– Electronic Supplementary Information –

Extended H-Bond Networks based on Guanidinium H-donors and $[Zr(A)_4]^{4-}$ H-acceptor units: Modulation of the assemblage and guest accessible volume by chemical design (A = Oxalate, dihydrobenzoquinonate, chloranilate)

*Georges Mouchaham, Nans Roques, Carine Duhayon, Inhar Imaz, and Jean-Pascal Sutter**

Figure S1 ORTEP view of the asymmetric unit of $\{(H\text{-}Guan)_4[Zr(Ox)_4]\}$, **1** with ellipsoids cut at the 30% probability level.

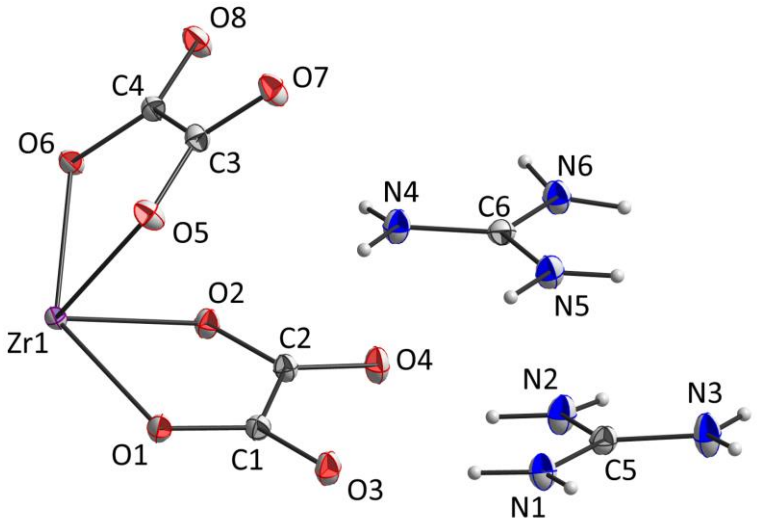

Figure S2 H-bonds between $[Zr(Ox)_4]^{4-}$ and bridging/non-bridging $(H\text{-}Guan)^{+}$ cations in the supramolecular architecture of $\{(H\text{-}Guan)_4[Zr(Ox)_4]\}$, **1**. Colour codes: Zr, violet; C, grey; O, red; H, black; N, blue. Symmetry operations: (a) x, 2-y, -0.5+z; (b) 1-x, y, 0.5-z; (c) 1-x, 1-y, 1-z.

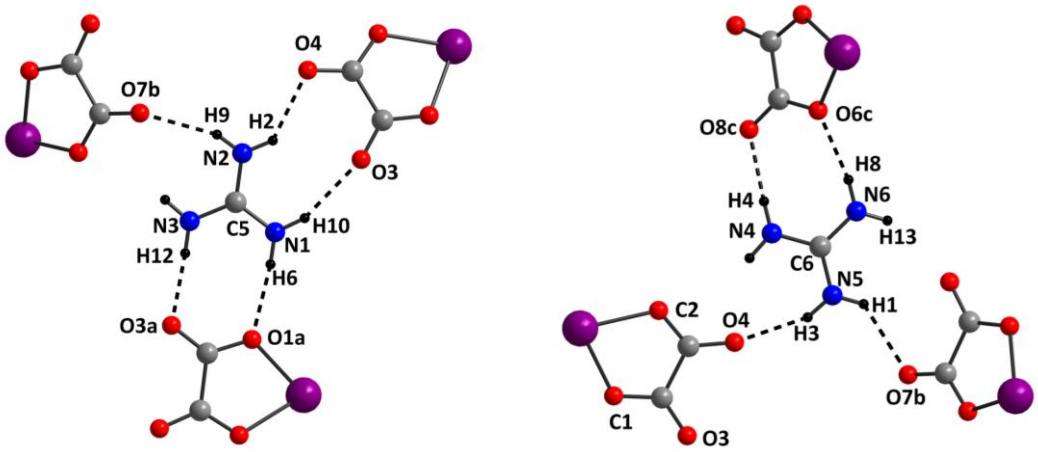

Figure S3 ORTEP view of the asymmetric unit of $\{(H\text{-}AIm)_4[Zr(Ox)_4]\}\cdot 5H_2O$, **2**, with ellipsoids cut at the 30% probability level.

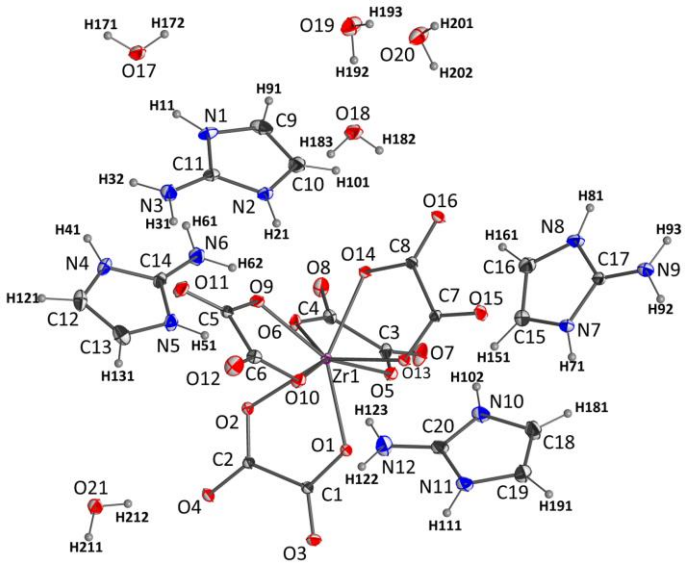

Figure S4 H-bonds between $[Zr(Ox)_4]^{4-}$ and bridging/non-bridging $(H\text{-}AIm)^+$ cations in the supramolecular architecture of $\{(H\text{-}AIm)_4[Zr(Ox)_4]\}\cdot 5H_2O$, **2**. Colour codes: Zr, violet; C, grey; O, red; H, black; N, blue. Symmetry operations: (a) 1-x, 1-y, 0.5+z; (b) 1-x, 1-y, -0.5+z; (c) 1-x, 2-y, -0.5+z; (d) x, y, -1+z ; (e) 1-x, 2-y, -1.5+z.

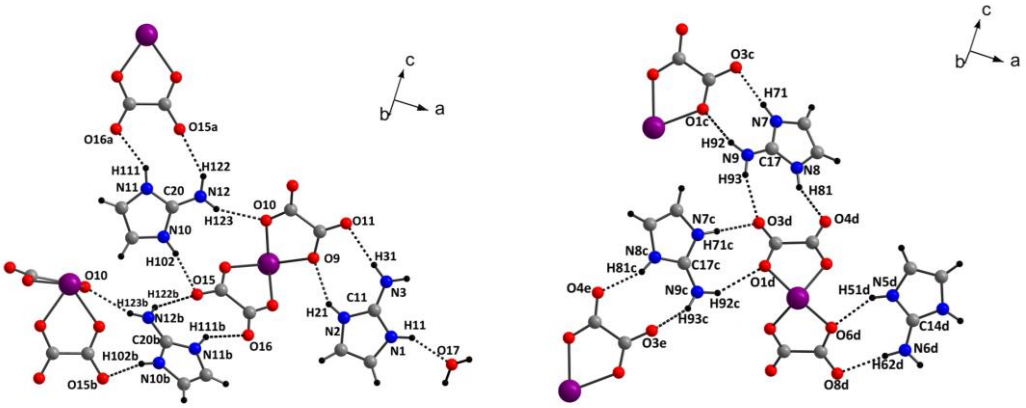

Figure S5 ORTEP view of the asymmetric unit of $\{(H\text{-}DmG)_4[Zr(Ox)_4]\}\cdot 0.5H_2O$, **3**, with ellipsoids cut at the 30% probability level. H atoms are omitted for the sake of clarity.

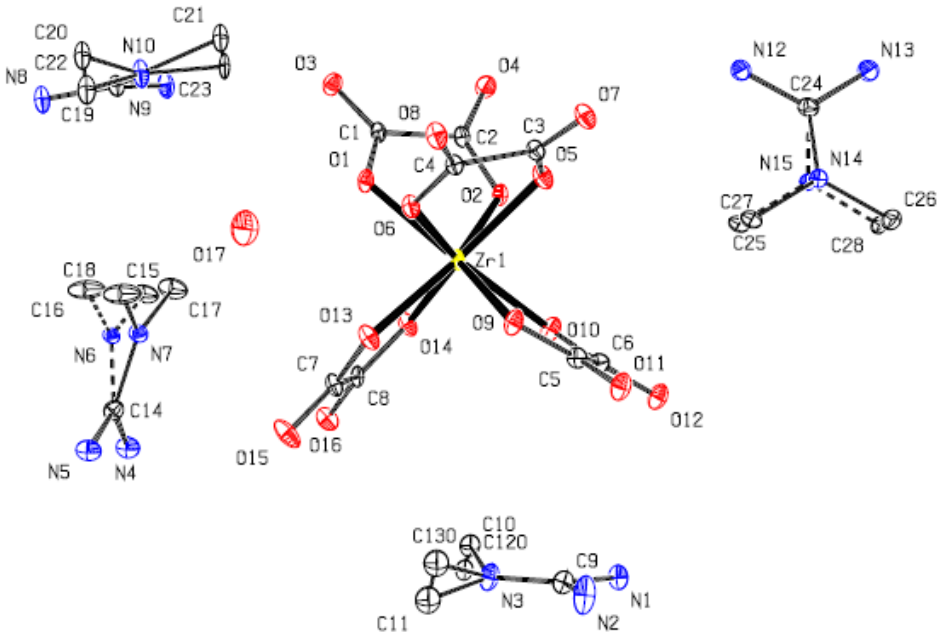

Figure S6 Space filling representation of the supramolecular architecture of $\{(H\text{-}DmG)_4[Zr(Ox)_4]\}\cdot 0.5H_2O$, **3**. Methyl groups of the (H-DmG)+ cation are shown in "ball and stick". H_2O molecules are omitted for the sake of clarity.

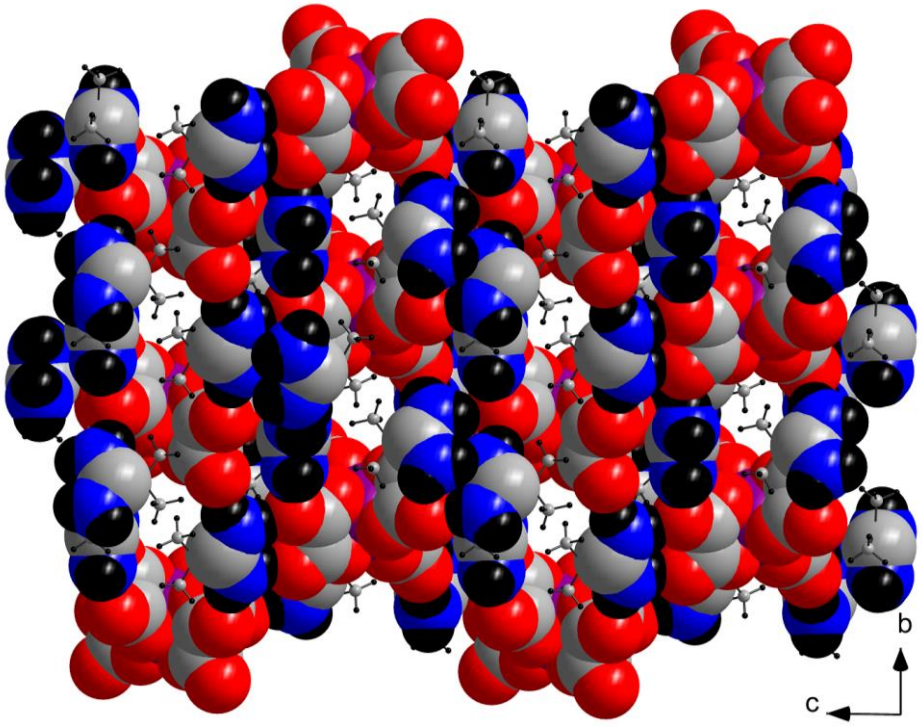

Figure S7 ORTEP view of the asymmetric unit of $\{(H\text{-}Guan)_4[Zr(DBQ)_4]\}\cdot 1.5H_2O$, **4**, with ellipsoids cut at the 30% probability level. O2W has an occupancy factor of 0.5.

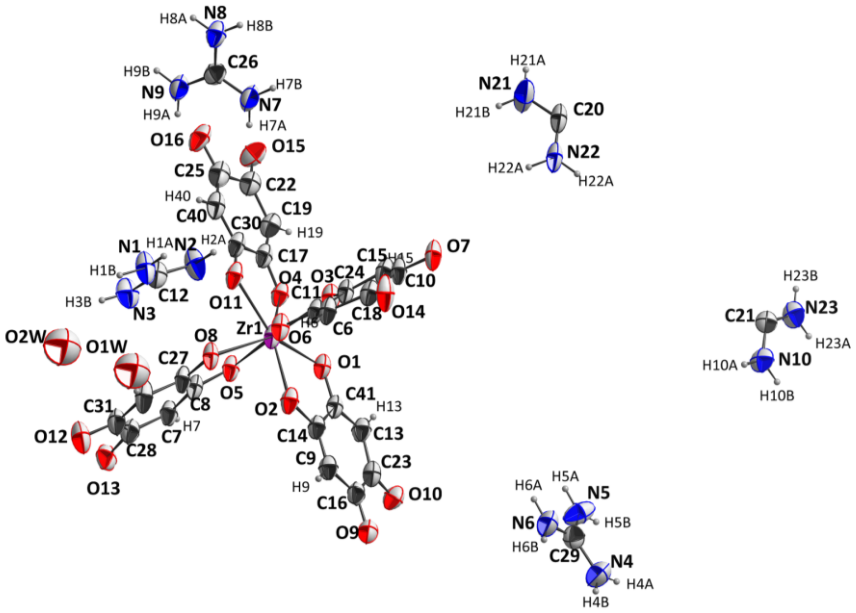

Figure S8 H-bonds between $[Zr(DBQ)_4]^{4-}$ and $(H\text{-}Guan)^+$ cations in the supramolecular architecture of $\{(H\text{-}Guan)_4[Zr(DBQ)_4]\}\cdot 1.5H_2O$, **4**. Colour codes: Zr, violet; C, grey; O, red; H, black; N, blue. Symmetry operations: (a) 1-x, y, 0.5-z ; (b) 0.5-x, 1.5-y, 0.5+z ; (c) -0.5+x, 0.5+y, 0.5-z ; (d) 1.5-x, 1.5-y, -0.5+z ; (e) 1.5-x, -0.5+y, z ; (f) 0.5+x, 0.5+y, 0.5-z ; (g) x, 2-y, -0.5+z.

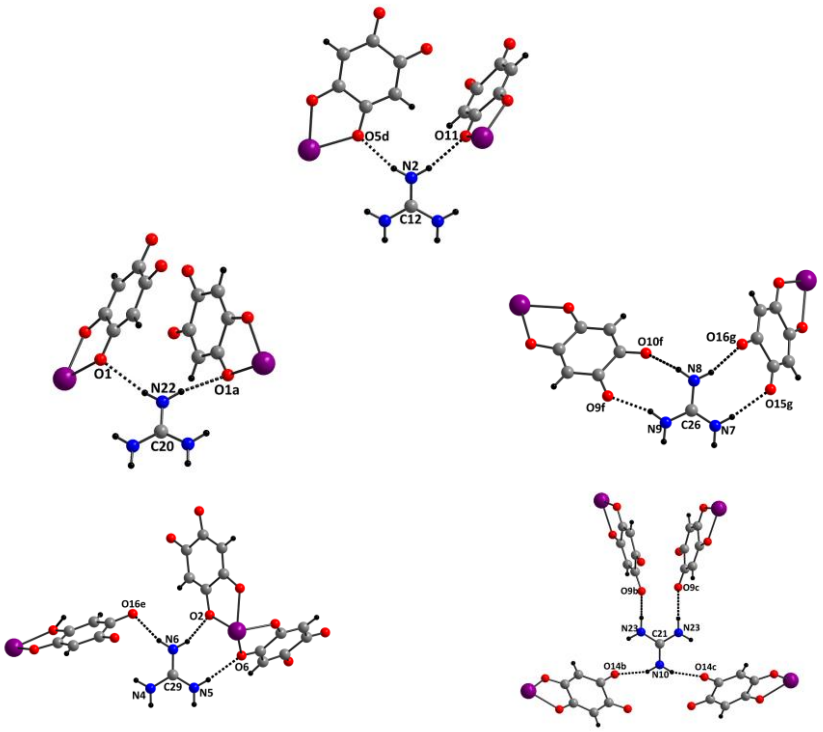

Figure S9 π···π interactions (dashed red lines) and C–H···π interactions (dashed blue lines) between DBQ ligands of consecutive metallotectons in the supramolecular architecture of **4**.

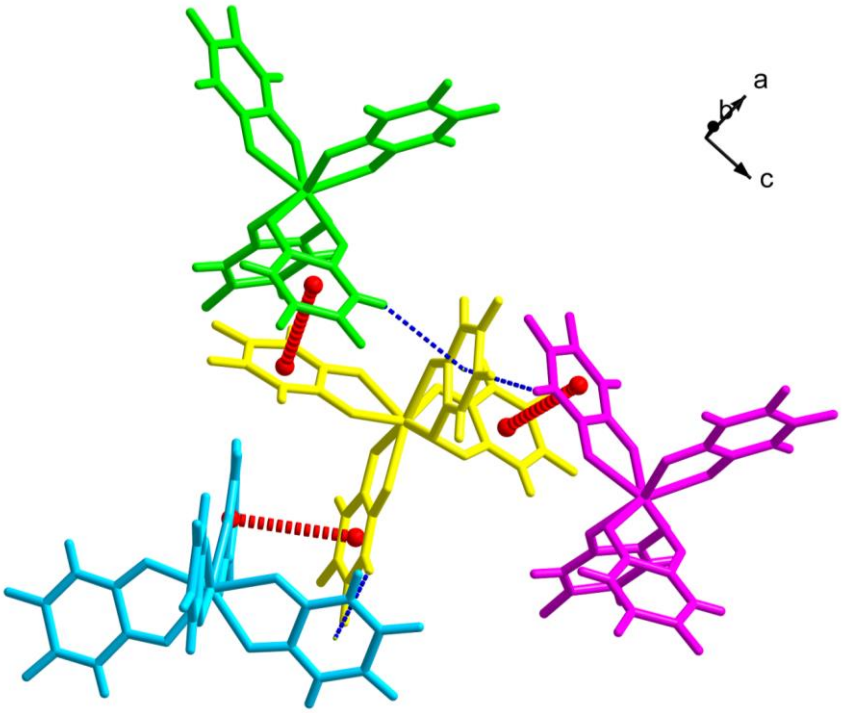

Figure S10 3D H-bonded supramolecular architecture of **4**.

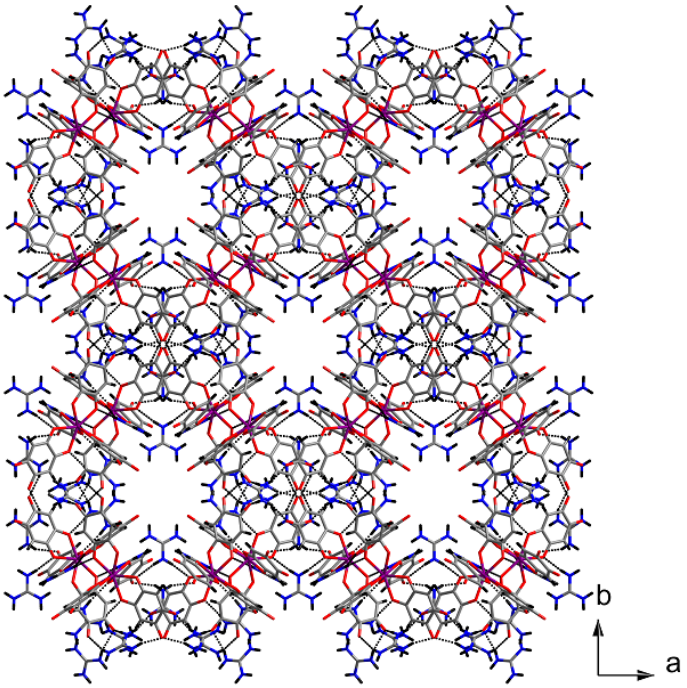

Figure S11 ORTEP view of the asymmetric unit of $\{(H\text{-}Guan)_4[Zr(CA)_4]\}\cdot 5.85H_2O$, **5**, with ellipsoids cut at the 30% probability level.

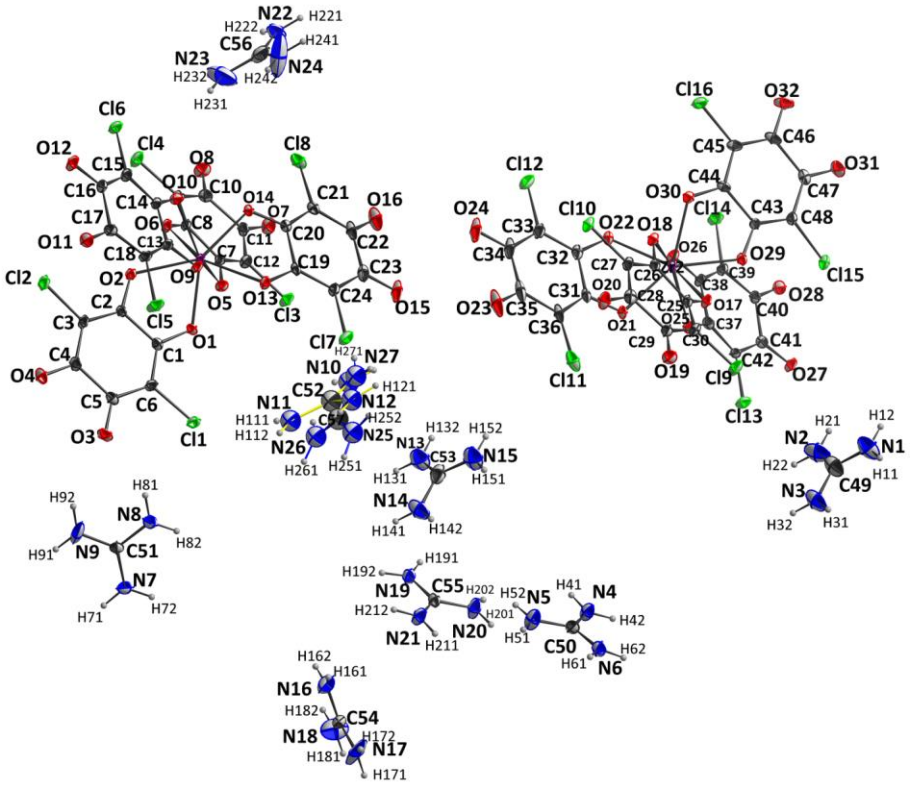

Figure S12 H-bonds between $[Zr(CA)_4]^{4-}$ and $(H\text{-}Guan)^+$ cations in the supramolecular architecture of **5**. Colour codes: Zr, violet; C, grey; O, red; H, black; N, blue. Symmetry operations: (a) x, -1+y, z ; (b) 1-x, -y, 1-z ; (c) 1-x, 1-y, 1-z ; (d) 1+x, 1+y, 1+z ; (e) 1-x, 2-y, 1-z ; (f) x, 1+y, 1+z.

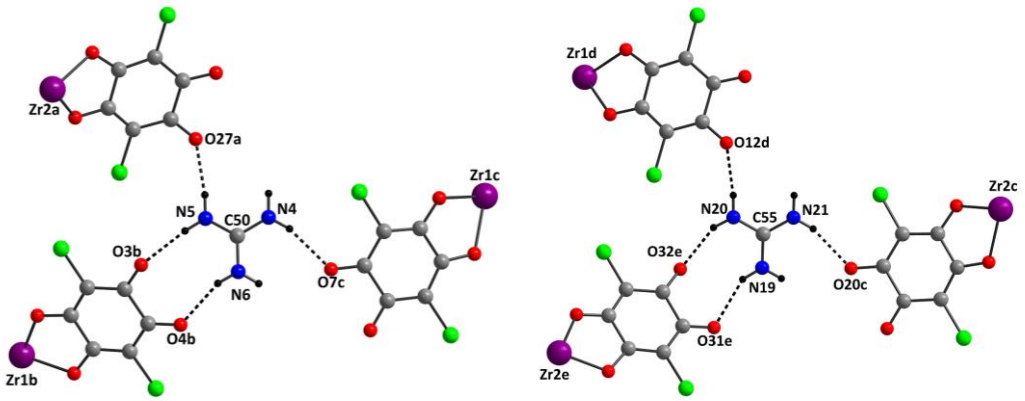

Figure S13 ORTEP view of the asymmetric unit of $\{(H\text{-}AIm)_4[Zr(CA)_4]\}\cdot H_2O$, **6**, with ellipsoids cut at the 30% probability level.

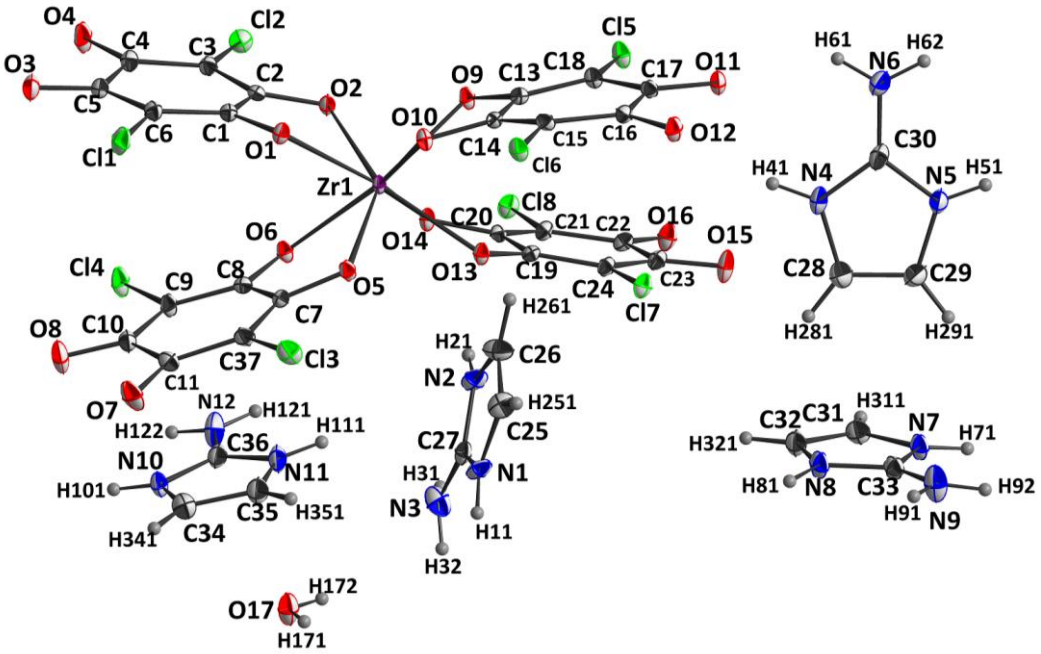

Figure S14 H-bonds between $[Zr(CA)_4]^{4-}$ and bridging/non-bridging $(H\text{-}AIm)^+$ cations in the supramolecular architecture of $\{(H\text{-}AIm)_4[Zr(CA)_4]\}\cdot H_2O$, **6**. Colour codes: Zr, violet; C, grey; O, red; H, black; N, blue. Symmetry operations: (a) 1-x, 1-y, 1-z; (b) x, 1.5-y, 0.5+z; (c) 1+x, y, z; (d) 1+x, y, 1+z; (e) –x, 1-y, -z.

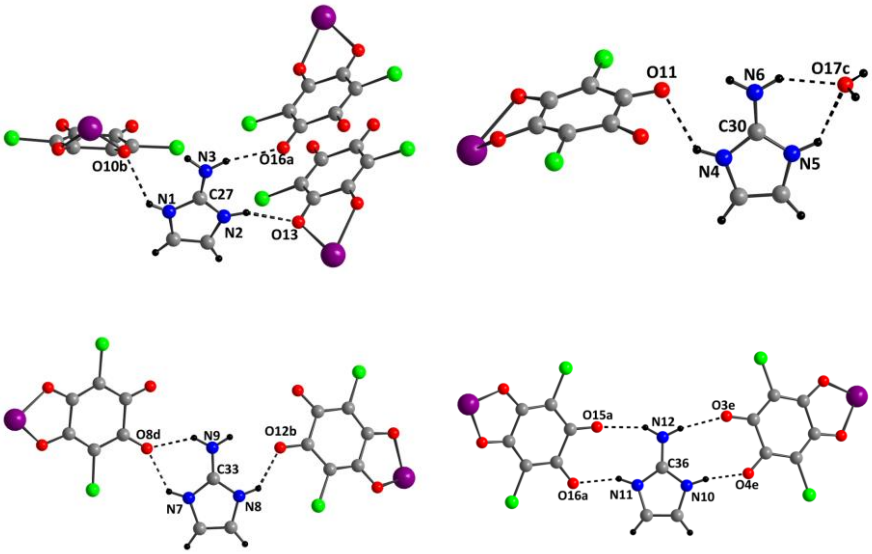

Figure S15 ORTEP view of the asymmetric unit of $\{K_2(H_2O)_3(H\text{-}DmG)_2[Zr(DBQ)_4]\}\cdot H_2O$, **7**, with ellipsoids cut at the 30% probability level.

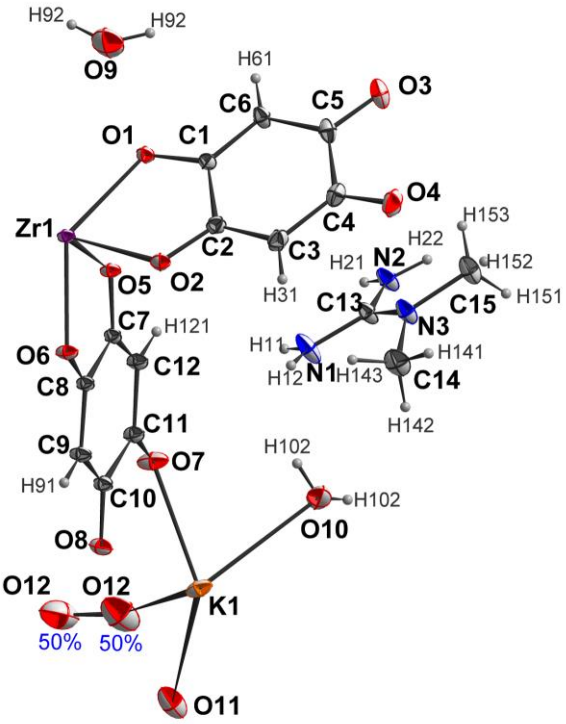

Figure S16 Space filling representation of the network **7** (view along the *c* axis). Colour codes: Zr, violet; K, orange; C, grey; O, red; H, black; N, blue.

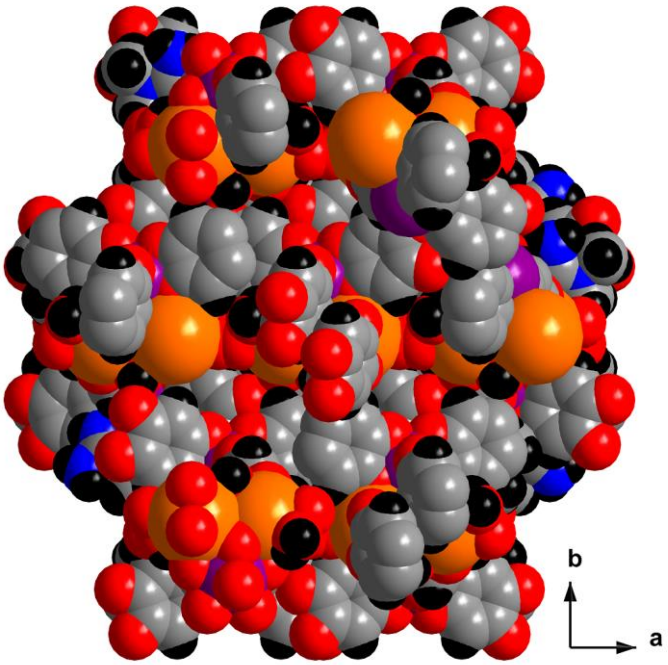

Figure S17 H-bonds between $[Zr(DBQ)_4]^{4-}$ and bridging/non-bridging $(H\text{-}DmG)^+$ cations in the supramolecular architecture of $\{K_2(H_2O)_3(H\text{-}DmG)_2[Zr(DBQ)_4]\}\cdot H_2O$, **7**. Colour codes: Zr, violet; C, grey; O, red; H, black; N, blue. Symmetry operations: (a) 0.5+x, 1.5-y, 1-z ; (b) 1-x, 1-y, 1-z ; (c) -0.5+x, 1.5-y, 1-z.

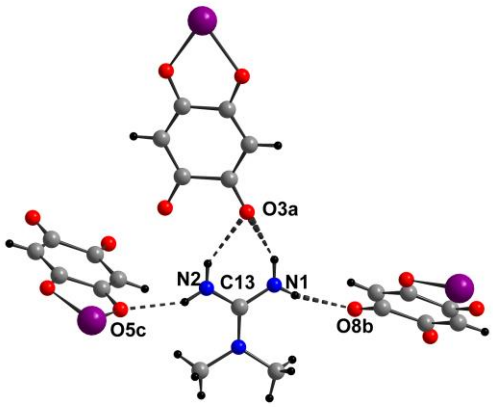

Figure S18 TGA curves for compounds **2** (a) and **5** (b) recorded under N_2 flow.

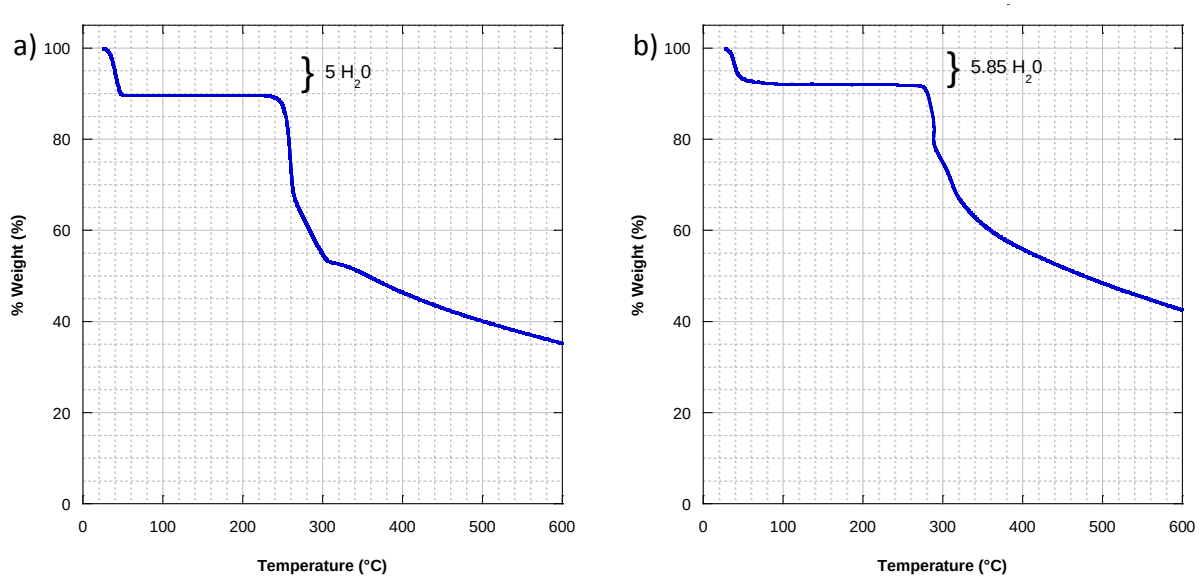

Figure S19 Variable temperature PXRD diffractograms under air atmosphere for compounds **2** (a) and **5** (b). (RT (1) and (2) stand for the diffractogram registered at Room Temperature before heating and after cooling, respectively).

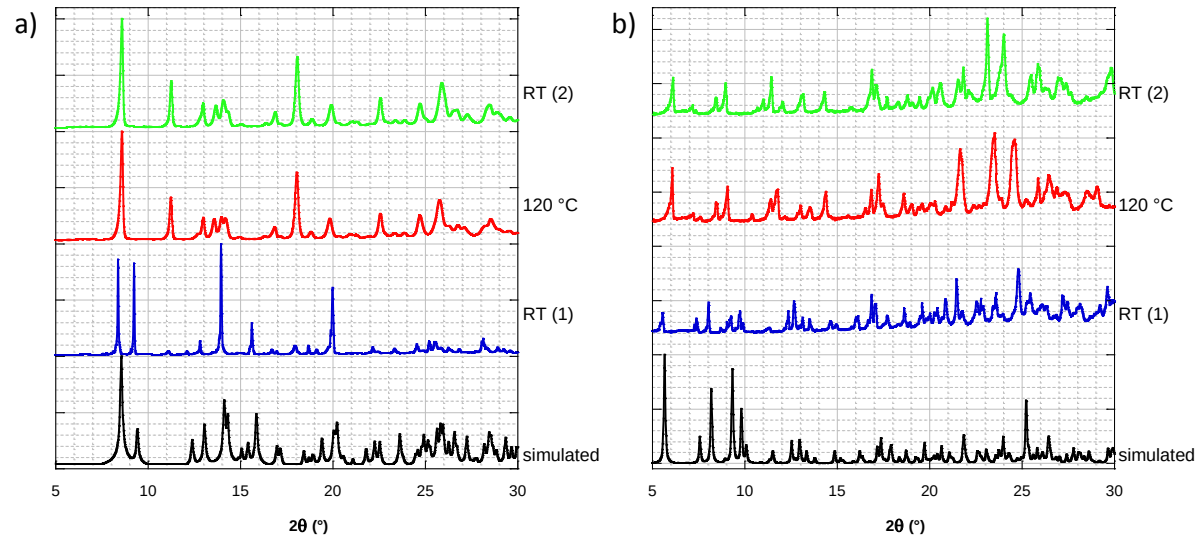

Table S1. Selected Hydrogen bonds for compounds **1-7**.

Atoms D−H···A	Dist. D−H (Å)	Dist. H−A (Å)	Dist. D−A (Å)	Angle D−H−A (°)
		{(H-Guan)$_4$[Zr(Ox)$_4$]} (1)$^{\#}$		
N1−H6···O1a	0.87	2.12	2.985(2)	170
N1−H10···O3a	0.88	2.18	3.007(2)	158
N2−H9···O7b	0.86	2.14	2.950(2)	158
N2−H2···O4	0.88	2.11	2.837(2)	139
N3−H12···O3a	0.87	1.97	2.839(2)	177
N4−H4···O8c	0.87	2.06	2.896(2)	163
N5−H1···O7b	0.86	2.27	2.958(2)	138
N5−H3···O4	0.88	2.08	2.898 (2)	156
N6−H8···O6c	0.88	2.04	2.917(2)	171
		{(H-AIm)$_4$[Zr(Ox)$_4$]}·5H$_2$O (2)$^{\#}$		
N6d−H62d···O8d	0.87	2.13	2.997(2)	175
N5d−H51d···O6d	0.86	2.13	2.905(2)	149
N7−H71···O3c	0.87	1.93	2.807(2)	179
N9−H92···O1c	0.87	2.30	3.025(2)	141
N9−H93···O3d	0.87	2.09	2.898(2)	155
N8−H81···O4d	0.87	2.03	2.818(2)	150
N2−H21···O9	0.86	2.11	2.883(2)	149
N3−H31···O11	0.89	2.13	3.010(2)	177
N10−H102···O15	0.88	1.99	2.840(2)	164
N12−H123···O10	0.87	2.23	3.037(2)	155
N12−H122···O15a	0.87	2.24	2.987(2)	145
N11−H111···O16a	0.89	2.08	2.844(2)	143
		{(H-DmG)$_4$[Zr(Ox)$_4$]}·0.5H$_2$O (3)$^{\#}$		
N1−H11···O16a	0.86	2.06	2.850(5)	153
N1−H12···O11b	0.85	2.21	2.965(6)	147
N2−H21···O15c	0.86	2.11	2.871(6)	147
N2−H22···O12c	0.85	1.98	2.809(7)	162
N4−H43···O15e	0.86	1.97	2.807(5)	166
N4−H44···O11d	0.87	2.09	2.876(6)	151
N5−H53···O16e	0.86	2.07	2.931(5)	175
N5−H54···O12f	0.85	2.12	2.944(5)	162
N8−H81···O8d	0.86	1.98	2.772(6)	152
N8−H82···O4f	0.86	2.08	2.881(5)	155
N8−H83···O4f	0.85	2.08	2.881(5)	155
N8−H84···O8d	0.86	1.92	2.772(6)	170
N9−H91···O7d	0.86	2.05	2.864(6)	157
N9−H92···O3	0.86	2.07	2.891(6)	159
N9−H93···O7d	0.86	2.01	2.864(6)	175
N9−H94···O3	0.87	2.11	2.891(6)	150
N12−H123···O4g	0.85	2.00	2.827(5)	164
N12−H124···O7	0.87	2.12	2.820(4)	155
N13−H131···O3g	0.85	2.00	2.846(4)	170
N13−H132···O8g	0.84	2.12	2.891(5)	153
		{(H-Guan)$_4$[Zr(DBQ)$_4$]}·1.5H$_2$O (4)$^{\#}$		
N22−H22A···O1	0.86	2.23	3.032(9)	154
N22−H22B···O1a	0.86	2.23	3.032(9)	154
N10−H10B···O14b	0.86	2.06	2.861(7)	155
N23−H23B···O9b	0.86	2.23	2.956(1)	142
N2−H2A···O5d	0.86	2.07	2.895(1)	162
N2−H2B···O11	0.86	2.13	2.971(1)	167
N6−H6A···O2	0.86	2.00	2.815(1)	157
N5−H5A···O6	0.86	2.18	3.034(1)	173

N6−H6B···O16e	0.86	2.08	2.901(1)	160
N8−H8A···O10f	0.86	2.03	2.815(9)	151
N8−H8B···O16g	0.86	2.12	2.926(1)	155
N7−H7B···O15g	0.86	2.15	2.976(1)	161
N9−H9B···O9f	0.86	2.04	2.875(9)	163

{(H-Guan)$_4$[Zr(CA)$_4$]}·5.85H$_2$O (5)$^{\#}$

N4−H42···O7c	0.86	2.23	2.946(7)	163
N5−H51···O3b	0.87	2.23	2.927(7)	170
N5−H52···O27a	0.86	2.06	2.940(7)	172
N6−H61···O4b	0.86	2.23	2.858(8)	147
N19−H191···O31e	0.86	2.06	2.968(8)	149
N20−H202···O32e	0.86	2.13	2.910(9)	156
N20−H201···O12d	0.86	2.00	2.925(7)	173
N21−H212···O20c	0.86	2.18	2.915(7)	163
N1−H12···O11f	0.86	2.08	2.974(1)	149
N8−H81···O3c	0.87	2.03	3.106(6)	157
N16−H162···O26c	0.86	2.12	3.012(7)	157
N15−H152···O28e	0.86	2.15	2.595(1)	149
N22−H222···O19	0.86	2.04	2.913(8)	147

{(H-AIm)$_4$[Zr(CA)$_4$]}·H$_2$O (6)$^{\#}$

N2−H21···O13	0.87	2.16	2.951(3)	151
N3−H31···O16a	0.87	2.26	3.113(3)	167
N1−H11···O10b	0.85	2.24	2.864(3)	130
N4−H41···O11	0.88	2.18	2.869(3)	136
N5−H51···O17c	0.88	2.16	2.843(3)	134
N6−H61···O17c	0.88	2.08	2.837(3)	145
N7−H71···O8d	0.88	2.07	2.769(2)	135
N8−H81···O12b	0.88	2.05	2.775(3)	140
N9−H92···O8d	0.89	2.07	2.803(3)	139
N10−H101···O4e	0.87	1.88	2.747(3)	169
N11−H111···O16a	0.86	2.01	2.814(2)	154
N12−H121···O15a	0.87	2.13	2.913(3)	150
N12−H122···O3e	0.86	2.09	2.940(3)	168

{K$_2$(H$_2$O)$_3$(H-DMG)$_4$[Zr(DBQ)$_4$]}·H$_2$O (7)$^{\#}$

N1−H11···O3a	0.85	2.31	3.01	140
N1−H12···O8b	0.85	2.17	2.99	163
N2−H22···O5c	0.85	2.12	2.90	153
N2−H21···O3a	0.85	2.22	2.97	149
N2−H21···O4	0.85	2.30	2.98	138

#Symmetry operations:

For **1**: (a) x, 2-y, -0.5+z; (b) 1-x, y, 0.5-z; (c) 1-x, 1-y, 1-z.

For **2**: (a) 1-x, 1-y, 0.5+z; (b) 1-x, 1-y, -0.5+z; (c) 1-x, 2-y, -0.5+z; (d) x, y, -1+z ; (e) 1-x, 2-y, -1.5+z.

For **3** : (a) 1-x, -y, 1-z ; (b) x, -1+y, z ; (c) x, 1+y, z ; (d) 1+x, y, z ; (e) 2-x, 1-y, z ; (f) 2-x, -y, -z ; (g) 1-x, -y, -z ; (h) 1-x, 1-y, -z.

For **4** : (a) 1-x, y, 0.5-z ; (b) 0.5-x, 1.5-y, 0.5+z ; (c) -0.5+x, 0.5+y, 0.5-z ; (d) 1.5-x, 1.5-y, -0.5+z; (e) 1.5-x, -0.5+y, z ; (f) 0.5+x, 0.5+y, 0.5-z ; (g) x, 2-y, -0.5+z.

For **5** : (a) x, -1+y, z ; (b) 1-x, -y, 1-z ; (c) 1-x, 1-y, 1-z ; (d) 1+x, 1+y, 1+z ; (e) 1-x, 2-y, 1-z ; (f) x, 1+y, 1+z.

For **6** : (a) 1-x, 1-y, 1-z ; (b) x, 1.5-y, 0.5+z ; (c) 1+x, y, z ; (d) 1+x, y, 1+z ; (e) –x, 1-y, -z.

For **7** : (a) 0.5+x, 1.5-y, 1-z ; (b) 1-x, 1-y, 1-z ; (c) -0.5+x, 1.5-y, 1-z.