Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Fluorescent chemosensing for aromatic compounds by supramolecular complex composed of tin(IV) porphyrin, viologen, and cucurbit[8]uril

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Experimental Section

All operations were carried out using standard Schlenk line techniques under nitrogen atmosphere. ^{1}H NMR spectra were obtained on a Bruker BIOSPIN/AVANCE III 400 spectrometer. Fluorescence spectra were recorded on a Shimadzu PF-5300PC spectrophotometer. ESI mass spectra were recorded on a Thermo Finnigan Linear Ion Trap Quadrupole mass spectrometer**.**

***meso*-Tetrakis[4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl]porphyrin**

To a solution containing [2-[2-(2-methoxyethoxy)ethoxy]ethoxy]*p*-toluenesulfonate (0.14 g, 0.50 mmol) and *meso*-tetrakis(4-hydroxyphenyl)porphyrin (0.10 g, 0.15 mmol) in DMF (30 mL), K_2CO_3 (0.17 g, 1.25 mmol) was added. The reaction mixture was heated at reflux for 24h. After the solvent was removed in vacuo, the product was separated and purified by column chromatography using an eluent of CH_2Cl_2 on silica gel. Yield: 0.18 g (93 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 8H), 8.16 (d, 8H), 7.29 (d, 8H), 4.25 (t, 8H), 3.91 (t, 8H), 3.73 (t, 8H), 3.66 (t, 8H), 3.58 (t, 8H), 3.46 (t, 8H), 3.29 (s, 12H), -2.90 (s, 2H) ppm.

***trans*-Dichloro[tetrakis{4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl}porphyrinato]tin(IV):** To a solution of tetrakis[4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl] porphyrin (0.10 g, 0.79 mmol) in 50 mL pyridine, anhydrous tin(II) chloride (200 mg, 1.05 mmol) was added. After refluxing for 7 hours, the solution was filtered through a celite pad. The product was recrystallized from CH_2Cl_2/*n*-hexane. Yield: 0.09 g (78 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.28 (s, 12H), 3.50 (m, 8H), 3.60 (m, 8H), 3.65 (m, 8H), 3.73 (m, 8H), 3.95 (t, 8H), 4.44 (t, 8H), 7.49 (d, 8H), 8.21 (d, 8H), 9.28 (s, 8H) ppm.

***trans*-Dihydroxo[tetrakis{4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl}porphyrinato]tin(IV):**

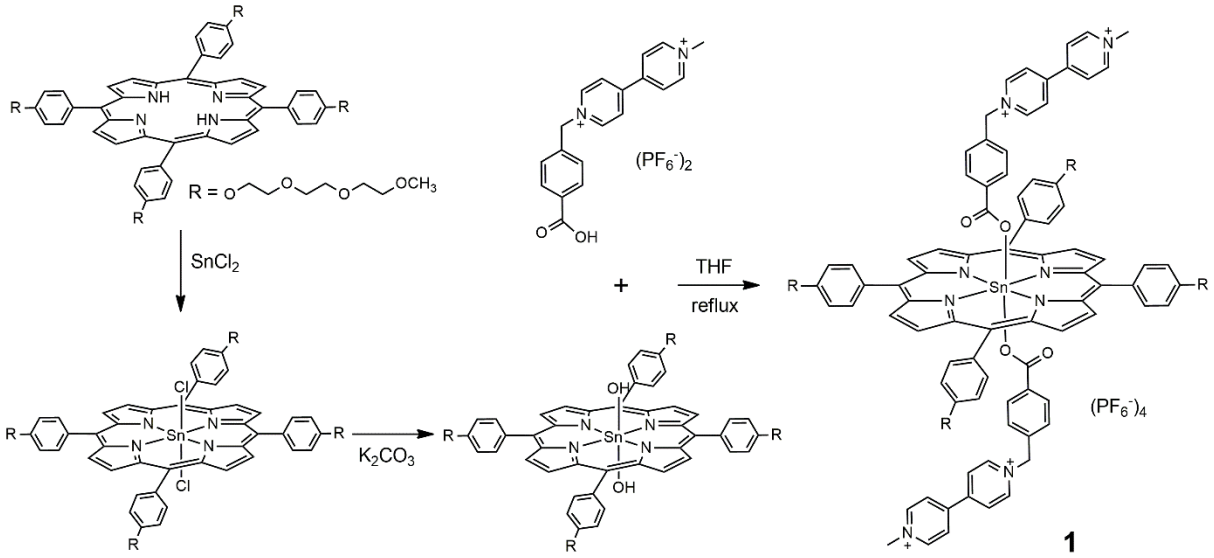
To a solution of (por)$SnCl_2$ (0.2 g, 0.13 mmol) in 100 mL of THF, a solution of K_2CO_3 (0.325 g, 2.21 mmol) in distilled water (30 mL) was added. After refluxing for 3 hours, the solvent was evaporated and the residue was carried on the extraction using CH_2Cl_2/water. The organic layers were then combined, dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure and the product was recrystallized from CH_2Cl_2/*n*-hexane. Yield: 0.14 g (72 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.28 (s, 12H), 3.50 (m, 8H), 3.61 (m, 8H), 3.65 (m, 8H), 3.73 (m, 8H), 3.95 (t, 8H), 4.43 (t, 8H), 7.46 (d, 8H), 8.18 (d, 8H), 9.05 (s, 8H) ppm.

***trans*-Bis(1-(4-Carboxybenzyl)-1'-methyl-4,4'-bipyridinium)[tetrakis{4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl}porphyrinato]tin(IV) hexafluorophosphate (1):** To a solution of (por)$Sn(OH)_2$ (0.05 g, 0.04 mmol) in 40 mL of THF, 1-(4-carboxybenzyl)-4,4′-bipyridinium

hexafluorophosphate (0.05 g, 0.08 mmol) was added. After refluxing for 48 h, the solvent was evaporated under reduced pressure. The residue was recrystallized from THF/*n*-hexane to produce **1**. Yield: 0.07 g (80 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.28 (s, 12H), 3.50 (m, 8H), 3.61 (m, 8H), 3.65 (m, 8H), 3.73 (m, 8H), 3.95 (t, 8H), 4.37 (s, 6H), 4.43 (t, 8H), 4.76 (s, 4H), 5.42 (d, 4H), 6.61 (d, 4H), 7.95 (m, 16H), 8.16 (d, 4H), 8.52 (d, 4H), 8.54 (d, 4H), 9.02 (d, 4H), 9.22 (s, 8H) ppm.

1:2 Supramolecular complex of 1 and cucurbit[8]uril (1•CB[8]): ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.28 (s, 12H), 3.50 (m, 8H), 3.61 (m, 8H), 3.65 (m, 8H), 3.73 (m, 8H), 3.95 (t, 8H), 4.21 (d, 32H, CB[8]), 4.43 (t, 8H), 4.53 (s, 6H), 5.39 (s, 32H, CB[8]), 5.58 (d, 32H, CB[8]), 6.08 (s, 4H), 6.99 (d, 4H), 7.08 (d, 4H), 7.30 (d, 4H), 7.97 (m, 8H), 8.12 (d, 8H), 8.31 (d, 4H), 8.91 (d, 4H), 8.96 (d, 4H), 9.25 (s, 8H) ppm.

Scheme S1. A series of reactions for the synthesis of **1**.



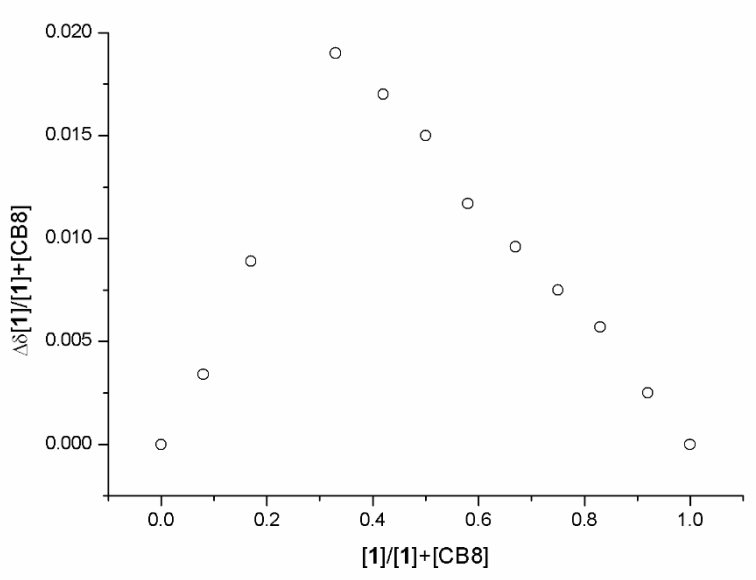


Fig. S1 Job's plot of **1** (c = 2 mM) with CB[8] in DMSO-d_6. Considering $\Delta\delta$ (= δ_{free} − $\delta_{complex}$) of α protons from the N-CH_3 end of bipyridinium moiety of **1**. Showing the maximum $\Delta\delta$ at ~0.33.

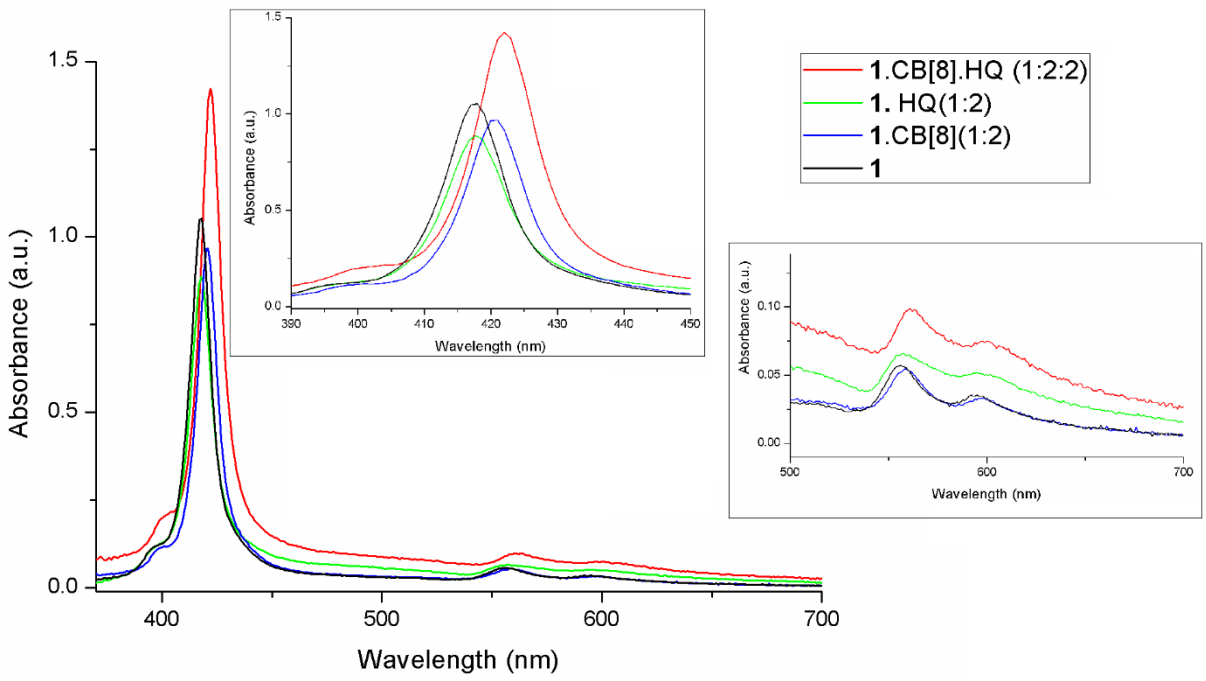


Fig. S2 Absorption spectra of **1**, CB[8], and HQ in water. All spectra were recorded with 2 μM solutions.

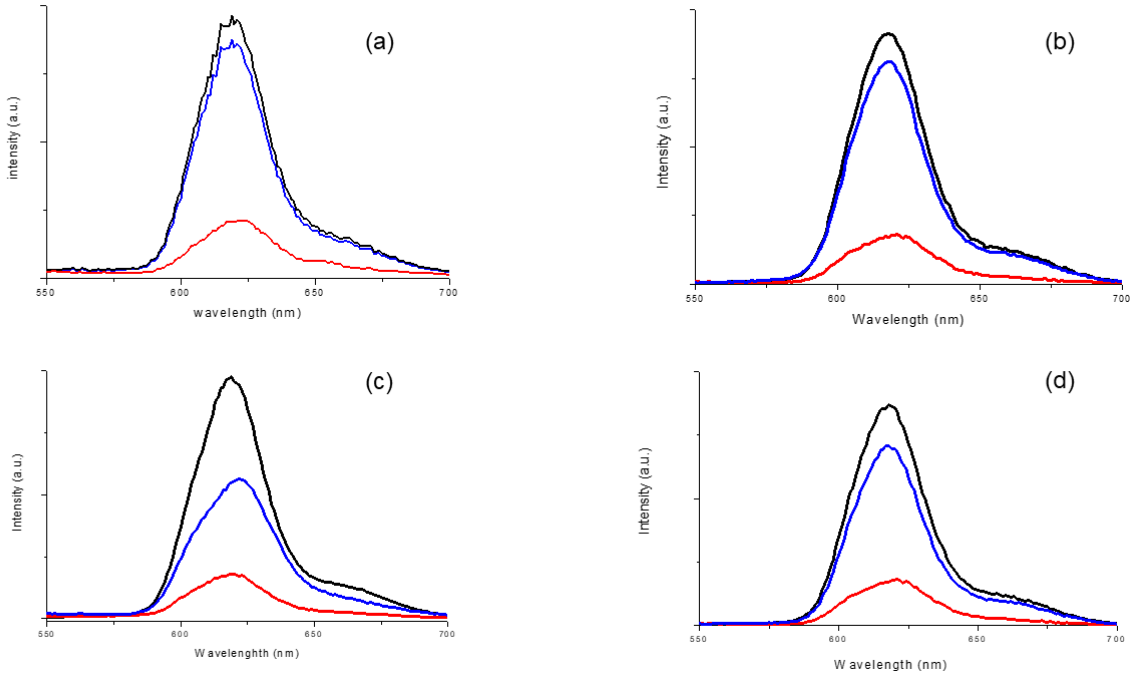


Fig. S3 Fluorescence spectral changes for **1** in aqueous solutions (c = 2 μM, using sodium phosphate buffer at pH 7.0) upon the supramolecular complexation. Each black and red curve correspond to **1** itself and the complexation with 2 equivalents of CB[8], respectively. The blue curves depict in the additional presence of 2 equivalent aromatic compounds; (a) 2,6-dihydroxynaphthalene, (b) tyrosine, (c) tryptophan, and (d) dopamine. The fluorescence was yielded by the excitation at 422 nm.

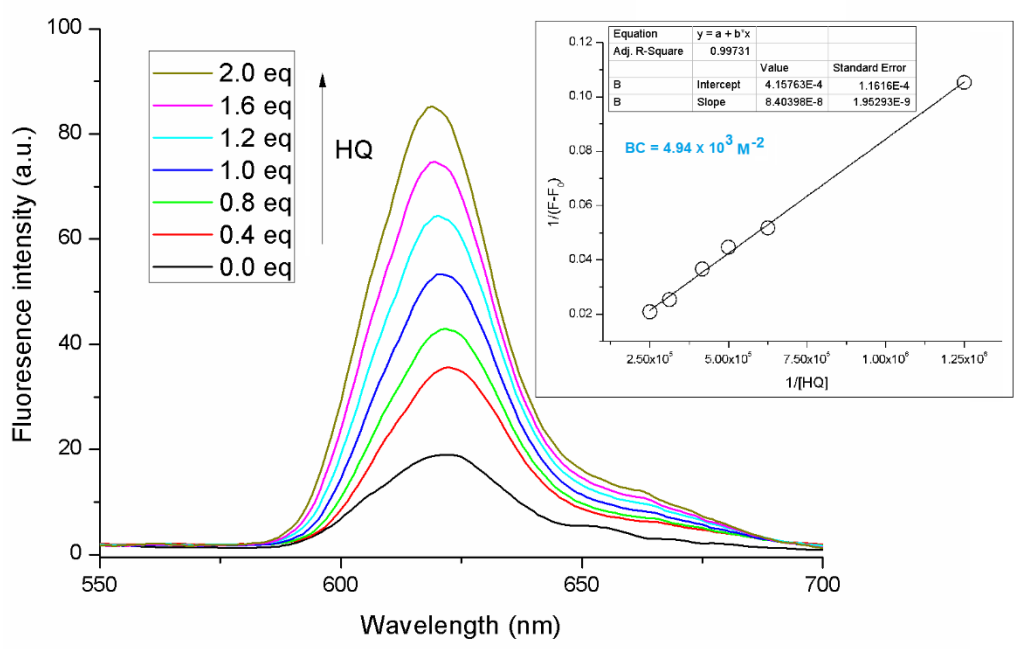


Fig. S4 Fluorescence titration experiment of **1**•CB[8] (c = 2 μM, using sodium phosphate buffer at pH 7.0) and hydroquinone in water (λ_{ex} = 422 nm). The inset shows the linear fitting curve.

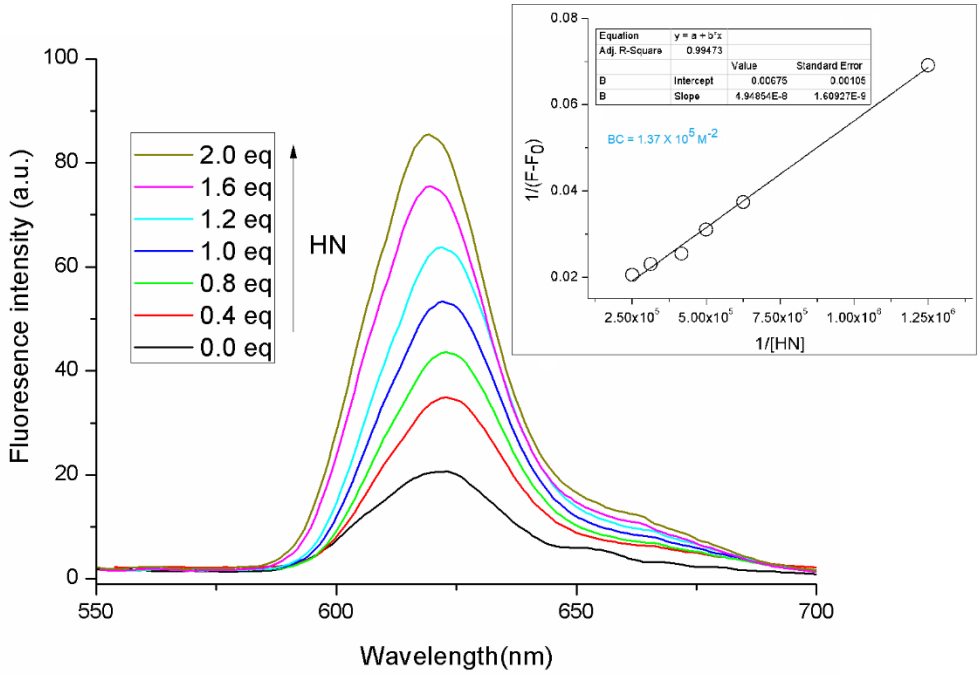


Fig. S5 Fluorescence titration experiment of **1**•CB[8] (c = 2 μM, using sodium phosphate buffer at pH 7.0) and 2,6-dihydroxynaphthalene in water (λ_{ex} = 422 nm). The inset shows the linear fitting curve.

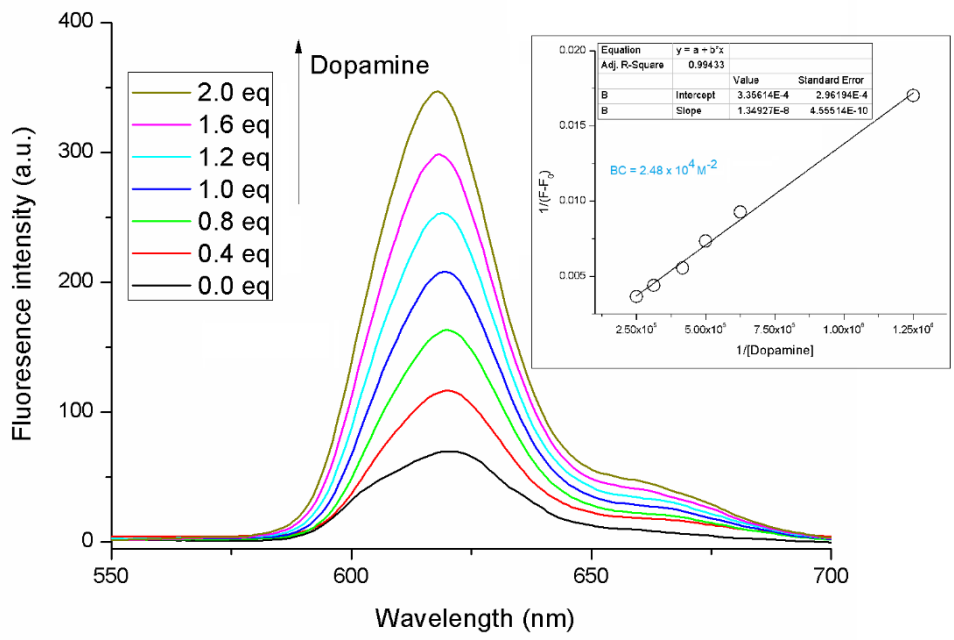


Fig. S6 Fluorescence titration experiment of **1**•CB[8] (c = 2 μM, using sodium phosphate buffer at pH 7.0) and dopamine in water (λ_{ex} = 422 nm). The inset shows the linear fitting curve.

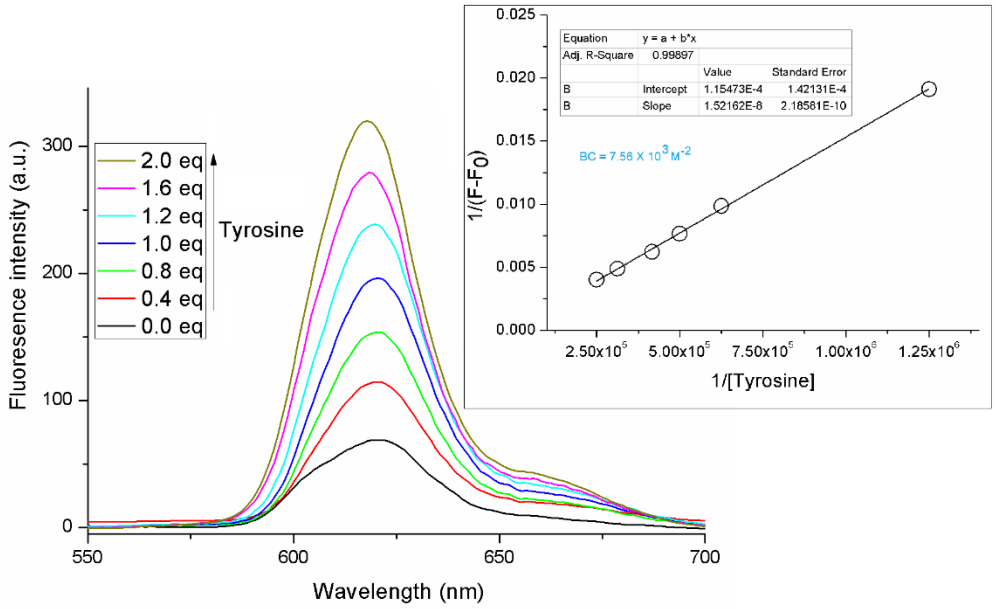


Fig. S7 Fluorescence titration experiment of **1**•CB[8] (c = 2 μM, using sodium phosphate buffer at pH 7.0) and tyrosine in water (λ_{ex} = 422 nm). The inset shows the linear fitting curve.

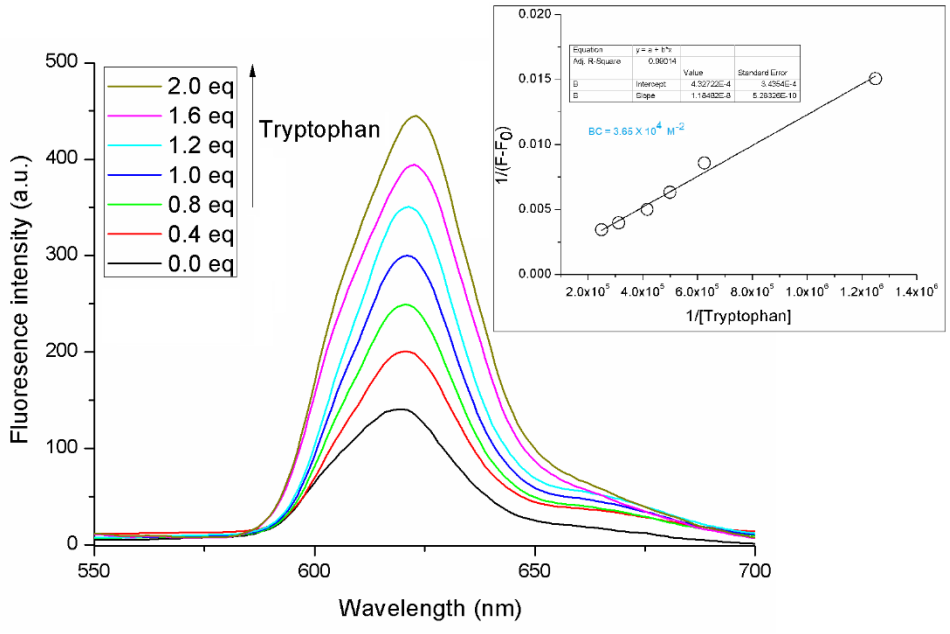


Fig. S8 Fluorescence titration experiment of **1**•CB[8] (c = 2 μM, using sodium phosphate buffer at pH 7.0) and tryptophan in water (λ_{ex} = 422 nm). The inset shows the linear fitting curve.

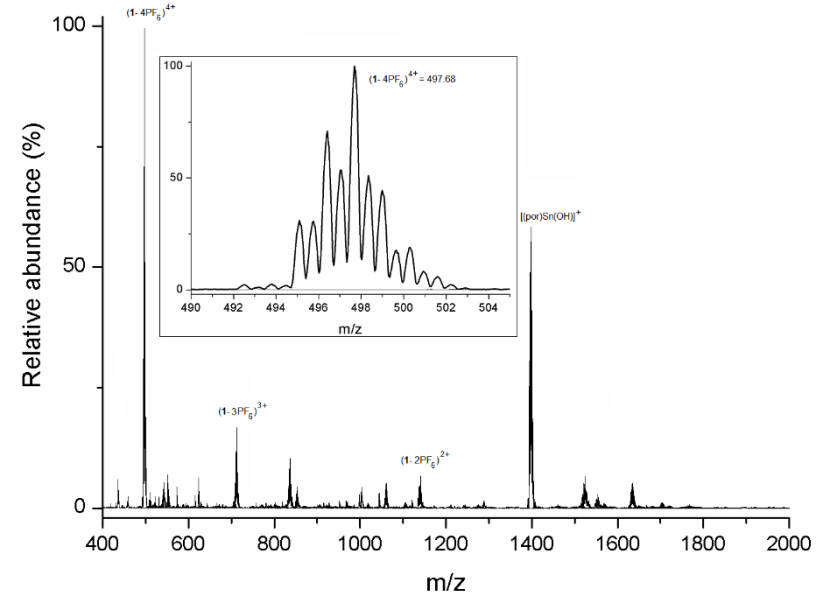


Fig. S9 ESI-MS spectrum for **1.**

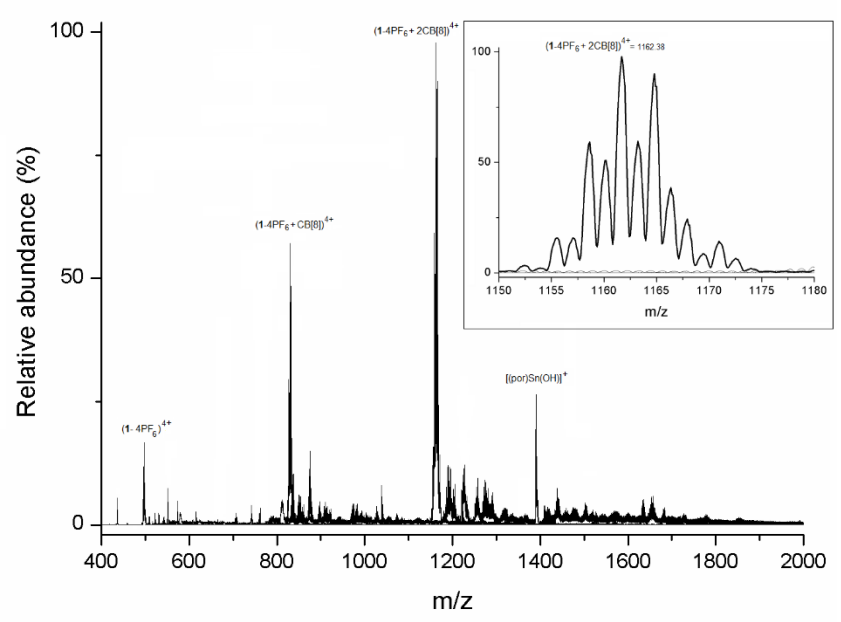


Fig. S10 ESI-MS spectrum for the 1:2 complex of **1** and CB[8]**.**

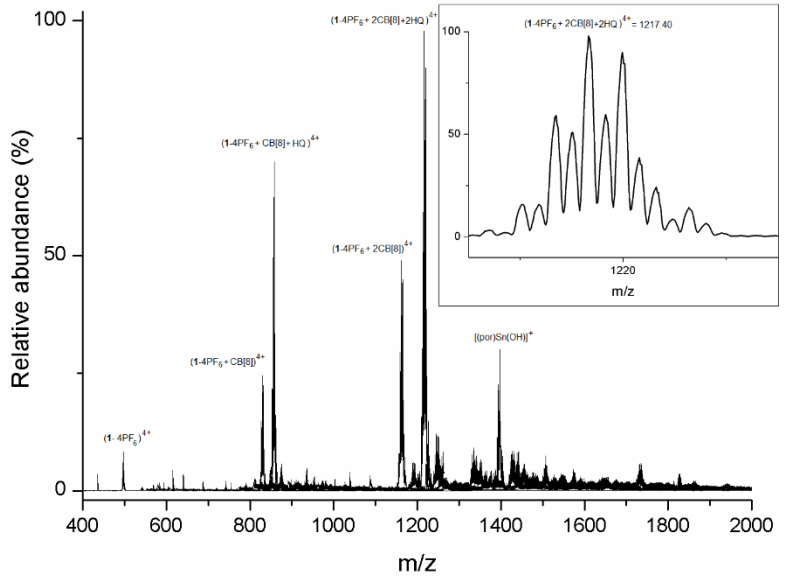


Fig. S11 ESI-MS spectrum for the 1:2:2 complex of **1,** CB[8], and hydroquinone (HQ)**.**