Supporting Information

A new ionophore for chemical sensing of F\textsuperscript{-}, CN\textsuperscript{-} and Co\textsuperscript{2+} using voltammetric, colorimetric and spectrofluorimetric techniques

Rashmi Sharma, Manmohan Chhibber, Susheel K Mittal*

School of Chemistry & Biochemistry
Thapar University, Patiala, India-147004.
E-mail: smittal@thapar.edu

Synthesis Procedure

Compound (TPEI), was prepared by reacting 2-hydroxy-1-naphtaldehyde with (b), 4-(3-(4-aminophenoxy)phenoxy)benzenamine by following steps:

**Synthesis of compound 1,3-bis(2-nitrophenoxy)benzene (a)**

To a solution of 1-fluoro-2-nitrobenzene (1.57 mL, 41.9 mmol) in DMF (25 mL) were added K\textsubscript{2}CO\textsubscript{3} (8.06 g, 83.9 mmol), resorcinol (2.0 g, 26.3 mmol) and 18-crown-6 (36 mg, 0.2 mmol). The mixture was stirred at room temperature for 12 h. After the reaction is complete (Thin Layer Chromatography monitoring), the reaction mixture was diluted with dichloromethane (100 mL), washed with water (50 mL), 1 N NaOH (3×10 mL), water (until neutral to litmus paper), brine and dried over Na\textsubscript{2}SO\textsubscript{4}. Evaporation of the organic solvent gave yellow solid which was purified using SiO\textsubscript{2} column chromatography and solvent (Pet. ether/ethyl acetate = 95:05) to afford product (a). Yield: 89.75%.

1,3-bis(2-nitrophenoxy)benzene : Melting point: 105-106\degree C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 6.73 (t, \(J = 2.3\) Hz, 1H), 6.8 (dd, \(J = 10.5, 2.7\)Hz, 2H), 7.2 (m, 2H), 7.3 (t, \(J = 9.2\)Hz, 1H), 7.5 (m, 2H), 7.9 (dd, \(J = 11.9, 2.7\)Hz, 2H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}): \(\delta\)109.5, 114.4, 121.2, 123.9, 125.8, 131.0, 134.4, 149.7, 157.3.

**Synthesis of 2-(3-(2-aminophenoxy)phenoxy)benzenamine (b)**
1,3-bis(2-nitrophenoxy)benzene (1.0 g, 4.1 mmol) was dissolved in 100 ml of dried methanol and catalytic amount of Pd/C (10 mg) was added. The solution was stirred at room temperature for 2 hours in the presence of H₂ gas. The yellow color was slowly disappeared that indicates the reduction of nitro group. Finally Pd/C was filtered off from reaction mixture. The solvent was evaporated using rota-vapor and product was obtained. Yield: 80%.

2-(3-(2-aminophenoxy)phenoxy)benzenamine: **Melting point:** 110-112°C. **¹H NMR (400 MHz, CDCl₃):** δ 3.65 (bs, 4H), 6.5 (dd, J = Hz, 2H), 6.6 (s, 1H), 6.7 (m, 2H), 6.8 (dd, J = 1.36 Hz, 2H), 6.89 (t, J = 7.76 Hz, 2H), 6.9 (m, 2H), 7.1 (t, J = 8.28 Hz, 1H). **¹³C NMR (CDCl₃):** δ 158.8, 142.4, 138.6, 130.2, 125.1, 120.5, 118.7, 116.5, 110.6, 106.1.

**Synthesis of receptor (TPEI)**

Aldehyde (2.2 mmol, 2-hydroxy naphthaldehyde) was dissolved in ethanol (30 ml) and stirred at room temperature. To this solution, ethanol solution (5 ml) of 2-(3-(2-aminophenoxy)phenoxy)benzenamine (1 mmol) was added drop-wise under stirring. The resultant reaction mixture was refluxed for 2-3 h. Then the reaction mixture was brought to room temperature and the product was precipitated out. The formed precipitate was filtered and washed with ethanol and dried under vacuum. Yield: 85%.

**(TPEI):** **Melting Point:** 150-151 °C. **¹H NMR (400 MHz, CDCl₃):** δ 15.4 (s, 1H), 9.3 (s, 2H), 8.1 (d, J = 8.2 Hz, 2H), 7.8 (d, J = 9.1 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.5 (m, 2H), 7.36 (m, 7H), 7.13 (m, 6H) 6.78 (m, 3H). **¹³C NMR (CDCl₃):** δ 168.2, 158.8, 155.2, 155.0, 141.7, 136.2, 132.9, 130.6, 129.3, 128.0, 127.3, 123.5, 121.8, 121.6, 120.2, 118.8, 113.3, 109.3, 108.5. **m/z:** 601.2 observed (calcd. 600.6)
Fig. S1 ESI-Mass spectra of TPEI.

Fig. S1a ESI-Mass spectra of TPEI-Co$^{2+}$ complex.

Fig. S1b Job’s plot of TPEI with Co$^{2+}$ showing 1:1 stoichiometry.

Fig. S2 UV-vis variation of absorption of TPEI upon addition of Co$^{2+}$ (50 equivalents) with various competing ions (50 equivalents) at 675 nm.

Fig. S3 Job’s plot of TPEI with F$^-$ showing 1:1 stoichiometry.

Fig. S4 Job’s plot of TPEI with CN$^-$ showing 1:2 stoichiometry.

Fig. S5 Fluorescence spectra response of TPEI (10 µM) upon addition of CN$^-$ (50 equiv.) in the absence and presence of 50 equiv. of various competing anions.

Fig. S6 Differential Pulse Voltammogram of TPEI receptor solution (10$^{-5}$M) and on addition of Co$^{2+}$, F$^-$ and CN$^-$ (10 equivalents each) at pH 7.0 ± 0.1 (10 mM HEPES in CH$_3$CN: H$_2$O 95: 5, v: v), 0.1M TBAPF$_6$, scan rate: 50mV/sec.

Fig. S7 Calibration plot of peak current v/s concentration of cobalt ions.

Fig. S8 Calibration plot of peak current v/s concentration of fluoride ions.

Fig. S9 Calibration plot of peak current v/s concentration of cyanide ions.

Fig. S10 Voltammogram showing the interference of CN$^-$ in detection of F$^-$ and selectivity of CN$^-$ over F$^-$ when added in equal concentrations into TPEI solution.

Fig. S11 $^1$H NMR titrations of TPEI with F$^-$ and CN$^-$ in CDCl$_3$.

Table S1 Peak potential of TPEI receptor solution in the presence of cobalt ion (10 equivalents) and interfering ion (10 equivalents).
Fig. S1 ESI-Mass spectra of TPEI.
Fig. S1a ESI-Mass spectra of TPEI-Co^{2+} complex.
**Fig. S1b** Job’s plot of TPEI with Co$^{2+}$ showing 1:1 stoichiometry.

**Fig. S2** UV-vis Variation of absorption of TPEI upon addition of Co$^{2+}$ (50 equivalents) with various competing ions (50 equivalents) at 675 nm.
**Fig. S3** Job’s plot of TPEI with F⁻.

**Fig. S4** Job’s plot of TPEI with CN⁻.
Fig. S5 Fluorescence spectra response of TPEI (10 µM) upon addition of CN− (50 equiv.) in the absence and presence of 50 equiv. of various competing anions.

Fig. S6 Differential Pulse Voltammogram of TPEI receptor solution (10⁻⁵M) and on addition of Co²⁺, F⁻ and CN⁻ (10 equivalents each) at pH 7.0 ± 0.1 (10 mM HEPES in CH₃CN: H₂O 95: 5, v: v), 0.1M TBAPF₆, scan rate: 50mV/sec.
Fig. S7 Calibration plot of peak current v/s concentration of cobalt ions.

Fig. S8 Calibration plot of peak current v/s concentration of fluoride ions.
**Fig. S9** Calibration plot of peak current v/s concentration of cyanide ions.

**Fig. S10** Voltammogram showing the interference of CN⁻ in detection of F⁻ and selectivity of CN⁻ over F⁻ when added in equal concentrations into TPEI solution.
Figure S11 $^1$H NMR titrations of TPEI with $F^-$ and $CN^-$ in CDCl$_3$. 
**Table S1** Peak potential of TPEI receptor solution in the presence of cobalt ion (10 equivalents) and interfering ions (10 equivalents).

<table>
<thead>
<tr>
<th>Metal studied</th>
<th>TPEI ligand</th>
<th>E_{pa1} (V)</th>
<th>E_{pa2} (V)</th>
<th>E_{pa3} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co^{2+} only</td>
<td>TPEI</td>
<td>0.55</td>
<td>0.78</td>
<td>--</td>
</tr>
<tr>
<td>Co^{2+} +K^{+}</td>
<td>TPEI</td>
<td>0.60</td>
<td>0.80</td>
<td>0.95</td>
</tr>
<tr>
<td>Co^{2+} +Mg^{2+}</td>
<td>TPEI</td>
<td>0.61</td>
<td>0.81</td>
<td>0.96</td>
</tr>
<tr>
<td>Co^{2+} +Ni^{2+}</td>
<td>TPEI</td>
<td>0.62</td>
<td>0.81</td>
<td>0.96</td>
</tr>
<tr>
<td>Co^{2+} +Ca^{2+}</td>
<td>TPEI</td>
<td>0.62</td>
<td>0.80</td>
<td>0.98</td>
</tr>
<tr>
<td>Co^{2+} +Ag^{+}</td>
<td>TPEI</td>
<td>0.62</td>
<td>0.81</td>
<td>0.95</td>
</tr>
<tr>
<td>Co^{2+} +Cu^{2+}</td>
<td>TPEI</td>
<td>0.61</td>
<td>0.81</td>
<td>0.96</td>
</tr>
<tr>
<td>Co^{2+} +Zn^{2+}</td>
<td>TPEI</td>
<td>0.60</td>
<td>0.79</td>
<td>0.95</td>
</tr>
<tr>
<td>Co^{2+} +Ba^{2+}</td>
<td>TPEI</td>
<td>0.59</td>
<td>0.81</td>
<td>0.93</td>
</tr>
<tr>
<td>Co^{2+} +Hg^{2+}</td>
<td>TPEI</td>
<td>0.61</td>
<td>0.81</td>
<td>0.97</td>
</tr>
<tr>
<td>Co^{2+} +Cd^{2+}</td>
<td>TPEI</td>
<td>0.62</td>
<td>0.80</td>
<td>0.95</td>
</tr>
<tr>
<td>Co^{2+} +Al^{3+}</td>
<td>TPEI</td>
<td>0.62</td>
<td>0.81</td>
<td>0.98</td>
</tr>
<tr>
<td>Co^{2+} +Pb^{2+}</td>
<td>TPEI</td>
<td>0.61</td>
<td>0.81</td>
<td>0.96</td>
</tr>
<tr>
<td>Co^{2+} +Na^{+}</td>
<td>TPEI</td>
<td>0.62</td>
<td>0.81</td>
<td>0.98</td>
</tr>
<tr>
<td>Co^{2+} +Li^{2+}</td>
<td>TPEI</td>
<td>0.62</td>
<td>0.80</td>
<td>0.98</td>
</tr>
</tbody>
</table>