Electronic supplementary information (ESI)

Template synthesis and photochromism of a layered zinc diphosphonate

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Experimental Section

Materials and methods.

All chemicals were reagent grade and used as purchased without further purification.

Elemental analyses (C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra were performed on a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. Electron paramagnetic resonance (EPR) spectroscopy was obtained using a JEOL JES-FA200 EPR spectrometer. Simulation of the PXRD curve was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org.

Synthesis of 2,4,6-tri(4-pyridyl)-1,3,5-triazine (TPT)

TPT was prepared according to literature procedure.[1]

Synthesis of 1

A mixture of ZnO (0.08 g, 0.1 mmol), TPT (0.05 g, 0.15 mmol), HEDP (0.15 mL, 0.62 mmol) and H_2O (5 mL) was sealed in a Teflon-lined autoclave (20 mL) and heated to 160 °C for 7 days then slowly cooled to 30 °C in 12 h. Yield: ca. 60% based on TPT. Elemental analysis (%): calcd for $C_{22}H_{26}N_6O_{16}P_4Zn_3$ (950.48): C, 27.80; H, 2.76; N, 8.84. Found: C, 27.56; H, 3.12; N, 8.56. IR (KBr pellets, cm^{-1}): 3467(s), 2966(s), 2923(s), 2854(w), 2640(w), 2144(s), 1639(s), 1575(s), 1515(s), 1448(s), 1375(s), 1313(m), 1247(m), 1155(s), 1065(s), 968(s), 937(s), 794(s), 648(s), 575(s).

X-ray Crystallography.

The crystallographic data of **1** was collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å). The program *CrystalClear* was used for the integration of the diffraction profiles.[2] The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semiempirical absorption corrections were applied by using the SADABS program).[3,4] Zn atoms were located from the *E*-maps, and other nonhydrogen atoms were subsequently located in successive difference Fourier

synthesis and refined anisotropically. Detailed crystallographic data for **1** is summarized in Table S1 and the selected bond lengths and angles are given in Table S2. Full crystallographic data for **1** has been deposited with the CCDC (1509226), which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

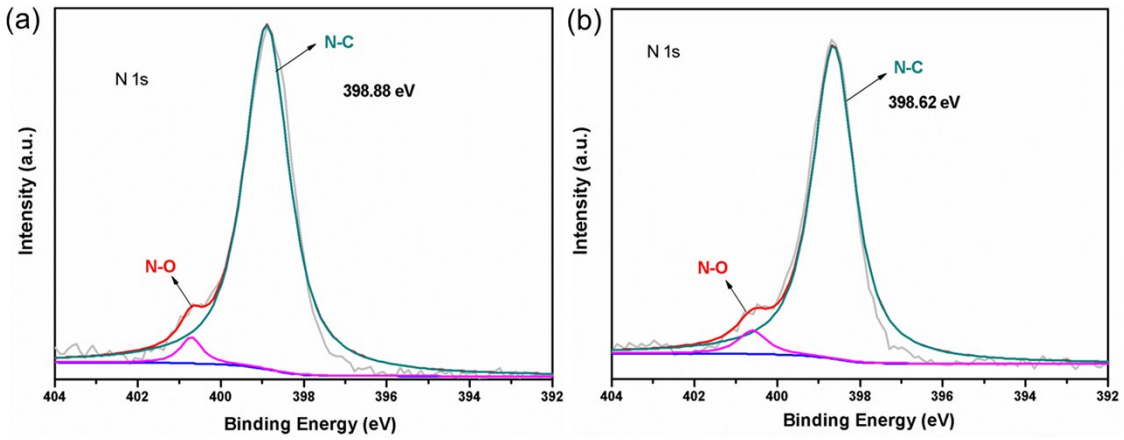

Fig. S1. The XPS spectra of N1s for **1**: before light irradiation (a), and after light irradiation (b).

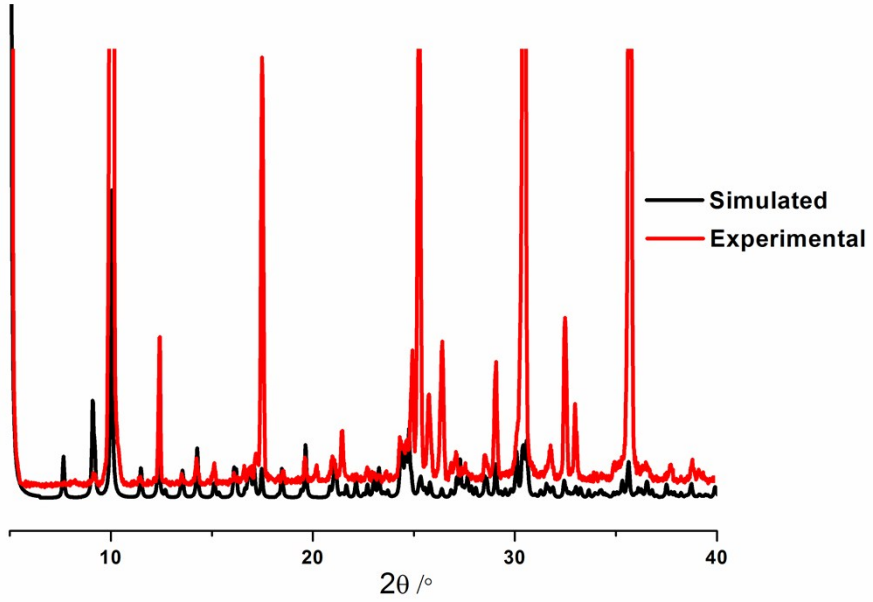

Fig. S2 PXRD pattern of **1** after light irradiation.

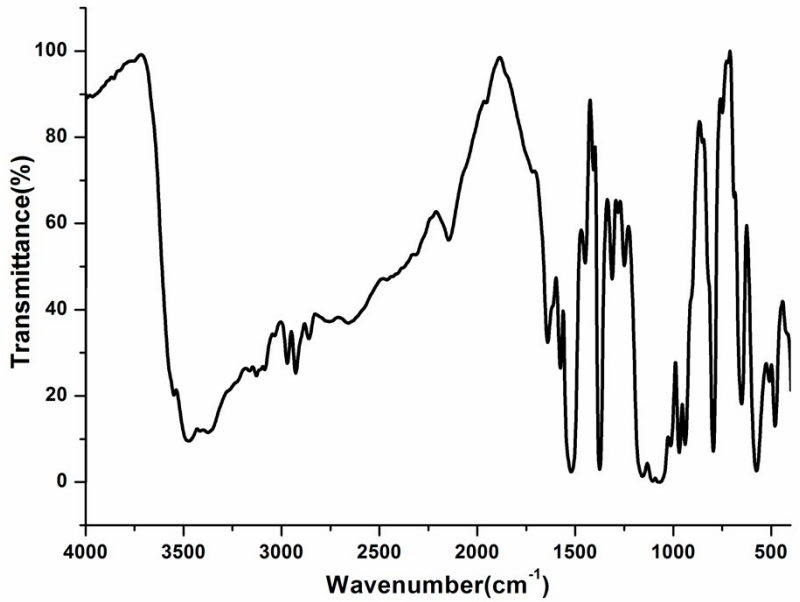

Fig. S3 IR pattern of **1**.

Table S1. Crystal data and structure refinement parameters for **1**

	1	
Formula	$C_{22}H_{26}N_6O_{16}P_4Zn_3$	
*M*r (g mol^{-1})	950.48	
Space group	*P*-1	
Crystal system	Triclinic	
a (Å)	8.0895(16)	
b (Å)	11.829(2)	
c (Å)	18.063(4)	
α (°)	86.63(3)	
β (°)	77.32(3)	
γ (°)	77.33(3)	
V (Å^3)	1645.2(6)	
Z	2	
F(000)	956	
Dc (gcm^{-3})	1.919	
μ (mm^{-1})	2.447	
R_{int}	0.0338	
limiting indices	-10≤ h ≤10 -15≤ k ≤15 -23≤ l ≤23	
Collected reflections	17583	
Unique reflections	7547	
GOF on F^2	1.056	
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0389	0.0742
R_1, wR_2 [all data]	0.0560	0.0794

a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. b $wR_2 = \{\sum[w(F_o^2 - F_c^2)2] / \sum w(F_o^2)2\}1/2$

Table S2. Selected bond lengths (Å) and angles (°) for **1**

O(2)-Zn(1)#2	1.952(2)	O(4)-Zn(2)	1.957(2)
O(5)-Zn(1)	1.961(2)	O(11)-Zn(2)	1.936(2)
O(8)-Zn(1)#3	1.936(2)	O(6)-Zn(2)#1	1.958(2)
O(9)-Zn(1)	1.940(2)	O(4)-Zn(3)	2.316(2)
Zn(1)-O(8)#3	1.936(2)	O(3)-Zn(3)	1.994(2)
Zn(1)-O(2)#4	1.952(2)	O(7)-Zn(3)	2.027(2)
Zn(2)-O(1)#1	1.935(2)	O(10)-Zn(3)	1.990(2)
Zn(2)-O(6)#1	1.958(2)	O(14)-Zn(3)	2.3992(19)
O(1)-Zn(2)#1	1.935(2)	O(15)-Zn(3)	2.1183(17)
O(8)#3-Zn(1)-O(9)	110.55(10)	O(3)-Zn(3)-O(7)	162.58(9)
O(8)#3-Zn(1)-O(2)#4	102.21(10)	O(10)-Zn(3)-O(15)	102.87(9)
O(9)-Zn(1)-O(2)#4	115.05(10)	O(3)-Zn(3)-O(15)	89.68(8)
O(8)#3-Zn(1)-O(5)	100.60(11)	O(7)-Zn(3)-O(15)	91.34(8)
O(9)-Zn(1)-O(5)	125.14(9)	O(10)-Zn(3)-O(4)	92.01(9)
O(2)#4-Zn(1)-O(5)	100.21(9)	O(3)-Zn(3)-O(4)	85.01(9)
O(1)#1-Zn(2)-O(11)	107.56(10)	O(7)-Zn(3)-O(4)	89.59(9)
O(1)#1-Zn(2)-O(4)	120.06(10)	O(15)-Zn(3)-O(4)	164.94(7)
O(11)-Zn(2)-O(4)	102.61(9)	O(10)-Zn(3)-O(14)	169.75(8)
O(1)#1-Zn(2)-O(6)#1	101.19(9)	O(3)-Zn(3)-O(14)	79.65(8)
O(11)-Zn(2)-O(6)#1	113.53(10)	O(7)-Zn(3)-O(14)	83.03(8)
O(4)-Zn(2)-O(6)#1	112.27(10)	O(15)-Zn(3)-O(14)	87.29(6)
O(10)-Zn(3)-O(3)	101.47(10)	O(4)-Zn(3)-O(14)	77.90(7)
O(10)-Zn(3)-O(7)	95.25(10)		

Symmetry codes: #1: -x, -y+2, -z+2; #2: x-1, y, z; #3: -x+1, -y+1, -z+2; #4: x+1, y, z.

References

1. D. Tian, Q. Chen, Y. Li, Y. H. Zhang, Z. Chang and X. H. Bu, *Angew. Chem., Int. Ed.*, 2014, **53**, 837.
2. Rigaku, *Process-Auto*, Rigaku Americas Corporation, The Woodlands, Texas, 1998.
3. G. M. Sheldrick, *SHELXS97 Program for Crystal Structure Solution*, University of Göttingen: Göttingen, Germany, **1997**.
4. G. M. Sheldrick, *SHELXL97 Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, **1997**.