Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Sulfonatocalix[4]arene-Based Light-Harvesting Amphiphilic Supramolecular Assemblies for Sensing Sulfites in Cells

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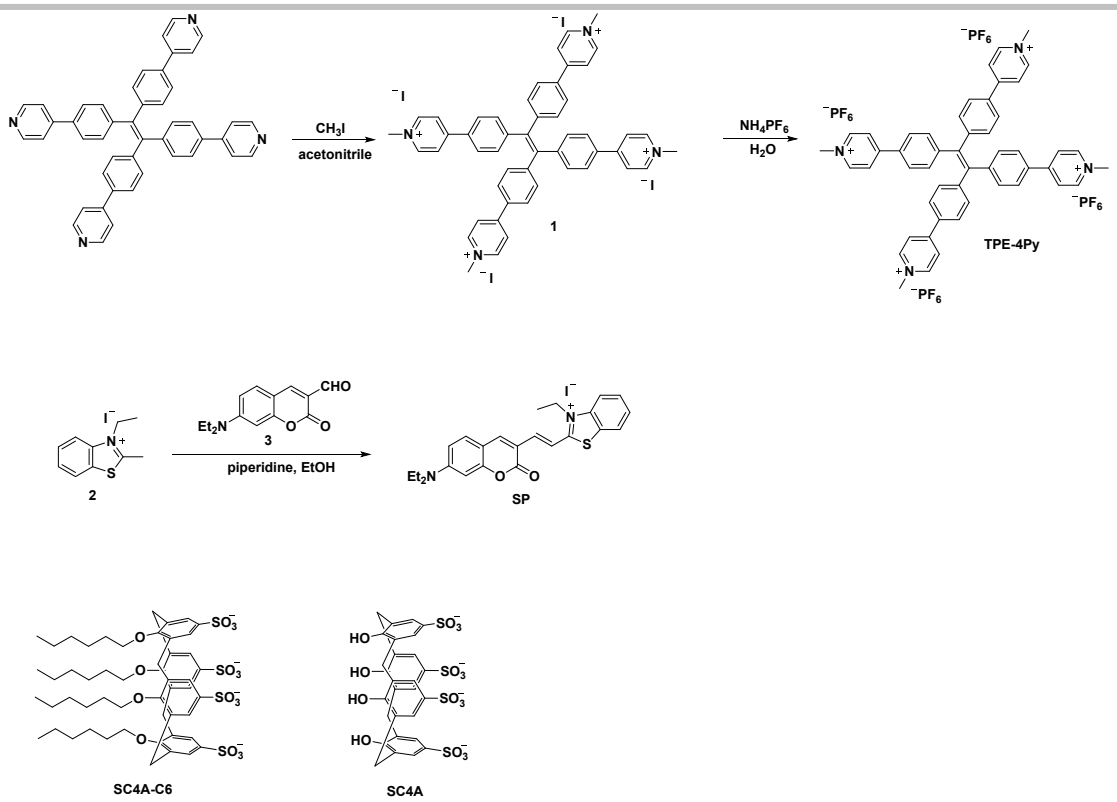

Scheme S1. Synthesis of **TPE-4Py** and **SP**, and the structure of **SC4A-C6**, **SC4A**.

Compound 1

Compound **1**, **2**, **3**, **SC4A** and **SC4A-C6** were synthesized according to the reported references, respectively.[1-4]

TPE-4Py

Compound **1** (100 mg, 0.08 mmol) was dissolved in H_2O (5 mL) and the solution was stirred at room temperature for 1h. After that, NH_4PF_6 saturated solution (20 mL) was added dropwise, and the reaction mixture was stirred overnight. After that, filtered and drip washing with H_2O (100 mL) to achieve **TPE-4Py** (85 mg, 81%) as a yellow solid.

^{1}H NMR (400 MHz, DMSO) δ 8.97 (d, J = 6.6 Hz, 8H), 8.45 (d, J = 6.6 Hz, 8H), 8.01 (d, J = 8.3 Hz, 8H), 7.38 (d, J = 8.3 Hz, 8H), 4.31 (s, 12H).

HRMS-ESI (m/z): $[M+]^{4+}$ calcd for $C_{24}H_{25}IN_2O_2S$: 175.0886; found: 175.0889.

SP

To a solution of compound **3** (200 mg, 0.82 mmol) in absolute ethyl alcohol, compound **2** (299 mg, 1.63 mmol) and piperidine (16.2 μL, 0.16 mmol) were added, and the reaction was refluxed overnight. Cooling to room temperature to obtain a large amount of precipitate, filtered and recrystallized in absolute ethyl alcohol to afford **SP** as a dark green solid (261 mg, 59.9%).

^{1}H NMR (400 MHz, DMSO) δ 8.64 (s, 1H), 8.40 (d, J = 7.8 Hz, 1H), 8.28 (d, J = 8.5 Hz, 1H), 8.05 (s, 2H), 7.85 (t, J = 7.8 Hz, 1H), 7.76 (t, J = 7.7 Hz, 1H), 7.59 (d, J = 9.1 Hz, 1H), 6.89 (dd, J = 9.1, 2.2 Hz, 1H), 6.70 (d, J = 2.1 Hz, 1H), 4.80 (q, J = 7.1 Hz, 2H), 3.55 (q, J = 6.9 Hz, 4H), 1.49 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.0 Hz, 6H).

HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{24}H_{25}IN_2O_2S$: 405.1631; found: 405.1635.

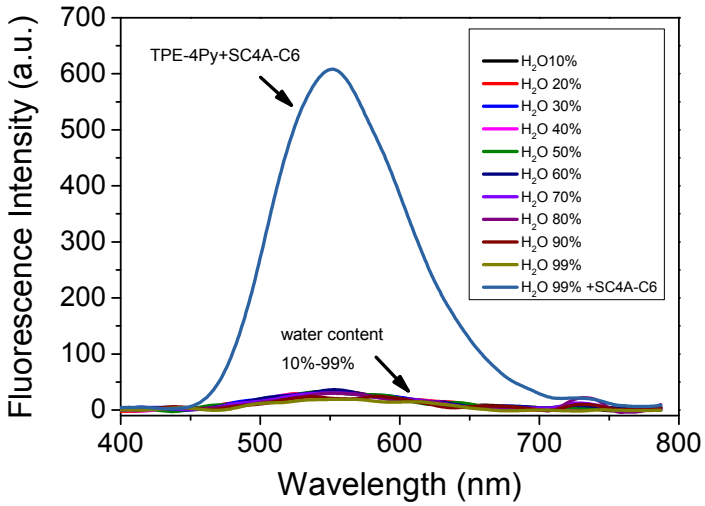

Figure S1. Fluorescence spectra of **TPE-4Py** (10 μM) in H_2O/THF mixtures with different H_2O fractions and in the presence of **SC4A-C6** at the H_2O content of 99% (λ_{ex} = 365 nm; slit: 2.5/5 nm).

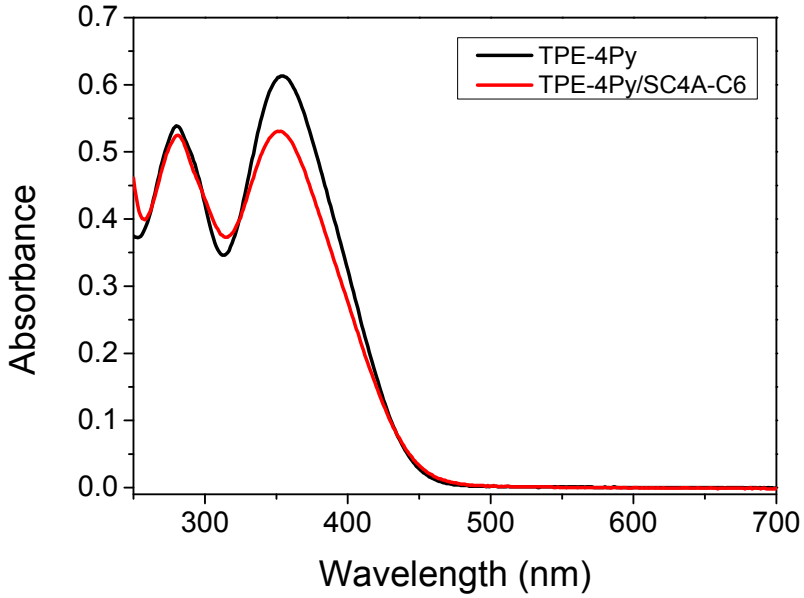

Figure S2. UV-vis absorption spectrum of **TPE-4Py** (14 μM) and **TPE-4Py/SC4A-C6** ([**SC4A-C6**] =12 μM, [**TPE-4Py**] = 14 μM) in PBS buffer solution.

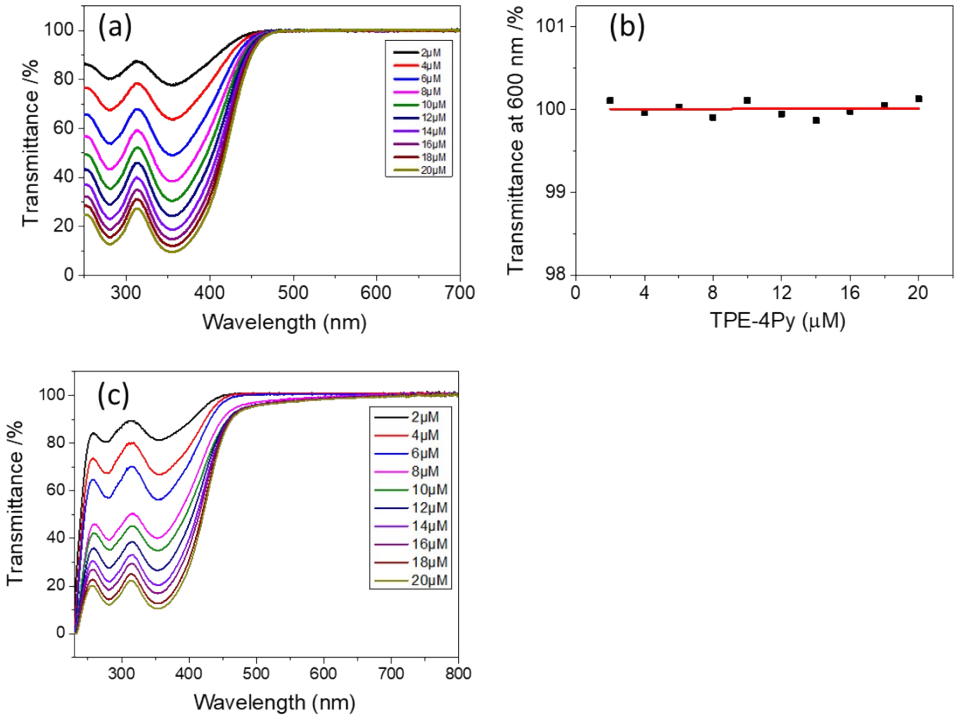

Figure S3. (a) Optical transmittance of **TPE-4Py** at different concentrations in PBS buffer solution. (b) Dependence of the optical transmittance at 600 nm at different concentrations of **TPE-4Py**. (c) Optical transmittance of **TPE-4Py** at different concentrations in the presence of **SC4A-C6** (10 μM) in PBS buffer solution.

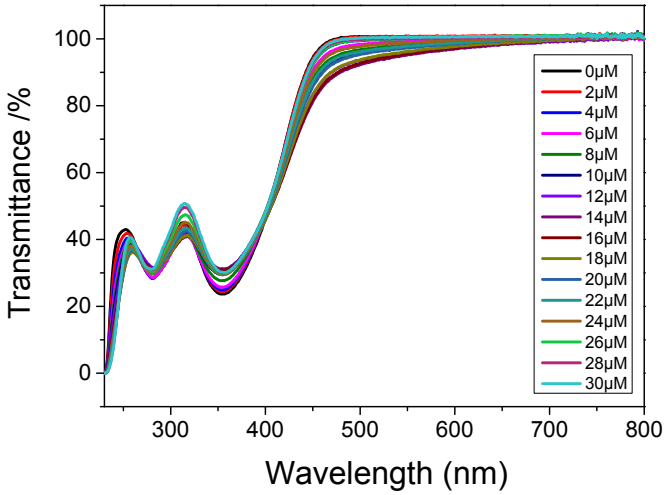

Figure S4. Optical transmittance of **SC4A-C6** on different concentrations in the presence of **TPE-4Py** (12 μM).

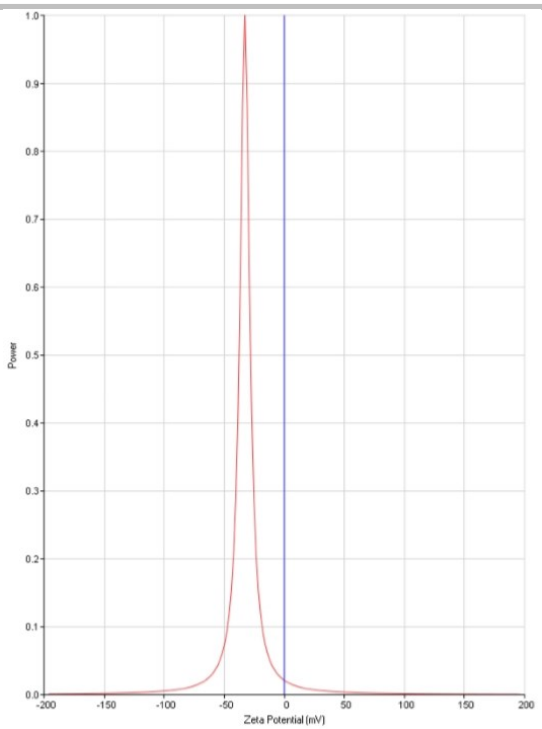

Figure S5. Zeta potential of **TPE-4Py/SC4A-C6** ([**SC4A-C6**] =12 μM, [**TPE-4Py**] = 14 μM).

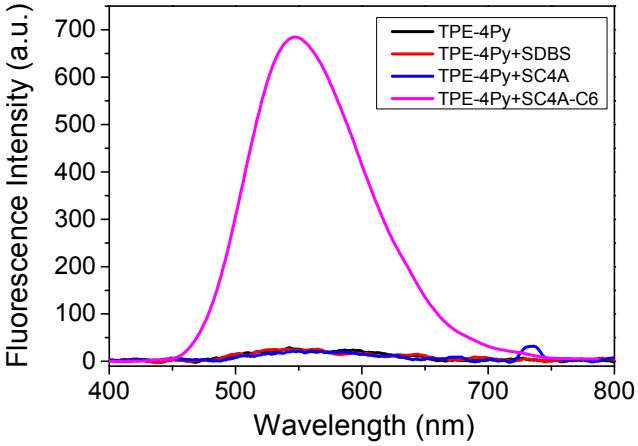

Figure S6. Fluorescence spectra of **TPE-4Py** (12 μM) in the presence **SC4A** (14 μM); **SC4A-C6** (14 μM), SDBS [sodium dodecyl benzene sulfonate (14 μM)] in PBS buffer solution (λ_{ex} = 365 nm; slit: 2.5/5 nm).

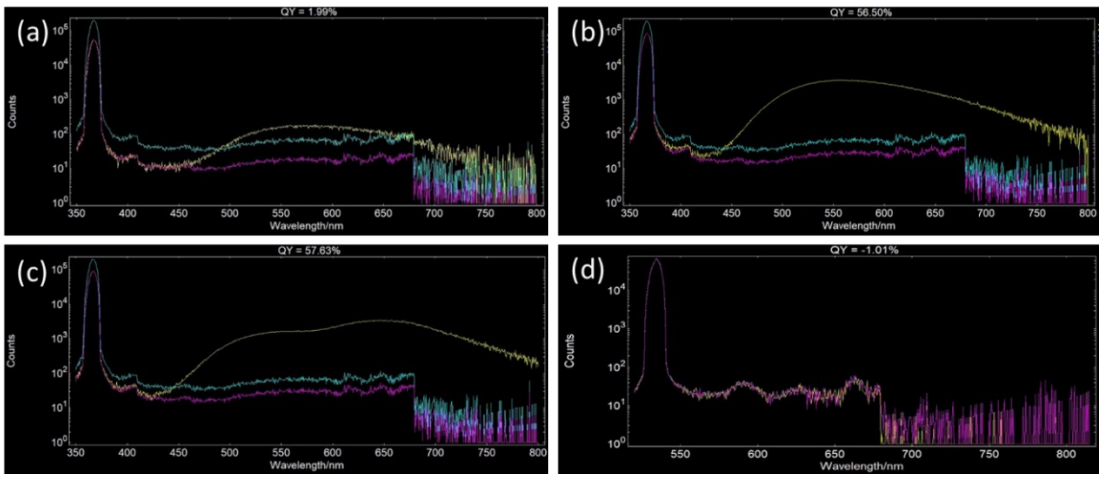

Figure S7. Quantum yields of (a) **TPE-4Py**, (b) **TPE-4Py/SC4A-C6**, (c) **TPE-4Py/SC4A-C6/SP** and (d) **SP** in PBS buffer solution (pH 7.4, 10 mM).

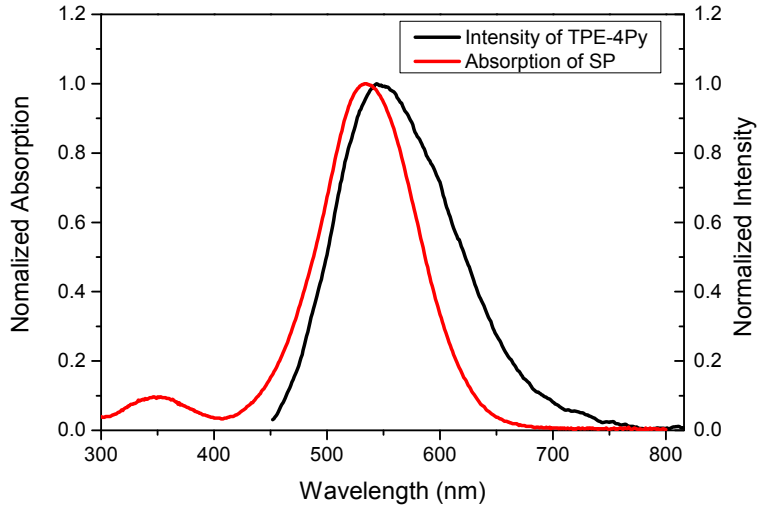

Figure S8. Normalized emission spectrum of **TPE-4Py** and absorption spectrum of **SP**.

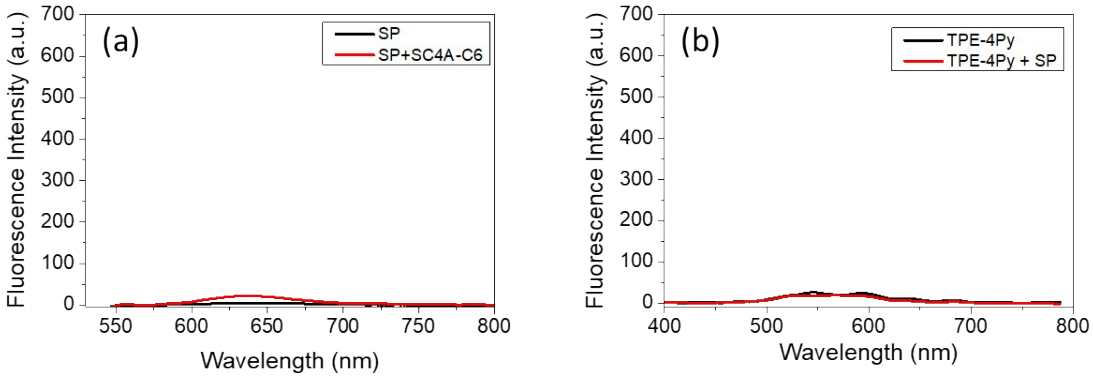

Figure S9. Fluorescence spectra of **SC4A-C6/SP** ([**SC4A-C6**] =12 μM, [**SP**] = 216 nM) and **TPE-4Py/SP** ([**TPE-4Py**] =12 μM, [**SP**] = 216 nM) in PBS buffer solution (10 mM, pH 7.4). (a) (λ_{ex} = 533 nm slit: 2.5/5 nm); (b) (λ_{ex} = 365 nm; slit: 2.5/5 nm).

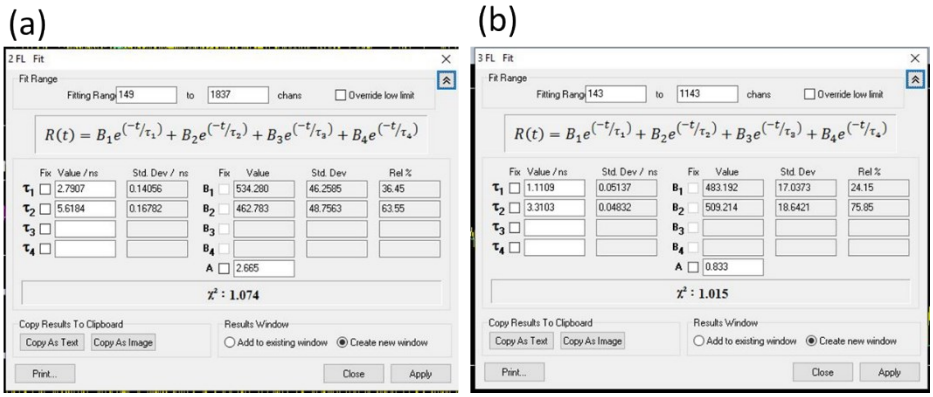

Figure S10. Fluorescence decay profiles of **TPE-Py/SC4A-C6** (a), and **TPE-Py/SC4A-C6/SP** (b) in PBS buffer solution ([**TPE-Py**] = 12 μM, [**SC4A-C6**] = 14 μM, [**SP**] = 216 nM) (λ_{ex} = 365 nm, λ_{em} = 350–800 nm).

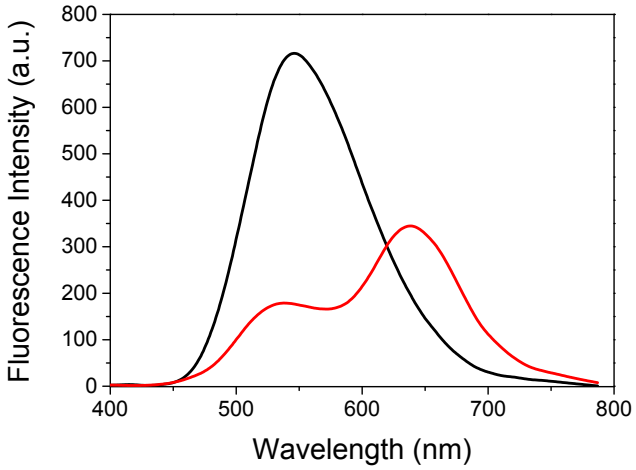

Figure S11. Fluorescence spectra of **TPE-4Py/SC4A-C6** (black) and **TPE-4Py/SC4A-C6/SP** (red) in PBS (10 mM, pH 7.4) ([**TPE-4Py**] = 12 μM, [**SC4A-C6**] = 14 μM, [**SP**] = 216 nM) (λ_{ex} = 365 nm; slits: 2.5/5 nm).

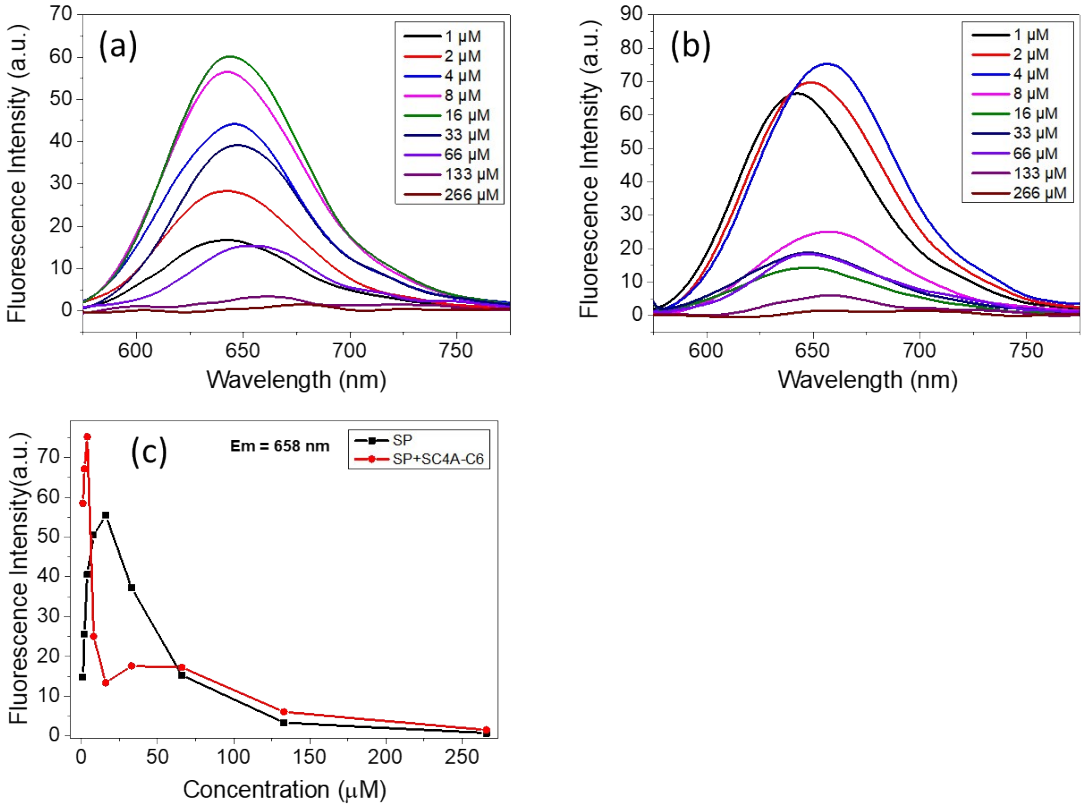

Figure S12. Fluorescence spectra of **SP** (a) and **SC4A-C6/SP** (b) at different concentrations in PBS buffer solution. (c) The fluorescence intensity of **SP** and **SC4A-C6/SP** at 658 nm in different concentration. (λ_{ex} = 533 nm; slit: 2.5/5 nm).

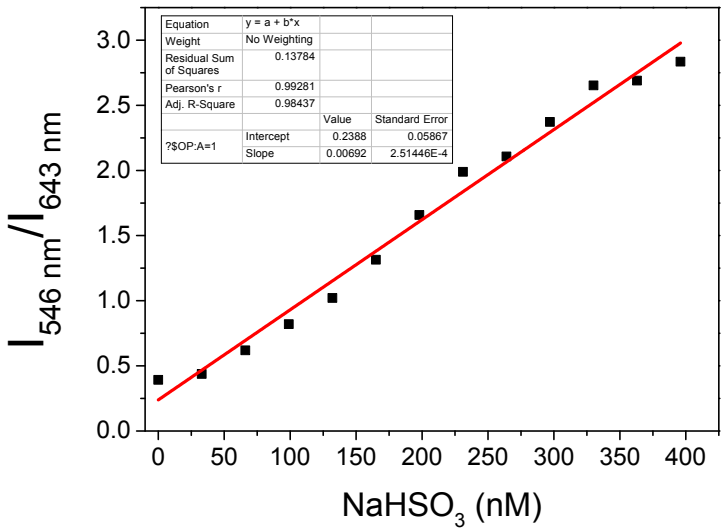

Figure S13. Fluorescent intensity ratio ($I_{546\ nm}/I_{643\ nm}$) changes of **TPE-4Py/SC4A-C6/SP** as a function of the concentration of $NaHSO_3$ in PBS buffer (pH 7.4, 10 mM). Each spectrum was recorded after 8 min (λ_{ex} = 365 nm; slits: 2.5/5 nm).

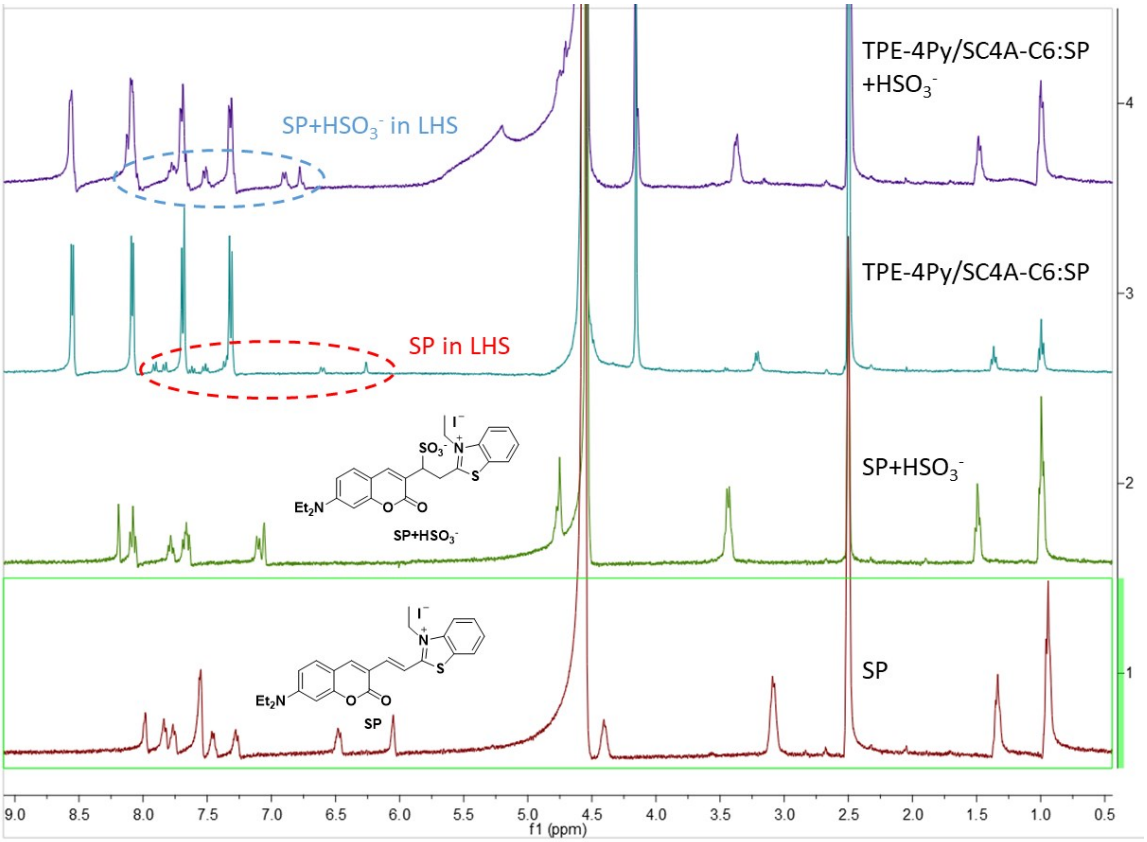

Figure S14. ^1H NMR spectra of **SP** and **TPE-4Py/SC4A-C6/SP** in the presence of HSO_3^- (DMSO-d_6/D_2O).

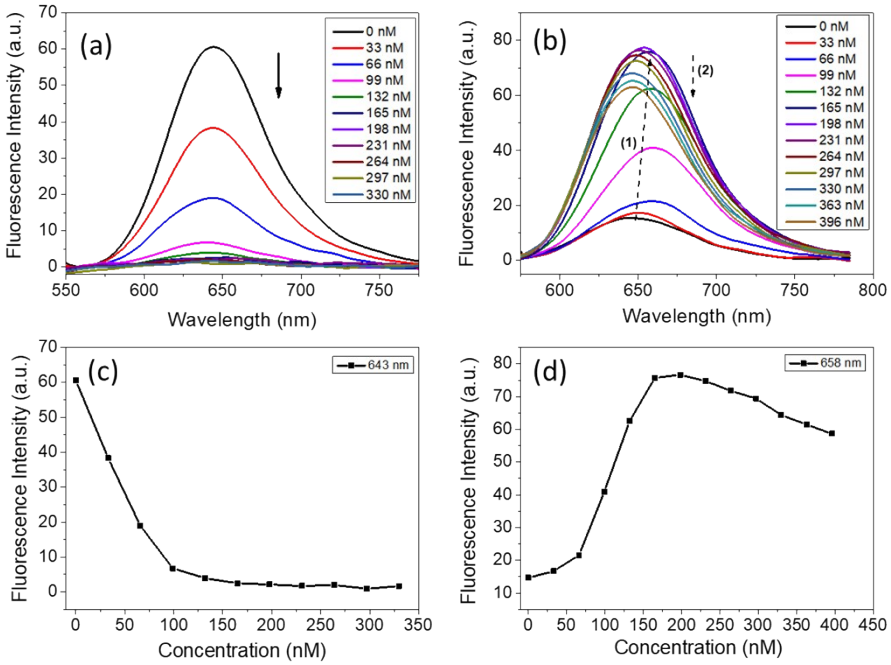

Figure S15. (a) Fluorescence spectra of **SP** (14 μM) upon gradual addition of HSO_3^- in PBS buffer. (b) Fluorescence spectra of **SC4A-C6/SP** ([**SP**] = 14 μM, [**SC4A-C6**] = 12 μM) upon gradual addition of HSO_3^- in PBS buffer solution. (c) The fluorescence intensity of **SP** at 643 nm upon gradual addition of HSO_3^- in PBS buffer. (D) The fluorescence intensity of **SC4A-C6/SP** at 658 nm upon gradual addition of HSO_3^- in PBS buffer solution. (λ_{ex} = 533 nm; slit: 2.5/5 nm).

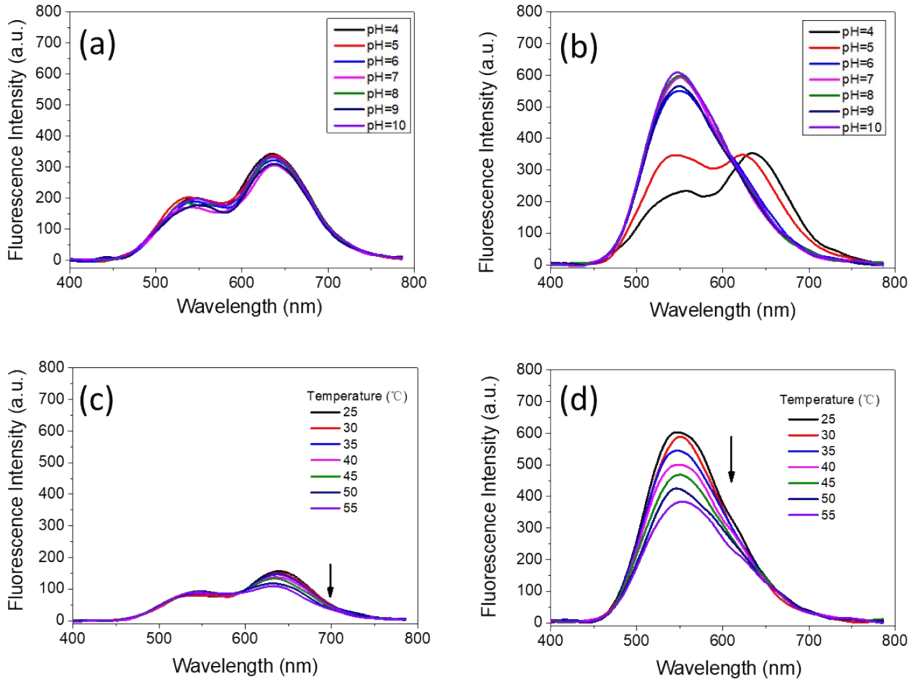

Figure S16. (a) Fluorescence spectra of **TPE-4Py/SC4A-C6/SP** at different pH values. (b) Fluorescence spectra of **TPE-4Py/SC4A-C6/SP** toward HSO_3^- (0.4 mM) at different pH values. (c) Fluorescence spectra of **TPE-4Py/SC4A-C6/SP** at different temperatures. (b) Fluorescence spectra of **TPE-4Py/SC4A-C6/SP** toward HSO_3^- (0.4 mM) at different temperatures. ([**TPE-4Py**] = 12 μM, [**SC4A-C6**] = 14 μM, [**SP**] = 216 nM) (λ_{ex} = 365 nm; slit: 2.5/5 nm).

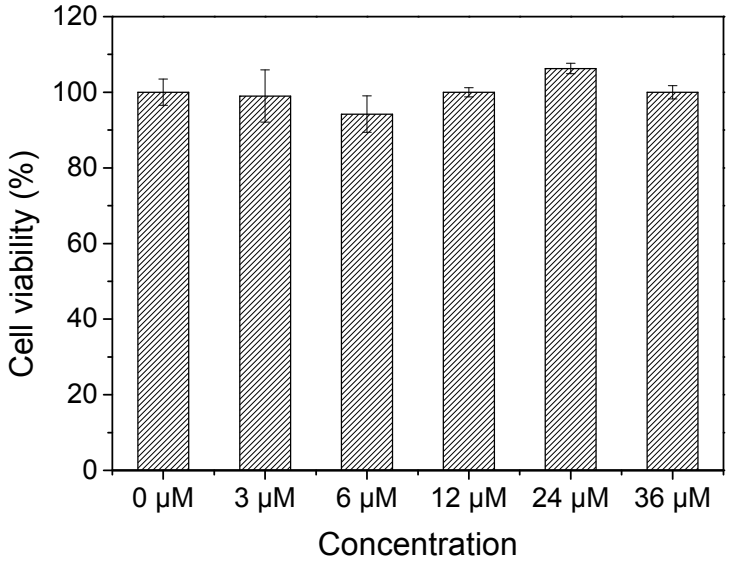

Figure S17. Cell viability revealed by CCK-8 assays with different concentration of **TPE-4Py/SC4A-C6/SP** based on **TPE-4Py** concentration.

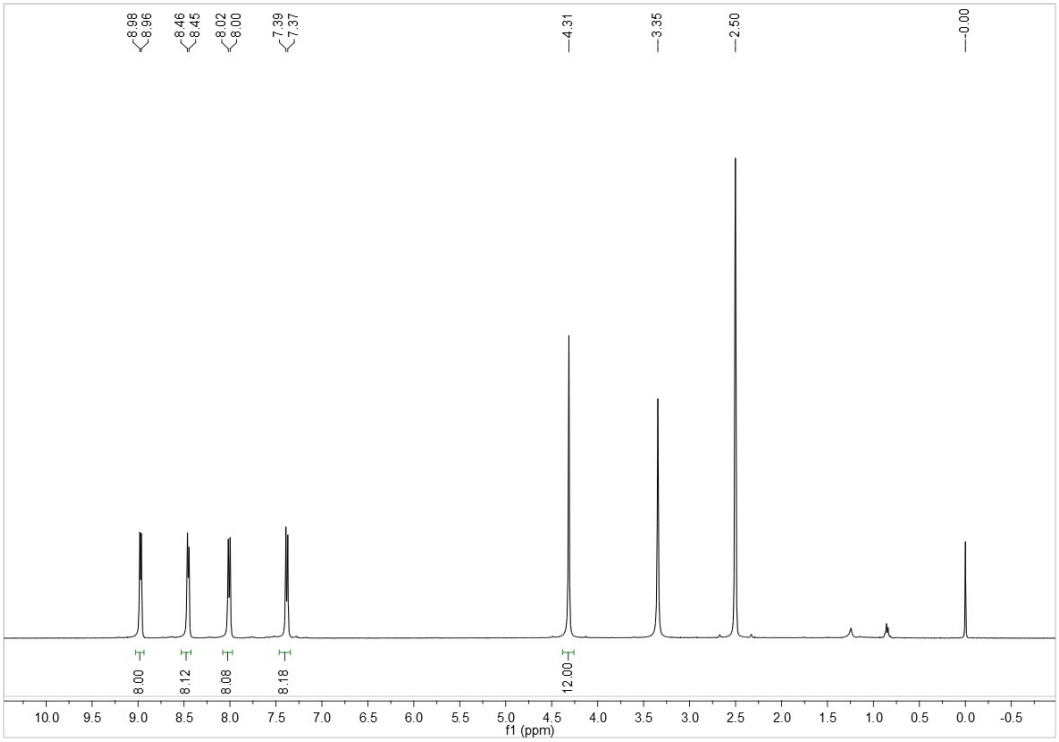

Figure S18. ^{1}H-NMR spectrum of **TPE-4Py** (400 MHz, DMSO-d_6).

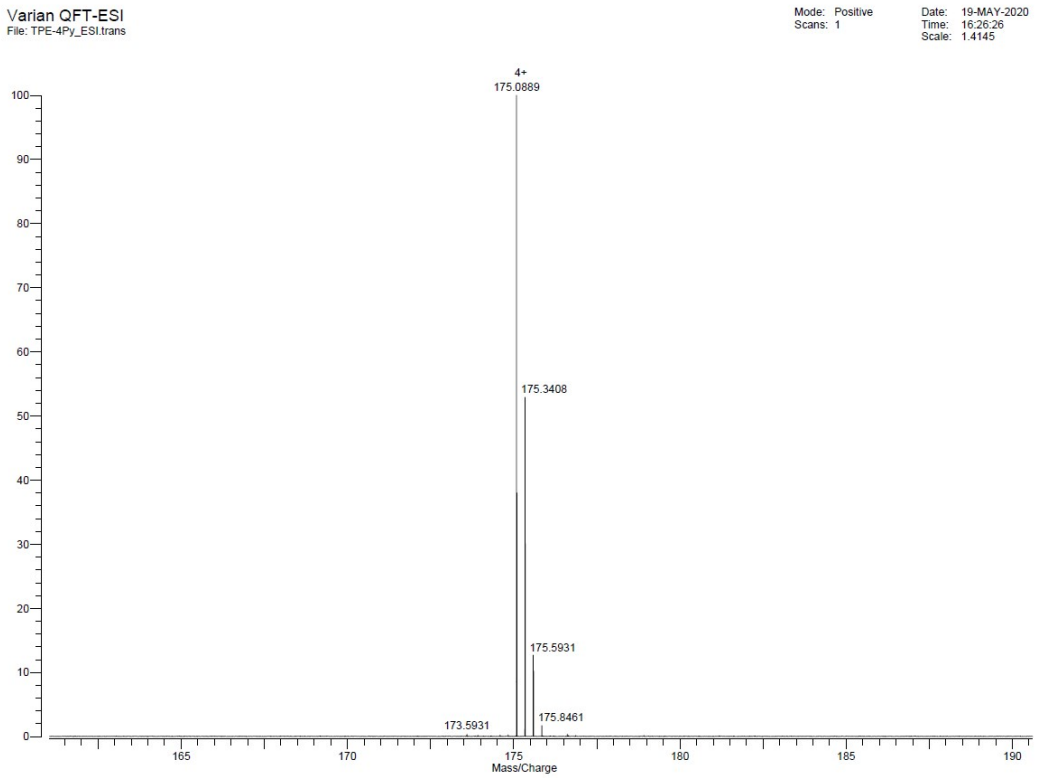

Figure S19. HRMS spectrum of **TPE-4Py**.

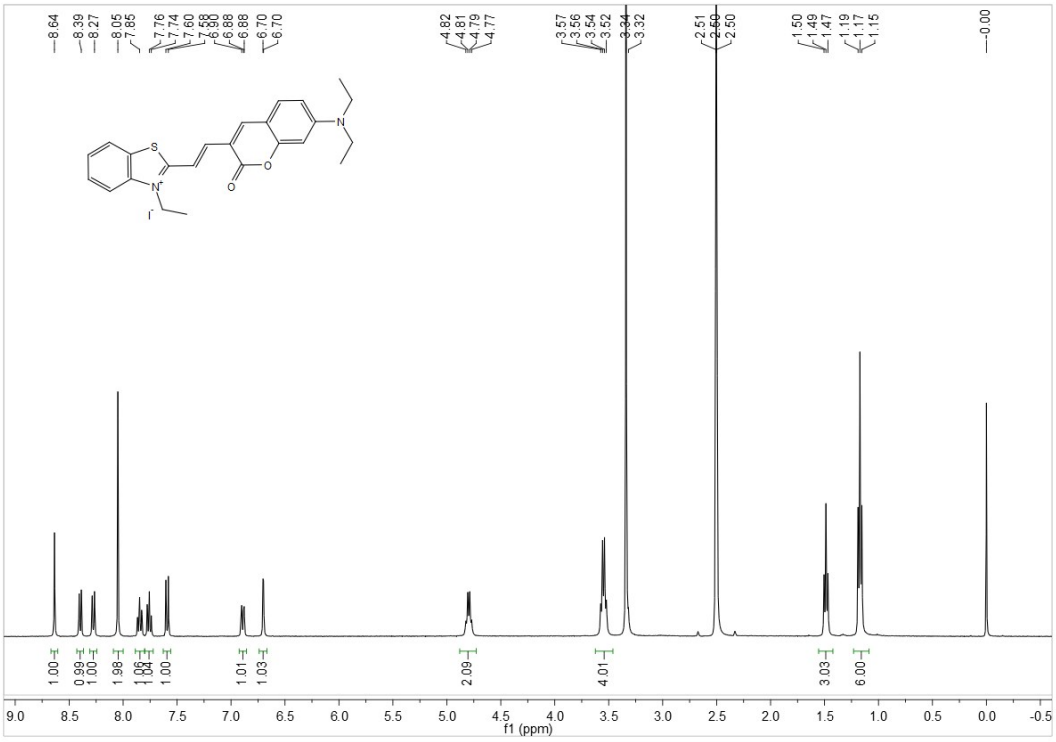

Figure S20. ^{1}H-NMR spectrum of **SP** (400 MHz, DMSO-d_6).

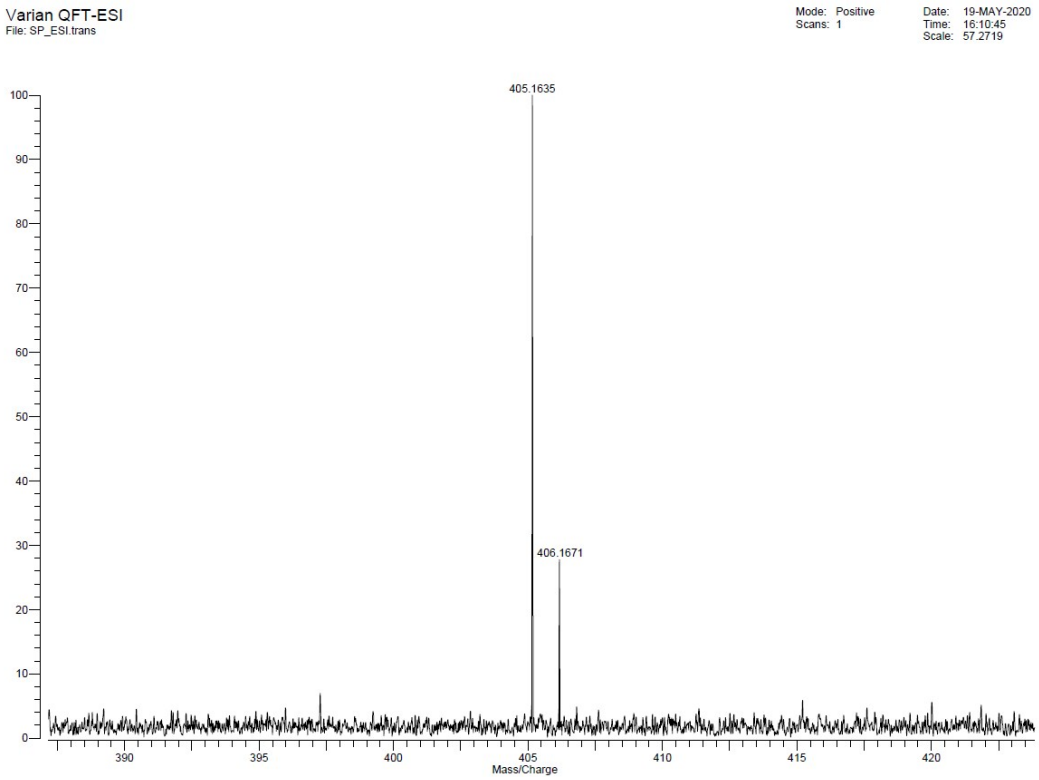

Figure S21. HRMS spectrum of **SP**.

References

1. T. Zhang, Y. Li, Z. Zheng, R. Ye, Y. Zhang, R. T. K. Kwok, J. W. Y. Lam and B. Z. Tang, *J. Am. Chem. Soc.*, 2019, **141**, 5612-5616.
2. Y. Q. Sun, J. Liu, J. Zhang, T. Yang and W. Guo, *Chem. Commun.*, 2013, **49**, 2637-2639.
3. X.-Y. Hu, Y. Chen and Y. Liu, *Chin. Chem. Lett.*, 2015, **26**, 862-866.
4. S. Peng, J. Gao, Y. Liu and D. S. Guo, *Chem. Commun.*, 2015, **51**, 16557-16560.

Author Contributions

Z. Liu and Prof. Y. Liu conceived and directed the study. X. Sun measured the fluorescence quantum yield. X. Dai performed the cytotoxicity test. J. Li performed the Zeta potential experiment. P. Li synthesized the SC4A-C6. Z. Liu wrote the main manuscript and prepared the Figures. Prof. Y. Liu supervised the work and edited the manuscript. All authors reviewed the manuscript. All authors have given approval to the final version of the manuscript.