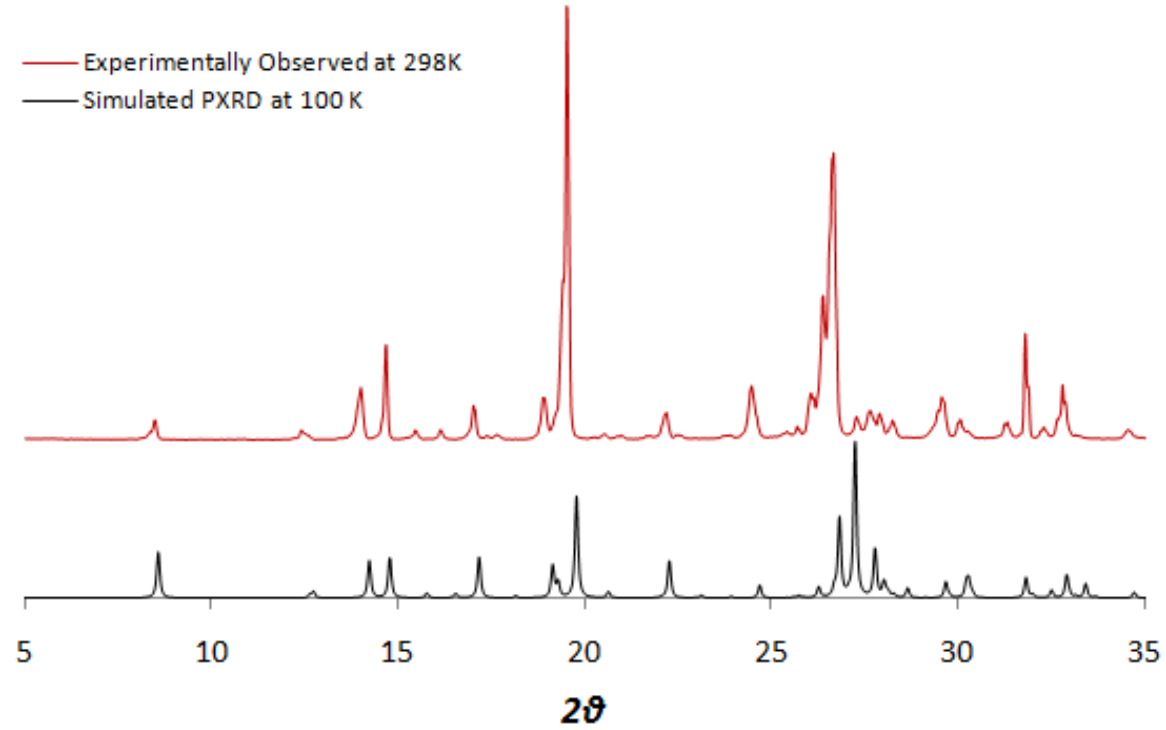

Figure S12. PXRD of 1,4-bis(2-hydroxyethylpiperazinium)•$(HPzDCA)_2$

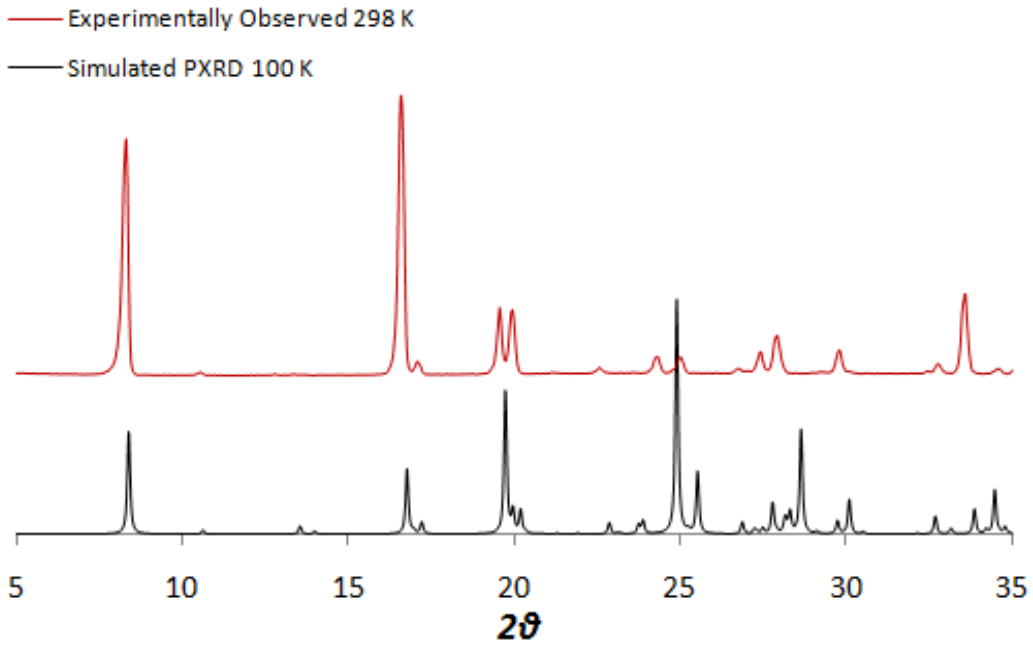

Figure S13. PXRD of $TMEDAH_2$•$(HPzDCA)_2$

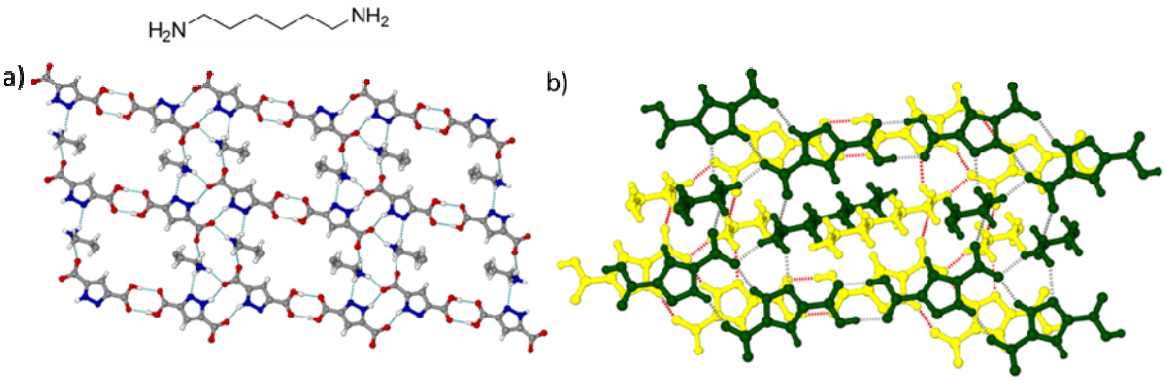

Figure S14. Structural features of: a) hydrogen bonded network of hexane-1,6-diaminonium•$(HPzDCA)_2$ (compound **7**); b) Overlay of layers of **7** showing the occupation of intra-layer voids by adjacent layers. (Hydrogen bonds within the "green" layer are colored grey, while those in the "yellow" layer are colored red.)

Table S1. Summary of Crystallographic Data for Compound **7**.

Empirical formula	$C_{16}H_{24}N_6O_8$	
Formula weight	428.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 4.5537(6) Å	□= 79.342(4)°.
	b = 9.3845(11) Å	□= 85.338(5)°.
	c = 11.1398(14) Å	□ = 85.904(4)°.
Volume	465.52(10) Å^3	
Z	1	
Density (calculated)	1.528 Mg/m^3	
Absorption coefficient	0.124 mm^{-1}	
F(000)	226	
Crystal size	0.23 x 0.20 x 0.14 mm^3	
Theta range for data collection	1.86 to 29.74°.	
Index ranges	-6≤h≤6, -13≤k≤13, -15≤l≤15	
Reflections collected	12441	
Independent reflections	2637 [R(int) = 0.0318]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9827 and 0.9725	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2637 / 0 / 138	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0935	
R indices (all data)	R1 = 0.0446, wR2 = 0.0980	
Largest diff. peak and hole	0.433 and -0.280 e.Å^{-3}	