Supplementary Material (ESI) for CrystEngComm

<Supporting Information>

Reversible Formation of Regular Pentagonal Dodecahedral $(H_2O)_{20}$ in 2-D Metal-Organic Framework

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Experimental Section

The reagents and solvents employed were commercially available and used as received without further purification. 1, 1'-di(ethylpropionato)-2, 2'-biimidazole ($Epra_2biim$) was synthesized in accordance with a published procedure[1]. Na_2Pra_2biim was prepared by hydrolyzing $Epra_2biim$ and characterized by IR spectra and ^1H NMR.

Physical Measurements

The C, H, and N microanalyses were carried out with a Vario EL III elemental analyzer. Infrared spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the 4000-400cm^{-1}. TGA were recorded with a Netzsch STA449C apparatus under a nitrogen atmosphere. Powder X-ray diffraction (XRD) data were collected on a RIGAKU DMAX2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å). A step size of 0.05^o and a counting time of 1.2 s/step were applied in a 2θ range of 5.00-45.00^o.

Crystallographic Analyses

X-ray diffraction data of **1** (0.28 × 0.24 × 0.10 mm) was collected on a Saturn 70 CCD diffractometer at 163K and 293K, respectively. The direct methods and successive difference Fourier maps reveal all non-hydrogen atoms that are refined anisotropically. All hydrogen (H) atoms of the organic ligand are located at calculated positions. The water H atoms are unambiguously located from difference Fourier map and refined with the fixed O-H distance of 0.95 Å. At 293K, the riding mode is applied due to the enhanced thermal vibration of the water H atoms. Crystal data for **1**: hexagonal, space group $R\bar{3}$. $a = b$ =20.1966(6), c = 25.1389(15) Å, V = 8880.4(6) Å^3. Z = 18, d_{calcd} = 1.979 g cm^{-3}, 2.03° < θ < 27.48, μ = 2.038 mm-^{1}, 4340 unique reflections. $R1$ = 0.0229 and w$R2$ = 0.0509 for $I \geq 2\sigma(I)$ (3689 reflections), and $R1$ = 0.0288, w$R2$ = 0.0536 for all data. at 293K: $a = b$ = 20.222(3), c = 25.168(5) Å, V = 8913(2) Å^3. Z = 18, d_{calc} = 1.972 g cm-^{3}, 2.46° < θ < 27.47, μ = 2.030 mm^{-1}, 4440 unique reflections. $R1$ = 0.0310 and w$R2$ = 0.0678 for $I \geq 2\sigma(I)$ (3487 reflections), and $R1$ = 0.0420, w$R2$ = 0.0675 for all data. CCDC-645476 and CCDC-645477 contain the supplementary data for this paper. These data can be obtained online free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the cambridge crystallographic Data Centre 12, Union Road, Cambridge CB2 1EZ, UK; fax:(+44)1223-033; or deposite@ccdc.cam.ac.ck.

Table 1S. Selected bond lengths (Å) and angles (º) for compounds **1**[a]

Ag(1)-N(1)	2.1275(18)	Ag(1)-N(3)	2.1392(18)
Ag(2)-O(7)	2.2120(15)	Ag(2)-O(10)	2.291(2)
Ag(2)-O(7)#1	2.4696(15)	Ag(1)-Ag(2)	3.0303(3)
N(1)-Ag(1)-N(3)	168.76(7)	N(1)-Ag(1)-Ag(2)	100.45(5)
O(7)-Ag(2)-O(10)	168.81(7)	O(7)-Ag(2)-O(7)#1	77.71(6)
O(10)-Ag(2)-O(7)#1	104.54(6)	N(3)-Ag(1)-Ag(2)	70.84(5)
O(7)-Ag(2)-Ag(1)	86.41(4)	O(10)-Ag(2)-Ag(1)	85.44(5)
O(7)#1-Ag(2)-Ag(1)	142.80(4)		

[a] Symmetry code: #1 -x+5/3,-y+4/3,-z+4/3。

Table 2S Hydrogen bond lengths (Å) and angles (°) in $(H_2O)_{20}$

D–H…A	∠ (HDH)		d(D...A)		∠ (DHA)	
	163K	293K	163K	293K	163K	293K
O(1)-H(1)···O(8)	107	113	2.744(2)	2.742(4)	166	172
O(1)-H(2)···O(3)			2.851(3)	2.871(4)	162	161
O(2)-H(3)···O(1)	104	111	2.830(3)	2.834(4)	172	160
O(2)-H(4)···O(3)			2.785(3)	2.810(5)	148	132
O(3)-H(5)···O(2)	106	105	2.754(3)	2.771(5)	169	163
O(3)-H(6)···O(9)			2.899(3)	2.907(5)	168	162
O(4)-H(7)···O(1)	110	107	2.843(2)	2.882(4)	167	177
O(5)-H(8)···O(9)	99	113	2.814(3)	2.828(4)	167	158
O(5)-H(9)···O(8)			2.899(3)	2.917(4)	167	160
O(6)-H(10)···O(6)’	98	107	2.900(3)	3.156(5)	170	178
O(6)-H(11)···O(10)			2.915(3)	2.928(5)	145	165

Table 3S Hydrogen-bond O···O···O angles

	Angles	
	163K	293K
O2···O1···O3	102.7	103.1
O2···O1···O4	106.8	106.3
O3···O1···O4	112.0	111.9
O1···O2···O3	112.7	113.7
O1···O2···O3	110.7	110.0
O3···O2···O3	106.9	106.0
O1···O3···O2	103.4	103.1
O1···O3···O2	111.2	111.4
O2···O3···O2	108.1	109.0
O1···O4···O1	105.0	104.9

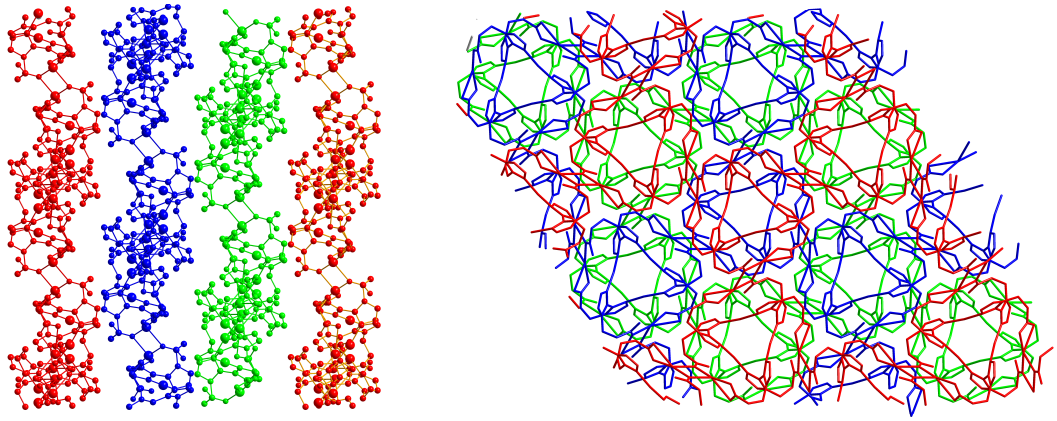


Fig. S1 Packing view of the 6^3 layers along *a*-axis (left) in ABC fashion and along *c*-axis (right). Three adjacent layers are represented in red, blue and green. Water molecules were omitted for clarity.

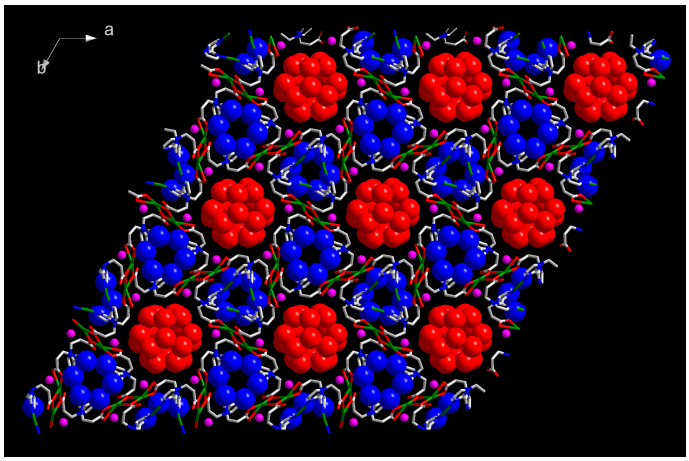
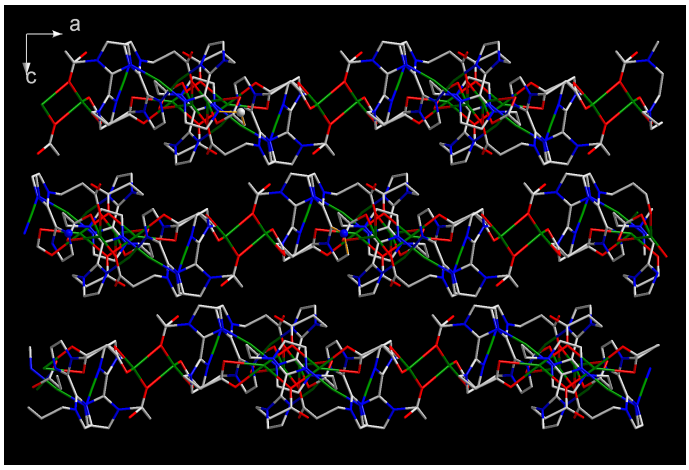
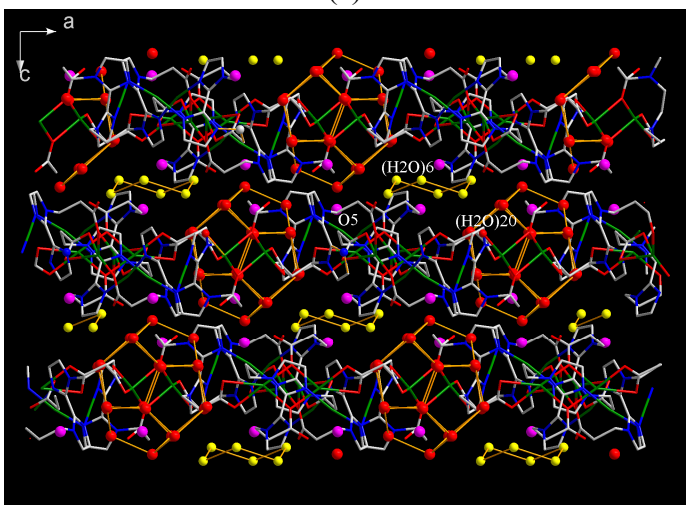


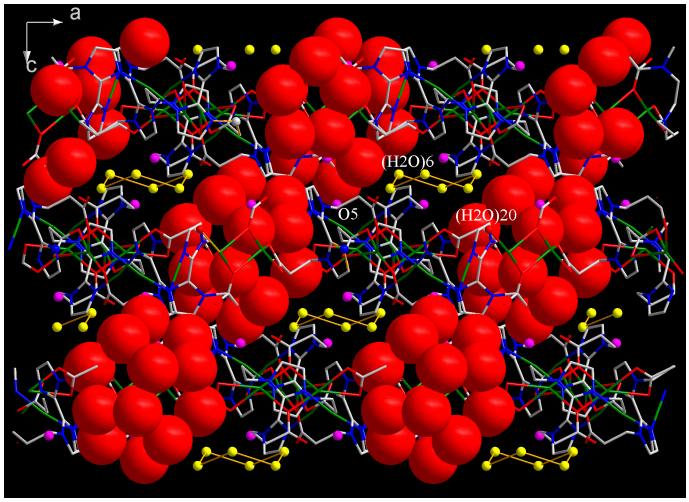
Fig. S2 View of the 6^3 layers along *c*-axis. The pentagonal dodecahedron of $(H_2O)_{20}$ are represented in red (O1-O4), the chair hexamer in blue (O6), and the lattice molecule (O5) in pink. Hydrogen atoms are omitted for clarity.



(a)

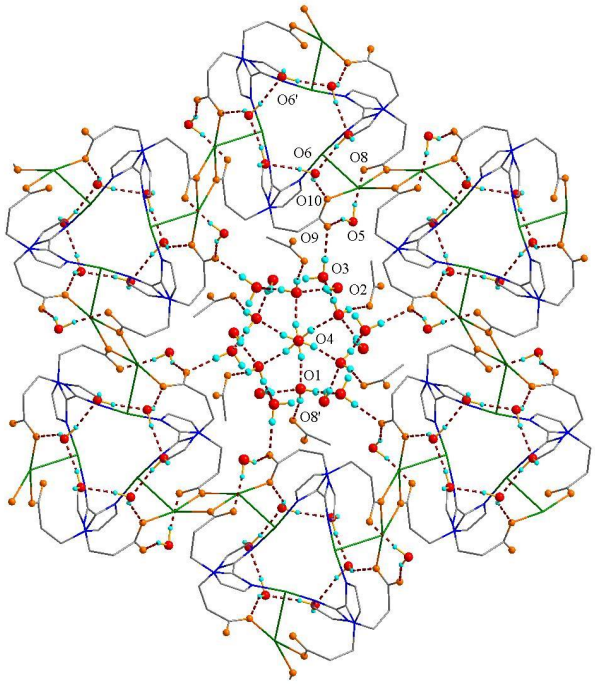


(b)

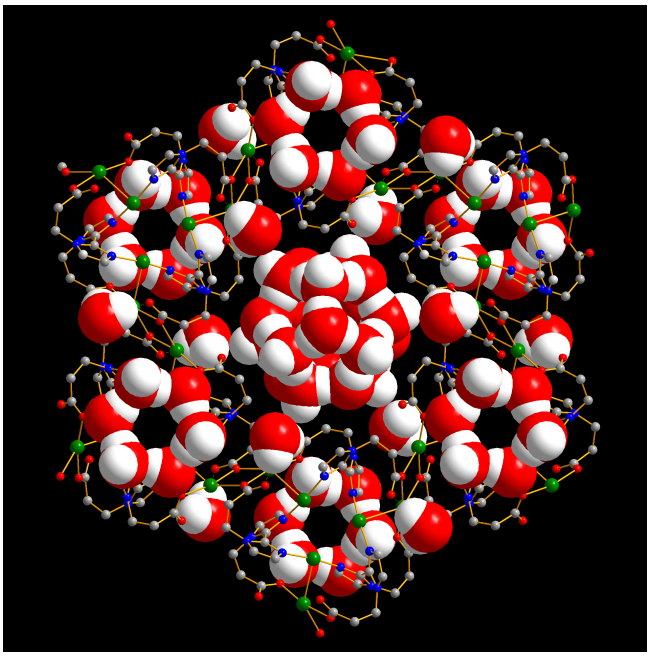


(c)

Fig. S3 Packing views of (a) the wires-sticks representation, showing the layers along *b*-axis in ABCABC fashion; (b) the 3D structure, showing the pentagonal dodecahedron of $(H_2O)_{20}$ (red), one lattice water molecule (O5) (pink) and the chair-shaped cyclic water hexamers (O6) (yellow, ball-sticks) are localed in the channels; (c) the 3D structure, showing the $(H_2O)_{20}$ (space-filling), one lattice water molecule (O5) and the chair-shaped cyclic water hexamers (O6) (ball-sticks) are localed in the channels. The hydrogen atoms are omitted for clarity.



(a)



(b)

Fig. S4 (a) View of the hydrogen bonding network in the structure of **1**. (b) View of the X-ray crystal structure of **1**on the *ab* plane, showing the water molecules (space-filling) in the host framework.

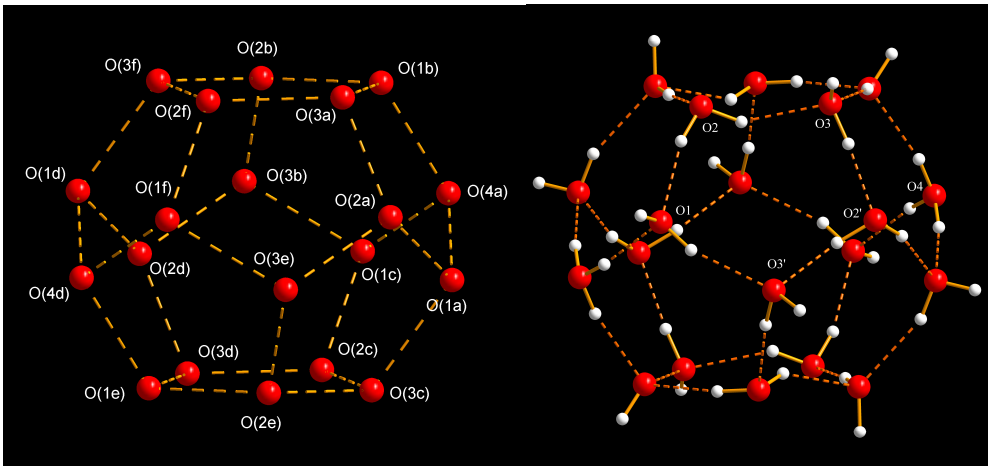


Fig. S5 Perspective view of pentagonal dodecahedron of $(H_2O)_{20}$. Symmetry codes: a: 1/3+x, -1/3+y, 2/3+z; b: 4/3-y, 2/3+x-y, 2/3+z; c: 1/3-x+y, 2/3-x, 2/3+z; d: 1-x, 1-y, -z; e: y, -x+y, -Z; f: 1+x-y, x, -z.

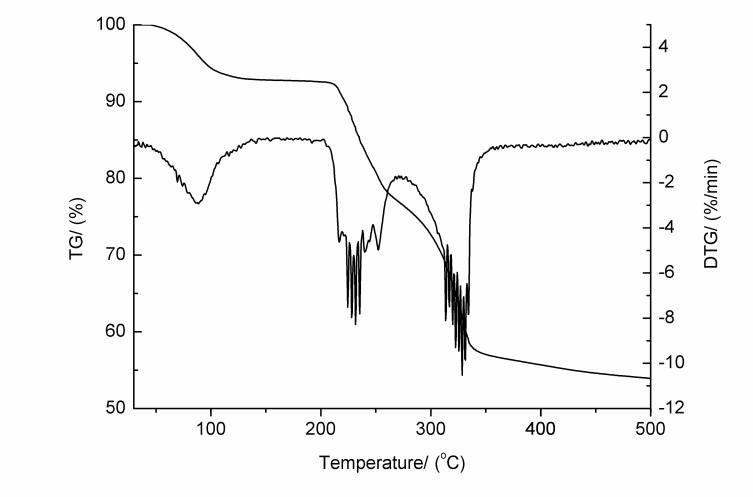


Fig. S6 TGA curve of 1

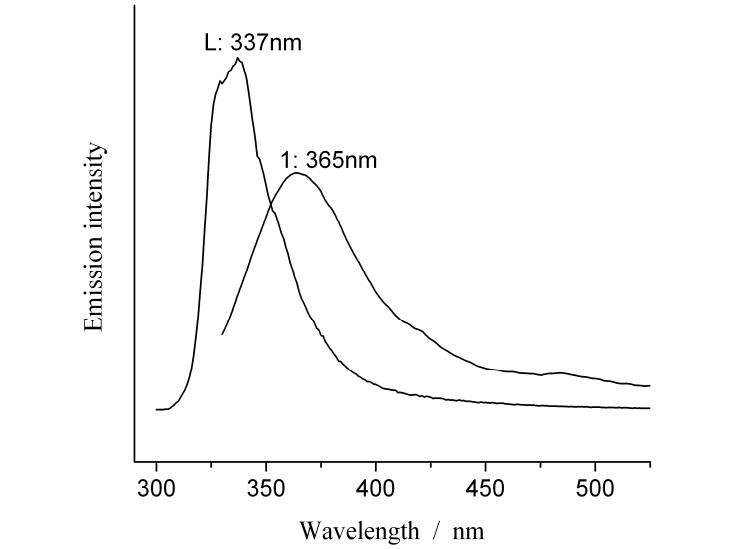


Fig. S7 The solid-state photoluminescence spectra of L (λ_{ex} = 280 nm) and **1** (λ_{ex} = 295 nm) recorded at room temperature.