Supporting Information

Three Novel Organic-Inorganic Complexes Based on Decavanadate $[V_{10}O_{28}]^{6-}$ Units: Special Water Layers, Open 3D Frameworks and Blue/Yellow Luminescences

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Table S1 Selected bond lengths (Å) for **1-3**

Complex 1

Zn(1)-O(10)	**2.013(4)**	**V(4)-O(7)**	**2.004(4)**	**V(1)-O(6)**	**2.039(4)**
Zn(1)-N(5)	**2.013(5)**	**V(4)-O(8)#1**	**2.044(4)**	**V(1)-O(11)**	**2.313(4)**
Zn(1)-N(3)	**2.013(6)**	**V(4)-O(11)**	**2.254(4)**	**V(5)-O(14)**	**1.602(5)**
Zn(1)-O(15)	**2.013(7)**	**V(2)-O(5)**	**1.598(4)**	**V(5)-O(2)**	**1.834(4)**
Zn(1)-O(16)	**2.013(8)**	**V(2)-O(4)**	**1.801(4)**	**V(5)-O(13)**	**1.865(4)**
V(3)-O(6)	**2.013(9)**	**V(2)-O(3)**	**1.849(4)**	**V(5)-O(4)**	**1.903(4)**
V(3)-O(12)	**2.013(10)**	**V(2)-O(7)#1**	**1.962(4)**	**V(5)-O(12)#1**	**2.022(4)**
V(3)-O(7)	**2.013(11)**	**V(2)-O(8)**	**2.055(4)**	**V(5)-O(11)**	**2.343(4)**
V(3)-O(8)	**2.013(12)**	**V(2)-O(11)**	**2.291(4)**	**V(5)-V(3)#1**	**3.0740(16)**
V(3)-O(11)	**2.013(13)**	**V(2)-V(4)#1**	**3.1150(17)**	**O(7)-V(2)#1**	**1.962(4)**
V(3)-O(11)#1	**2.013(14)**	**V(1)-O(1)**	**1.601(4)**	**O(11)-V(3)#1**	**2.121(4)**
V(4)-O(9)	**2.013(15)**	**V(1)-O(3)**	**1.830(4)**	**O(8)-V(4)#1**	**2.044(4)**
V(4)-O(13)	**2.013(16)**	**V(1)-O(2)**	**1.838(4)**	**O(12)-V(5)#1**	**2.022(4)**
V(4)-O(10)	**2.013(17)**	**V(1)-O(10)**	**1.949(4)**		

Symmetry transformations used to generate equivalent atoms: #1: -x, -y+1, -z.

Complex 2

Zn(1)-N(4)	**2.107(5)**	**V(1)-O(3)**	**1.816(4)**	**V(3)-O(11)**	**2.047(4)**
Zn(1)-O(31)	**2.110(4)**	**V(1)-O(16)**	**1.998(4)**	**V(3)-O(10)**	**2.331(4)**
Zn(1)-O(30)	**2.121(5)**	**V(1)-O(15)**	**2.016(4)**	**V(7)-O(17)**	**1.608(4)**
Zn(1)-O(29)	**2.122(4)**	**V(1)-O(10)**	**2.256(4)**	**V(7)-O(23)**	**1.813(4)**
Zn(1)-N(7)	**2.133(5)**	**V(5)-O(9)**	**1.683(4)**	**V(7)-O(22)**	**1.844(4)**
Zn(1)-N(1)	**2.140(5)**	**V(5)-O(18)**	**1.695(4)**	**V(7)-O(15)**	**1.989(4)**

Zn(2)-N(10)	2.151(5)	V(5)-O(16)	1.901(4)	V(7)-O(16)	2.003(4)
Zn(2)-N(8)	2.155(5)	V(5)-O(14)	2.009(4)	V(7)-O(19)	2.262(4)
Zn(2)-N(13)	2.179(5)	V(5)-O(10)	2.108(4)	V(10)-O(28)	1.602(5)
Zn(2)-N(2)	2.183(5)	V(5)-O(19)	2.115(4)	V(10)-O(27)	1.821(4)
Zn(2)-N(5)	2.188(5)	V(4)-O(12)	1.613(4)	V(10)-O(23)	1.890(4)
Zn(2)-N(16)	2.189(5)	V(4)-O(8)	1.807(4)	V(10)-O(25)	1.904(4)
Zn(3)-O(34)	2.101(4)	V(4)-O(7)	1.823(4)	V(10)-O(20)	2.057(4)
Zn(3)-N(17)	2.103(5)	V(4)-O(13)	1.999(4)	V(10)-O(19)	2.346(4)
Zn(3)-O(32)	2.123(5)	V(4)-O(14)	2.032(4)	V(2)-O(4)	1.606(4)
Zn(3)-O(33)	2.132(5)	V(4)-O(10)	2.257(4)	V(2)-O(5)	1.816(4)
Zn(3)-N(11)	2.133(5)	V(8)-O(21)	1.619(4)	V(2)-O(7)	1.874(4)
Zn(3)-N(14)	2.143(5)	V(8)-O(25)	1.799(4)	V(2)-O(2)	1.902(4)
V(6)-O(20)	1.690(4)	V(8)-O(24)	1.839(4)	V(2)-O(9)	2.079(4)
V(6)-O(11)	1.691(4)	V(8)-O(13)	1.977(4)	V(2)-O(10)	2.311(4)
V(6)-O(13)	1.923(4)	V(8)-O(14)	2.065(4)	V(9)-O(26)	1.604(4)
V(6)-O(15)	1.959(4)	V(8)-O(19)	2.257(4)	V(9)-O(27)	1.831(4)
V(6)-O(19)	2.113(4)	V(3)-O(6)	1.592(4)	V(9)-O(24)	1.868(4)
V(6)-O(10)	2.123(4)	V(3)-O(5)	1.835(4)	V(9)-O(22)	1.897(4)
V(1)-O(1)	1.614(4)	V(3)-O(3)	1.872(4)	V(9)-O(18)	2.058(5)
V(1)-O(2)	1.810(4)	V(3)-O(8)	1.906(4)	V(9)-O(19)	2.306(4)

Complex 3

Zn(3)-N(3)#1	1.979(3)	V(3)-V(5)#3	3.0795(9)	V(4)-O(11)	1.869(3)
Zn(3)-N(6)#2	1.986(4)	V(3)-V(4)	3.1043(9)	V(4)-O(9)	1.913(3)
Zn(3)-O(18)	1.988(6)	V(5)-O(12)	1.611(3)	V(4)-O(14)	2.054(3)
Zn(3)-N(9)	1.995(3)	V(5)-O(11)	1.827(3)	V(4)-O(6)	2.306(2)
Zn(1)-O(3)	1.976(2)	V(5)-O(5)	1.827(3)	V(4)-V(1)	3.0609(10)

Zn(1)-N(4)	**2.022(3)**	**V(5)-O(7)#3**	**1.994(2)**	**V(2)-O(2)**	**1.689(3)**
Zn(1)-N(8)	**2.028(3)**	**V(5)-O(13)#3**	**2.008(2)**	**V(2)-O(2)#3**	**1.689(3)**
Zn(1)-N(1)	**2.105(4)**	**V(5)-O(6)**	**2.274(2)**	**V(2)-O(7)**	**1.930(2)**
Zn(1)-O(15)	**2.221(4)**	**V(5)-V(3)#3**	**3.0795(9)**	**V(2)-O(7)#3**	**1.930(2)**
Zn(2)-O(17)	**2.116(3)**	**V(5)-V(1)**	**3.1075(9)**	**V(2)-O(6)#3**	**2.109(2)**
Zn(2)-N(2)	**2.119(3)**	**V(5)-V(4)**	**3.1128(9)**	**V(2)-O(6)**	**2.109(2)**
Zn(2)-O(19)	**2.128(3)**	**V(6)-O(14)#3**	**1.691(2)**	**V(2)-V(1)#3**	**3.0601(7)**
Zn(2)-N(5)	**2.143(3)**	**V(6)-O(14)**	**1.691(2)**	**V(2)-V(1)**	**3.0601(7)**
Zn(2)-N(7)	**2.162(3)**	**V(6)-O(13)**	**1.937(2)**	**V(1)-O(1)**	**1.603(3)**
Zn(2)-O(16)	**2.170(3)**	**V(6)-O(13)#3**	**1.937(2)**	**V(1)-O(4)**	**1.829(3)**
V(3)-O(8)	**1.608(3)**	**V(6)-O(6)**	**2.115(2)**	**V(1)-O(5)**	**1.864(3)**
V(3)-O(9)	**1.791(3)**	**V(6)-O(6)#3**	**2.115(2)**	**V(1)-O(3)**	**1.918(3)**
V(3)-O(3)	**1.862(2)**	**V(6)-V(4)**	**3.0771(6)**	**V(1)-O(2)**	**2.044(3)**
V(3)-O(13)	**1.981(2)**	**V(6)-V(4)#3**	**3.0771(6)**	**V(3)-O(7)**	**2.043(2)**
V(4)-O(10)	**1.598(3)**	**V(3)-O(6)**	**2.250(2)**	**V(4)-O(4)**	**1.821(3)**

Symmetry transformations used to generate equivalent atoms: #1: -x+1/2, y+1/2, z; #2: x, -y, z+1/2; #3: -x, y, -z+1/2.

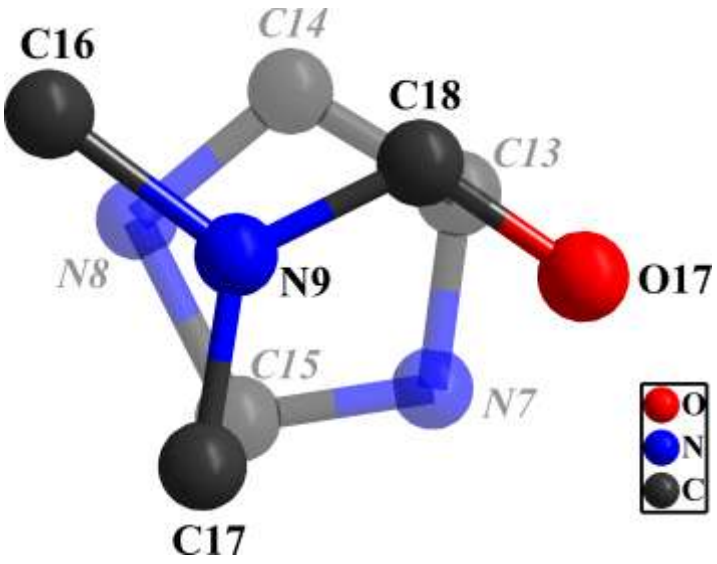


Fig. S1 Statistical distribution is shown in the structure of complex **1,** with two disordered parts including imidazole (C13-C14-C15-N7-N8) and DMF (C16-C17-C18-N9-O17).

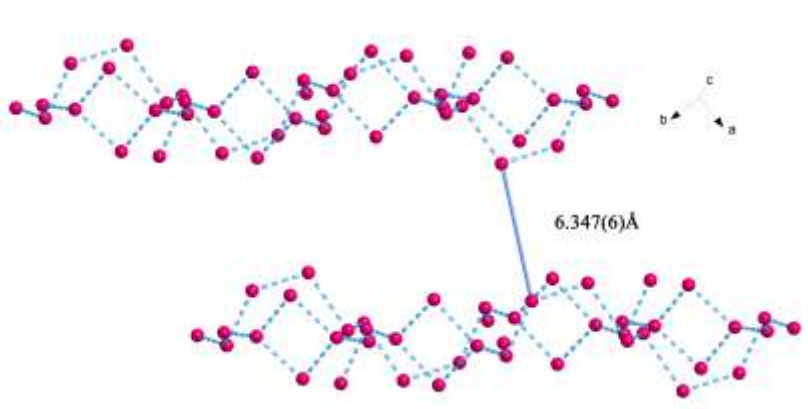


Fig. S2 Ball representation of the corrugated water sheets pile along the c-axis of the crystal cell in **2**.

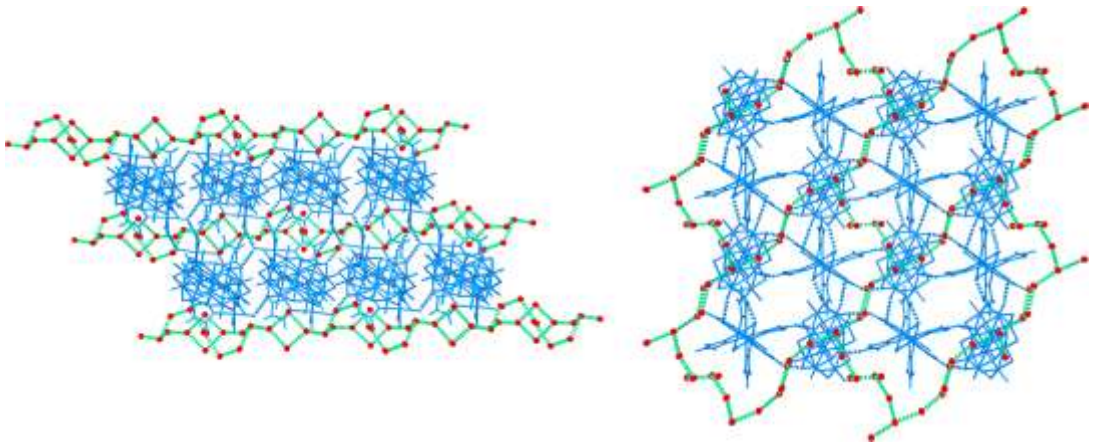


Fig. S3 Ball representation of the metalorganic-water supramolecular network constructed by H-bonds in **2**

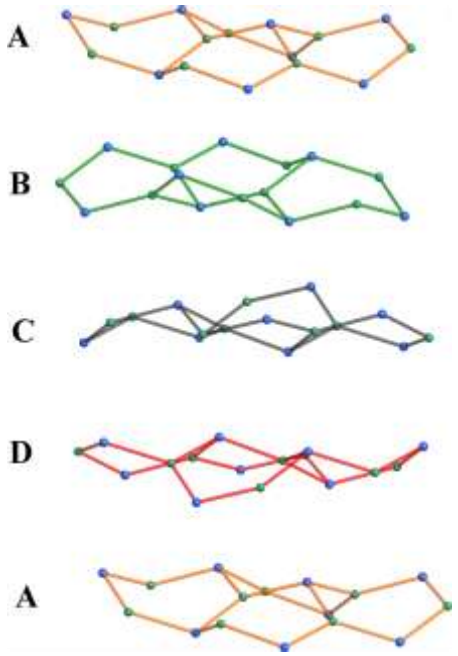


Fig. S4 The hexagonal grid sheets of **3** stack in ABCD mode.

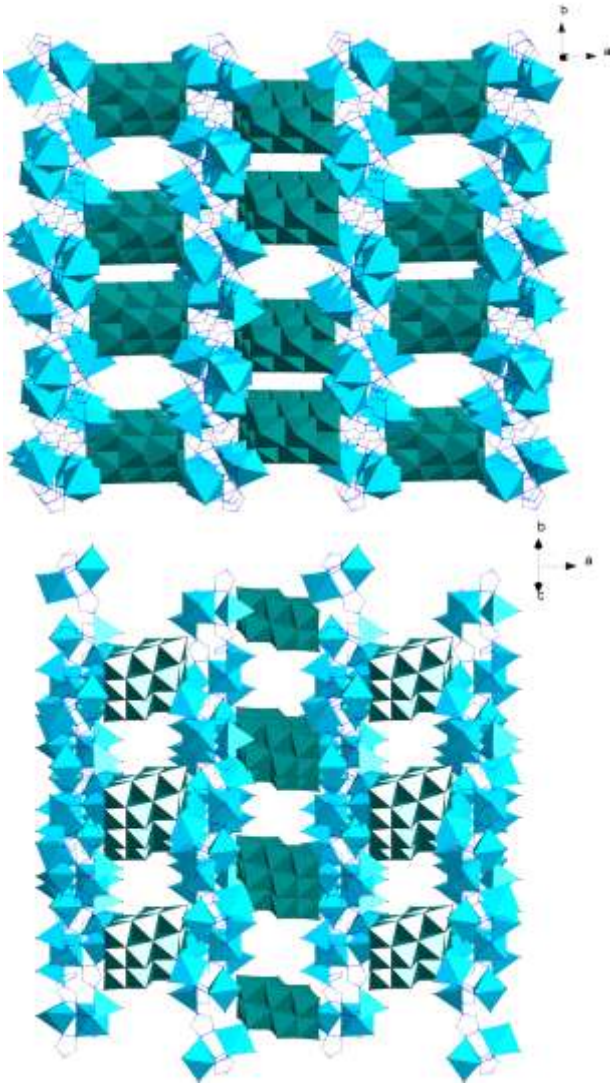


Fig. S5 Projection of complex **3** along the *c* axis and [011] direction

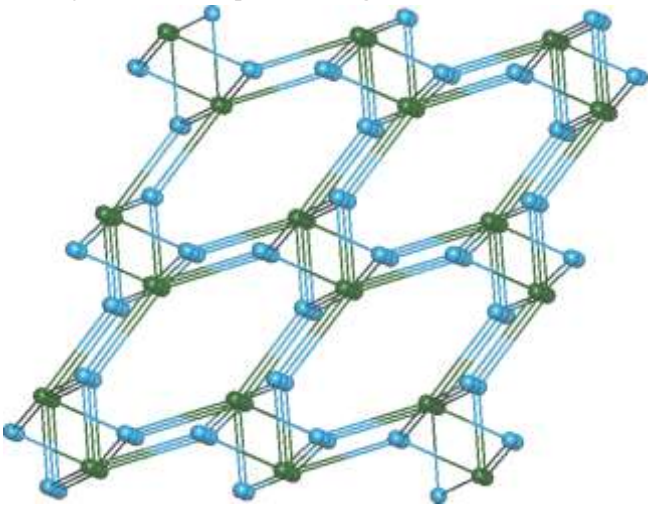


Fig. S6 The α-PbO_2 type topology with the $\{V_{10}Zn_4\}$ units as the 6-connected nodes and mononuclear Zn(II) ions as 3-connected nodes. Cyan and green colors represent mononuclear Zn(II) ions and $\{V_{10}Zn_4\}$ units respectively.

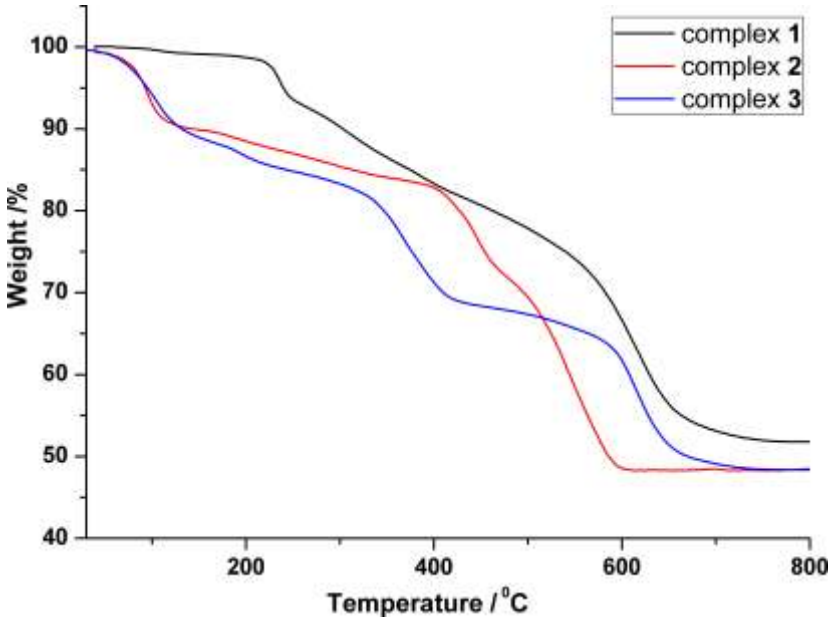


Fig. S7 The TG curves of complexes **1**, **2** and **3**.

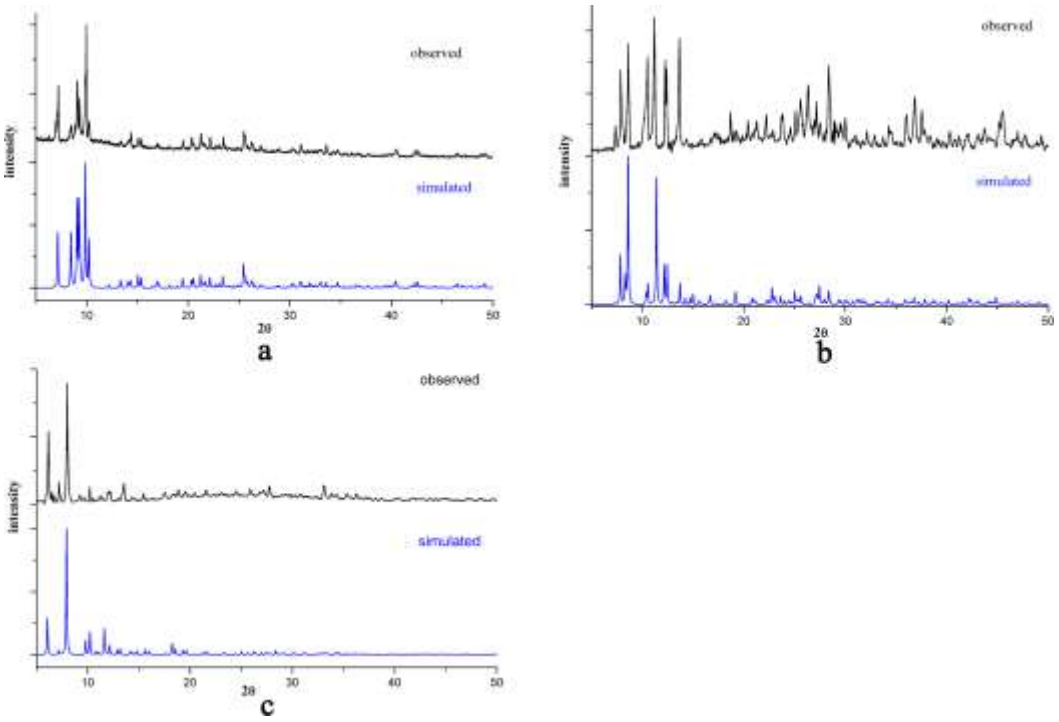
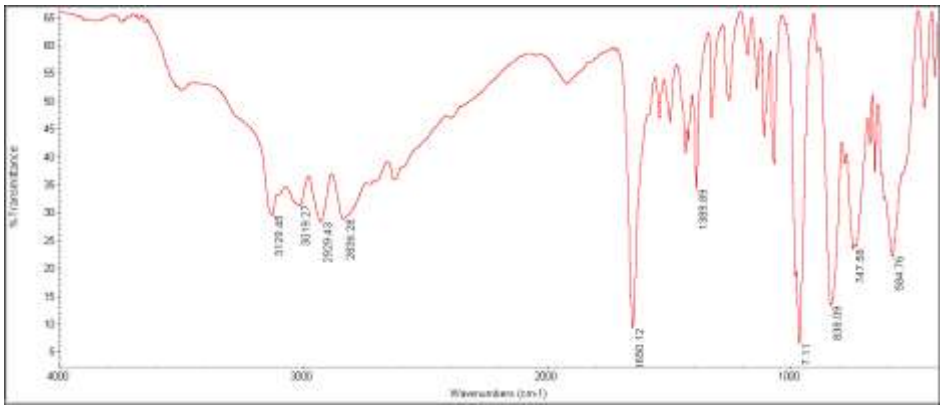
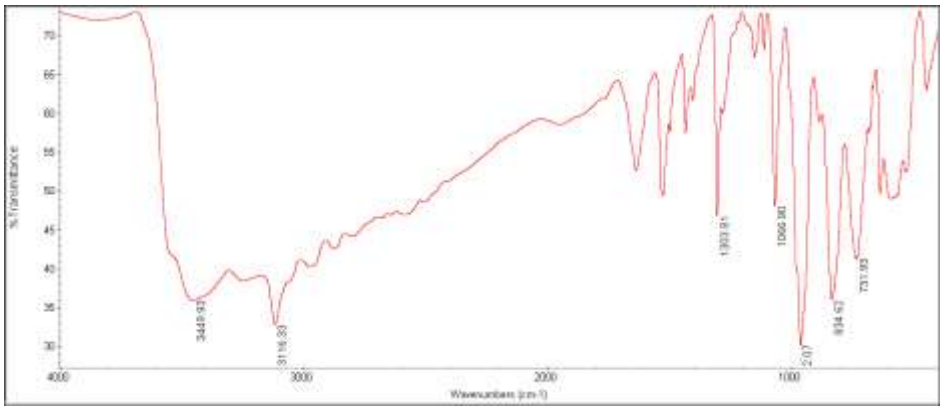


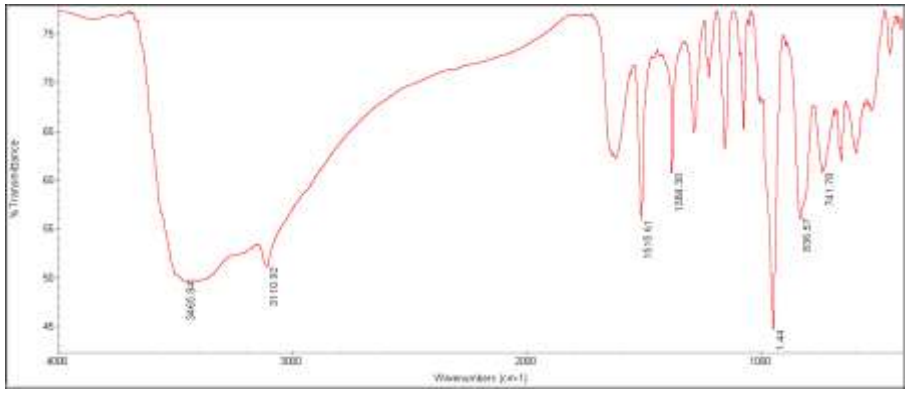
Fig. S8 Simulated and observed PXRD patterns of complexes **1** (a), **2**(b) and **3**(c).



a

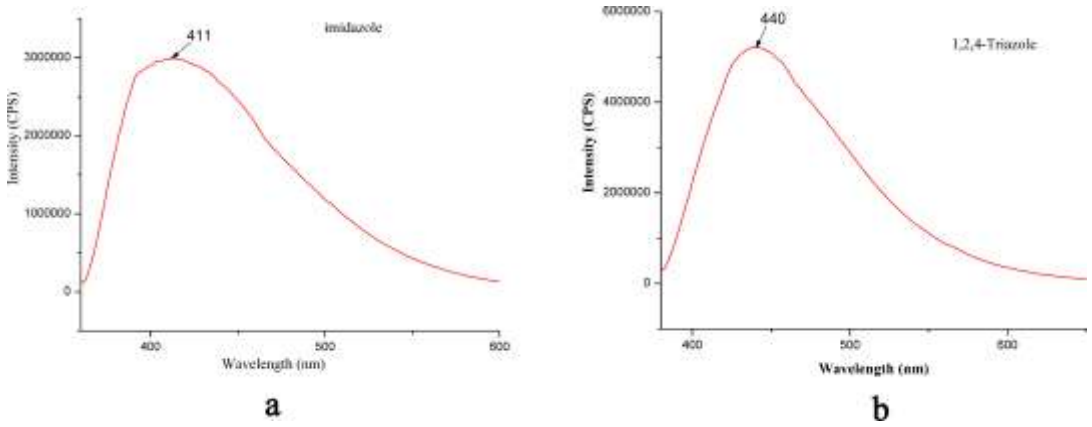


b



c

Fig. S9 IR spectra of complexes **1**(a), **2**(b) and **3**(c)



a b

Fig. S10 The solid-state photoluminescence spectra of imidazole and 1,2,4-triazole recorded at room temperature (λ_{ex}=360nm).

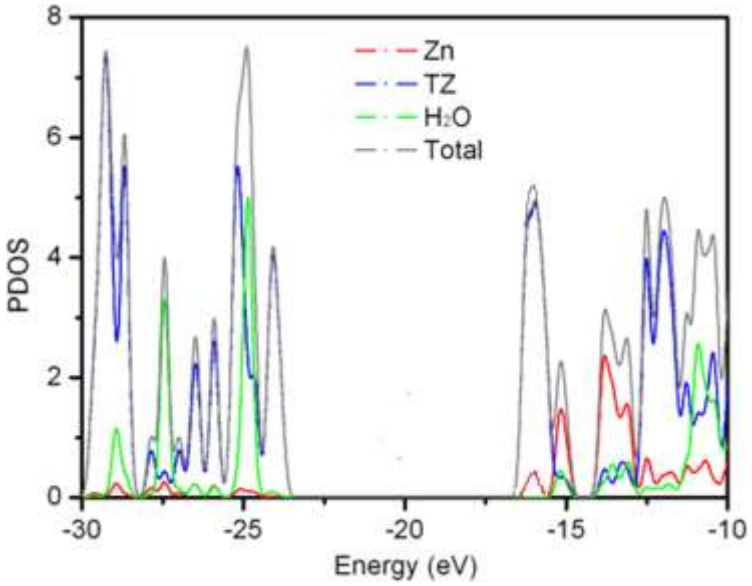


Fig. S11 Partial density of states (PDOS) diagram of complex **2** with contribution of

different groups of Zn atoms (Zn), triazole ligands (TZ), and coordinated water moleculars (H_2O).

Computational study

All the calculations were carried out by using the Gaussian 03 program package.[1] The computational method used was the density functional theory (DFT) with the B3P86 functional which combines the Becke's three-parameter hybrid exchange functional[2] with the Perdew's gradient correlation functional.[3] The initial structure was extracted as a isolated molecule carrying six positive charges derived from the experimentally geometry obtained from the X-ray crystallographic data, without considering the VO cluster and uncoordinated triazole molecule. The geometry in the ground state was fully optimized with S_6 symmetry constraint. In the optimization process, the convergent values of maximum force, root-mean-square (RMS) force, maximum displacement, and RMS displacement are set by default. Then, fifty lowest simple excited states of this complex were calculated by the time-dependent DFT (TD-DFT)[4] calculation to determine the vertical excitation energies of this coordination complex with the same functional based on the optimized geometrical structure. The self-consistent field (SCF) convergence criterions of RMS density matrix and maximum density matrix are set at 10^{-8} and 10^{-6} a.u., respectively, in all the electronic structure calculations. The iterations of excited states continue until the changes on energies of states are no more than 10^{-7} a.u. between the iterations, and then convergences are reached in all the excited states. In these calculations, the Lanl2dz[5] effective core potential (ECP) was employed to describe the core electrons of zinc atoms, and the associated double-ζ basis set was used for the remainling outer electrons, and the 6-31G(p) all-electron basis set was used for the remaining non-metal atoms. The partial density of states (PDOS) spectrum was obtained by calculating the percent contributions of each group to the molecular orbitals based on Mulliken Population Analysis in the help with GaussSum 2.2.5.[6] The PDOS spectrum was created by convoluting the molecular orbital information with Gaussian curves of unit height and the specified full width at hafl-maximum of 0.3 eV.

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