Supporting Information

Three Zn(II)-triazole-H_3btc Complexes Regulated by Mixed Ligands Protonation upon Stepwise Crystallization

En-Cui Yang,[a] Zhong-Yi Liu,[a] Xiu-Guang Wang,[a] Stuart R. Batten[b] and Xiao-Jun Zhao[*, a]

College of Chemistry and Life Science, Key Laboratory of Molecular Structure and Materials Performance, Tianjin Normal University, Tianjin 300387, P. R. China, and School of Chemistry, Monash University, Victoria 3800, Australia

Experiment Section

Materials.

All reagents were purchased commercially and used without further purification. Doubly deionized water was used for the conventional synthesis. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer in the range 4000 – 400 cm^{-1} region. X-ray powder diffraction (XRPD) data were recorded on a Rigaku D/max-2500 diffractometer at 60 kV and 300 mA for Cu K_α radiation (λ = 1.5406 Å), with a scan speed of 2 deg/min and a step size of 0.02° in 2θ. The calculated XRPD patterns based on the single-crystal diffraction data were produced by Mercury 1.3 software, available from the Cambridge Crystallographic Data Center. Thermogravimetric analysis (TGA) experiments were carried out on Shimadzu simultaneous DTG-60A thermal analysis instrument from room temperature to 800°C under N_2 atmosphere at a heating rate of 5 °C/min. Fluorescence spectra of the polycrystalline powder samples were performed on a Cary Eclipse fluorescence spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

Synthesis of 1 ~ 3.

Htrz (10.5mg, 0.15mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (29.7mg, 0.1 mmol), and H_3btc (10.5 mg, 0.05 mmol) were dissolved in 10mL water and the initial pH value of the mixture was adjusted to 3.6 by slow addition of an appropriate amount of triethylamine. Then the mixture was transferred into a Teflon-lined stainless steel vessel (20ml) and heated to 150 ^{o}C for four days under autogenous pressure. After the mixture was cooled to room temperature, the colorless block-shaped single crystals **1** suitable for X-ray diffraction were obtained directly, washed with ethanol, and air-dried (yield 2.3 mg, 10% based on Zn salt). Anal.Calcd. for $C_{13}H_{13}Zn_{2.5}N_6O_9$: C, 27.85; H, 2.34; N, 14.99%. Found: C, 27.89; H, 2.60; N,14.73%. IR (KBr, cm^{-1}): 3469br, 3132w, 2368w, 1623s, 1564s, 1520m, 1426m,1368s, 1346s, 1289m, 1204w, 1165m, 1085m, 1011m, 895w, 764m, 735m, 661m, 552w, 467w. The resulting mixture was filtrated. Upon slow evaporation of the filtrate at room temperature, pale-yellow single crystals **2** were produced within three days, washed by ethanol and air-dried (yield 8.8 mg, 32% based on Zn salt). Anal. Calcd. for $C_{20}H_{14}Zn_{2.5}N_3O_{14}$: C, 35.13; H, 2.06; N, 6.15%. Found: C, 35.33; H, 2.20; N, 6.33. IR (KBr, cm^{-1}): 3442br, 3136m, 1707s, 1617s, 1546s, 1441s, 1360s, 1302m, 1258m, 1228s, 1177m, 1092m, 1038w, 1005w, 867w, 836w, 791w, 754m, 731w, 678m, 656m, 547w. Further slow evaporation of the filtrate, colorless block single crystals **3** produced within two weeks, washed by ethanol and air-dried (yield 22.0 mg, 55% based on Zn salt). Anal.Calcd for $C_{22}H_{26}Zn_2N_6O_{18}$: C, 33.31; H, 3.30; N, 10.59%. Found: C, 33.41; H, 3.20; N, 10.63. IR (KBr, cm^{-1}): 3469br 3129w, 1724s, 1618s, 1575s, 1510m, 1368w, 1297m, 1234s, 1160s, 1073m, 786m, 730m, 677m, 539m, 453w.

X-ray Data Collection and Structure Determinations. Diffraction intensities for complexes **1 – 3** were collected on Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the φ-ω scan technique at ambient temperature. There was no evidence of crystal decay during data collection. Semiempirical absorption corrections were applied (SADABS), and the program SAINT was used for integration of the diffraction profiles. [1] The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.[2] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The oxygen atoms of the water of crystallization in **1** are disordered: one, O(8), varies among three positions with occupancies that refined to 0.35 for O(8), 0.30 for O(8′) and 0.35 for O(8″); while O(10) also varies among three positions with occupancies that refined to 0.40 for O(10), 0.25 for O(10′) and 0.35 for O(10″). The organic hydrogen atoms were generated geometrically; the H atoms of the water molecules except for the splitting water molecules were located from difference maps and refined with isotropic temperature factors. No attempts have been performed to locate hydrogen atoms of the splitting water molecules. CCDC-664695 **1**; CCDC-664694 **2**; CCDC-664697 **3**; contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

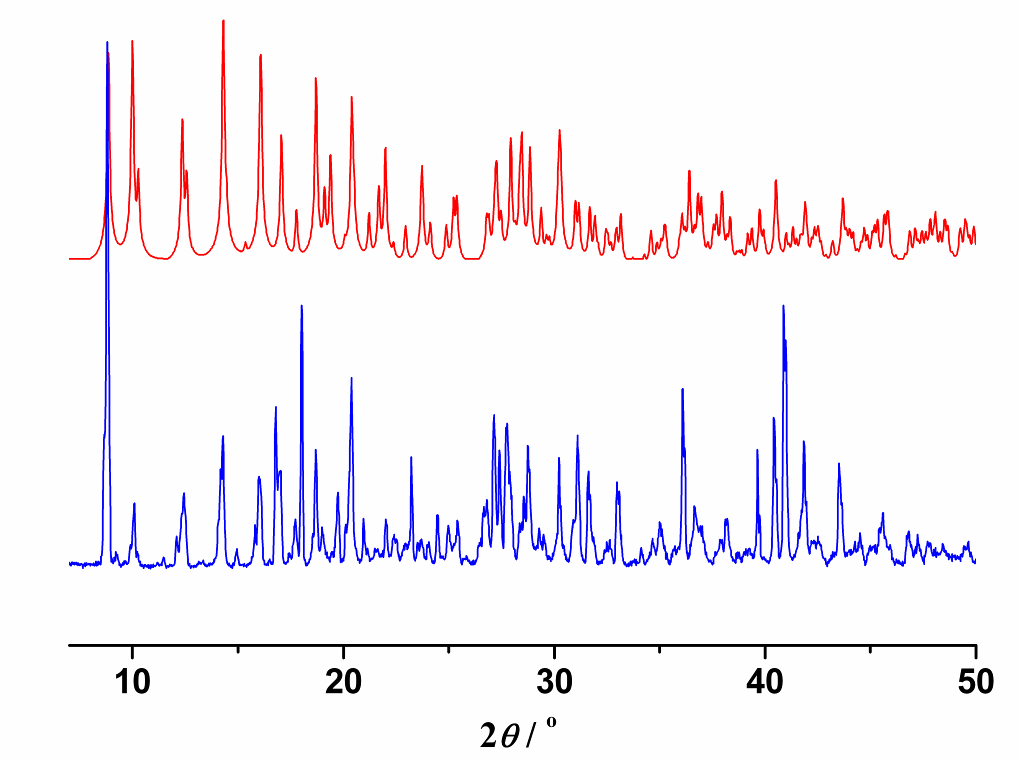


Fig. S1 Calculated (red line) and experimental (blue line) X-ray powder diffraction patterns for **1**.

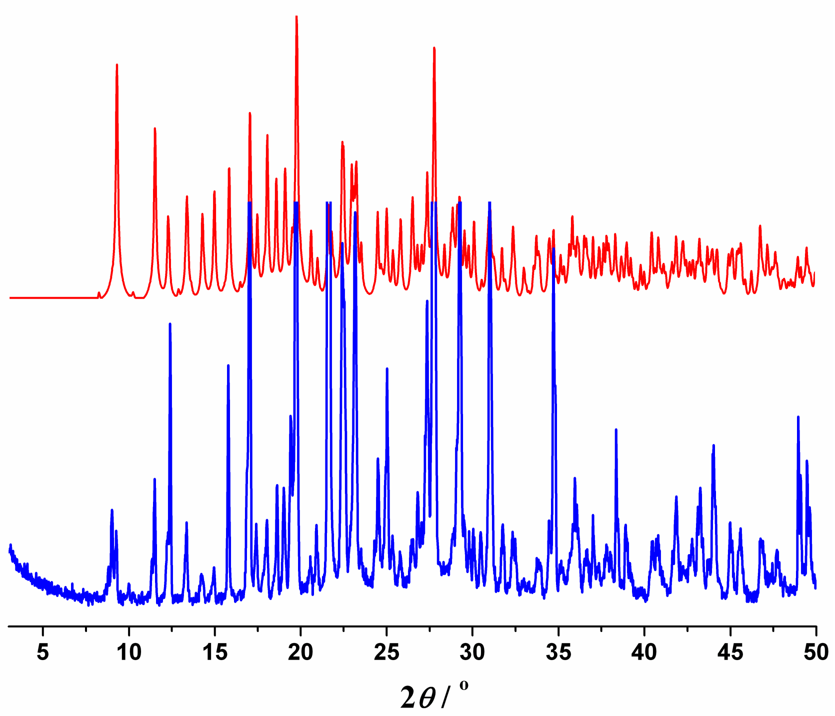


Fig. S2 Calculated (red line) and experimental (blue line) X-ray powder diffraction patterns for **2**.

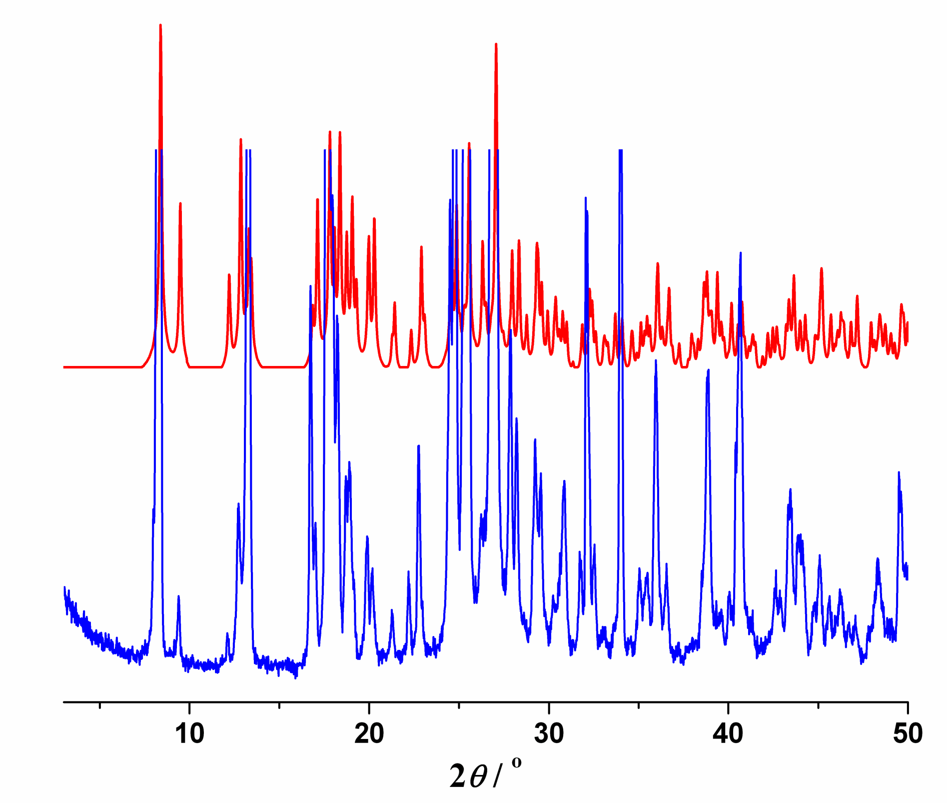


Fig. S3 Calculated (red line) and experimental (blue line) X-ray powder diffraction patterns for **3**.

IR spectra for 1 – 3. In their IR spectra, the broad band located at *ca*. 3450 cm^{-1} confirms the existence of coordinated/lattice and guest water molecules. The absence of peaks between 1730 and 1690 cm^{-1} indicates the full deprotonation of H_3btc in **1**. In contrast, a peak appeared at 1707 for **2** and 1724 cm^{-1} for **3**, suggesting the coexistence of -COOH and -COO$^-$. In addition, the differences (Δv) in v_{as}(COO$^-$) and v_s(COO$^-$) are much larger than 95 cm^{-1} in **3**, implying a unidentate coordination mode for the carboxylate groups (see Table S1). [3] The Δv in **1** and **2** (138, 255 and 105, 257 cm^{-1}) indicates the carboxylate groups behave as chelating/bridging bidentate and unidentate coordinated ligands, which is agreement with the results of single-crystal X-ray diffraction and significantly dominates the dimensionality of the complexes.

Table S1. The vibration frequencies of carboxylate groups in **1 – 3** (in cm^{-1})

	v_{as}(COO$^-$)	v_s(COO$^-$)	Δv
1	1623, 1564	1426, 1368	255, 138
2	1617, 1546	1441, 1360	257, 105
3	1618, 1575	1368	250, 207

Table S2. Selected hydrogen bond lengths (Å) and angles (˚) for **1 – 3**.

Donor–H···Acceptor	D – H	H···A	D···A	D – H···A
1				
O7–H7B···O2[a]	0.850	1.922	2.724(6)	156.79
2				
O3–H3···O1[a]	0.820	1.891	2.651(1)	153.66
O11–H11···O9[b]	0.820	1.796	2.588(7)	162.07
O13–H13A···O4[b]	0.850	2.001	2.832(5)	165.58
O13–H13B···O7[c]	0.850	2.069	2.883(8)	160.52
O13–H13B···O10[d]	0.850	2.652	3.149(2)	118.64
O14–H14A···O4[b]	0.850	2.141	2.886(2)	146.23
O14–H14A···O12[e]	0.850	2.619	3.124(2)	119.31
O14–H14B···O6[f]	0.850	1.878	2.696(9)	161.38
3				
O3–H3···O8[a]	0.820	1.840	2.646(8)	167.72
O7–H7A···N1[b]	0.850	1.980	2.785(0)	157.72
O7–H7B···O4[c]	0.850	1.952	2.782(5)	165.28
N2–H2'···O9[d]	0.860	2.009	2.763(2)	145.86
O8–H8A···O6[e]	0.850	1.800	2.626(9)	163.88
O8–H8B···O9[f]	0.850	1.894	2.743(1)	177.06
O9–H9A···O2[c]	0.850	1.846	2.672(2)	163.66
O9–H9B···O8[a]	0.850	2.064	2.844(6)	152.43

Symmetry Codes: for **1** [a] *x* – 1/4, – *y* + 1/4, *z* + 3/4, for **2** [a] *x* – 1, *y*, *z*, [b] *x* + 1, *y*, *z*, [c] –*x* + 1, *y* + 1/2, – *z* + 1/2, [d] – *x* + 1, – *y* + 1, – *z*, [e] *x*, – *y* + 1/2, *z* + 1/2, [f] – *x* + 1, – *y* + 1, – *z* + 1, for **3** [a] –*x* + 1, – *y* + 1, – *z* + 2, [b] *x* – 1, *y*, *z*, [c] – *x* + 1, – *y* + 1, – *z* + 1, [d] *x* + 1, *y* + 1, *z* – 1, [e] – *x* + 2, – *y* + 1, – *z* + 1, [f] *x* + 1, *y*, *z*.

Table S3. Selected bond lengths (Å) and angles (°) for complex **1 – 3**^{a}.

1			
Zn(1)–N(5)	2.110(3)	Zn(2)–N(6)	1.991(3)
Zn(1)–N(2)^{a}	2.129(3)	Zn(3)–N(4)	1.997(3)
Zn(1)–O(1)	2.129(2)	Zn(3)–N(1)	2.013(3)
Zn(2)–O(3)^{b}	1.977(2)	Zn(3)–O(6)^{d}	1.962(3)
Zn(2)–N(3)^{c}	1.976(3)	Zn(3)–O(2)	2.001(2)
Zn(2)–O(7)	1.997(3)		
N(5)–Zn(1)–N(5)^{a}	89.13(18)	O(3)^{b}–Zn(2)–N(3)^{c}	123.28(14)
N(5)–Zn(1)–N(2)^{a}	176.82(11)	O(3)^{b}–Zn(2)–N(6)	110.89(14)
N(5)–Zn(1)–N(2)	91.98(11)	N(3)^{c}–Zn(2)–N(6)	112.81(12)
N(2)^{a}–Zn(1)–N(2)	87.08(18)	O(3)^{b}–Zn(2)–O(7)	104.95(12)
N(5)–Zn(1)–O(1)	90.91(12)	N(3)^{c}–Zn(2)–O(7)	99.74(15)
N(5)^{a}–Zn(1)–O(1)	87.91(12)	N(6)–Zn(2)–O(7)	101.71(15)
N(2)^{a}–Zn(1)–O(1)	92.11(12)	O(6)^{d}–Zn(3)–O(2)	101.52(11)
N(2)–Zn(1)–O(1)	90.91(12)	O(6)^{d}–Zn(3)–N(4)	105.19(13)
N(5)–Zn(1)–O(1)^{a}	87.91(12)	O(2)–Zn(3)–N(4)	114.14(13)
N(5)^{a}–Zn(1)–O(1)^{a}	90.91(12)	O(6)^{d}–Zn(3)–N(1)	128.36(13)
N(2)^{a}–Zn(1)–O(1)^{a}	89.09(13)	O(2)–Zn(3)–N(1)	105.75(13)
O(1)–Zn(1)–O(1)^{a}	178.3(2)	N(4)–Zn(3)–N(1)	102.34(11)
2			
Zn(1)–O(7)	1.9997(15)	Zn(2)–O(14)^{c}	2.0641(16)
Zn(1)–N(1)^{a}	2.0083(18)	Zn(2)–O(13)	2.1541(17)
Zn(1)–N(2)^{b}	2.0287(17)	Zn(3)–N(3)	2.0027(18)
Zn(1)–O(1)	2.0661(15)	Zn(3)–O(10)^{d}	1.9363(15)
Zn(1)–O(2)	2.2659(16)	Zn(3)–O(8)	1.9995(15)
Zn(2)–O(5)	2.0579(15)	Zn(3)–O(6)^{e}	2.0019(16)
O(7)–Zn(1)–N(1)^{a}	118.78(7)	O(5)–Zn(2)–O(13)	86.97(7)
O(7)–Zn(1)–N(2)^{b}	96.84(7)	O(14)–Zn(2)–O(13)	91.81(7)

N(1)^{a}–Zn(1)–N(2)^{b}	106.05(7)	O(5)–Zn(2)–O(14)	87.80(6)
O(7)–Zn(1)–O(1)	113.12(6)	O(5)–Zn(2)–O(14)^{c}	92.20(6)
N(1)^{a}–Zn(1)–O(1)	116.98(7)	O(14)–Zn(2)–O(14)^{c}	180.00(8)
N(2)^{b}–Zn(1)–O(1)	100.55(7)	O(14)–Zn(2)–O(13)^{c}	88.19(7)
O(7)–Zn(1)–O(2)	87.26(6)	O(5)–Zn(2)–O(13)	86.97(7)
N(1)^{a}–Zn(1)–O(2)	88.64(7)	O(6)^{e}–Zn(3)–N(3)	102.56(7)
N(2)^{b}–Zn(1)–O(2)	160.16(6)	O(8)–Zn(3)–N(3)	96.59(7)
O(1)–Zn(1)–O(2)	60.28(6)	O(10)^{d}–Zn(3)–O(8)	114.99(6)
O(5)^{c}–Zn(2)–O(5)	180.0	O(10)^{d}–Zn(3)–O(6)^{e}	113.84(6)
O(13)–Zn(2)–O(13)^{c}	180.00(7)	O(8)–Zn(3)–O(6)^{e}	97.66(6)
O(5)^{c}–Zn(2)–O(13)	93.03(7)	O(10)^{d}–Zn(3)–N(3)	126.41(7)
3			
Zn(1)–O(5)^{a}	1.9679(14)	Zn(1)–N(3)	2.0055(17)
Zn(1)–O(1)	1.9838(14)	Zn(1)–O(7)	2.0094(17)
O(5)^{a}–Zn(1)–O(1)	100.62(6)	O(5)^{a}–Zn(1)–O(7)	106.41(7)
O(5)^{a}–Zn(1)–N(3)	125.96(7)	O(1)–Zn(1)–O(7)	113.58(6)
O(1)–Zn(1)–N(3)	110.51(6)	N(3)–Zn(1)–O(7)	100.14(7)

Symmetry Codes: for **1** ^{a} $-x+1, -y, z$, ^{b} $x-1/2, y, z+1/2$, ^{c} $x, y, z+1$, ^{d} $-x+5/4, y+1/4, z+1/4$; for **2** ^{a} $-x, -y+1, -z$, ^{b} $x+1, y, z$, ^{c} $-x+1, -y+1, -z+1$ ^{d} $\mathrm{x}, -y+1/2, z+1/2$, ^{e} $-x, y-1/2, -z+1/2$; for **3** ^{a} $x-1, y+1, z$.

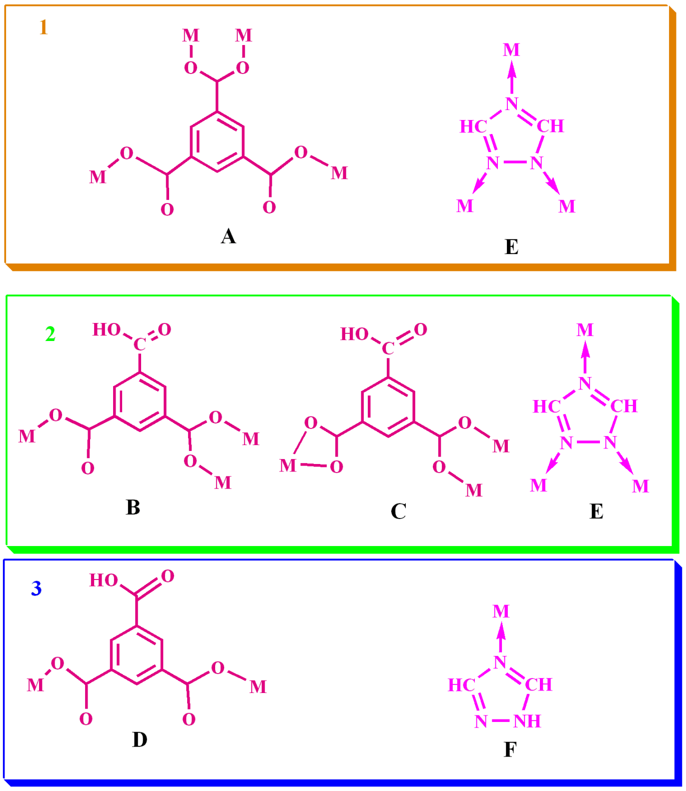
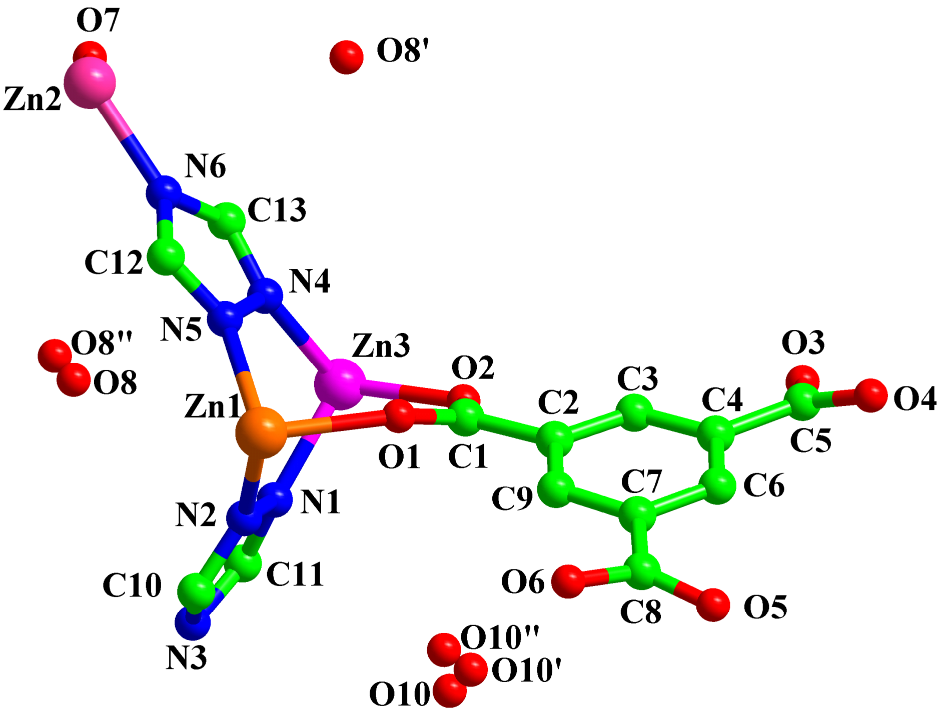


Fig. S4. Coordination modes of H$_3$btc and Htrz in **1 – 3**.



(a)

Fig. S5. Asymmetric unit of **1** with atomic labels (hydrogen atoms are omitted for clarity).

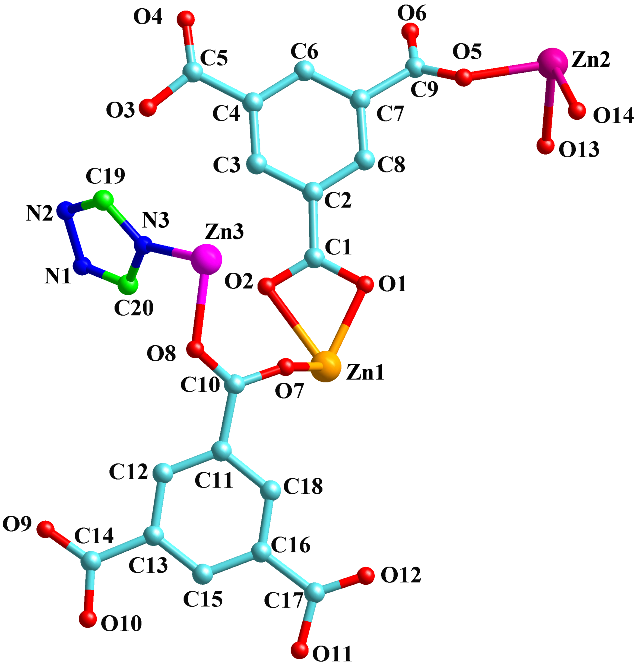
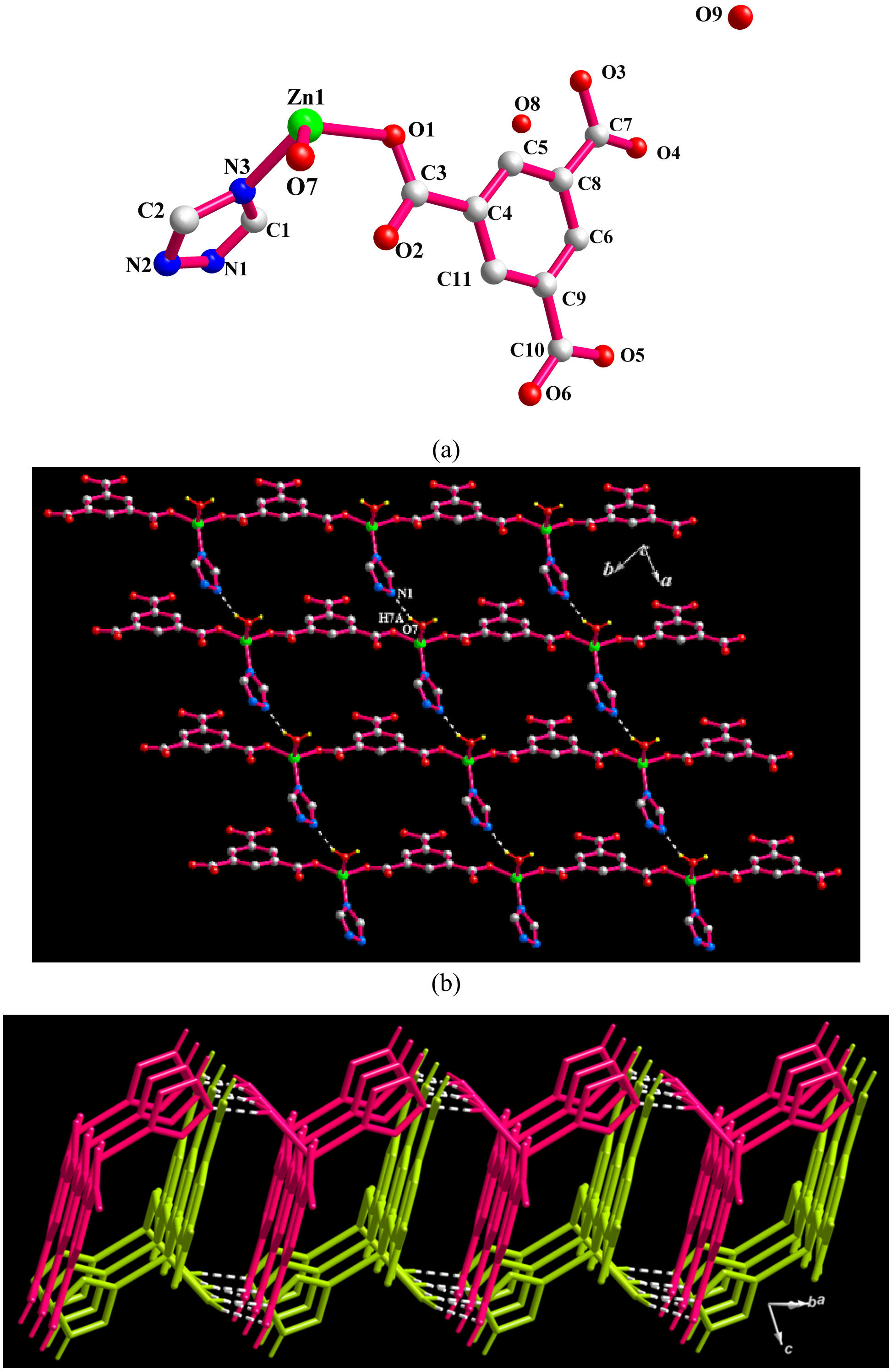


Fig. S6 Asymmetric unit of **2** with atomic labels (hydrogen atoms are omitted for clarity).



(a)

(b)

(c)

Fig. S7. (a) Asymmetric unit of **3** with atomic labels (hydrogen atoms are omitted for clarity). (b) 2-D layer of **3** formed by interchain O–H···N H-bonds interactions. (c) Two face-to-face 2-D layers of **3** formed by interlayer O–H···O H-bonds interactions.

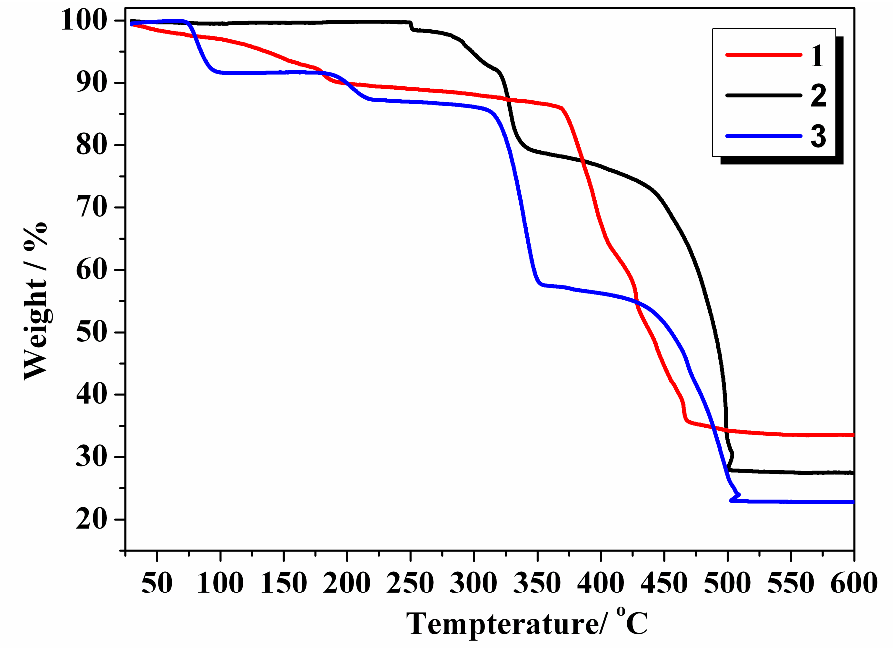


Fig. S8. TG curves for **1 – 3.**

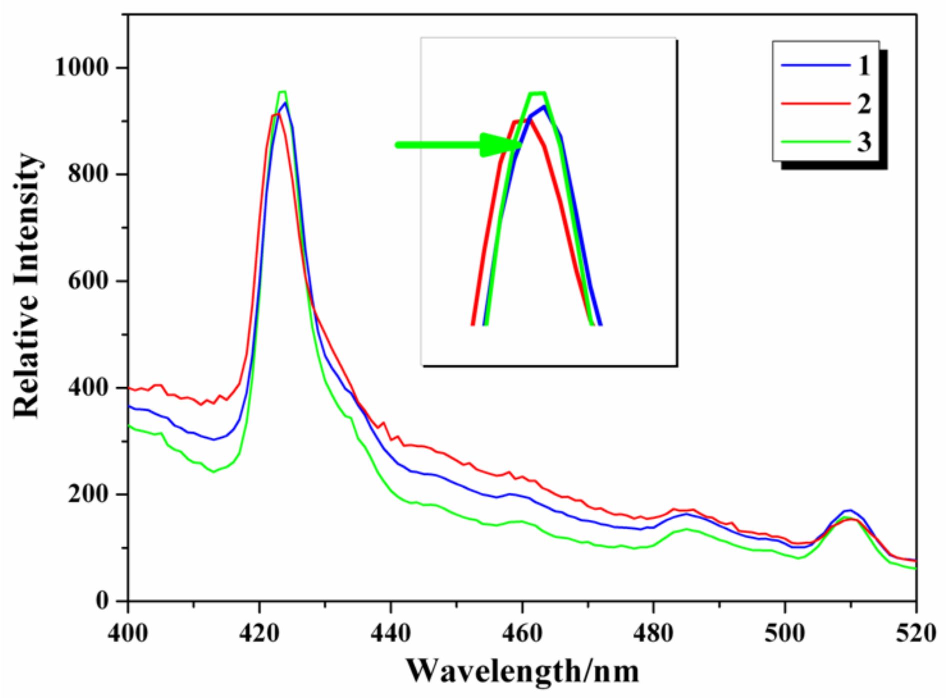


Fig. S9. The solid emission spectra of **1** ~ **3** at room temperature.

References

1. *SAINT*; Bruker AXS: Madison, WI, **1998**.

2. G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*; Göttingen University: Göttingen, Germany, 1997; Sheldrick, G. M. *SHELXS-97, Program for X-ray Crystal Structure Solution*; Göttingen University: Göttingen, Germany, 1997.

3. Deacon, G. B.; Phillips, R. *J. Coord. Chem. Rev*. 1980, 33, 227; L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958