

## Supporting Information

### Caption of Figures

**Fig. S1** Different non-covalent interactions in molecular structure of salt **1**. Color code: C, grey; O, red; N, blue.

**Fig. S2** Six membered cyclic cavity of H<sub>3</sub>BTC in **1** with included two molecules of Pz<sup>Me<sub>2</sub></sup>H. Color code: C, grey; H, white; O, red; N, blue.

**Fig. S3** Cavities align to form channels in which Pz<sup>Me<sub>2</sub></sup>H molecules in salt **1**. Color code: C, grey; H, white; O, red; N, blue. Hydrogen atoms have been omitted for clarity

**Fig. S4** ORTEP drawing with 50% probability of salt **2**.

**Fig. S5** Six membered hexagonal cavity of H<sub>3</sub>BTC with included two molecules of Pz<sup>iPr<sub>2</sub></sup>H in salt **2**. Color code: C, grey; H, white; N, blue; O, red

**Fig. S6** Different non-covalent interactions in molecular structure of salt **2**. Color code: C, grey; O, red; N, blue.

**Fig. S7** ORTEP drawing with 50% probability of salt **3**.

**Fig. S8** Six membered hexagonal cavity in salt **3** formed by H<sub>3</sub>BTC having Pz<sup>tBu, iPr</sup>H molecules. Color code: C, grey; H, white; N, blue; O, red.

**Fig. S9** Different non-covalent interactions in molecular structure of salt **3**. Color code: C, grey; O, red; N, blue.

**Fig. S10** C-H... $\pi$  interactions in salt **3**.

**Fig. S11** ORTEP drawing with 50% probability of co-crystal **4**.

**Fig. S12** Four membered cyclic cavity of H<sub>3</sub>BTC in **4**, with hydrogen bonded Pz<sup>Ph, Me</sup>H molecules outside the cavity.

**Fig. S13** Different non-covalent interactions in molecular structure of salt **4**. Color code: C, grey; O, red; N, blue.

**Fig. S14** Three dimensional packing of co-crystal **4**.

**Fig. S15** ORTEP drawing with 50% probability of salt **5**.

**Fig. S16** Hexagonal cavity formed by H<sub>3</sub>BTC in **5** having 3-cumenyl-5-methylpyrazole. Color code: C, grey; H, white; N, blue; O, red.

**Fig. S17** Different non-covalent interactions in molecular structure of salt **5**. Color code: C, grey; O, red; N, blue.

**Fig. S18**  $\pi$ ... $\pi$  interactions in salt **5**.

**Fig. S19** ORTEP drawing with 50% probability of salt **6**.

**Fig. S20** Different non-covalent interactions in molecular structure of salt **6**. Color code: C, grey; O, red; N, blue.

**Fig. S21** Hydrogen bonded discrete hexameric unit in **6**.

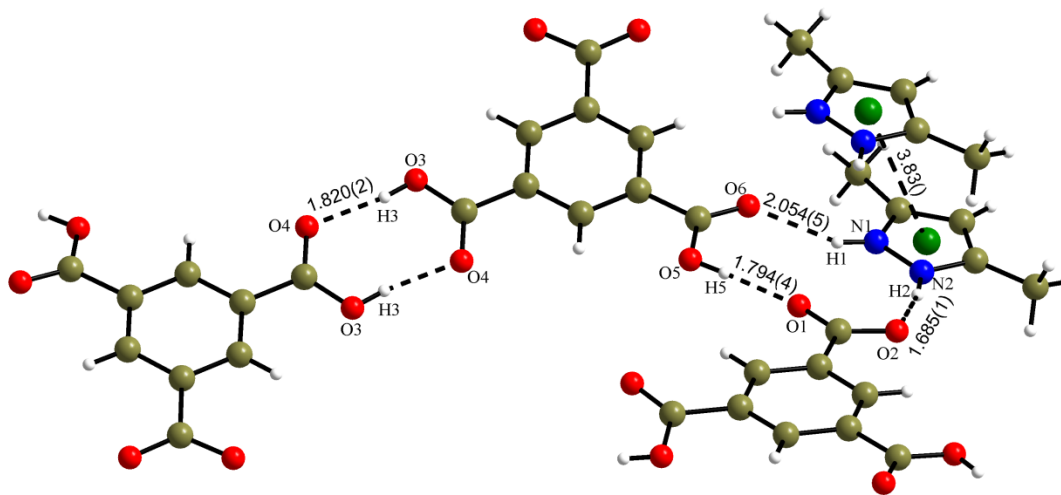
**Fig. S22** ORTEP drawing with 50% probability of salt **7**.

**Fig. S23** Six membered rectangular cavity of H<sub>3</sub>BTC in salt **7**, filled with two BPz H<sub>2</sub> and one methanol molecule.

**Fig. S24** Different non-covalent interactions in molecular structure of salt **7**. Color code: C, grey; O, red; N, blue.

**Fig. S25** Thermogravimetric curves for **1-7**.

**Fig. S26** Representative powder XRD patterns of salt **1** and co-crystal **4**. The left and right patterns in each case correspond to experimental and simulated, respectively.



**Fig. S1**

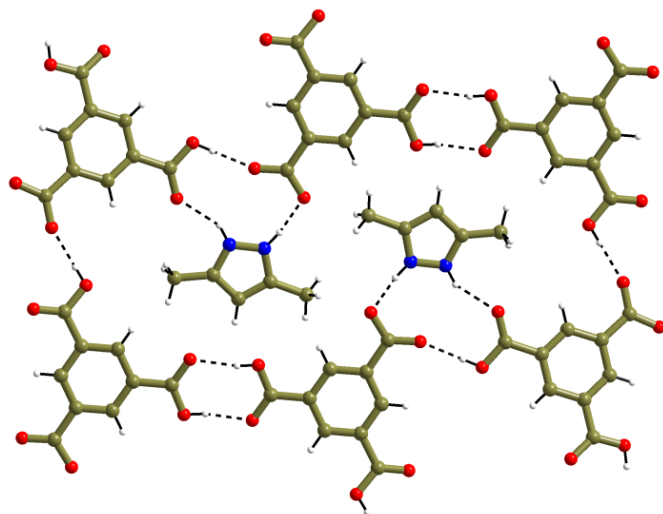


Fig. S2

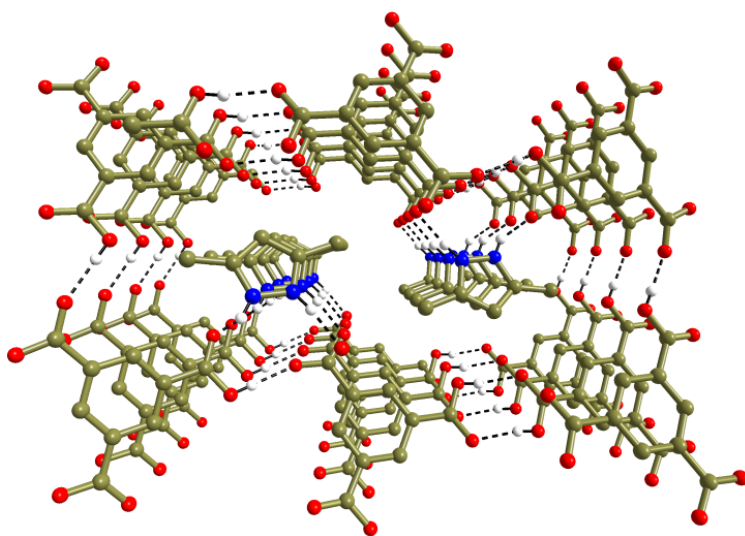


Fig. S3

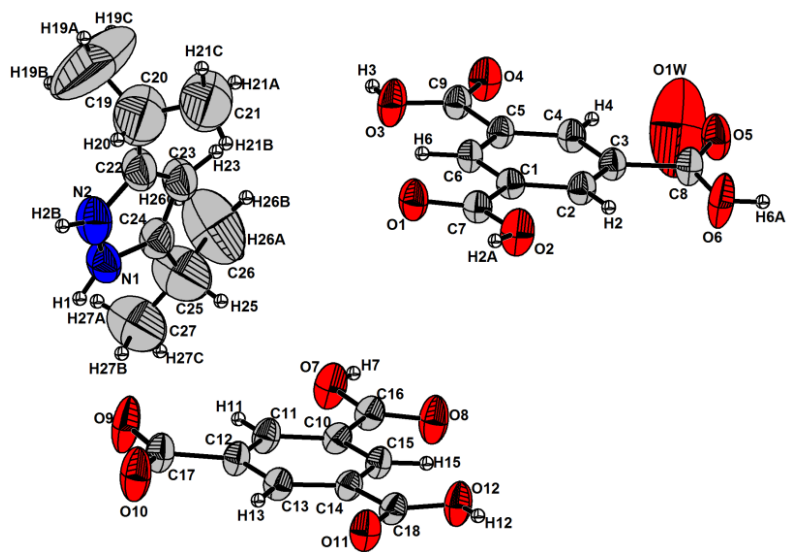


Fig. S4

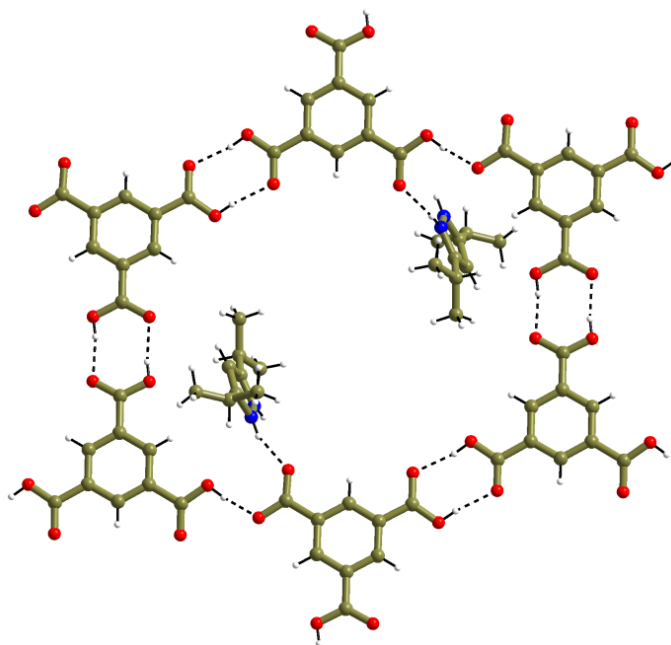


Fig. S5

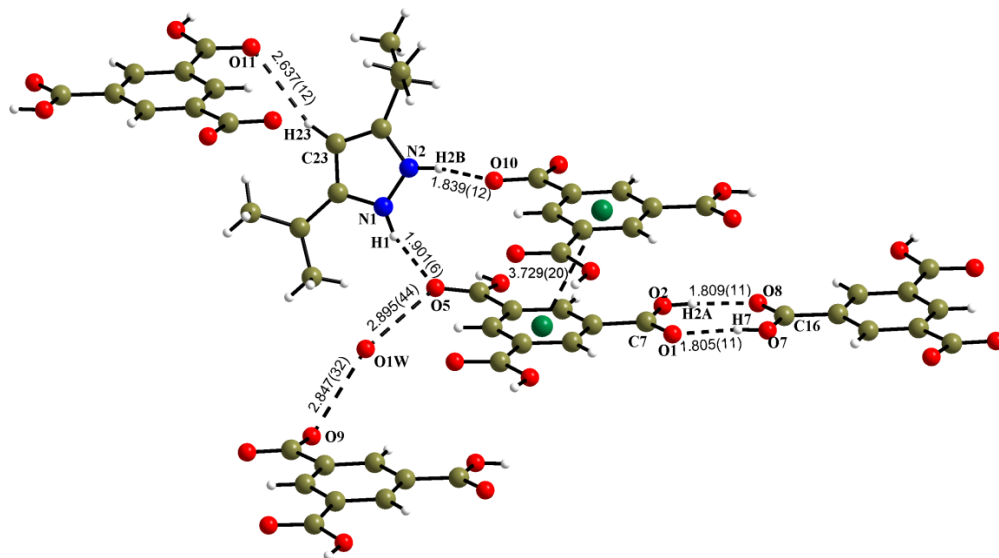


Fig. S6

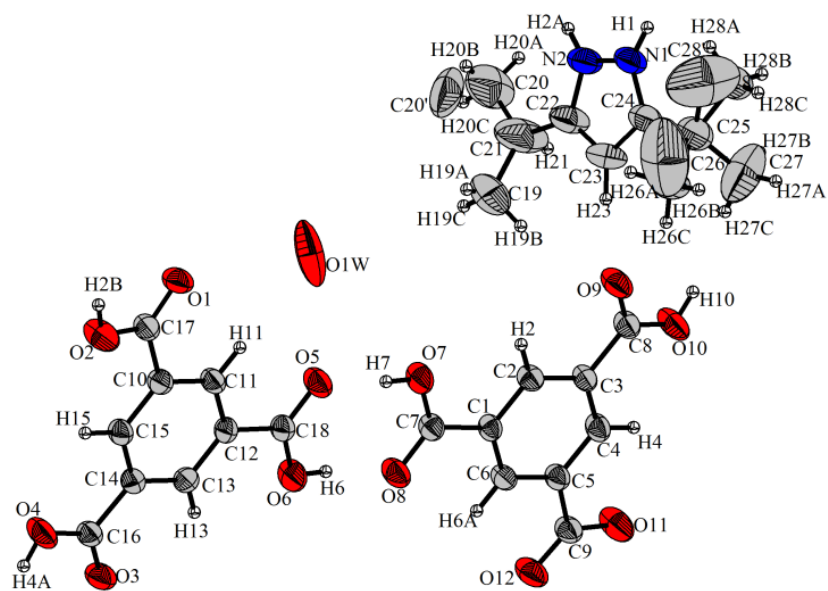


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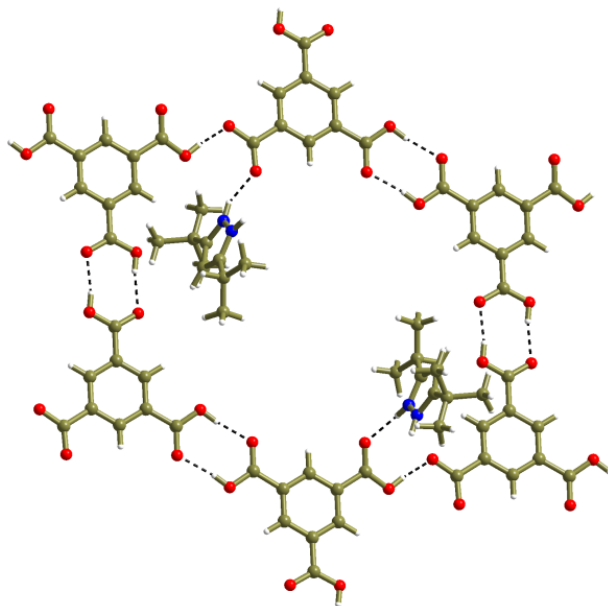


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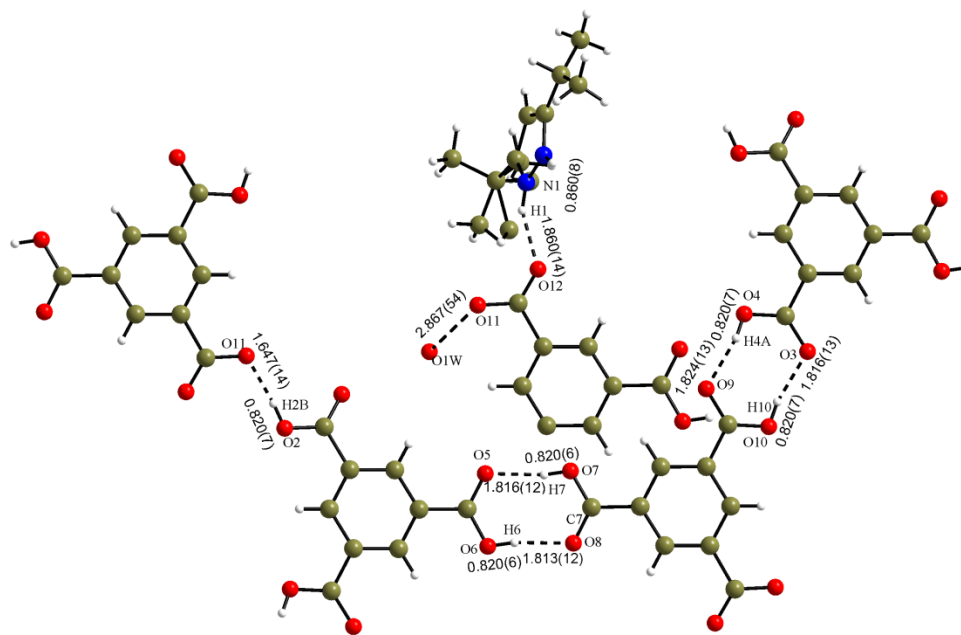


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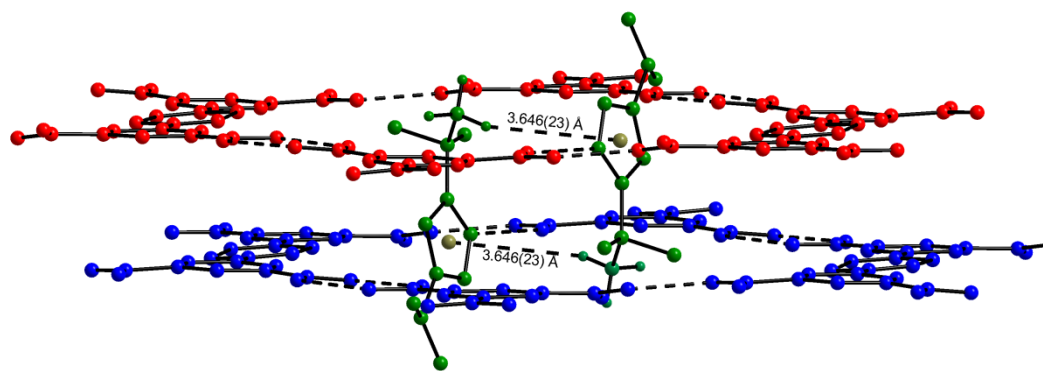


Fig. S10

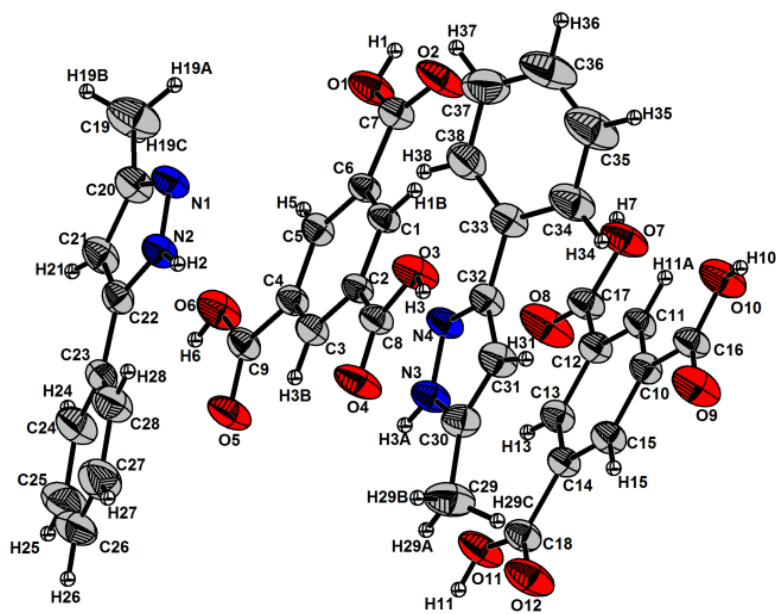


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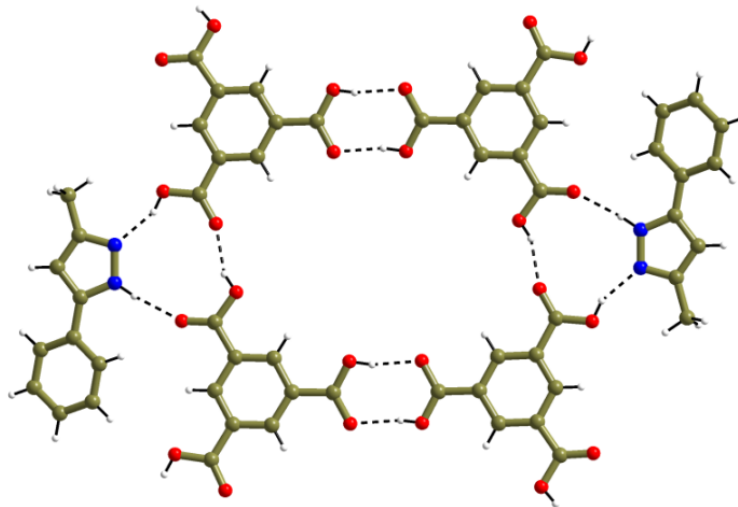


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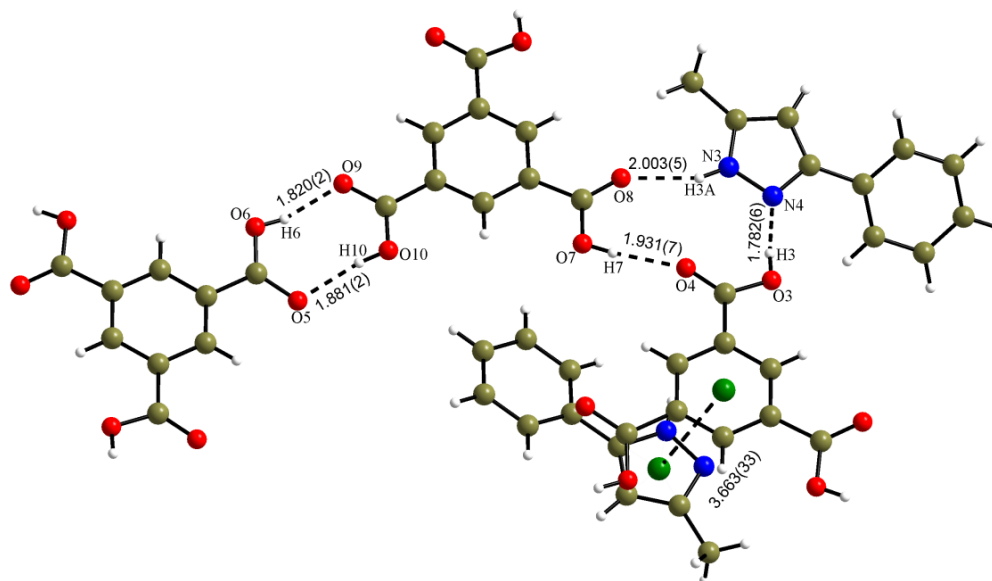


Fig. S13



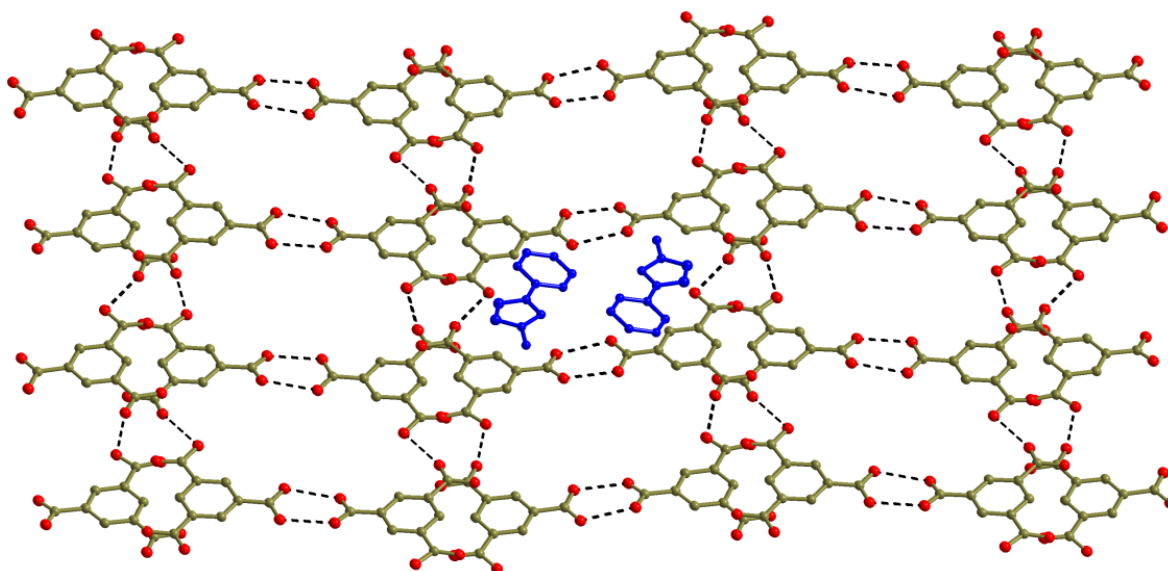


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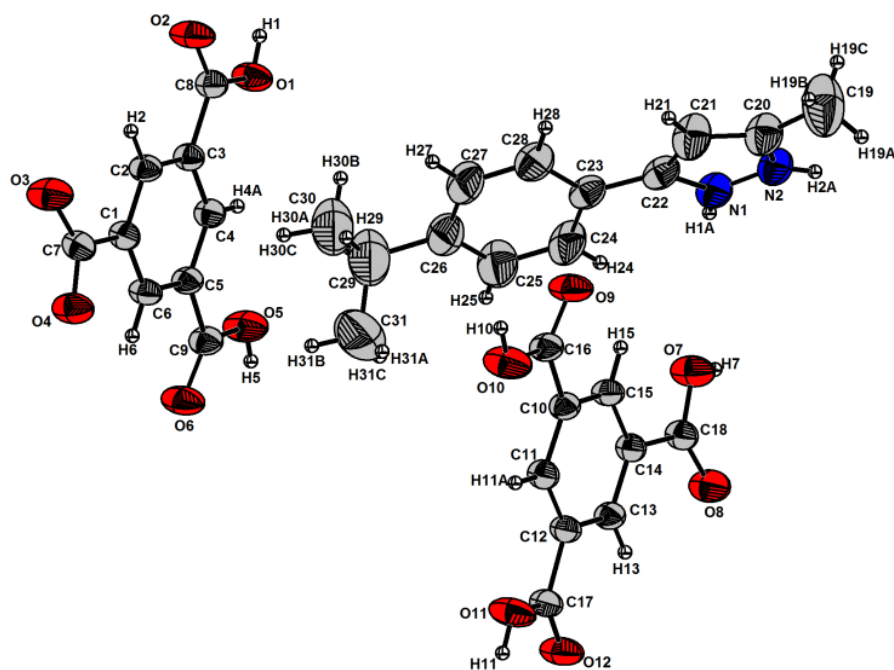


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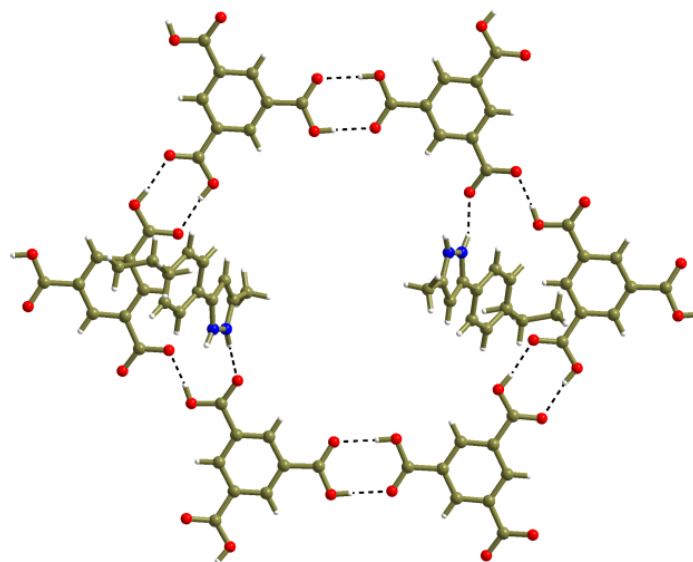


Fig. S16

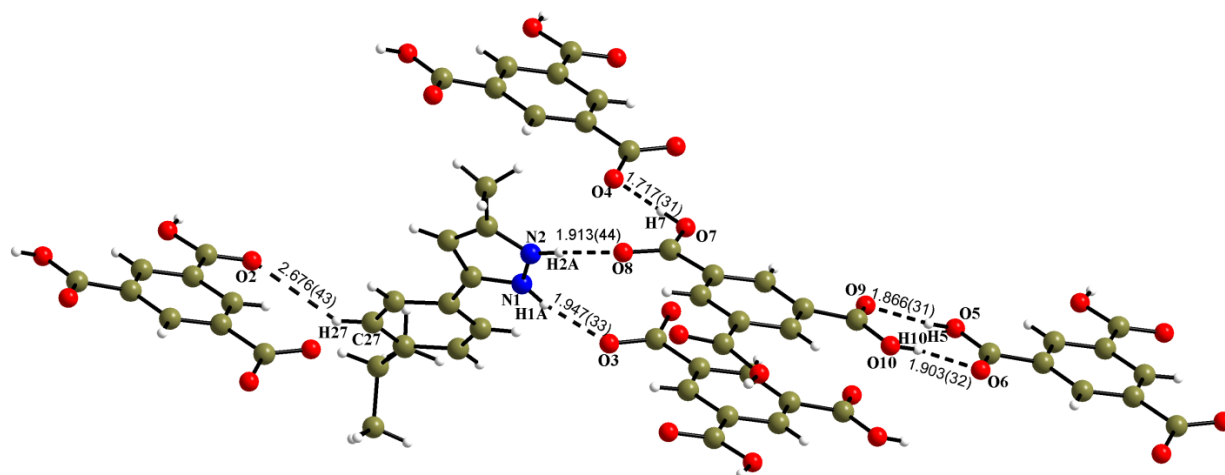


Fig. S17

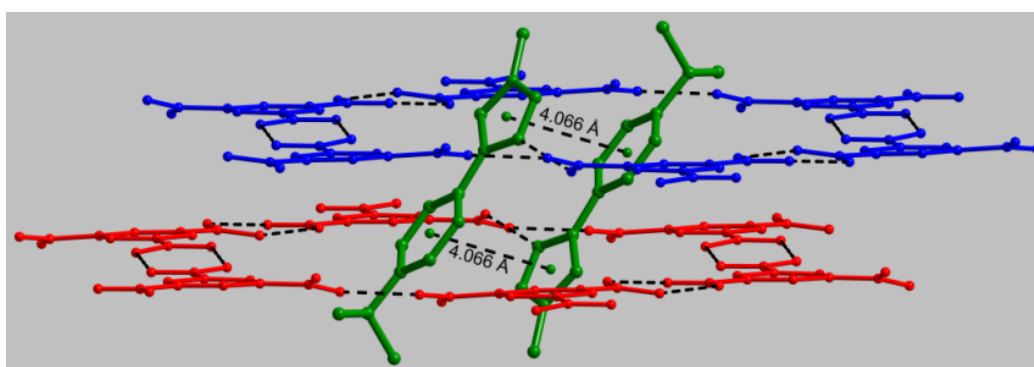


Fig. S18

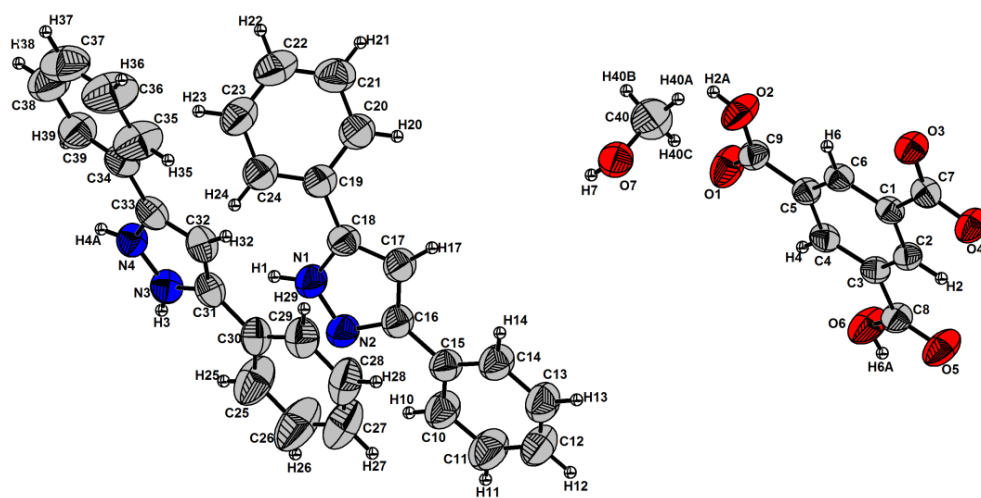


Fig. S19

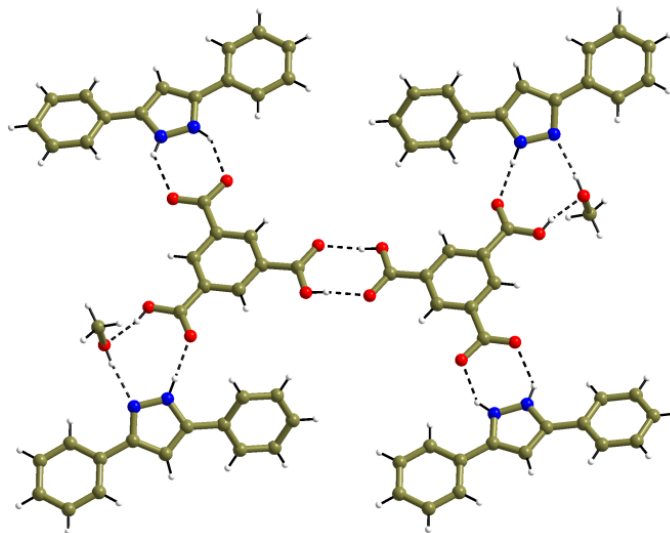


Fig. S20

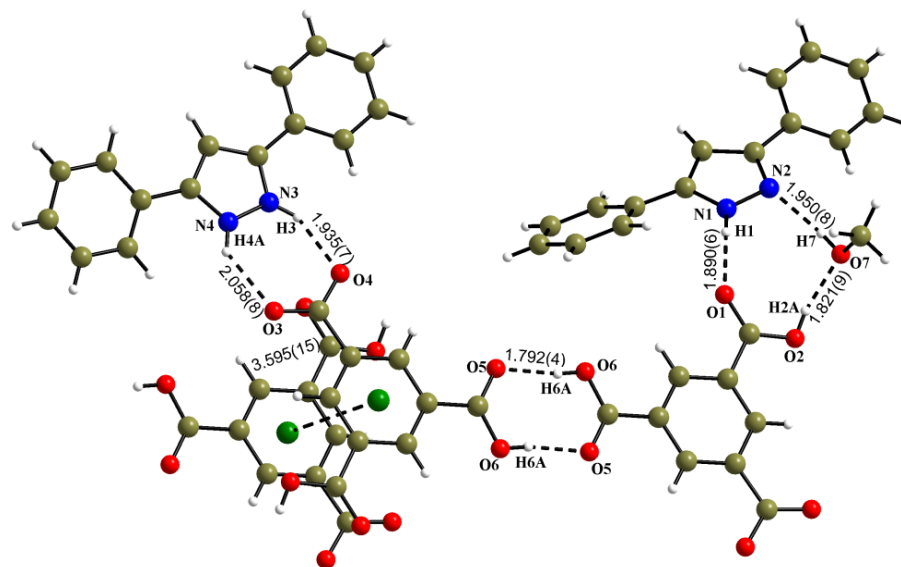


Fig. S21

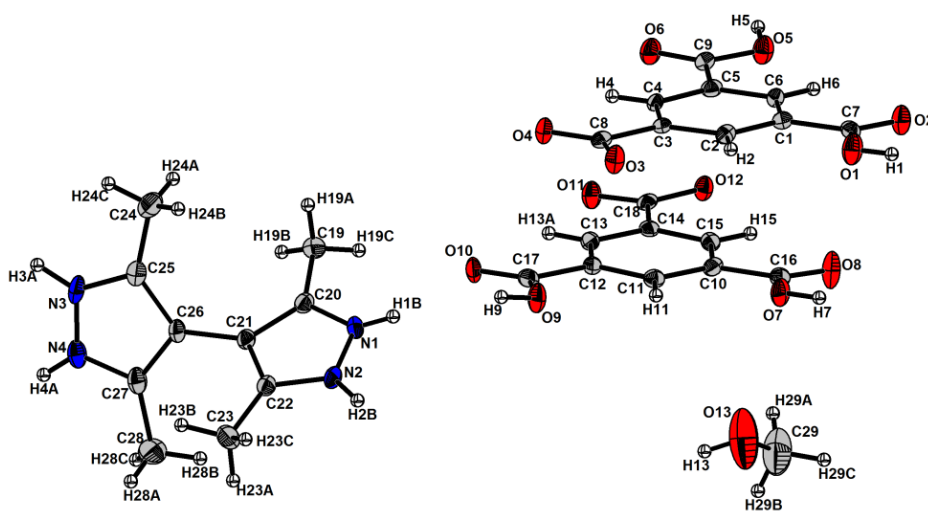


Fig. 22

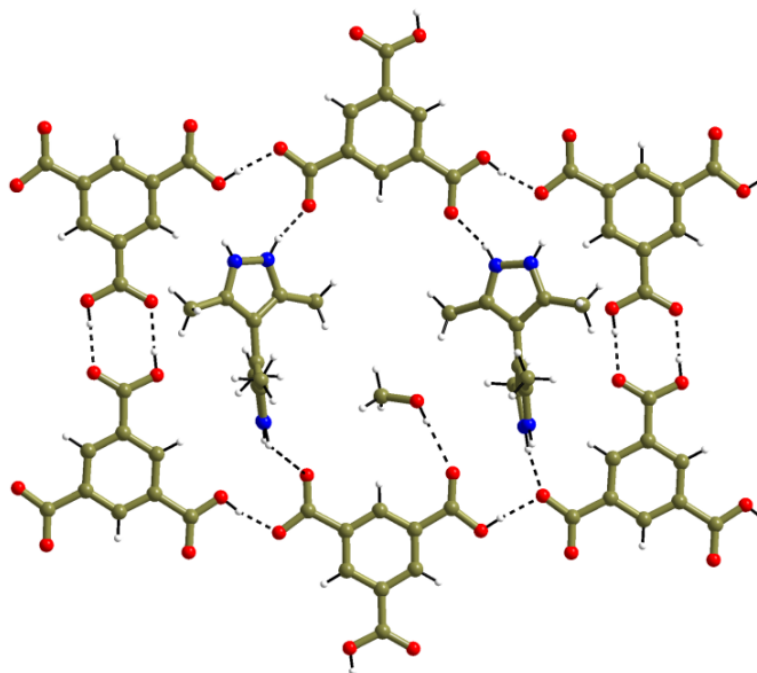


Fig. S23

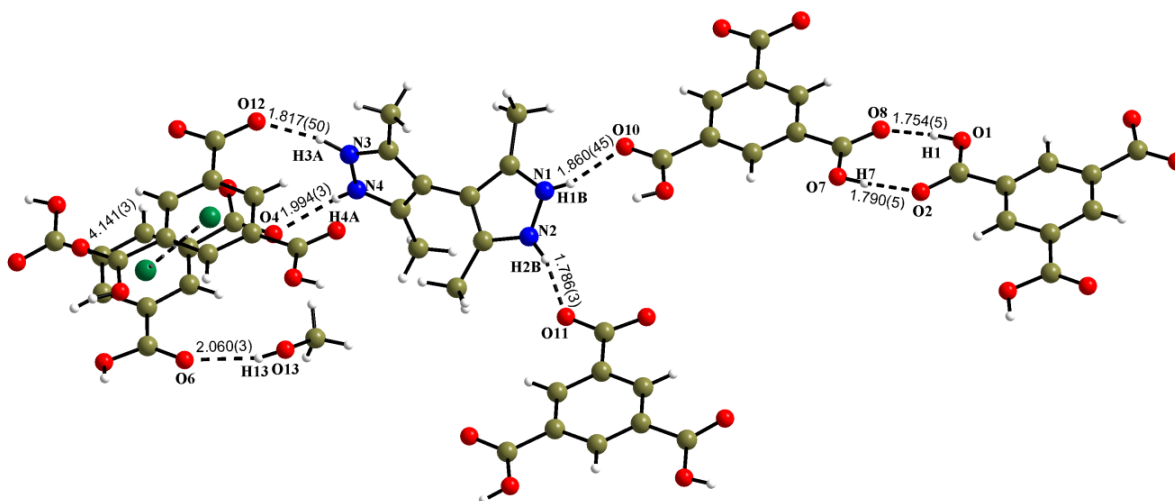


Fig. S24

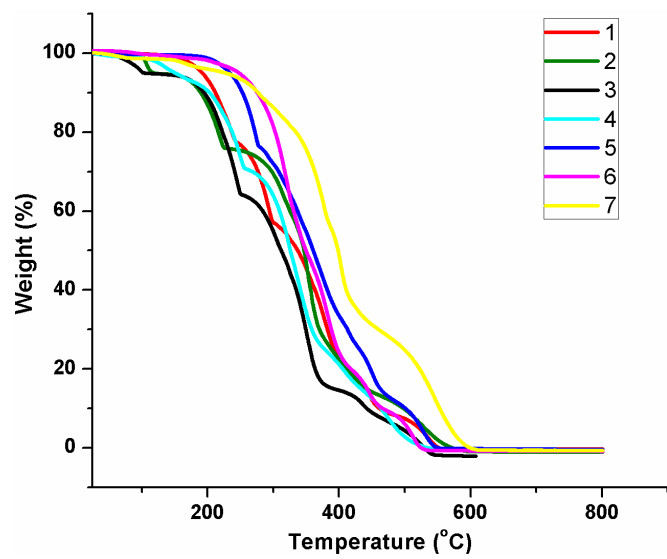


Fig. S25

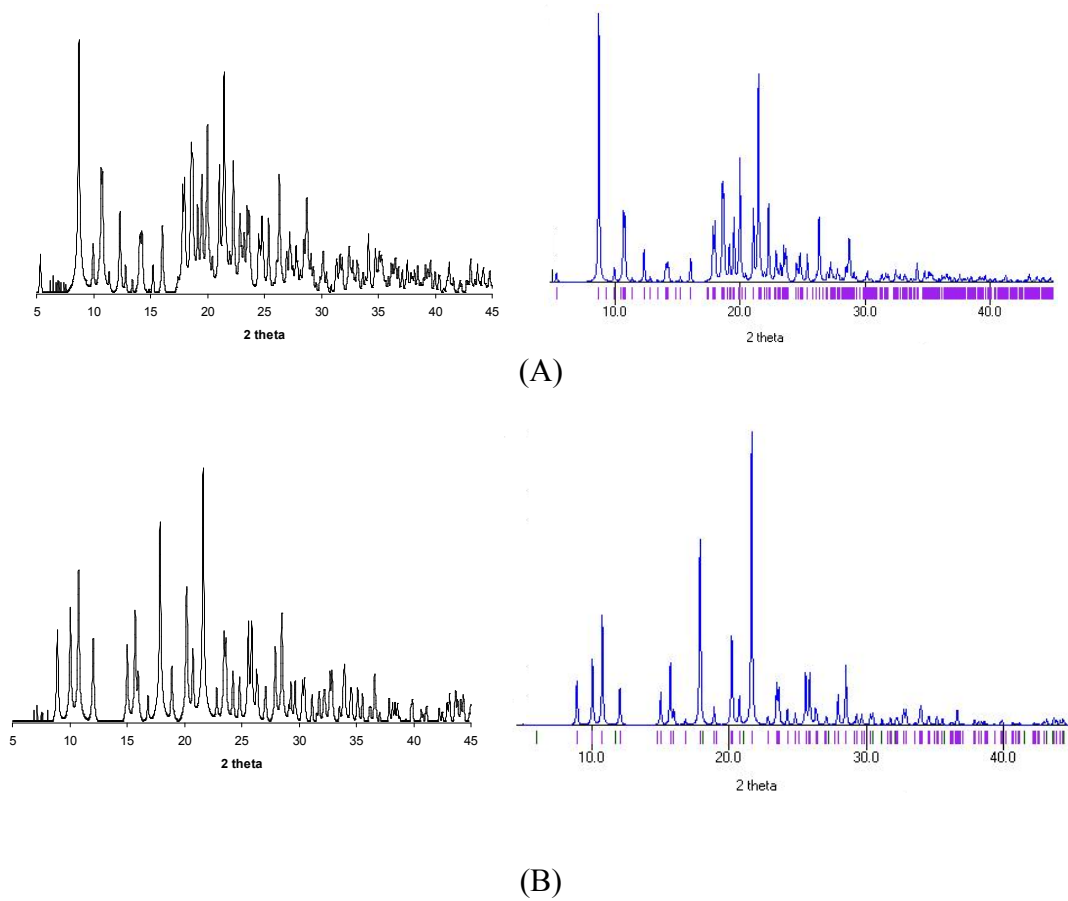


Fig. S26

**Table S1 Details of the thermal analysis**

Compound No.	Temperature range (°C) and weight loss (%)	Thermal stability (°C)
1	(i) No weight loss upto 187 °C. (ii) I <sup>st</sup> weight loss (~25 %) upto 250 °C. (iii) II <sup>nd</sup> weight loss (~45 %) upto 318 °C. (iv) Last continuous step of weight loss (100 %) upto 550 °C.	187 °C
2	(i) No loss upto 110 °C. (ii) I <sup>st</sup> weight loss (~5 %) upto 124 °C and stable upto 177 °C. (iii) II <sup>nd</sup> weight loss (~26 %) upto 230 °C. (iv) Last continuous step of weight loss (100 %) upto 555 °C.	177 °C
3	(i) No loss upto 88 °C. (ii) I <sup>st</sup> weight loss (~4.8 %) upto 115 °C and stable upto 180 °C. (iii) II <sup>nd</sup> weight loss (~38 %) upto 240 °C. (iv) Last continuous step of weight loss (100 %) upto 530 °C.	180 °C
4	(i) No loss upto 150 °C. (ii) I <sup>st</sup> weight loss (~5 %) upto 202 °C.	

	(iii) II <sup>nd</sup> weight loss (~32 %) upto 268 °C.  (iv) Last continuous step of weight loss (100 %) upto 526 °C.	202 °C
5	(i) No loss upto 218° C.  (ii) I <sup>st</sup> weight loss (~26 %) upto 270 °C.  (iv) Last continuous step of weight loss (100 %) upto 530 C.	218 °C
6	(i) No loss upto 236°C.  (ii) Last continuous step of weight loss (100 °C) upto 520 °C.	236 °C
7	(i) No loss upto 168 °C.  (ii) I <sup>st</sup> weight loss (~3.8 %) upto 230 °C.  (iii) Last continuous step of weight loss (100 %) upto 596 °C.	230 °C