

Supplementary information

New 3D metal phosphonates with bright tunable luminescence for the reversible sensing of nitrobenzene

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Materials and instrumentation

1,4-((H₂O₃PCH₂)(HOOCCH₂)NCH₂)₂C₆H₄ was prepared by N-alkylation reaction. Other 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. Photoluminescent properties were investigated in the solid state at room temperature with a F-7000 FL spectrophotometer and an Edinburgh FLS920 fluorescence spectrometer. Thermogravimetric/Differential Thermal analysis (TG-DTA) 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 under ambient environment. The mass spectrum was recorded on a Varian 4000 gas chromatograph-mass spectrometer.

Synthesis of [Zn₂(H₂L)] (1). A mixture of H₆L (0.0716 g, 0.163 mmol) and Zn(CH₃COO)₂·2H₂O (0.0457 g, 0.208 mmol) in 8.0 mL distilled water with the pH value adjusted to 2.6, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at 140 °C for 120 h. After slow cooling to room temperature with a rate of 0.045 °C · min⁻¹, colorless crystals were obtained. Yield: 0.0338 g (57 %). Anal. Calc. for C₁₄H₁₈N₂O₁₀P₂Zn₂: C 29.66, H 3.20, N 4.94 %. Found: C 29.55, H 3.27, N 4.93 %. Except for few additional small peaks at high angle, experimental powder XRD patterns for solid **1** are consistent with those of simulated from single-crystal X-ray data of compound **1**. Furthermore, luminescent excitation and emission spectra of as-prepared **1** are same to those of single crystal of **1**. These results indicate the final product is almost pure. IR (KBr pellet, cm⁻¹): 3347w($\nu_{\text{O-H}}$), 3011w, 2947w($\nu_{\text{C-H}}$), 2926w, 2761w, 2691w, 2598w, 1651s(ν_{asCO}), 1456m, 1430w, 1413w, 1396w, 1385m, 1337m, 1312w, 1283w, 1177s($\nu_{\text{P-O}}$), 1116s($\nu_{\text{P-O}}$), 1046s($\nu_{\text{P-O}}$), 984w, 974w, 941w, 924w, 882w, 849w, 730m, 600w, 559w, 525w.

Synthesis of [Co₂(H₂L)] (2). A mixture of H₆L (0.0504 g, 0.114 mmol) and Co(CH₃COO)₂·4H₂O (0.0487 g, 0.196 mmol) in 6.0 mL distilled water with the pH

value adjusted to 2.0, was sealed into a Parr Teflon-lined autoclave (23 mL) and heated at 140 °C for 120 h. After slow cooling to room temperature with a rate of 0.045 °C·min⁻¹, red crystals were obtained as a homogenous phase based on powder XRD patterns. Yield: 0.0021 g (3.9%). Anal. Calc. for C₁₄H₁₈N₂O₁₀P₂Co₂: C 30.35, H 3.27, N 5.06 %. Found: C 30.58, H 3.42, N 5.01 %. IR (KBr pellet, cm⁻¹): 3434s(ν_{O-H}), 2948w(ν_{C-H}), 2914w, 1568s(ν_{asCO}), 1450m, 1438w, 1423m, 1337m, 1314w, 1278w, 1184s(ν_{P=O}), 1150s(ν_{P-O}), 1057s(ν_{P-O}), 979w, 966w, 941m, 894m, 831w, 742m, 636m, 583m, 520w, 492w.

Heating treatment: Solids **1-250** and **1-300** were obtained after polycrystalline of **1** was heated at 250 and 300 °C for two hours under an air atmosphere, respectively, and then naturally cooled to room temperature. Anal. Calc. for solid **1-300** (C₁₄H₁₈N₂O₁₀P₂Zn₂): C 29.66, H 3.20, N 4.94 %. Found: C 28.96, H 3.40, N 4.98.

X-Ray crystallography

X-ray data for **1-2** were collected at 293(2) K on a Rigaku Mercury CCD/AFC diffractometer using graphite-monochromated Mo Kα radiation ($\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$). Data of **1-2** 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. Positions of Hydrogen atoms were located from a difference Fourier map and assigned with fixed isotropic thermal parameters. Crystallographic data for compounds **1-2** are summarized in Table S1. Selected bond lengths and angles for compounds **1** and **2** are listed in Table S2 and S3, respectively. CCDC 875032 (**1**) and 875033 (**2**).

Table S1. Crystallographic data for compounds **1** and **2**

Compounds	1	2
Formula	C ₁₄ H ₁₈ N ₂ O ₁₀ P ₂ Zn ₂	C ₁₄ H ₁₈ N ₂ O ₁₀ P ₂ Co ₂
FW	566.98	554.10
Space group	C2/c	C2/c
a (Å)	23.334(16)	23.255(5)
b (Å)	9.933(5)	9.9714(17)
c (Å)	8.938(5)	8.8080(18)
β (deg)	112.509(7)	112.174(9)
V (Å ³)	1913.9(19)	1891.4(6)
Z	4	4
T(K)	293(2)	293(2)
Measured/unique/ observed reflections	7319 / 2174 / 1974	6851 / 2160 / 1775
D _{calcd} (g cm ³)	1.968	1.946
μ (mm ⁻¹)	2.733	1.983
GOF on F ²	1.088	1.201
R _{int}	0.0226	0.0387
R1 ^a [I>2σ(I)]	0.0305	0.0465
wR2 ^b [all data]	0.0782	0.1833
^a R1 = Σ(F _o - F _c) / Σ F _o . ^b wR2 = {Σw [(F _o ² - F _c ²)] / Σw [(F _o ²) ²]} ^{0.5} .		

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

Zn(1)-O(1)	2.039(2)	Zn(1)-O(5) ^b	2.093(2)
Zn(1)-O(2) ^a	1.991(2)	Zn(1)-N(1)	2.239(2)
Zn(1)-O(4)	2.067(2)		
O(1)-Zn(1)-O(2) ^a	96.22(9)	O(2) ^a -Zn(1)-O(5) ^b	92.87(9)
O(1)-Zn(1)-O(4)	117.02(8)	O(2) ^a -Zn(1)-N(1)	174.15(7)
O(1)-Zn(1)-O(5) ^b	141.85(8)	O(4)-Zn(1)-O(5) ^b	98.49(9)
O(1)-Zn(1)-N(1)	84.83(8)	O(4)-Zn(1)-N(1)	77.82(7)
O(2) ^a -Zn(1)-O(4)	96.62(8)	O(5) ^b -Zn(1)-N(1)	89.81(8)

Symmetry codes: a - x + 1/2, y - 1/2, - z + 1/2; b x, - y, z - 1/2.

Table S3. Selected bond lengths (Å) and angles (°) for **2**

Co(1)-O(1)	2.030(3)	Co(1)-O(5) ^b	2.091(3)
Co(1)-O(2) ^a	2.003(3)	Co(1)-N(1)	2.236(3)
Co(1)-O(4)	2.064(3)		
O(1)-Co(1)-O(2) ^a	96.46(13)	O(2) ^a -Co(1)-O(5) ^b	93.81(14)
O(1)-Co(1)-O(4)	115.58(13)	O(2) ^a -Co(1)-N(1)	174.31(13)
O(1)-Co(1)-O(5) ^b	143.79(14)	O(4)-Co(1)-O(5) ^b	97.39(14)
O(1)-Co(1)-N(1)	84.47(12)	O(4)-Co(1)-N(1)	77.63(13)
O(2) ^a -Co(1)-O(4)	96.95(13)	O(5) ^b -Co(1)-N(1)	88.66(13)

Symmetry codes: a - x + 1/2, y - 1/2, - z + 1/2; b x, - y, z + 1/2.

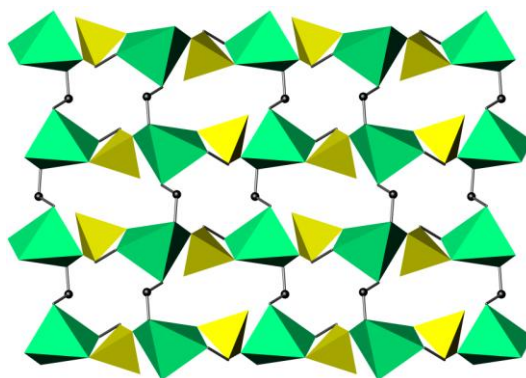


Fig. S1 Polyhedral view of the 2D hybrid layer in **1**.

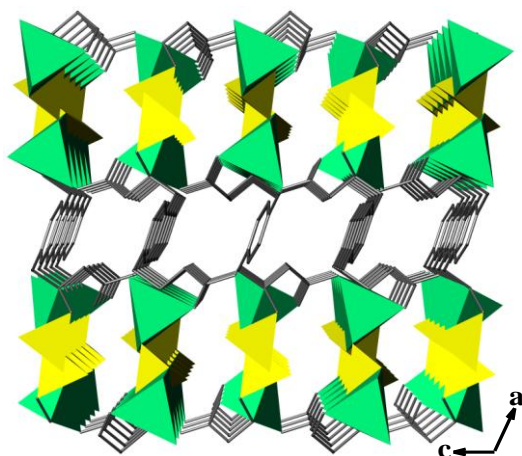


Fig. S2 Polyhedral view of the 3D framework in **1**.

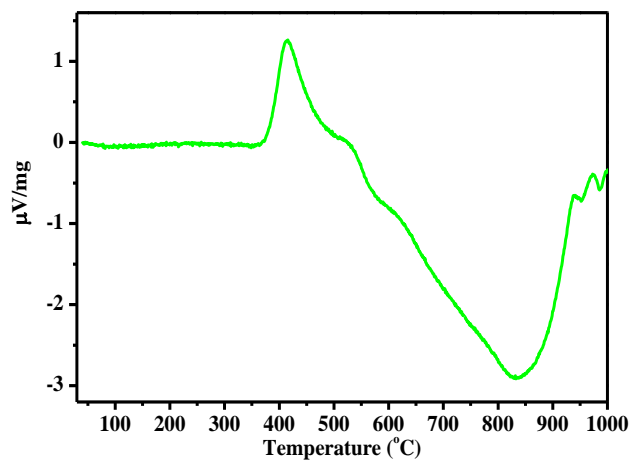
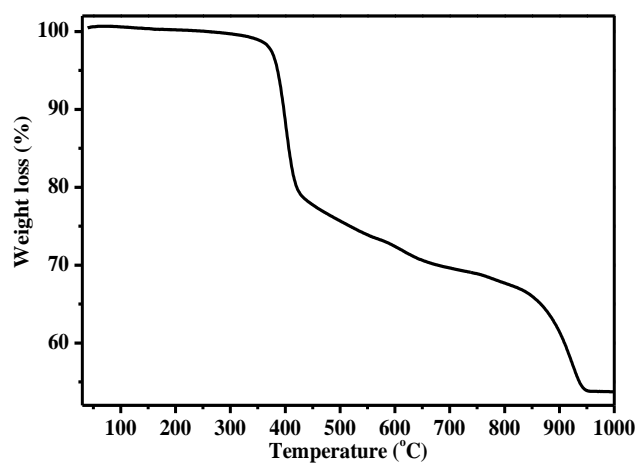


Fig. S3 TGA (top) and DTA (bottom) curves of **1**.

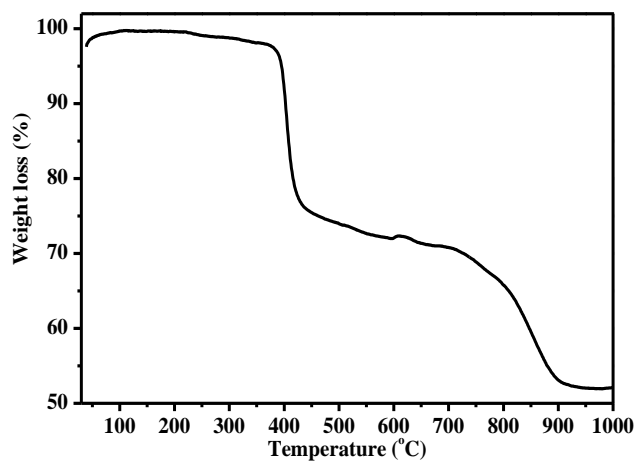


Fig. S4 TGA curve of **2**.

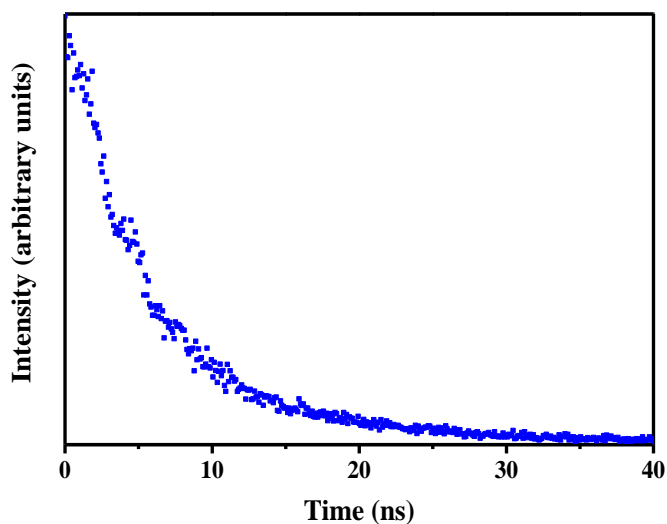


Fig. S5 Room-temperature solid-state fluorescent intensity as a function of time for solid **1** with $\lambda_{em} = 399$ nm under excitation of 335nm.

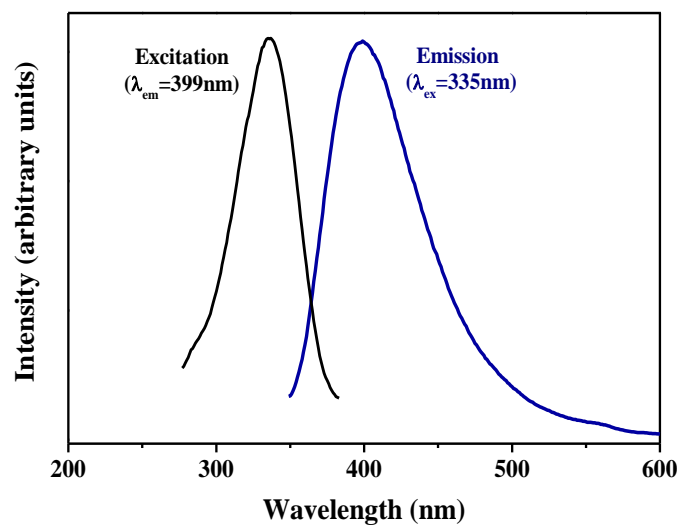


Fig. S6 Emission and excitation spectra of as-prepared **1** under ambient temperature.

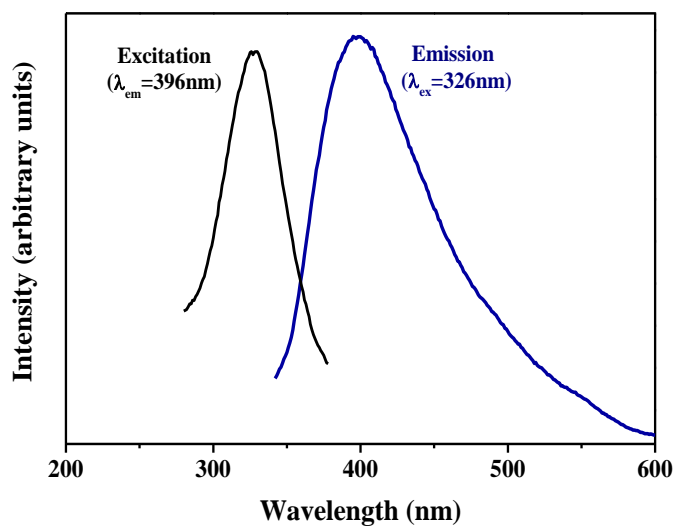


Fig. S7 Emission and excitation spectra of solid **1-250** under ambient temperature.

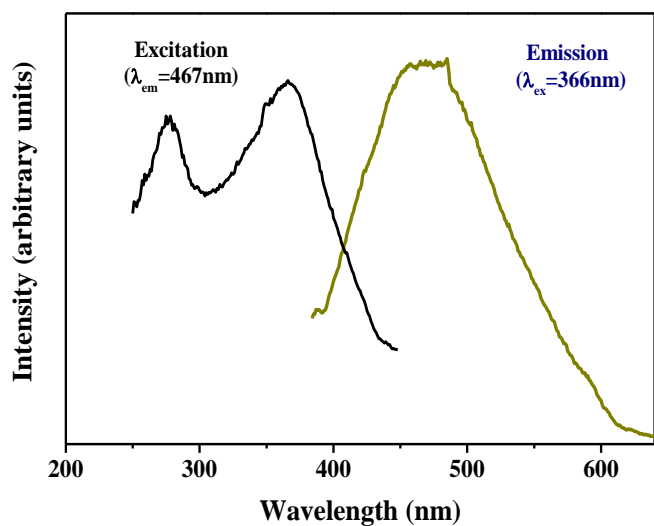


Fig. S8 Emission and excitation spectra of solid **1-300** under ambient temperature.

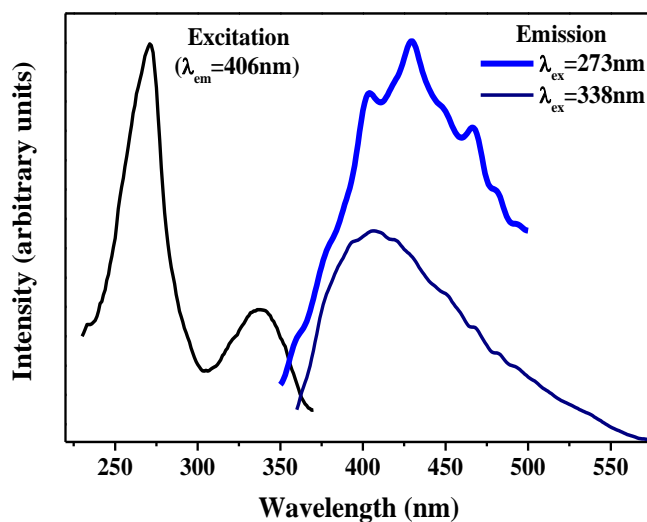


Fig. S9 Normalized emission and excitation spectra of solid **1** at 10 K.

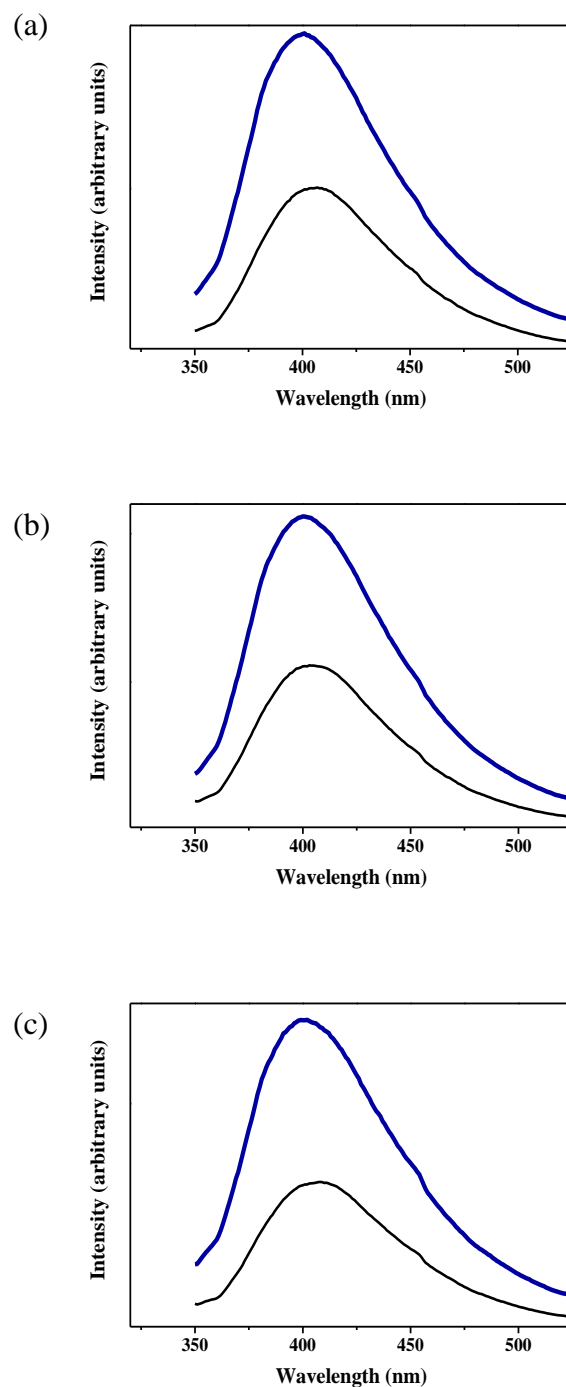


Fig. S10 Room-temperature relative emission intensities of emission for solid **1** (purple), as well as solid **1** has been exposed to the equilibrated vapors of nitrobenzene (black) for 3-10 days: (a) first cycle, (b) second cycle and (c) third cycle.

References

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