Supporting Information

Pentaquinone based Probe for Nanomolar Detection of Zinc Ion: Chemosensing Ensemble as Antioxidant

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General Experimental Methods

Quantum yield
Florescence quantum yield\(^1\) was determined using optically matching solutions of diphenylanthracene (\(\Phi_{fr} = 0.9\) in ethanol) as standard at an excitation wavelength of 360 nm and quantum yield is calculated using the equation:

\[
\Phi_{fs} = \Phi_{fr} \times \left(1 - 10^{-\text{ArLr}} / 1 - 10^{-\text{AsLs}}\right) \times (N_s^2 / N_r^2) \times (D_s / D_r)
\]

\(\Phi_{fs}\) and \(\Phi_{fr}\) are the radiative quantum yields of sample and the reference respectively, \(\text{As}\) and \(\text{Ar}\) are the absorbance of the sample and the reference respectively, \(D_s\) and \(D_r\) the respective areas of emission for sample and reference. \(L_s\) and \(L_r\) are the lengths of the absorption cells of sample and reference respectively. \(N_s\) and \(N_r\) are the refractive indices of the sample and reference solutions (pure solvents were assumed) respectively.

Calculation of Anti-oxidation activity
Oxidation (O) % = \(\left(\frac{I_0 - I_i}{I_0 - I_c}\right) \times 100\)

Where
- \(I_i\) = Fluorescence intensity of \(\beta\)-hydroxy naphthaldehyde in the presence of the 3a-Zn + H\(_2\)O\(_2\) or in the presence of the PG + H\(_2\)O\(_2\).
- \(I_0\) = Fluorescence intensity of \(\beta\)-hydroxy naphthaldehyde in the absence of any analyte.
- \(I_c\) = Fluorescence intensity of \(\beta\)-hydroxy naphthaldehyde in the presence of H\(_2\)O\(_2\).

Anti-oxidation activity \(A = (100 - O)\) %

Figure S1. $^1$H NMR (CDCl$_3$, 300 MHz, ppm) spectrum of 3a.
**Figure S2.** IR spectrum of 3a.
Figure S3. MALDI-TOF mass of 3a.
**Figure S4.** UV-vis spectra of 3a (5 µM) in response to the presence of different metal ions (10 equiv each) in THF.
To determine the detection limit, fluorescence titration of compound 3a with zinc ions was carried out by adding aliquots of zinc solution of minimum concentration and the fluorescence intensity as a function of Zn$^{2+}$ ions added was then plotted.

Equation used for calculating detection limit (DL):

$$DL = C_L \times E_T$$

$C_L$ = Conc. of Ligand;  $E_T$ = Equiv. of Titrant at which change observed.

Thus;

$$DL = 5 \times 10^{-6} \times 0.007 = 0.0035 \times 10^{-6} = 3.5 \times 10^{-9}$$

or = 3.5 nanomolar

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Figure S6. Job’s plot of 3a with Zn$^{2+}$ ions in THF representing stoichiometry 1:1.
Figure S7. IR spectrum of 3a-Zn.
Figure S8. MALDI-TOF mass of 3a-Zn.

[3a + Zn + H]^+
Figure S9. Fluorescence response of 3a (5 µM) in the presence of various metal ions (0-1.0 equiv) in THF.
Figure S10. $^1$H NMR (CDCl$_3$, 300 MHz, ppm) spectrum of 3b.
Figure S11. Mass spectrum of 3b.
**Figure S12.** Fluorescence spectrum of 3b (5 µM) in THF.

**Figure S13.** Fluorescence response of 3b (5 µM) in the presence of Zn$^{2+}$ ions (0-50 equiv.) in THF.
**Figure S14.** Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of H₂O₂ (183 μM) in presence of 2 μM of TP in THF.

**Figure S15.** Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of H₂O₂ (183 μM) in presence of 2 μM of PG in THF.
Figure S16. Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of H₂O₂ (95 μM) in presence of 2 μM of BHA in THF.

Figure S17. Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of H₂O₂ (142 μM) in presence of 2 μM of BHT in THF.
Figure S18. Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of H₂O₂ (95 μM) in presence of 2 μM of SA in THF.
Figure S19. Calculation of anti-oxidation activity

The method of measurement of anti-oxidation activity can be explained as follows:

Oxidation (O) % = \((I_0-I_c/I_0-I_c) \times 100\)

Where \(I_c\) = Fluorescence intensity of β-hydroxy naphthaldehyde in the presence of the 3a-Zn + H\(_2\)O\(_2\) or in the presence of the PG + H\(_2\)O\(_2\).

\(I_0\) = Fluorescence intensity of β-hydroxy naphthaldehyde in the absence of any analyte.

\(I_c\) = Fluorescence intensity of β-hydroxy naphthaldehyde in the presence of H\(_2\)O\(_2\).

Anti-oxidation activity \(A = (100 - O) \%\).

For 3a-Zn
\[
(O) \% = \left(\frac{80.2 - 62.77}{80.2 - 10.74}\right) \times 100
\]
\[
= 0.25 \times 100
\]
\[
= 25.09
\]
\[
A = (100 - O) \% = 74.91
\]

For PG
\[
(O) \% = \left(\frac{80.2 - 48.79}{80.2 - 10.74}\right) \times 100
\]
\[
= 45.22
\]
\[
A = (100 - O) \% = 54.78
\]

For TP
\[
(O) \% = \left(\frac{80.2 - 48.95}{80.2 - 10.74}\right) \times 100
\]
\[
= 44.98
\]
\[
A = (100 - O) \% = 55.02
\]

For BHT
\[
(O) \% = \left(\frac{80.2 - 43.005}{80.2 - 10.74}\right) \times 100
\]
\[
= 0.5354 \times 100
\]
\[
= 53.54
\]
\[
A = (100 - O) \% = 46.46
\]

For BHA
(O) % = \frac{(80.2-24.57)/(80.2-10.74)}{100} 
= 80.08 
A = (100-\text{O}) \% = 19.9 

For SA

(O) % = \frac{(80.2-23.97)/(80.2-10.74)}{100} 
= 80.95 
A = (100-\text{O}) \% = 19.05
Figure S20. Comparison of receptor 3a with Zn$^{2+}$ sensors reported in the literature

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reference</th>
<th>Selectivity/ interference</th>
<th>Detection limit</th>
<th>Peroxide detection with Zn$^{2+}$ ensemble</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T. Mukherjee, J. C. Pessoa, A. Kumar, A. R. Sarkar, <em>Dalton Trans.</em>, 2012, 41, 5260.</td>
<td>Responds to Cr$^{3+}$ and Cd$^{2+}$ also.</td>
<td>$40 \times 10^{-5}$ M</td>
<td>NO</td>
</tr>
<tr>
<td>2</td>
<td>S. Kotha, D. Goyal, S. Banerjee, A. Datta, <em>Analyst</em>, 2012, 137, 2871.</td>
<td>Responds to Hg$^{2+}$ and Cd$^{2+}$ also.</td>
<td>$34 \times 10^{-8}$ M</td>
<td>NO</td>
</tr>
<tr>
<td>10</td>
<td>X. Y. Chen, J. Shi, Y. M. Li, F. L. Wang, X. Wu, Q. X.</td>
<td>Responds to Cd$^{2+}$ also.</td>
<td>*</td>
<td>NO</td>
</tr>
<tr>
<td>No.</td>
<td>Authors</td>
<td>Journal and Volume</td>
<td>Response</td>
<td>Concentration</td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>--------------------</td>
<td>----------</td>
<td>---------------</td>
</tr>
<tr>
<td>11</td>
<td>Y. Xu, Y. Pang</td>
<td><em>Dalton Trans.</em>, 2011, 40, 1503.</td>
<td>Respond to Hg$^{2+}$ and Cu$^{2+}$ also.</td>
<td>*</td>
</tr>
<tr>
<td>13</td>
<td><strong>Receptor 3a</strong></td>
<td></td>
<td>Highly selective to Zn$^{2+}$ ion and no interference with other metal ions.</td>
<td>3.5 × 10$^{-9}$ M</td>
</tr>
</tbody>
</table>

* No data available