Electronic Supplementary Information for Dalton Transactions

Construction of different dimensional inorganic–organic hybrid materials based on polyoxometalates and metal-organic units via changing metal ions: from non-covalent interactions to covalent connections

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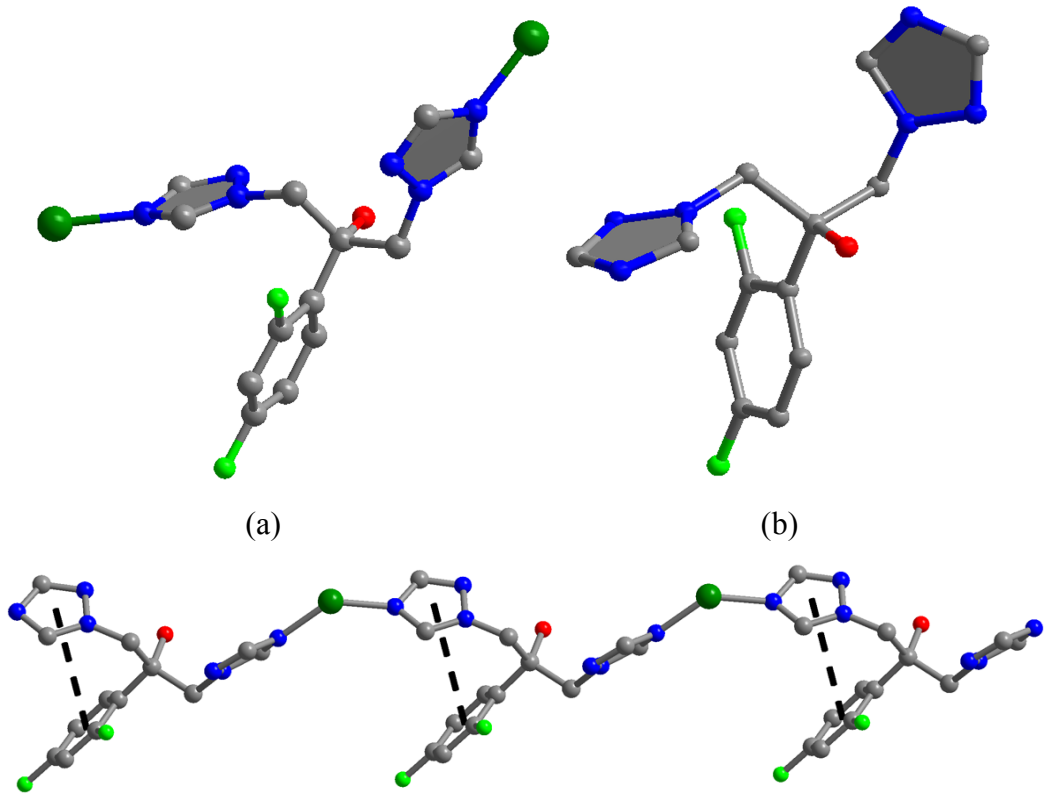
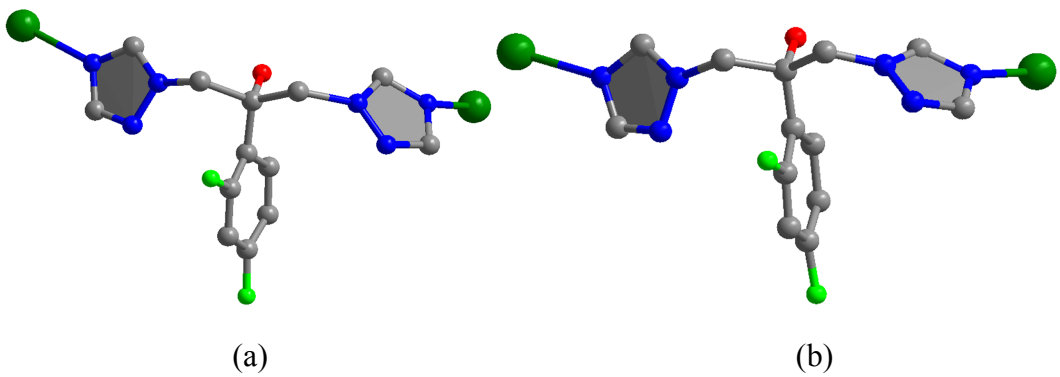
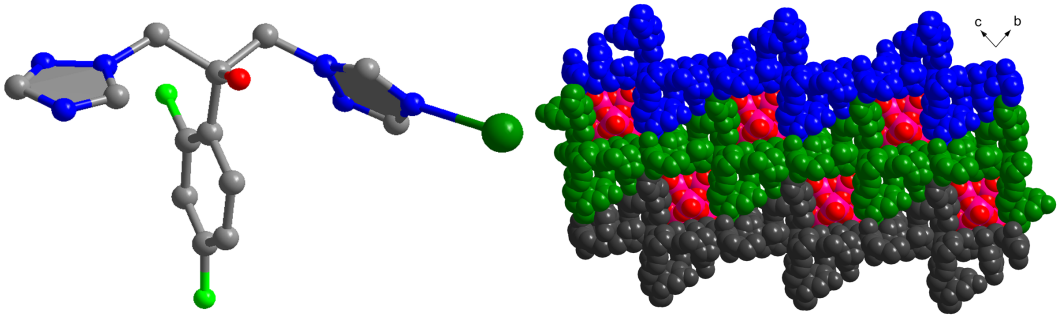
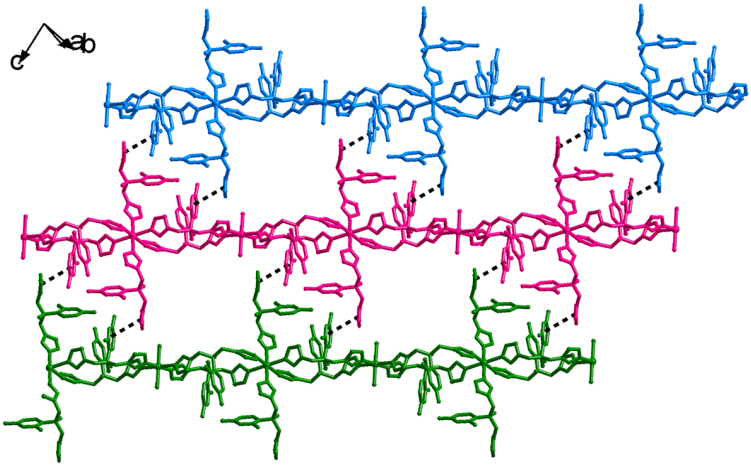


Fig. S1 (a) and (b) Ball-stick representations of the coordination modes of Hfcz1 and Hfcz2 ligands in **1**. (c) The $\pi\cdots\pi$ stacking in the same chain.



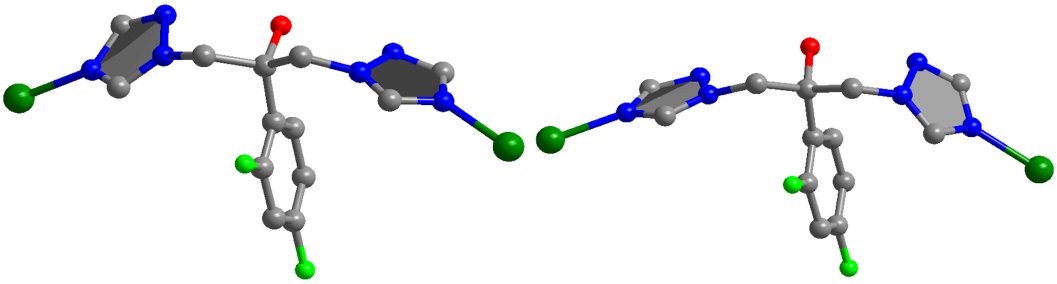


(c) (d)

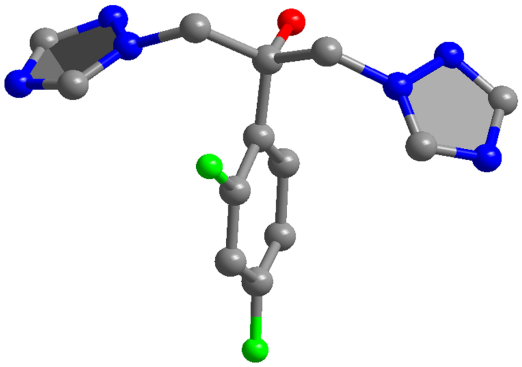


(e)

Fig. S2 (a), (b) and (c) Ball-stick representations of the coordination modes of three kinds of Hfcz ligands in **2**, respectively. (d) Space filling representation of the arrangement of **2**. (e) View of the 2D supramolecular structure formed by the $\pi\cdots\pi$ stacking between adjacent chains.



(a) (b)



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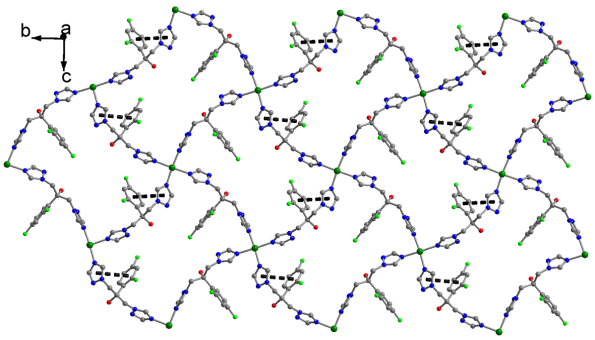
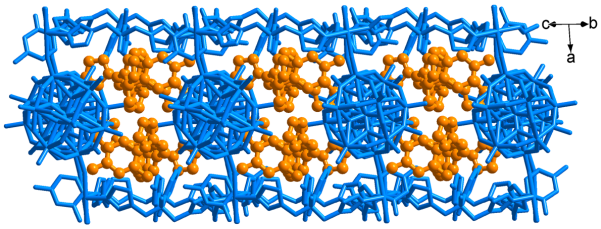


(d)



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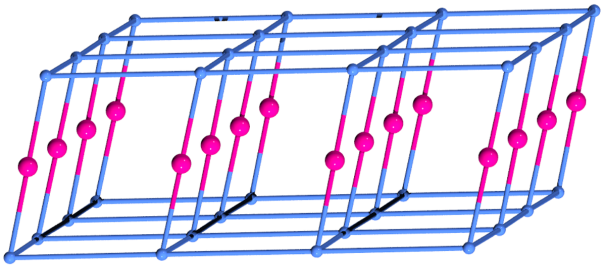
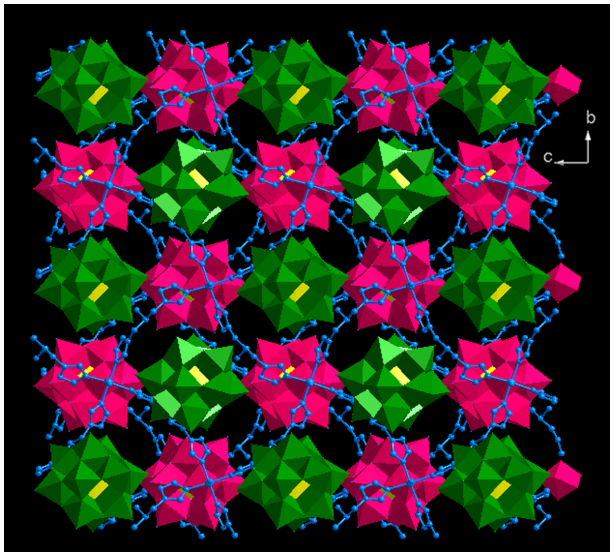
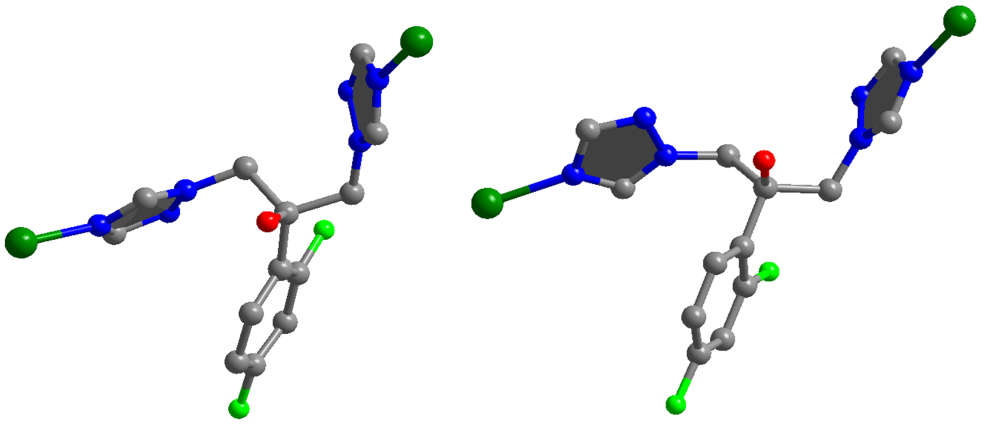


(f)

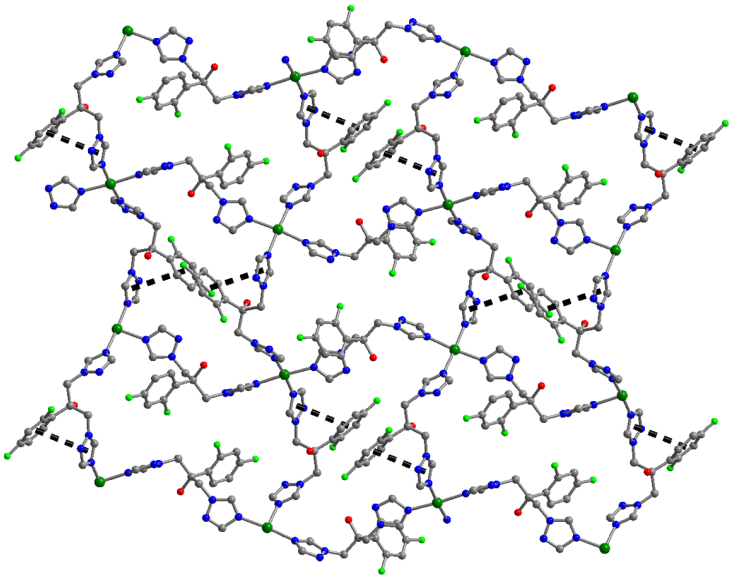


(g)

Fig. S3 (a), (b) and (c) Ball-stick representations of the coordination modes of three kinds of Hfcz ligands in **3**, respectively. (d) The $\pi\cdots\pi$ stacking in the same ligand. (e) Blue and yellow ball-stick representations of the sandwich double sheet and dissociative $(H_3fcz)^{2+}$ ligands. (f) Ball-stick representation of the sandwich double sheet. (g) Ball-stick and polyhedral representations of compound **3** (all DFP groups are omitted for clarity).



(a) (b)



(c)

Fig. S4 (a) and (b) Ball-stick representations of the coordination modes of Hfcz ligands in **4**. (c) The $\pi\cdots\pi$ stacking in the same ligand.

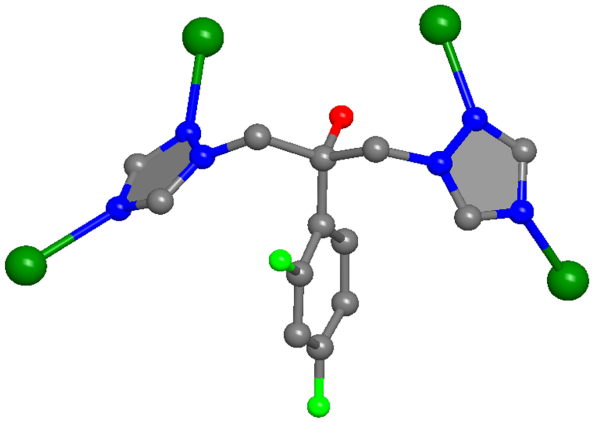


Fig. S5 Ball-stick representation of the coordination mode of Hfcz ligands in **5**.

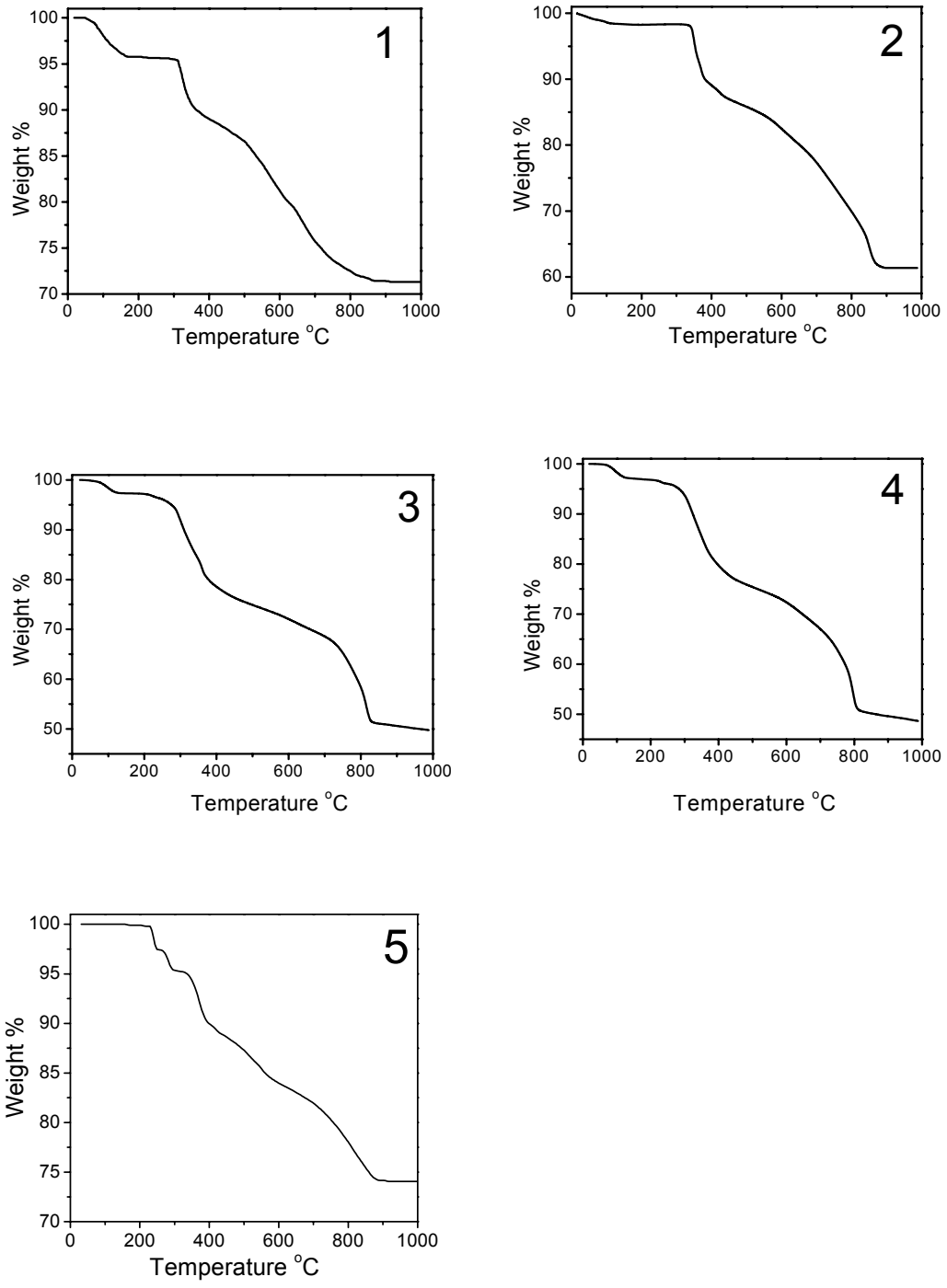


Fig. S6 TGA curves of **1-5**.

Table S1. Conformation (B) of L (A), Dihedral Angle of Two Imidazole Rings (C) (deg), Dihedral Angle Between Imidazole Rings and Phenyl Ring of Ligand (D) (deg), and Torsion Angles (E) (deg) in Compounds **1**-**5**

	A	B	C	D		E	
1	Hfcz1	GT	118.8	24.3	123.6	N1-C3-C7-C6	C3-C7-C6-N5
						-40.8	-169.9
	Hfcz2	GT	107.7	37.6	118.5	N8-C16-C17-C18	C16-C17-C18-N7
						56.6	176.1
2	Hfcz1	TT	70.7	47.8	101.1	N7-C16-C17-C18	C16-C17-C18-N10
						-171.4	171.4
	Hfcz2	TT	108.2	69.5	57.2	N13-C31-C30-C29	C31-C30-C29-N16
						-176.4	173.5
	Hfcz3	TT	119.8	86.4	45.9	N1-C3-C4-C5	C3-C4-C5-N4
						178.6	176.6
3	Hfcz1	TT	47.4	108.0	67.1	N2-C3-C4-C11	C3-C4-C11-N4
						172.1	170.4
	Hfcz2	TT	60.1	84.9	142.7	N7-C24-C17-C16	C24-C17-C16-N11
						-166.7	178.3
	Hfcz3	TT	58.2	56.8	104.5	N15-C29-C30-C31	C29-C30-C31-N16
						-164.8	173.6
4	Hfcz1	GT	108.3	142.4	42.4	N4-C5-C4-C3	C5-C4-C3-N3
						58.6	174.4
	Hfcz2	GT	83.4	42.4	52.0	N11-C20-C19-C18	C20-C19-C18-N8
						78.1	176.7
5	Hfcz	TT	96.8	38.1	60.4	N4-C11-C4-C3	C11-C4-C3-N3
						-165.9	-174.8

Table S2. Hydrogen-bond geometries for compounds **1**, **2** and **3**. (lengths in Å and angles in degrees) [a]

D-H···A	D-H	H···A	D···A	<D-H···A
Compound **1**				
O(1W)-H(1B)...O(8)#3	0.883(10)	1.998(12)	2.865(4)	167(3)
O(2W)-H(2A)...O(30)#4	0.884(10)	2.237(19)	3.054(4)	154(3)
O(2W)-H(2B)...O(6W)	0.89(3)	1.946(17)	2.779(7)	156(3)
O(41)-H(41)...O(40)#5	0.82	2.28	3.065(4)	159.3
O(42)-H(42)...O(6)#6	0.82	2.02	2.838(4)	177.4
Compound **2**				
O(23)-H(23)...O(15)	0.82	2.38	3.10(2)	147.5
Compound **3**				
N(13)-H(13A)...N(8)#7	0.86	2.08	2.888(16)	157.4
N(18)-H(18)...O(3W)#8	0.86	1.88	2.708(18)	160.8
O(41)-H(41)...O(9)	0.82	2.25	2.962(13)	145.2
O(42)-H(42)...N(8)	0.82	2.33	2.962(14)	134.9
O(42)-H(42)...N(13)#9	0.82	2.13	2.829(15)	143.7
O(43)-H(43)...O(3)#10	0.82	2.34	3.082(15)	150.4

[a]Symmetry operations: For **1:** #3 -x+1, -y, -z+1; #4 x+1/2, -y+1/2, z+1/2; #5 -x+1, -y+1, -z+1; #6 -x+2, -y, -z+1; for **3**: #7 x, y-1, z; #8 x, y-1, z+1; #9 x, y+1, z; #10 -x+1, -y+1, -z+1.