Electronic Supplementary Material (ESI) for Chemical Communications

Turn-on the fluorescence of tetra(4-pyridylphenyl)ethylene by the synergic interactions of mercury (II) cation and hydrogen sulfate anion

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1. General Information

^{1}H NMR spectra were recorded on Bruker Avance 400 MHz. Fluorescence spectra were studied on a Hitachi F-4500 spectrometer. Absorption spectra were measured on a Hitachi U3010 spectrometer. Dynamic light scattering (DLS) experiments were carried out with Malvern Instrument (Nano Series). The sample solutions were filtered through a Millipore filtration system prior to DLS experiments. All solvents were purified and dried following standard procedures unless special statements.

Single crystal of **1** was grown by slow evaporation from dichloromethane/methanol (v/v 1:1) at room temperature. All diffraction data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator Mo-Kα radiation (λ = 0.71073 Å) at 113 K. Intensities were corrected for absorption effects using the multi-scan technique SADABS. The structure was solved by direction methods and refined by a full matrix least squares technique based on F^2 using SHELXL 97 program (Sheldrick, 1997). Methanol molecules located in each crystal cell could not be satisfactorily resolved because of severe disorder. The SQUEEZE routine within the crystallographic program PLATON was employed in the treatment of the disordered methanol molecules of the crystal.

2. Intermolecular arrangements within the crystal of 1

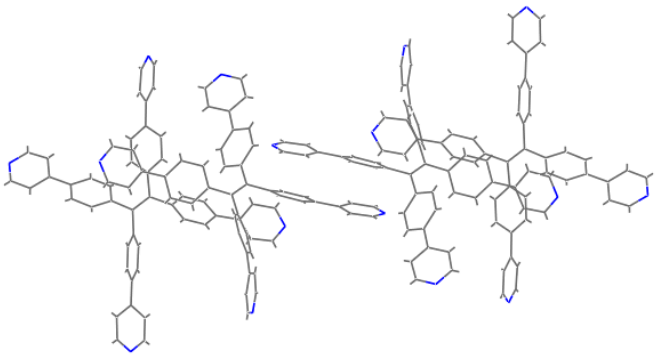


Figure S1. Four unique molecules of **1** in the unit cell of crystal; solvent molecules of methanol were omitted for clarity.

3. Plot of the fluorescence quantum yield of 1 vs the water content

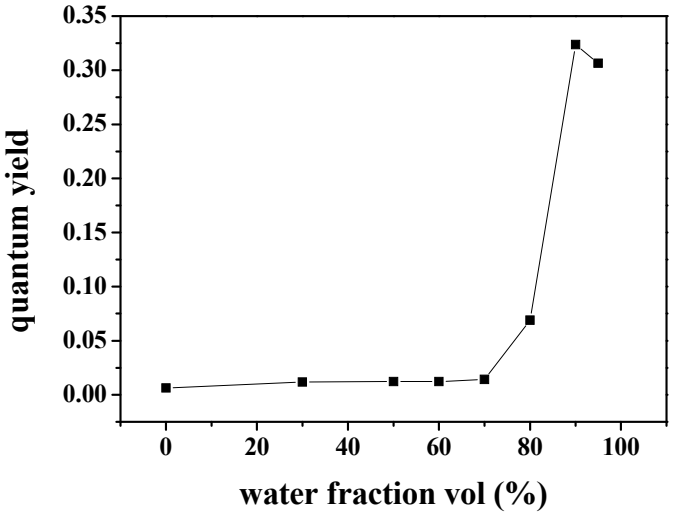
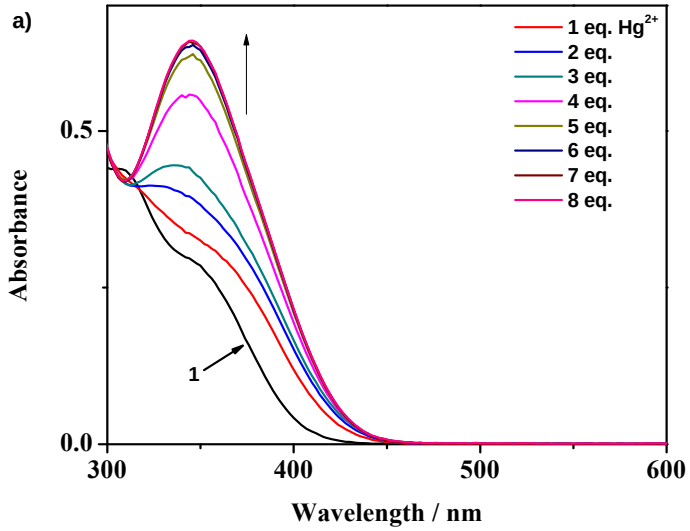


Figure S2. Plot of the fluorescence quantum yield of **1** vs the water content of DMF/water mixture; the fluorescence quantum yields (Φ_f) were measured with quinine sulfate in 0.1 M H_2SO_4 (Φ_f = 54%) as the standard; the absorbance of each solution at 360 nm (the excitation wavelength) was adjusted to be less than 0.05.

4. Absorption and fluorescence spectra of 1 (0.1 mM) in the presence of different amounts of $Hg(ClO_4)_2$



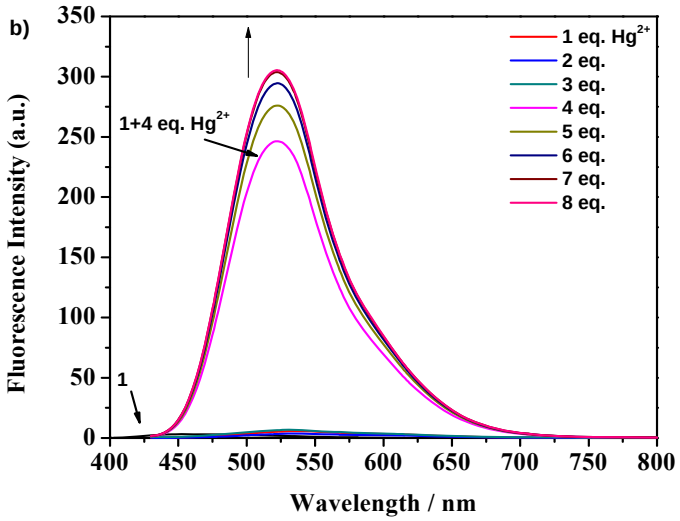


Figure S3. Absorption (a) and fluorescence (b) spectra (0.1 mM in DMF) upon addition of increasing amounts of $Hg(ClO_4)_2$ up to 8.0 equiv.

5. ^{1}H NMR spectra of 1 in the presence of different amounts of $Hg(ClO_4)_2$

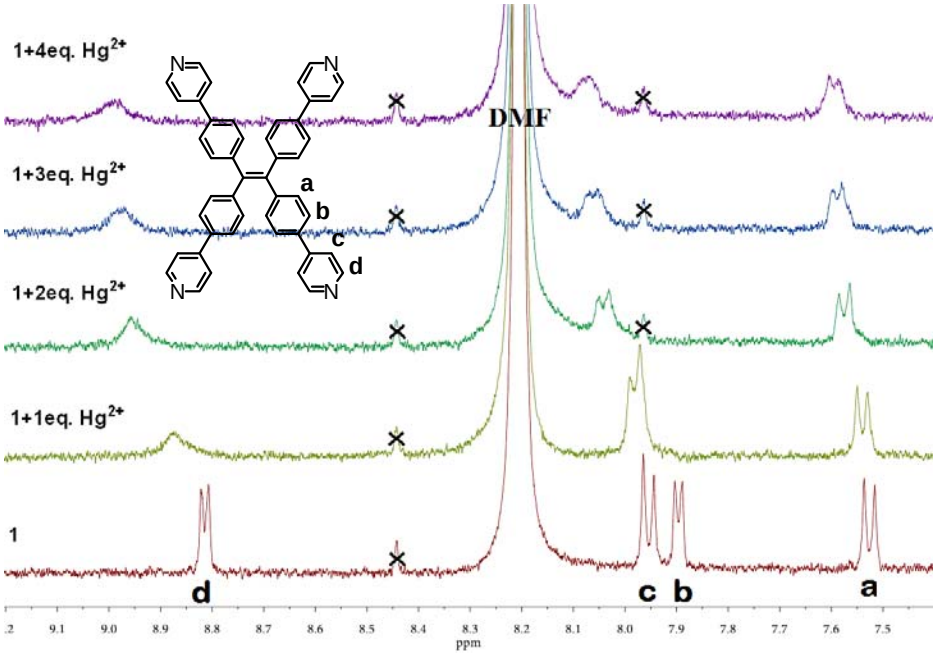


Figure S4. ^{1}H NMR spectra of **1** (0.125 mM) in DMF-d_7 upon addition of 1.0-4.0 equiv. of $Hg(ClO_4)_2$

6. DLS profile for 1 (0.1 mM) in the presence of 4.0 equiv. $Hg(ClO_4)_2$

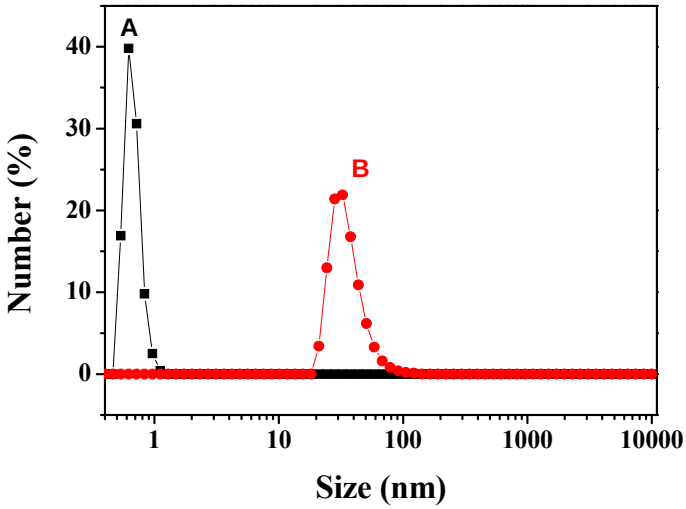


Figure S5. DLS profile for **1** (0.1 mM) in DMF (A) and after the addition of 4.0 equiv. of $Hg(ClO_4)_2$ (B)

7. Absorption spectra of 1 (10 μM) in the presence of different amounts of $Hg(ClO_4)_2$

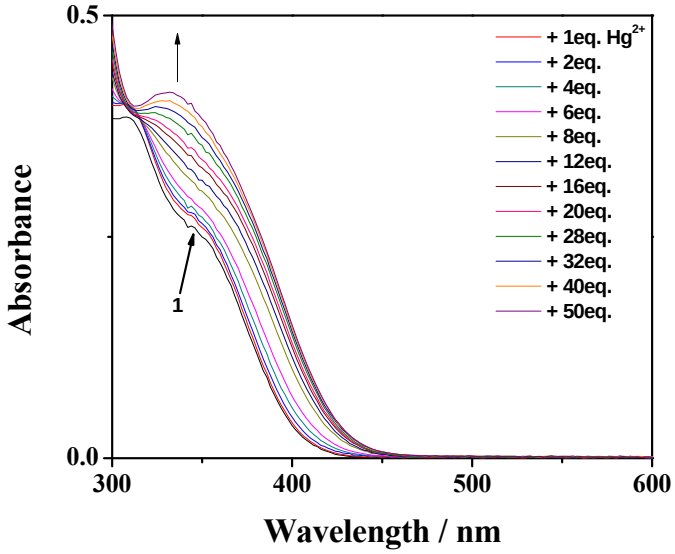


Figure S6. Absorption spectra of **1** (10 μM in DMF) upon addition of 1.0–50.0 equiv. of $Hg(ClO_4)_2$

8. DLS profiles for 1 (10 μM) in the presence of $Hg(ClO_4)_2$ and Bu_4NHSO_4

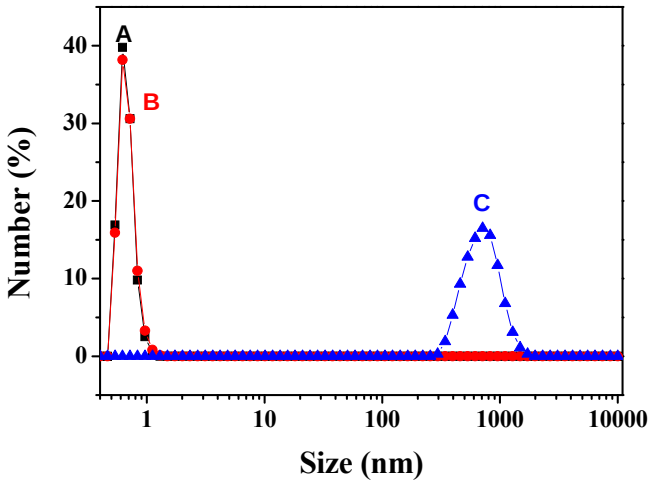


Figure S7. DLS profiles for **1** (10 μM) in DMF (A), after the addition of 4.0 equiv. of $Hg(ClO_4)_2$ (B), and after further addition of 8.0 equiv. of Bu_4NHSO_4 (C).

9. Absorption spectra of 1 (10 μM) after addition of Bu_4NHSO_4 in the presence of $Hg(ClO_4)_2$

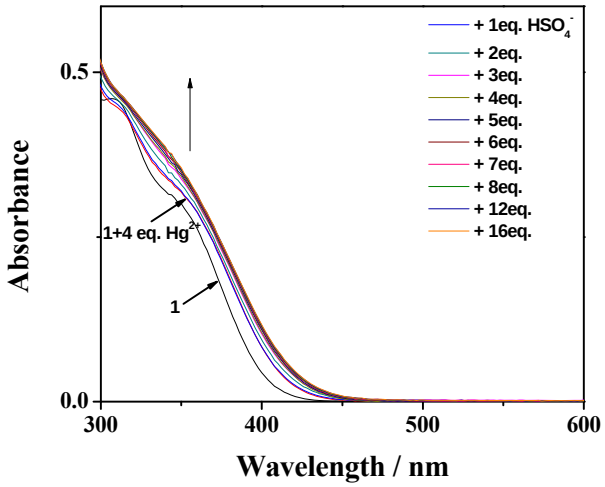


Figure S8. Absorption spectra of **1** (10 μM) in DMF after addition of Bu_4NHSO_4 (1.0-16.0 equiv.) in the presence of 4.0 equiv. of $Hg(ClO_4)_2$.

10. Fluorescence spectra of 1 (10 μM) after addition of $Hg(ClO_4)_2$ in the presence of Bu_4NHSO_4

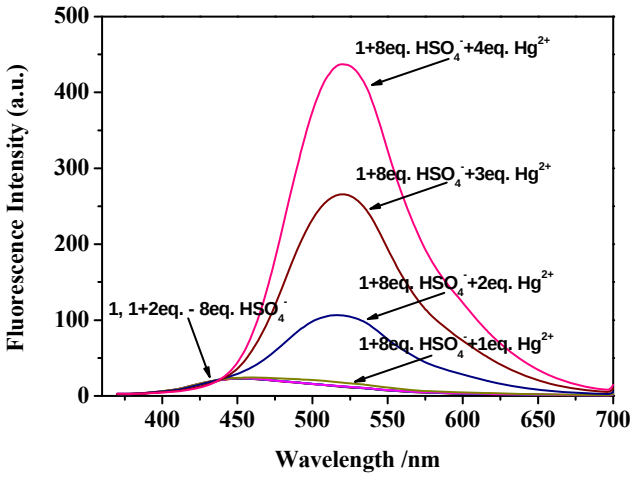
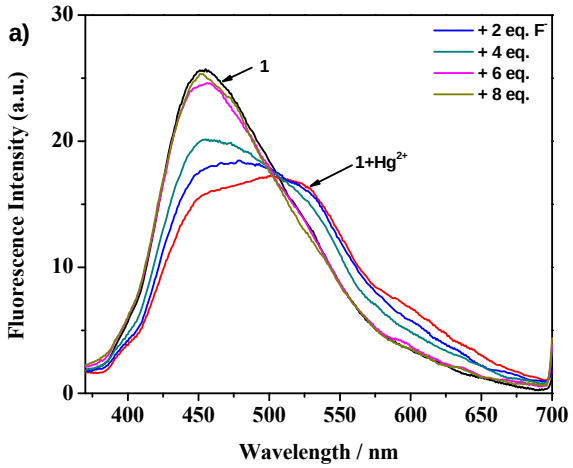
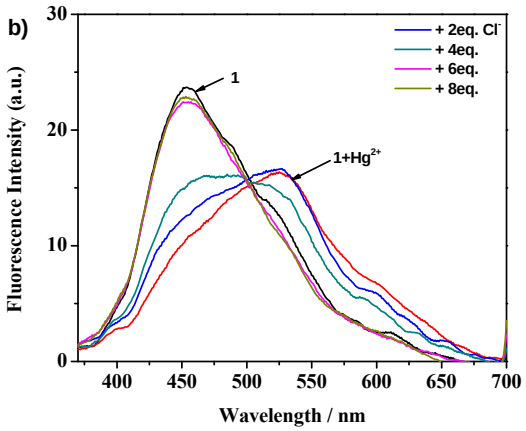
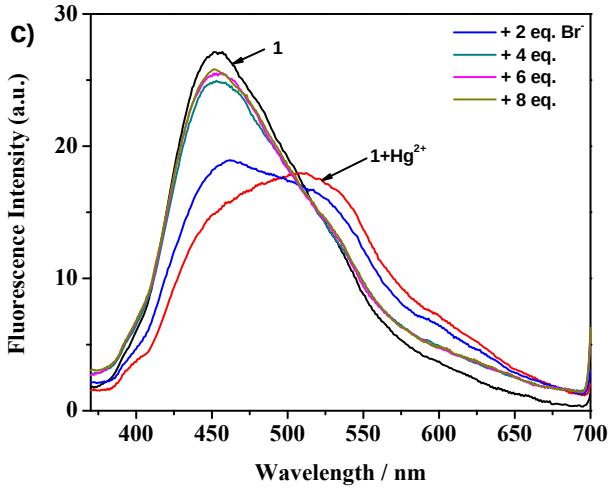


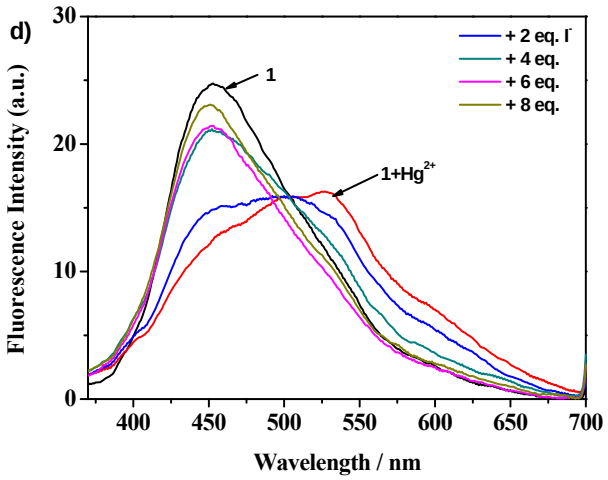
Figure S9. Fluorescence spectra of **1** (10 μM in DMF) containing 8.0 equiv. of Bu_4NHSO_4 after addition of 1.0 - 4.0 equiv. of $Hg(ClO_4)_2$.

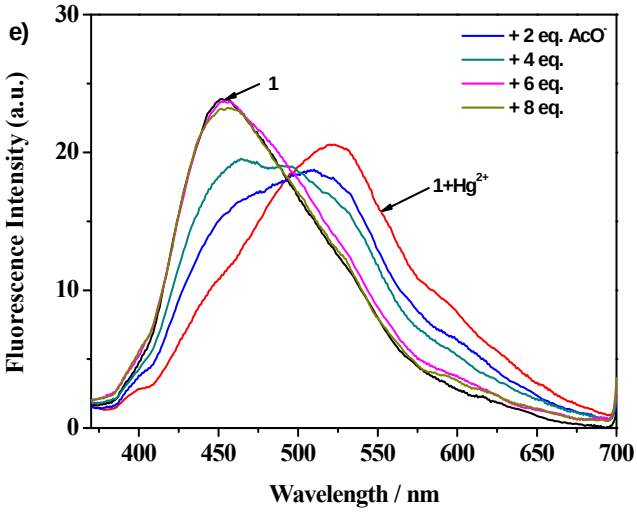
11. Fluorescence spectra of 1 (10 μM) after addition of various anions in the presence of $Hg(ClO_4)_2$

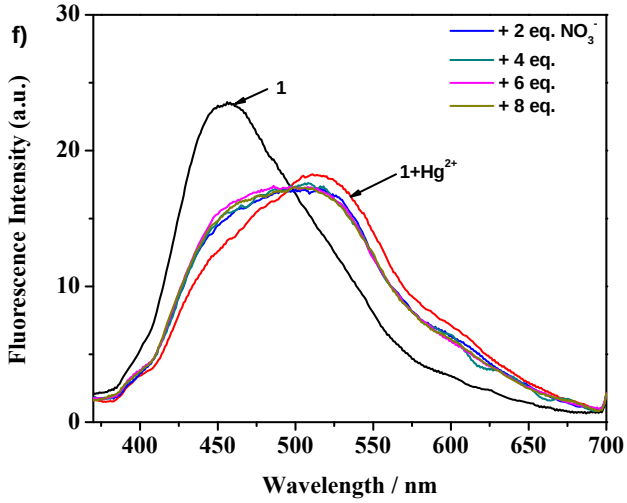


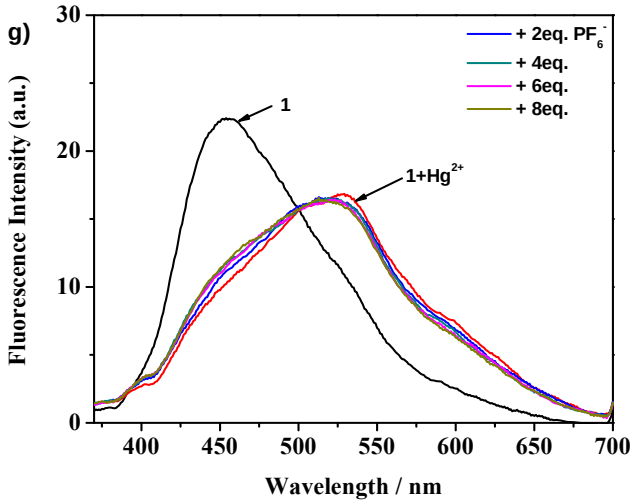


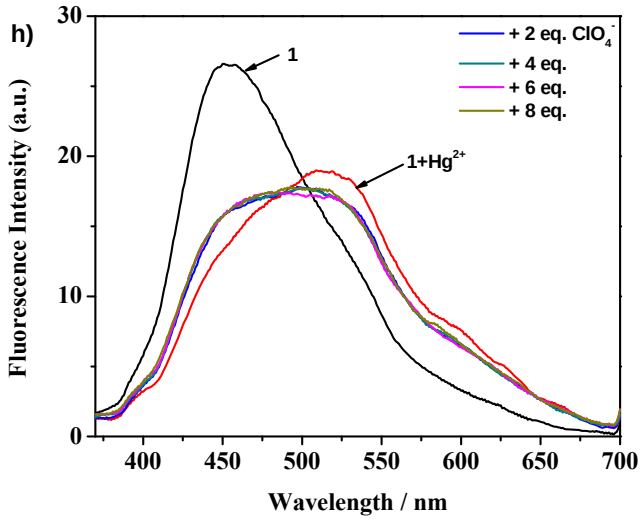

c)
Fluorescence Intensity (a.u.)
Wavelength / nm
+ 2 eq. Br-
+ 4 eq.
+ 6 eq.
+ 8 eq.
1
1+Hg2+


d)
Fluorescence Intensity (a.u.)
Wavelength / nm
+ 2 eq. I-
+ 4 eq.
+ 6 eq.
+ 8 eq.
1
1+Hg2+


e)
Fluorescence Intensity (a.u.)
Wavelength / nm
+ 2 eq. AcO-
+ 4 eq.
+ 6 eq.
+ 8 eq.
1
1+Hg2+


f)
+ 2 eq. NO3-
+ 4 eq.
+ 6 eq.
+ 8 eq.
1
1+Hg2+
Fluorescence Intensity (a.u.)
Wavelength / nm


g)
+ 2eq. PF6-
+ 4eq.
+ 6eq.
+ 8eq.
1
1+Hg2+
Fluorescence Intensity (a.u.)
Wavelength / nm


h)
+ 2 eq. ClO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.
1
1+Hg2+
Fluorescence Intensity (a.u.)
Wavelength / nm

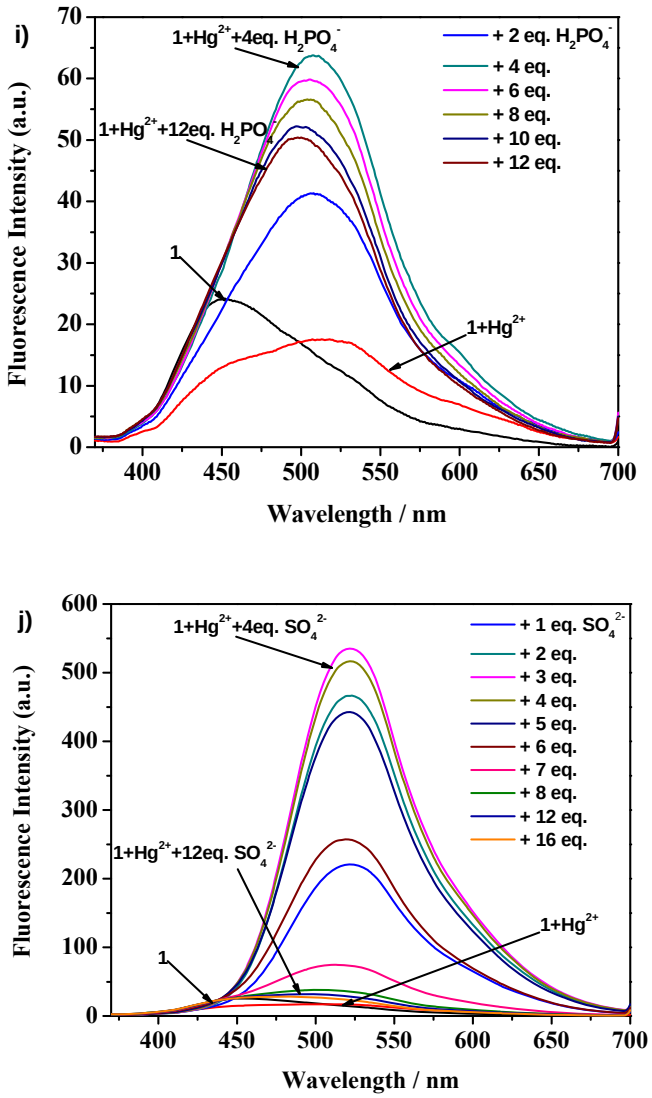
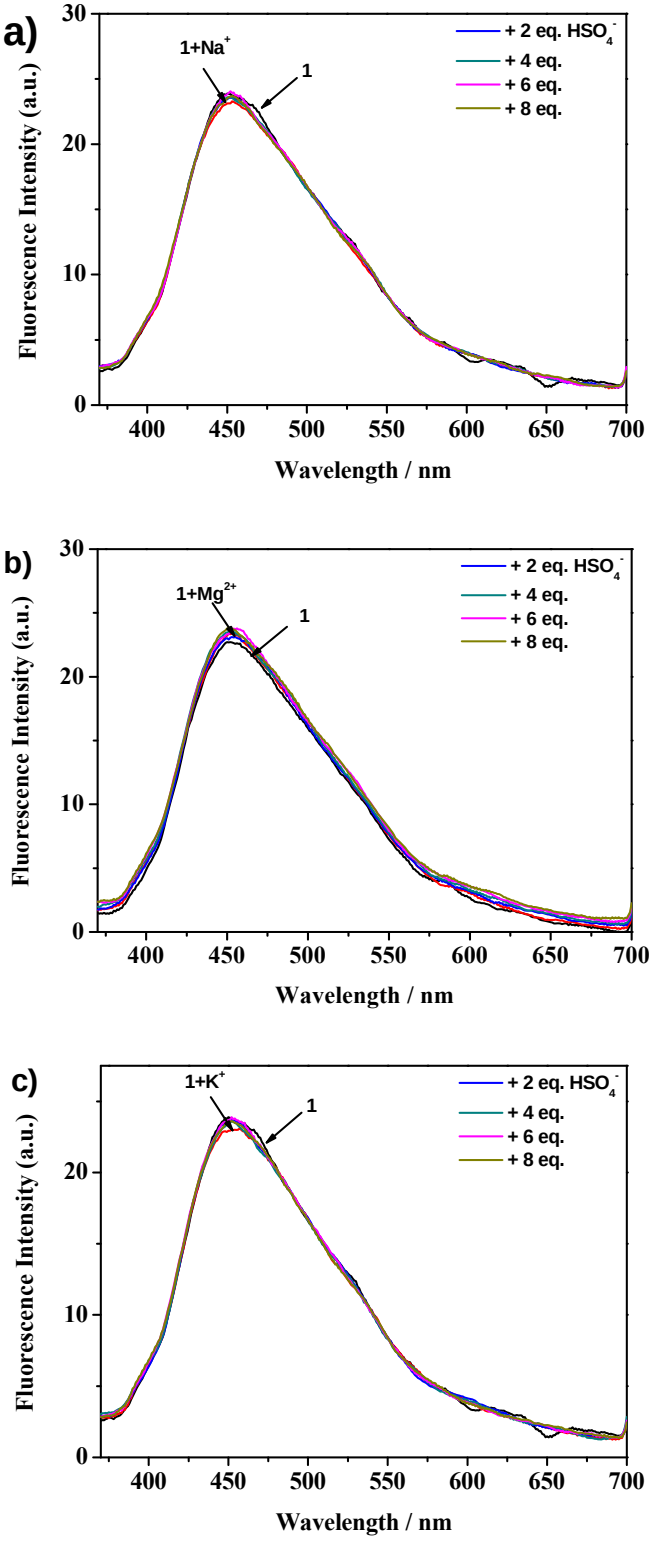
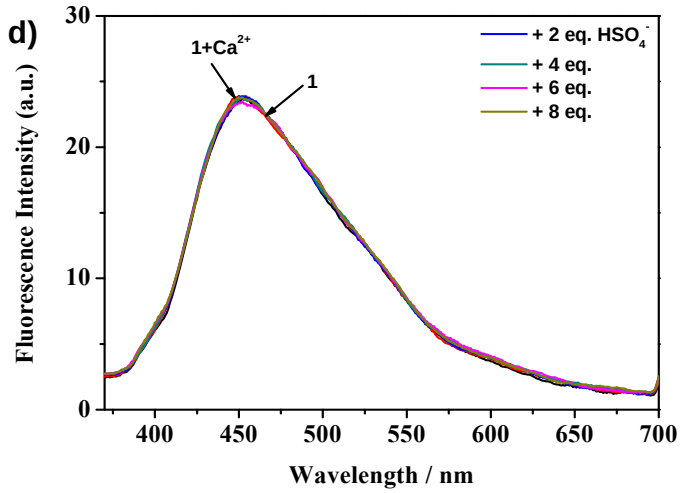
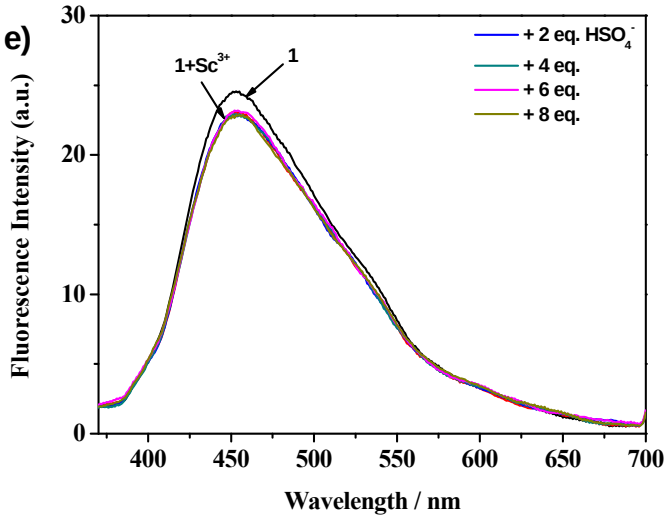


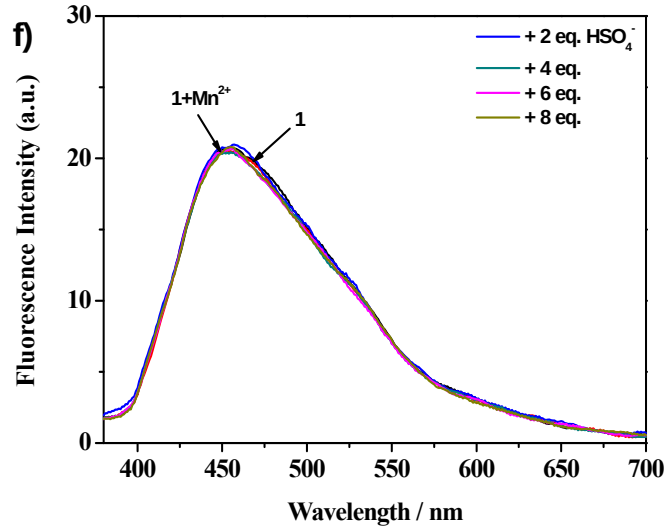
Figure S10. Fluorescence spectra of the ensemble of **1** (10 μM) (black) and 4.0 equiv. of $Hg(ClO_4)_2$ (red) in DMF after addition of various anions: a) Bu_4NF (2.0-8.0 equiv.), b) Bu_4NCl (2.0-8.0 equiv.), c) Bu_4NBr (2.0-8.0 equiv.), d) Bu_4NI (2.0-8.0 equiv.), e) Bu_4NAcO (2.0-8.0 equiv.), f) Bu_4NNO_3 (2.0-8.0 equiv.), g) Bu_4NPF_6 (2.0-8.0 equiv.), h) Bu_4NClO_4 (2.0-8.0 equiv.), i) $Bu_4NH_2PO_4$ (2.0-12.0 equiv.), j) $(Bu_4N)_2SO_4$ (1.0-16.0 equiv.).

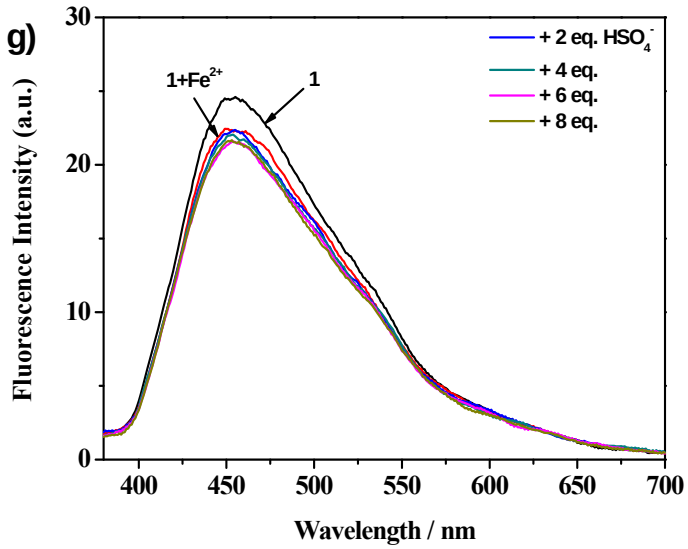
12. Fluorescence spectra of 1 (10 μM) after addition of Bu_4NHSO_4 in the presence of various metal cations

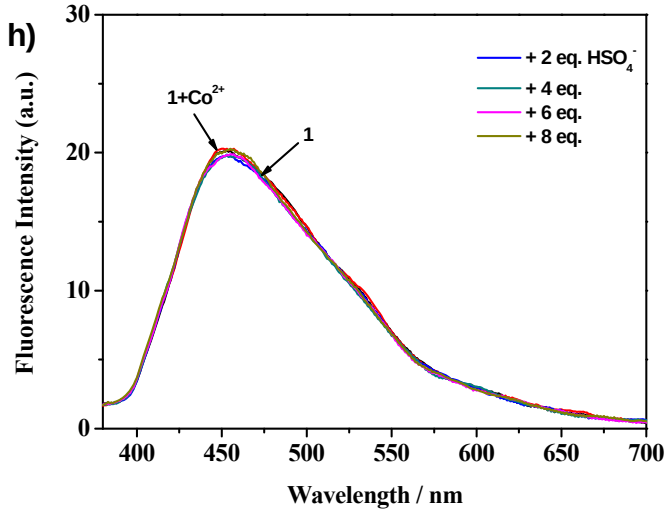


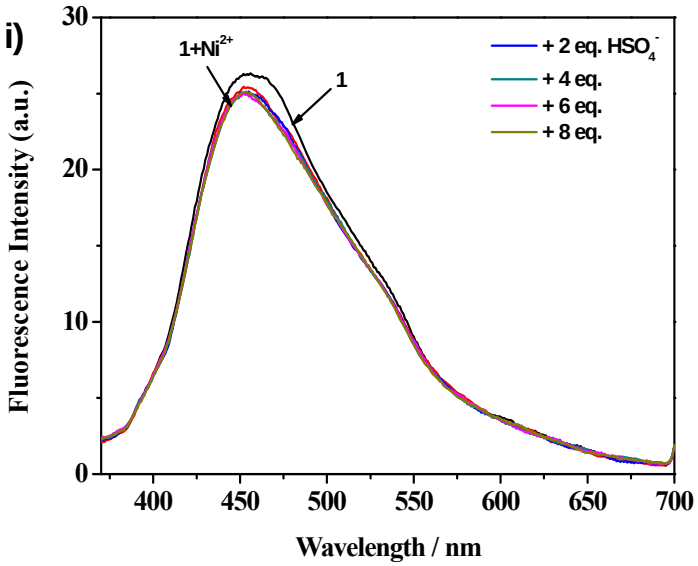

d)
1+Ca2+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.
Fluorescence Intensity (a.u.)
Wavelength / nm

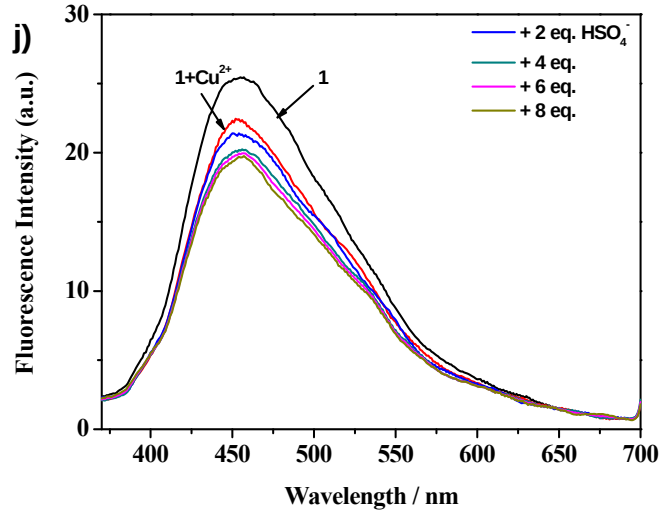

e)
1+Sc3+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.
Fluorescence Intensity (a.u.)
Wavelength / nm

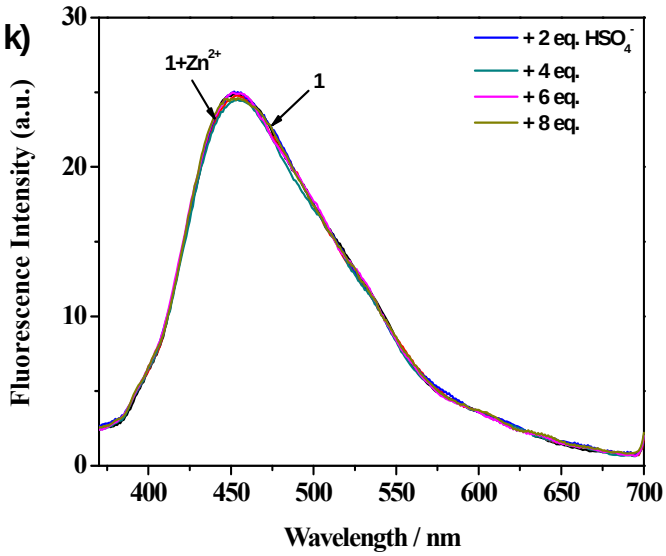

f)
1+Mn2+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.
Fluorescence Intensity (a.u.)
Wavelength / nm

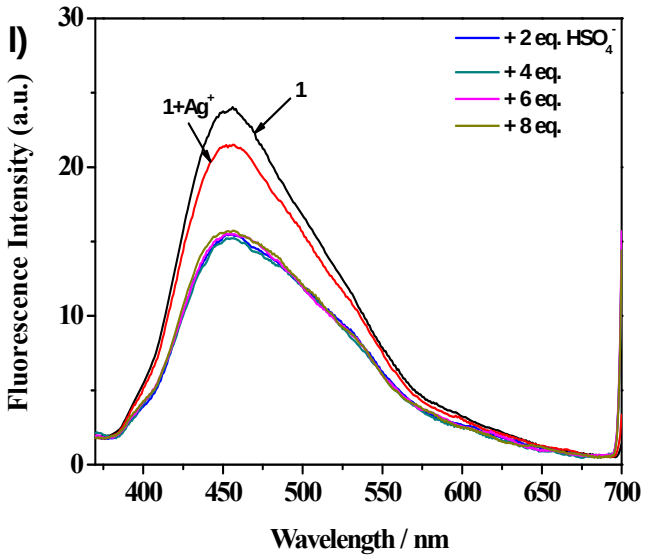

g)
1+Fe2+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.
Fluorescence Intensity (a.u.)
Wavelength / nm


h)
1+Co2+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.
Fluorescence Intensity (a.u.)
Wavelength / nm


i)
1+Ni2+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.
Fluorescence Intensity (a.u.)
Wavelength / nm


j)
Fluorescence Intensity (a.u.)
Wavelength / nm
1+Cu2+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.


k)
Fluorescence Intensity (a.u.)
Wavelength / nm
1+Zn2+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.


l)
Fluorescence Intensity (a.u.)
Wavelength / nm
1+Ag+
1
+ 2 eq. HSO4-
+ 4 eq.
+ 6 eq.
+ 8 eq.

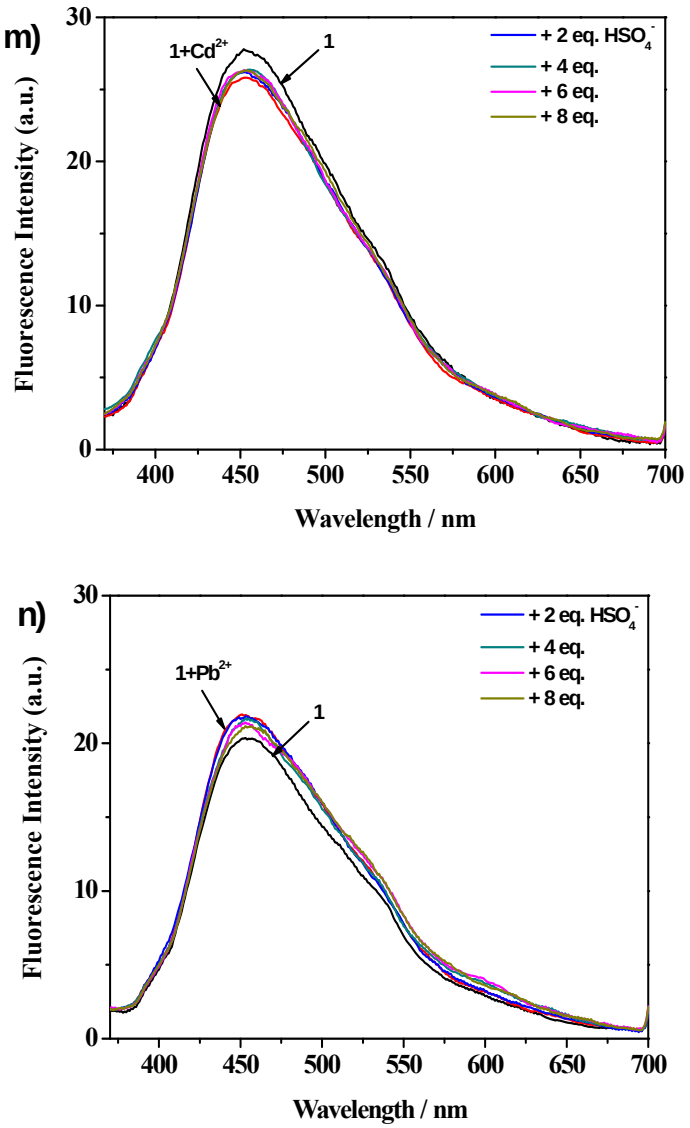


Figure S11. Fluorescence spectra of **1** (10 μM) (black) in DMF after addition of Bu_4NHSO_4 (2.0-8.0 equiv.) in the presence of 4.0 equiv. of various metal cations (red): a) $NaClO_4$, b) $Mg(ClO_4)_2$, c) $KClO_4$, d) $Ca(ClO_4)_2$, e) $Sc(ClO_4)_3$, f) $Mn(ClO_4)_2$, g) $Fe(ClO_4)_2$, h) $Co(ClO_4)_2$, i) $Ni(ClO_4)_2$, j) $Cu(ClO_4)_2$, k) $Zn(ClO_4)_2$, l) $AgClO_4$, m) $Cd(ClO_4)_2$ and n) $Pb(ClO_4)_2$.

13. ^{1}H NMR spectra of 1 after addition of Bu_4NHSO_4 in the presence and absence of $Hg(ClO_4)_2$

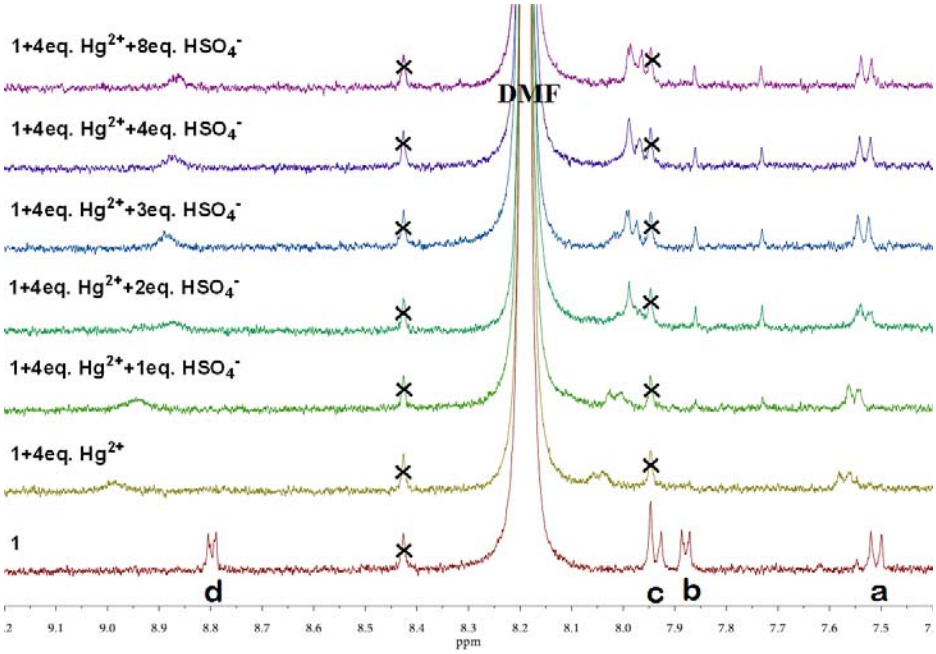


Figure S12. ^{1}H NMR spectra of **1** (20 μM) in DMF-d_7 upon addition of 4.0 equiv. of $Hg(ClO_4)_2$ and 1.0-8.0 equiv. of Bu_4NHSO_4.

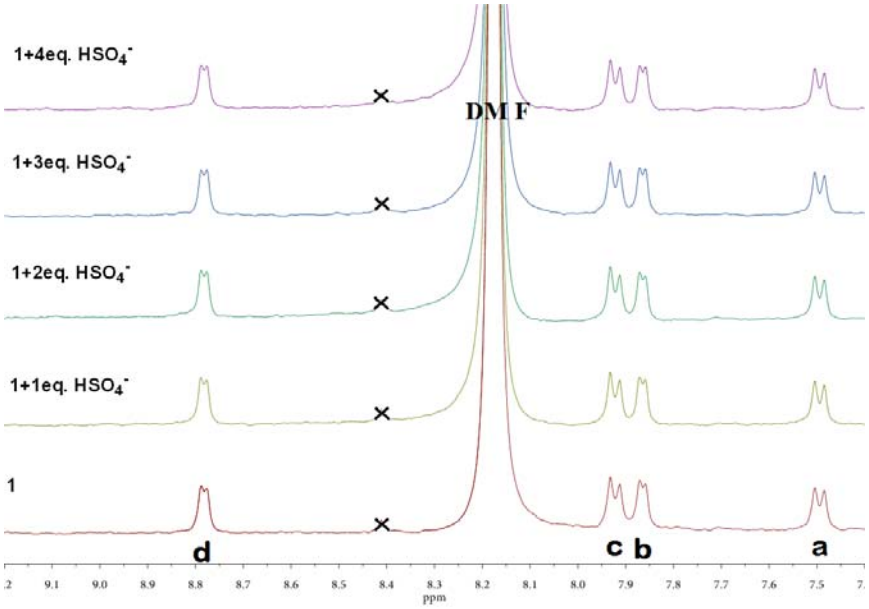


Figure S13. ^{1}H NMR spectra of **1** (0.1 mM) in DMF-d_7 upon addition of 1.0-4.0 equiv. of Bu_4NHSO_4.

14. XPS spectra of 1 after addition of $Hg(ClO_4)_2$ in the presence and absence of Bu_4NHSO_4

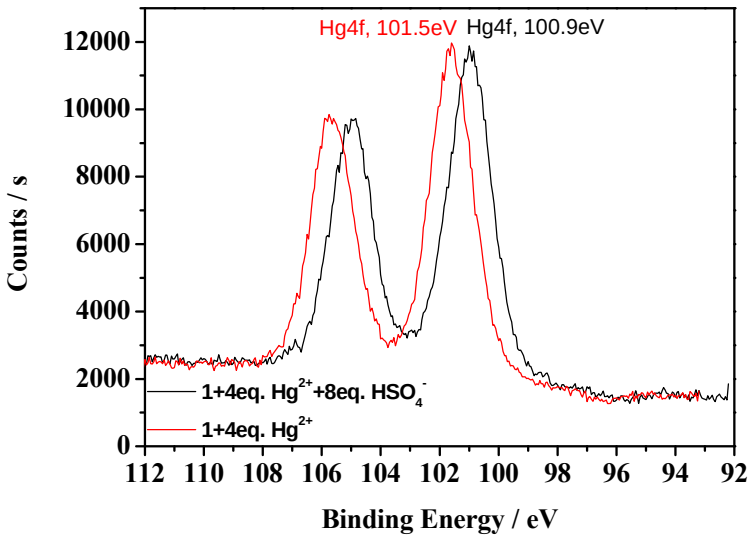


Figure S14. XPS data of Hg4f for **1** after addition of $Hg(ClO_4)_2$ in the presence and absence of Bu_4NHSO_4.

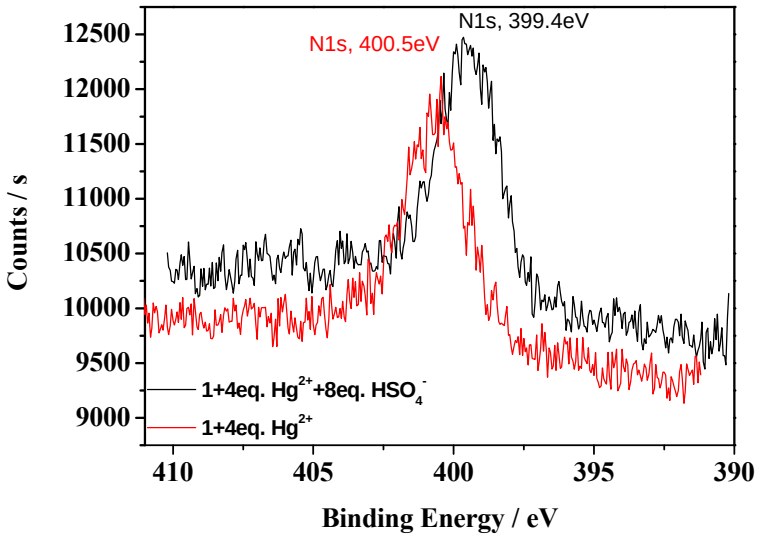


Figure S15. XPS data of N1s for **1** after addition of $Hg(ClO_4)_2$ in the presence and absence of Bu_4NHSO_4.