Supplementary information

Two fluorescent lead phosphonates for highly selective sensing of nitro aromatics (NACs), Fe$^{3+}$ and MnO$_4^{-}$ ions

Bo Xing, Huan-Yu Li, Yan-Yu Zhu, Zhou Zhao, Zhen-Gang Sun*, Dan Yang and Jing Li

School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P. R. China
Table S1. Selected Bond Distances (Å) and Angles (deg) for 1

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Dist/deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(1)−O(2)#1</td>
<td>2.290(4)</td>
</tr>
<tr>
<td>Pb(1)−O(5)#2</td>
<td>2.348(4)</td>
</tr>
<tr>
<td>Pb(1)−O(4)</td>
<td>2.446(4)</td>
</tr>
<tr>
<td>Pb(1)−O(1)#3</td>
<td>2.578(4)</td>
</tr>
<tr>
<td>P(1)−O(1)</td>
<td>1.500(4)</td>
</tr>
<tr>
<td>P(1)−O(2)</td>
<td>1.507(4)</td>
</tr>
<tr>
<td>O(2)#1−Pb(1)−O(5)#2</td>
<td>97.16(14)</td>
</tr>
<tr>
<td>O(2)#1−Pb(1)−O(4)</td>
<td>84.17(14)</td>
</tr>
<tr>
<td>O(5)#2−Pb(1)−O(4)</td>
<td>81.92(13)</td>
</tr>
<tr>
<td>O(2)#1−Pb(1)−O(1)#3</td>
<td>86.08(13)</td>
</tr>
<tr>
<td>O(5)#2−Pb(1)−O(1)#3</td>
<td>79.83(13)</td>
</tr>
<tr>
<td>O(4)−Pb(1)−O(1)#3</td>
<td>158.04(13)</td>
</tr>
<tr>
<td>O(1)−P(1)−O(2)</td>
<td>117.7(2)</td>
</tr>
<tr>
<td>O(1)−P(1)−O(3)</td>
<td>106.0(2)</td>
</tr>
<tr>
<td>O(2)−P(1)−O(3)</td>
<td>108.8(2)</td>
</tr>
<tr>
<td>O(1)−P(1)−C(3)</td>
<td>109.2(2)</td>
</tr>
<tr>
<td>O(2)−P(1)−C(3)</td>
<td>108.7(3)</td>
</tr>
<tr>
<td>O(3)−P(1)−C(3)</td>
<td>105.8(3)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 x − 1, y + 1, z, #2 x − 1, y, z, #3 x − 2, y + 1, z, #4 x + 1, y − 1, z, #5 x + 2, y − 1, z, #6 x + 1, y, z.
| Bond Distance/Angle | 2.403(8) | 2.406(6) | 2.513(5) | 2.727(6) | 2.740(6) | 2.266(6) | 2.368(6) | 2.368(6) | 2.378(5) | 2.309(6) | 2.386(5) | 84.9(3) | 110.2(2) | 146.0(2) | 78.6(2) | 95.11(19) | 69.7(2) | 49.60(18) | 79.2(2) | 80.3(2) | 86.6(2) | 90.1(3) | 158.7(2) | 73.31(19) | 89.7(2) | 79.26(19) | 78.61(18) | 2.517(5) | 2.731(6) | 1.478(6) | 1.515(6) | 1.603(7) | 1.484(8) | 1.499(5) | 1.572(8) | 1.495(6) | 1.518(5) | 1.594(6) | 50.89(17) | 123.19(17) | 111.4(4) | 105.6(4) | 114.6(4) | 114.6(4) | 113.1(4) | 105.4(4) | 134.3(3) | 136.1(5) | 108.2(5) | 110.9(5) |

Symmetry transformations used to generate equivalent atoms:
#1 $-x + 1$, $-y + 2$, $-z$
#2 $-x + 2$, $-y + 1$, $-z$
#3 $x - 1$, $y$, $z$
#4 $-x + 1$, $-y + 2$, $-z + 1$
#5 $x + 1$, $y$, $z$. 

Table S2. Selected Bond Distances (Å) and Angles (deg) for 2
Table S3. The ICP result of filtrate.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Units</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>Fe</td>
</tr>
<tr>
<td>1</td>
<td>ppm</td>
<td>1.4826</td>
</tr>
<tr>
<td>2</td>
<td>ppm</td>
<td>1.9319</td>
</tr>
</tbody>
</table>

Fig. S1 The experimental powder XRD pattern and the simulated XRD pattern of compound 1.

Fig. S2 The experimental powder XRD pattern and the simulated XRD pattern of compound 2.
Fig. S3 (a) A 2D layer structure of compound 1 viewed in $ab$–plane; (b) the 30–atom windows in compound 1.

Fig. S4 The double layer structure of compound 2 viewed in $ac$–plane.
Fig. S5 The IR spectrum of compound 1.

Fig. S6 The IR spectrum of compound 2.
Fig. S7 The TG–DTG curves (10 K/min) of compound 1.

Fig. S8 The TG–DTG curves (10 K/min) of compound 2.
Fig. S9 The PXRD patterns for (a) 1 on heating from 25 to 240 °C and (b) 2 on heating from 25 to 220 °C.

Fig. S10 The solid-state emission spectra of compound 1 (a) and compound 2 (b) at room temperature.
Fig. S11 The emission spectra of (a, b) compound 1 in various solvents at room temperature.

Fig. S12 The emission spectra of (a, b) compound 2 in various solvents at room temperature.
**Fig. S13** The room temperature emission spectra of compounds 1 and 2 in ethanol.

**Fig. S14** The fluorescence properties of compound 1 suspension in the presence of various contents of nitromethane.
**Fig. S15** The fluorescence properties of compound 1 suspension in the presence of various contents of m-dinitrobenzen.

**Fig. S16** The fluorescence properties of compound 1 suspension in the presence of various contents of o-nitrophenol.
Fig. S17 The fluorescence properties of compound 1 suspension in the presence of various contents of 2,6-dinitrotoluene.

Fig. S18 The fluorescence properties of compound 1 suspension in the presence of various contents of nitrobenzene.
Fig. S19 The fluorescence properties of compound 1 suspension in the presence of various contents of 4-nitrotoluene.

Fig. S20 The fluorescence properties of compound 1 suspension in the presence of various contents of p-nitrophenol.
Fig. S21 The fluorescence properties of compound 2 suspension in the presence of various contents of 4-nitrotoluene.

Fig. S22 The fluorescence properties of compound 2 suspension in the presence of various contents of 2,6-dinitrotoluene.
**Fig. S23** The fluorescence properties of compound 2 suspension in the presence of various contents of m-dinitrobenzen.

**Fig. S24** The fluorescence properties of compound 2 suspension in the presence of various contents of o-nitrophenol.
**Fig. S25** The fluorescence properties of compound 2 suspension in the presence of various contents of nitromethane.

**Fig. S26** The fluorescence properties of compound 2 suspension in the presence of various contents of nitrobenzene.
Fig. S27 The fluorescence properties of compound 2 suspension in the presence of various contents of p-nitrophenol.

Fig. S28 The possible weak interaction mechanisms of o-nitrophenol.
Fig. S29 (a) The luminescence spectra of compound 1 in ethanol with different concentration of p-NP; (b) The linear correlation for the plot of $(I_o/I) - 1$ vs concentration of p-NP.

Fig. S30 (a) The luminescence spectra of compound 2 in ethanol with different concentration of p-NP; (b) The linear correlation for the plot of $(I_o/I) - 1$ vs concentration of p-NP.
linear correlation for the plot of $(I_0/I) - 1$ vs concentration of p-NP.

**Fig. S31** Stern–Volmer plots for the fluorescence quenching of compound 1 (a) and 2 (b) (as a stable suspension in ethanol) upon gradual addition of various NACs.

**Fig. S32** The reproducibility of the quenching efficiency of the ethanol suspension of compounds 1 (a) and 2 (b) towards 4 mM p-NP solution.
Fig. S33 The color change of the luminescent responses for sensing the different metal ions (M = Zn$^{2+}$, Al$^{3+}$, Pb$^{2+}$, Sr$^{2+}$, Li$^+$, Mg$^{2+}$, Na$^+$, Ba$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Cr$^{3+}$, Cu$^{2+}$ and Fe$^{3+}$) in aqueous solution for (a) 1, (b) 2 by the ultraviolet light.

Fig. S34 (a) The luminescent intensity compound 1 treated with $1.0 \times 10^{-3}$ M various cations for 12 h; (b) Percentage of fluorescence quenching by introducing different metal cations aqueous solution.
**Fig. S35** (c) The luminescent spectra of compound 1 in the presence of Fe$^{3+}$ ion with different concentrations (10–100 μM); (d) Stern–Volmer plot of I$_0$/I versus the Fe$^{3+}$ concentration.

**Fig. S36** (c) The luminescent spectra of compound 2 in the presence of Fe$^{3+}$ ion with different concentrations (10–100 μM); (d) Stern–Volmer plot of I$_0$/I versus the Fe$^{3+}$ concentration.
Fig. S37 (a) The luminescent intensity compound 1 treated with $1.0 \times 10^{-3}$ M various cations for 12 h; (b) Percentage of fluorescence quenching by introducing different metal cations ethanol solution; (c) The luminescent spectra of compound 1 in the presence of Fe$^{3+}$ ion with different concentrations (10–100 μM). (d) Stern–Volmer plot of I$_o$/I versus the Fe$^{3+}$ concentration.
Fig. S38 (a) The luminescent intensity compound 2 treated with $1.0 \times 10^{-3}$ M various cations for 12 h; (b) Percentage of fluorescence quenching by introducing different metal cations ethanol solution; (c) The luminescent spectra of compound 2 in the presence of Fe$^{3+}$ ion with different concentrations (10−100 μM). (d) Stern–Volmer plot of $I_0/I$ versus the Fe$^{3+}$ concentration.
**Fig. S39** The room temperature emission spectra of compounds 1 (a) and 2 (b) in ethanol and aqueous solution.

![Emission Spectra](image1)

**Fig. S40**
(c) The luminescent spectra of compound 1 in the presence of MnO$_4^-$ ion with different concentrations (10–100 μM); (d) Stern–Volmer plot of $I_0/I$ versus the MnO$_4^-$ concentration.

![Stern–Volmer Plot](image2)

**Fig. S41**
(c) The luminescent spectra of compound 2 in the presence of MnO$_4^-$ ion with different concentrations (10–100 μM); (d) Stern–Volmer plot of $I_0/I$ versus the MnO$_4^-$ concentration.
Fig. S42 (a) The luminescent intensity compound 1 treated with $1.0 \times 10^{-3}$ M various anions for 12 h; (b) Percentage of fluorescence quenching by introducing different anions ethanol solution; (c) The luminescent spectra of compound 1 in the presence of MnO$_4^-$ ion with different concentrations (10–100 µM); (d) Stern–Volmer plot of $I_0/I$ versus the MnO$_4^-$ concentration.
Fig. S43 (a) The luminescent intensity compound 2 treated with $1.0 \times 10^{-3}$ M various anions for 12 h; (b) Percentage of fluorescence quenching by introducing different anions ethanol solution; (c) The luminescent spectra of compound 2 in the presence of MnO$_4^-$ ion with different concentrations (10−100 μM); (d) Stern–Volmer plot of $I_0/I$ versus the MnO$_4^-$ concentration.
Fig. S44 (a), (c) The quenching and recovery test of compound 1 dispersed in aqueous solution in the presence of Fe$^{3+}$ and MnO$_4^-$ solution; (b) (d) the quenching and recovery test of compound 2 dispersed in aqueous solution in the Fe$^{3+}$ and MnO$_4^-$ solution. Red bar: emission of sample before sensing of Fe$^{3+}$ and MnO$_4^-$; Blue and green bars: emission of sample after sensing of Fe$^{3+}$ and MnO$_4^-$ respectively.
Fig. S45 The XRD patterns of compound 1 before and after treatment with p-NP (a), Fe$^{3+}$ (b) and MnO$_4^-$ (c) solutions.

Fig. S46 The XRD patterns of compound 2 before and after treatment with p-NP (a), Fe$^{3+}$ (b) and MnO$_4^-$ (c) solutions.
Fig. S47 UV-Vis absorption spectra of the Fe$^{3+}$ (a), MnO$_4^-$ (b) in aqueous solutions and compounds 1 and 2 (c).
**Fig. S48** The solid sample color change of compound 1 immersed into the Fe$^{3+}$ (a) and MnO$_4^-$ (b) aqueous solutions.

**Fig. S49** The solid sample color change of compound 2 soaked in the Fe$^{3+}$ (a) and MnO$_4^-$ (b) aqueous solutions.