

Supplementary information

New zinc diphosphonates with bright tunable luminescence and 12-member ring channels

Ruibiao Fu*, Shengmin Hu, Xintao Wu*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian, 350002 China

* Corresponding author. E-mail: wxt@fjirsm.ac.cn

Materials and instrumentation

All chemicals were obtained from commercial sources without further purification. Elemental analyses were carried out with a Vario EL III element analyzer. Infrared spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer. Photoluminescence properties were investigated in solid state at room temperature with F-7000 FL, FLS920 and LifeSpec-ps spectrophotometers. Thermogravimetric analysis (TGA) was performed on a Netzsch STA449C at a heating rate of 10 °C · min⁻¹ from room temperature to 1000 °C under an air gas flow. Powder XRD patterns were acquired on a DMAX-2500 diffractometer using CuK α radiation at ambient environment.

Synthesis of (C₆H₁₀N₂)_{0.5}[Zn₃(L)(HL)]·3H₂O (1). A mixture of H₄L·H₂O (0.0610 g, 0.202 mmol), Zn(CH₃COO)₂·2H₂O (0.0405 g, 0.185 mmol), and 4-picolylamine (0.8 mL, 7.9 mmol) in 6.0 mL distilled water with the pH value adjusted to 3.74, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at 160 °C for 120 h. After slow cooling to room temperature, colorless crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0425 g (80 %). Anal. Calc. for C₁₇H₂₆N₃O₁₇P₄Zn₃: C 23.19, H 2.98, N 4.77 %. Found: C 22.88, H 2.96, N 4.85 %. IR (KBr pellet, cm⁻¹): 3434m(ν_{O-H}), 3190m(ν_{O-H}), 3105w, 2955w(ν_{C-H}), 2929w, 2857w, 1614m, 1592w, 1490w, 1442m, 1384w, 1356w, 1317w, 1134s($\nu_{P=O}$), 1117s(ν_{P-O}), 1082s(ν_{P-O}), 1057s(ν_{P-O}), 1033s(ν_{P-O}), 1005m(ν_{P-O}), 986m(ν_{P-O}), 864w, 814m, 704m, 677w, 660m, 626m, 610w, 567m, 529w.

Synthesis of (H₂G)_{0.5}[Zn₃(L)(HL)]·3H₂O (G = 3-picolylamine (2), piperazine (3), 2-methylpiperazine (4), 1,2-ethanediamine (5), 1,3-propanediamine (6), 1,4-butane diamine (7), 1,2-propanediamine (8), 3-aminopropylmethylamine (9)) and (H₄G)_{0.25}[Zn₃(L)(HL)]·3H₂O (G = tri(2-aminoethyl)amine (10)). Compounds 2-10 were synthesized by the similar procedure as 1 except for replacement of 4-picolylamine with 3-picolylamine, piperazine, 2-methylpiperazine, 1,2-ethanediamine, 1,3-propanediamine, 1,4-butanediamine, 1,2-propanediamine,

3-aminopropylmethylamine and tri(2-aminoethyl)amine, respectively. These patterns of powder XRD were in accord with that simulated from single-crystal X-ray data of **1**, which indicated homogeneous phase of respective product. Anal. Calc. for $C_{16}H_{27}N_3O_{17}P_4Zn_3$ (**2**): C 23.19, H 2.98, N 4.77 %; Found: C 23.16, H 3.03, N 4.82 %. For $C_{17}H_{26}N_3O_{17}P_4Zn_3$ (**3**): C 22.52, H 3.19, N 4.92 %; Found: C 22.12, H 3.06, N 4.92 %. For $C_{16.5}H_{27}N_3O_{17}P_4Zn_3$ (**4**): C 23.06, H 3.17, N 4.89 %; Found: C 22.72, H 3.22, N 4.77 %. For $C_{15}H_{26}N_3O_{17}P_4Zn_3$ (**5**): C 21.44, H 3.12, N 5.00 %; Found: C 20.85, H 3.01, N 4.69 %. For $C_{15.5}H_{27}N_3O_{17}P_4Zn_3$ (**6**): C 21.97, H 3.21, N 4.96 %; Found: C 21.64, H 3.07, N 4.75 %. For $C_{16}H_{28}N_3O_{17}P_4Zn_3$ (**7**): C 22.49, H 3.30, N 4.92 %; Found: C 22.56, H 3.21, N 5.02 %. For $C_{15.5}H_{27}N_3O_{17}P_4Zn_3$ (**8**): C 21.97, H 3.21, N 4.96 %; Found: C 21.25, H 2.86, N 4.55 %. For $C_{16}H_{28}N_3O_{17}P_4Zn_3$ (**9**): C 22.49, H 3.30, N 4.92 %; Found: C 22.12, H 3.13, N 4.63 %. For $C_{15.5}H_{26.5}N_3O_{17}P_4Zn_3$ (**10**): C 21.98, H 3.15, N 4.96 %; Found: C 22.03, H 3.12, N 5.19 %.

X-Ray crystallography

X-ray data for **1** were collected at 293(2) K on a Rigaku Mercury CCD/AFC diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda(\text{Mo-}K\alpha) = 0.71073 \text{ \AA}$). Data of **1** were reduced with CrystalClear v1.3. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL-97.¹ All non-hydrogen atoms were treated anisotropically. The protonated 4-picolylamine lies disordered about inversion centres. Hydrogen atoms of 1-hydroxyl-2-(3-pyridyl)ethylidene-1,1-diphosphonate group were generated geometrically. While no attempts were performed to locate other hydrogen atoms. Crystallographic data for **1** are summarized in Table S1. Selected bond lengths for **1** are listed in Table S2. CCDC-817237 (**1**) and 838869 (**4**).

Table S1. Crystallographic data for **1**

Compound	1
Formula	C ₁₇ H ₂₆ N ₃ O ₁₇ P ₄ Zn ₃
FW	864.40
Space group	P2(1)/c
a (Å)	9.655(3)
b (Å)	9.344(3)
c (Å)	30.965(9)
α (deg)	90
β (deg)	93.859(5)
γ (deg)	90
V (Å ³)	2787.4(13)
Z	4
T(K)	293(2)
Measured/unique/ observed reflections	21087 / 6381 / 5711
D _{calcd} (g cm ³)	2.060
μ (mm ⁻¹)	2.876
GOF on F ²	1.089
R _{int}	0.0383
R1 ^a [I>2σ(I)]	0.0545
wR2 ^b [all data]	0.1427
^a R1 = $\sum(F_o - F_c) / \sum F_o $. ^b wR2 = $\{\sum w [(F_o^2 - F_c^2)] / \sum w [(F_o^2)^2]\}^{0.5}$.	

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

Zn(1)-O(1)	1.944(4)	Zn(2)-O(10) ^a	1.929(3)
Zn(1)-O(4)	1.926(4)	Zn(2)-O(13)	1.949(4)
Zn(1)-O(8)	1.978(3)	Zn(3)-O(2)	1.935(3)
Zn(1)-O(12)	1.937 (4)	Zn(3)-O(3) ^c	2.000(3)
Zn(2)-N(2) ^b	2.017 (4)	Zn(3)-O(5) ^c	1.923(3)
Zn(2)-O(9)	1.995(3)	Zn(3)-O(11) ^d	1.950(3)
O(1)-Zn(1)-O(4)	103.19(15)	O(9)-Zn(2)-O(10) ^a	109.52(14)
O(1)-Zn(1)-O(8)	101.96(15)	O(9)-Zn(2)-O(13)	99.40(14)
O(1)-Zn(1)-O(12)	118.53(16)	O(10) ^a -Zn(2)-O(13)	109.09(16)
O(4)-Zn(1)-O(8)	108.71(15)	O(2)-Zn(3)-O(3) ^c	110.54(14)
O(4)-Zn(1)-O(12)	121.40(17)	O(2)-Zn(3)-O(5) ^c	109.00(15)
O(8)-Zn(1)-O(12)	101.11(14)	O(2)-Zn(3)-O(11) ^d	114.12(15)
N(2) ^b -Zn(2)-O(9)	106.69(16)	O(3) ^c -Zn(3)-O(5) ^c	105.48(14)
N(2) ^b -Zn(2)-O(10) ^a	118.11(16)	O(3) ^c -Zn(3)-O(11) ^d	105.57(14)
N(2) ^b -Zn(2)-O(13)	112.35(17)	O(5) ^c -Zn(3)-O(11) ^d	111.75(15)
Symmetry codes: a - x + 1, - y + 1, - z; b x + 1, y, z; c - x + 1, y + 1/2, - z + 1/2; d - x + 1, y - 1/2, - z + 1/2.			

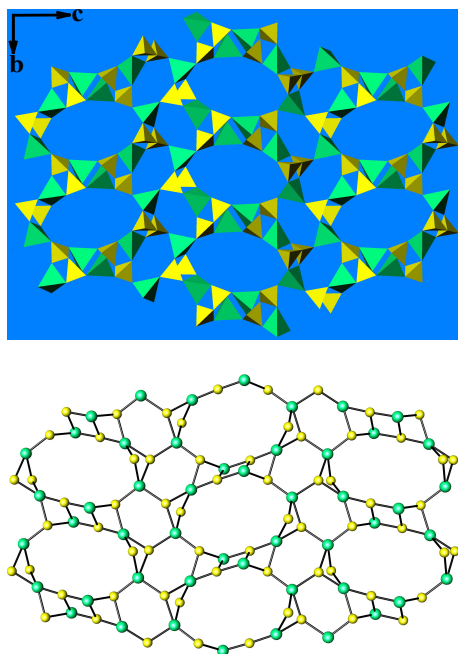


Fig. S1 Polyhedral (top) and Ball-stick (bottom) view of the 2D layer in **1**.

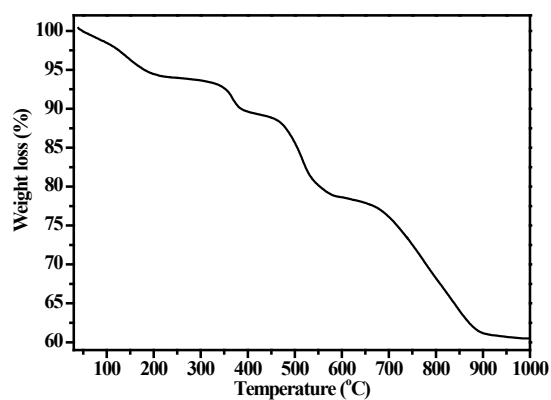


Fig. S2 TGA curve of **1**.

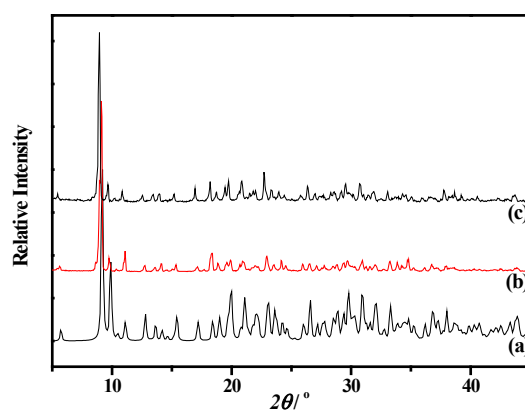


Fig. S3 XRD patterns of **1** (a) simulated from X-ray single crystal data, (b) polycrystalline as newly synthesized, and (c) polycrystalline annealed at 250 °C.

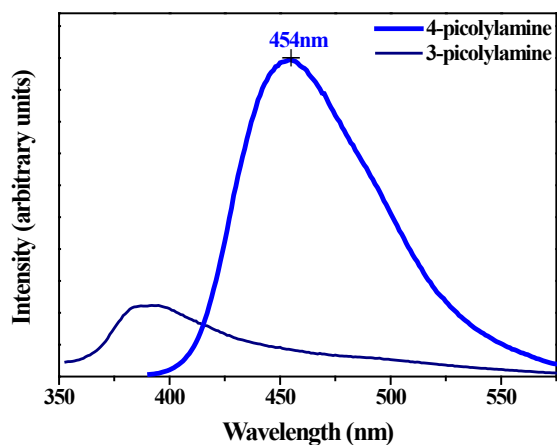


Fig. S4 Emission spectra of 4-picolylamine and 3-picolylamine.

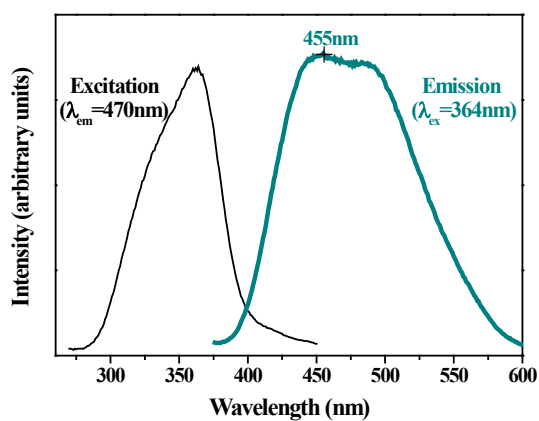


Fig. S5 Emission and excitation spectra of 4-picolylamine hydrochloride solution.

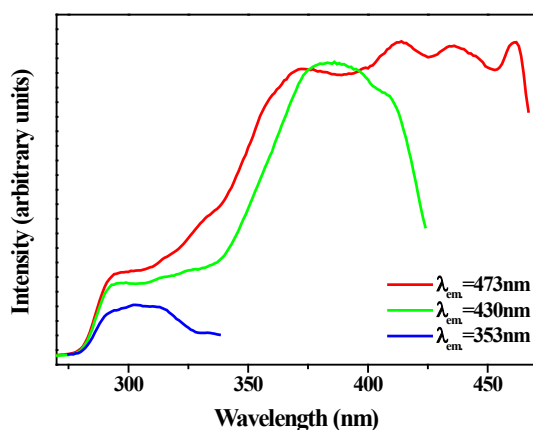


Fig. S6 Relative intensity of excitation spectra for **1** with emission fixed at 473, 430 and 353 nm, respectively.

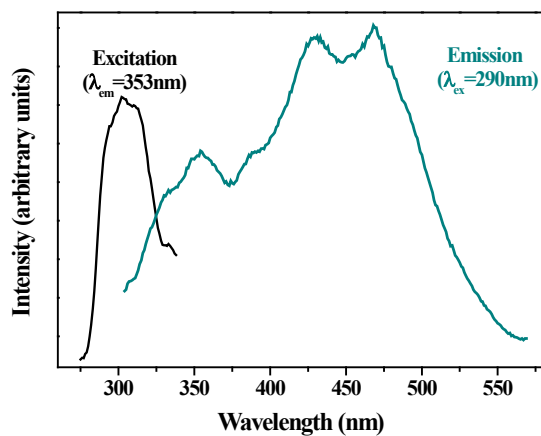


Fig. S7 Emission and excitation spectra of as-prepared **1**.

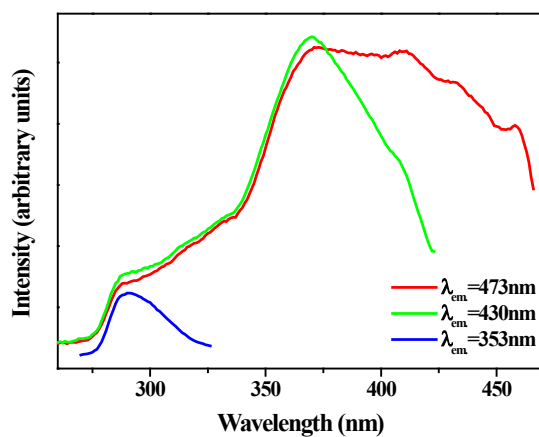


Fig. S8 Relative intensity of fluorescent excitation spectra for **1-250** with emission fixed at 473, 430 and 353 nm, respectively.

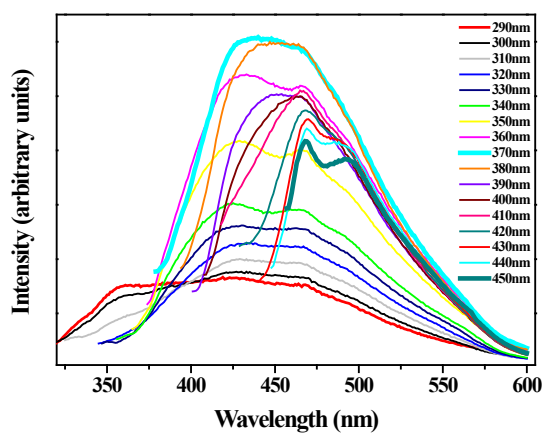


Fig. S9 Relative intensities of emission for **1-250** upon different wavelengths of excited light.

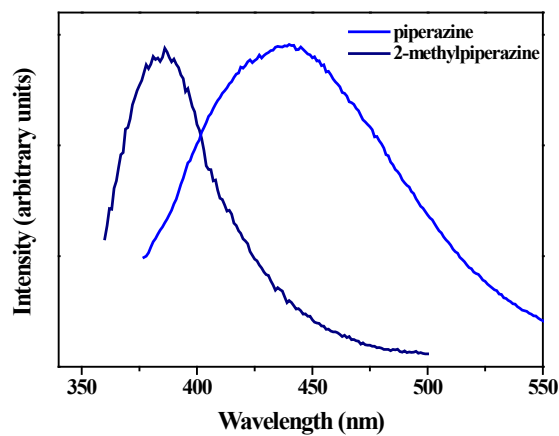


Fig. S10 Emission spectra of piperazine and 2-methylpiperazine.

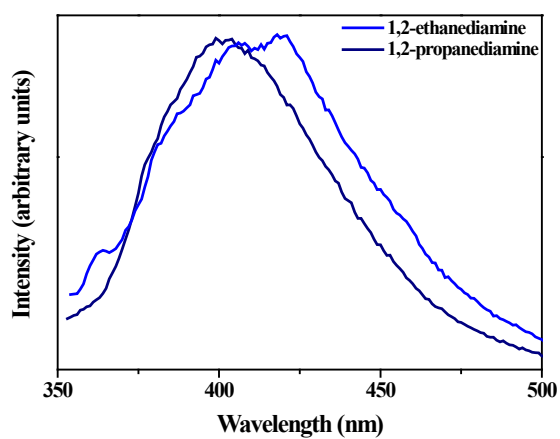


Fig. S11 Emission spectra of 1,2-ethanediamine and 1,2-propanediamine.

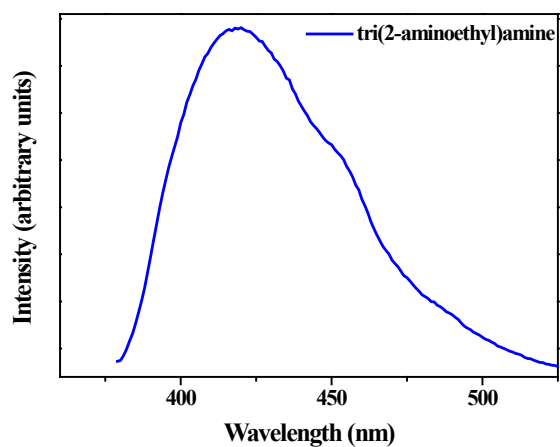


Fig. S12 Emission spectrum of tri(2-aminoethyl)amine.

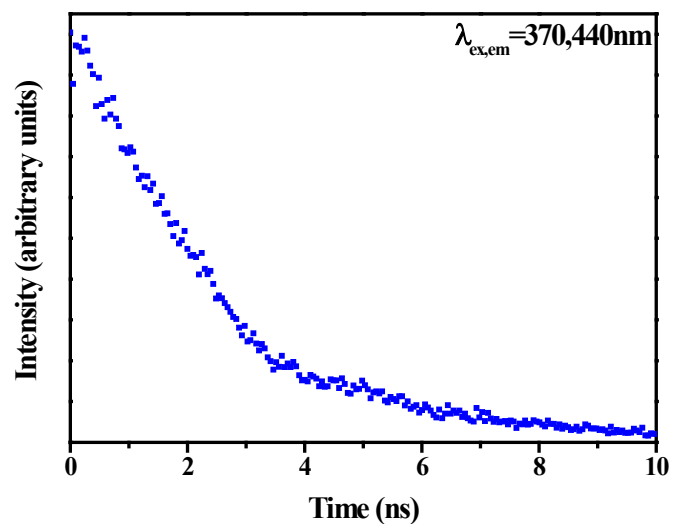


Fig. S13 Room-temperature solid-state fluorescent intensity as a function of time for solid **1-250**.

References

- (1) G. M. Sheldrick, SHELXT 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.