Electronic Supporting Information (ESI)

for

Structure modulation in zinc-ditetrazolate coordination polymers by *in situ* ligand synthesis

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Figures in Supporting Information

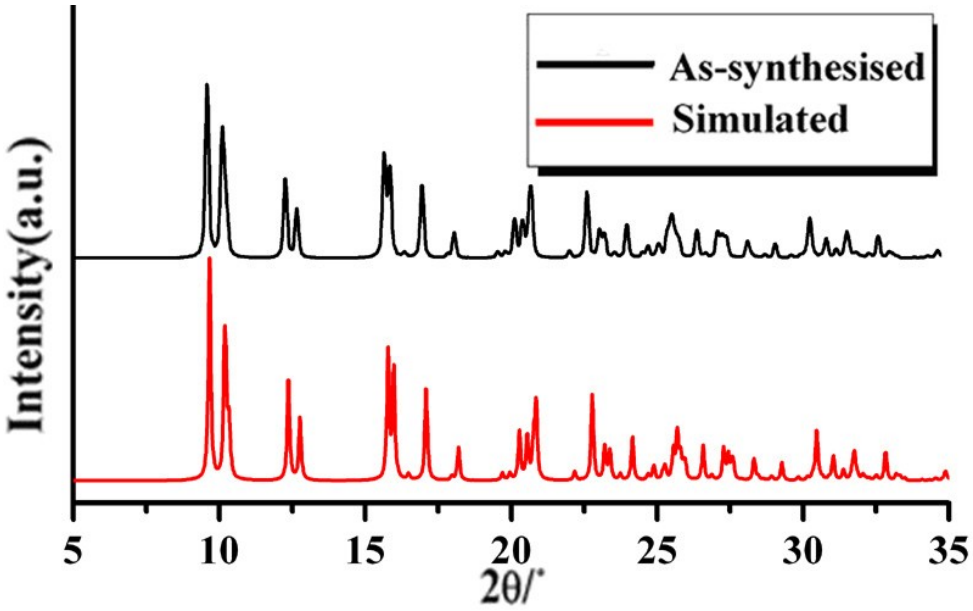

Fig. S1. XRPD patterns for **1**.

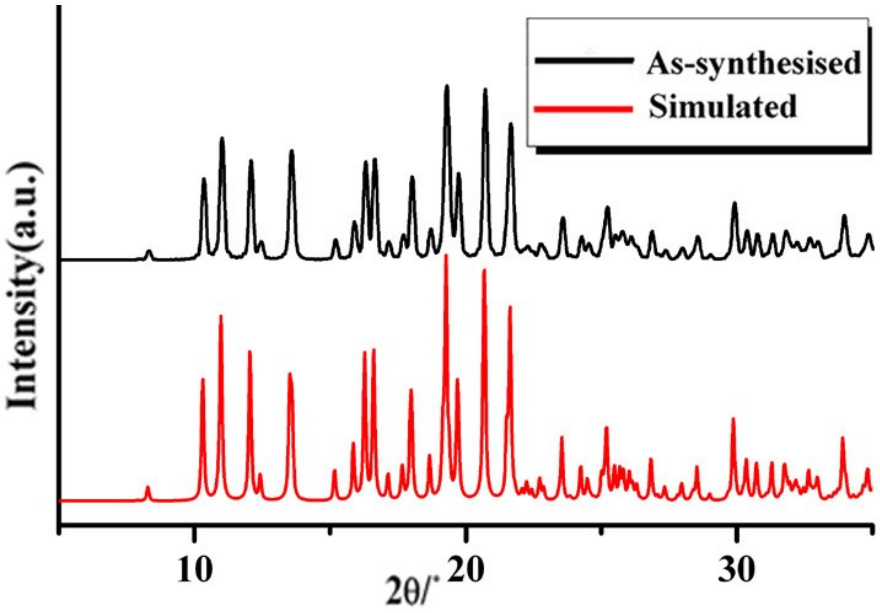

Fig. S2. XRPD patterns for **2**.

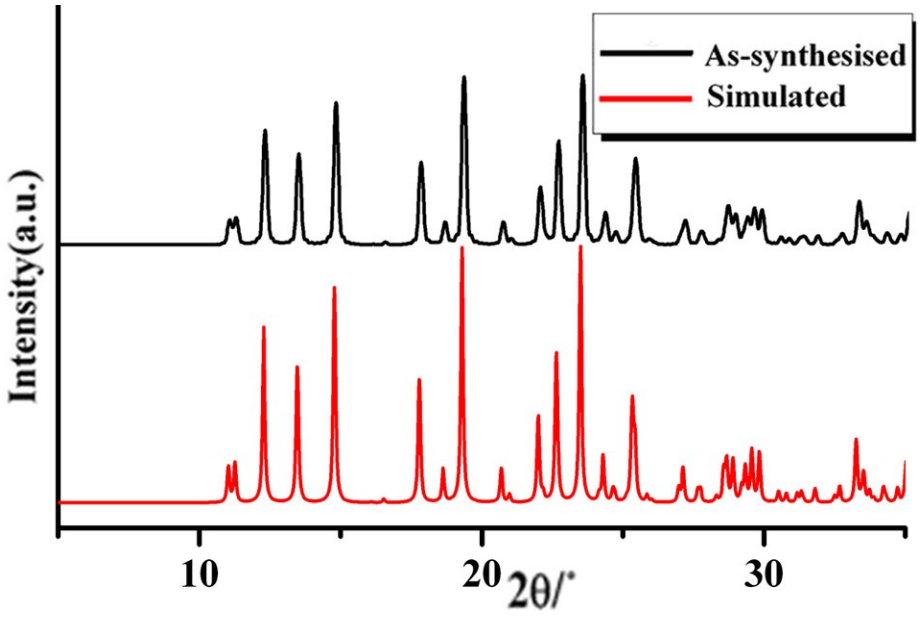

Fig. S3. XRPD patterns for **3**.

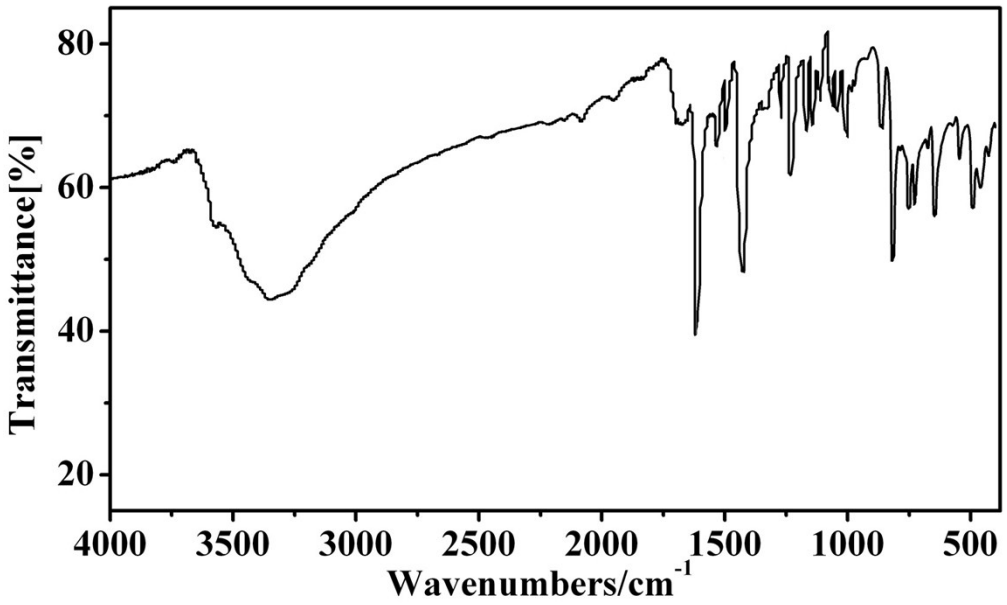

Fig. S4. IR spectrum of compound **1**.

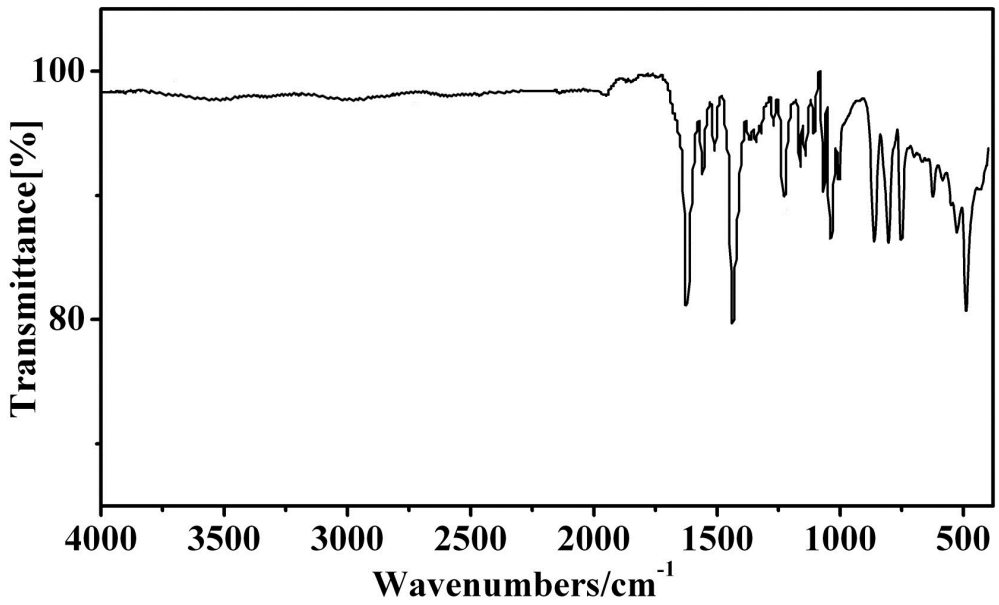

Fig. S5. IR spectrum of compound **2**.

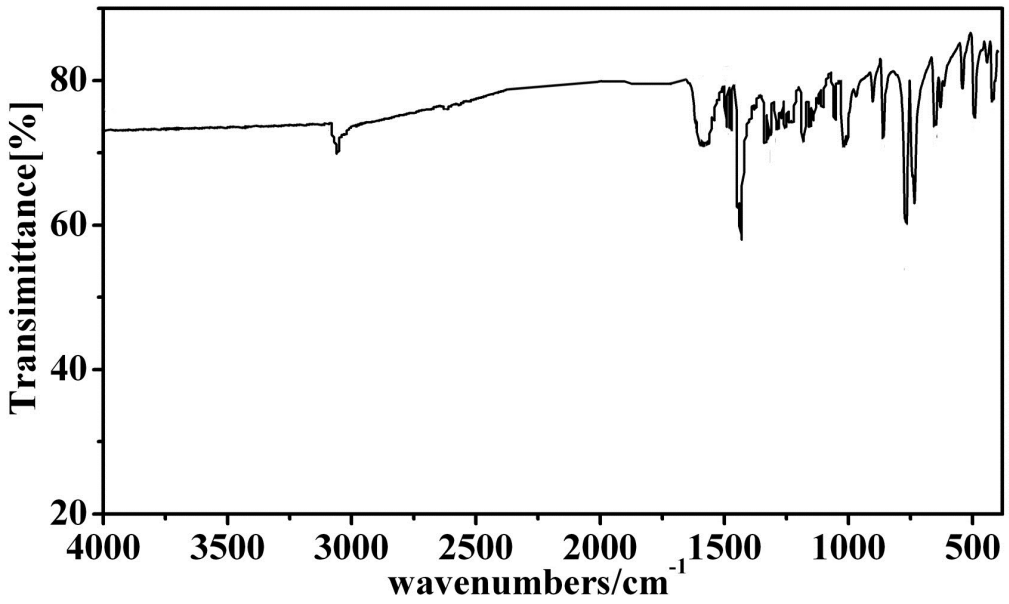

Fig. S6. IR spectrum of compound **3**.

The π-π stacking interactions

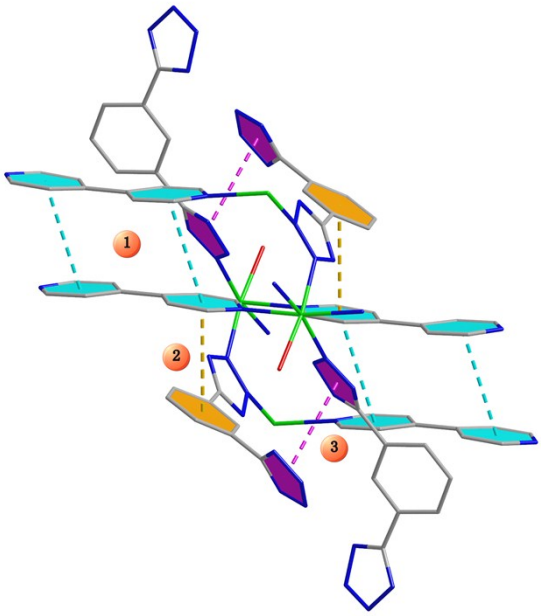

Fig. S7. The *π-π* stacking interactions (blue, orange and purple dished lines) in **1**. Color codes: Zn-(green), C-(gray), O-(red), N-(blue). Hydrogen atoms are omitted for clarity.

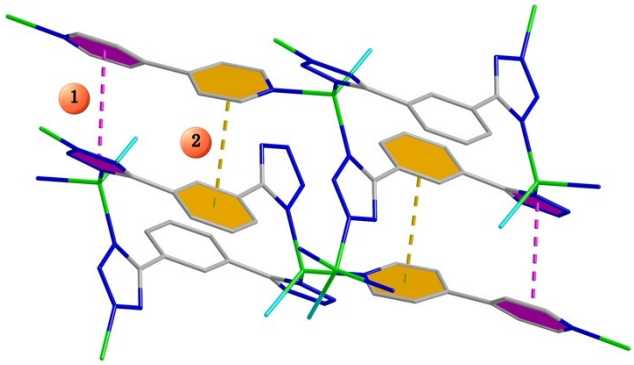

Fig. S8. The *π-π* stacking interactions (orange and purple dished lines) in **2**. Color codes: Zn-(green), C-(gray), O-(red), N-(blue). Hydrogen atoms are omitted for clarity.

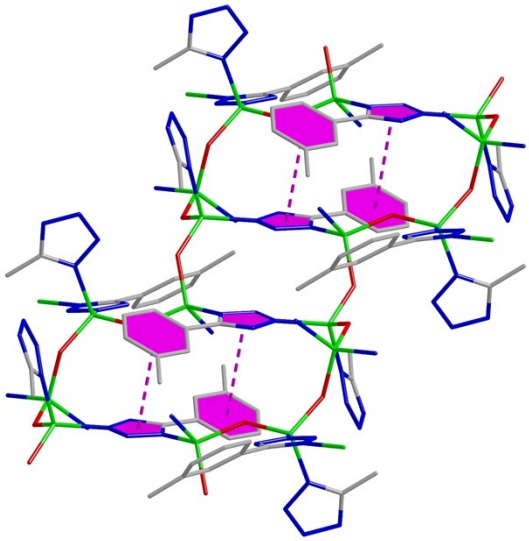

Fig. S9. The π-π stacking interactions (purple dished lines) in **3**. Color codes: Zn-(green), C-(gray), O-(red), N-(blue). Hydrogen atoms are omitted for clarity.

Table S1 π-π contacts (Å and ˚) in **1-3**.

	Group 1 ··· Group 2	CCD	DA
1	$Cg_{(purple)}$ ··· $Cg_{(purple)}$	3.799(3)	3.3(2)
	$Cg_{(blue)}$ ··· $Cg_{(blue)}$	3.797(3)	6.8(2)
	$Cg_{(blue)}$ ··· $Cg_{(orange)}$	3.759(3)	23.99(17)
2	$Cg_{(purple)}$ ··· $Cg_{(purple)}$	3.640(2)	2.5(2)
	$Cg_{(orange)}$ ··· $Cg_{(orange)}$	4.065(2)	16.14(19)
3	$Cg_{(purple)}$ ··· $Cg_{(purple)}$	3.916(5)	25.8(4)

“Cg” means the different kind of rings, “CCD” is the centroid-to-centroid distance and “DA” is the dihedral angle between rings.

The Uv-vis spectra

The UV-vis absorption spectra of the samples **1-3** in the solid state are shown in Fig. S10. These three compounds all exhibit low energy bands from 200 to 320 nm. Compounds **1** and **2** show two similar absorption energy bands at maximum 209 and 237 nm, 209 and 236 nm, respectively, which can be assigned to ligand-to-metal charge transfer transitions.[S1] While compound **3** reveals three absorption energy bands at maximum 212, 246 and 303 nm, which also can be ascribed to ligand-to-metal charge transfer transitions. The presence of the third absorption band at 303 nm is probably the effect of the OH^- groups which links two different Zn^{2+} ions to give a binuclear $\{Zn_2\}$ cluster.[S2]

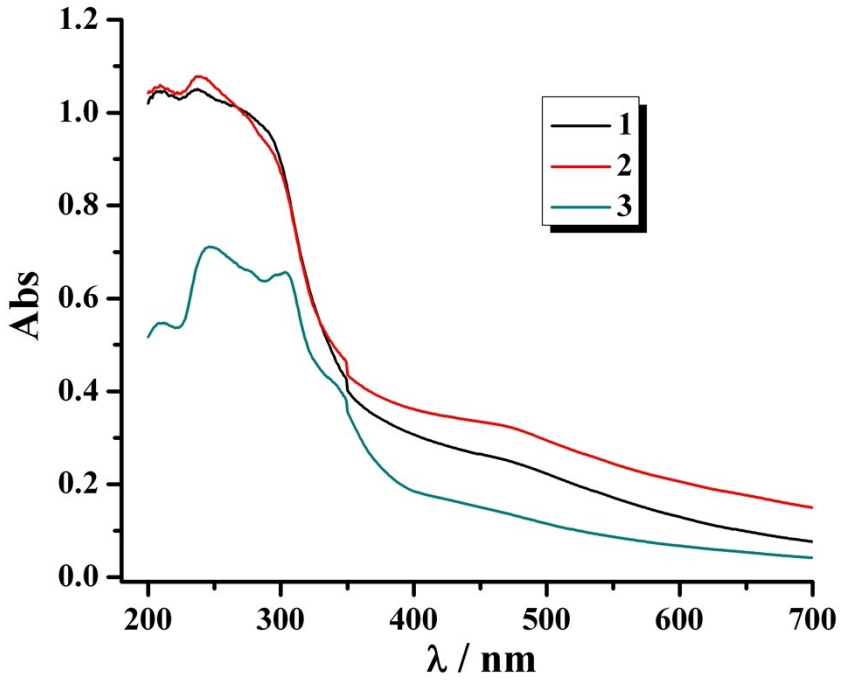

Fig. S10. Uv-vis spectrum of compounds **1-3**.

S1. (1) Z. Q. Shi, Y. Z. Li, Z. J. Guo and H. G. Zheng, *CrystEngComm.*, 2014, **16**, 900; (b) W. W. Xiong, E. U. Athresh, Y. T. Ng, J. F. Ding, T. Wu and Q. C. Zhang, *J. Am. Chem. Soc.*, 2013, **135**, 1256.

S2. (a) V. Béreau, *Inorg. Chem. Commun.*, 2004, **7**, 829; (b) B. Liu, J. Yang, G. C. Yang, J. F. Ma, *Inorg. Chem.*, 2013, **52**, 84.

The fluorescence lifetime

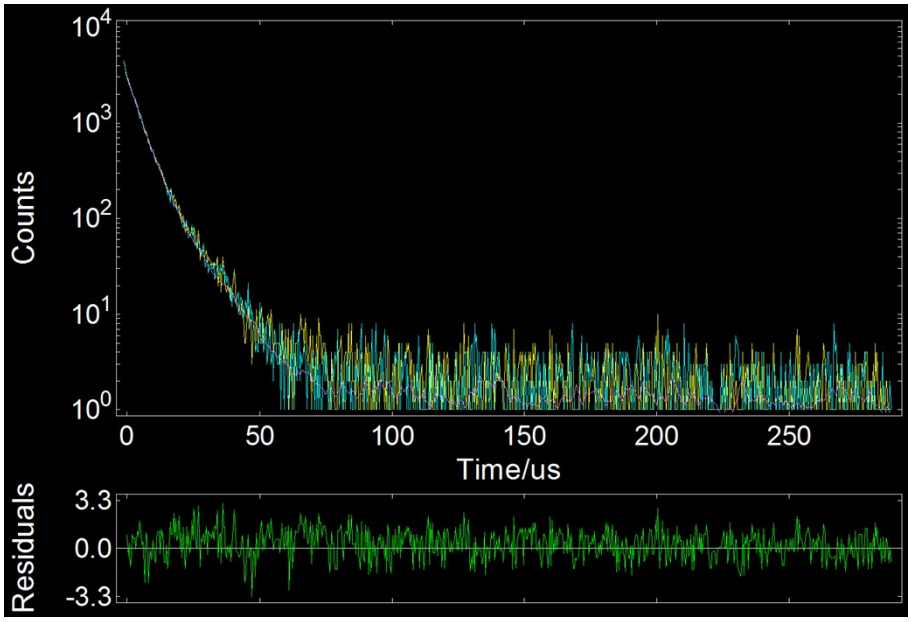

Fig. S11. Fluorescence decay curves for compound **1**. The scattering points are experimental data and the solid lines are the fitting results.

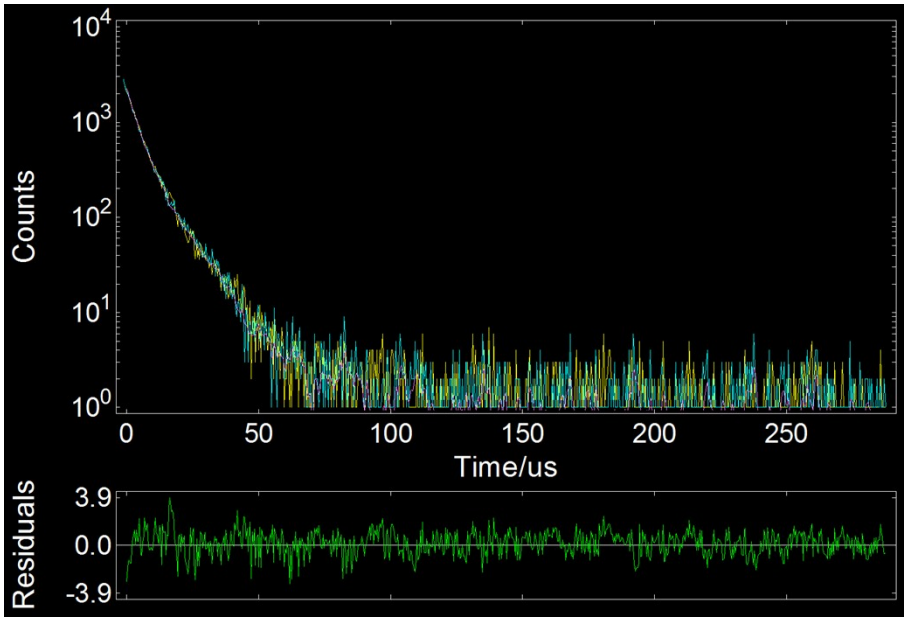

Fig. S12. Fluorescence decay curves for compound **2**. The scattering points are experimental data and the solid lines are the fitting results.

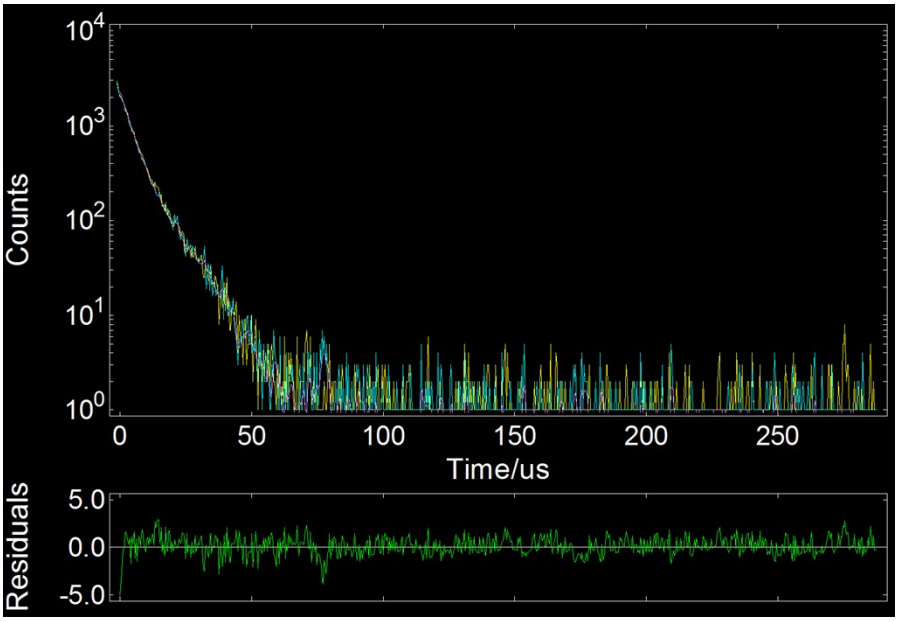

Fig. S13. Fluorescence decay curves for compound **3**. The scattering points are experimental data and the solid lines are the fitting results.

Table S2 The selected bond lengths [Å] and angles [º] of compound **1**.

		1	
Zn(1)-O(1)	1.910(5)	Zn(2)-N(8)#2	2.026(5)
Zn(1)-O(2)	1.912(5)	Zn(2)-N(4)#3	2.037(5)
Zn(1)-N(2)	2.004(6)	N(4)-Zn(2)#6	2.037(5)
Zn(1)-N(5)	2.029(6)	N(8)-Zn(2)#7	2.026(5)
Zn(2)-O(2)#1	1.904(5)	O(2)-Zn(2)#8	1.904(5)
Zn(2)-O(1)	1.933(5)		
O(1)-Zn(1)-O(2)	105.1(2)	O(2)#1-Zn(2)-O(1)	103.0(2)
O(1)-Zn(1)-N(2)	112.6(2)	O(2)#1-Zn(2)-N(8)#2	118.0(2)
O(2)-Zn(1)-N(2)	115.0(2)	O(1)-Zn(2)-N(8)#2	109.7(2)
O(1)-Zn(1)-N(5)	109.9(2)	O(2)#1-Zn(2)-N(4)#3	109.3(2)
O(2)-Zn(1)-N(5)	108.2(2)	O(1)-Zn(2)-N(4)#3	113.8(2)
N(2)-Zn(1)-N(5)	106.0(2)	N(8)#2-Zn(2)-N(4)#3	103.4(2)

Symmetry transformations used to generate equivalent atoms: #1: x, -y+3/2, z-1/2; #2: x-1, -y+3/2, z-1/2; #3: -x+1, y-1/2, -z+3/2; #6: -x+1, y+1/2, -z+3/2; #7: x+1, -y+3/2, z+1/2; #8: x, -y+3/2, z+1/2.

Table S3 The selected bond lengths [Å] and angles [º] of compound **2**.

		2	
Zn(1)-N(1)	2.013(3)	Zn(2)-N(10)#3	2.031(3)
Zn(1)-N(9)	2.035(3)	Zn(2)-Cl(2)	2.1889(13)
Zn(1)-N(5)#1	2.038(3)	N(5)-Zn(1)#1	2.038(3)
Zn(1)-Cl(1)	2.2006(13)	N(7)-Zn(2)#4	2.000(3)
Zn(2)-N(7)#2	2.000(3)	N(10)-Zn(2)#5	2.031(3)
Zn(2)-N(3)	2.010(3)		
N(1)-Zn(1)-N(9)	106.39(12)	N(7)#2-Zn(2)-N(3)	103.85(13)
N(1)-Zn(1)-N(5)#1	103.72(12)	N(7)#2-Zn(2)-N(10)#3	111.47(13)
N(9)-Zn(1)-N(5)#1	106.60(12)	N(3)-Zn(2)-N(10)#3	105.16(13)
N(1)-Zn(1)-Cl(1)	117.10(9)	N(7)#2-Zn(2)-Cl(2)	117.29(10)
N(9)-Zn(1)-Cl(1)	108.44(10)	N(3)-Zn(2)-Cl(2)	108.86(10)
N(5)#1-Zn(1)-Cl(1)	113.88(9)	N(10)#3-Zn(2)-Cl(2)	109.37(9)

Symmetry transformations used to generate equivalent atoms: #1: -x+1, -y+2, -z; #2: x, y, z+1; #3: x+1, y+1, z; #4: x, y, z-1; #5: x-1, y-1, z.

Table S4 The selected bond lengths [Å] and angles [º] of compound **3**.

		3	
Zn(1)-O(1)	1.910(5)	Zn(2)-N(8)#2	2.026(5)
Zn(1)-O(2)	1.912(5)	Zn(2)-N(4)#3	2.037(5)
Zn(1)-N(2)	2.004(6)	N(4)-Zn(2)#6	2.037(5)
Zn(1)-N(5)	2.029(6)	N(8)-Zn(2)#7	2.026(5)
Zn(2)-O(2)#1	1.904(5)	O(2)-Zn(2)#8	1.904(5)
Zn(2)-O(1)	1.933(5)		
O(1)-Zn(1)-O(2)	105.1(2)	O(2)#1-Zn(2)-O(1)	103.0(2)
O(1)-Zn(1)-N(2)	112.6(2)	O(2)#1-Zn(2)-N(8)#2	118.0(2)
O(2)-Zn(1)-N(2)	115.0(2)	O(1)-Zn(2)-N(8)#2	109.7(2)
O(1)-Zn(1)-N(5)	109.9(2)	O(2)#1-Zn(2)-N(4)#3	109.3(2)
O(2)-Zn(1)-N(5)	108.2(2)	O(1)-Zn(2)-N(4)#3	113.8(2)
N(2)-Zn(1)-N(5)	106.0(2)	N(8)#2-Zn(2)-N(4)#3	103.4(2)

Symmetry transformations used to generate equivalent atoms: #1: x, -y+3/2, z-1/2; #2: x-1, -y+3/2, z-1/2; #3: -x+1, y-1/2, -z+3/2; #6: -x+1, y+1/2, -z+3/2; #7: x+1, -y+3/2, z+1/2; #8: x, -y+3/2, z+1/2