Supporting Information

Novel water soluble pillar[5]arene and phenazine derivatives self-assembled pseudorotaxane sensor for selective detection of Hg$^{2+}$ and Ag$^{+}$ with high selectivity and sensitivity

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1. Experimental

1.1 Materials and instruments

All reagents were purchased from commercial supplies and used without further purification. Solvents and twice-distilled water were purified by standard methods. Fresh double distilled water was used throughout the experiment. Solutions of metal ions were prepared from the perchlorate salts of Fe$^{3+}$, Hg$^{2+}$, Ag$^+$, Ca$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cr$^{3+}$ and Mg$^{2+}$ ($4 \times 10^{-4}$ M). $^1$H NMR spectra were recorded on a Mercury−600 BB spectrometer at 600 MHz and $^{13}$C NMR spectra were recorded on a Mercury−600 BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsililane (TMS, $\delta$ scale with solvent resonances as internal standards). Low-resolution mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

1.2 General procedure for fluorescence experiments

Fluorescence spectroscopy was carried out keeping the host concentration constant in water solution on a Shimadzu RF-5301PC spectrofluorophotometer.

1.3 General procedure for $^1$H NMR titrations

For $^1$H NMR titrations, three stock solutions were prepared: one of them contained the host only in D$_2$O, the second one contained an appropriate concentration of guest in DMSO-$d_6$. The third one contained an appropriate concentration of host and guest in D$_2$O. Aliquots of the two solutions were mixed directly in NMR tubes.

1.4 Synthesis and characterization of WP5

1.4.1 Synthesis of compound P5

A solution of compound 1 (3.80 g, 10.00 mmol) in 1, 2-dichloroethane (200 mL), paraformaldehyde (0.68 g, 20.00 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (BF$_3$·O(C$_2$H$_5$)$_2$, 1.42 g, 10.00 mmol) was added to
the solution and the mixture was stirred at room temperature for 4 h. A green solution was obtained. After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with petroleummethane/dichloromethane (1:1 v/v) as the eluent to get a white powder compound P5 (1.57 g, 40%). m. p. 124 - 126 °C. 

$^1$H NMR (600 MHz, CDCl$_3$, Fig. S4) $\delta$: 6.86 (s, 10H), 3.96 (s, 20H), 3.76 (d, $J = 8.0$ Hz, 10H), 3.50 (s, 10H), 3.29 (s, 10H), 2.12 (s, 20H), 1.99 (s, 20H). $^{13}$C NMR (150 MHz, CDCl$_3$, Fig. S5) $\delta$: 149.55, 128.15, 67.33, 33.83, 32.09, 30.12 and 28.57. MS: ESI (Fig. S6) m/z for P5 C$_{75}$H$_{104}$K$_2$Br$_{10}$O$_{10}$Na$_6$, found: 2180.89, calcd : 2180.82.

1.5 Synthesis of WP5

The compound P5 (1.00 g, 0.51 mmol) and trimethylamine (33 % in ethanol, 6.89 mL, 25.5 mmol) were added to ethanol (50 mL). The solution was refluxed over night. Then the solvent was removed by evaporation, deionized water (20 mL) was added. After filtration, a clear solution was obtained. Then the water was removed by evaporation to obtain WAP as a white solid (1.28 g, 95%). m. p. 218 - 220 °C. $^1$H NMR (600 MHz, D$_2$O, Fig. S7) $\delta$ 6.78 (s, 11H), 3.82 (d, $J = 38.2$ Hz, 31H), 3.25 (s, 21H), 2.97 (s, 90H), 1.78 (s, 41H). The $^{13}$C NMR spectrum of WAP is shown in Fig. S8. $^{13}$C NMR (150 MHz, D$_2$O) $\delta$: 150.12, 129.22, 116.81, 68.46, 65.87, 52.87, 25.78 and 19.46. HRESI-MS (Fig. S9) m/z for WAP [M - 3Br + 9Na + 2NH$_4$]$^{3+}$ C$_{105}$H$_{198}$Br$_7$N$_{12}$Na$_9$O$_{10}$, found: 848.9418, calcd: 848.9554.
1.6 Synthesis of G

2, 3-Diamino-phenazine ([S1]) (F) (0.42 g, 2.00 mmol), 1-octanal (0.31 g, 2.40 mmol) and catalytic amount of acetic acid (AcOH) were combined in hot absolute DMF (5 mL) (Scheme S2). The solution was stirred under reflux conditions for 8 h, and then the reaction system was poured into 50 mL H₂O and the yellow floccules was filtrated, collected the solid crude product and purified by column chromatography with ethyl acetate / petroleum ether = 20 : 1 (v/v) as eluent, finally got yellow solid 0.47 g, yield: 73.8 % and m. p : 143 - 145°C. ¹H NMR (400 MHz, CDCl₃, Fig. S10) δ 9.63 (s, 1H), 8.55 (s, 1H), 8.21 (s, 4H), 7.77 (m, J = 6.7, 3.4 Hz, 3H), 3.01 (t, J = 7.7 Hz, 2H), 1.94 (m, J = 15.2, 7.5 Hz, 2H), 1.49 – 1.41 (m, 3H), 1.32 (d, J = 14.8 Hz, 4H), 1.37 – 1.15 (m, 2H).

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2 \overset{FeCl₃, HCl}{\underset{r.t. \ H₂O}{\longrightarrow}} \text{product} + \text{product}
\]
Scheme S2. Synthesis of G.

2. ESI-MS spectrum of G-WAP

Fig. S1 ESI-MS spectrum of WAP and G, indication a 1:1 stoichiometry.
3. Determination of detection limit of Ag$^+$. 

![Graph with linear equation and calculations]

Fig. S2 The photograph of the linear range

Linear Equation: $Y = -206.57843 \times X + 671.15235$, 
$R^2 = 0.99892$ 
$S = 2.061 \times 10^8$ 
$\delta = \sqrt{\frac{\sum (F_0 - F_i)^2}{N-1}} = 0.83$ 

$\text{LOD} = K \times \delta / S$, $K=3$ 
$\text{LOD} = 1.20 \times 10^{-8} \text{M}$
4. ESI-MS spectrum of \([G + 2\text{AgClO}_4 + \text{H}]^+\).

Fig. S3 Electrospray ionization mass spectrum of \([G + 2\text{AgClO}_4 + \text{H}]^+\).
**Fig. S4** $^1$H NMR (600 MHz, 298 K) spectra of product P5 in CDCl$_3$.

**Fig. S5** $^{13}$C NMR (150 MHz, 298K) spectra of product P5 in CDCl$_3$. 
Fig. S6 Electrospray ionization mass spectrum of compound P5.

Fig. S7 $^1$H NMR (600 MHz, 298K) spectra of product WAP in D$_2$O.
Fig. S8 $^{13}$C NMR (150MHz, 298K) spectra of product WAP in D$_2$O.

Fig. S9 Electrospray ionization mass spectrum of compound WAP.
**Fig. S10** $^1$H NMR (600 MHz, 298K) spectra of product G.

**Fig. S11** $^{13}$C NMR (150MHz, 298K) spectra of product G.
Fig. S12 Electrospray ionization mass spectrum of compound G.

References: