Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Supramolecular isomerism, single-crystal to single-crystal transformation induced by release of *in situ* generated I_2 between two supramolecular frameworks

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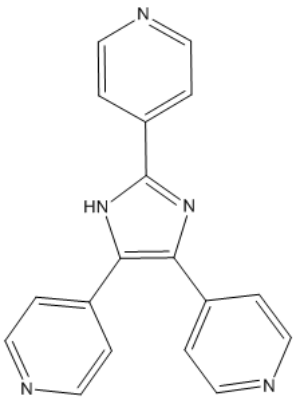

Fig. S1 The structure of 2,4,5-Tris(4-pyridinyl)-imidazole (Htpim).

The synthesis of 2,4,5-Tris(4-pyridinyl)-imidazole is according to the reported literature.[1]

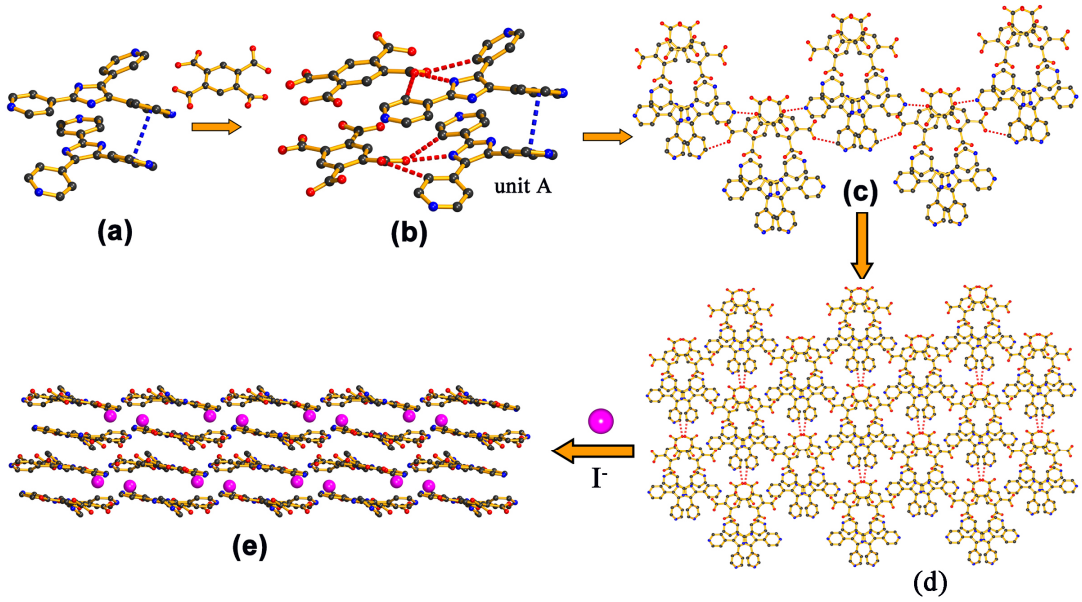

Fig. S2 (a) A cationic dimer. (b) The unit A constructed by two H_4betc and two protonated H_2tpim. (c) The infinite supramolecular chain formed by the unit A. (d) The 2D cationic layer. (e) The 3D supramolecular structure along the *b*-axis. The hydrogen atoms are omitted for clarity (red dot line: Hydrogen bond; blue dot line: π···π contact).

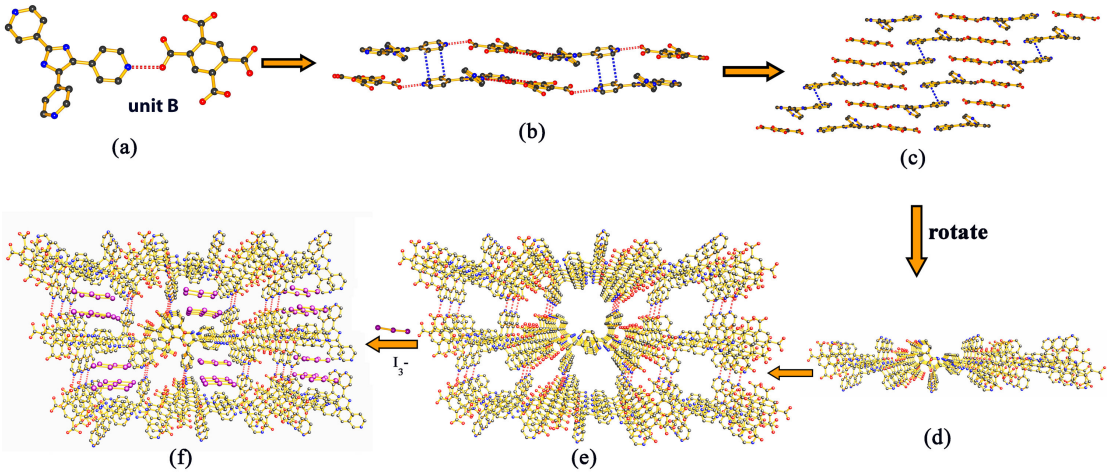

Fig. S3 (a) The unit B constructed by one H_4betc and one protonated H_2tpim. (b) The infinite supramolecular chain formed by the unit B. (c, d) The 2D cationic layer. (e) The 3D supramolecular framework with positive charges. (f) The electrically neutral architecture. The hydrogen atoms are omitted for clarity (red dot line: Hydrogen bond; blue dot line: π···π contact).

Table S1. Hydrogen Bonding Parameters for Compound **1**

D−H···A	d(H···A) (Å)	d(D···A) (Å)	∠D−H···A (deg)
N(3)−H(3)···O(8)	1.92	2.769(3)	170
O(1)−H(1A)···N(5)	1.93(9)	2.733(4)	162(13)
C(2)−H(2B)···O(8)	2.20	3.106(5)	164
C(10)−H(10)···O(7)	2.29	3.137(4)	151
C(16)−H(16)···O(6)	2.38	3.002(5)	124
C(17)−H(17)···O(3)	2.58	3.190(4)	123

Table S2. Hydrogen Bonding Parameters for Compound **2**

D−H···A	d(H···A) (Å)	d(D···A) (Å)	∠D−H···A (deg)
O(6)−H(6)···N(4)	1.89	2.644(8)	152
N(2)−H(2A)···O(2)	1.95	2.804(6)	170
C(4)−H(4)···O(2)	2.33	3.227(8)	162
C(1)−H(1)···O(3)	2.32	3.228(9)	164
O(7)−H(7)···N(5)	1.91	2.656(7)	150

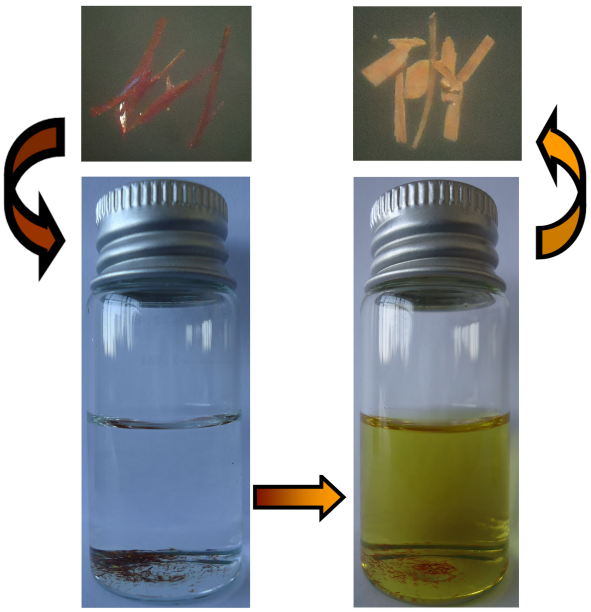

Fig. S4 Color change from brown to yellow of crystals of **2** soaked in MeOH.

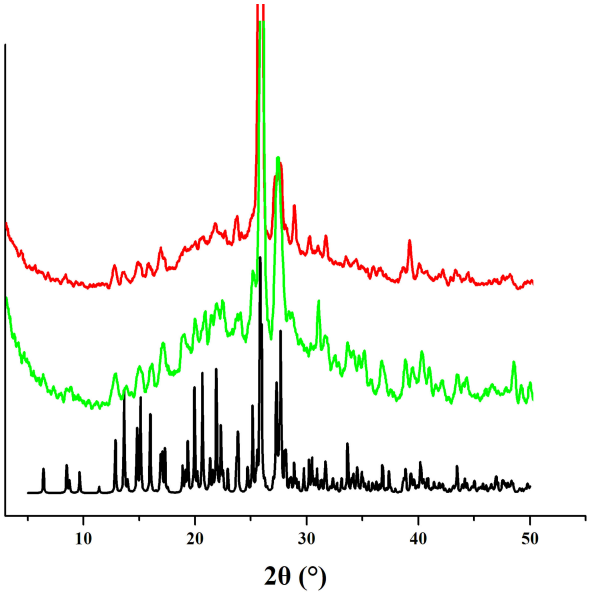

Fig. S5 Experimental (**1**: green; **2**': red) and simulated (black) powder X-Ray diffraction patterns for **1**.

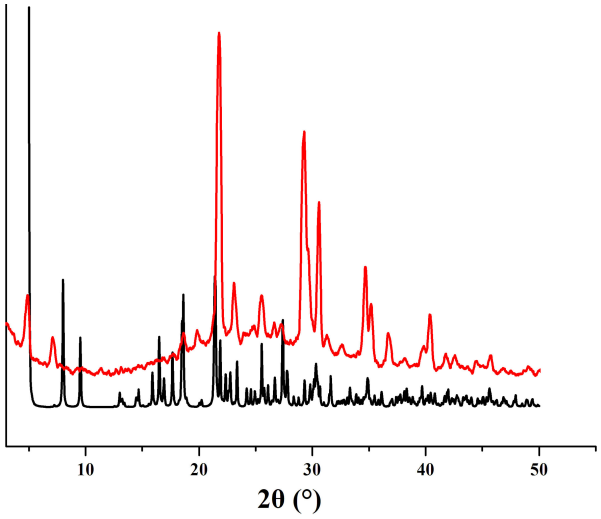

Fig. S6 Experimental (red) and simulated (black) powder X-Ray diffraction patterns for **2.**

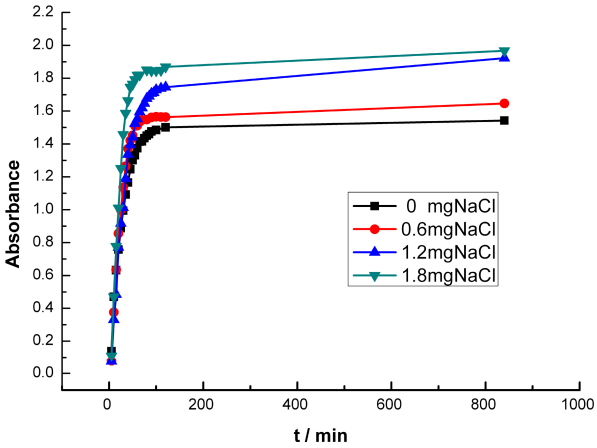

Fig. S7 The delivery of I_2 containing different amount of NaCl in 50 mL methanol solution.

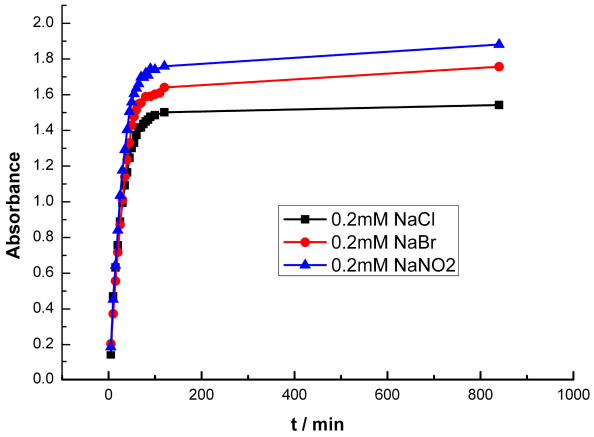

Fig. S8 The delivery of I_2 containing various ions with the same amount (0.2 mM

NaCl, NaBr or $NaNO_2$) in methanol solution.

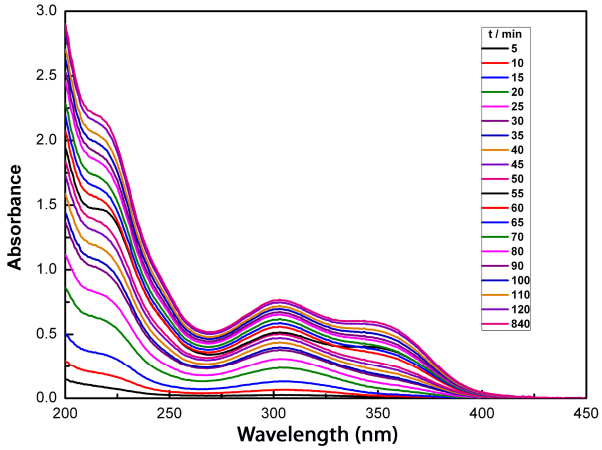

Fig. S9 Temporal evolution of UV/vis absorption spectra for the I_2 delivery from 5mg of compound **2** in 50 mL water.

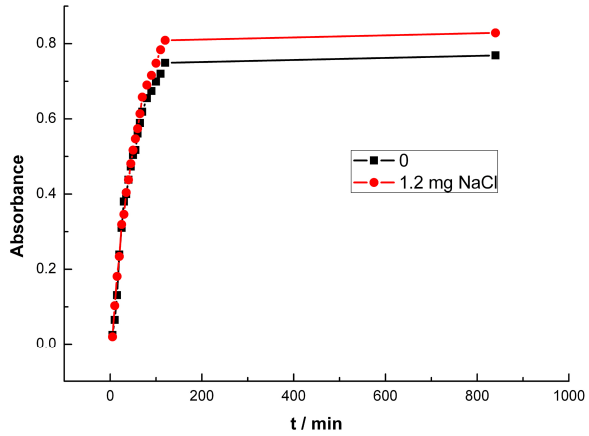

Fig. S10 The delivery of I_2 in water solution.

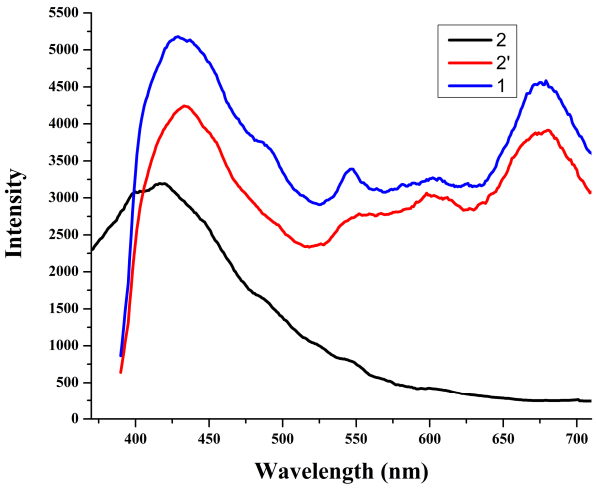

Fig. S11 Solid-state luminescent spectra of **2** (black), **2'** (red) and **1** (blue) at room

temperature.

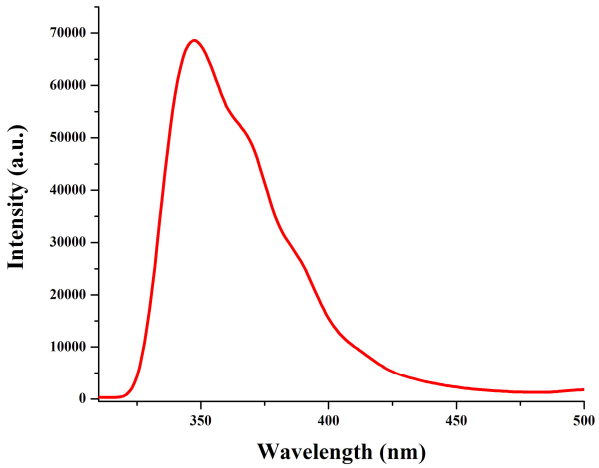

Fig. S12 Solid-state luminescent spectrum of H_4betc.

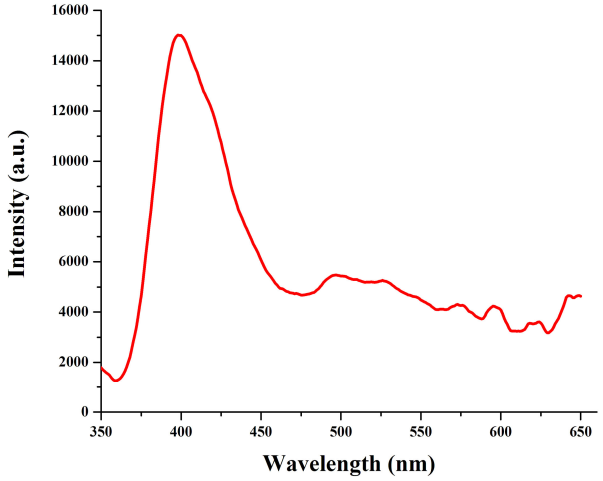

Fig. S13 Solid-state luminescent spectrum of Htpim.

The solid-state luminescent spectra of **1**, **2** and **2'** have been studied at room temperature. **1** and **2'** show the strong emission at 428 nm, 550 nm, 600 nm and 680 nm upon excitation at 300 nm. **2** only exhibits the emission maxima at 417 nm upon excitation at 300 nm, and the disappeared peaks and decrease in intensity of the luminescence may be due to the host–guest photoinduced electron transfer effect (Fig. S11†).[2] For the sake of understanding the mechanism of the emission, we examine the luminescent properties of the free ligands Htpim and H_4betc in the solid state at room temperature. We find that the strong emission peaks at 400, 500, and 645 nm upon excitation at 340 nm for Htpim (Fig. S13†) and at 348 nm upon excitation at 284 nm for H_4betc (Fig. S12†), respectively. The emissions of

the ligands may be attributed to n→ π* and π→ π* transitions of the intraligands. In comparison with the emission peaks of the Htpim, the luminescent emission wavelengths of **1** and **2** show red shifts (Fig. S11†). As far as we know, the emissions of **1** and **2** are neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT), and may be ascribed to intraligand charge transitions.[3]

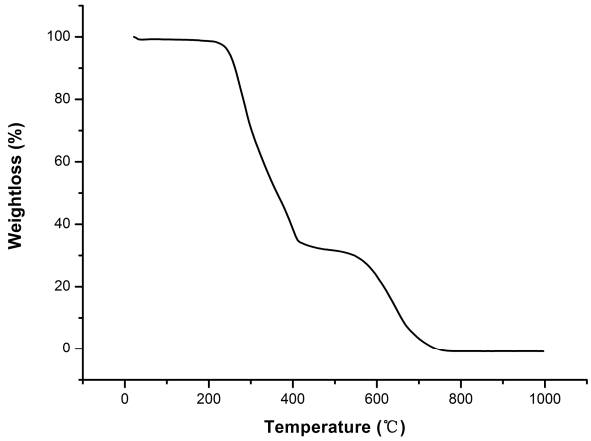

Fig. S14 The TGA curve of compound **1**

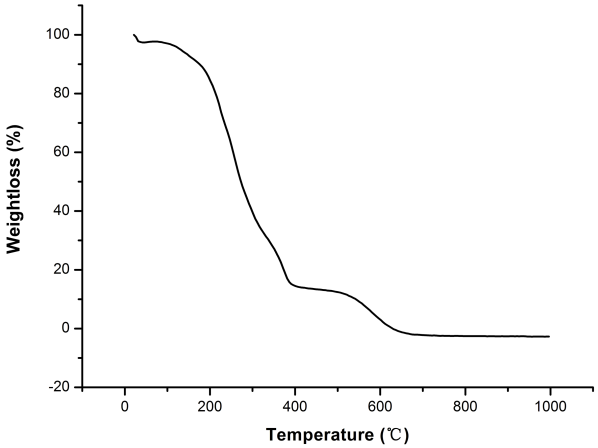

Fig. S15 The TGA curve of compound **2**.

1 M. V. Proskurnina, N. A. Lozinskaya, S. E. Tkachenko and N. S. Zefirov, *Russ. J. Org. Chem.*, 2002, **38**, 1200.

2 B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 15394.

3 (*a*) L. Y. Zhang, J. P. Zhang, Y. Y. Lin and X. M. Chen, *Cryst. Growth Des.*, 2006, **6**, 1685; (*b*) Q. Chu, G. X. Liu, Y. Q. Huang, X. F. Wang and W. Y. Sun, *Dalton Trans.*, 2007, 4302.