

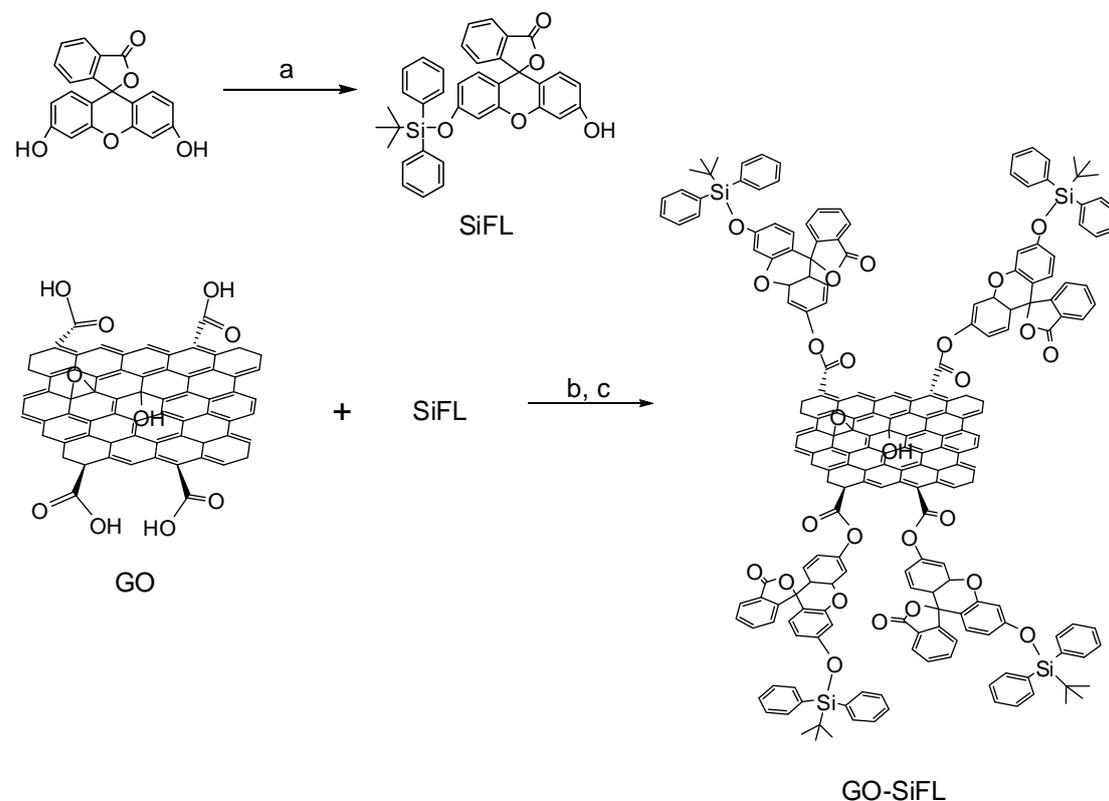
Supporting Information

A nanohybrid of graphene oxide-fluorescein derived silyl ether for photocurrent generation triggered by F^- ions †

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Scheme S1. The synthesis strategy of GO-SiFL. a. DBU, $t\text{BuPh}_2\text{SiCl}$, nitrogen gas protection; b. GO, oxalyl chloride; c. THF, TEA, argon gas protection

Synthesis and Characterization of SiFL: The compound SiFL was prepared according to the synthesis strategy shown in Scheme S1, and characterized by ^1H NMR, ^{13}C NMR, and high resolution Mass spectrometry as seen in Figure S1-3.

Synthesis of SiFL: Dihydroxyfluorane (0.487 g, 1.47 mmol) was dissolved in anhydrous dichloromethane (15 mL) and 1, 8-diazabi-cyclo [5.4.0] undec-7-ene (DBU, 0.3 mL) was added dropwise under nitrogen at 0 °C using a syringe. The mixture was stirred for 3 h at room temperature. Then tert-butyldiphenylchlorosilane (0.4 mL) was added dropwise using a syringe at room temperature. The mixture was stirred for an addition hour at room temperature, before it was poured into HCl (2 M, 15 mL). The mixture was extracted with dichloromethane until the pH value reached to 7. The combined organic layer was washed with the brine twice, dried over MgSO_4 , filtrated, and concentrated. The yellow residue was purified by column chromatography (silica gel, CH_2Cl_2 /ethyl acetate 20:1) to give the compound (0.376 g, 40%) as a yellow solid. ^1H NMR ppm δ_{H} (d_6 -DMSO) 10.16 (1, s), 7.99 (1, m), 7.78 (1, m), 7.71 (5, m) 7.47 (2, m), 7.39 (4, m), 7.26 (1, m), 6.70 (1, s), 6.61 (1, m), 6.56 (4, m), 1.04 (3, s), 0.96 (6, s). ^{13}C NMR ppm δ_{C} (d_6 -DMSO) 168.62, 159.49, 156.68, 152.37, 151.83, 151.53, 153.31, 136.33, 135.63, 135.55, 134.97, 134.45, 131.39, 130.44, 130.08, 129.08, 128.19, 127.49, 126.15, 125.93, 124.61, 123.98, 116.21, 112.81, 112.58, 112.16, 109.55, 109.26, 106.66, 102.22, 83.07, 82.42, 26.52, 26.15, 18.90, 18.67. TOF MS (ES^+): calcd for $[\text{C}_{36}\text{H}_{31}\text{O}_5\text{Si}]^+$, m/z 571.1941, found m/z 571.1948.

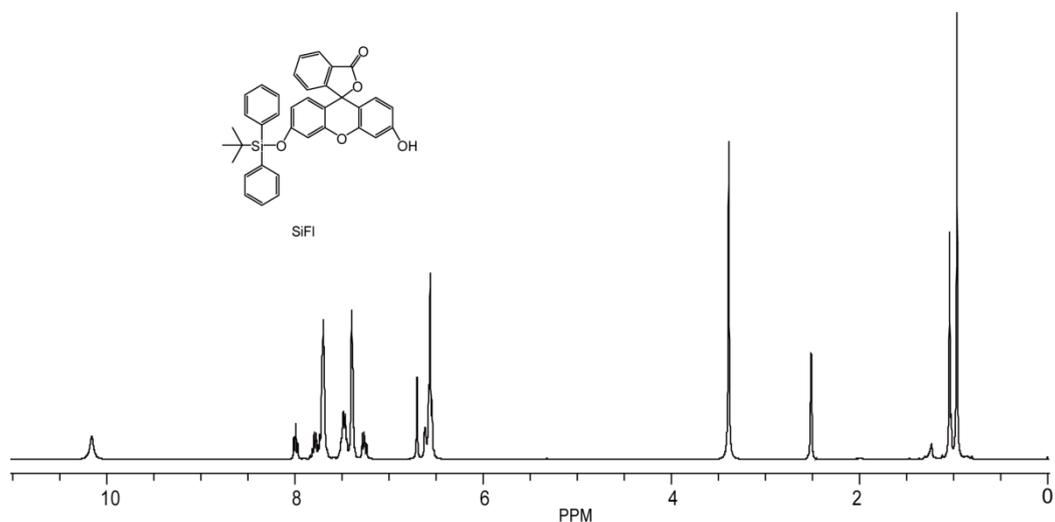


Figure S1. ^1H NMR spectrum of SiFL in d_6 -DMSO.

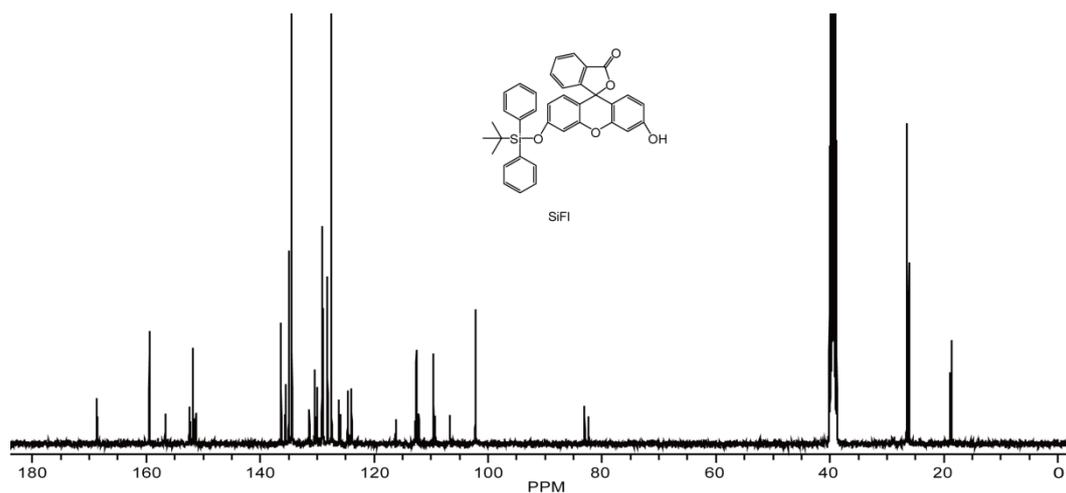


Figure S2. ^{13}C NMR spectrum of SiFL in d_6 -DMSO.

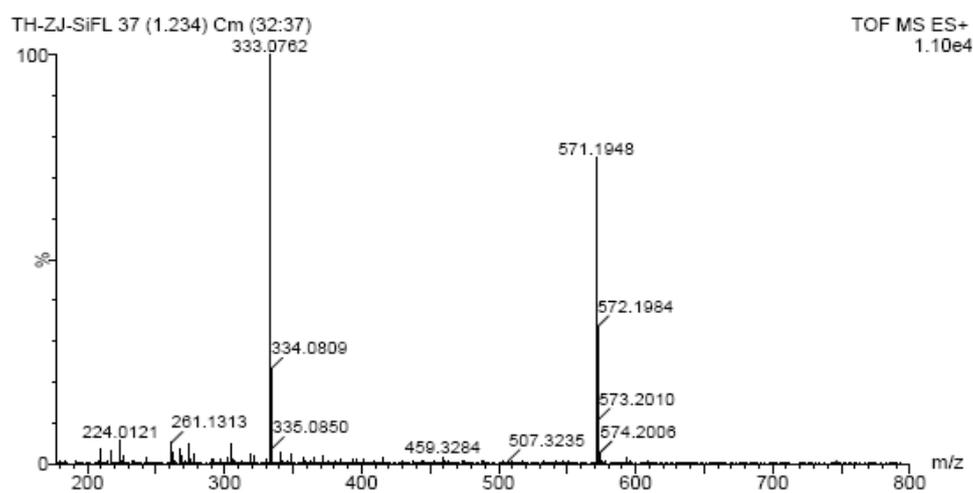


Figure S3. High resolution mass spectrum for SiFL.

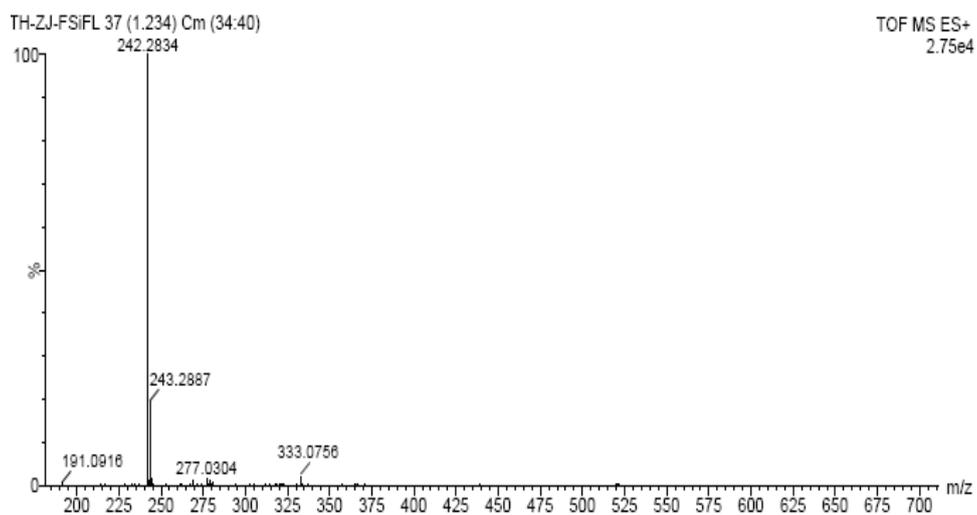


Figure S4. High resolution mass spectrum for SiFL incubated with excess F^- ions.

Synthesis of GO-SiFL: GO (35 mg) was stirred in oxalyl chloride (20 mL) at 80 °C for 24 h. Then the reaction mixture was evaporated to remove the excess oxalyl chloride. In the presence of triethylamine (0.6 mL), the above product was allowed to react with SiFL (35 mg) in dry THF (20 mL), refluxed for 72 h under argon. After the reaction, the solution was poured into ether (300 mL) to precipitate the product. The product was isolated by filtration on a Nylon membrane (0.22 μm). The excess SiFL and other impurities were removed through five washing cycles, which including sonication, centrifugation and re-suspension of the solid in CH₂Cl₂ (50 mL). The precipitate was washed with CHCl₃ five times, following the above procedure. UV spectroscopy and thin-layer chromatography were used to check the filtrate to ensure no SiFL existed in the final washing. The GO-SiFL was then washed with a small quantity of water to remove excess SiFL and Et₃N·HCl, and finally dried under vacuum to yield the hybrid GO-SiFL.

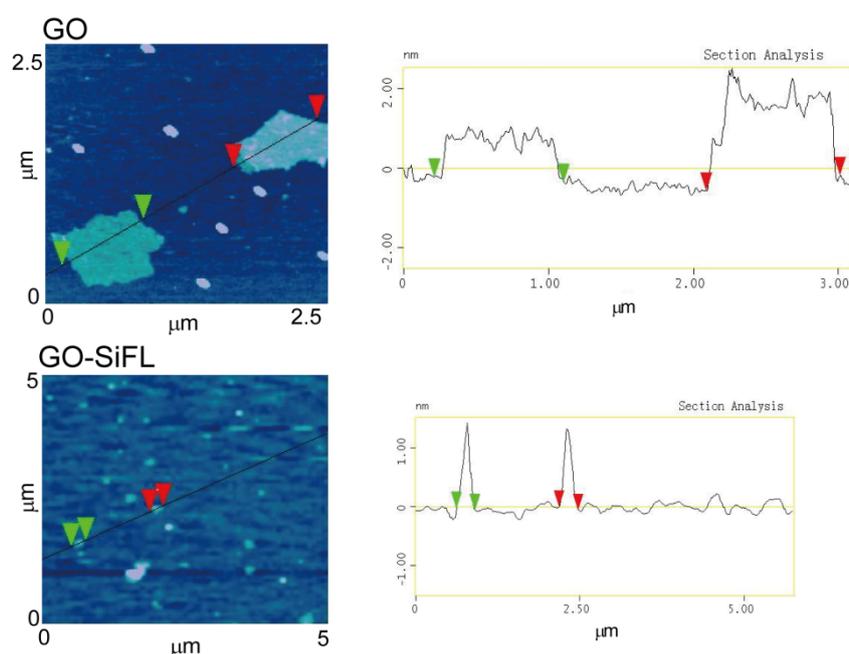


Figure S5. Representative AFM images of GO and GO-SiFL, and the profile analysis showing a height of ~1 nm for both GO and GO-SiFL, respectively.

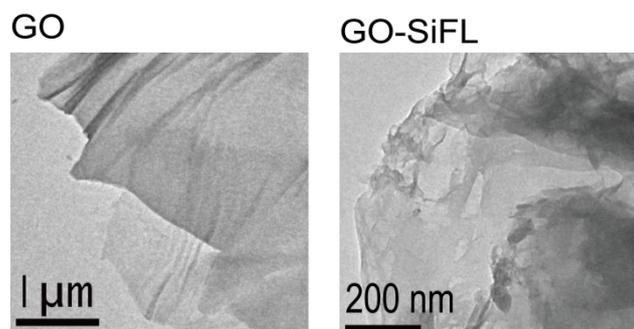


Figure S6. Representative TEM images of GO and GO-SiFL.

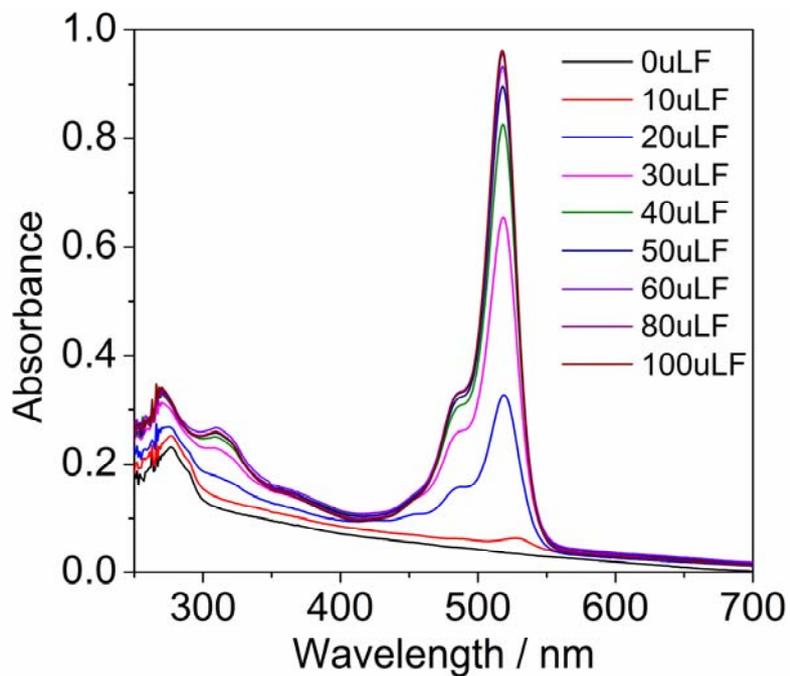


Figure S7. UV-vis spectra of 35.1 mg·L⁻¹ GO-SiFL titrated by 1 mM F⁻ ions in DMF.

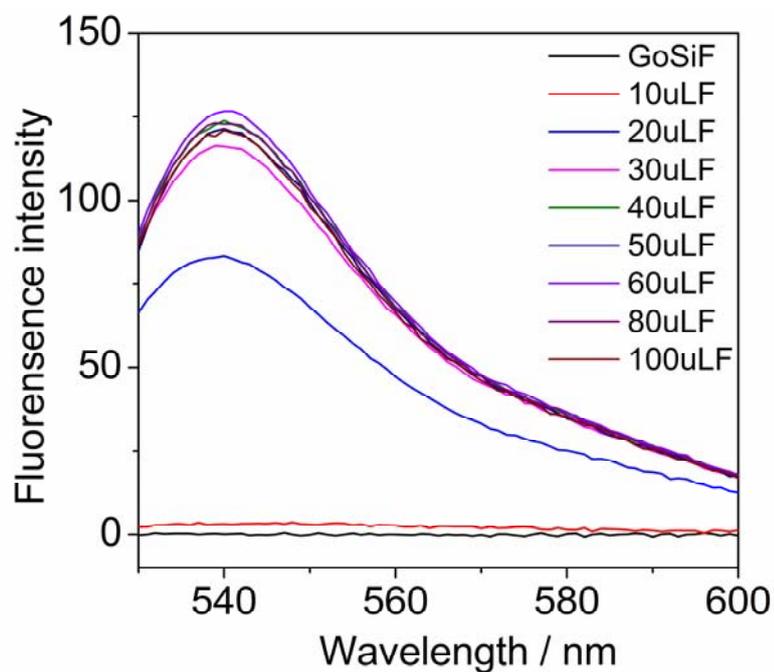


Figure S8. Fluorescence spectra of 35.1 mg·L⁻¹ GO-SiFL titrated by 1 mM F⁻ ions in DMF.

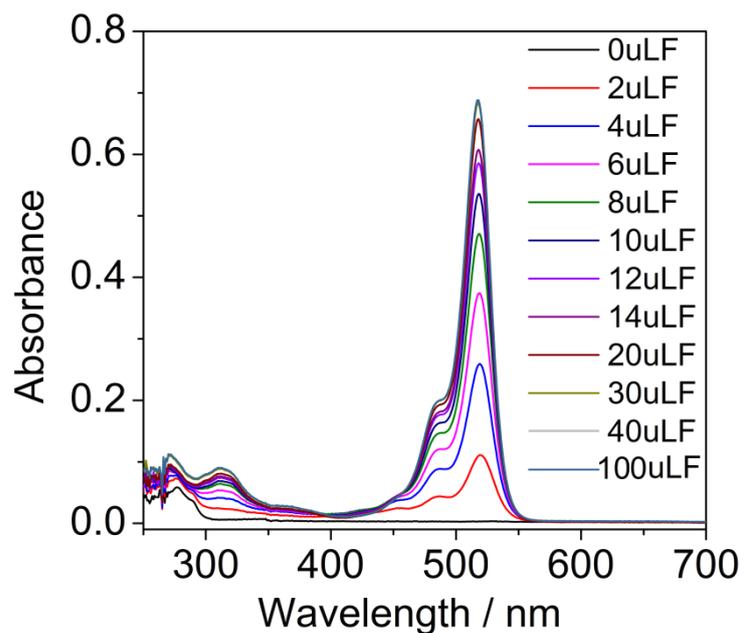


Figure S9. UV-vis spectra of 2.2 mg·L⁻¹ SiFL titrated by 1 mM F⁻ ions in DMF.

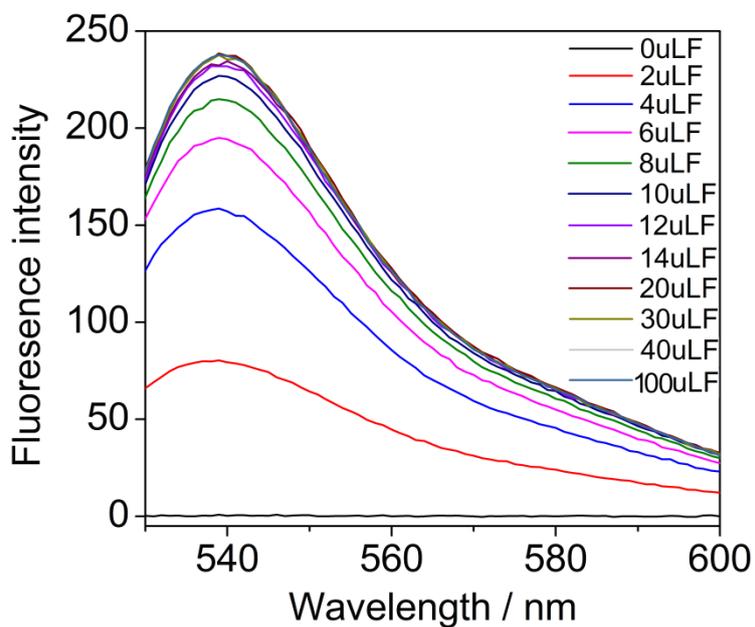


Figure S10. Fluorescence spectra of 2.2 mg·L⁻¹ SiFL titrated by 1 mM F⁻ in DMF excited at 519 nm.

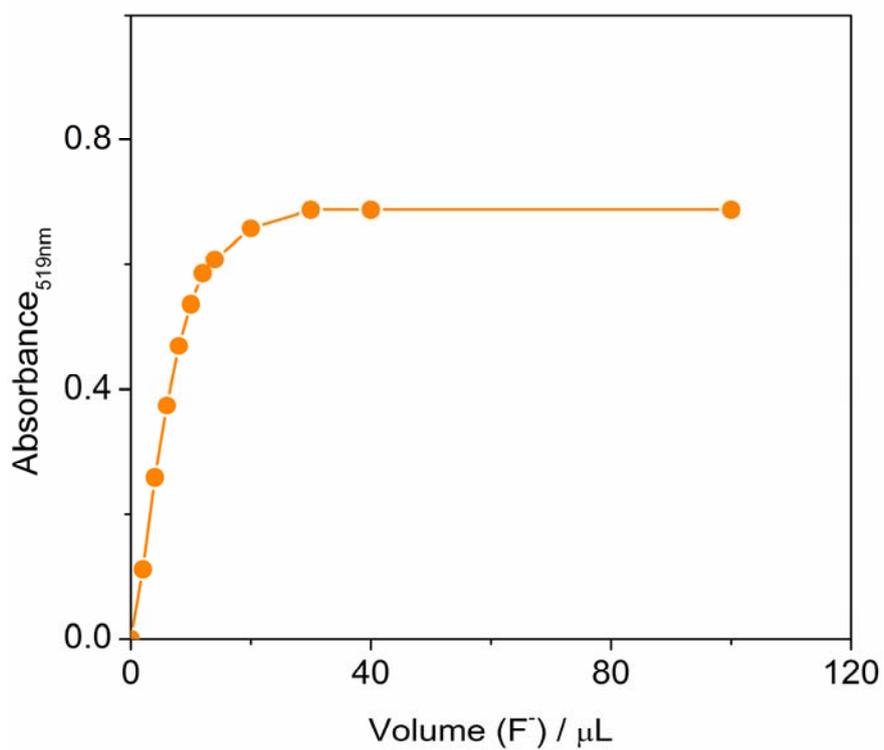


Figure S11. The absorption changes at 519 nm resulted from the F⁻ anions titration on SiFL in DMF.

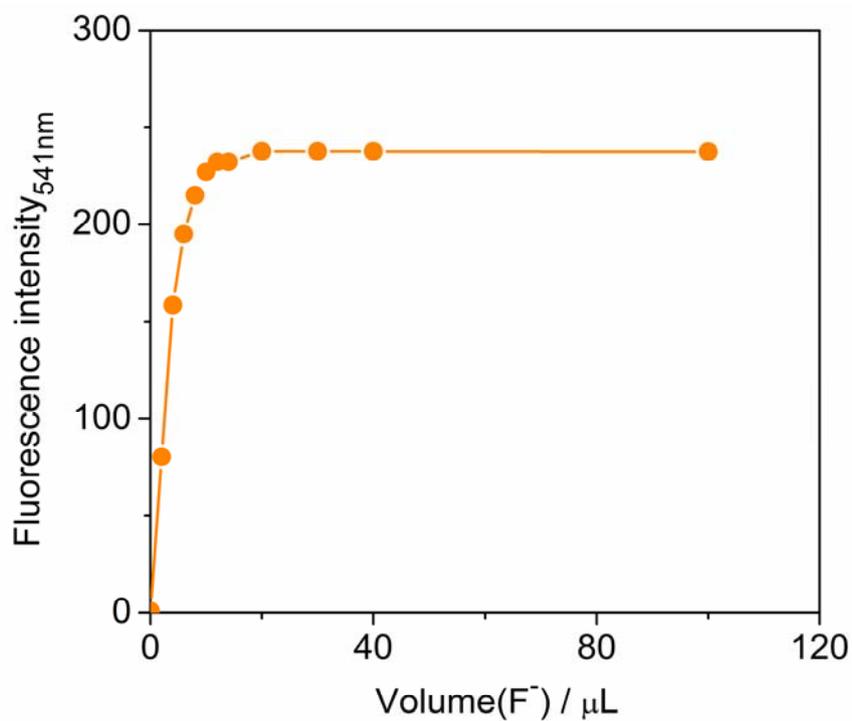


Figure S12. The emission changes at 541 nm resulted from the F⁻ anions titration on SiFL in DMF.

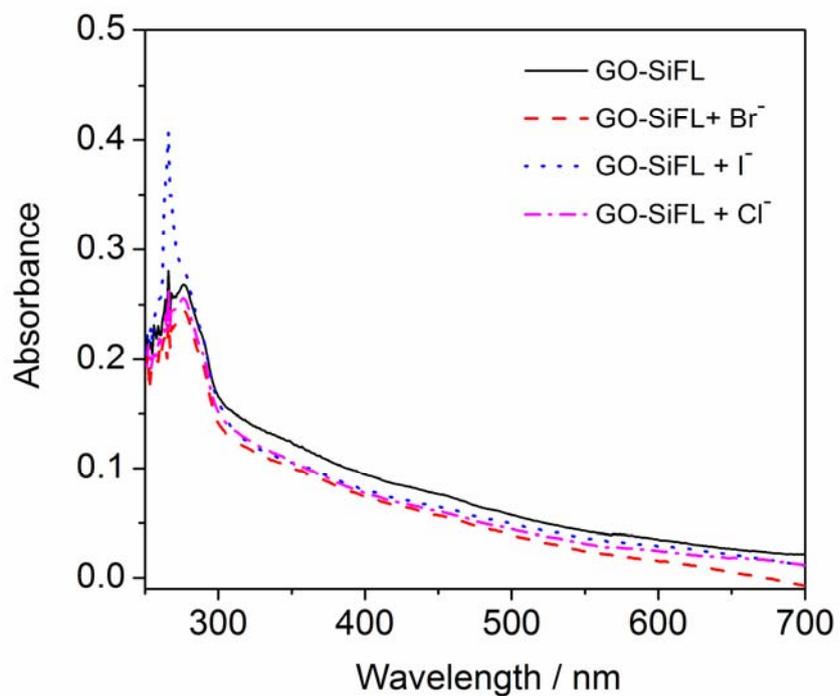


Figure S13. UV-vis spectra for GO-SiFL upon addition of excess Cl⁻, Br⁻, I⁻ ions in DMF, respectively.

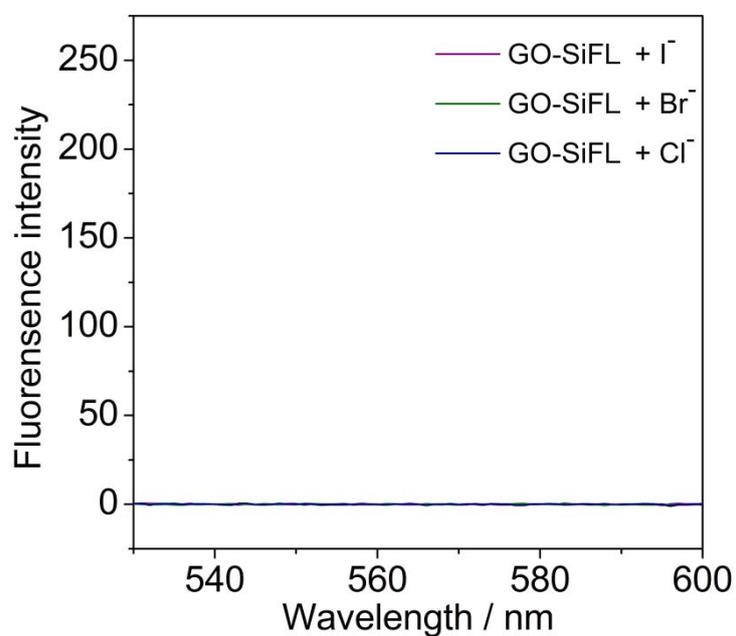


Figure S14. Fluorescence emission spectra (ex 519 nm) of GO-SiFL upon addition of excess Cl⁻, Br⁻, I⁻ ions in DMF, respectively.

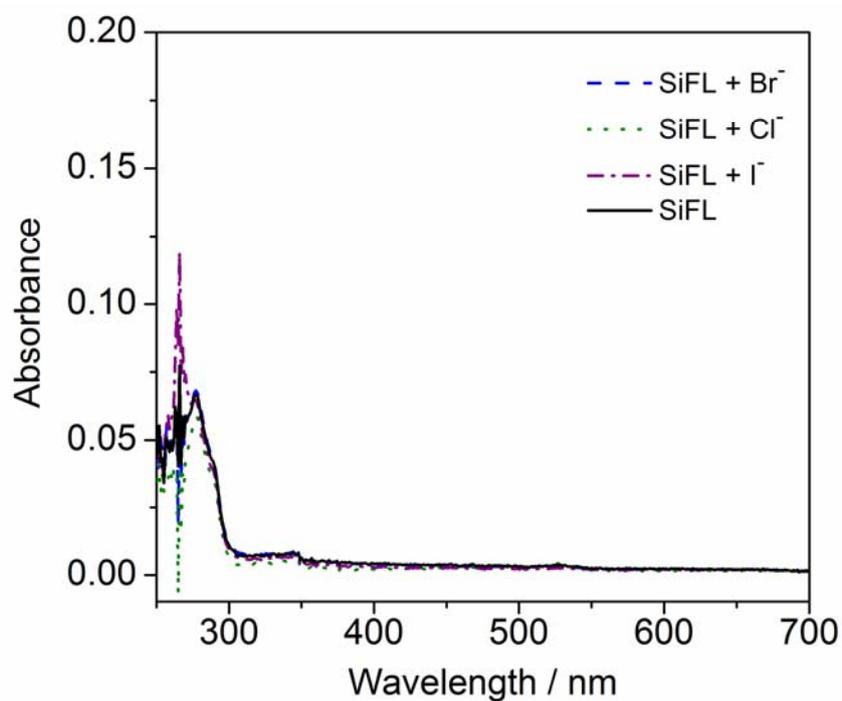


Figure S15. Changes of UV-vis absorption for $2.2 \text{ mg}\cdot\text{L}^{-1}$ SiFL upon the addition of excess Cl^- , Br^- , I^- ions in DMF.

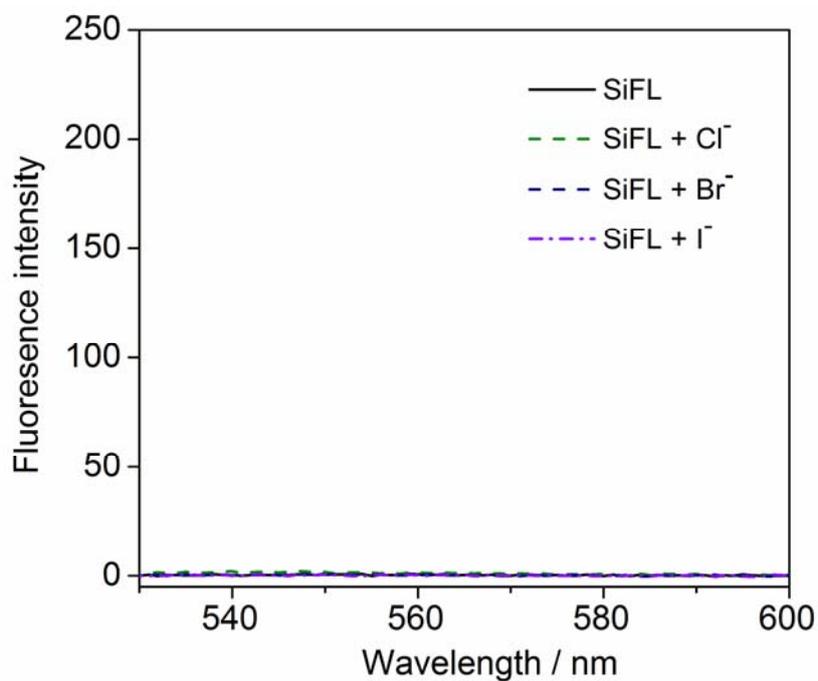


Figure S16. Changes of Fluorescence emission spectra for $2.2 \text{ mg}\cdot\text{L}^{-1}$ SiFL upon the addition of excess Cl^- , Br^- , I^- ions in DMF.

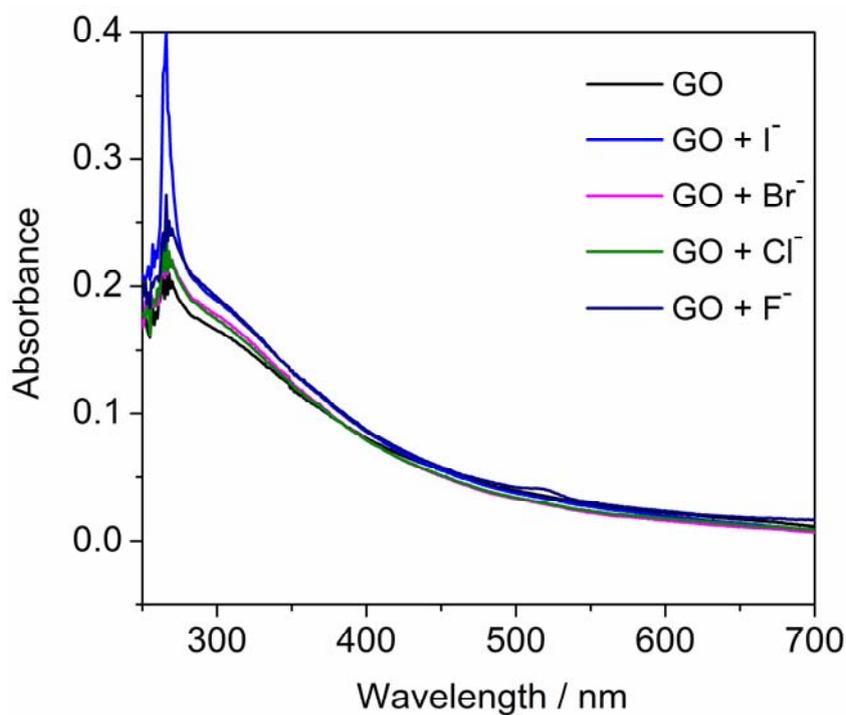


Figure S17. Changes of UV-vis absorption for 13.3 mg·L⁻¹ GO upon the addition of excess F⁻, Cl⁻, Br⁻, I⁻ ions in DMF.

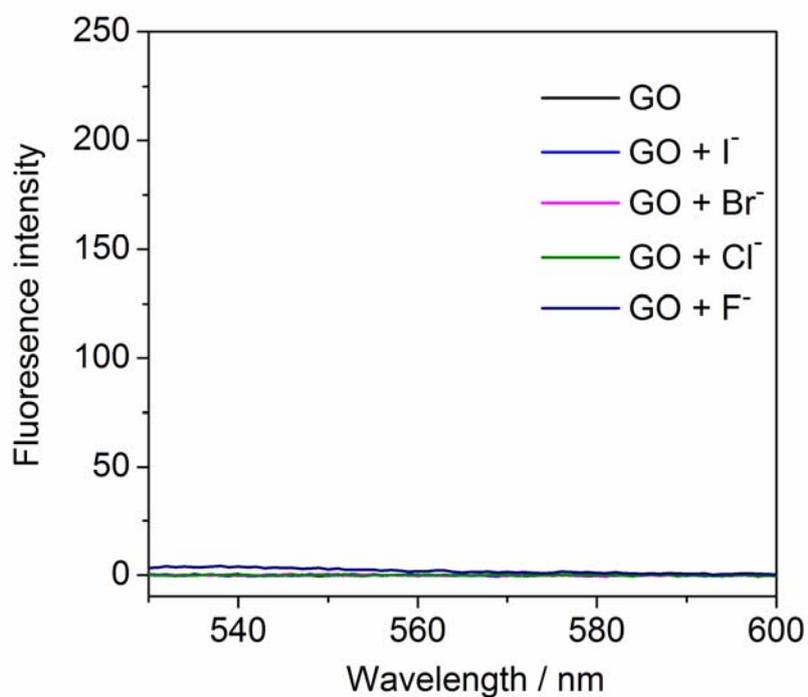


Figure S18. Changes of Fluorescence emission spectra for 13.3 mg·L⁻¹ GO upon the addition of excess F⁻, Cl⁻, Br⁻, I⁻ ions in DMF.

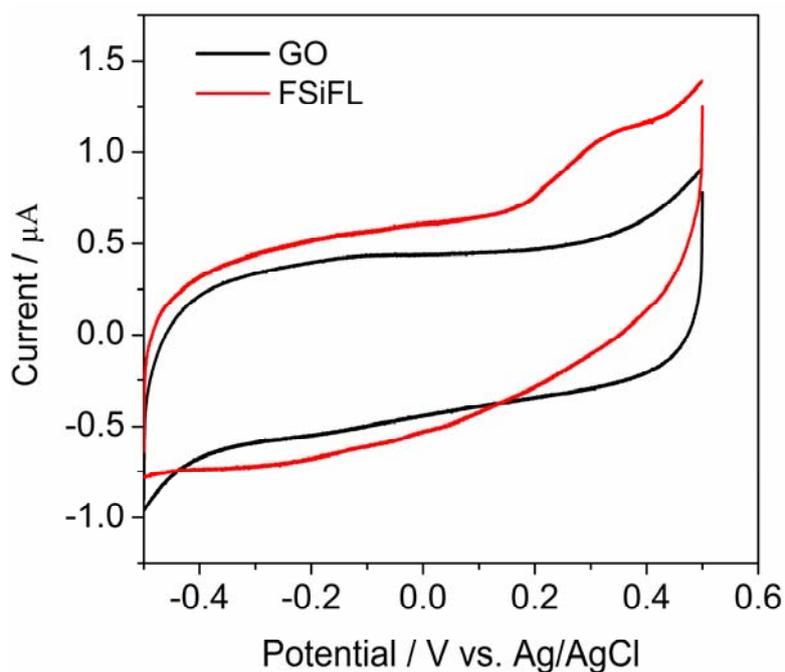


Figure S19. Cyclic voltammograms (CVs) of $35\text{mg}\cdot\text{L}^{-1}$ GO ($13.3\text{ mg}\cdot\text{L}^{-1}$, black), and FSiFL ($2.2\text{ mg}\cdot\text{L}^{-1}$ SiFL upon addition of F^- , red) in 0.1 M TBAP DMF solution at the scan rate $0.1\text{ V}\cdot\text{s}^{-1}$, using glassy carbon as working electrode, Pt wire as counter electrode, Ag/AgCl. as reference electrode.

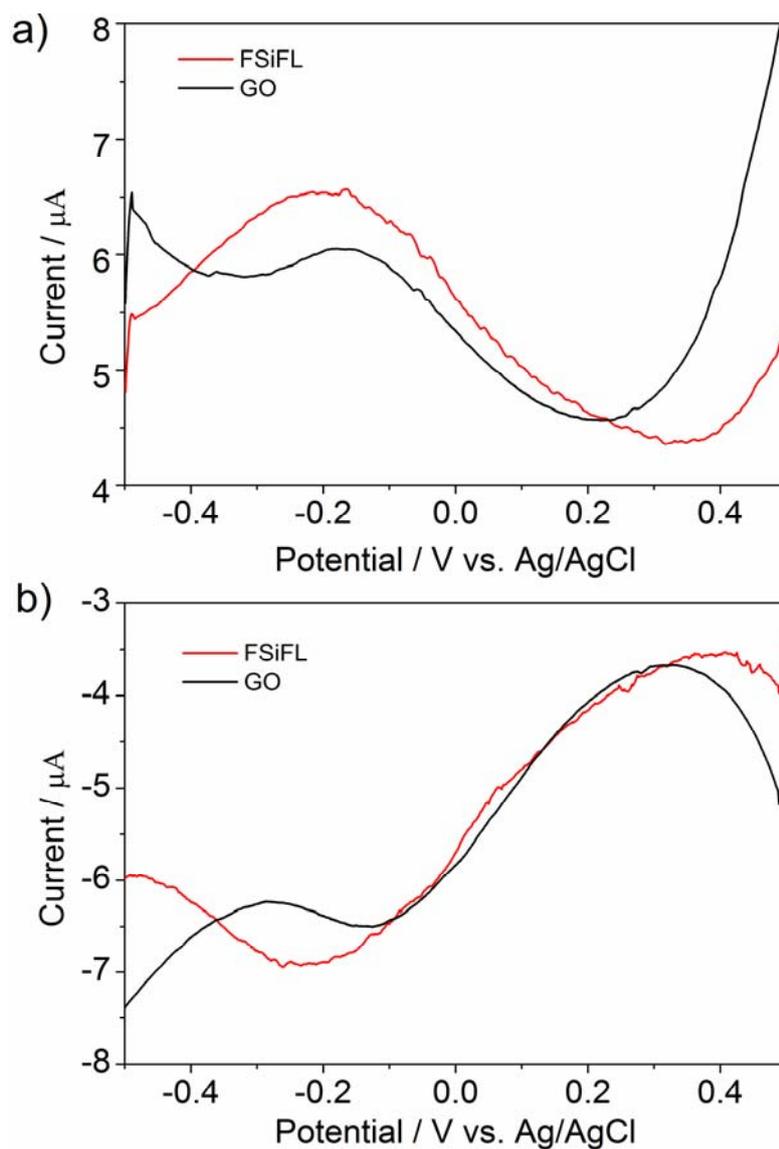


Figure S20. Differential pulse voltammograms (DPVs) of GO ($13.3 \text{ mg}\cdot\text{L}^{-1}$, black) and FSiFL ($2.2 \text{ mg}\cdot\text{L}^{-1}$ SiFL upon addition of F^- , red) in 0.1 M TBAP DMF solution at the scan rate $0.1 \text{ V}\cdot\text{s}^{-1}$, 50 mV pulse amplitude and 50 ms pulse width, using glassy carbon as working electrode, Pt wire as counter electrode, Ag/AgCl. as reference electrode. a). scanning from -0.5 V to 0.5 V; b). scanning from 0.5 V to -0.5 V).