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 CuKα 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 C₁₄H₁₈N₂O₁₀P₂Zn₉: 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(νO-H), 3011w, 2947w(νC-H), 2926w, 2761w, 2691w, 2598w, 1651s(νasCO₂), 1456m, 1430w, 1413w, 1396w, 1385m, 1337m, 1312w, 1283w, 1177s(νP=O), 1116s(νP=O), 1046s(νP=O), 984w, 974w, 941w, 924w, 882w, 849w, 730w, 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 C_{14}H_{18}N_{2}O_{10}P_{2}Co_{2}: 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(υO-H), 2948w(υC-H), 2914w, 1568s(υasCO), 1450m, 1438w, 1423m, 1337m, 1314w, 1278w, 1184s(υP=O), 1150s(υP-O), 1057s(υP-О), 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 (C_{14}H_{18}N_{2}O_{10}P_{2}Zn_{2}): 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 (λ(Mo-Kα) = 0.71073 Å). 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 F² 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

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<thead>
<tr>
<th>Compounds</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{14}$H$</em>{18}$N$<em>2$O$</em>{10}$P$_2$Zn$_2$</td>
<td>C$<em>{14}$H$</em>{18}$N$<em>2$O$</em>{10}$P$_2$Co$_2$</td>
</tr>
<tr>
<td>FW</td>
<td>566.98</td>
<td>554.10</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>23.334(16)</td>
<td>23.255(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.933(5)</td>
<td>9.9714(17)</td>
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<tr>
<td>c (Å)</td>
<td>8.938(5)</td>
<td>8.8080(18)</td>
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<tr>
<td>β (deg)</td>
<td>112.509(7)</td>
<td>112.174(9)</td>
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<tr>
<td>V (Å$^3$)</td>
<td>1913.9(19)</td>
<td>1891.4(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
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<tr>
<td>T(K)</td>
<td>293(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Measured/unique/observed reflections</td>
<td>7319 / 2174 / 1974</td>
<td>6851 / 2160 / 1775</td>
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<tr>
<td>$D_{\text{calc}}$ (g cm$^{-3}$)</td>
<td>1.968</td>
<td>1.946</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>2.733</td>
<td>1.983</td>
</tr>
<tr>
<td>GOF on $F^2$</td>
<td>1.088</td>
<td>1.201</td>
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<tr>
<td>$R_{\text{int}}$</td>
<td>0.0226</td>
<td>0.0387</td>
</tr>
<tr>
<td>$R1^a [I&gt;2\sigma(I)]$</td>
<td>0.0305</td>
<td>0.0465</td>
</tr>
<tr>
<td>wR2$^b$ [all data]</td>
<td>0.0782</td>
<td>0.1833</td>
</tr>
</tbody>
</table>

$^a$ $R1 = \Sigma([F_o] - |F_c|)/\Sigma |F_o|$.

$^b$ $wR2 = \{ \Sigma w [(F_o^2 - F_c^2)] / \Sigma w [(F_o^2)] \}^{0.5}$.  

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

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
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</thead>
<tbody>
<tr>
<td>Zn(1)-O(1)</td>
<td>2.039(2)</td>
<td>Zn(1)-O(5)(^b)</td>
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<td>Zn(1)-O(2)(^a)</td>
<td>1.991(2)</td>
<td>Zn(1)-N(1)</td>
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<td>Zn(1)-O(4)</td>
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<tr>
<td>O(1)-Zn(1)-O(2)(^a)</td>
<td>96.22(9)</td>
<td>O(2)(^a)-Zn(1)-O(5)(^b)</td>
<td>92.87(9)</td>
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<tr>
<td>O(1)-Zn(1)-O(4)</td>
<td>117.02(8)</td>
<td>O(2)(^a)-Zn(1)-N(1)</td>
<td>174.15(7)</td>
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<td>O(1)-Zn(1)-O(5)(^b)</td>
<td>141.85(8)</td>
<td>O(4)-Zn(1)-O(5)(^b)</td>
<td>98.49(9)</td>
</tr>
<tr>
<td>O(1)-Zn(1)-N(1)</td>
<td>84.83(8)</td>
<td>O(4)-Zn(1)-N(1)</td>
<td>77.82(7)</td>
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<td>O(2)(^a)-Zn(1)-O(4)</td>
<td>96.64(8)</td>
<td>O(5)(^b)-Zn(1)-N(1)</td>
<td>89.81(8)</td>
</tr>
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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

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
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<tr>
<td>Co(1)-O(1)</td>
<td>2.030(3)</td>
<td>Co(1)-O(5)(^b)</td>
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<td>Co(1)-O(2)(^a)</td>
<td>2.003(3)</td>
<td>Co(1)-N(1)</td>
<td>2.236(3)</td>
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<td>Co(1)-O(4)</td>
<td>2.064(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)-Co(1)-O(2)(^a)</td>
<td>96.46(13)</td>
<td>O(2)(^a)-Co(1)-O(5)(^b)</td>
<td>93.81(14)</td>
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<tr>
<td>O(1)-Co(1)-O(4)</td>
<td>115.58(13)</td>
<td>O(2)(^a)-Co(1)-N(1)</td>
<td>174.31(13)</td>
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<tr>
<td>O(1)-Co(1)-O(5)(^b)</td>
<td>143.79(14)</td>
<td>O(4)-Co(1)-O(5)(^b)</td>
<td>97.39(14)</td>
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<tr>
<td>O(1)-Co(1)-N(1)</td>
<td>84.47(12)</td>
<td>O(4)-Co(1)-N(1)</td>
<td>77.63(13)</td>
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<td>O(2)(^a)-Co(1)-O(4)</td>
<td>96.95(13)</td>
<td>O(5)(^b)-Co(1)-N(1)</td>
<td>88.66(13)</td>
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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