Supporting Information

Hydrogen bond-assisted aggregation-induced emission and application in the detection of Zn(II) ion

Dan Wang[a], Shu-Mu Li[b], Yu-Fei Li[a], Xiang-Jun Zheng*[, a] and Lin-Pei Jin[a]

[a] *Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing, 100875, P. R. China.*

[b]*Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.*

1. General Information and Materials

All solvents and reagents (analytical grade) were used as received. Elemental analyses were conducted using a Vario EL elemental analyzer. Fourier transform infrared (FT-IR) was measured on an Avatar 360 Nicolet 380 FT-IR spectrometer using KBr pellets. Powder X-ray diffraction (XRD) analyses were performed on a PANalytical X' Pert PRO MPD diffractometer for Cu-Kα radiation (λ = 1.5406 Å), with a scan speed of 2°·min^{-1} and a step size of 0.02° in 2θ. The solutions of metal ions were prepared from LiCl, NaCl, KCl, $MgCl_2·6H_2O$, $CrCl_3·6H_2O$, $Mn(ClO_4)_2·6H_2O$, $Fe(ClO_4)_2·xH_2O$, $CaCl_2$, $Co(ClO_4)_2·6H_2O$, $Ni(ClO_4)_2·6H_2O$, $Cu(Ac)_2·H_2O$, $Hg(ClO_4)_2$, $Cd(ClO_4)_2·H_2O$, $Zn(Ac)_2·2H_2O$, $Al(ClO_4)_3·9H_2O$, and $Pb(ClO_4)_2·3H_2O$, respectively. UV-Vis absorption spectra were recorded by a spectrophotometer UV-2600 and fluorescence spectra were recorded on a FS5 fluorescence spectrophotometer, with a quartz cuvette (path length = 1 cm). DLS (dynamic light scattering) results were obtained on Brookhaven Zeta Plus Zeta Potential Analyzer. SEM images were obtained on JEOL JSM-6701F SEM. Mass spectra (ESI) were obtained on LCT Premier XE time-of-flight (TOF) mass spectrometer.

2. Structural determination

Single-crystal data were collected on a Bruker APEX II CCD diffractometer (Germany) with graphite monochromated Mo-Kα radiation (λ) at 293 K. The structure was solved by the direct method and refined by full matrix least squares based on F^2 using the SHELX 97 program.[1] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Crystal data for **1** and the Zn(II) complex **2** are summarized in Table S1, Selected bond lengths and bond angles for **1** and the complex **2** are tabulated in Table S2.

3. Recrystallization of 0.5[$C_5H_5N_2COOK{\cdot}C_5H_5N_2COOH$] (1)

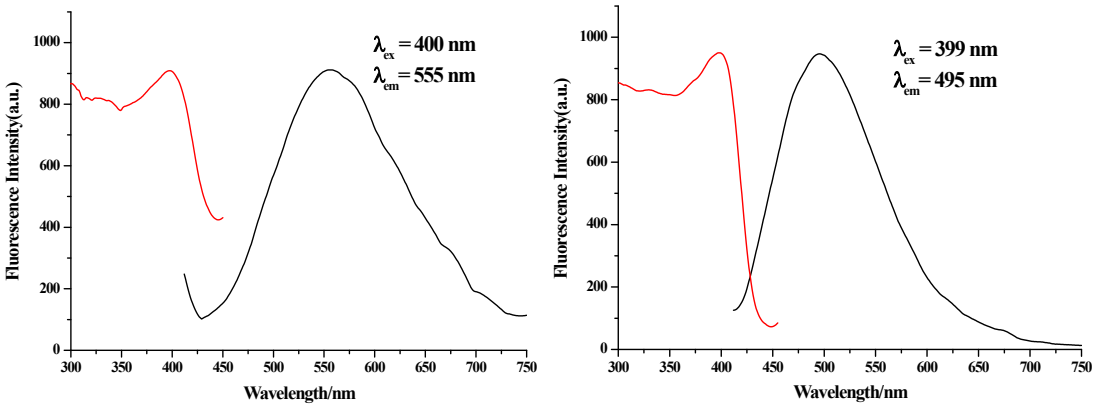
The powder of 3-amino-2-pyridinecarboxylic acid purchased (0.0276 g) and 6 mL absolute alcohol were mixed in a closed 25 mL Teflon-lined autoclave and heated at 80 °C for 12 h and this mixture was filtered before it was completely cooled down. Then pale yellow crystals suitable for X-ray crystallography were recrystallized from the filtrate at room temperature in a yield (0.0089g, 32.2%). Anal. Calcd for $C_6H_{5.5}K_{0.5}N_2O_2$: C, 45.85; H, 3.53; N, 17.82. Found: C, 45.83; H, 4.01; N, 17.85. IR (KBr pellet, cm^{-1}): 3414s, 3269m, 2851m, 1676sm 1572m, 1530vs, 1366w, 1329m, 1209m, 1194m, 1007m, 800s, 789s.

4. Preparation of the Zn(II) complex crystal (2)

The Zn(II) complex was synthesized by mixing **1** (0.0314 g, 0.2 mmol) and $Zn(Ac)_2{\cdot}2H_2O$ (0.0219 g, 0.1 mmol) and 6 mL HAc-NaAc buffer solution (0.1 M, pH 5.7) in a closed 25 mL Teflon-lined autoclave and heated at 100 °C for 72 h and cooling to room temperature naturally. Yellow crystals of suitable for X-ray crystallography were collected and washed with deionized water, and air-dried in a yield (0.0214 g, 40.1 %). Anal. Calcd for $C_{12}H_{12}N_4O_5Zn$: C, 40.30; N, 15.67; H; 3.38. Found: C, 40.42; N, 15.72; H, 3.28. IR (KBr pellet, cm-1): 3449s, 3335s, 1611vs, 1551vs, 1458m, 1395s, 1275m, 1261s, 1150w, 897w, 700w.

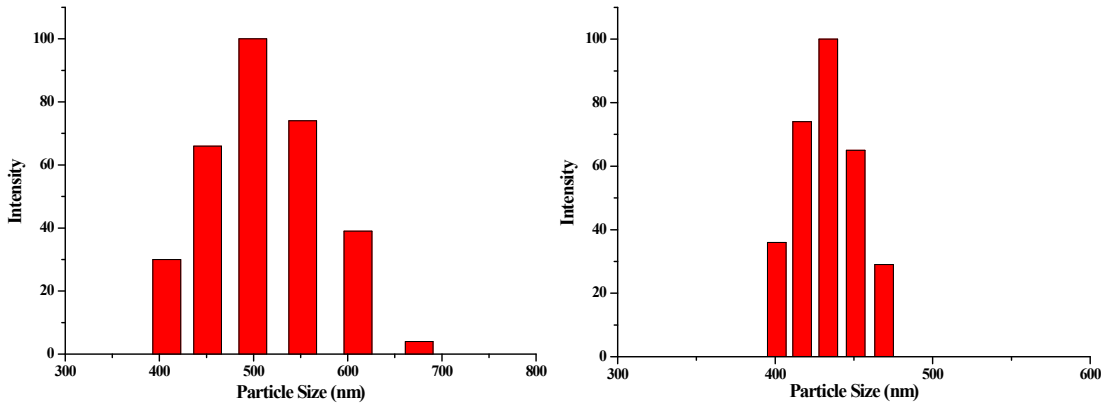
5. Preparation of the Zn(II) complex powder (2')

The aqueous solution of **1** (0.0942 g, 0.6 mmol) and the aqueous solution of $Zn(Ac)_2{\cdot}2H_2O$ (0.0657 g, 0.3 mmol) were mixed and stirred at room temperature for 2 h. Then yellow powder was obtained in a yield (0.0562 g, 37.8%). Anal. Calcd for $C_{12}H_{12}N_4O_5Zn$: C, 40.30; N, 15.67; H; 3.38. Found: C, 40.50; N, 15.83; H, 3.68. IR (KBr pellet, cm-1): 3449s, 3333s, 1616vs, 1551vs, 1456m, 1395s, 1275m, 1261s, 1150w, 895w, 700w. Elemental analysis, IR and PXRD (Fig. S1) confirmed that the powder product is the same as **2**.



(a) (b)

Fig. **S**1 Fluorescence spectra of **1** (a) and **2** (b) for their solids.



(a) (b)

Fig. **S**2 (a) Particle size distribution of **1** in DMF/H_2O (8:2, v/v); (b) Particle size distribution of **2** in DMF/H_2O (3:7, v/v).

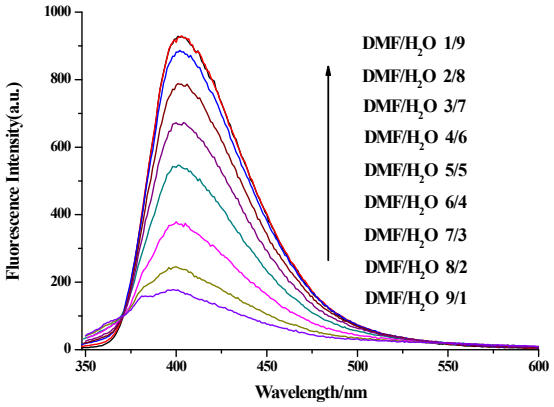


Fig. **S**3 Fluorescence spectra of **1** (50 μM) upon addition of 0.5 equiv. Zn^{2+} in DMF/H_2O mixtures with different water fractions, λ_{ex}=334 nm.

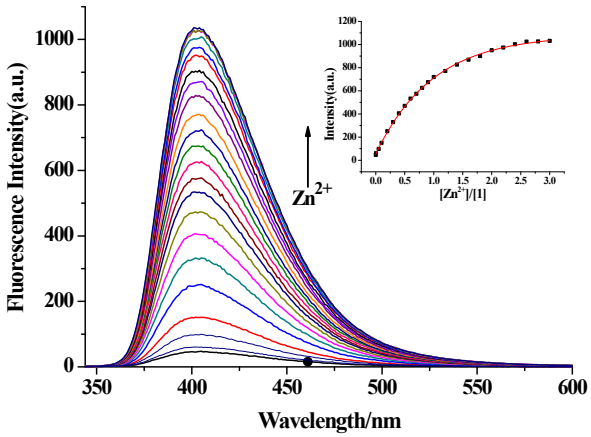


Fig. **S**4 Changes of fluorescence spectra of 40 μM **1** upon addition of 0, 0.005, 0.05, 0.10, 0.20 , 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, and 3.0 equiv. Zn^{2+} in DMF/H_2O (1:9, v/v). Inset: Fluorescence intensity at 403 nm as a function of [Zn^{2+}]/[**1**].

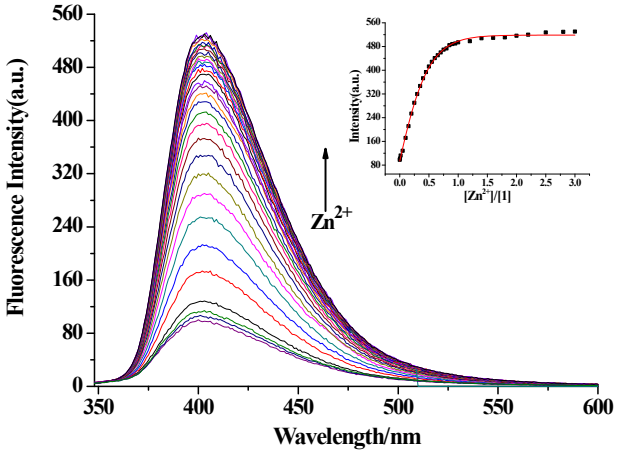


Fig. **S**5 Changes of fluorescence spectra of 40 μM **1** upon addition of 0, 0.005, 0.015, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.8, and 3.0 equiv. Zn^{2+} in DMF/H_2O (3:7, v/v). Inset: Fluorescence intensity at 403 nm as a function of [Zn^{2+}]/[**1**].

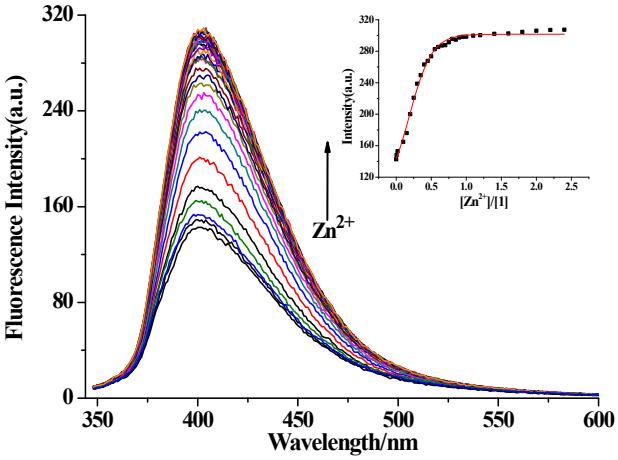


Fig. **S**6 Changes of fluorescence spectra of 40 μM **1** upon addition of 0, 0.005, 0.02, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, and 2.4 equiv. Zn^{2+} in DMF/H_2O (5:5, v/v). Inset: Fluorescence intensity at 403 nm as a function of [Zn^{2+}]/[**1**].

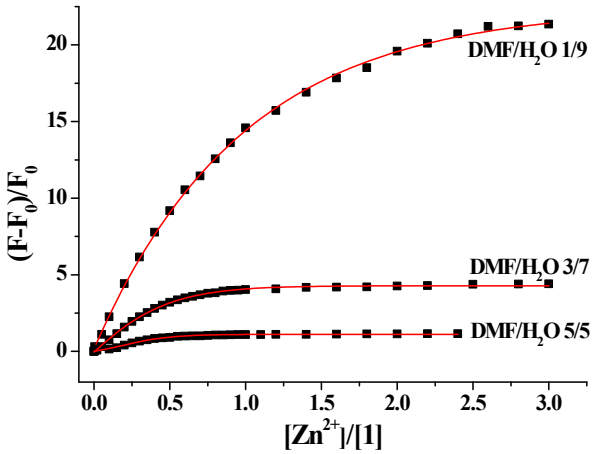


Fig. **S**7 Relative fluorescence intensity curves for **1** upon addition of Zn^{2+} in DMF/H_2O (1:9, v/v), DMF/H_2O (3:7, v/v) and DMF/H_2O (5:5, v/v).

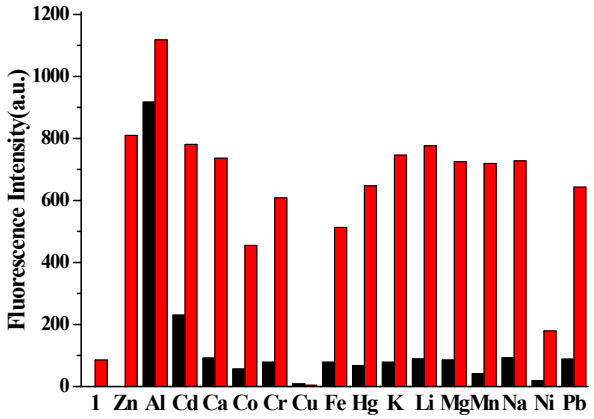


Fig. **S**8 Fluorescence emission intensity of complexes of **1** and Zn^{2+} in the presence of various metal ions at 403 nm. Black bars: **1** (20 μM) with 1.0 equiv. of the metal ions stated. Red bars: **1** (20 μM) with 1.0 equiv. of Zn^{2+} and 1.0 equiv. of the other metal ions stated.

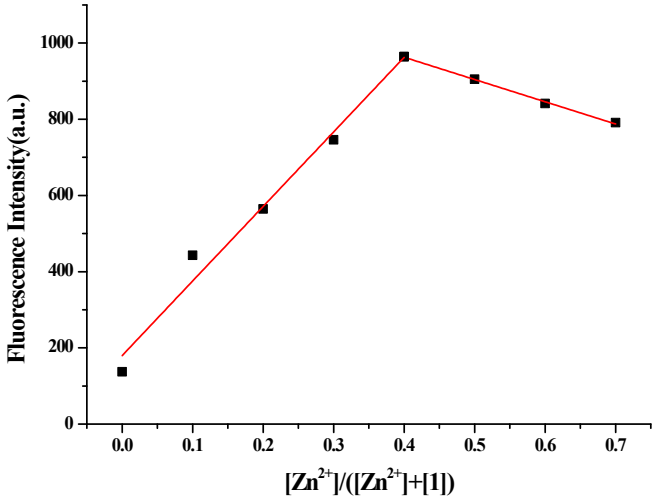
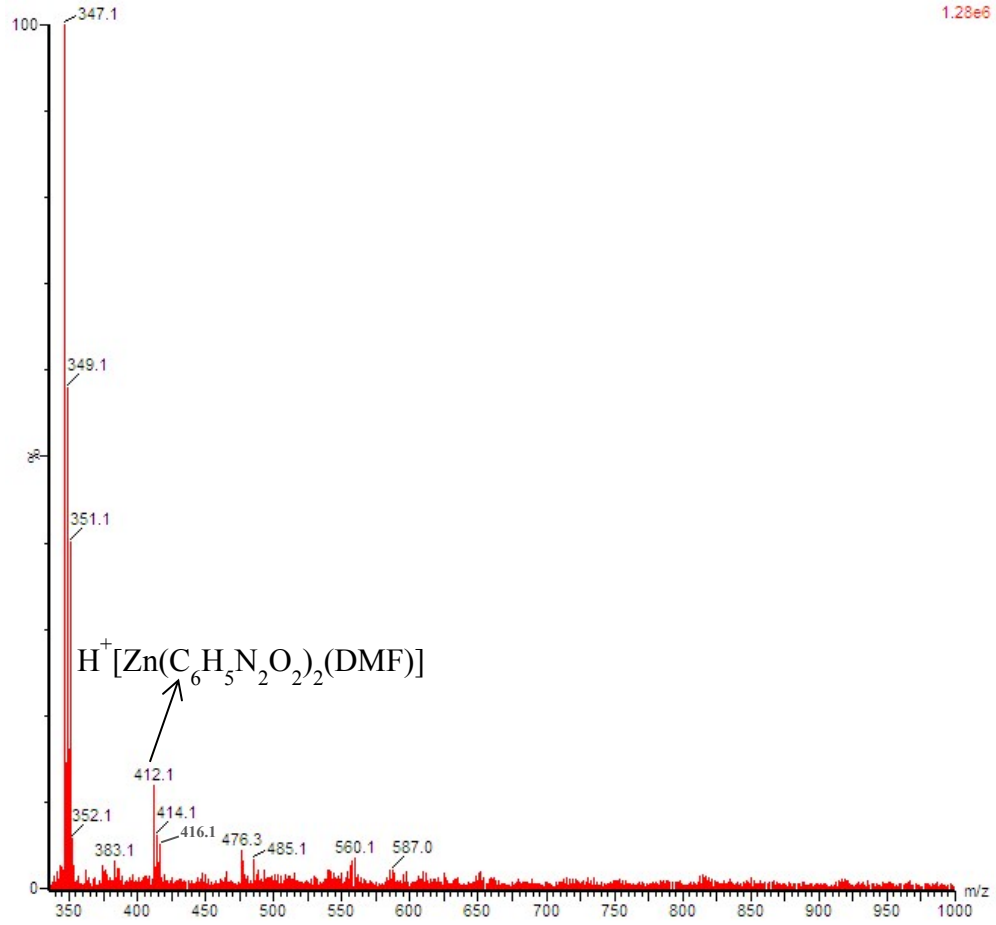
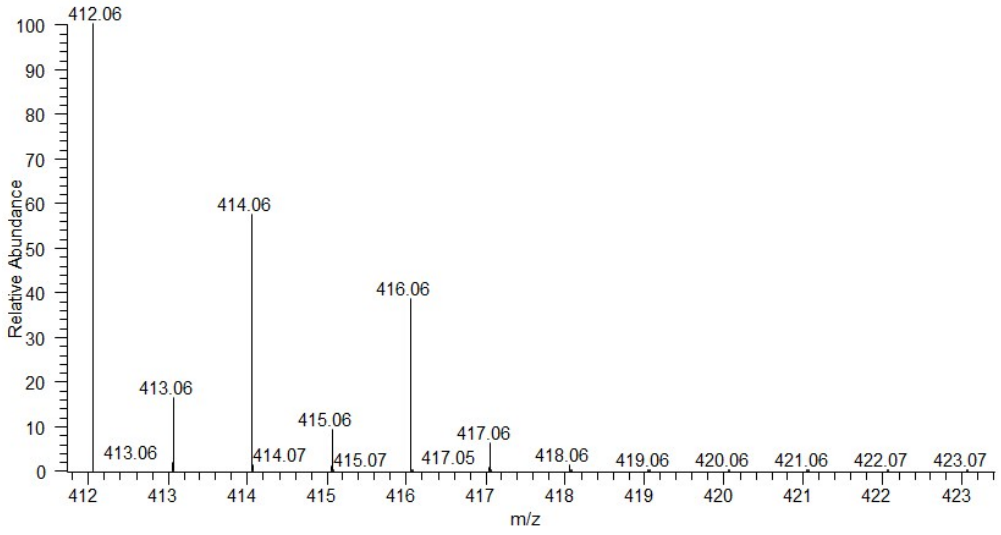


Fig. **S**9 Job plot for the determination of the stoichiometry of **1** and Zn^{2+} in the complex.



(a)



(b)

Fig. **S**10 (a) ESI-MS spectrum of probe **1** (10 μM) after treatment with 0.5 equiv. Zn^{2+}; (b) The simulation pattern of $H^+[Zn(C_6H_5N_2O_2)_2(DMF)]$.

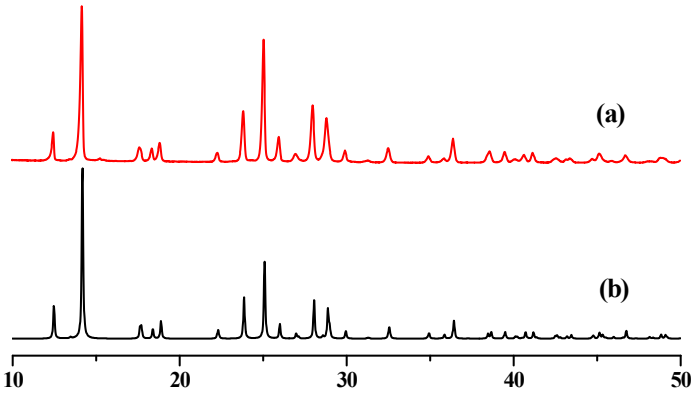


Fig. **S**11 PXRD patterns of (a) **2'**; (b) **2** simulated from the single-crystal X-ray diffraction data.

Table S1 DLS results of the compounds **1** and **2** in DMF/H_2O mixture.

	Effective Diameter (nm)	Polydispersity
1 in H_2O	0.0	0.000
1 in DMF/H_2O (8:2, v/v)	460.2	0.263
2 in DMF	0.0	0.000
2 in DMF/H_2O (3:7, v/v)	272.3	0.140

Table S2 Crystal data and structure refinement parameters of the compounds **1** and **2**.

Compound	**1**	**2**
Formula	$C_6H_{5.5}K_{0.5}N_2O_2$	$C_{12}H_{11}N_4O_5Zn$
Fw	157.17	356.62
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)/c*	*C2/c*
a (Å)	8.135(8)	10.017(3)
b (Å)	11.441(12)	10.064(3)
c (Å)	14.604(15)	13.150(4)
α (°)	90	90
β (°)	98.293(17)	89.992(5)
γ (°)	90	90
V (Å^3)	1345(2)	1325.6(6)
Z	8	4
calculated density (g/cm^3)	1.552	1.787
F (000)	648	724
Reflections collected/unique	8717 / 3098 [R(int) = 0.0414]	4212 / 1523 [R(int) = 0.0222]
Goodness-of-fit on F^2	1.060	1.150
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0630, wR_2 = 0.1997	R_1 = 0.0269, wR_2 = 0.0816
R indices (all data)	R_1 = 0.0735, wR_2 = 0.2112	R_1 = 0.0296, wR_2 = 0.0835
CCDC no.	1448462	1448463

$R_1 = \Sigma(|F_o| - |F_c|)/|F_o|$; $wR_2 = \{\Sigma[(w|F^2_o| - |F^2_c|)^2/\Sigma w(F^2_o)^2]\}^{1/2}$.

Table S3 Selected bond distances (Å) and angles (deg) for the compounds **1** and **2**.

1			
C(5)-N(2)	1.326(4)	C(11)-O(1)	1.222(4)
C(5)-C(18)	1.390(4)	C(11)-O(2)	1.269(4)
C(7)-N(1)	1.355(3)	C(13)-N(1A)	1.354(4)
C(7)-C(15)	1.410(4)	C(13)-C(2A)	1.412(4)
C(7)-C(9)	1.482(4)	C(15)-N(4)	1.342(4)
C(8)-N(2)	1.356(3)	C(15)-C(20)	1.411(4)
C(8)-C(13)	1.400(4)	C(17)-C(20)	1.357(4)
C(8)-C(11)	1.497(4)	C(17)-C(19)	1.379(4)
C(9)-O(4)	1.224(4)	C(18)-C(2A)	1.361(4)
C(9)-O(3)	1.292(4)	C(19)-N(1)	1.332(4)
N(2)-C(5)-C(18)	118.8(3)	N(1A)-C(13)-C(8)	122.7(2)
N(1)-C(7)-C(15)	118.8(2)	N(1A)-C(13)-C(2A)	120.0(2)
N(1)-C(7)-C(9)	116.4(2)	C(8)-C(13)-C(2A)	117.3(2)
C(15)-C(7)-C(9)	124.8(2)	N(4)-C(15)-C(7)	122.9(3)
N(2)-C(8)-C(13)	118.6(2)	N(4)-C(15)-C(20)	120.1(3)
N(2)-C(8)-C(11)	115.7(2)	C(7)-C(15)-C(20)	117.0(2)
C(13)-C(8)-C(11)	125.6(2)	C(20)-C(17)-C(19)	120.0(3)
O(4)-C(9)-O(3)	126.8(3)	C(2A)-C(18)-C(5)	119.5(3)
O(4)-C(9)-C(7)	119.9(3)	N(1)-C(19)-C(17)	119.0(3)
O(3)-C(9)-C(7)	113.2(2)	C(17)-C(20)-C(15)	121.3(3)
O(1)-C(11)-O(2)	127.0(3)	C(18)-C(2A)-C(13)	121.4(3)
O(1)-C(11)-C(8)	120.0(2)	C(19)-N(1)-C(7)	123.9(2)
O(2)-C(11)-C(8)	113.0(2)	C(5)-N(2)-C(8)	124.4(2)
2			
N(2)-Zn(1)	2.0937(19)	Zn(1)-O(1)#1	2.0397(16)
O(1)-Zn(1)	2.0397(16)	Zn(1)-N(2)#1	2.0937(18)
O(2)-Zn(1)	1.998(2)		
C(5)-N(2)-Zn(1)	126.83(15)	O(2)-Zn(1)-N(2)#1	96.31(5)
C(7)-N(2)-Zn(1)	112.71(13)	O(1)#1-Zn(1)-N(2)#1	79.57(6)
C(8)-O(1)-Zn(1)	115.72(13)	O(1)-Zn(1)-N(2)#1	94.58(6)
Zn(1)-O(2)-H(2)	109.5	O(2)-Zn(1)-N(2)	96.31(5)
O(2)-Zn(1)-O(1)#1	117.42(5)	O(1)#1-Zn(1)-N(2)	94.58(6)
O(2)-Zn(1)-O(1)	117.42(5)	O(1)-Zn(1)-N(2)	79.57(6)
O(1)#1-Zn(1)-O(1)	125.15(11)	N(2)#1-Zn(1)-N(2)	167.38(9)

[1] G. M. Sheldrick, in SHELXS-97, Program for solution of crystal structures, University of Göttingen, Germany, (1997).