Supporting information

pH- and mol-ratio dependent formation of zinc(II) coordination polymers with iminodiacetic acid: Synthesis, crystal structure, spectroscpic and thermal studies

Lu-Bin Ni[a], Rong-Hua Zhang[a], Qiong-Xin Liu[a], Wen-Sheng Xia[a], Hongxin Wang[b], Zhao-Hui Zhou[a,b,*]

[a] *State Key Laboratory of Physical Chemistry of Solid Surface, , National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China,* [b] *Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

Figure S7. EDS results of (a) $(NH_4)_n[Zn(Hida)Cl_2]_n$ (**1**) calcined at 500^oC for 4h; (b) $[Zn(ida)(H_2O)_2]_n$ (**2**) calcined at 500^oC for 4h; (c) $[Zn(Hida)]_n \cdot 4H_2O$ (**3**) calcined at 500^oC for 4h

Figure S8. SEM image of $[Zn(Hida)]_n \cdot 4H_2O$ (**3**) and $[Zn(ida)(phen)(H_2O)] \cdot 2H_2O$ (**4)** calcined at 500^oC for 4h.

Figure S9. ^1H NMR spectra of $(NH_4)_n[Zn(Hida)Cl_2]_n$ (**1**), $[Zn(ida)(H_2O)_2]_n$ (**2**) and $[Zn(Hida)_2]_n \cdot 4nH_2O$ (**3**) in D_2O.

Figure S10. IR spectra of the zinc complexes $(NH_4)_n[Zn(Hida)Cl_2]_n$ (**1**), $[Zn(ida)(H_2O)_2]_n$ (**2**), $[Zn(ida)(phen)(H_2O)] \cdot 2H_2O$ (**4**) and $[Zn(Hida)_2]_n \cdot 4nH_2O$ (**3**).

Figure S11. UV-Vis diffuse reflection spectra of H_2ida, $(NH_4)_n[Zn(Hida)Cl_2]_n$ (**1**), $[Zn(ida)(H_2O)_2]_n$ (**2**) and $[Zn(Hida)_2]_n \cdot 4nH_2O$ (**3**).

Figure S12. UV-Vis diffuse reflection spectra of 1,10-phen, $[Zn(ida)(phen)(H_2O)] \cdot 2H_2O$ (**4**).

Figure S1

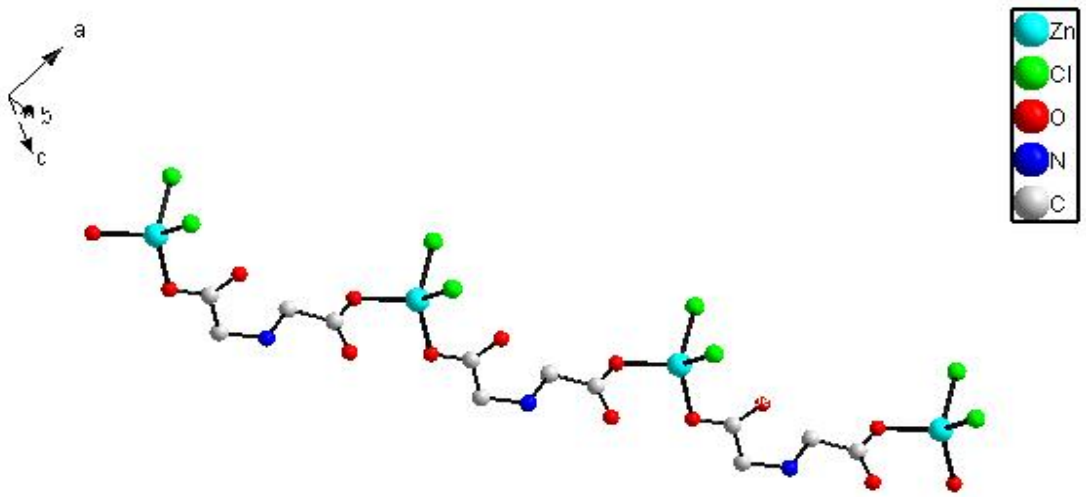


Figure S2

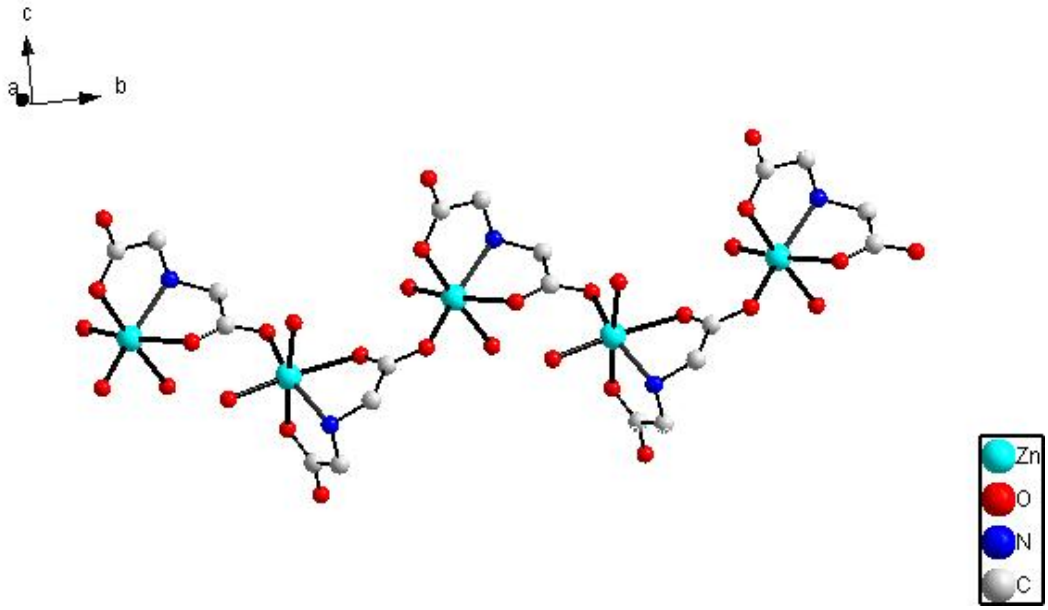


Figure S3

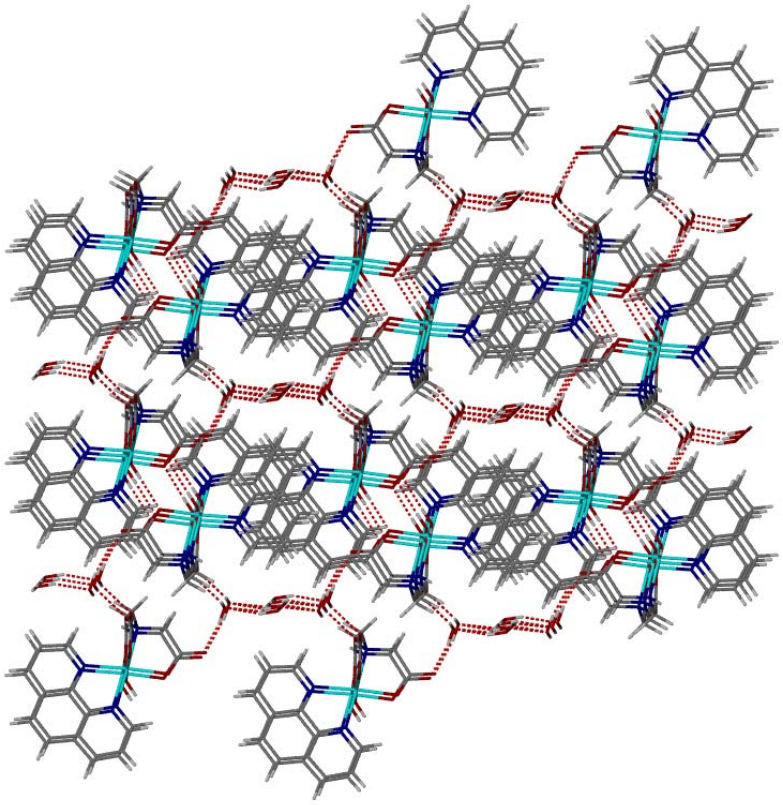


Figure S4

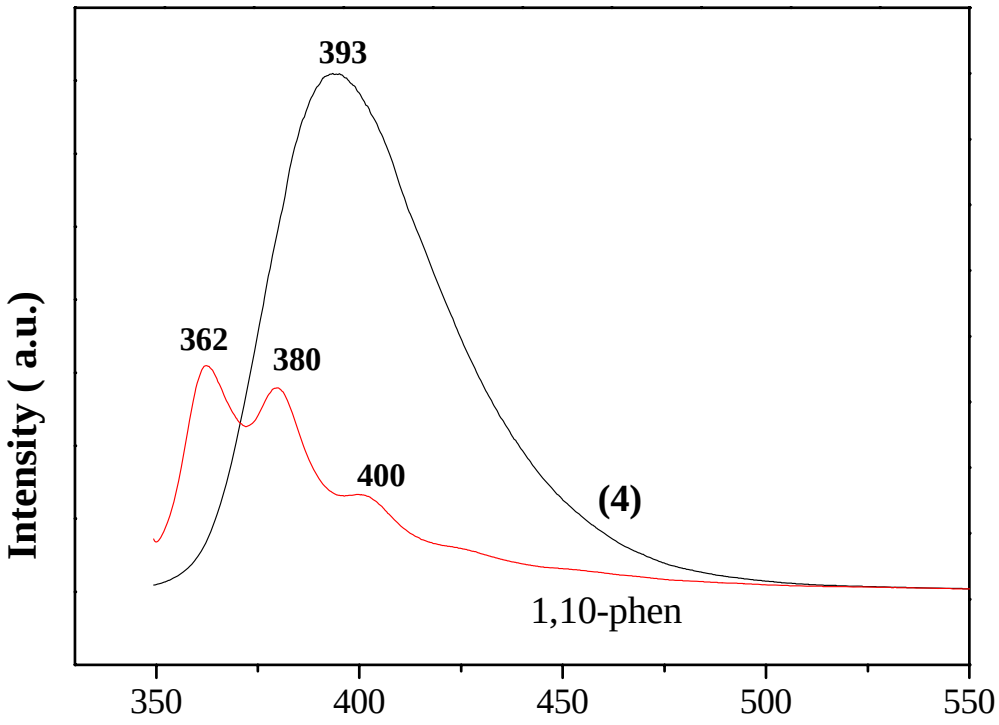
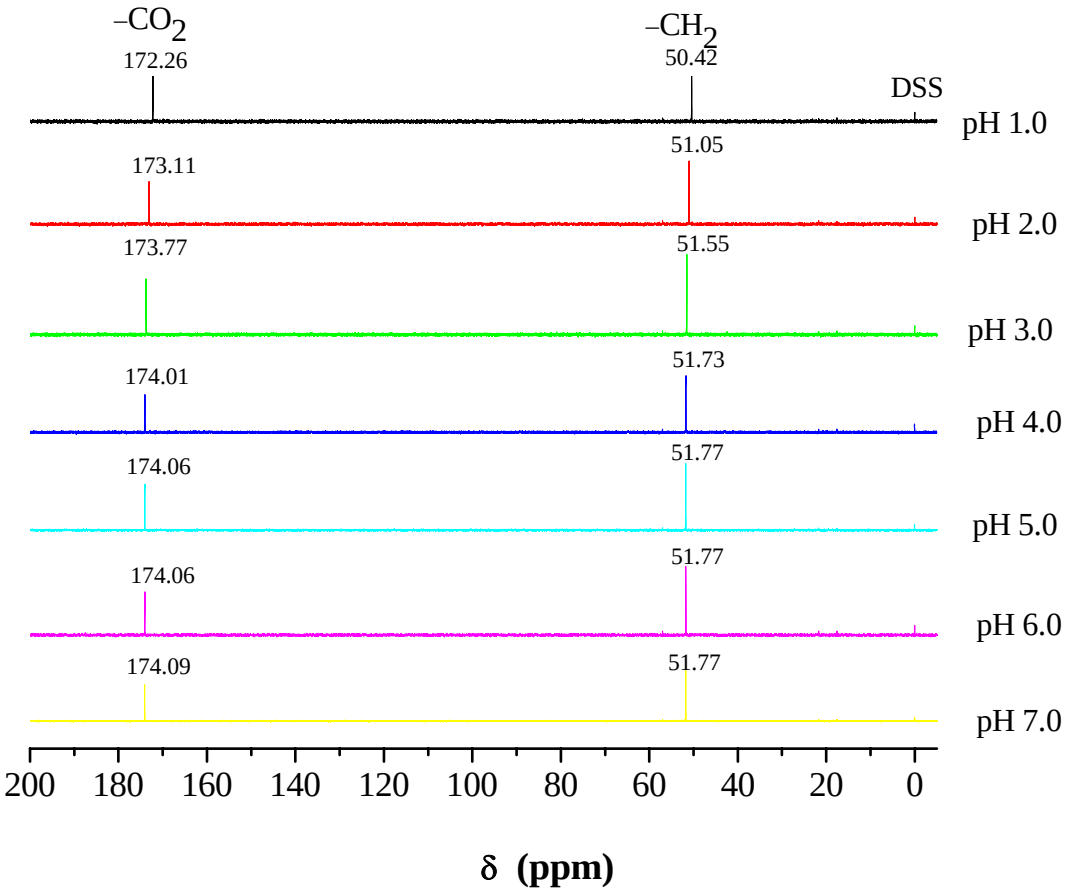


Figure S5



NMR Experimental section

Preparations of the solutions of free iminodiacetate ligand at various pH values for NMR studies

Iminodiacetic acid (6.70g, 50mmol) was dissolved in 10ml of water. The resulting solution was divides into seven parts. The pH value of each solution was adjusted (1.0 to 7.0) with ammonium hydroxide respectively. The ^{13}C NMR spectra of the solutions were recorded in D_2O after 24 h.

Figure S6

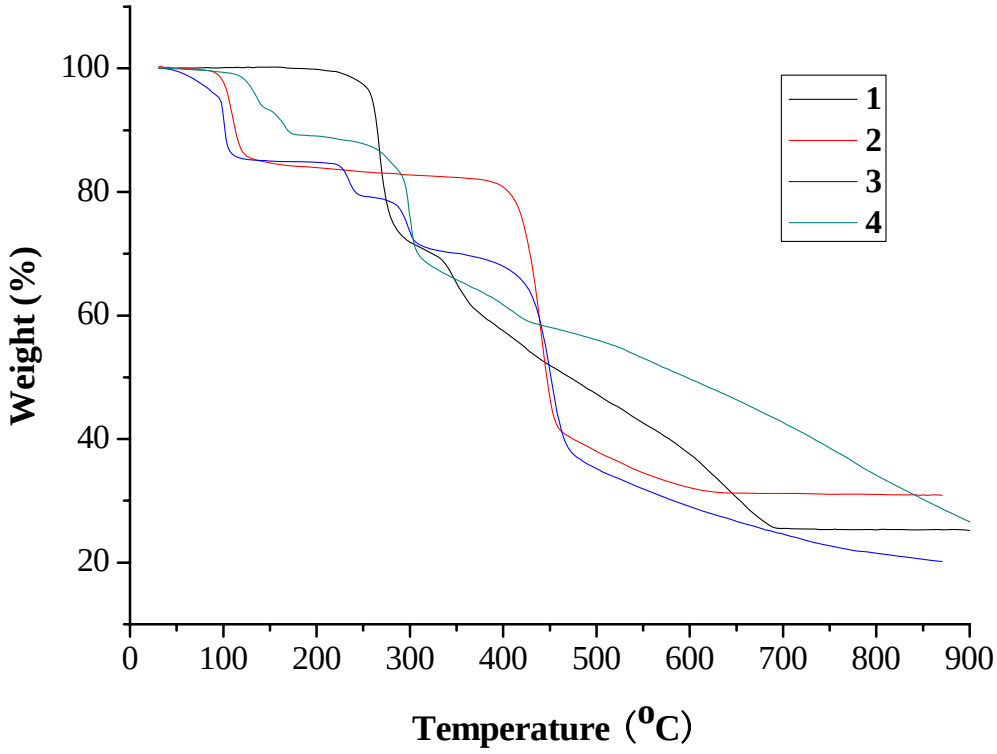
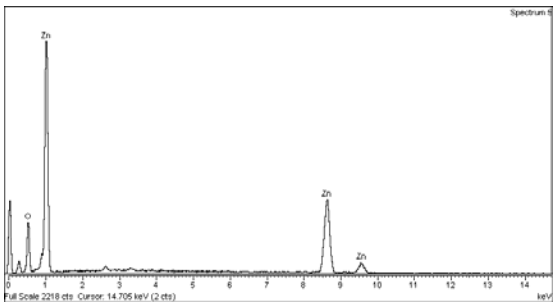

100
80
60
40
20
Weight (%)
0
100
200
300
400
500
600
700
800
900
Temperature (°C)
1
2
3
4

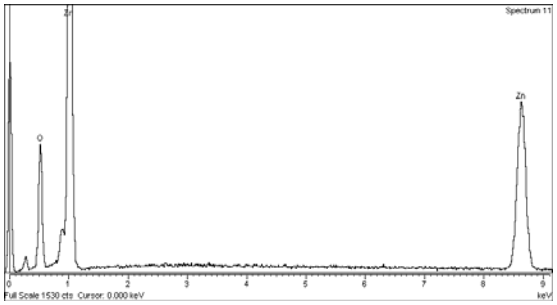
Figure S7

(a)



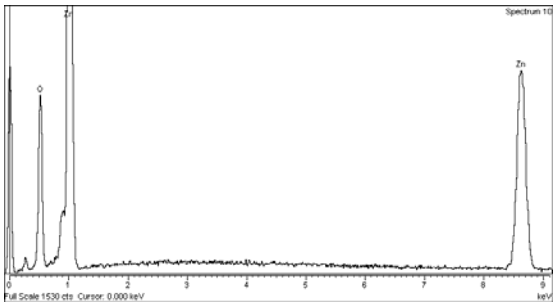
Element	Weight%	Atomic%
O	23.33	55.43
Zn	76.67	44.57
Totals	100.00	

(b)



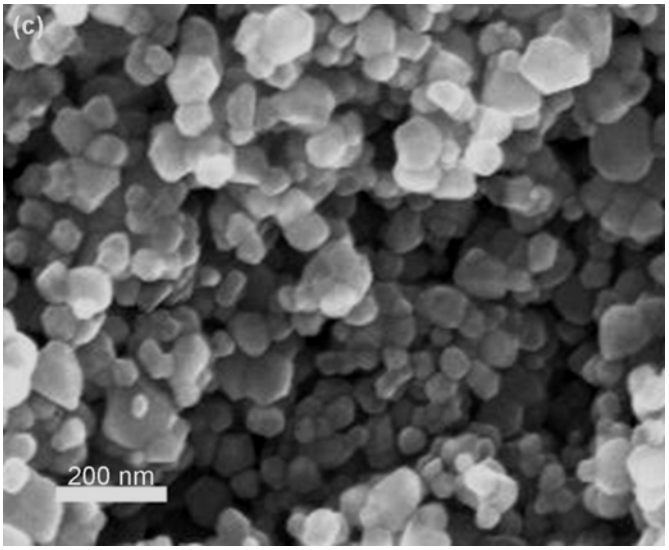
Element	Weight%	Atomic%
O	18.42	47.99
Zn	81.58	52.01
Totals	100.00	

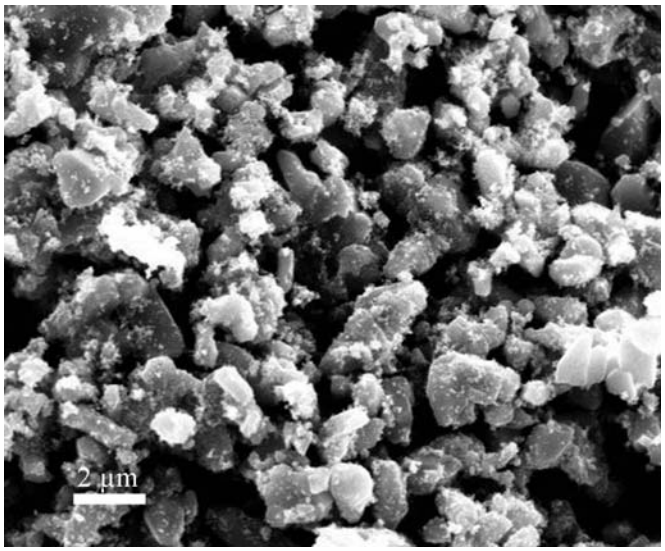
(c)

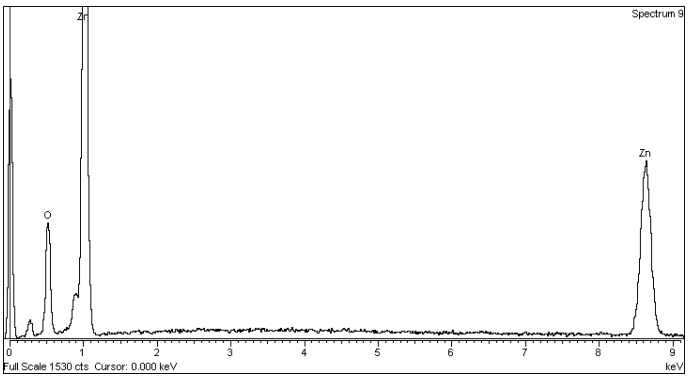


Element	Weight%	Atomic%
O K	20.57	51.42
Zn K	79.43	48.58
Totals	100.00	

Figure S8







Element	Weight%	Atomic%
O K	17.70	46.77
Zn K	82.30	53.23
Totals	100.00	

Figure S9

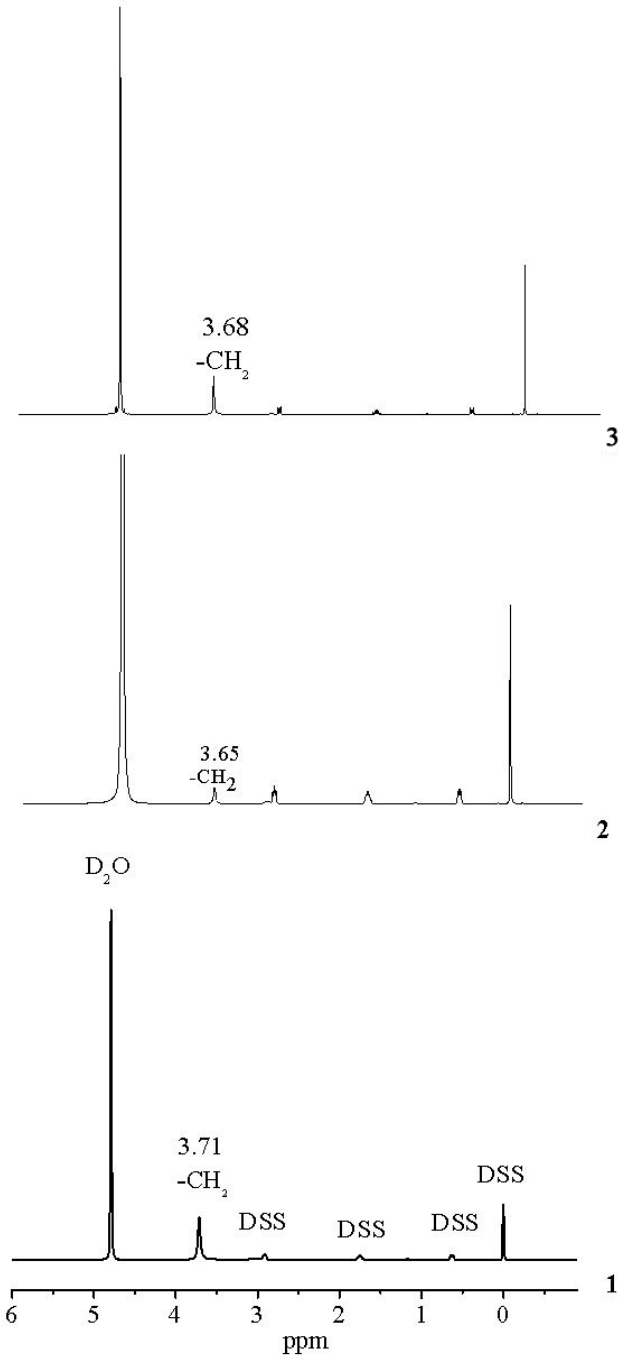


Figure S10

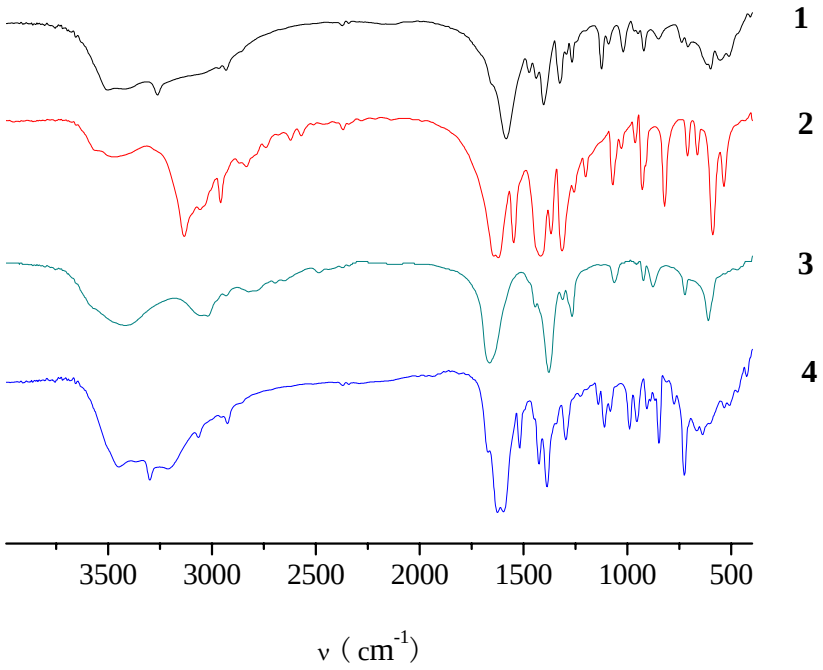


Figure S11

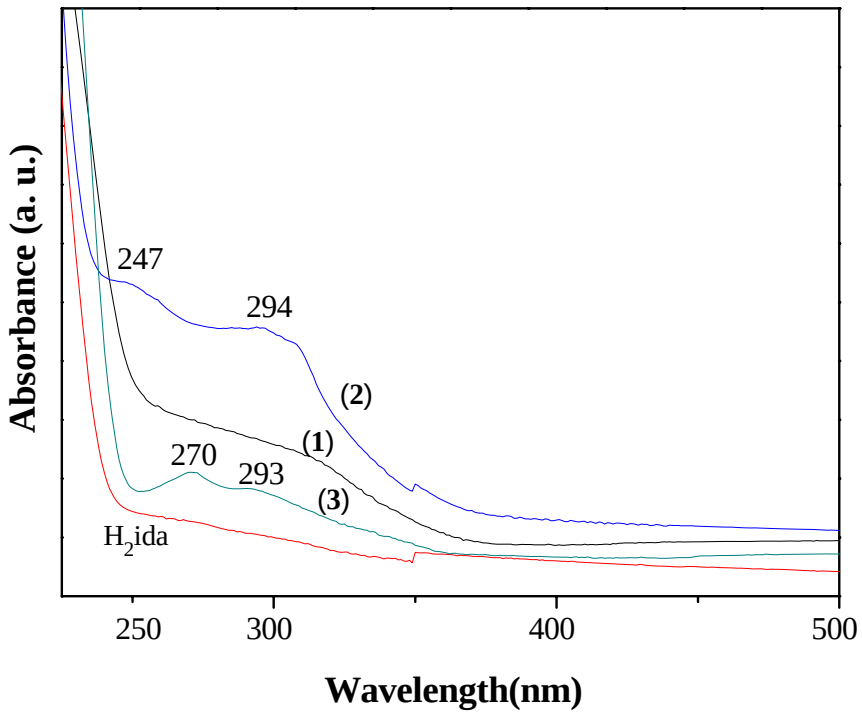

Absorbance (a. u.)
247
294
(2)
(1)
270
293
(3)
H2ida
250
300
400
500
Wavelength(nm)

Figure S12

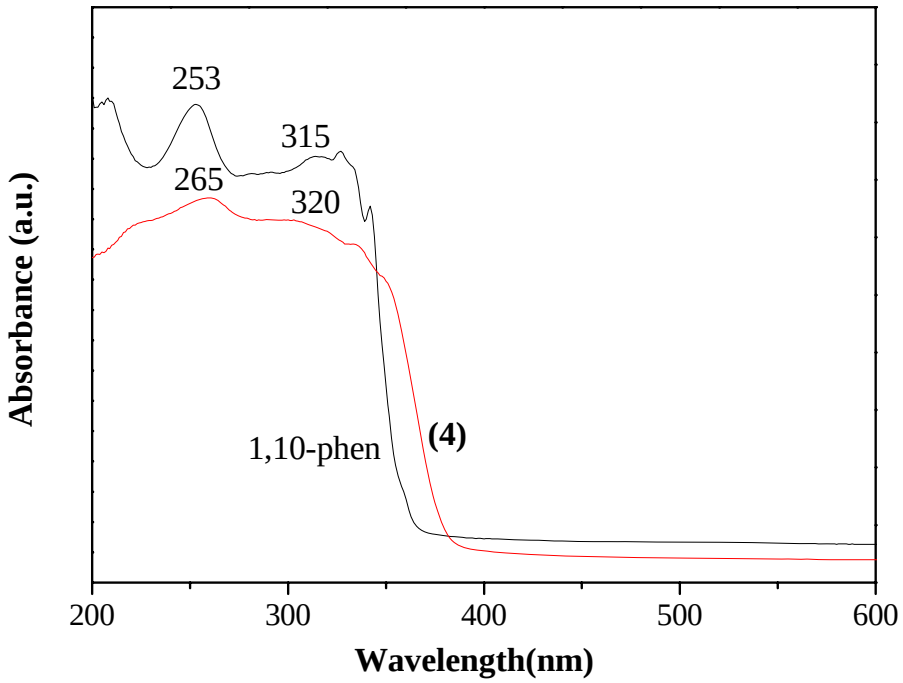

253
315
265
320
1,10-phen
(4)
Absorbance (a.u.)
200
300
400
500
600
Wavelength(nm)

Table S1. Selected bond lengths (Å) and angles (º) for 1–4.

1					
Zn(1)–O(2a)	1.989(1)	Zn(1)–O(4)	1.966(1)	Zn(1)–Cl(1)	2.2538(6)
Zn(1)–Cl(2)	2.2784(5)				
O(4)–Zn(1)–O(2a)	102.84(6)	O(4)–Zn(1)–Cl(1)	115.96(5)	O(2a)–Zn(1)–Cl(1)	117.39(4)
O(4)–Zn(1)–Cl(2)	102.95(5)	O(2a)–Zn(1)–Cl(2)	113.93(4)	Cl(1)–Zn(1)–Cl(2)	103.21(2)
2					
Zn(1)–O(1)	2.092(2)	Zn(1)–O(3)	2.251(2)	Zn(1)–O(4a)	2.010(2)
Zn(1)–O(1w)	2.161(2)	Zn(1)–O(2w)	2.107(2)	Zn(1)–N(1)	2.114(2)
O(4a)–Zn(1)–O(1)	87.66(7)	O(4a)–Zn(1)–O(2w)	106.27(7)	O(1)–Zn(1)–O(2w)	94.53(8)
O(4a)–Zn(1)–N(1)	159.02(7)	O(1)–Zn(1)–N(1)	81.53(7)	O(2 w)–Zn(1)–N(1)	92.53(7)
O(4a)–Zn(1)–O(1w)	94.01(8)	O(1)–Zn(1)–O(1w)	176.11(7)	O(2w)–Zn(1)–O(1w)	88.38(7)
N(1)–Zn(1)–O(1 w)	95.79(7)	O(4a)–Zn(1)–O(3)	86.93(7)	O(1)–Zn(1)–O(3)	92.24(7)
O(2 w)–Zn(1)–O(3)	165.38(6)	N(1)–Zn(1)–O(3)	75.65(8)	O(1 w)–Zn(1)–O(3)	84.35(7)
3					
Zn(1)–O(3)	1.963(2)	Zn(1)–O(1)	1.973(2)	Zn(1)–O(3a)	1.963(2)
Zn(1)–O(1a)	1.973(2)				
O(3)–Zn(1)–O(3a)	109.0(1)	O(3)–Zn(1)–O(1a)	115.81(8)	O(3a)–Zn(1)–O(1a)	103.5(1)
O(3)–Zn(1)–O(1)	103.5(1)	O(3a)–Zn(1)–O(1)	115.81(8)	O(1a)–Zn(1)–O(1)	109.8(1)
4					
Zn(1)–O(1)	2.187(2)	Zn(1)–O(3)	2.070(2)	Zn(1)–O(1w)	2.176(2)
Zn(1)–N(1)	2.132(2)	Zn(1)–N(2)	2.153(2)	Zn(1)–N(3)	2.091(2)
O(3)–Zn(1)–N(3)	98.36(8)	O(3)–Zn(1)–N(1)	83.23(8)	N(3)–Zn(1)–N(1)	172.90(8)
O(3)–Zn(1)–O(1w)	88.02(7)	N(3)–Zn(1)–O(1w)	92.55(8)	N(1)–Zn(1)–O(1w)	94.42(8)
O(3)–Zn(1)–N(2)	175.75(8)	N(3)–Zn(1)–N(2)	79.15(9)	N(1)–Zn(1)–N(2)	99.67(9)
N(1)–Zn(1)–O(1)	79.16(8)	N(2)–Zn(1)–O(1)	92.73(8)	O(1w)–Zn(1)–O(1)	173.57(7)
N(2)–Zn(1)–O(1w)	88.65(8)	O(3)–Zn(1)–O(1)	90.88(7)	N(3)–Zn(1)–O(1)	93.87(8)

Symmetric transformation for **1**: a, x–1, y, z–1; **2**: a, –x+2, y–1/2, –z ; **3**: a, –x+3/2, –y+1/2, z ;