

Electronic Supplementary Information

Specific ratiometric fluorescent sensing of Hg²⁺ via the formation of mercury(II) barbiturate coordination polymers

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Contents

1. General remarks
2. Synthesis and characterization of **AnB**
3. Influence of pH on the self-aggregation of **AnB**
4. Absorption study on the binding stoichiometry between Hg²⁺ and **AnB**
5. Mass spectrometric evidence for the Hg(II)-**AnB** coordination polymer
6. Dynamic light scattering study on the reaction of **AnB** with Hg²⁺
7. Influence of reaction time and pH on Hg²⁺ sensing

1. General remarks

9-Anthraldehyde, barbituric acid and piperidine were purchased from Sigma-Aldrich Co., Ltd. They were used without any further purification. All other reagents were of analytical grade or better and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance II 400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the residual DMSO peak (2.50 ppm in the ¹H NMR and 39.43 ppm in the ¹³C NMR) and coupling constants (*J*) are reported in Hertz (Hz). Electrospray ionisation (ESI) mass spectra were recorded on a Bruker ESQUIRE-3000⁺ mass spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker-Dalton Reflex III mass spectrometer. Absorption and fluorescence spectra were acquired with a Hitachi U-3900 ultraviolet-visible spectrophotometer and a Hitachi F-7000 fluorophotometer, respectively. Dynamic light scattering (DLS) data were collected from a Malvern Zetasizer Nano-zsMPT-2 particle size and zeta potential analyzer.

2. Synthesis and characterization of AnB (Fig. S1–S3)

A mixture of 9-anthraldehyde (206 mg, 1.0 mmol), barbituric acid (164 mg, 1.0 mmol) and piperidine (1 mL) in ethanol (40 mL) was refluxed under nitrogen atmosphere for about 7 h and then cooled to room temperature to give a red precipitate. The solid was collected by filtration, washed with methanol and dried under vacuum. Yield: 240 mg, 75%. The selected spectroscopic data of **1** are as follows. ^1H NMR (400MHz, DMSO- d_6 , ppm): δ = 8.99 (s, 1H), 8.67 (s, 1H), 8.15 (d, 2H, J = 7.6 Hz), 7.97 (d, 2H, J = 8.8 Hz), 7.57-7.49 (m, 4H). ^{13}C NMR (100MHz, DMSO- d_6 , ppm): δ = 162.85, 160.99, 151.70, 150.98, 131.02, 129.99, 129.15, 128.24, 128.12, 126.70, 126.01, 125.84. ESI-MS: m/z calcd for $[\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_3]^+$, 316.31; found, 316.5.

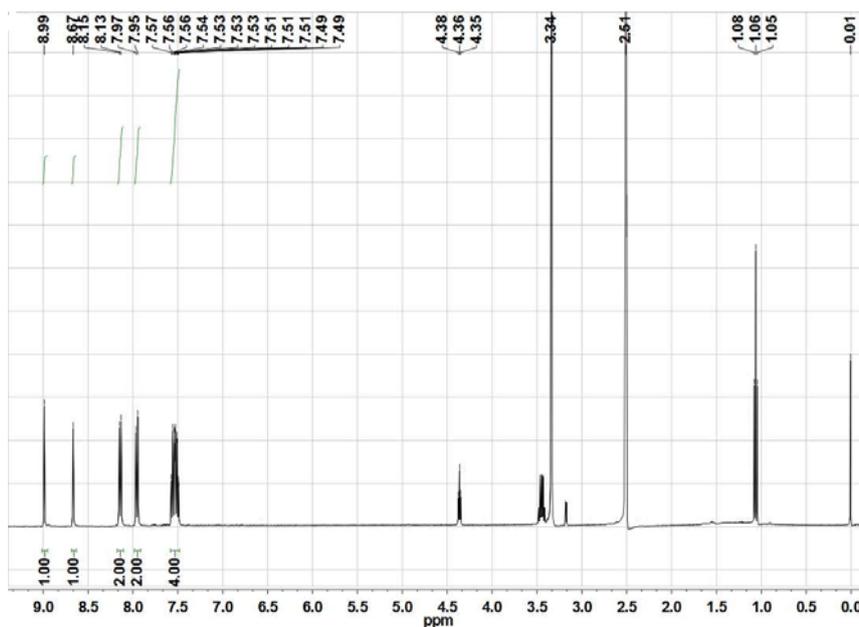


Fig. S1 ^1H NMR spectrum (400MHz, DMSO- d_6) of **AnB**. The signals for N-H were not obtained in DMSO- d_6 because of the hydrogen bonding interaction between the barbitol moieties.

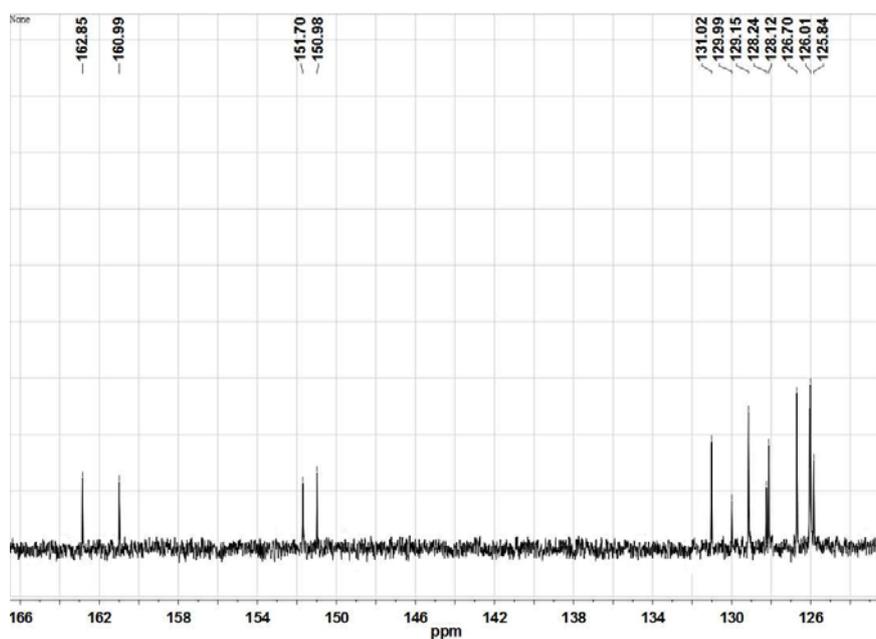


Fig. S2 ^{13}C NMR spectrum (100MHz, DMSO- d_6) of **AnB**.

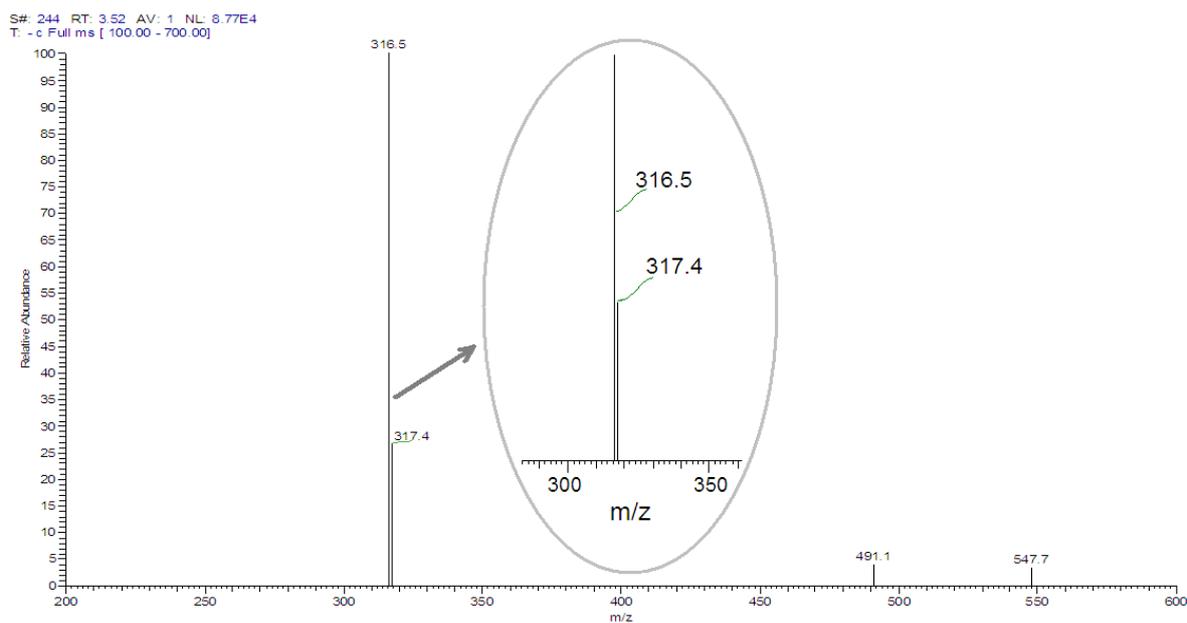


Fig. S3 ESI mass spectrum of AnB.

3. Influence of pH on aggregation of AnB (Fig. S4)

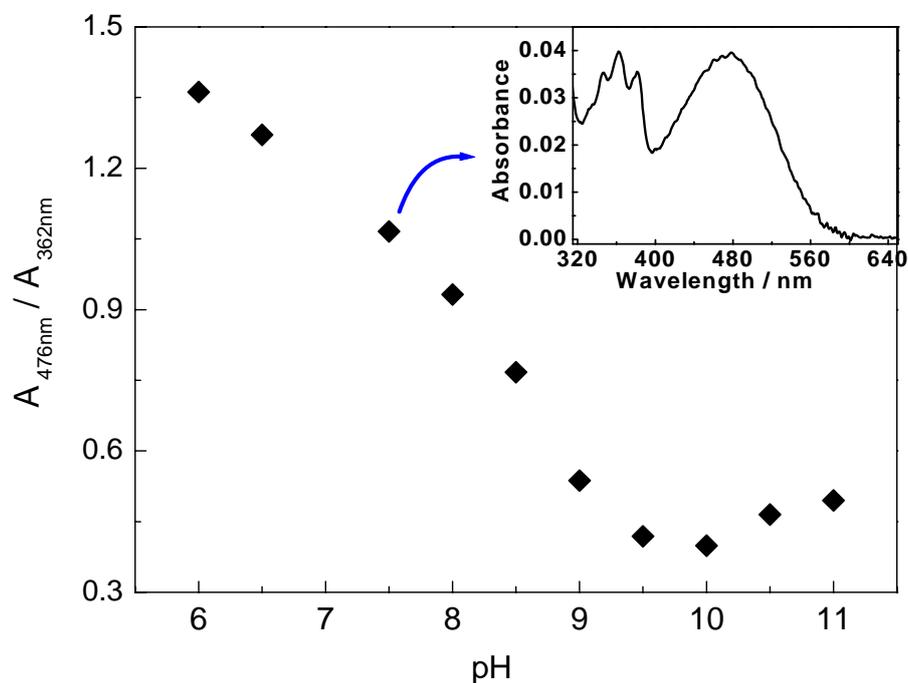


Fig. S4 Influence of pH on absorption of AnB (1.00×10^{-5} M) in aqueous solution. pH 5.8–8.0: buffered by 0.02 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$; pH 8.5–11.0: buffered by 0.02 M $\text{NH}_4\text{Cl-NH}_3$. Inset: absorption spectrum at pH 7.5.

4. Absorption spectral study of the stoichiometry between Hg^{2+} and AnB (Fig. S5)

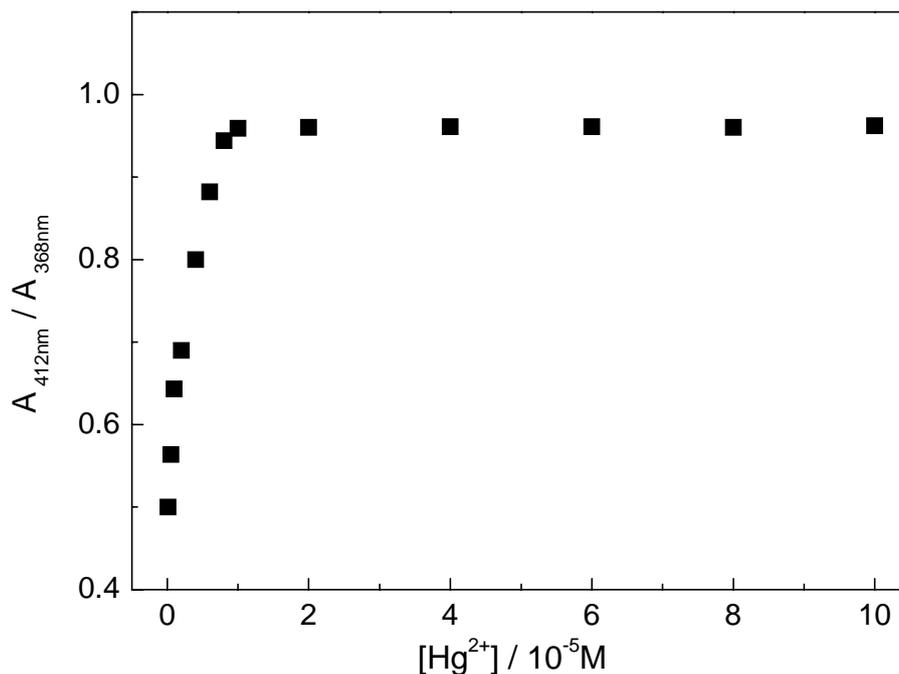


Fig. S5 Absorbance ratio (412 nm to 368 nm) of AnB ($1.00 \times 10^{-5} \text{ M}$) as a function of Hg^{2+} concentration in aqueous solution. pH: 9.0, buffered by 0.02 M $\text{NH}_4\text{Cl-NH}_3$.

5. Mass spectrometric evidence for Hg^{2+} -AnB coordination polymer (Fig. S6)

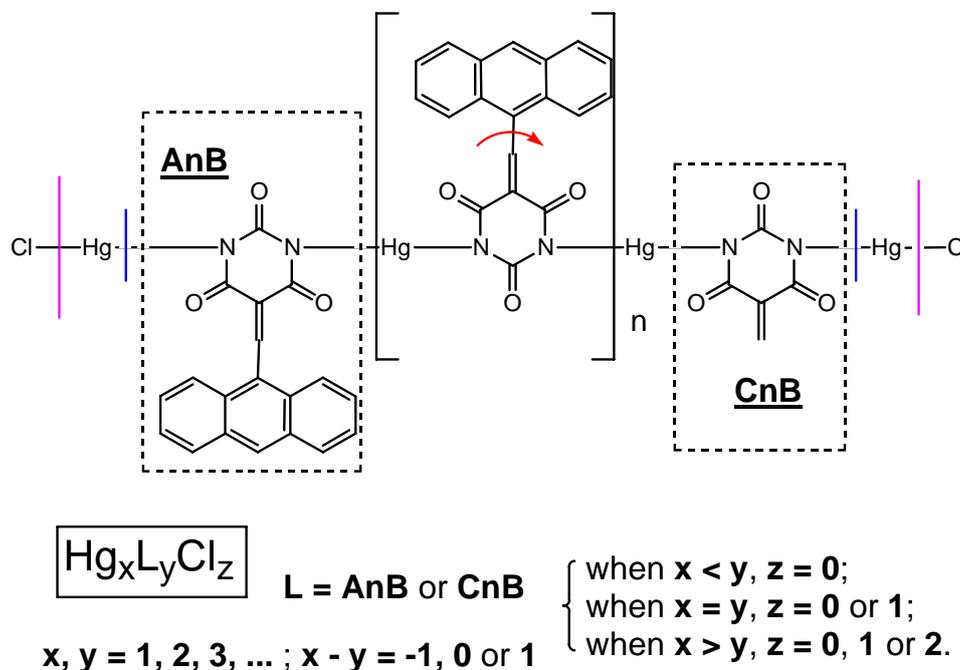


Fig. S6 Proposed fragments of Hg^{2+} -AnB coordination polymer in mass spectrometric analysis (Figure3). MS signals at m/z 674.63, 878.74, 1068.03, 1301.57, 1507.51, 1746.89 and 1924.54 are assigned to $\{2 \text{ CnB} + 2 \text{ Hg}\}$, $\{2 \text{ CnB} + 3 \text{ Hg}\}$, $\{2 \text{ AnB} + 2 \text{ Hg} + \text{Cl}\}$, $\{2 \text{ AnB} + 3 \text{ Hg} + 2\text{Cl}\}$, $\{2 \text{ AnB} + 2 \text{ CnB} + 3 \text{ Hg}\}$, $\{3 \text{ AnB} + 4 \text{ Hg}\}$ and $\{3 \text{ AnB} + \text{CnB} + 4 \text{ Hg} + \text{Cl}\}$, respectively.

6. Dynamic light scattering study on the reaction of AnB with Hg^{2+} (Fig. S7)

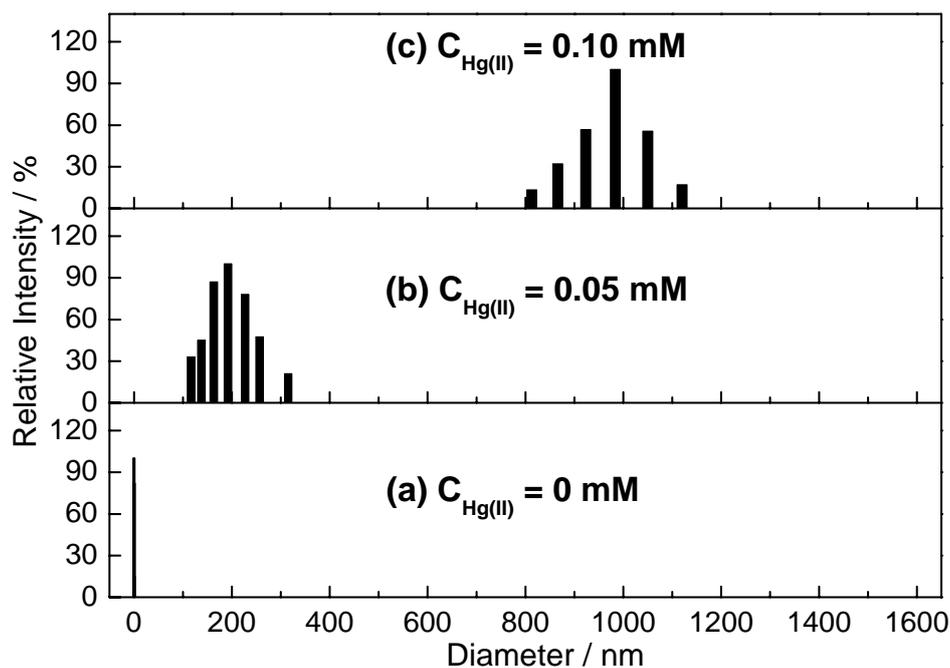


Fig. S7. Sizes of the particles in the aqueous solutions of **AnB** ($1.00 \times 10^{-5} \text{ M}$) in the presence of different amount of HgCl_2 as revealed by the dynamic light scattering experiments. pH: 9.0, buffered by 0.02 M $\text{NH}_4\text{Cl-NH}_3$.

7. Influence of reaction time and pH on Hg^{2+} sensing (Fig. S8–S9)

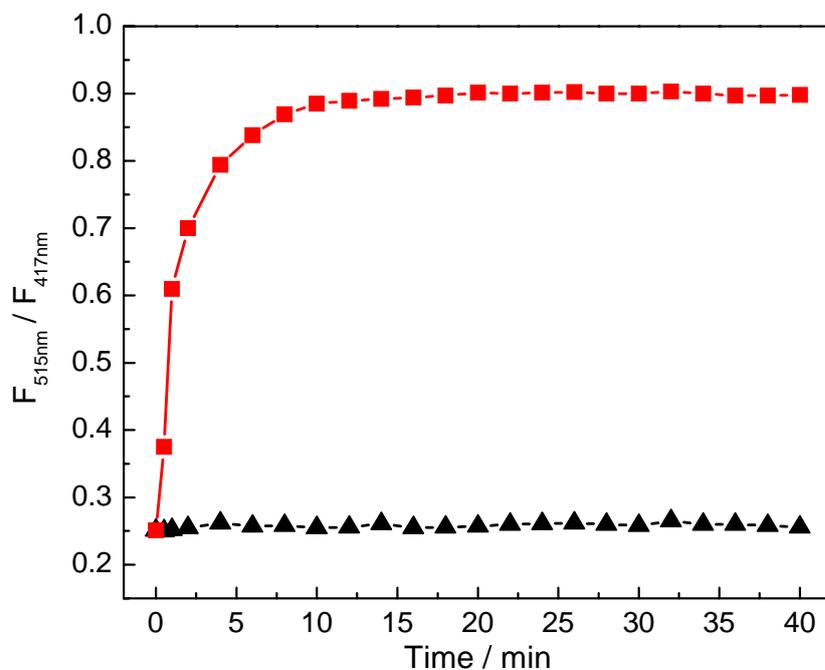


Fig. S8 Time dependence of fluorescence emission of **AnB** ($1.00 \times 10^{-5} \text{ M}$) in the absence (triangles) and presence (squares) of HgCl_2 ($1.00 \times 10^{-5} \text{ M}$). pH: 9.0, buffered by 0.02 M $\text{NH}_4\text{Cl-NH}_3$. Excitation wavelength: 367 nm.

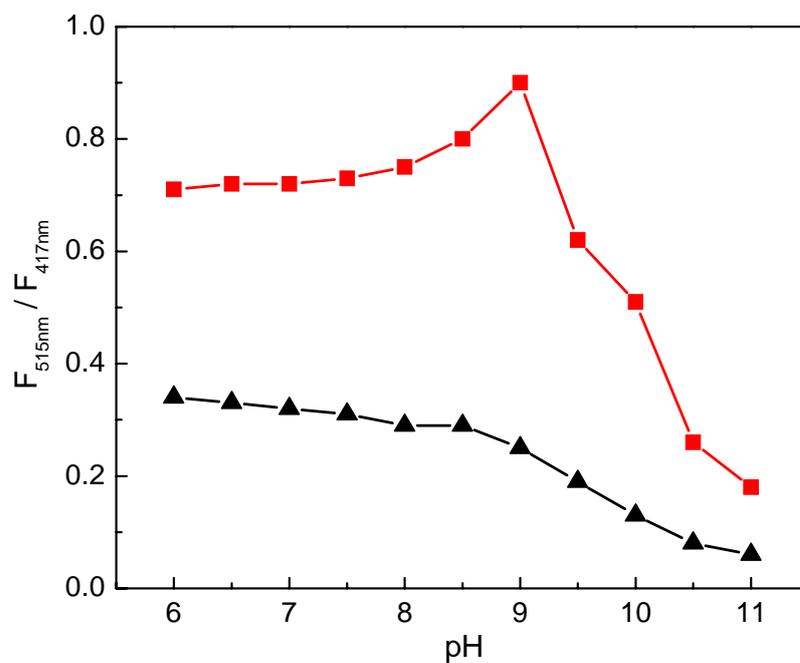


Fig. S9 Influence of pH on fluorescence emission of **AnB** (1.00×10^{-5} M) in the absence (triangles) and presence (squares) of HgCl_2 (1.00×10^{-5} M). pH 5.8–8.0: buffered by 0.02 M $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$; pH 8.5–11.0: buffered by 0.02 M $\text{NH}_4\text{Cl-NH}_3$. Excitation wavelength: 367 nm.