Synthesis, Structure and Adsorption of Coordination Polymers Constructed from 3,3',5,5'-Azobenzenetetracarboxylic Acid and Zn Ions

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Supporting Information

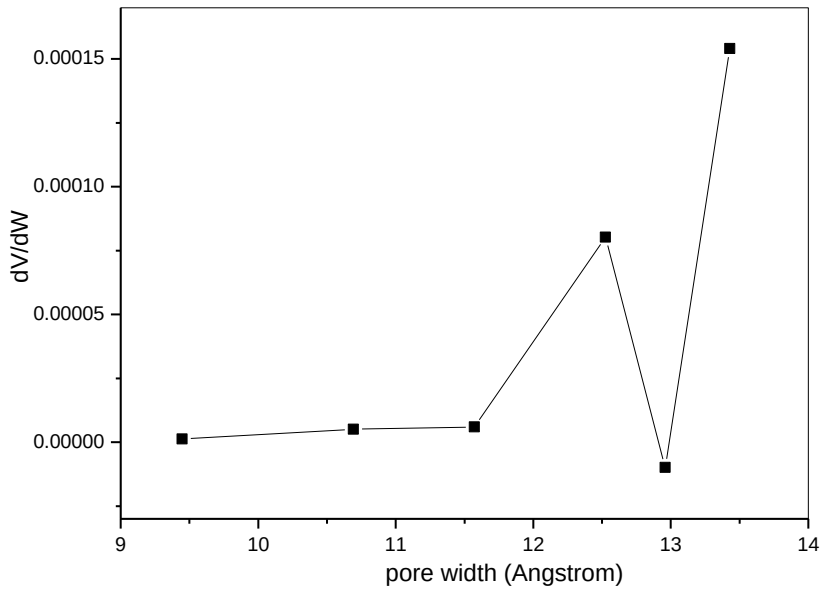

Fig. S1. Pore size distribution curve of $\{(Hap)_2\ [Zn_3(\eta_9\text{-aobtc})_2] \cdot 2H_2O\}^3_n$ (**3**) .

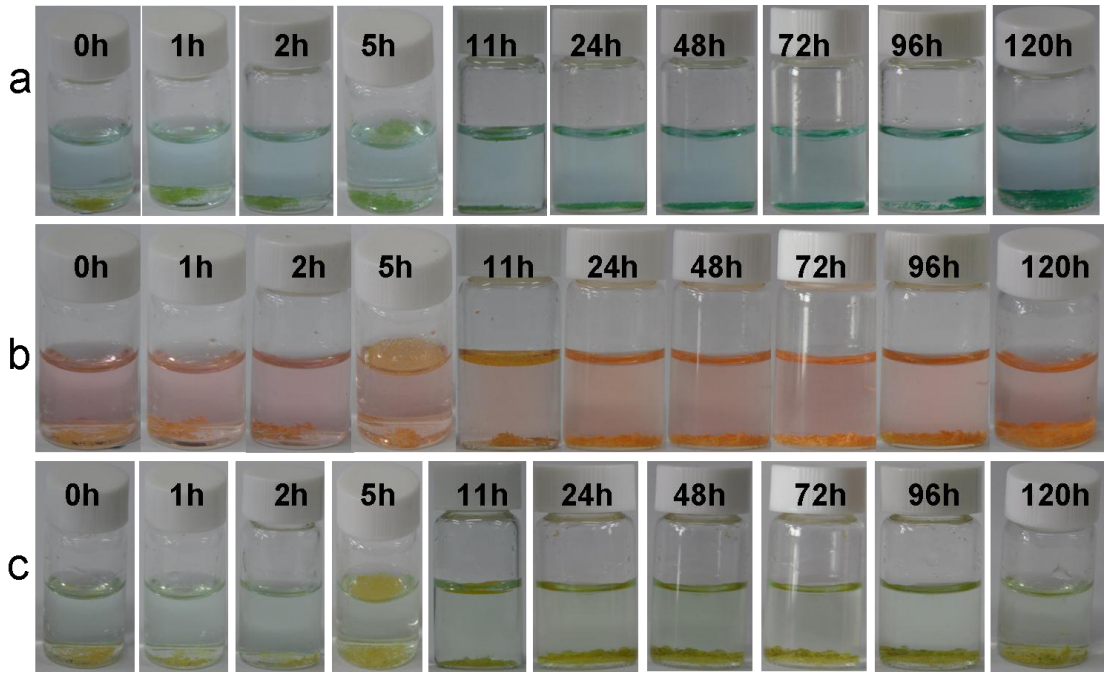

Fig. S2. Photographs showing the visual color change when some crystal of complex **2** was immersed in the solution of (a) 10 mg/ml $Cu(NO_3)_2$, (b) 10mg/ml $Co(NO_3)_2$, (c) 10mg/ml $Ni(NO_3)_2$.

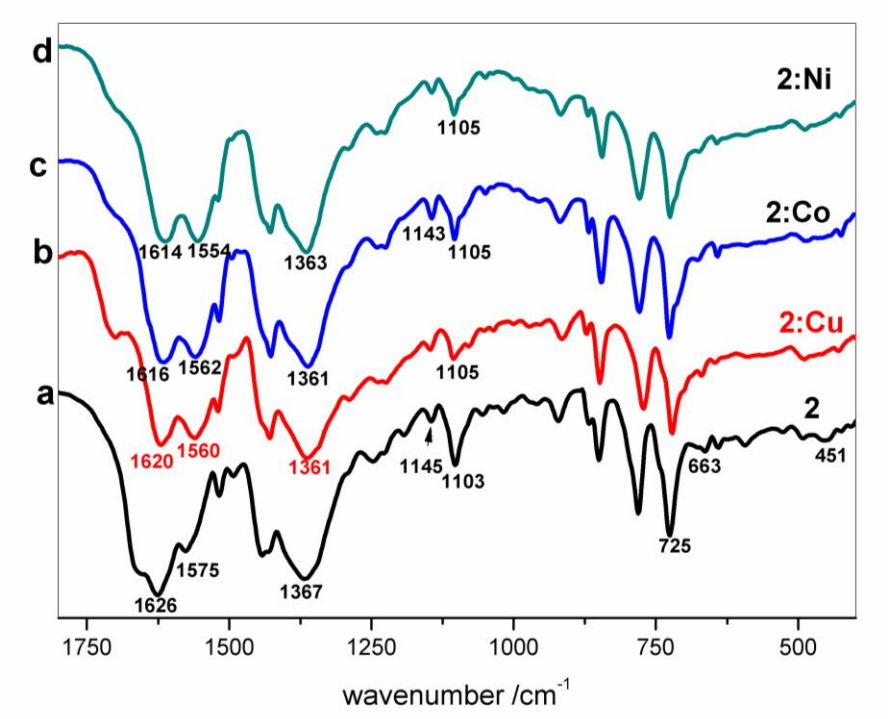

Fig. S3. IR spectra of **2** before and after metal ion exchanges. (a) **2** before exchange; (b) Cu-exchanged; (c) Co –exchanged; (d) Ni -exchanged product.

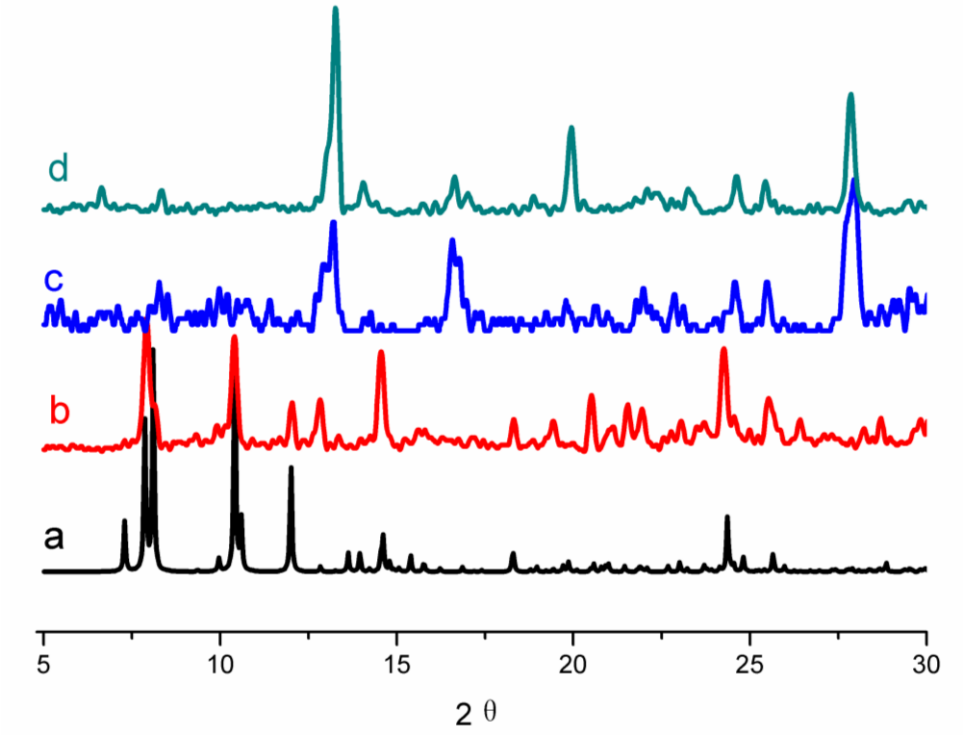

Fig. S4. PXRD patterns of complex **2.** (a) Simulated; (b) Experimental; (c) Co –exchanged; (d) Ni -exchanged.

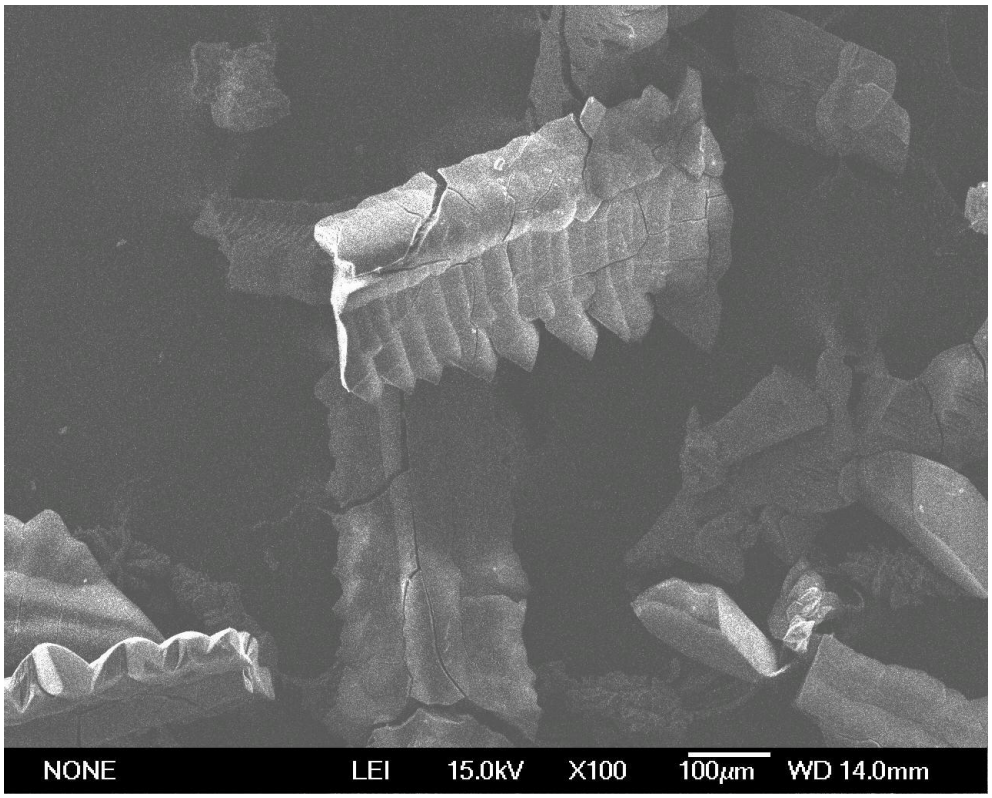

Fig. S5. Typical SEM image of Cu(II)-exchanged products from complex **2.**

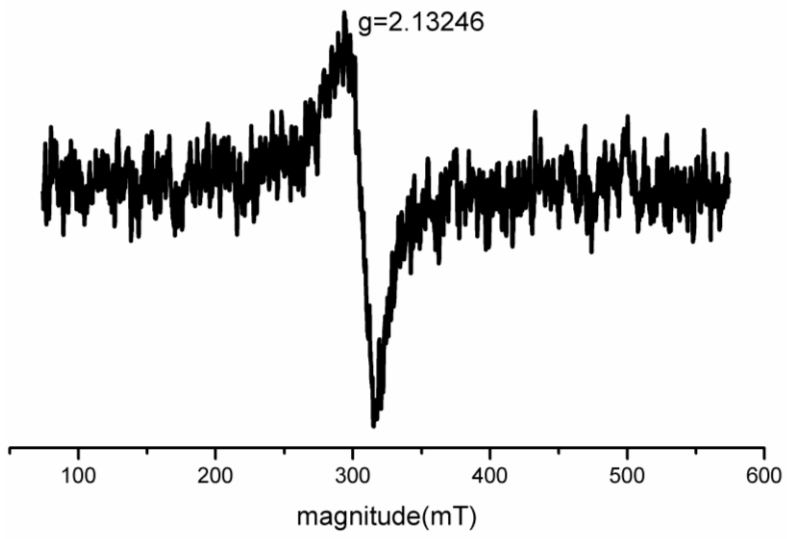

Fig. S6 EPR spectra of Cu(II)-exchanged products from complex **2.**

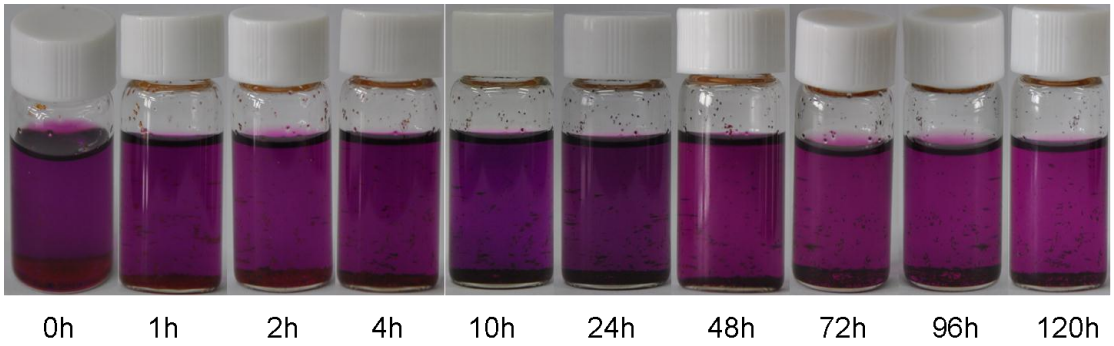

Fig. S7. I_2 enrichment progress when 30 mg of crystals **2** were soaked in cyclohexane solution of I_2 (0.005 mol/L) (totle volume is 4 ml).

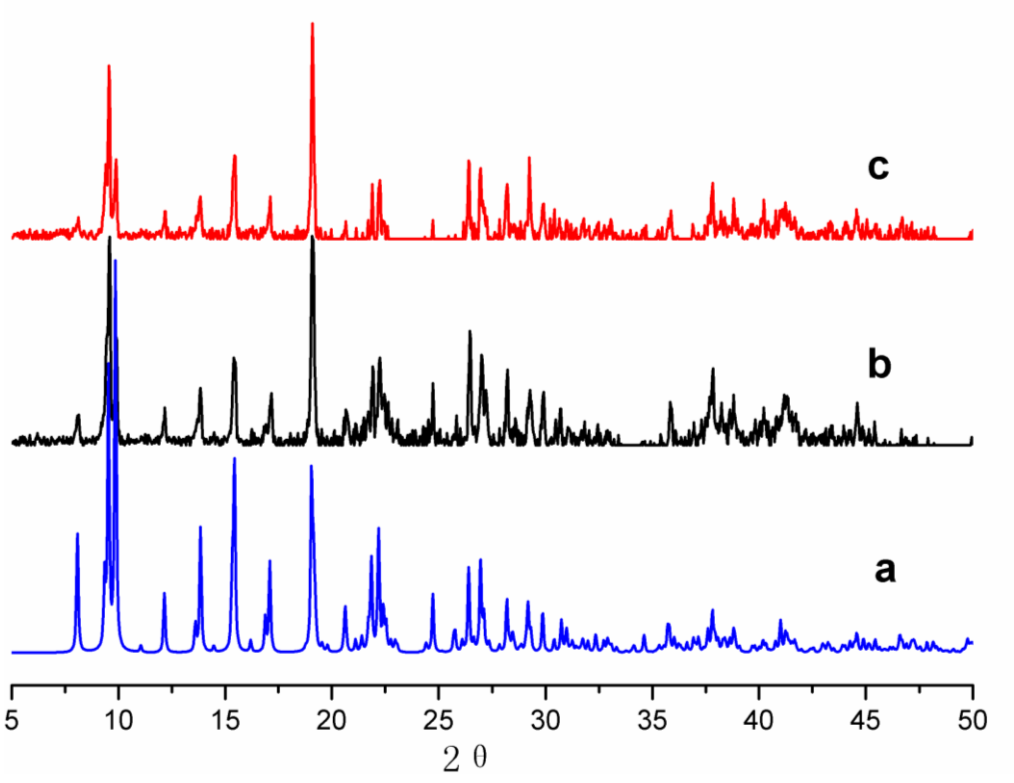

Fig. S8. PXRD patterns of complex **3.** (a) simulated; (b) experimental; (c) after immersing in methylene blue.

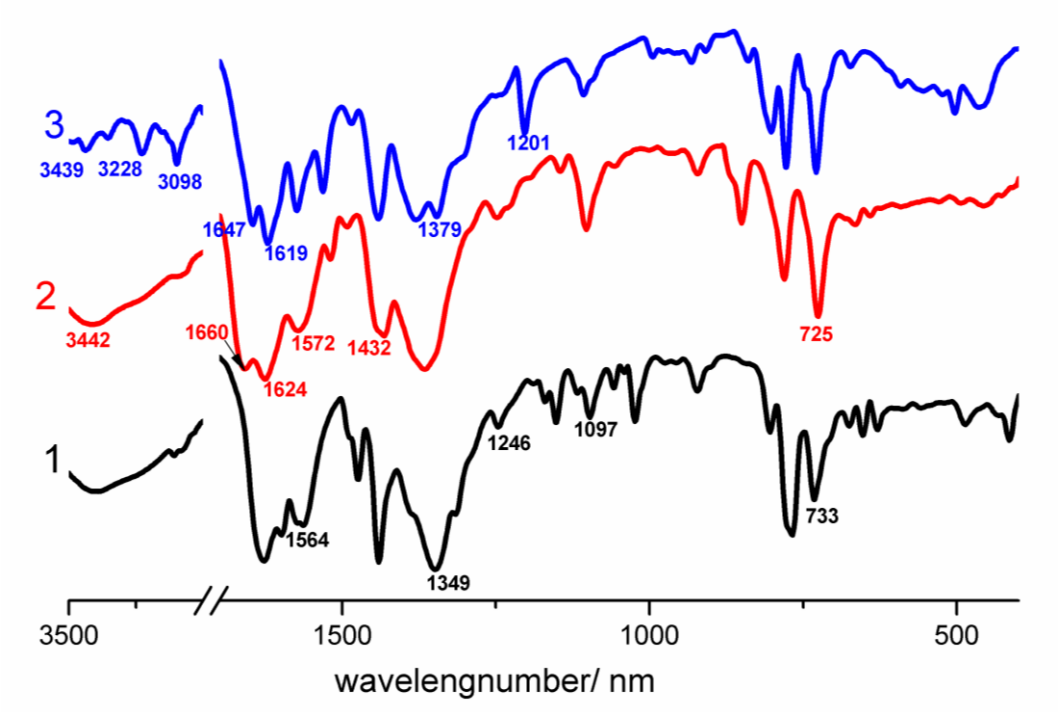

Fig. S9. IR spectra of complexes **1-3**.

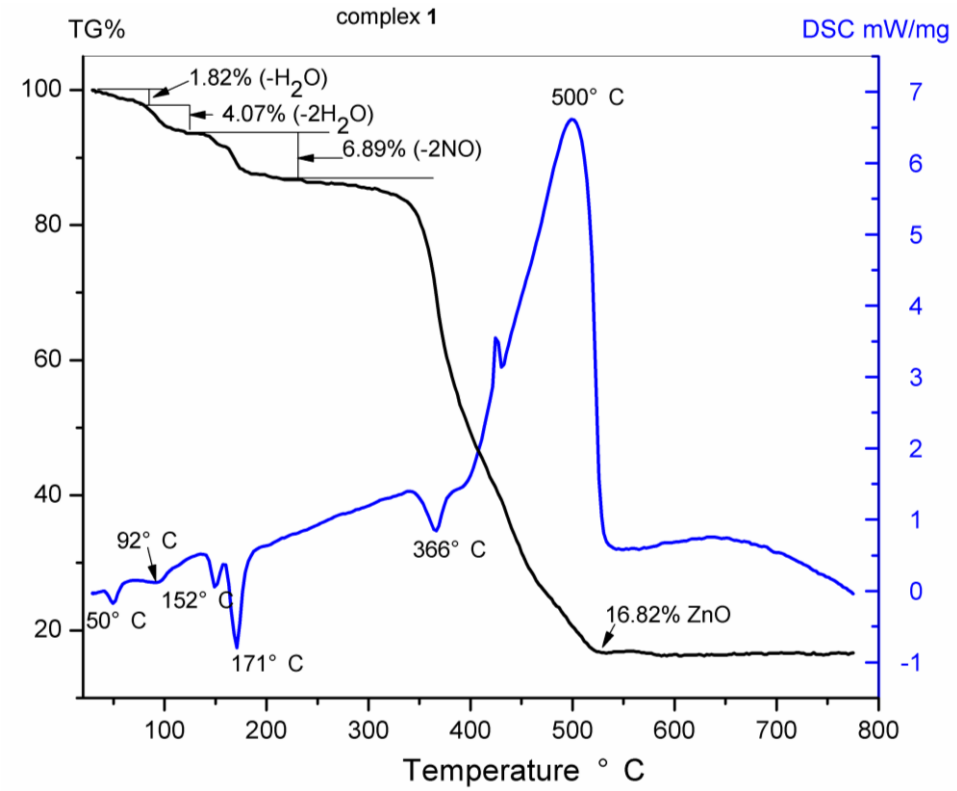

Fig. S10 TG and DSC of $\{[Zn_2(\eta_6\text{-}ao_2btc)\ (\eta_2\text{-}2,2'\text{-}bpy)_2(H_2O)_2]\bullet 2H_2O\}^1{}_n$ (**1**).

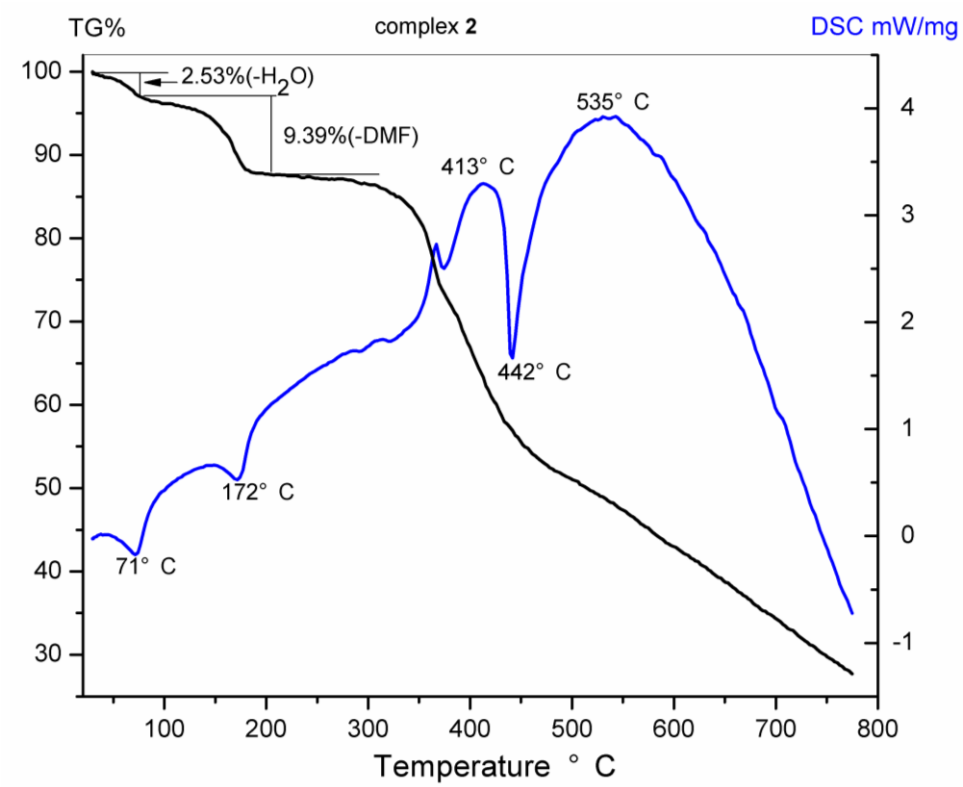

Fig. S11 TG and DSC of $\{[Zn_2(\eta_8\text{-aobtc})(\eta_2\text{-phen})(H_2O)]\bullet DMF\}^3_n$ (**2**).

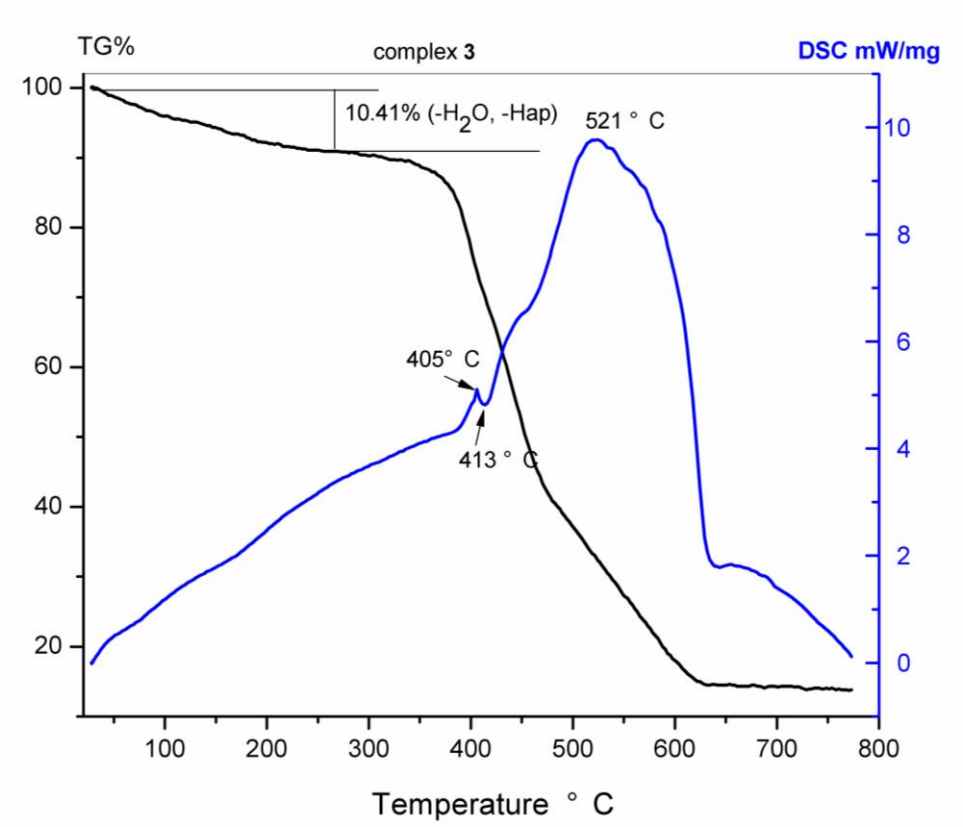

Fig. S12 TG and DSC of $\{(Hap)_2\ [Zn_3(\eta_9\text{-aobtc})_2]\bullet 2H_2O\}^3_n$ (**3**).

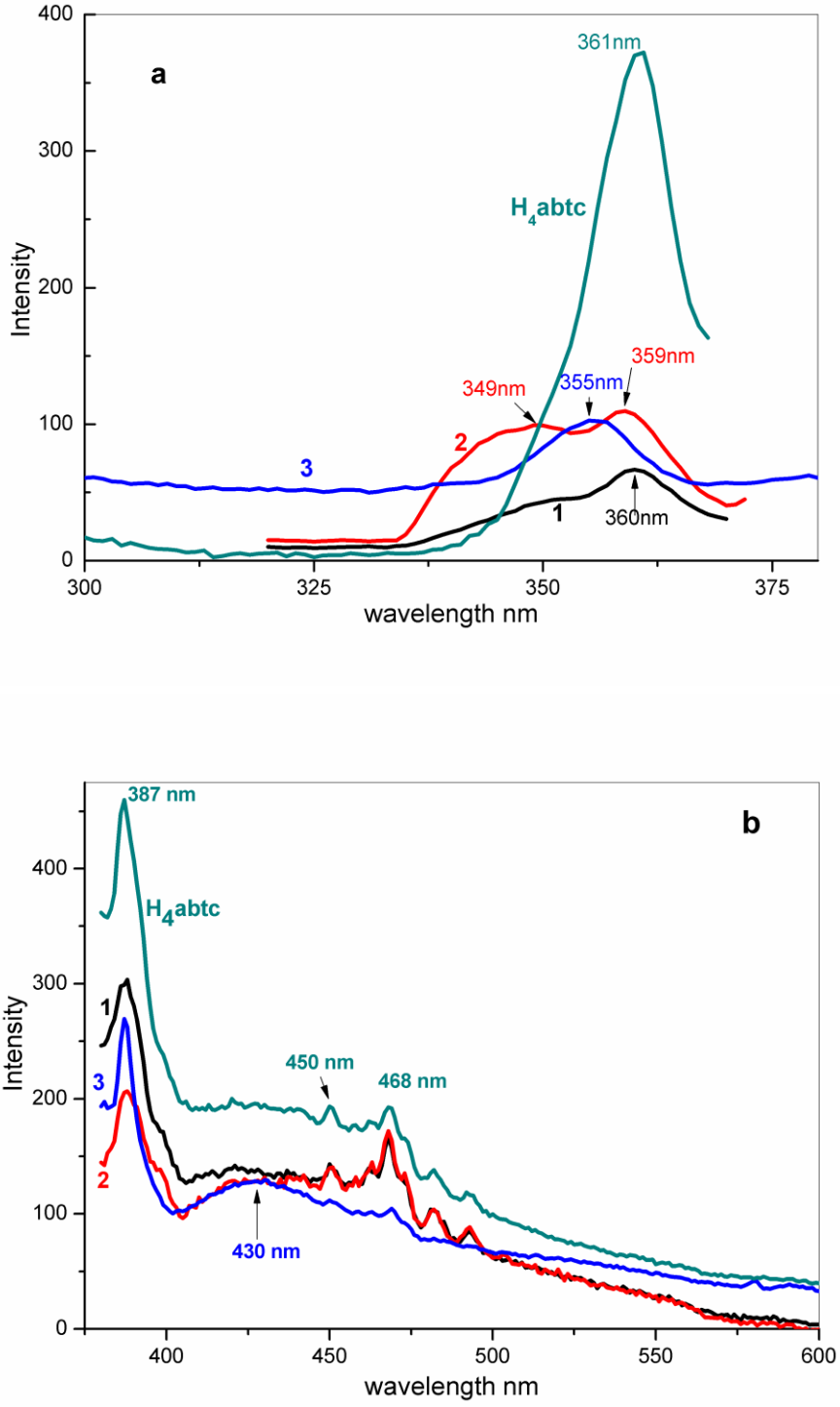

Fig. S13 Fluorescence excitation of ligand H_4abtc and complex **1- 3** in solid state (Em 387nm) (a). Fluorescence emssions of ligand H_4abtc and complex **1- 3** in solid state (Ex 360nm) (b).

Table S1. Bond lengths [Å] and angles [°] for complex **1-3.**

Complex **1**			
Zn(1)-O(2)	2.035(6)	Zn(1)-N(1)	2.102(7)
Zn(1)-O(1W)	2.117(7)	Zn(1)-N(2)	2.137(8)
Zn(1)-O(3)#1	2.232(10)	Zn(1)-O(4)#1	2.317(11)
O(3)-Zn(1)#2	2.253(7)	O(4)-Zn(1)#2	2.317(8)
O(2)-Zn(1)-O(1W)	88.93(39)	N(1)-Zn(1)-O(1W)	93.53(3)
O(2)-Zn(1)-N(2)	92.1(3)	N(1)-Zn(1)-N(2)	76.8(3)
O(1W)-Zn(1)-N(2)	168.3(3)	O(2)-Zn(1)-O(3)#1	143.4(4)
N(1)-Zn(1)-O(3)#1	87.6(4)	O(1W)-Zn(1)-O(3)#1	89.3(3)
N(2)-Zn(1)-O(3)#1	96.8(3)	O(2)-Zn(1)-O(4)#1	87.8(3)
N(1)-Zn(1)-O(4)#1	142.0(3)	O(1W)-Zn(1)-O(4)#1	97.0(3)
N(2)-Zn(1)-O(4)#1	94.7(3)	O(3)#1-Zn(1)-O(4)#1	56.2(4)
Symmetry transformations used to generate equivalent atoms: #1 x,y,z+1; #2 -x,-y,-z; #3 x,y,z-1.			
Complex **2**			
Zn(1)-O(7) #1	2.061(10)	Zn(1)-O(1W)	2.084(12)
Zn(1)-O(6) #2	2.083(11)	Zn(1)-N(1)	2.138(14)
Zn(1)-N(2)	2.147(13)	Zn(1)-O(1)	2.259(10)
Zn(2)-O(5) #3	1.967(9)	Zn(2)-O(8) #4	2.000(10)
Zn(2)-O(4)	2.036(15)	Zn(2)-O(1) #5	2.067(9)
Zn(2)-O(3)	2.437(13)	Zn(2)-O(2)#5	2.472(13)
O(7)#1-Zn(1)-O(6)#2	100.6(4)	O(7)#1-Zn(1)-O(1W)	96.8(5)
O(6)#2-Zn(1)-O(1W)	85.7(5)	O(7)#1-Zn(1)-N(1)	91.7(5)
O(6)#2-Zn(1)-N(1)	167.5(5)	O(1W)-Zn(1)-N(1)	91.1(5)
O(7)#1-Zn(1)-N(2)	167.5(5)	O(6)#2-Zn(1)-N(2)	90.0(5)
N(1)-Zn(1)-N(2)	78.0(6)	O(7)#1-Zn(1)-O(1)	85.4(4)
O(6)#2-Zn(1)-O(1)	90.8(4)	O(1W)-Zn(1)-O(1)	176.2(5)
N(1)-Zn(1)-O(1)	92.0(4)	N(2)-Zn(1)-O(1)	87.9(4)
O(5)#3-Zn(2)-O(8)#4	99.2(4)	O(5)#3-Zn(2)-O(4)	103.1(5)
O(8)#4-Zn(2)-O(4)	105.7(5)	O(5)#3-Zn(2)-O(1)#5	114.7(4)
O(8)#4-Zn(2)-O(1)#5	97.7(4)	O(4)-Zn(2)-O(1)#5	131.3(5)
O(5)#3-Zn(2)-O(3)	156.8(5)	O(8)#4-Zn(2)-O(3)	94.7(5)
O(4)-Zn(2)-O(3)	55.0(6)	O(1)#5-Zn(2)-O(3)	81.3(5)
O(5)#3-Zn(2)-O(2)#5	93.0(4)	O(8)#4-Zn(2)-O(2)#5	152.4(4)
O(4)-Zn(2)-O(2)#5	95.4(5)	O(1)#5-Zn(2)-O(2)#5	54.6(4)
O(3)-Zn(2)-O(2)#5	82.8(4)	Zn(2)#6-O(1)-Zn(1)	101.6(4)
Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z; #2 x+1,-y+3/2,z+1/2; #3 -x,-y+1,-z; #4 x,-y+3/2,z+1/2; #5 -x+1,y-1/2,-z+1/2; #6 -x+1,y+1/2,-z+1/2; #7 x-1,-y+3/2,z-1/2; #8 x,-y+3/2,z-1/2.			
Complex **3**			
Zn(1)-O(1)#1	2.010(4)	Zn(1)-O(1)	2.010(4)
Zn(1)-O(7)#2	2.043(4)	Zn(1)-O(7)#3	2.043(4)
Zn(1)-O(3)#4	2.252(4)	Zn(1)-O(3)#5	2.252(4)

Zn(2)-O(2)#6	1.972(4)	Zn(2)-O(8)#7	1.998(5)
Zn(2)-O(5)#8	2.006(4)	Zn(2)-O(3)	2.012(4)
O(2)-Zn(2)#4	1.972(4)	O(3)-Zn(1)#6	2.252(4)
O(5)-Zn(2)#9	2.006(4)	O(7)-Zn(1)#10	2.044(4)
O(8)-Zn(2)#11	1.998(4)		
O(1)#1-Zn(1)-O(1)	179.999(1)	O(1)#1-Zn(1)-O(7)#2	96.21(18)
O(1)-Zn(1)-O(7)#2	83.79(18)	O(1)#1-Zn(1)-O(7)#3	83.86(18)
O(1)-Zn(1)-O(7)#3	96.21(18)	O(7)#2-Zn(1)-O(7)#3	180.00(2)
O(1)#1-Zn(1)-O(3)#4	91.34(17)	O(1)-Zn(1)-O(3)#4	88.66(17)
O(7)#2-Zn(1)-O(3)#4	92.57(16)	O(7)#3-Zn(1)-O(3)#4	87.43(16)
O(1)#1-Zn(1)-O(3)#5	88.66(17)	O(1)-Zn(1)-O(3)#5	91.34(17)
O(7)#2-Zn(1)-O(3)#5	87.436(16)	O(7)#3-Zn(1)-O(3)#5	92.57(16)
O(3)#4-Zn(1)-O(3)#5	180.0	O(2)#6-Zn(2)-O(8)#7	107.23(19)
O(2)#6-Zn(2)-O(5)#8	105.64(18)	O(8)#7-Zn(2)-O(5)#8	101.79(18)
O(2)#6-Zn(2)-O(3)	112.25(18)	O(8)#7-Zn(2)-O(3)	101.71(17)
O(5)#8-Zn(2)-O(3)	126.28(18)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1; #2 -x+1,-y,-z; #3 x+1,y,z+1 #4 x+1,y,z; #5 -x+1,-y,-z+1; #6 x-1,y,z; #7 x,y,z+1; #8 x,y+1,z+1; #9 x,y-1,z-1; #10 x-1,y,z-1; #11 x,y,z-1.

Table **S2.** Hydrogen bonds for **1**-**3** [Å and °].

D-H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	<(DHA)
Complex **1**				
O(1W)-H(1WB)...O(2)#4	0.90	1.89	2.762(9)	164.1
O(1W)-H(1WA)...O(4)#5	0.82	2.23	2.975(12)	151.2
Symmetry codes: #1 x,y,z+1; #2 -x,-y,-z, #3 x,y,z-1; #4 –x+1,-y+1,-z+1; #5 -x+1,-y,-z;				
Complex **2**				
O(1W)-H(1WB)...O(7)#1	0.85	2.58	3.100(17)	120.2
Symmetry codes: #1 -x+1,-y+2,-z; #2 x+1,-y+3/2,z+1/2; #3 -x,-y+1,-z; #4 x,-y+3/2,z+1/2; #5 -x+1,y-1/2,-z+1/2; #6 -x+1,y+1/2,-z+1/2; #7 x-1,-y+3/2,z-1/2; #8 x,-y+3/2,z-1/2.				
Complex **3**				
N(4)-H(4A)...O(1W)#12	0.86	2.40	3.147(10)	146.0
N(4)-H(4B)...O(1W)	0.86	2.25	3.101(10)	170.6
O(1W)-H(1WA)...O(6)#8	0.85	2.15	2.939(8)	154.2
O(1W)-H(1WB)...O(6)#13	0.85	2.12	2.940(8)	162.3
N(3)-H(3A)...O(4)#11	0.86	2.00	2.844(9)	168.2
Symmetry codes: #1 -x+2,-y,-z+1; #2 -x+1,-y,-z; #3 x+1,y,z+1; #4 x+1,y,z; #5 -x+1,-y,-z+1 #6 x-1,y,z; #7 x,y,z+1; #8 x,y+1,z+1; #9 x,y-1,z-1; #10 x-1,y,z-1; #11 x,y,z-1; #12 -x,-y,-z; #13 -x+1,-y+1,-z+1.				

Table S3. N_2 adsorption data of complex **3.**

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(V4.00 H)

Sample:	xff-01		
Operator:	wwj		
Submitter:			
File:	C:\2020\DATA\ZMB-MIC.SMP		
Started:	5/27/2012 10:16:51AM	Analysis Adsorptive:	N2
Completed:	5/27/2012 11:56:03AM	Analysis Bath Temp.:	-195.767 癈
Report Time:	5/28/2012 1:28:39PM	Thermal Correction:	No
Sample Mass:	0.0487 g	Warm Free Space:	27.9585 cm?Entered
Cold Free Space:	84.7784 cm	Equilibration Interval:	30 s
Ambient Temperature:	22.00 癈	Low Pressure Dose:	3.000 cm?g STP
Automatic Degas:	Yes		

Horvath-Kawazoe Differential Pore Volume Plot

Sphere Pore Geometry

xff-01

Pore Width (?	dV/dw (cm?g放)
9.447	1.28922E-06
10.6917	5.01834E-06
11.57207631	5.92535E-06
12.5250901	8.01892E-05
12.95979262	-9.92112E-06
13.42901053	0.000153996

Summary Report

Horvath-Kawazoe

Maximum pore volume at P/Po = 0.010018259:	0.000168 cm?g
Median pore width:	12.405