

Electronic supplementary information (ESI)

An inorganic-organic hybrid framework from the assembly of electron-rich diphosphonate and electron-deficient tripyridyl moiety

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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. The luminescence data were recorded on an F-7000 FL spectrophotometer. Electron spin resonance (ESR) spectroscopy was recorded on a JEOL JES-FA200 EPR spectrometer. X-ray photoelectron spectroscopy (XPS) was measured on Thermo ESCALAB 250Xi. 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, 0.10 mmol), TPT (0.05 g, 0.15 mmol), LiF (0.10 g, 4 mmol), HEDP (0.55 mL, 2.30 mmol), and H₂O (5 mL) was sealed in a Teflon-lined autoclave (20 mL) and heated to 145 °C for 7 days then slowly cooled to 30 °C in 12 h. Yield: ca. 60% based on TPT. Elemental analysis (%): calcd for C₄₀H₃₈N₁₂O₁₆P₄Zn₃ (1262.92): C, 38.04; H, 3.03; N, 13.31. Found: C, 38.35; H, 3.26; N, 13.04. IR (KBr pellets, cm⁻¹): 3420(s), 2970(w), 2924(w), 2368(w), 1624(m), 1580(w), 1521(s), 1372(s), 1320(w), 1139(s), 1062(s), 994(w), 944(m), 802(s), 648(s), 582(w), 539(m).

X-ray Crystallography.

The single-crystal X-ray diffraction data of **1** and **2** (the photo-activated one) were collected on an XtaLAB-mini diffractometer at 293(2) K with Mo-K α radiation (λ = 0.71073 Å) and ω scan

mode. SHELX-2016 software was used to solve the structure.² Detailed crystallographic data for **1** and **2** are summarized in Table S1 and the selected bond lengths and angles are given in Table S2. The hydrogen bonds are given in Table S3. Full crystallographic data have been deposited with the CCDC 1841357 for **1** and CCDC 1857523 for **2**.

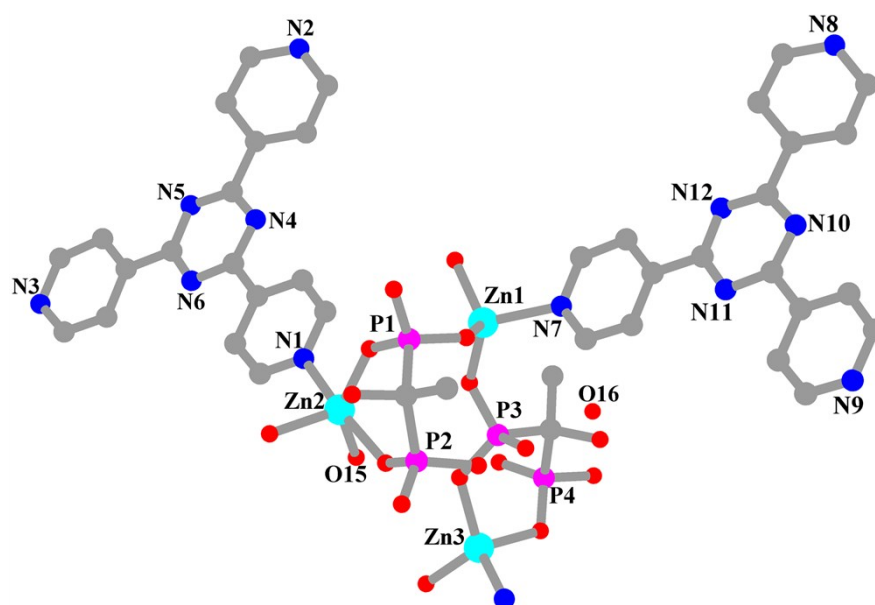


Fig. S1 The asymmetric unit of **1** (H atoms are omitted for clarity).

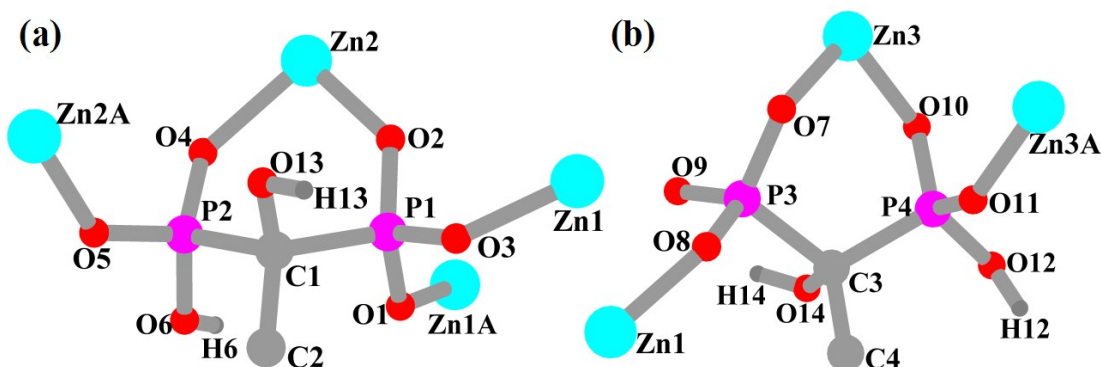


Fig. S2 The coordination mode of diphosphonate ligand in **1** (H atoms for CH₃ group are omitted for clarity).

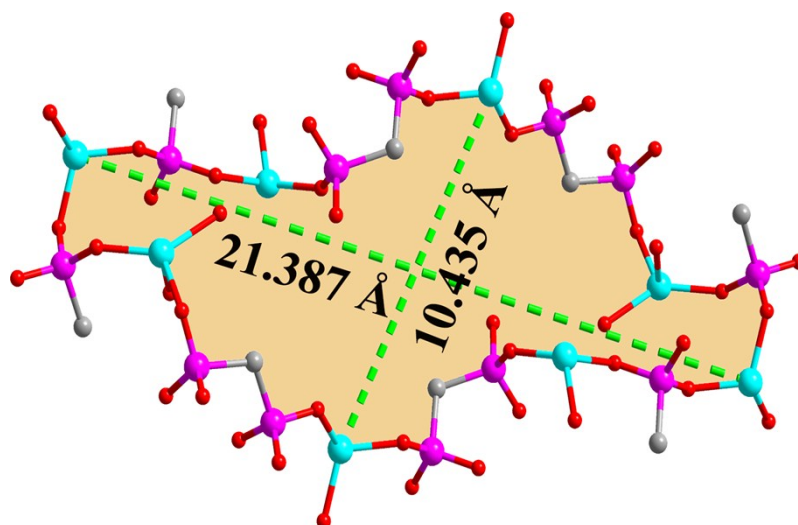


Fig. S3 The ball and stick view of the 20-MR building units.

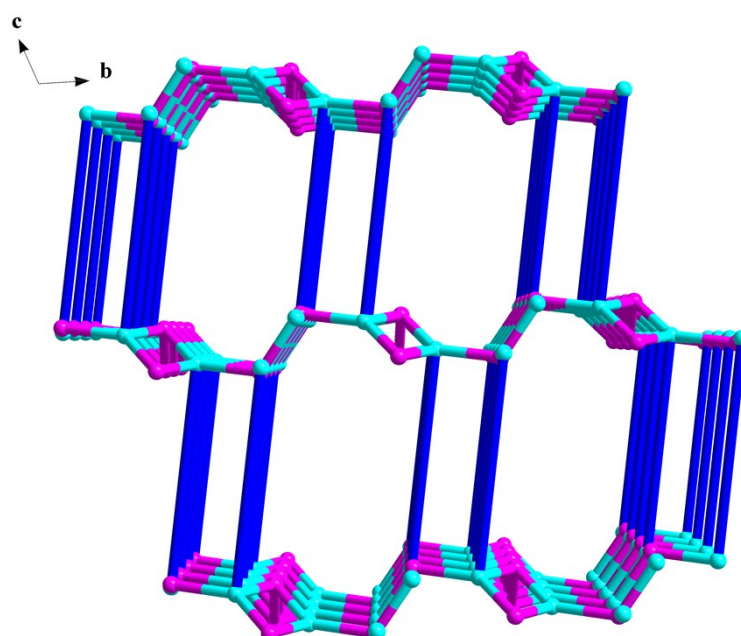


Fig. S4 The topological network of **1**.

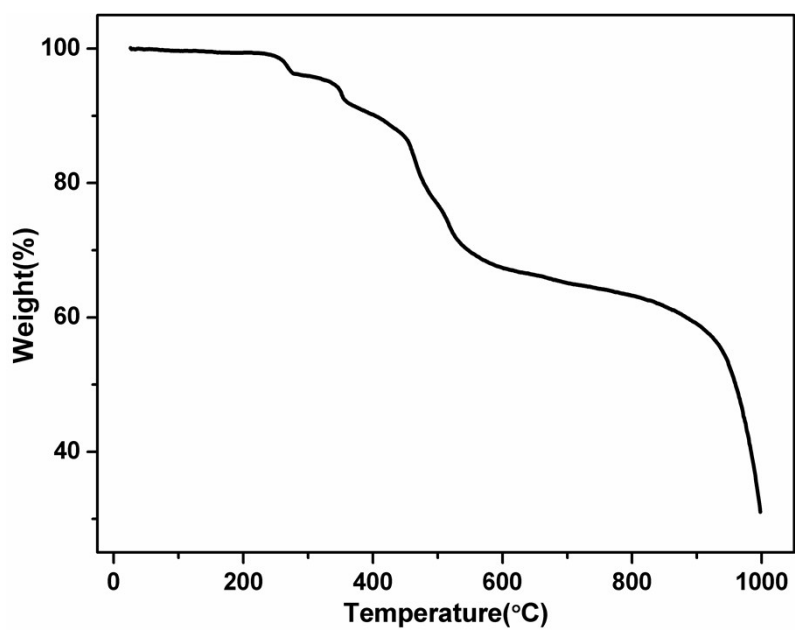


Fig. S5 The TG plot of **1**.

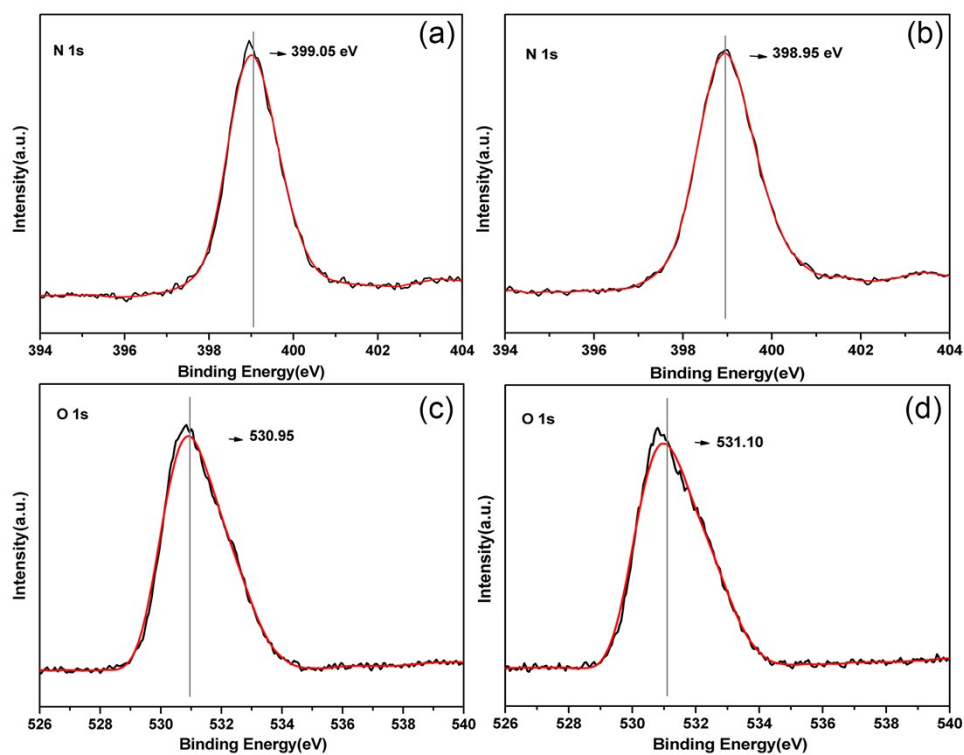


Fig. S6 The XPS spectra for **1**: (a) Before light irradiation of N1s; (b) After light irradiation of N1s; (c) Before light irradiation of O1s; (d) After light irradiation of O1s.

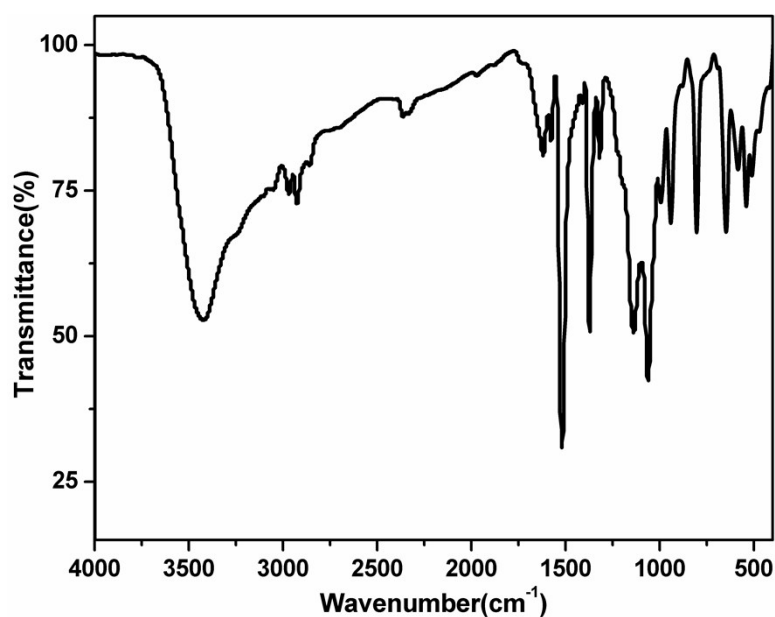


Fig. S7 IR plot of **1**.

Table S1. Crystallographic data for **1** and **2** (the photo-activated one).

	1	2
Formula	C ₄₀ H ₃₈ N ₁₂ O ₁₆ P ₄ Zn ₃	C ₄₀ H ₃₈ N ₁₂ O ₁₆ P ₄ Zn ₃
Mr (g mol ⁻¹)	1262.92	1262.92
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Crystal system	Triclinic	Triclinic
<i>a</i> (Å)	10.9781(10)	10.9701(7)
<i>b</i> (Å)	14.0982(11)	14.1004(6)
<i>c</i> (Å)	16.9572(13)	16.9569(8)
α (°)	105.647(7)	105.651(4)
β (°)	108.800(8)	108.779(5)
γ (°)	100.832(7)	100.702(4)
<i>V</i> (Å ³)	2281.1(4)	2281.9(2)
<i>Z</i>	2	2
<i>F</i> (000)	1276	1276
<i>D</i> _c (gcm ⁻³)	1.836	1.835
μ (mm ⁻¹)	1.794	1.793
<i>R</i> _{int}	0.0436	0.0325
limiting indices	-13 ≤ <i>h</i> ≤ 12 -16 ≤ <i>k</i> ≤ 16 -20 ≤ <i>l</i> ≤ 18	-12 ≤ <i>h</i> ≤ 13 -16 ≤ <i>k</i> ≤ 16 -20 ≤ <i>l</i> ≤ 17
Collected reflections	12010	13191
Unique reflections	8037	8039
GOF on <i>F</i> ²	1.002	1.028
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0523 0.1108	0.0411 0.1003
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0874 0.1261	0.0655 0.1092

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

Zn(1)-N(7)	2.066(4)	Zn(2)#3-O(5)	1.977(3)
Zn(1)-O(1)	1.937(4)	Zn(2)-O(15)	2.068(4)
Zn(1)#2-O(3)	1.935(3)	Zn(3)-O(7)	1.931(3)
Zn(1)-O(8)	1.903(4)	Zn(3)-O(10)	1.956(4)
Zn(2)-N(1)	2.122(5)	Zn(3)#4-O(11)	1.890(4)
Zn(2)-O(2)	1.941(3)	Zn(3)#1-N(9)	2.027(5)
Zn(2)-O(4)	2.084(3)		
O(8)-Zn(1)-O(3)#2	111.04(16)	O(15)-Zn(2)-O(4)	85.16(15)
O(8)-Zn(1)-O(1)	109.86(16)	O(2)-Zn(2)-N(1)	89.40(16)
O(3)#2-Zn(1)-O(1)	118.67(15)	O(5)#3-Zn(2)-N(1)	91.29(15)
O(8)-Zn(1)-N(7)	117.56(16)	O(15)-Zn(2)-N(1)	86.73(17)
O(3)#2-Zn(1)-N(7)	106.49(16)	O(4)-Zn(2)-N(1)	169.52(16)
O(1)-Zn(1)-N(7)	92.37(17)	O(11)#4-Zn(3)-O(7)	113.45(16)
O(2)-Zn(2)-O(5)#3	115.47(16)	O(11)#4-Zn(3)-O(10)	116.66(18)
O(2)-Zn(2)-O(15)	139.36(16)	O(7)-Zn(3)-O(10)	97.73(14)
O(5)#3-Zn(2)-O(15)	105.05(15)	O(11)#4-Zn(3)-N(9)#1	104.20(18)
O(2)-Zn(2)-O(4)	92.43(14)	O(7)-Zn(3)-N(9)#1	120.34(18)
O(5)#3-Zn(2)-O(4)	97.21(14)	O(10)-Zn(3)-N(9)#1	104.73(17)

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

Table S3 Details of Hydrogen Bond Interactions in **1**

D-H...A	<i>d</i> (D-H) (Å)	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	∠(DHA) (deg)
O6-H6A...O9	0.903	1.714	2.609	170.51
O12-H12A... O16	0.909	1.658	2.561	172.37
O13-H13A... O16	0.820	2.225	3.036	170.46
O14-H14A... O9	0.820	2.109	2.714	130.43
O16-H16A... O3	0.917	1.971	2.885	173.92
O16-H18A... N3	0.902	1.951	2.844	170.31

References

1. D. Tian, Q. Chen, Y. Li, Y. H. Zhang, Z. Chang and X. H. Bu, *Angew. Chem., Int. Ed.*, 2014, **53**, 837-841.
2. G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.