Supporting Information (SI)

A Coordination Driven ‘heat-set’ Zr-Gel: Efficient Fluorophore Probe for Selective Detection of Fe$^{3+}$, Nitrofuran based Antibiotics and Smart Approach towards UV Protection

Sumit Mondal†, and Debajit Sarma*†

†Department of Chemistry, Indian Institute of Technology Patna, Bihar 801106, India

*E-mail: debajit@iitp.ac.in
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Methods:
Time-resolved PL measurements:

Fitting either a single-exponential or a bi-exponential function to the ensuing lifetime decays is demonstrated by equation S1, where the reduced $\chi^2$ is used to determine the virtue of the fitting.

$$I_t = A + \sum_{i=1}^{n} B_i \exp\left(-\frac{t}{\tau_i}\right) \quad \text{equation S1}; \text{ where } n \text{ is } 1 \text{ or } 2$$

In order to determine the average lifetime, we employ the fitted parameters, which include the lifetime components $\tau_i$’s and their respective relative contributions, $B_i$’s, as shown in equation S2:

$$\tau_{avg} = \frac{\sum_{i=1}^{n} B_i \tau_i^2}{\sum_{i=1}^{n} B_i \tau_i} \quad \text{equation S2}; \text{ where } n \text{ is } 1 \text{ or } 2$$

Characterization:
The Powder X-Ray Diffraction (PXRD) pattern was recorded using a PANalytical X’Pert Pro Diffractometer that ran at 45 mA and 40 kV with Cu K radiation. The $^1$H and $^{13}$C NMR spectra were performed using a Bruker Avance II 400 spectrometer. Using an SDT Q600 (TA Instruments) and a N$_2$ gas flow rate of 100 mL/min, a thermogravimetric analysis (TGA) of the xerogel was carried out. The temperature was raised from room temperature to 800 °C at a rate of 10 °C min$^{-1}$. The surface morphology of the xerogel was examined using a Field Emission Scanning Electron Microscope (FESEM; ZEISS GEMINISEM500 assembled with an energy-dispersive X-ray spectroscopy detector). The xerogel sample was examined using a transmission electron microscope (JEOL-JEM-F200) at a 200 kV potential. The FT-IR spectra of all the samples were recorded using an ATR sampling method on a PerkinElmer Spectrum 400 instrument. The rheological measurements were carried out using a Modular Compact Rheometer by Anton Paar (MCR 302). In order to determine the storage modulus ($G'$) and loss modulus ($G''$), the metallogel was scanned on a parallel plate with a 9-millimeter diameter while being subjected to 0.1% strain. All UV-Vis spectra were performed using a Shimadzu UV2500 spectrophotometer. Utilizing two-sided transparent square-faced quartz cuvettes, solution phase data from the instrument was taken (1 cm path-length). Solid-state UV-Vis spectra were collected on a JASCO V-650 spectrometer. Utilizing a Horiba Jobin Yvon Fluoromax-4 fluorescence spectrophotometer, photoluminescence (PL) spectra were acquired. In order to conduct the dispersed phase fluorescence investigation, a 4 mL four-faced transparent quartz cuvette was used. All the solution and dispersed phase photoluminescence spectra were measured using fresh Milli-Q water. The Edinburgh Instrument (model: lifeSpec II, U.K) of fluorescence spectrophotometer was used for Time-Resolved Photoluminescence (TRPL) analysis. The data was taken using a Hamamatsu MCP PMT (3809U) detector.
NMR data of the H₃TATAB linker:

**Figure S1**: $^1$H-NMR spectrum of the H₃TATAB linker (400 MHz, in DMSO-$d_6$).

**Figure S2**: $^{13}$C-NMR spectrum of the H₃TATAB ligand (400 MHz, in DMSO-$d_6$).
Synthesis, characterization of the metallogel and xerogel:
Table S1: Gelation study in various solvent combinations

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Solvent used</th>
<th>Gelation ability</th>
<th>Temperature</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>DMF/Water</td>
<td>Gel formation happen</td>
<td>90 °C</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>2.</td>
<td>DMF/MeOH</td>
<td>White precipitate</td>
<td>90 °C</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>3.</td>
<td>DMF/EtOH</td>
<td>Little turbidity</td>
<td>90 °C</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>4.</td>
<td>DMSO/Water</td>
<td>Weak gelation</td>
<td>90 °C</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>5.</td>
<td>DMSO/MeOH</td>
<td>White precipitate</td>
<td>90 °C</td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>6.</td>
<td>DMSO/EtOH</td>
<td>Clear solution</td>
<td>90 °C</td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>Solvent</td>
<td>Linker solubility</td>
<td>Result</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>----------</td>
<td>---------------------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>THF</td>
<td>Linker is not soluble</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Hexane</td>
<td>Linker is not soluble</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Chloroform</td>
<td>Linker is not soluble</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Figure S3: Turbidity measurements which correlates with naked eye test and transmittance (100 T% at 500 nm wavelength) at different time interval of the gelation process.

Figure S4: FT-IR analysis of the linker and different time interval gelation process.
Figure S5: DRS spectra analysis of reaction mixtures (in different time interval for sol to gel transition).

Figure S6: Dynamic angular frequency sweep vs. gain modulus (G') and loss modulus (G'') of the Zr-CPG.
Figure S7: Dynamic Strain sweep vs. gain modulus ($G'$) and loss modulus ($G''$) of the Zr-CPG.

Figure S8: PXRD pattern of Zr-CPG xerogel.
Figure S9: TGA analysis of Zr-CPG xerogel.

Figure S10: EDS analysis of the Zr-CPG xerogel with elemental dot mapping image.
Photophysical properties of the Zr-CPG xerogel:

**Figure S11:** Solid state UV-Vis spectra of (a) linker (H$_3$TATAB) and (b) Zr-CPG xerogel.

**Figure S12:** Solid state photoluminescence spectra of (a) linker (H$_3$TATAB) and (b) Zr-CPG xerogel.
Figure S13: Solvent dependent photoluminescence study of the Zr-CPG xerogel.

Figure S14: Leaching test for Zr-CPG xerogel suspension in water.
Quenching behaviour of Zr-CPG’s luminescent peak upon addition of different metal ions (Figure S15a-S15i):

**Figure 15a:** Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Fe$^{2+}$(10 mM, up to 200 µL).

**Figure S15b:** Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Zn$^{2+}$ (10 mM, up to 200 µL).
Figure S15c: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Na⁺ (10 mM, up to 200 μL).

Figure S15d: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Al³⁺ (10 mM, up to 200 μL).
**Figure S15e:** Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Co$^{2+}$ (10 mM, up to 200 μL).

**Figure S15f:** Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Cu$^{2+}$ (10 mM, up to 200 μL).
Figure S15g: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Cr\(^{3+}\) (10 mM, up to 200 μL).

Figure S15h: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Hg\(^{2+}\) (10 mM, up to 200 μL).
**Figure S15i**: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of K⁺ (10 mM, up to 200 μL).

**Figure S15j**: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Ca²⁺ (10 mM, up to 200 μL).
Figure S15k: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Ni$^{2+}$ (10 mM, up to 200 μL).

Figure S15l: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of Cd$^{2+}$ (10 mM, up to 200 μL).
**Figure S16**: Fluorescence intensity changes of Zr-CPG xerogel with a function of Fe$^{3+}$ concentration.

**Fe$^{3+}$ sensing in presence of interference metal ions (Figure S17a-S17l):**

**Figure 17a**: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Fe$^{2+}$ followed by Fe$^{3+}$ in water.
Figure S17b: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Cd$^{2+}$ followed by Fe$^{3+}$ in water.

Figure S17c: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Al$^{3+}$ followed by Fe$^{3+}$ in water.
Figure S17d: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Hg$^{2+}$ followed by Fe$^{3+}$ in water.

Figure S17e: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of K$^+$ followed by Fe$^{3+}$ in water.
Figure S17f: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Na⁺ followed by Fe³⁺ in water.

Figure S17g: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Cr³⁺ followed by Fe³⁺ in water.
Figure S17h: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Cu$^{2+}$ followed by Fe$^{3+}$ in water.

Figure S17i: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Ca$^{2+}$ followed by Fe$^{3+}$ in water.
Figure S17j: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Zn$^{2+}$ followed by Fe$^{3+}$ in water.

Figure S17k: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Co$^{2+}$ followed by Fe$^{3+}$ in water.
Figure S17: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of Ni$^{2+}$ followed by Fe$^{3+}$ in water.

Figure S18: Bar diagram representation of Fe$^{3+}$ quenching in presence of interfering ions.
Recyclability test for Fe\(^{3+}\) sensing:

**Figure S19:** Recyclability of Fe\(^{3+}\) sensing using Zr-CPG xerogel.

**Figure S20:** FT-IR spectra before and after completion of five cycles of NFT sensing.
Fe$^{3+}$ sensing in physiological conditions:

Figure S21: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of NFT in physiological condition.

Quenching behaviour of Zr-CPG’s characteristic luminescent peak upon addition of different antibiotics (Figure S22a-S22h):

Figure S22a: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of SDZ (10 mM, up to 200 μL).
Figure S22b: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of SMZ (10 mM, up to 200 μL).

Figure S22c: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of CAP (10 mM, up to 200 μL).
Figure S22d: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of DTZ (10 mM, up to 200 μL).

Figure S22e: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of RDZ (10 mM, up to 200 μL).
**Figure S22f:** Quenching of the luminescent peak of Zr-CPG xerogel upon addition of ODZ (10 mM, up to 200 μL).

**Figure S22g:** Quenching of the luminescent peak of Zr-CPG xerogel upon addition of NFZ (10 mM, up to 200 μL).
Figure S22h: Quenching of the luminescent peak of Zr-CPG xerogel upon addition of FZD (10 mM, up to 200 μL).

Figure S23: Fluorescence intensity changes of Zr-CPG xerogel with a function of NFT concentration.
NFT sensing in presence of interference antibiotics (Figure S24a-S24f):

**Figure S24a:** Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of SDZ followed by NFT in water.

**Figure S24b:** Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of SMZ followed by NFT in water.
**Figure S24c:** Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of CAP followed by NFT in water.

**Figure S24d:** Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of DTZ followed by NFT in water.
**Figure S24e**: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of RDZ followed by NFT in water.

**Figure S24f**: Quenching behaviour of Zr-CPG xerogel characteristic peak after adding 10 mM solution of ODZ followed by NFT in water.
Figure S25: Quenching efficiency for NFT antibiotic in presence of other antibiotics (interference test).

Recyclability test for NFT sensing:

Figure S26: Recyclability of NFT sensing using Zr-CPG xerogel.
Fluorescence kinetic study for NFT sensing:

![Graph showing quenching efficiency over time for different volumes of NFT (10 µL, 100 µL, 200 µL)].

**Figure S27:** Kinetic study through fluorescence titration method for NFT sensing (variation in different volumes).
Comparison table of Fe³⁺ and NFT sensing for Zr-CPG xerogel with other reported materials:

Table S2: Comparison table for Fe³⁺ sensing of Zr-CPG xerogel with other reported materials.

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Sensor probe</th>
<th>Ksv Value (M⁻¹)</th>
<th>LOD value</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Zr-CPG</td>
<td>7.16×10³</td>
<td>68 ppb</td>
<td>Water</td>
<td>This work</td>
</tr>
<tr>
<td>2.</td>
<td>[Zn₃(bpg)₁.₅(azdc)₃]⁺(DMF)₅.₉·(H₂O)₁₀.₅</td>
<td>2.54 × 10⁴</td>
<td>1.71 ppm</td>
<td>DMF</td>
<td>¹</td>
</tr>
<tr>
<td>3.</td>
<td>[Tb(HL)(DMF)(H₂O)₂]·3H₂O</td>
<td>4.479×10³</td>
<td>1.03 ppm</td>
<td>Water</td>
<td>²</td>
</tr>
<tr>
<td>4.</td>
<td>Al-MIL-53-N₃</td>
<td>6.13 × 10³</td>
<td>0.03 μM</td>
<td>Water</td>
<td>³</td>
</tr>
<tr>
<td>5.</td>
<td>EuL₃</td>
<td>4.1 × 10³</td>
<td>0.0005 mol/L</td>
<td>Water</td>
<td>⁴</td>
</tr>
<tr>
<td>6.</td>
<td>[Zn₂(L₁)₂(HBPT)₂]·H₂O</td>
<td>3.38 × 10⁴</td>
<td>72 ppb</td>
<td>DMF</td>
<td>⁵</td>
</tr>
<tr>
<td>7.</td>
<td>Au NRs</td>
<td>-</td>
<td>100 ppb</td>
<td>Water</td>
<td>⁶</td>
</tr>
<tr>
<td>8.</td>
<td>AuNCs</td>
<td>-</td>
<td>3.5 μM</td>
<td>Water</td>
<td>⁷</td>
</tr>
<tr>
<td>9.</td>
<td>[Cd(p-CNPhHIDC)(4,4'-bipy)₀.₃]ₙ</td>
<td>1.99 × 10³</td>
<td>5 × 10⁻³ M</td>
<td>Water</td>
<td>⁸</td>
</tr>
<tr>
<td>10.</td>
<td>[Zn(p-CNPhHIDC)(4,4'-bipy)]ₙ</td>
<td>1.37 × 10³</td>
<td>5 × 10⁻³ M</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>BTP-1</td>
<td>-</td>
<td>0.74 nM</td>
<td>Water</td>
<td>⁹</td>
</tr>
<tr>
<td>12.</td>
<td>[Zn₂(2,6-NDC)₂(L)ₓG]ₙ</td>
<td>-</td>
<td>0.052 ppm</td>
<td>DMF/Water</td>
<td>¹⁰</td>
</tr>
</tbody>
</table>

Table S3: Comparison table for NFT sensing of Zr-CPG xerogel with other reported materials.

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Sensor probe</th>
<th>Ksv Value (M⁻¹)</th>
<th>LOD value</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Zr-CPG</td>
<td>1.53×10⁴</td>
<td>50 ppb</td>
<td>Water</td>
<td>This work</td>
</tr>
<tr>
<td>2.</td>
<td>Copper nanoclusters</td>
<td>4.3 × 10³</td>
<td>0.73 μM</td>
<td>Phosphate buffer saline solution</td>
<td>¹¹</td>
</tr>
<tr>
<td>3.</td>
<td>Tb-(TATMA)(H₂O)·2H₂O</td>
<td>3.35 × 10⁴</td>
<td>-</td>
<td>Water</td>
<td>¹²</td>
</tr>
<tr>
<td>4.</td>
<td>CTGU-8</td>
<td>9.25 × 10³</td>
<td>52 ppb</td>
<td>Water</td>
<td>¹³</td>
</tr>
<tr>
<td>5.</td>
<td>Tb-AIP MMMs</td>
<td>4.0 × 10⁴</td>
<td>0.30 μM</td>
<td>Water</td>
<td>¹⁴</td>
</tr>
<tr>
<td>6.</td>
<td>Eu-BCA thin-film</td>
<td>1.6 × 10⁴</td>
<td>0.21 μM</td>
<td>Water</td>
<td>¹⁵</td>
</tr>
<tr>
<td>7.</td>
<td>[Zn(IPT)₂]ₙ</td>
<td>1.4 × 10⁴</td>
<td>-</td>
<td>Water</td>
<td>¹⁶</td>
</tr>
<tr>
<td>8.</td>
<td>[Cd(tptc)₁₀.₅(bpy)]ₙ</td>
<td>7.63 × 10³</td>
<td>184 ppb</td>
<td>Water</td>
<td>¹⁷</td>
</tr>
<tr>
<td>9.</td>
<td>Zn(L)(aip)·(H₂O)</td>
<td>-</td>
<td>100 ppm</td>
<td>Water</td>
<td>¹⁸</td>
</tr>
<tr>
<td>10.</td>
<td>Zn(L)(ip)·(DMF)(H₂O)₁.₅</td>
<td>-</td>
<td>80 ppm</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Zn(L)(HBTC)·(H₂O)₂</td>
<td>-</td>
<td>45 ppm</td>
<td>Water</td>
<td></td>
</tr>
</tbody>
</table>
Fluorescence quenching mechanism explanation:

Table S4: Average excited-state lifetime ($<\tau>$) values of pristine Zr-CPG after the addition of 10 mM aqueous solution of Fe$^{3+}$ ion and NFT.

<table>
<thead>
<tr>
<th></th>
<th>$B_1$ (%)</th>
<th>$B_2$ (%)</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\chi^2$</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-CPG</td>
<td>45.89</td>
<td>54.11</td>
<td>0.69</td>
<td>2.76</td>
<td>1.04</td>
<td>2.40</td>
</tr>
<tr>
<td>Zr-CPG after adding Fe$^{3+}$</td>
<td>37.41</td>
<td>62.59</td>
<td>0.41</td>
<td>2.12</td>
<td>1.13</td>
<td>1.94</td>
</tr>
<tr>
<td>Zr-CPG after adding NFT</td>
<td>36.34</td>
<td>66.66</td>
<td>0.47</td>
<td>2.40</td>
<td>1.17</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Figure S28: FT-IR spectra of Zr-CPG xerogel before and after Fe$^{3+}$ sensing.
**Figure S29:** EDS analysis of Zr-CPG xerogel after NFT sensing.

**Figure S30:** FT-IR spectra of Zr-CPG xerogel before and after NFT sensing.
Figure S31: Temperature dependent quenching study (a-c), (d) corresponding line graph to dictate quenching efficiency.
Figure S32: HOMO-LUMO energy levels of the linker (H₃TATAB) and all antibiotics (except NFT).
**Table S5**: HOMO-LUMO energy levels of the linker (H$_3$TATAB) and all antibiotics with calculated band gaps.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HUMO (eV)</th>
<th>LUMO (eV)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$TATAB</td>
<td>-6.51</td>
<td>-2.04</td>
<td>4.47</td>
</tr>
<tr>
<td>NFT</td>
<td>-6.99</td>
<td>-3.34</td>
<td>3.65</td>
</tr>
<tr>
<td>FZD</td>
<td>-6.84</td>
<td>-3.22</td>
<td>3.62</td>
</tr>
<tr>
<td>NFZ</td>
<td>-6.85</td>
<td>-3.30</td>
<td>3.55</td>
</tr>
<tr>
<td>ODZ</td>
<td>-7.14</td>
<td>-3.45</td>
<td>3.69</td>
</tr>
<tr>
<td>RDZ</td>
<td>-7.50</td>
<td>-3.64</td>
<td>3.86</td>
</tr>
<tr>
<td>DTZ</td>
<td>-7.30</td>
<td>-3.56</td>
<td>3.74</td>
</tr>
<tr>
<td>CAP</td>
<td>-7.67</td>
<td>-2.95</td>
<td>4.72</td>
</tr>
<tr>
<td>SMZ</td>
<td>-6.24</td>
<td>-1.26</td>
<td>4.98</td>
</tr>
<tr>
<td>SDZ</td>
<td>-6.30</td>
<td>-1.55</td>
<td>4.75</td>
</tr>
</tbody>
</table>

**Figure S33**: DRS spectra of Zr-CPG.
Reference: