Supporting Information

2,2’-Biimidazole moiety containing conjugated polymers as a novel fluorescent sensing platform for pyrophosphate anion

Yinyin Bao†, Hu Wang†, Qianbiao Li†, Bin Liu†, Qing Li‡, Wei Bai‡, Bangkun Jin†, Ruke Bai†,*

†CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China.
‡Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States

* Corresponding author. Telephone: 86-551-3600722. Fax: 86-551-3631760. E-mail: bairk@ustc.edu.cn.

Table S1. Polymerization results and characterization of P1, P2, and P3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M_w</th>
<th>M_n</th>
<th>PDI</th>
<th>Absorbance (λ_max, nm)</th>
<th>Emission (λ_max, nm)</th>
<th>Quantum Yield</th>
<th>Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>8900</td>
<td>7000</td>
<td>1.27</td>
<td>335</td>
<td>423</td>
<td>0.22</td>
<td>0.13</td>
</tr>
<tr>
<td>P2</td>
<td>5200</td>
<td>4100</td>
<td>1.28</td>
<td>326</td>
<td>426</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>P3</td>
<td>12000</td>
<td>8500</td>
<td>1.40</td>
<td>336</td>
<td>425</td>
<td>0.41</td>
<td>0.05</td>
</tr>
</tbody>
</table>

† Estimated from GPC (eluent: DMF, polystyrene standards). † All spectra were recorded in DMF at a concentration of polymer-bound biimidazole of 8.0 µM. Emission spectra were measured with excitation at 338 nm. † The quantum yields of the polymers were determined in DMF. † The quantum yields of the polymers were determined in DMF-HEPES (4:1, v/v).
Figure S1. Fluorescence spectra of P1 in various organic solvents. $\lambda_{ex} = 338$ nm. $[P1] = 1.0 \times 10^{-5}$ M.

Figure S2. Fluorescence spectra of P2 in various organic solvents. $\lambda_{ex} = 338$ nm. $[P2] = 1.0 \times 10^{-5}$ M.
Figure S3. Fluorescence spectra of P1 in DMF-H₂O mixed solvents with different water contents. \( \lambda_{\text{ex}} = 338 \text{ nm} \). \([P1] = 8.0 \times 10^{-6} \text{ M}\).

Figure S4. Fluorescence spectra of P2 in DMF-H₂O mixed solvents with different water contents. \( \lambda_{\text{ex}} = 338 \text{ nm} \). \([P2] = 8.0 \times 10^{-6} \text{ M}\).
Figure S5. Emission intensity ratios $F_{550\text{nm}}/F_{423\text{nm}}$ of P2 in DMF-H$_2$O mixed solvents change with increasing water contents. $\lambda_{\text{ex}} = 338$ nm. [P2] = 8.0 × 10$^{-6}$ M.

Figure S6. Fluorescence spectra of P3 in DMF-H$_2$O mixed solvents with different water contents. $\lambda_{\text{ex}} = 338$ nm. [P3] = 8.0 × 10$^{-6}$ M.
Figure S7. Emission intensity ratio $F_0/F$ of $P_1$, $P_2$, and $P_3$ in DMF-H$_2$O mixed solvents as a function of water content. $\lambda_{\text{ex}} = 338$ nm. $[P_1] = [P_2] = [P_3] = 8.0 \times 10^{-6}$ M.

Figure S8. Stern-Volmer plot for $P_1$ in DMF-HEPES (pH = 7.4, v/v = 4:1) after the addition of Cu$^{2+}$. $\lambda_{\text{ex}} = 338$ nm. $[P_1] = 8.0 \times 10^{-6}$ M.
Figure S9. Fluorescence spectra of P2 upon the titration of Cu$^{2+}$ in DMF-HEPES (pH = 7.4, v/v = 4:1). $\lambda_{ex} = 338$ nm. [P1] = $8.0 \times 10^{-6}$ M.

Figure S10. Emission intensity ratios $F_{550\text{nm}}/F_{423\text{nm}}$ of P2 in DMF-H$_2$O mixed solvents change with increasing concentration of Cu$^{2+}$. $\lambda_{ex} = 338$ nm. [P2] = $8.0 \times 10^{-6}$ M.
Figure S11. Fluorescence intensity of P2 as a function of Cu$^{2+}$ concentration. $\lambda_{ex} = 338$ nm. [P2] = $8.0 \times 10^{-6}$ M.

Figure S12. Stern-Volmer plot for P2 in DMF-HEPES (pH = 7.4, v/v = 4:1) after the addition of Cu$^{2+}$. $\lambda_{ex} = 338$ nm. [P2] = $8.0 \times 10^{-6}$ M.
Figure S13. Fluorescence spectra of P3 upon the titration of Cu$^{2+}$ in DMF-HEPES (pH = 7.4, v/v = 4:1). $\lambda_{ex} = 338$ nm. \([P3] = 8.0 \times 10^{-6}$ M.

Figure S14. Fluorescence intensity of P3 as a function of Cu$^{2+}$ concentration. $\lambda_{ex} = 338$ nm. \([P3] = 8.0 \times 10^{-6}$ M.

Figure S15. Stern-Volmer plot for P3 in DMF-HEPES (pH = 7.4, v/v = 4:1) after the addition of Cu$^{2+}$. $\lambda_{ex} = 338$ nm. \([P2] = 8.0 \times 10^{-6}$ M.
Figure S16. Absorbance spectra of P1 + Cu$^{2+}$ in DMF-HEPES (pH = 7.4, v/v = 4:1) of increasing Cu$^{2+}$ concentrations. [P1] = 8.0 × 10$^{-6}$ M.

Figure S17. Absorbance spectra of P2 + Cu$^{2+}$ in DMF-HEPES (pH = 7.4, v/v = 4:1) of increasing Cu$^{2+}$ concentrations. [P2] = 8.0 × 10$^{-6}$ M.
Figure S18. Fluorescence spectra of P1 in the presence of various metal ions (25.0 equiv of Na\(^+\), K\(^+\), and 2.5 equiv Mg\(^{2+}\), Ca\(^{2+}\), Ag\(^+\), Zn\(^{2+}\), Cd\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Mn\(^{2+}\), Pb\(^{2+}\), Fe\(^{3+}\)) in DMF-HEPES (pH = 7.4, v/v = 4:1). \(\lambda_{ex} = 338\) nm. \([P1] = 8.0 \times 10^{-6}\) M.

Figure S19. Emission intensity ratios \(F_0/F\) of P1 in the presence of indicated metal ions in DMF-HEPES (pH = 7.4, v/v = 4:1). \(\lambda_{ex} = 338\) nm. \([P1] = 8.0 \times 10^{-6}\) M.
**Figure S20.** Fluorescence spectra of P2 in the presence of various metal ions (25.0 equiv of Na\(^+\), K\(^+\), and 2.5 equiv Mg\(^{2+}\), Ca\(^{2+}\), Ag\(^+\), Zn\(^{2+}\), Cd\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Mn\(^{2+}\), Pb\(^{2+}\), Fe\(^{3+}\)) in DMF-HEPES (pH = 7.4, v/v = 4:1). \(\lambda_{\text{ex}} = 338\) nm. [P2] = 8.0 \(\times\) 10\(^{-6}\) M.

**Figure S21.** Emission intensity ratios \(F_0/F\) of P2 in the presence of indicated metal ions in DMF-HEPES (pH = 7.4, v/v = 4:1). \(\lambda_{\text{ex}} = 338\) nm. [P2] = 8.0 \(\times\) 10\(^{-6}\) M.
Figure S22. Fluorescence spectra of P2-Cu$^{2+}$ complex upon the titration of PPI in DMF-HEPES (pH = 7.4, v/v = 4:1). $\lambda_{ex}$=338 nm. [P2] = $8.0 \times 10^{-6}$ M. [Cu$^{2+}$] = $2.0 \times 10^{-5}$ M.

Figure S23. Fluorescence intensity of P2-Cu$^{2+}$ complex as a function of PPI concentration. $\lambda_{ex}$=338 nm. [P2] = $8.0 \times 10^{-6}$ M. [Cu$^{2+}$] = $2.0 \times 10^{-5}$ M.
**Figure S24.** Fluorescence spectra of \( \text{P2-}\text{Cu}^{2+} \) complex upon the titration of PPI in DMF-HEPES (pH = 7.4, v/v = 4:1). \( \lambda_{\text{ex}} = 338 \text{ nm} \). \([\text{P2}] = 8.0 \times 10^{-6} \text{ M} \). \([\text{Cu}^{2+}] = 1.0 \times 10^{-5} \text{ M} \).

**Figure S25.** Fluorescence intensity of \( \text{P2-}\text{Cu}^{2+} \) complex as a function of PPI concentration. \( \lambda_{\text{ex}} = 338 \text{ nm} \). \([\text{P2}] = 8.0 \times 10^{-6} \text{ M} \). \([\text{Cu}^{2+}] = 1.0 \times 10^{-5} \text{ M} \).
Figure S26. Fluorescence spectra of P2-Cu$^{2+}$ complex and (b) intensity ratio F/F$_0$ of P2-Cu$^{2+}$ complex in the presence of $4.0 \times 10^{-5}$ M PPI and $8.0 \times 10^{-5}$ M various anions in DMF-HEPES (pH = 7.4, v/v = 4:1). $\lambda_{ex} = 338$ nm. [P2] = $8.0 \times 10^{-6}$ M. [Cu$^{2+}$] = $2.0 \times 10^{-5}$ M.

Figure S27. Intensity ratios F/F$_0$ of P2-Cu$^{2+}$ complex in the presence of $4.0 \times 10^{-5}$ M PPI and $8.0 \times 10^{-5}$ M various anions in DMF-HEPES (pH = 7.4, v/v = 4:1). $\lambda_{ex} = 338$ nm. [P2] = $8.0 \times 10^{-6}$ M. [Cu$^{2+}$] = $2.0 \times 10^{-5}$ M. 1, PPI; 2, F$^-$; 3, Cl$^-$; 4, Br$^-$; 5, I$^-$; 6, NO$_3^-$; 7, HSO$_4^-$; 8, ClO$_4^-$; 9, AcO$^-$. 10, HCO$_3^-$; 11, CO$_3^{2-}$; 12, H$_2$PO$_4^-$; 13, HPO$_4^{2-}$; 14, PO$_4^{3-}$. 
Figure S28. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of M0.

Figure S29. $^{13}$C NMR (CDCl$_3$, 400 MHz) spectrum of M0.
Figure S30. $^1$H NMR (CDCl₃, 400 MHz) spectrum of M1.

Figure S31. $^{13}$C NMR (CDCl₃, 400 MHz) spectrum of M1.
Figure S32. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of M2.

Figure S33. $^{13}$C NMR (CDCl$_3$, 400 MHz) spectrum of M1.
Figure S34. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P2.

Figure S35. $^1$H NMR (CDCl$_3$, 400 MHz) spectrum of P3.
Figure S36. FT-IR spectrum of P1.

Figure S37. FT-IR spectrum of P2.

Figure S38. FT-IR spectrum of P3.