Ultraselective Fluorescent Sensing of Hg^{2+} through Metal Coordination-Induced Molecular Aggregation

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Supporting Information

1. Materials and Methods.

Dideoxythymidine-perylene-3,4,9,10-tetracarboxylic diimide (TT-PTCDI) was synthesized following the standard condensation method developed by Langhals.\(^1\) Briefly, 3.6 mg (9.2 µmol) 3,4,9,10-perylene-tetracarboxylic dianhydride (Aldrich), 5 mg (21 µmol) 5’-amino-5’-deoxythymidine (Sigma), and 0.6 g imidazole (Fisher) were heated under argon at 120 °C for 3 h. The reaction mixture was cooled to room temperature and dispersed in 10 mL ethanol, followed by addition of 20 mL 2 M HCl. The mixture was stirred overnight. The resulting red solid was collected by vacuum filtration through a 0.45 µm membrane filter (Osmonics). The solid was then washed thoroughly with distilled water until the pH of washings turned to be neutral. The collected solid was dried in vacuum at 60 °C. TCL: R\(_f\) (silica gel/dioxane:CHCl\(_3\) = 75:25) = 0.83. All other chemicals were used as received.

Due to the limited solubility of TT-PTCDI in the common NMR solvents, it was challenging to run NMR measurement on this compound. Mass spectra were run on a MALDI instrument using angiotensin as an external standard. MS (M+2H\(^+\)), m/z: 840.29 (calc. 840.22).

UV-visible absorption spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer. Fluorescence spectra were measured using a Perkin Elmer LS55 fluorometer.

Fig. S1. Addition of 10 μM Hg\(^{2+}\) into a 5 μM TT-PTCDI solution in DMF/H\(_2\)O (70/30, vol) (left) results in complexation and aggregation of the molecules, which eventually leads to formation of redish flocs (middle). The floating flocs can be redissolved back to solution by addition of ca. 0.05 M HCl (right).

Fig. S2. Job’s plot of the complexation between TT-PTCDI and Hg\(^{2+}\). Total concentration of TT-PTCDI and Hg\(^{2+}\) was kept constant at 1 μM in DMF/H\(_2\)O (70/30, vol) solution.
Fig. S3. Absorption spectra of a 1 µM solution of TT-PTCDI in DMF/H₂O (70/30, vol) in the absence (black) and presence of 12.5 µM Cu²⁺ (red), showing no significant change in absorption. Similar results were obtained for all the other environmentally relevant metal ions including Ni²⁺, Fe²⁺, Co²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Mn²⁺, Cr³⁺, Mg²⁺, Ca²⁺, K⁺ and Na⁺.