Effect of Charge Transfer and Structural Rigidity on Divergent Luminescence Response of a Metal Organic Framework towards Different Metal Ions: Luminescence Lifetime Decay Experiments and DFT Calculations

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ELECTRONIC SUPPLEMENTARY INFORMATION
Fig. S1: Powder XRD (CuKα) patterns of [Cd(C12N2H8)(C7N1O4H3)], 1: (a) simulated from single crystal X-ray data of [Cd(phen)(2,5-pda)]∞ (Y. Wei, H. Hou,* L. Li, Y. Fan and Y. Zhu, Cryst. Growth Des., 2005, 5(4), 1405-1413) (b) experimental.
Fig. S2: IR spectrum of [Cd(C_{12}N_{2}H_{8})(C_{7}N_{1}O_{4}H_{3})], 1.
Fig. S3: Thermogravimetric analysis (TGA) of [Cd(C_{12}N_{2}H_{6})(C_{7}N_{1}O_{4}H_{3})], 1, in nitrogen atmosphere.
Fig. S4: Powder XRD (CuKα) patterns of [Cd(C\textsubscript{12}N\textsubscript{2}H\textsubscript{8})(C\textsubscript{7}N\textsubscript{1}O\textsubscript{4}H\textsubscript{3})], 1: (a) simulated from single crystal X-ray data, (b) after immersing in water for 2 days, (c) at pH=3 (d) at pH=6 and (e) at pH= 10.
Fig. S5: (a) Absorption spectra of compound 1, 2,5-pydc and 1,10-phenanthroline in the pH range 3 to 10. It shows the difference in the spectra of compound and the ligands in both peak positions as well as shape of the band. (b) Absorption spectra of compound 1, 2,5-pydc and 1,10-phenanthroline at pH = 2. In this pH, absorption spectra of compound nicely match (both peak position and the band shape of the spectra) with the absorption spectra of 2,5-pydc. (c) Absorption spectra of compound 1, 2,5-pydc and 1,10-phenanthroline at pH = 11. In this pH, absorption spectra of compound nicely match (both peak position and the band shape of the spectra) with the absorption spectra of 1,10-phenanthroline. Both (b) and (c) indicate that the compound in the pH ranges below 3 and above 10 breaks down and the free ligand is formed.
Fig. S6: Excitation and luminescence spectrum ($\lambda_{ex} = 280$ nm) of compound 1.
Fig. S7: Emission spectra of compound 1 dispersed in water upon incremental addition of Al$^{3+}$ solution ($\lambda_{ex} = 280$ nm). Final concentration of Al$^{3+}$ in the medium is indicated in the legend.
Fig. S8: Emission spectra of compound 1 dispersed in water upon incremental addition of Pb$^{2+}$ solution ($\lambda_{\text{ex}} = 280$ nm). Final concentration of Pb$^{2+}$ in the medium is indicated in the legend.
Fig. S9: Emission spectra of compound 1 dispersed in water upon incremental addition of Cd$^{2+}$ solution ($\lambda_{ex} = 280$ nm). Final concentration of Cd$^{2+}$ in the medium is indicated in the legend.
Fig. S10: Emission spectra of compound 1 dispersed in water upon incremental addition of K\(^+\) solution \((\lambda_{\text{ex}} = 280 \text{ nm})\). Final concentration of K\(^+\) in the medium is indicated in the legend.
Fig. S11: Emission spectra of compound 1 dispersed in water upon incremental addition of Mg$^{2+}$ solution ($\lambda_{ex} = 280$ nm). Final concentration of Mg$^{2+}$ in the medium is indicated in the legend.
Fig. S12: Emission spectra of compound 1 dispersed in water upon incremental addition of Na\(^+\) solution \((\lambda_{ex} = 280 \text{ nm})\). Final concentration of Na\(^+\) in the medium is indicated in the legend.
Fig. S13: Emission spectra of compound 1 dispersed in water upon incremental addition of Mn$^{2+}$ solution ($\lambda_{\text{ex}} = 280$ nm). Final concentration of Mn$^{2+}$ in the medium is indicated in the legend.
Fig. S14: Emission spectra of compound 1 dispersed in water upon incremental addition of Cr\(^{3+}\) solution (\(\lambda_{\text{ex}} = 280\) nm). Final concentration of Cr\(^{3+}\) in the medium is indicated in the legend.
Fig. S15: Time resolved fluorescence decay plot of compound 1 and with addition of Cu$^{2+}$. Final concentrations of metal ions in the medium are indicated in the legend.
Fig. S16: Time resolved fluorescence decay plot of compound 1 and with addition of Hg$^{2+}$. Final concentrations of metal ions in the medium are indicated in the legend.
Fig. S17: (a) Absorption spectra of compound 1 in water and pyrene in heptane (b) luminescence spectra of pyrene in heptanes upon excitation at 335 nm (c) luminescence spectra of compound 1 in water upon excitation at 272 nm.

**Determination of quantum yield:**

\[
Q_f^i = \frac{F_i f_s n_i^2}{F_s f_i n_s^2} Q_f^s
\]

where \(Q_f^i\) and \(Q_f^s\) are the fluorescence QYs of the sample and that of the standard, respectively; \(F_i\) and \(F_s\) are the integrated intensities (areas) of sample and standard spectra, respectively; \(f_s\) and \(f_i\) are the absorbance factor of standard and sample, respectively; the refractive indices of the sample and reference solution are \(n_i\) and \(n_s\), respectively.

\[
Q_f^i = \frac{20601 \times 0.21 \times 1.33^2}{37475 \times 0.24 \times 1.38^2} \times 0.3
\]

\[
Q_f^i = 0.13
\]
Fig. S18: Absorption spectra of compound 1 and compound 1 + 20 µM Zn$^{2+}$ in aqueous solution. It is also be noted that with the coordination of Zn$^{2+}$ ion, the absorption bands at 270 nm changes its shape which is the clear indication of increase in rigidity of the structure.
Fig. S19: Linear region of luminescence intensity (at 365 nm) of compound 1 upon addition of Zn\(^{2+}\) (R\(^2\) = 0.98876).

**Calculation of Detection Limit**

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<tr>
<th>Blank Reading (only 1)</th>
<th>Fluorescence Intensity</th>
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<tr>
<td>Reading 1</td>
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<td>Reading 2</td>
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<td>Reading 3</td>
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<td>Reading 4</td>
<td>767</td>
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<td>Reading 5</td>
<td>776</td>
</tr>
<tr>
<td>Standard deviation(σ)</td>
<td>14.59</td>
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<table>
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<tr>
<th>Standard Deviation (σ)</th>
<th>14.59</th>
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<tbody>
<tr>
<td>Slope from Graph (m)</td>
<td>142.6 μM(^{-1})</td>
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</table>

Thus, Limit of Detection (LOD) = \(3σ/m = (3 \times 14.59)/142.6 = 0.30 \mu M = 19\) ppb
Fig. S20: Emission spectra of the compound 1 dispersed in water upon addition of 5 μM solution of Co$^{2+}$ sequentially in two equal portion (2.5 μM in each portion) followed by 5 μM solution of Zn$^{2+}$ in similar way ($\lambda_{ex} = 280$ nm). The addition cycles were repeated for two more times. The final concentration of analytes solution (Co$^{2+}$ and Zn$^{2+}$) are as below: (a) 0 μM Co$^{2+}$ + 0 μM Zn$^{2+}$, (b) 2.5 μM Co$^{2+}$ + 0 μM Zn$^{2+}$, (c) 5 μM Co$^{2+}$ + 0 μM Zn$^{2+}$, (d) 5 μM Co$^{2+}$ + 2.5 μM Zn$^{2+}$, (e) 5 μM Co$^{2+}$ + 5 μM Zn$^{2+}$, (f) 7.5 μM Co$^{2+}$ + 5 μM Zn$^{2+}$, (g) 10 μM Co$^{2+}$ + 5 μM Zn$^{2+}$, (h) 10 μM Co$^{3+}$ + 7.5 μM Zn$^{2+}$, (i) 10 μM Co$^{2+}$ + 10 μM Zn$^{2+}$, (j) 12.5 μM Co$^{2+}$ + 10 μM Zn$^{2+}$, (k) 15 μM Co$^{2+}$ + 10 μM Zn$^{2+}$, (l) 15 μM Co$^{3+}$ + 12.5 μM Zn$^{2+}$, (m) 15 μM Co$^{2+}$ + 15 μM Zn$^{2+}$. 
Fig. S21: Emission spectra of the compound 1 dispersed in water upon addition of 5 μM solution of Hg$^{2+}$ sequentially in two equal portion (2.5 μM in each portion) followed by 5 μM solution of Zn$^{2+}$ in similar way ($\lambda_{ex} = 280$ nm). The addition cycles were repeated for two more times. The final concentration of analytes solution (Hg$^{2+}$ and Zn$^{2+}$) are as below: (a) 0 μM Hg$^{2+} + 0$ μM Zn$^{2+}$, (b) 2.5 μM Hg$^{2+} + 0$ μM Zn$^{2+}$, (c) 5 μM Hg$^{2+} + 0$ μM Zn$^{2+}$, (d) 5 μM Hg$^{2+} + 2.5$ μM Zn$^{2+}$, (e) 5 μM Hg$^{2+} + 5$ μM Zn$^{2+}$, (f) 7.5 μM Hg$^{2+} + 5$ μM Zn$^{2+}$, (g) 10 μM Hg$^{2+} + 5$ μM Zn$^{2+}$, (h) 10 μM Hg$^{2+} + 7.5$ μM Zn$^{2+}$, (i) 10 μM Hg$^{2+} + 10$ μM Zn$^{2+}$, (j) 12.5 μM Hg$^{2+} + 10$ μM Zn$^{2+}$, (k) 15 μM Hg$^{2+} + 10$ μM Zn$^{2+}$, (l) 15 μM Hg$^{2+} + 12.5$ μM Zn$^{2+}$, (m) 15 μM Hg$^{2+} + 15$ μM Zn$^{2+}$.
Fig. S22: Emission spectra of the compound 1 dispersed in water upon addition of 5 μM solution of Ni$^{2+}$ sequentially in two equal portion (2.5 μM in each portion) followed by 5 μM solution of Zn$^{2+}$ in similar way ($\lambda_{ex} = 280$ nm). The addition cycles were repeated for two more times. The final concentration of analytes solution (Ni$^{2+}$ and Zn$^{2+}$) are as below: (a) 0 μM Ni$^{2+}$ + 0 μM Zn$^{2+}$, (b) 2.5 μM Ni$^{2+}$ + 0 μM Zn$^{2+}$, (c) 5 μM Ni$^{2+}$ + 0 μM Zn$^{2+}$, (d) 5 μM Ni$^{2+}$ + 2.5 μM Zn$^{2+}$, (e) 5 μM Ni$^{2+}$ + 5 μM Zn$^{2+}$, (f) 7.5 μM Ni$^{2+}$ + 5 μM Zn$^{2+}$, (g) 10 μM Ni$^{2+}$ + 5 μM Zn$^{2+}$, (h) 10 μM Ni$^{2+}$ + 7.5 μM Zn$^{2+}$, (i) 10 μM Ni$^{2+}$ + 10 μM Zn$^{2+}$, (j) 12.5 μM Ni$^{2+}$ + 10 μM Zn$^{2+}$, (k) 15 μM Ni$^{2+}$ + 10 μM Zn$^{2+}$, (l) 15 μM Ni$^{2+}$ + 12.5 μM Zn$^{2+}$, (m) 15 μM Ni$^{2+}$ + 15 μM Zn$^{2+}$. 
Fig. S23: Emission spectra of the compound 1 dispersed in water upon addition of 5 μM solution of Fe$^{2+}$ sequentially in two equal portion (2.5 μM in each portion) followed by 5 μM solution of Zn$^{2+}$ in similar way ($\lambda_{ex} = 280$ nm). The addition cycles were repeated for two more times. The final concentration of analytes solution (Fe$^{2+}$ and Zn$^{2+}$) are as below: (a) 0 μM Fe$^{2+} + 0$ μM Zn$^{2+}$, (b) 2.5 μM Fe$^{2+} + 0$ μM Zn$^{2+}$, (c) 5 μM Fe$^{2+} + 0$ μM Zn$^{2+}$, (d) 5 μM Fe$^{2+} + 2.5$ μM Zn$^{2+}$, (e) 5 μM Fe$^{2+} + 5$ μM Zn$^{2+}$, (f) 7.5 μM Fe$^{2+} + 5$ μM Zn$^{2+}$, (g) 10 μM Fe$^{2+} + 5$ μM Zn$^{2+}$, (h) 10 μM Fe$^{2+} + 7.5$ μM Zn$^{2+}$, (i) 10 μM Fe$^{2+} + 10$ μM Zn$^{2+}$, (j) 12.5 μM Fe$^{2+} + 10$ μM Zn$^{2+}$, (k) 15 μM Fe$^{2+} + 10$ μM Zn$^{2+}$, (l) 15 μM Fe$^{2+} + 12.5$ μM Zn$^{2+}$, (m) 15 μM Fe$^{2+} + 15$ μM Zn$^{2+}$.
Fig. S24: Emission spectra of the compound 1 dispersed in water upon addition of 5 µM solution of Cu\textsuperscript{2+} sequentially in two equal portion (2.5 µM in each portion) followed by 5 µM solution of Zn\textsuperscript{2+} in similar way (λ\textsubscript{ex} = 280 nm). The addition cycles were repeated for two more times. The final concentration of analytes solution (Cu\textsuperscript{2+} and Zn\textsuperscript{2+}) are as below: (a) 0 µM Cu\textsuperscript{2+} + 0 µM Zn\textsuperscript{2+}, (b) 2.5 µM Cu\textsuperscript{2+} + 0 µM Zn\textsuperscript{2+}, (c) 5 µM Cu\textsuperscript{2+} + 0 µM Zn\textsuperscript{2+}, (d) 5 µM Cu\textsuperscript{2+} + 2.5 µM Zn\textsuperscript{2+}, (e) 5 µM Cu\textsuperscript{2+} + 5 µM Zn\textsuperscript{2+}, (f) 7.5 µM Cu\textsuperscript{2+} + 5 µM Zn\textsuperscript{2+}, (g) 10 µM Cu\textsuperscript{2+} + 5 µM Zn\textsuperscript{2+}, (h) 10 µM Cu\textsuperscript{2+} + 7.5 µM Zn\textsuperscript{2+}, (i) 10 µM Cu\textsuperscript{2+} + 10 µM Zn\textsuperscript{2+}, (j) 12.5 µM Cu\textsuperscript{2+} + 10 µM Zn\textsuperscript{2+}, (k) 15 µM Cu\textsuperscript{2+} + 10 µM Zn\textsuperscript{2+}, (l) 15 µM Cu\textsuperscript{2+} + 12.5 µM Zn\textsuperscript{2+}, (m) 15 µM Cu\textsuperscript{2+} + 15 µM Zn\textsuperscript{2+}. 
Fig. S25: Change of percentage in luminescence intensity upon the addition of quenchable metal ions (two steps, 2.5 µM + 2.5 µM) followed by the addition of Zn$^{2+}$ solution (two steps, 2.5 µM + 2.5 µM) and so on.
Fig. S26: (A) Emission spectra of 1 in aqueous solution upon the incremental addition of Zn$^{2+}$ solution in presence of 5 µM of quenchable metal ions solution ($\lambda_{ex} = 280$ nm). (B) Bar diagram showing the luminescence intensity (monitored at 365 nm) of 1 upon the incremental addition of Zn$^{2+}$ solution in presence of 5 µM of each quenchable metal ions solution. The composition and concentration of the system were as follows: (a) 1 in aqueous solution, (b) a + 5 µM Cu$^{2+}$, (c) b + 5 µM Hg$^{2+}$, (d) c + 5 µM Ni$^{2+}$, (e) d + 5 µM Co$^{2+}$, (f) e + 5 µM Fe$^{2+}$, (g) f + 2.5 µM Zn$^{2+}$, (h) g + 5 µM Zn$^{2+}$, (i) g + 7.5 µM Zn$^{2+}$, (j) g + 10 µM Zn$^{2+}$, (k) g + 12.5 µM Zn$^{2+}$, (l) g + 15 µM Zn$^{2+}$, (m) g + 17.5 µM Zn$^{2+}$, (n) g + 20 µM Zn$^{2+}$, (o) g + 22.5 µM Zn$^{2+}$ and (p) g + 25 µM Zn$^{2+}$. 