Specific Hg^{2+}-Mediated Perylene Bisimide Aggregation for Highly Sensitive Detection of Cysteine

Yi-Bin Ruan, Ai-Fang Li, Jin-Song Zhao, Jiang-Shan Shen and Yun-Bao Jiang*

Department of Chemistry, College of Chemistry and Chemical Engineering, and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China

E-mail: ybjiang@xmu.edu.cn.

Electronic Supporting Information

1. Materials and Methods

Perylene bisimide (PBI) was purchased from Liangang Pigment and Dyestuff Chemicals Co., Ltd (Liaoning, China) with a purity > 98%. All other chemicals were obtained from commercial suppliers and used as received. Absorption spectra were recorded on a Varian Cary 300 or a Thermo Scientific Evolution 300 UV-Vis absorption spectrometer. Fluorescence spectra were taken on a Hitachi F-4500 fluorescence spectrometer.

The tested metal salts included $Hg(ClO_4)_2$, $Cd(ClO_4)_2$, $Cu(ClO_4)_2$, $Ni(ClO_4)_2$, $Pb(ClO_4)_2$, $Zn(ClO_4)_2$, $AgNO_3$, $Ba(NO_3)_2$, $Fe(NO_3)_3$, $Mg(NO_3)_2$, $Fe(NH_3)_2SO_4$ and $CaCl_2$.

2. Detection of Cysteine

To the DMF/H_2O (9:1, v/v) solution containing 0.33 μM PBI, 100 nM Hg^{2+} was added. The resultant solution was incubated at room temperature for *ca*. 20 min to reach equilibrium. Varying concentration of Cys was subsequently added to the PBI-Hg^{2+} solution and the fluorescence spectra were then recorded.

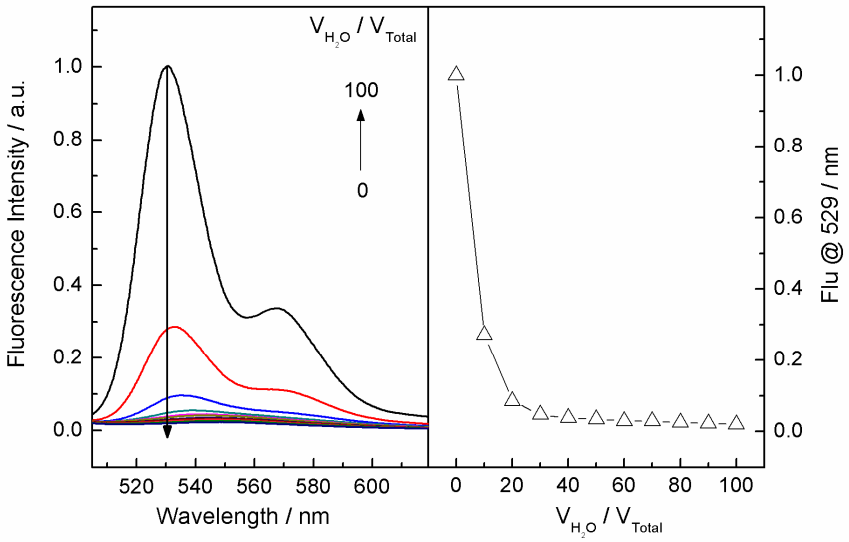

Fig. S1 Solvent dependent fluorescence spectra of PBI in DMF-H_2O solutions. [PBI] = 6.63 μM, λ_{ex} = 484 nm.

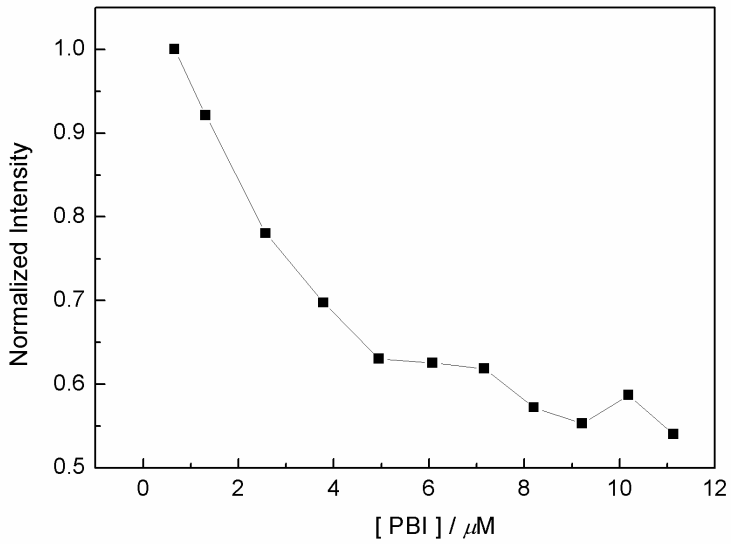

Fig. S2 Concentration dependent fluorescence intensity of PBI at 530 nm in 9:1 DMF/H_2O (v/v). λ_{ex} = 484 nm.

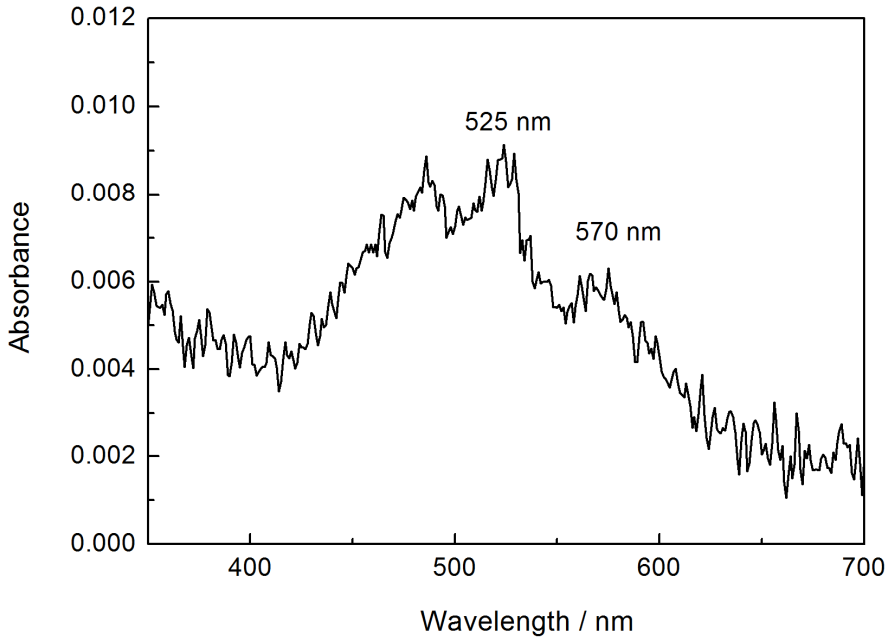

Fig. S3 Absorption spectrum of PBI in 9:1 DMF/H_2O. [PBI] = 0.33 μM.

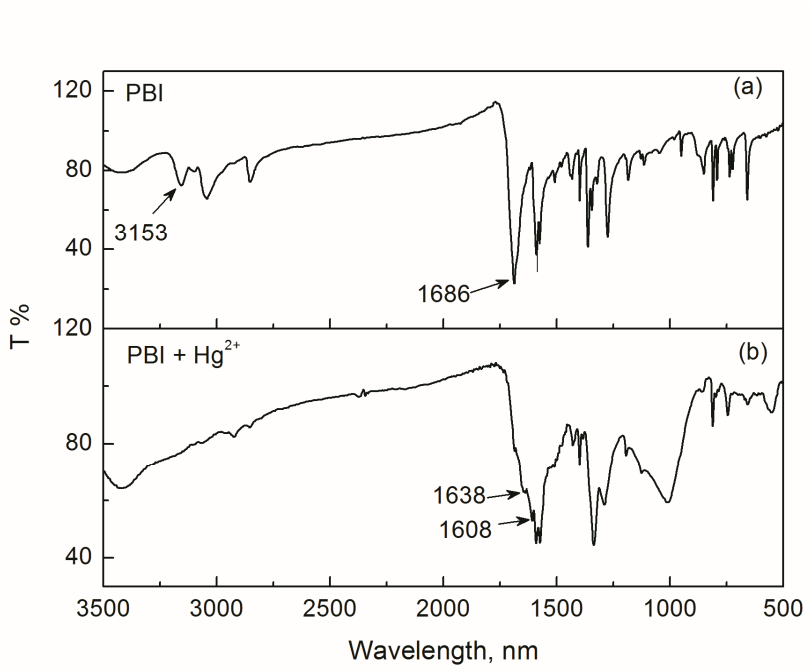

Fig. S4 IR spectra of (a) PBI and (b) Hg^{2+}-PBI complex

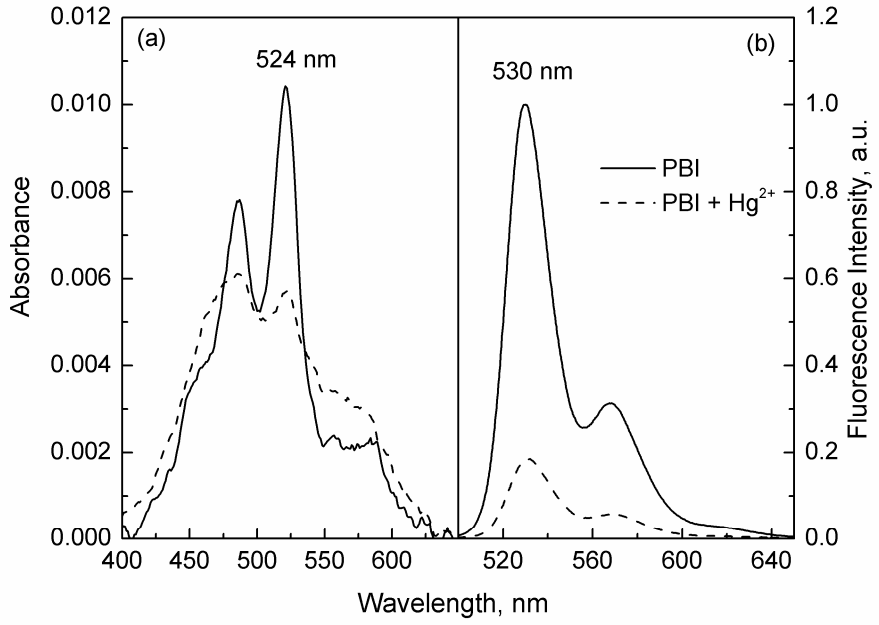

Fig. S5 Absorption (a) and fluorescence (b) spectra of PBI in DMF in the absence and presence of Hg^{2+}. [PBI] = 0.33 μM, [Hg^{2+}] = 1.0 μM, λ_{ex} = 484 nm.

Hill plot analysis for Hg^{2+}-PBI interaction

Hill equation describes the degree of cooperativity of the ligand binding to receptor.[1] log[Y/(1-Y)] = n log[G] + log K_{app}, where Y, n, [G] and K_{app} represent the fraction of ligand binding sites filled, Hill coefficient, concentration of guest (here Hg^{2+}) and the apparent association constant, respectively. When appropriate, the value of Hill coefficient describes the cooperativity of ligand binding in the following way: n > 1, positive cooperativity; n = 1, noncooperativity and n < 1, negative cooperativity. Y was determined by the equation of (I-I_0)/(I_{max}-I_0), where I_0, I, and I_{max} are the fluorescence intensity at 532 nm in the absence, in the presence and in the presence of excess amount of Hg^{2+}. Similar analysis was also applied for the dissociation of "Hg^{2+}-PBI" aggregates by Cys (see Fig. S8).

1. S. Shinkai, M. Ikeda, A. Sugasaki and M. Takeuchi, *Acc. Chem. Res.*, 2001, **34**, 494.

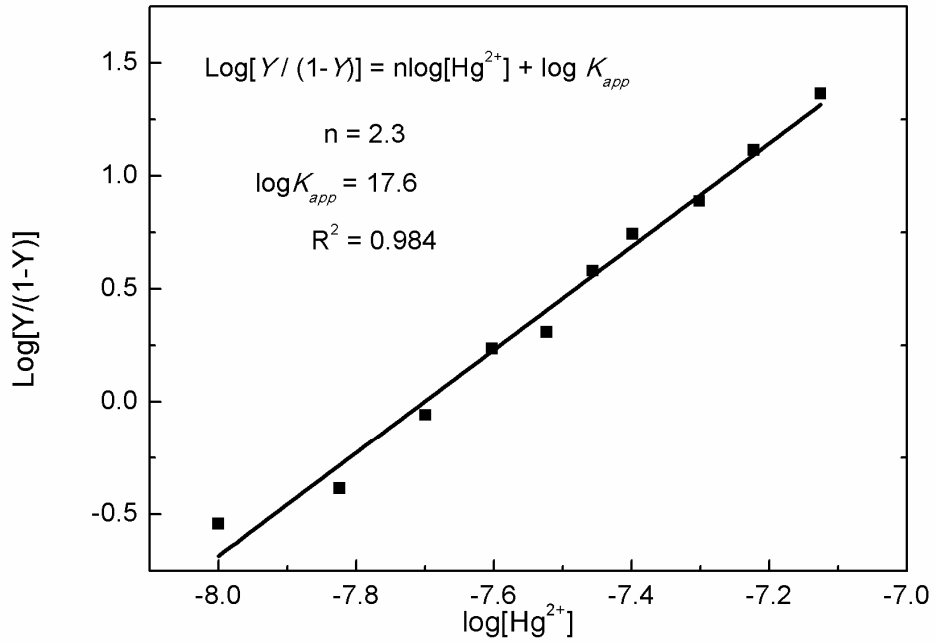

Fig. S6 Hill plot for binding of Hg^{2+} to PBI in 9:1 DMF/H_2O based on fluorescence intensity changes in low Hg^{2+} concentration range.

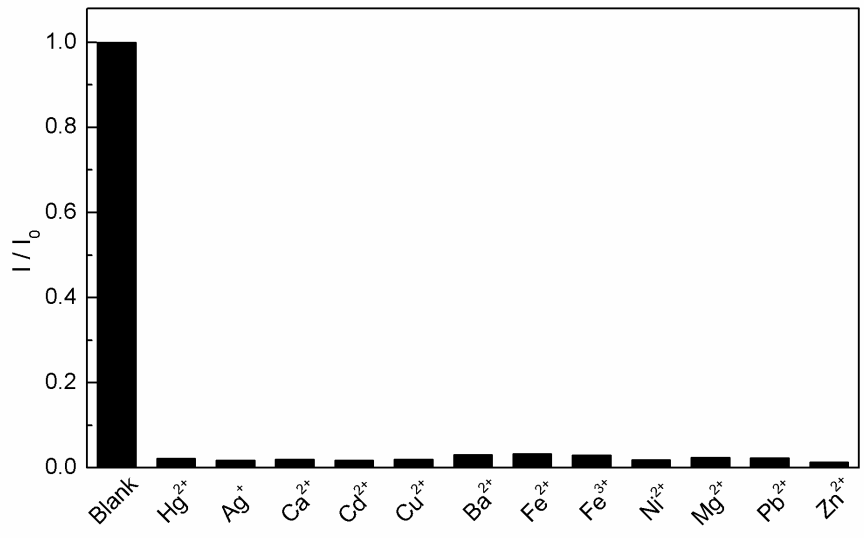

Fig. S7 Competitive experiment for PBI binding with Hg^{2+} (500 nM) in 9:1 DMF/H_2O in the presence of another metal ion at 2.5 μM. I_0 and I are fluorescence intensities of PBI at 532 nm before and after addition of the metal ion, respectively.

Hill plot analysis for Cys-Hg^{2+}/PBI assemble interaction

Hill equation here is $\log[Y/(1-Y)] = n \log[Cys] + \log K_{app}$, where Y, n, [Cys] and K_{app} represent the fraction of ligand binding sites filled, Hill coefficient, Cys concentration and the apparent association constant, respectively. When appropriate, the value of Hill coefficient describes the cooperativity of ligand binding in the following way: n > 1, positive cooperativity; n = 1, noncooperativity and n < 1, negative cooperativity.[1] Y was determined by the equation of $(I-I_0)/(I_{max}-I_0)$, where I_0, I, and I_{max} are the fluorescence intensity at 532 nm in the absence, in the presence and in the presence of excess amount of Cys. For reference 1 see Fig. S6.

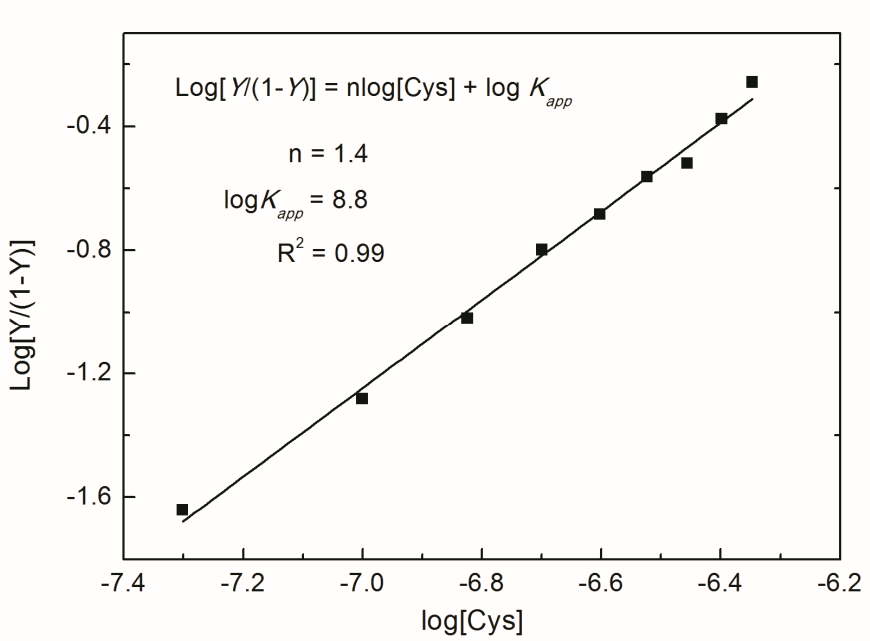

Fig. S8 Hill plot for interaction of Cys with PBI-Hg ensemble in 9:1 DMF/H_2O based on fluorescence intensity changes in low Cys concentration range.

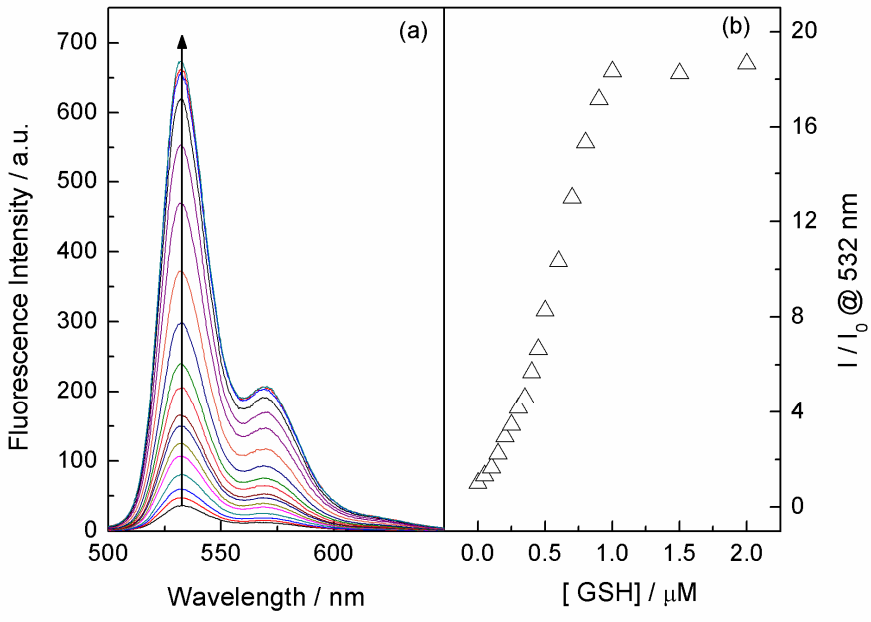

Fig. S9 (a) Fluorescence spectra of PBI-Hg in the presence of GSH of increasing concentration and (b) plot of fluorescence intensity at 532 nm versus GSH concentration. [PBI] = 0.33 μM, [Hg^{2+}] = 0.10 μM, λ_{ex} = 484 nm.

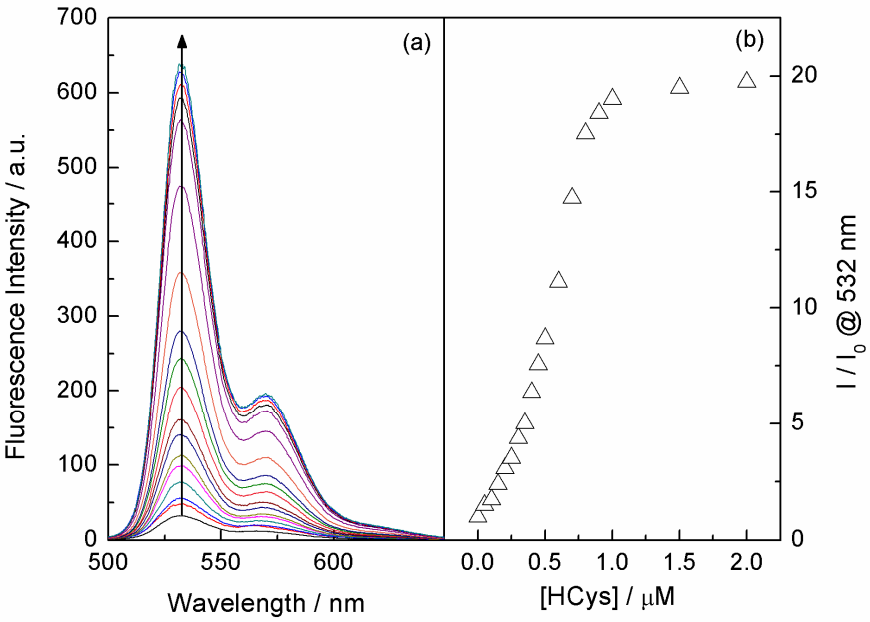

Fig. S10 (a) Fluorescence spectra of PBI-Hg in the presence of HCys of increasing concentration and (b) plot of fluorescence intensity at 532 nm versus HCys concentration. [PBI] = 0.33 μM, [Hg^{2+}] = 0.10 μM, λ_{ex} = 484 nm.

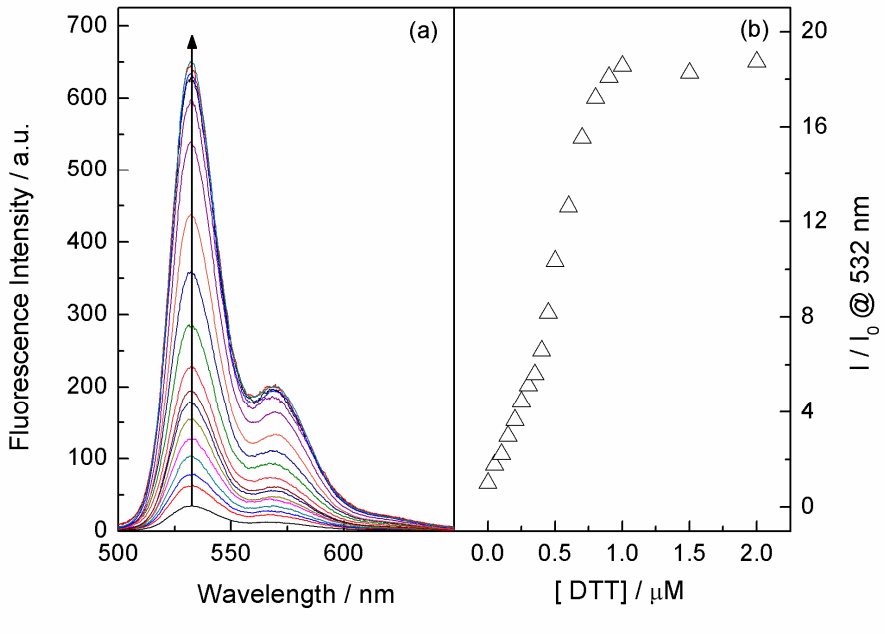

Fig. S11 (a) Fluorescence spectra of PBI-Hg in the presence of DTT of increasing concentration and (b) plot of fluorescence intensity at 532 nm versus DTT concentration. [PBI] = 0.33 μM, [Hg^{2+}] = 0.10 μM, λ_{ex} = 484 nm.

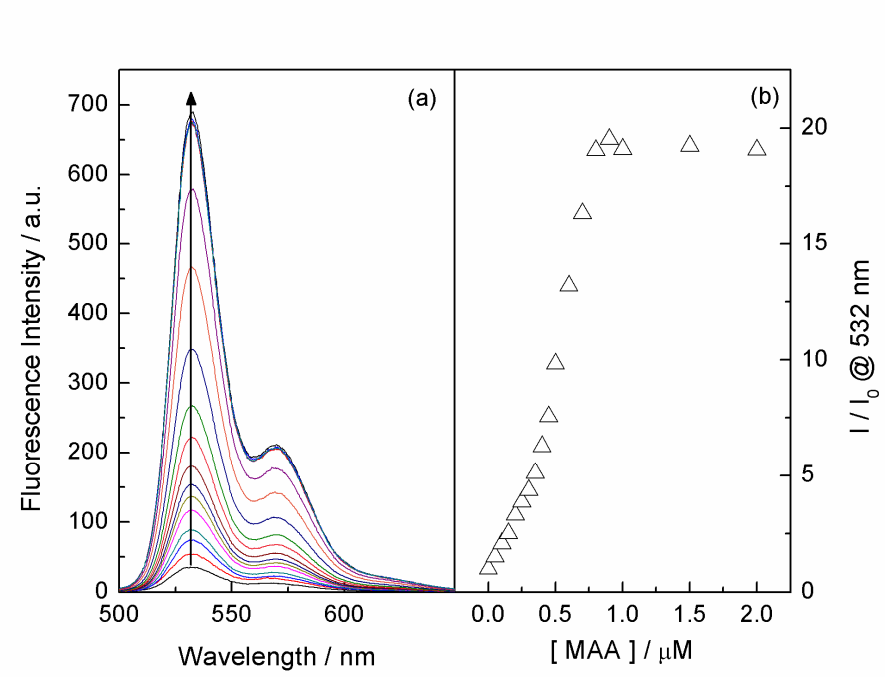

Fig. S12 (a) Fluorescence spectra of PBI-Hg in the presence of MAA of increasing concentration and (b) plot of fluorescence intensity at 532 nm versus MAA concentration. [PBI] = 0.33 μM, [Hg^{2+}] = 0.10 μM, λ_{ex} = 484 nm.

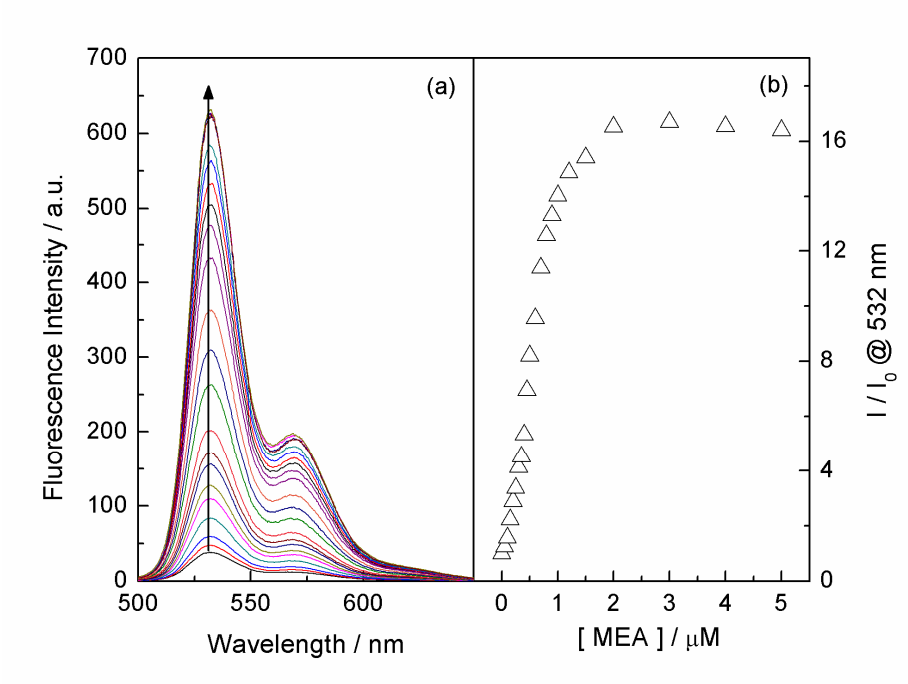

Fig. S13 (a) Fluorescence spectra of PBI-Hg in the presence of MEA of increasing concentration and (b) plot of fluorescence intensity at 532 nm versus MEA concentration. [PBI] = 0.33 μM, [Hg^{2+}] = 0.10 μM, λ_{ex} = 484 nm.