Electronic Supplementary Information

An AIE luminogens-Based Electropolymerized Film: Ultrasensitive Fluorescent Probe for TNP and Fe\textsuperscript{3+} in Water

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1. Experimental Procedures

General

All chemicals and solvents were used as received from commercial sources, unless otherwise noted. Tetrahydrofuran (THF) was dried and distilled under argon atmosphere. $^1$H and $^{13}$C-NMR spectra were obtained using a Varian AV500 MHz NMR spectrometer (Varian, Inc., Palo Alto, CA, USA) with CDCl$_3$ solvent and tetramethylsilylane (TMS) as internal standard. Mass spectra (MS) were recorded on a Thermo MAT95XP-HRMS spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Elemental analysis (EA) was obtained on a Vario elemental analysis cube (Elementar Analysensysteme GmbH, Hanau, Germany). Fluorescence spectra were obtained on an FLS980 spectrometer (Edinburgh Instruments Ltd., UK). Ultraviolet-visible (UV-Vis) absorption spectrum was obtained on a Hitachi U-3900 spectrophotometer (Hitachi Instruments, Inc., Tokyo, Japan). Fourier transform-infrared (FT-IR) spectra were measured using a Bruker Vector 33 spectrometer (KBr pellet; Bruker Corp., Billerica, MA, USA). Dynamic light scattering measurement was using a Particle Size Analyzer-Zetasiser Nano ZS90. The film thickness was measured on a Veeco Dektak 150 profilometer. X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra DLD instrument (Kratos Analytical, Ltd., Manchester, UK) with photoelectrons generated by the nonmonochromatic Al-K$_{\alpha}$ irradiation (1486.6 eV). Powder X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray diffractometer (Rigaku Corp., Tokyo, Japan) in a scanning rate of 4°/min at 293K. Atomic force microscopic (AFM) experiments were performed on a SPA 400 (Seiko Instruments USA, Inc., CA, USA) with SPI 3800 probe station. Scanning electron microscopy (SEM) images were measured by a Gemini 500 field emission scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany). Transmission electron microscopic images (TEM) were recorded on a JEM-3010 electron microscope (JEOL Ltd., Tokyo, Japan) with an acceleration voltage of 300 kV. EP films were prepared using a cyclic voltammetry (CV) method with a CHI760D electrochemical workstation (CH Instruments, Inc., Austin, TX, USA) with SPI 3800 probe station. Scanning electron microscopy (SEM) images were measured by a Gemini 500 field emission scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany). Transmission electron microscopic images (TEM) were recorded on a JEM-3010 electron microscope (JEOL Ltd., Tokyo, Japan) with an acceleration voltage of 300 kV. EP films were prepared using a cyclic voltammetry (CV) method with a CHI760D electrochemical workstation (CH Instruments, Inc., Austin, TX, USA). Indium-tin oxide (ITO)-coated glass, Ag/Ag$^+$ and nonaqueous electrode, and titanium plate were used as the working, reference, and counter electrodes, respectively. EP films were produced on ITO-coated glass by multicyclic CV of PhTPECz (0.6 mg/mL) in a mixture of acetonitrile/dichloromethane (DCM; 1/4, v/v) containing the supporting electrolyte of tetrabutylammonium hexafluorophosphate (0.1 M) at room temperature.

Theoretical Calculations

Conformations were optimized employing density functional theory (DFT) at the B3LYP/6-31G (d, p) level. Calculations were carried out using the Gaussian 16 package and the frontier molecular orbital demonstrated using Gauss View 6 software.

Synthetic procedures

PhTPECz: Compound 1 (1.16 g, 1.62 mmol), compound 2 (0.22 g, 0.35 mmol), and a catalyst, Pd(dpdpf)Cl$_2$, (0.01 g, 0.01 mmol) were added to 25 mL of THF under an argon atmosphere and stirred. After 7 mL of NaHCO$_3$ solution (2 M) was added dropwise to the solution in a three-necked round bottom flask, the mixture was stirred at 70°C for 48 h, and then cooled to room temperature. After removing THF under reduced pressure, the mixture was then extracted with DCM and deionized water. The organic phase was collected, filtered, and dried with MgSO$_4$ overnight and DCM removed under reduced pressure. The obtained solid was purified by silica gel column chromatography using DCM/petroleum ether (PE; 1/1, v/v) as an eluent to obtain a yellow solid (0.52 g, 55%).

$^1$H-NMR (600 MHz, CDCl$_3$) δ 8.19 (dd, J = 15.3 and 7.7 Hz, 16H), 7.75–7.69 (m, 8H), 7.63 (dd, J = 15.0 and 8.3 Hz, 16H), 7.60–7.55 (m, 16H), 7.53 (s,8H), 7.52–7.41 (m, 32H), 7.34 (dt, J = 15.1 and 7.2 Hz, 16H), 7.27 (d, J = 13.3 Hz,4H), 7.25–7.20 (m, 16H);$^{13}$C-NMR (151 MHz, CDCl$_3$) δ 141.99, 140.93, 139.96, 139.73, 138.17, 137.31, 136.18, 135.10, 131.03, 129.16, 128.04, 126.37, 125.84, 125.49, 125.08, 119.43, 119.11, and 108.86; MS (MALDI-TOF), m/z: 2671.464 ([M+H]+ calc’d for C$_{200}$H$_{122}$N$_{8}$, 2669.057); Anal. Calc. for C$_{200}$H$_{122}$N$_{8}$: C 90.82, H 4.98, and N 4.19 and found: C 90.84, H 5.12, and N 4.03%.

Detection method

To explore the sensing properties of PhTPECz monomer and polyPhTPECz EP films, the fluorescence spectra of PhTPECz and polyPhTPECz EP films were recorded by adding different concentrations of quenchers to solutions. The polyPhTPECz EP films were immersed in an aqueous solution, after adding NACs or iron chloride for 5 s, then, the fluorescence measurement was taken. The following NACs were chosen for the fluorescence sensing studies: 2,4,6-trinitrophenol (TNP), 2,4-dinitrophenol (DNP), 2-nitrophenol (NP), 2,4,6-trinitrotoluene (TNT), 2-nitrotoluene (2-NT), and nitrobenzene (NB). The probe sensitivity was estimated by the Stern-Volmer constant ($K_v$), which was calculated from the slope of the Stern-Volmer curve, $I_0/I=K_v[Q]$. The $I_0$ was the original fluorescence intensity, $I$ the fluorescence intensity after exposure in quencher, and $[Q]$ the quencher concentration. Calculation of the limit of detection (LOD) was based on the fluorescence titration using the equation LOD = 3σ/m, where $\sigma$ was the standard deviation of the blank solution and $m$ the calibration curve slope between the fluorescence intensity change and quencher concentration.
Probe utility in TNP vapor detection was explored by placing TNP powder into the bottom of quartz cell for 60 min. After a constant TNP vapor was reached, the polyPhTPECz EP film was exposed to the saturated TNP vapor at room temperature and the fluorescence spectrum recorded at different time intervals.

Reusability was demonstrated, after exposing a film to TNP solution and vapor, by washing the polyPhTPECz film with ethanol for three times, dried under vacuum for 50°C for 4 h, and then reused in the next-round sensing to explore reusability. Film reusability in Fe$^{3+}$ detection was explored by washing EP films with ethylene diaminetetraacetic acid after being exposed to Fe$^{3+}$ and then dried and used again to detect Fe$^{3+}$.

Scheme S1. Synthetic routes for PhTPECz.

Figure S1. The $^1$H NMR spectrum of PhTPECz
Figure S2 The $^{13}$C NMR spectrum of PhTPECz

Figure S3 The MS (MALDI-TOF) spectrum of PhTPECz

Figure S4. The emission images of PhTPECz in THF and THF/water mixtures with different water fractions (under the illumination of 365 nm UV light at room temperature).
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Figure S22. The fluorescence lifetime decay curves of the polyPhTPECz films with or without the addition of Fe^{3+}.
Figure S23. The scheme of sensing mechanism of polyPhTPECz to TNP and Fe$^{3+}$.

Figure S24. The titration curves of polyPhTPECz EP films in the Fe$^{3+}$ aqueous solution.
Table S1 XPS data showing the binding energy for different elements present in the polyPhTPECz EP films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s</th>
<th>N1s</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C-C</td>
<td>C-N</td>
</tr>
<tr>
<td>Ep films</td>
<td>284.7</td>
<td>285.1</td>
</tr>
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</table>

Table S2 Fluorescence quenching data for TNP vapor from different literature.

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Fluorescence quenching rate (exposure time)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCzDPAn film</td>
<td>30% (60 s) 70% (240 s)</td>
<td>1</td>
</tr>
<tr>
<td>TCBzC</td>
<td>38.6% (120 s) 45.5% (300 s)</td>
<td>2</td>
</tr>
<tr>
<td>S1</td>
<td>21% (120 s) 80% (600 s)</td>
<td>3</td>
</tr>
<tr>
<td>F5 thin film</td>
<td>40% (60 s) 91% (210 s)</td>
<td>4</td>
</tr>
<tr>
<td>P4 thin film</td>
<td>37% (60 s) 81% (540 s)</td>
<td>5</td>
</tr>
<tr>
<td>polyPhTPECz film</td>
<td>32% (60 s) 73% (180 s)</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table S3 Fluorescence quenching data for detecting Fe³⁺.

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Type of sensor</th>
<th>Detecting system</th>
<th>Ksv</th>
<th>LOD</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYTPAG2 films</td>
<td>film</td>
<td>aqueous solution</td>
<td>4.5×10⁴ M⁻¹</td>
<td>0.085 μM</td>
<td>6</td>
</tr>
<tr>
<td>Sensor 1</td>
<td>solution</td>
<td>aqueous solution</td>
<td>4.31×10³ M⁻¹</td>
<td>6.95 μM</td>
<td>7</td>
</tr>
<tr>
<td>T3</td>
<td>solution</td>
<td>aqueous solution</td>
<td>1.8×10⁶ M⁻¹</td>
<td>0.36 μM</td>
<td>8</td>
</tr>
<tr>
<td>Probe 1</td>
<td>solution</td>
<td>aqueous solution</td>
<td>×</td>
<td>0.186 μM</td>
<td>9</td>
</tr>
<tr>
<td>DPYBT</td>
<td>solution</td>
<td>THF solution</td>
<td>×</td>
<td>3.04 μM</td>
<td>10</td>
</tr>
<tr>
<td>Fe-P-1</td>
<td>solution</td>
<td>aqueous media</td>
<td>×</td>
<td>0.8 ppb (14 nM)</td>
<td>11</td>
</tr>
<tr>
<td>Fe₂O₅@ZnO@L-Cys</td>
<td>nanoparticles</td>
<td>water</td>
<td>×</td>
<td>5 nM</td>
<td>12</td>
</tr>
<tr>
<td>Phen-MDI-CA</td>
<td>Solution</td>
<td>water</td>
<td>×</td>
<td>2.6 ppb (46 nM)</td>
<td>13</td>
</tr>
<tr>
<td>CD-based fluorescent probe</td>
<td>solution</td>
<td>buffer solution</td>
<td>×</td>
<td>0.28 μM</td>
<td>14</td>
</tr>
<tr>
<td>polyPhTPECz film</td>
<td>film</td>
<td></td>
<td>7.82×10⁴ M⁻¹</td>
<td>10.0 nM</td>
<td>This work</td>
</tr>
</tbody>
</table>

REFERENCES
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