Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

An NBD-armed thiacalix[4]arene-derived colorimetric and fluorometric chemosensor for silver cation: a metal-ligand receptor of anions

Yu Fu,[a] Lan Mu,[a] Xi Zeng,*[a] Jiang-Lin Zhao,[a] Carl Redshaw,[b] Xin-Long Ni,*[a] and Takehiko Yamato[c]

[a]Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China

[b] School of Chemistry, University of Hull, Hull, HU6 7RX (UK)

[c]Department of Applied Chemistry, Faculty of Science and Engineering Saga University 1 Honjo-machi 1, Saga-shi, Saga 840-8502, Japan

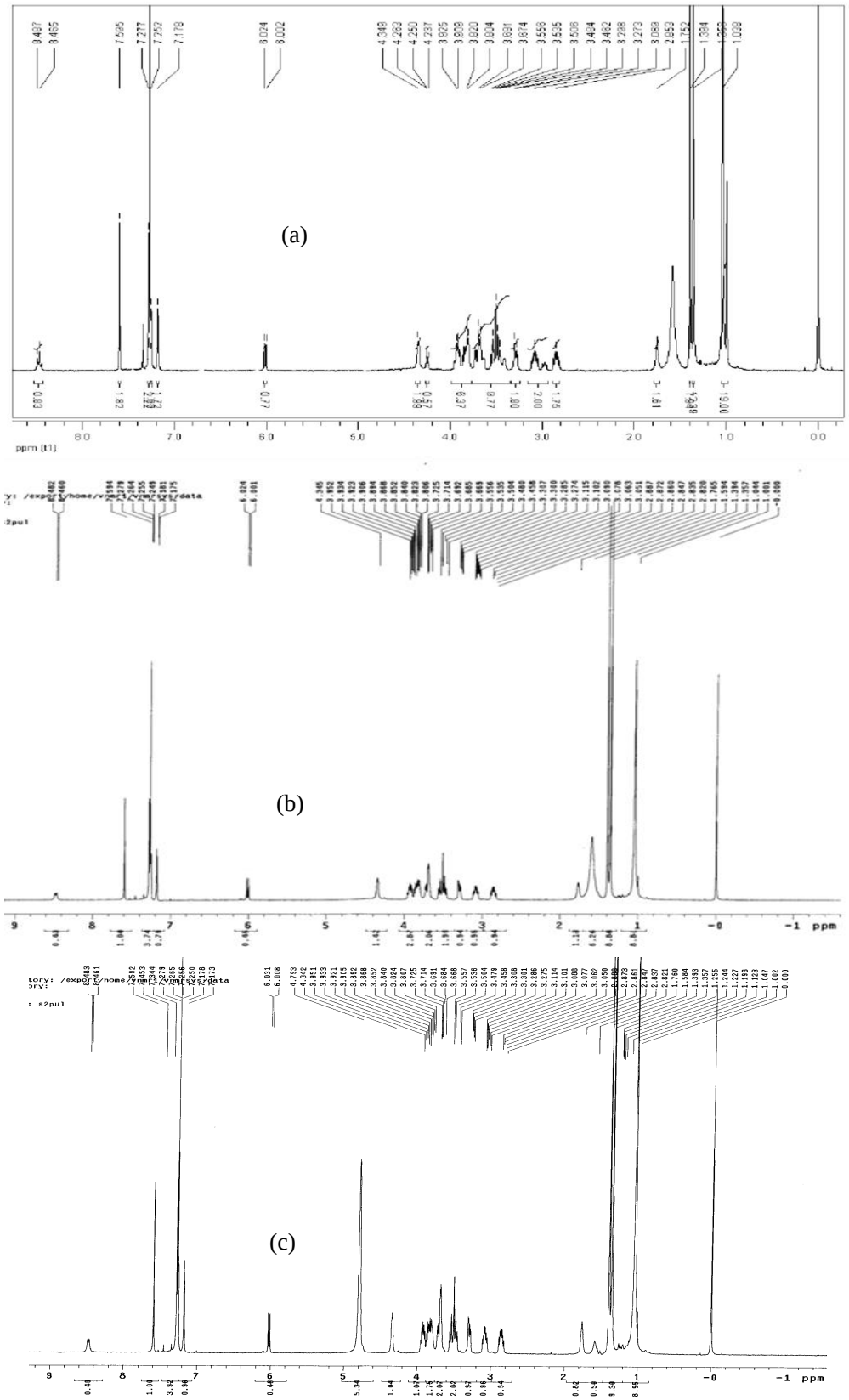


Figure S1. ^{1}H NMR spectra of compound **2a** in $CDCl_3$ (a) and (b), and in $CDCl_3/D_2O$ (10:1, v/v) (c).

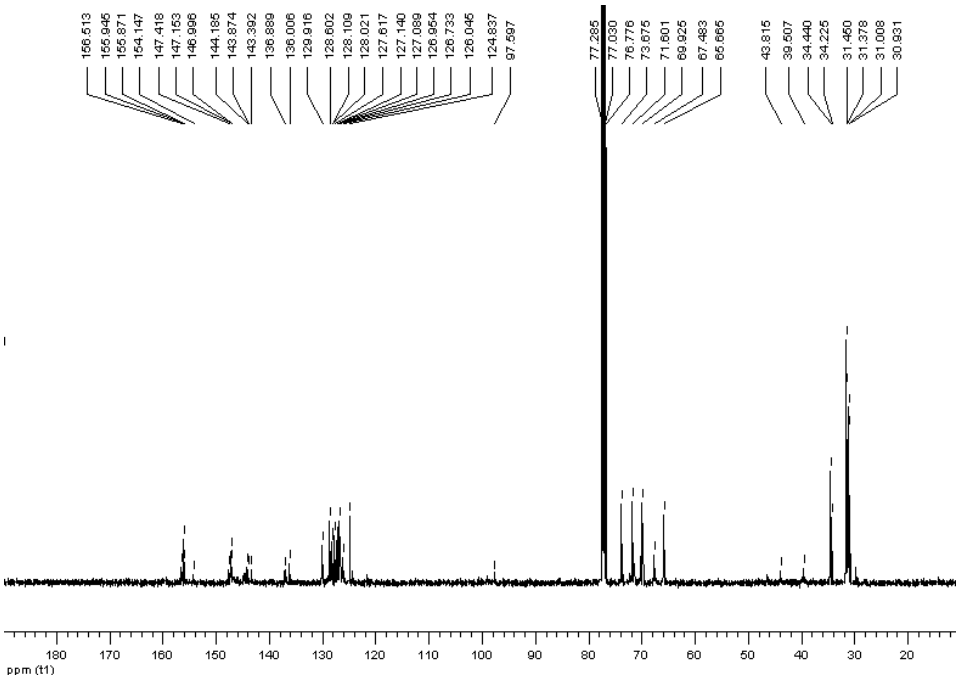


Figure S2. ^{13}C NMR spectra of compound **2a** in $CDCl_3$.

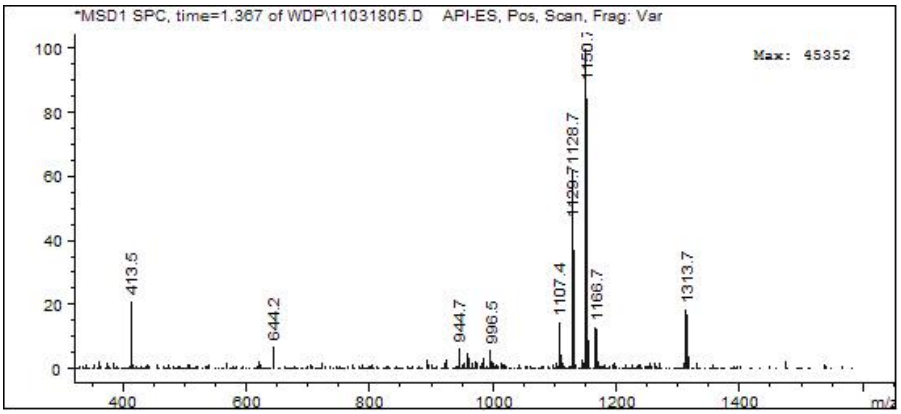


Figure S3. HPLC-ESI mass spectra (positive) of compound **2a**.

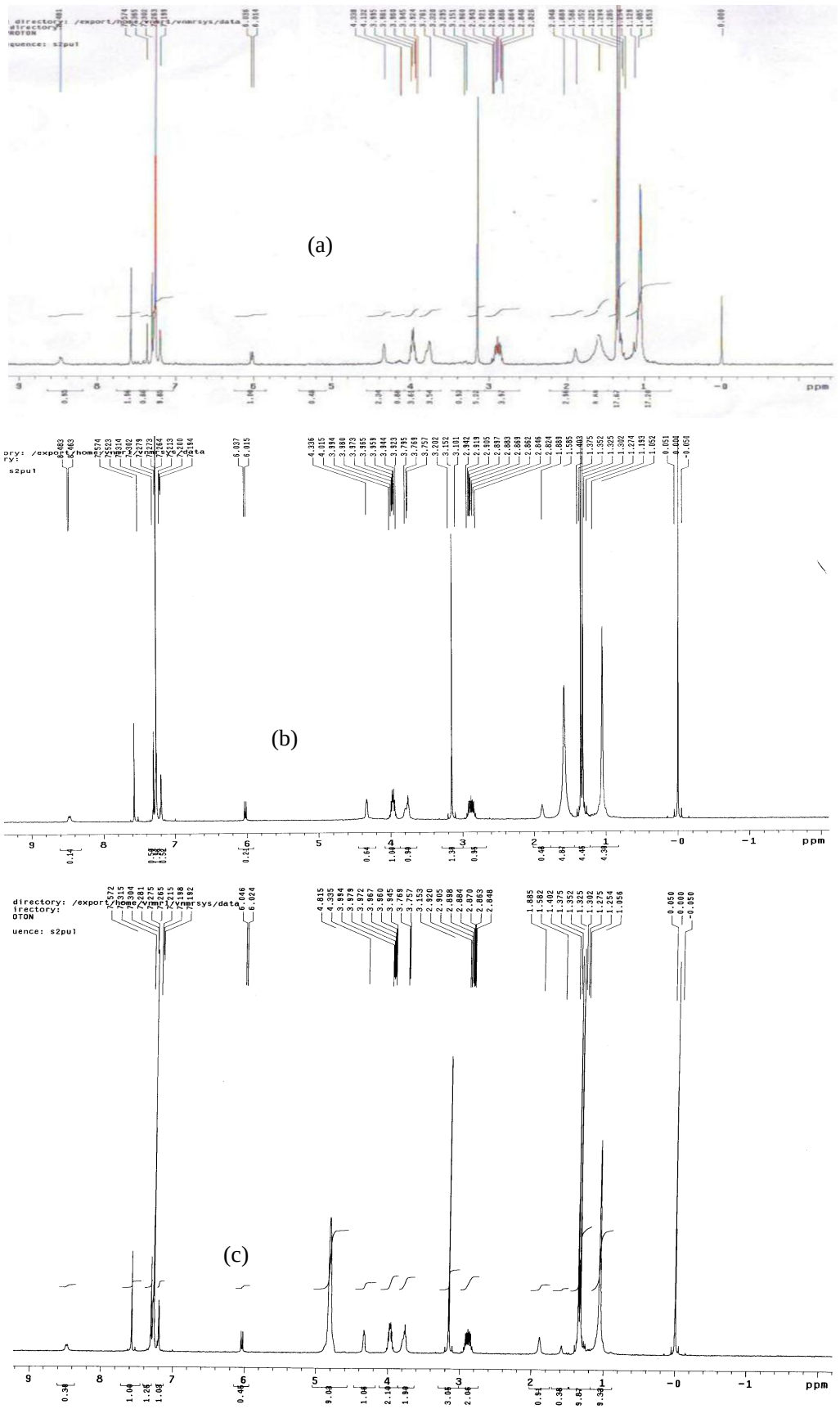


Figure S4. ^{1}H NMR spectra of compound **2a** in $CDCl_3$ (a) and (b), and in $CDCl_3/D_2O$ (10:1, v/v) (c).

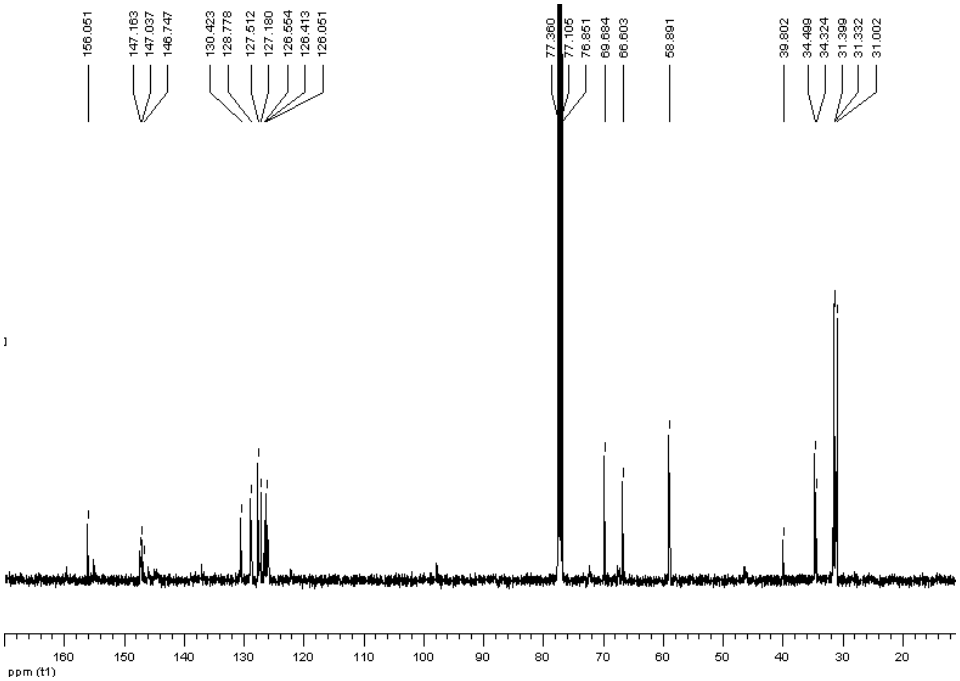


Figure S5. ^{13}C NMR spectra of compound **2b** in $CDCl_3$.

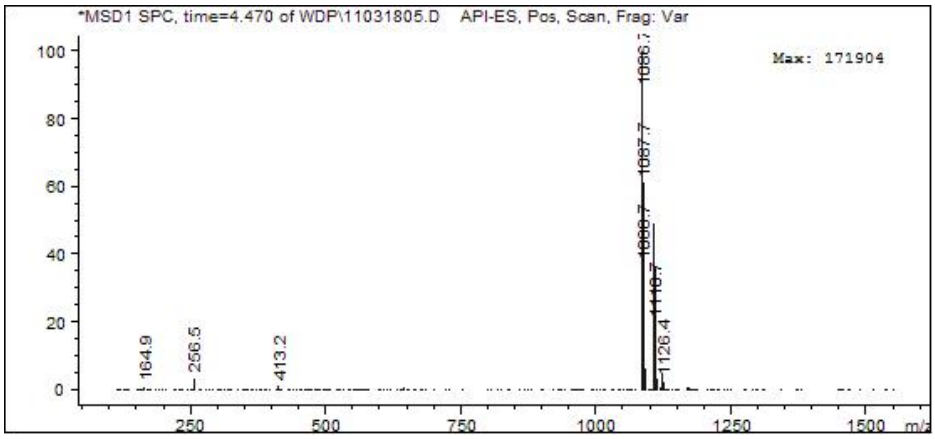


Figure S6. HPLC-ESI mass spectra (positive) of compound **2b.**

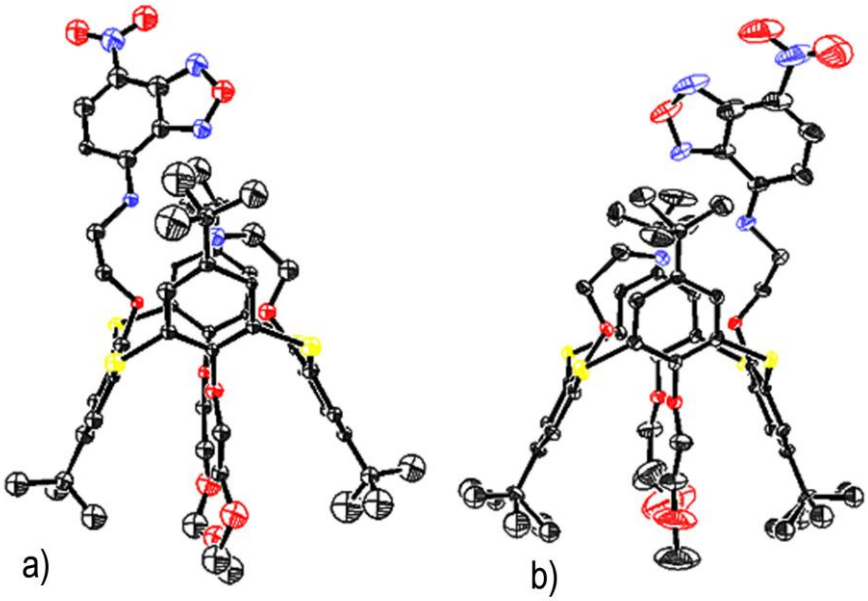
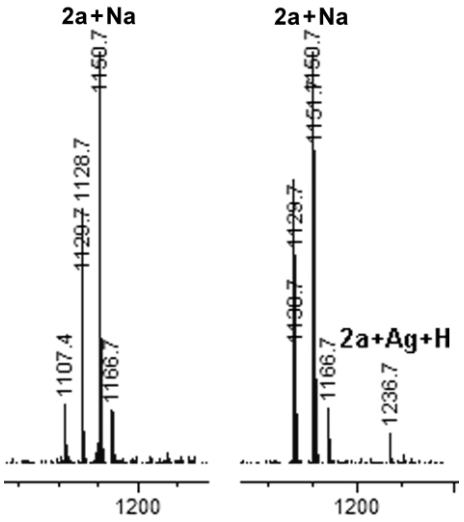


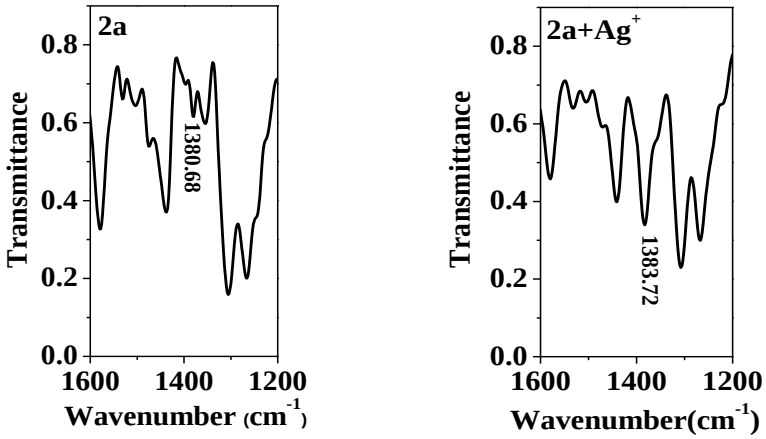
Figure S7. Side views of the X-ray crystal structure of a) **2a** and b) **2b**. The thermal ellipsoids are drawn at 50 % probability; hydrogen atoms are omitted for clarity.

X-ray crystal data for receptors 2a: Recrystallized from $CHCl_3/C_2H_5OH$ (4:1, v/v) in the presence small amount of benzene. Crystal data: $C_{58}H_{73}N_5O_{10}S_4$; M = 1128.4; crystal system: monoclinic; space group: P 21; a = 14.792(9), b = 13.313(8), c = 18.498(12) Å; α = 90.00°, β = 105.325(9)°, γ = 90.00°; V = 3513(4) Å^3; Z = 2; D_c = 1.366 g cm^{-3}; crystal dimensions 0.20 × 0.20 × 0.18 mm^3; T = 293(2) K; R_{int} = 0.1152, R [I > 2σ(I)][a] = 0.1883 for 7459 unique reflections.



a) b)

Figure S8. HPLC-ESI mass spectra (positive) of **2a** and **2a**/Ag^+; a) **2a** (10.0 μM), b) **2a** with Ag^+ (1.0 equiv.).



a) b)

Figure S9. IR studies of compound **2a** and **2a**/Ag^+; a) **2a** (10.0 μM), b) **2a** with Ag^+ (1.0 equiv.).

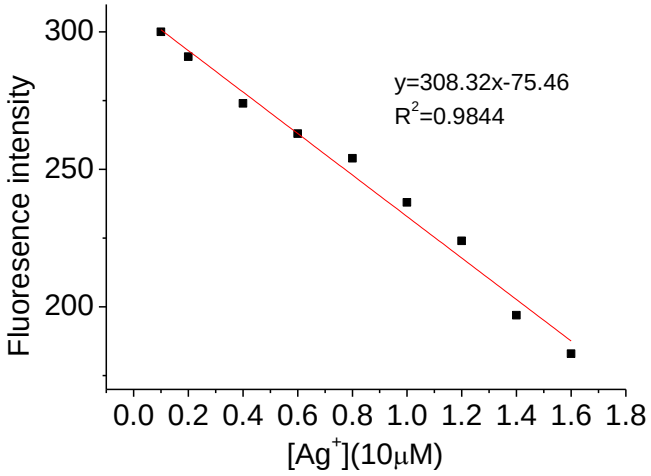


Figure S10. Plot of fluorescence intensity change (533 nm) of **2a** with varied concentrations of Ag^+ at 298 K, the limit of detection of Ag^+ was calculated to be 2.92 × 10^{-7} M by the formula (3σ/K).

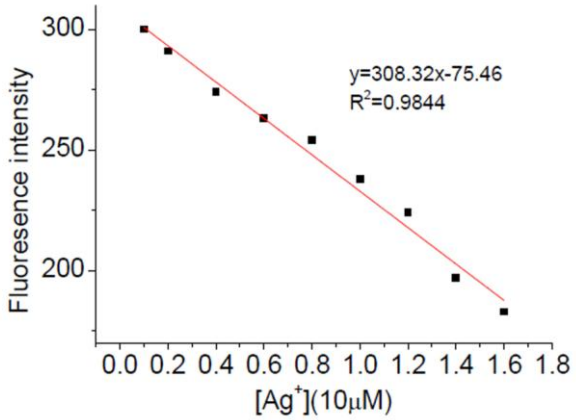


Figure S11. Plot of fluorescence intensity change (533 nm) of **2b** with varied concentrations of Ag^+ at 298 K, the limit of detection of Ag^+ was calculated to be 6.50 × 10^{-7} M by the formula (3σ/K).

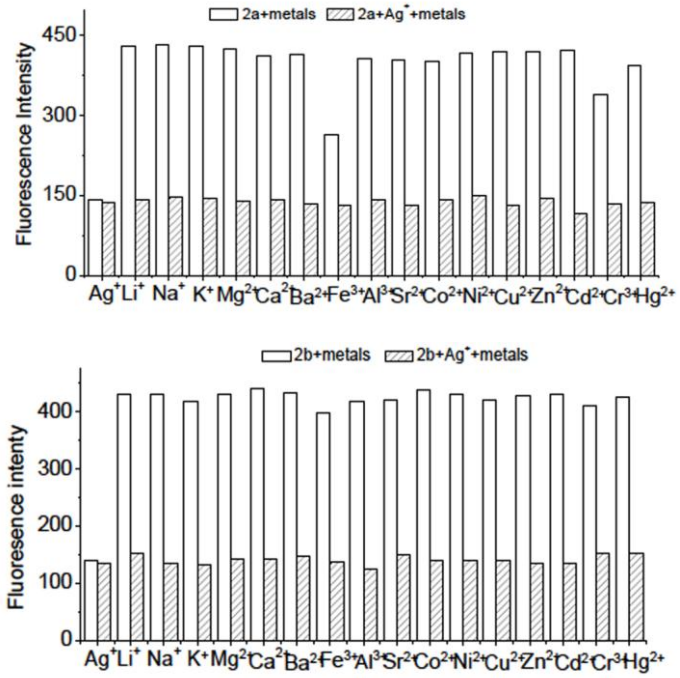


Figure S12. Fluorescence intensity responses of receptors **2a** and **2b** to 50 μM various tested ions (white bar) and to the mixture 50 μM tested cations with 50μM Ag^+ (gray bar) at 298 K. λ_{ex} = 466 nm.

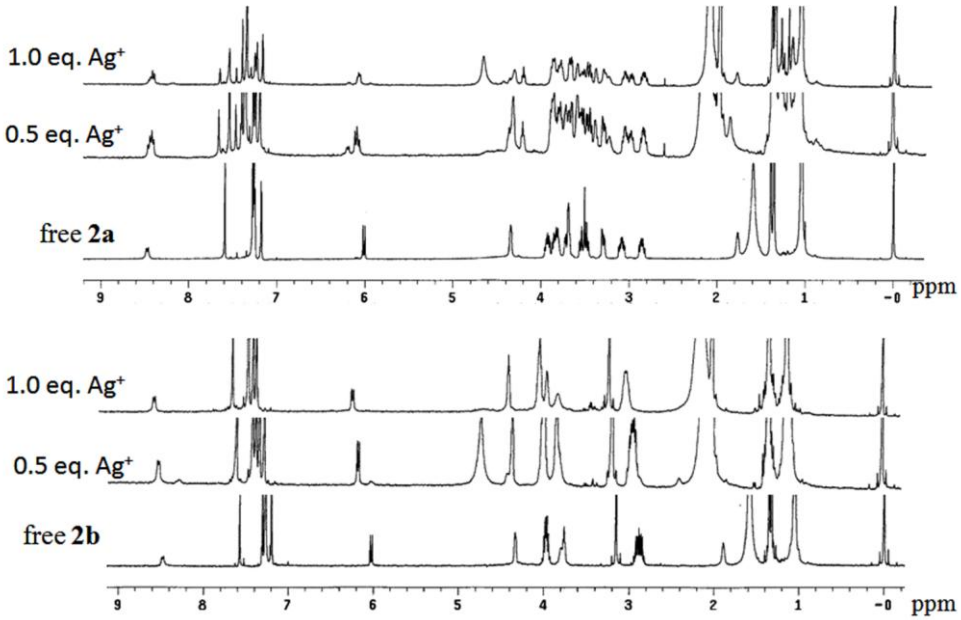


Figure S13. Partial ^{1}H NMR spectral changes of **2a** and **2b** (each at 5.0 mM) in $CDCl_3$/CDCN (10:1, v/v) upon addition of 0.5 and 1.0 eq. of $AgClO_4$ at 298 K.

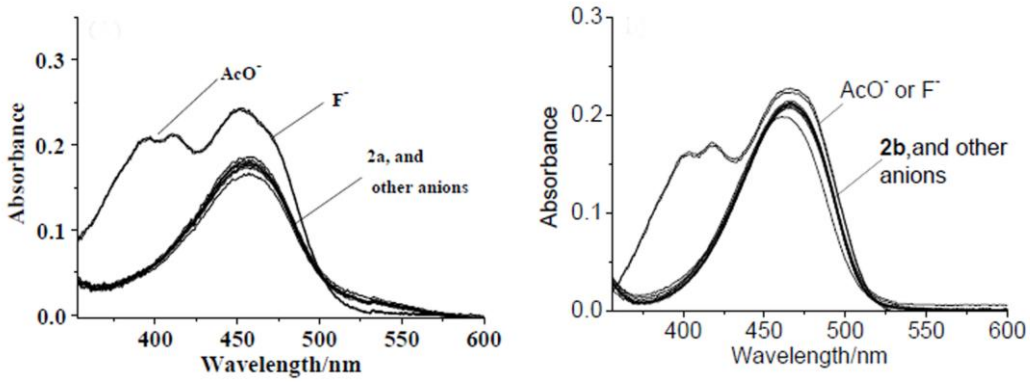


Figure S14. UV-vis absorption spectra changes of receptors a) **2a** and b) **2b** (each of 10.0 μM) with the addition of various anions (10.0 eq.) in THF solution at 298 K.

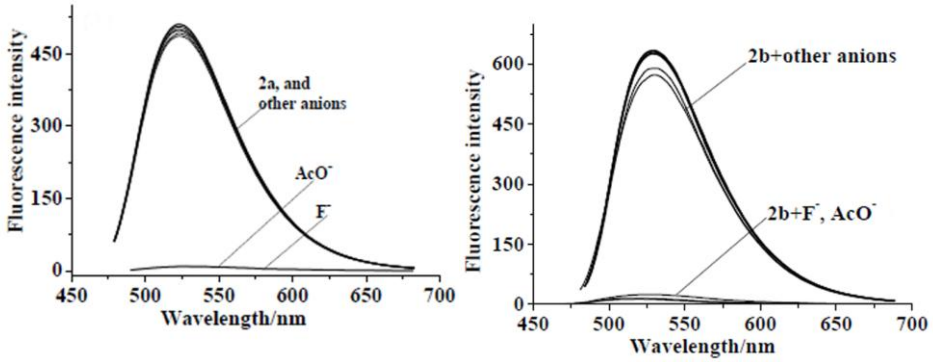


Figure S15. Fluorescence emission spectra changes of receptors a) **2a** and b) **2b** (each of 10.0 μM) upon addition of various anions (10.0 eq.) in THF solution at 298 K. λ_{ex} = 466 nm.

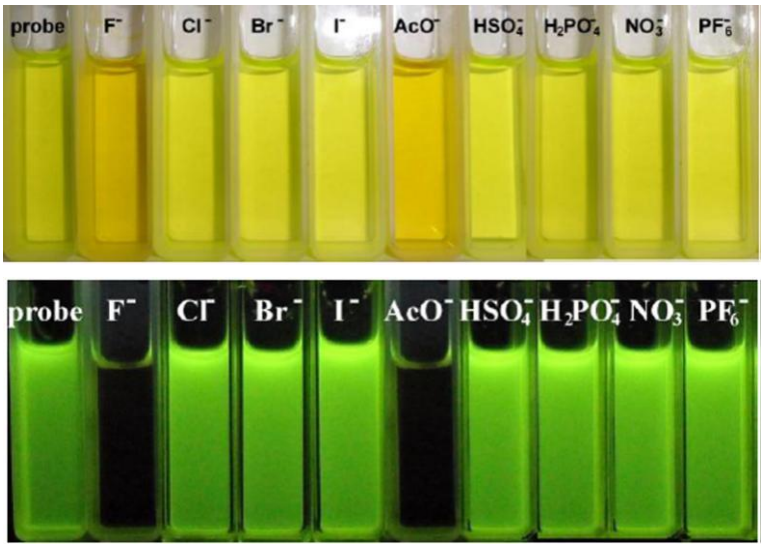


Figure S16. Visual color changes for receptor **2a** upon addition of various anions in THF solution.

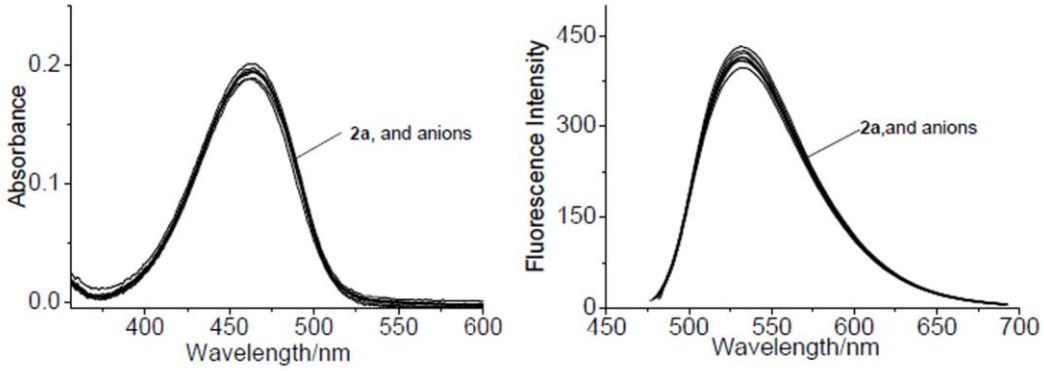


Figure S17. UV-vis and fluorescence spectra changes of receptor **2a** (10.0 μM) upon addition of various anions (10.0 eq.) in H_2O/THF (1:4, v/v, pH = 7.5) solution at 298 K. λ_{ex} = 466 nm.

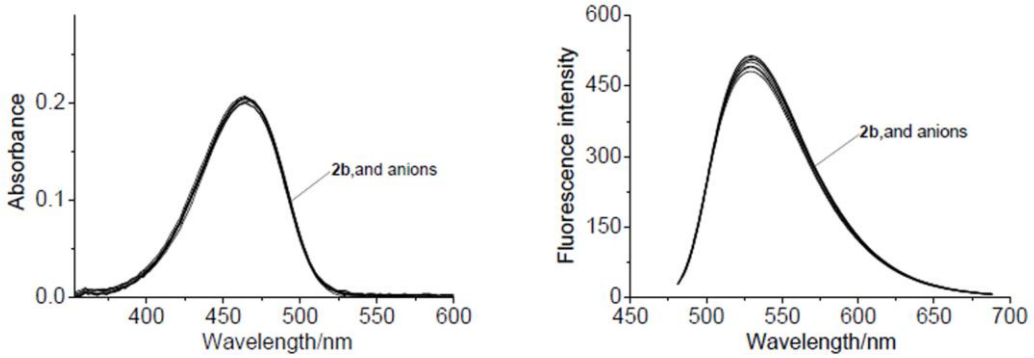


Figure S18. UV-vis and fluorescence spectra changes of receptor **2b** (10.0 μM) upon addition of various anions (10.0 eq.) in H_2O/THF (1:4, v/v, pH = 7.5) solution at 298 K. λ_{ex} = 466 nm.

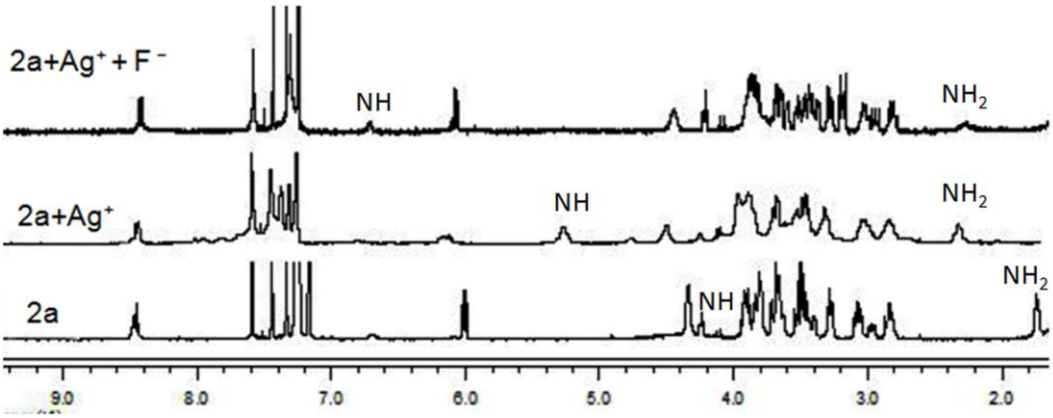


Figure S19. Partial ^{1}H NMR spectral changes of **2a** (5.0 mM) in $CDCl_3$ upon addition of 1.0 eq. of Ag^+ and F^- ions at 298 K.

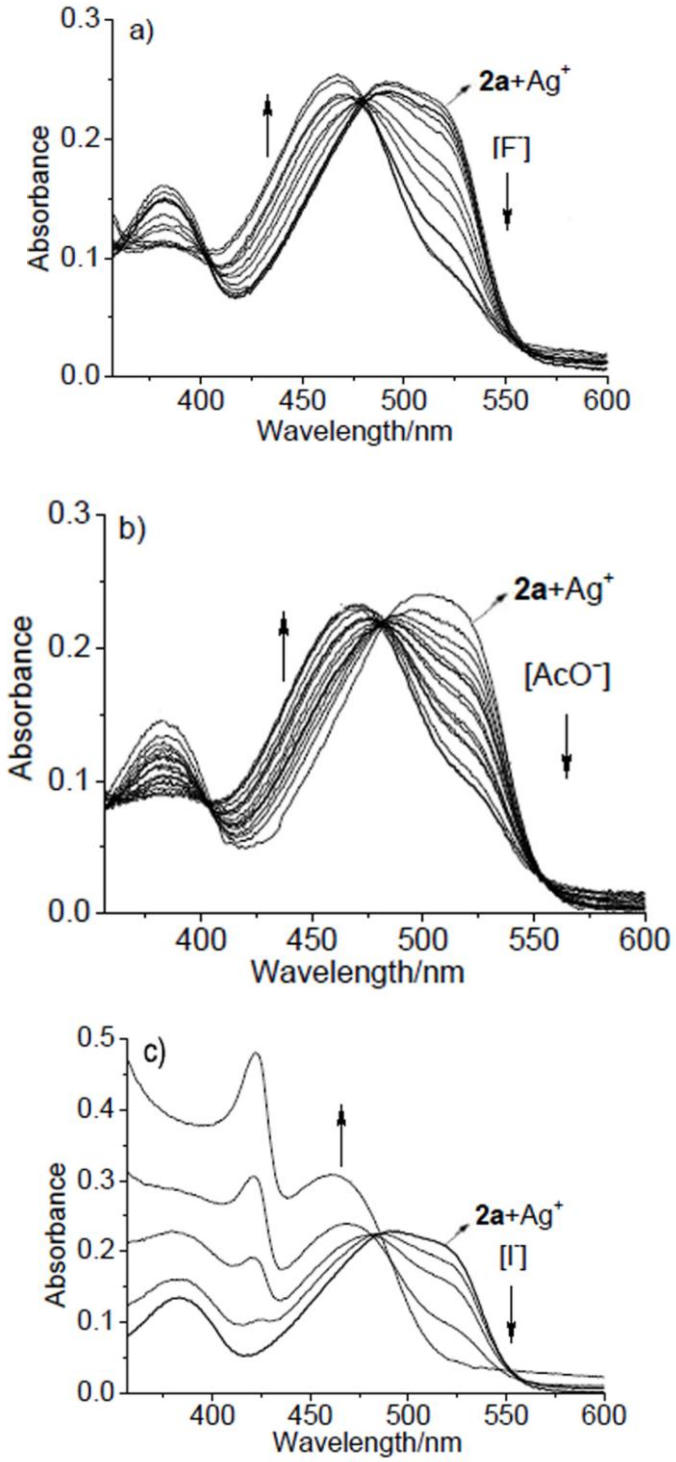


Figure S20. Changes in the UV-vis absorption spectra of receptor **2a**•Ag^{+} upon addition of increasing concentrations of a) F^{-}, b) AcO^{-} and c) I^{-} anions in aqueous solution (0−50 μM) at 298 K in H_2O/THF (1:4, v/v, pH = 7.5) solution.

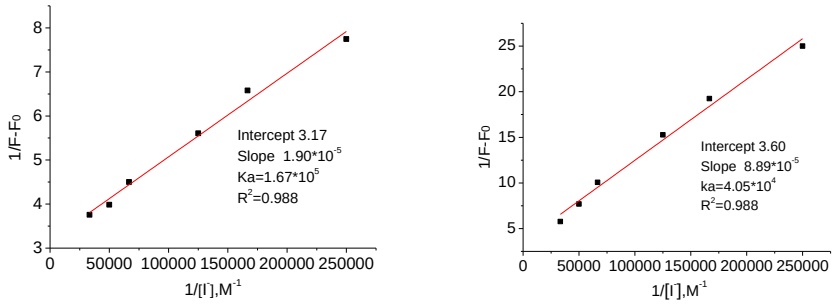


Figure S21. Benesi-Hilderbrand plot of **2a**•Ag^{+} and **2b**•$Ag^{+}$with I^{-} anion.

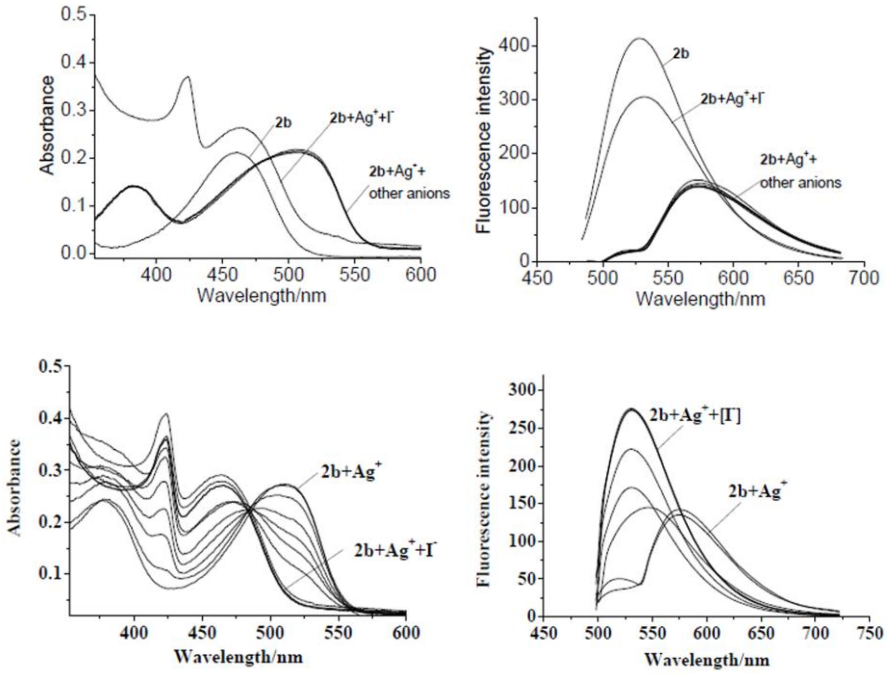


Figure S22. Changes in the UV-vis absorption and fluorescence emission spectra of receptor **2b**•Ag^{+} upon addition of various anions and I^{-} anion (5.0 eq.) at 298 K in H_2O/THF (1:4, v/v, pH = 7.5) solution.

Figure S23. Visual color changes for receptor a) **2b**, b) **2b**•Ag^{+}, c) **2b**•Ag^{+} + F^{-}, d) **2b**•Ag^{+} + AcO^{-}, e) **2b**•Ag^{+} + I^{-} in H_2O/THF (1:4, v/v, pH = 7.5) solution.