Electronic Supplementary Information (ESI)

Two hexaazatriphenylene-pyrene based Hg$^{2+}$ fluorescent chemosensors applicable to test paper detection

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Experimental

1. Materials and general methods

All the starting reagents and chemicals were purchased from commercial sources and used as received. Intermediates 2,7-di-tert-butylpyrene-4,5,9,10-tetraone, 2,7-di-tert-butylpyrene-4,5-dione and 2,3,8,9-tetraphenylpyrazino[2,3-f]quinoxaline-5,6-diamine were prepared according to literature procedures. The solvents used for fluorescence measurements were purified by standard procedures. $^1$H NMR spectra were recorded in CDCl$_3$ on a Bruker 300 MHz NMR spectrometer. High-resolution mass spectra were measured on an IonSpec 7.0T FT-ICR mass spectrometer. IR spectra were recorded on a TENSOR 27 OPUS Fourier transform infrared (FT-IR) spectrometer (Bruker) in the range of 4000−400 cm$^{-1}$ using KBr disks dispersed with sample powders. Elemental analyses (C, H, and N) were tested using a Perkin-Elmer 240C analyzer. Fluorescence spectra were measured at room temperature on a Varian Cary Eclipse fluorescence spectrometer. UV-vis absorption spectra were recorded by a Shimadzu UV-2450 UV-vis spectrophotometer.

2. Characterization data of compound 1

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 1.67 (s, 18H), 7.46 (s, 24H), 7.92 (q, 8H), 7.99 (q, 8H), 8.76 (d, 2H), 10.07 (d, 2H). $^{13}$C NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 31.98, 36.65, 128.50, 128.64, 129.85, 130.34, 138.27, 138.33, 139.36, 139.72, 141.28, 141.79, 152.46, 153.50, 154.35. MS-ESI calcd. for C$_{92}$H$_{63}$N$_{12}$ [M + H]$^+$ 1336.5, found 1336.5. Anal. Calcd. for C$_{92}$H$_{64}$N$_{12}$•2H$_2$O: C, 80.56; H, 5.58; N, 12.25%; Found: C, 80.41; H, 5.47; N, 12.14%. IR (KBr, cm$^{-1}$): 3132, 2917, 2849, 1586, 1472, 1369, 1247, 788, 594, 548.

3. Characterization data of compound 2

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) 1.75 (s, 18H), 7.46 (m, 12H), 7.93 (m, 4H), 8.05 (m, 6H), 8.38 (s, 2H), 10.03 (s, 2H). $^{13}$C NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 32.73, 36.55, 122.01, 124.66, 127.40, 128.48, 128.62, 129.68, 130.38, 131.24, 138.58, 139.38, 139.86, 140.68, 144.25, 149.70, 153.41, 153.87. MS-ESI calcd. for C$_{58}$H$_{42}$N$_6$ [M + H]$^+$ 825.4, found 825.8; calcd. for C$_{116}$H$_{89}$N$_{12}$ [2M + H]$^+$ 1650.7, found 1649.4. Anal. Calcd. for C$_{58}$H$_{42}$N$_6$•3H$_2$O: C, 79.25; H, 5.73; N, 9.56%; Found: C, 79.14; H, 5.76; N, 9.18%. IR (KBr, cm$^{-1}$): 3441, 3056, 2951, 1586, 1473, 1370, 905, 741, 695, 594.
Table S1  The Hg$^{2+}$ responsive chemosensors reported in recent years (2012-2014)

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<th>Detection limit (nM)</th>
<th>Ref.</th>
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<td>This work</td>
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<tr>
<td></td>
<td></td>
<td>3.1 for 2</td>
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<tr>
<td>2</td>
<td>acridinedione</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>anthracene and pyrene</td>
<td>2–4</td>
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</tr>
<tr>
<td>4</td>
<td>rhodamine</td>
<td>3</td>
<td>6</td>
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<tr>
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<tr>
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<td>8</td>
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Table S2  The energies of the frontier orbitals of compound 1 and 2

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<th>LUMO (eV)</th>
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<td>2</td>
<td>−5.462</td>
<td>−2.187</td>
<td>3.274</td>
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Fig. S1  Linear emission intensity change of (a) 1 and (b) 2 as a function of Hg$^{2+}$ concentration. $\lambda_{em}$ is 459 nm for 1 and 529 nm for 2.

Fig. S2  The linear fitting of fluorescence intensity change with $\log[(F_\infty-F)/(F-F_0)] = n\log[Hg^{2+}] + \log\beta$. $n$ is the complex-ratio of 1 or 2 to Hg$^{2+}$, $\beta$ is the stability constant of the formed complex, $F_0$, $F$ and $F_\infty$ are the fluorescence intensities of the solution of 1 or 2 after the addition of none, a given amount and excess amount of Hg$^{2+}$, respectively. (a) [1] = 10 $\mu$M, $\lambda_{em}$ = 459 nm. (b) [2] = 10 $\mu$M, $\lambda_{em}$ = 529 nm.
**Fig. S3**  Job’s plots of (a) 1 and (b) 2 to Hg\(^{2+}\) in CH\(_3\)CN-H\(_2\)O (v/v = 9/1) media obtained by fluorescence measurements.

**Fig. S4**  Possible binding sites of compounds 1 and 2.

**Fig. S5**  Absorption spectra of (a) 1 (50 \(\mu\)M) and (b) 2 (50 \(\mu\)M) in CH\(_3\)CN-H\(_2\)O (v/v = 9/1) media upon the addition of Hg\(^{2+}\) (0–220 \(\mu\)M for 1 and 0–500 \(\mu\)M for 2).
The linear fitting of absorbance change with \( \log\left(\frac{(A_\infty - A)}{(A - A_0)}\right) = n\log[Hg^{2+}] + \log\beta \). \( n \) is the complex-ratio of 1 or 2 to Hg\(^{2+}\), \( \beta \) is the stability constant of the formed complex, \( A_0, A \) and \( A_\infty \) are the absorbances of the solution of 1 or 2 after the addition of none, a given amount and excess amount of Hg\(^{2+}\), respectively. (a) \([1] = 50 \ \mu\text{M}, \lambda = 399 \ \text{nm}\). (b) \([2] = 50 \ \mu\text{M}, \lambda = 364 \ \text{nm}\).

Interfacial plots of the HOMO and LUMO of compounds (a) 1 and (b) 2. The molecular configurations of these compounds were optimized at B3LYP/6-31G(d) level previously. Gray, white and blue atoms of the molecular frameworks indicate the C, H and N atoms, respectively. Red and green parts on the interfacial plots refer to the different phases of the molecular wave functions, for which the isovalue is 0.02 au.
Fig. S8  ESI-MS spectrum of compound 1.

Fig. S9  ESI-MS spectrum of compound 2.
Fig. S10  The $^1$H NMR spectra of (a) 1 and (b) 2.
Fig. S11  The $^{13}$C NMR spectra of (a) 1 and (b) 2.
References


19. J. Weng, Q. Mei, B. Zhang, Y. Jiang, B. Tong, Q. Fan, Q. Ling and W. Huang, *Analyst*, 2013,
138, 6607.


