Electronic Supplementary Information

Template-Free H-Dimer and H-Aggregate Formation by Dimeric Carbocyanine Dyes

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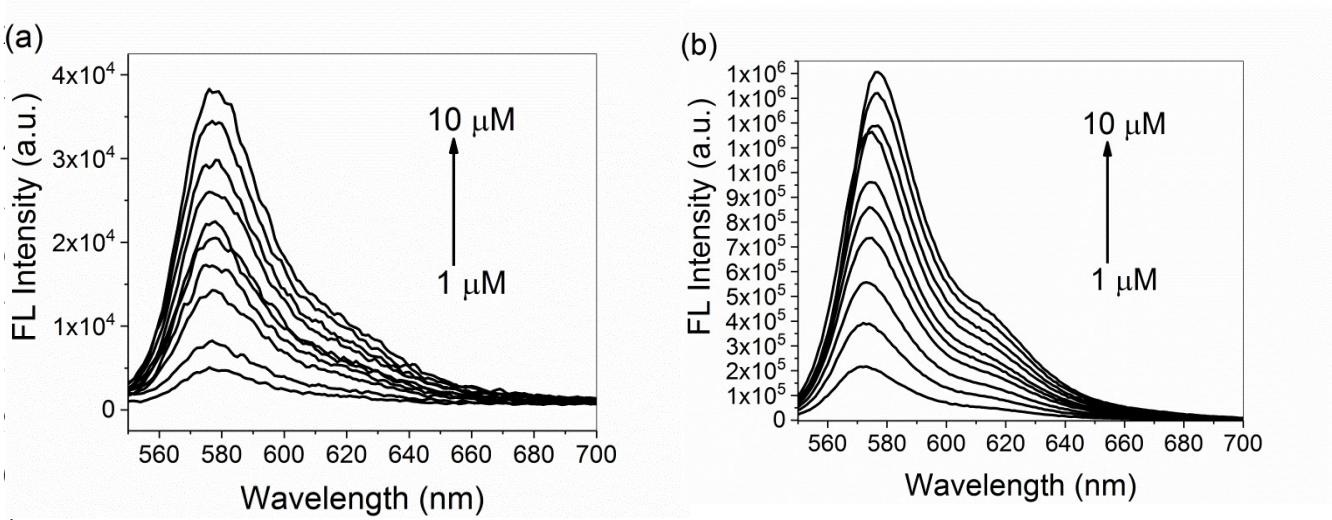

Figure S1. Fluorescence titration spectra of (a) **5a** and (b) **8a** in water, 10% MeOH (at 540 nm excitation).

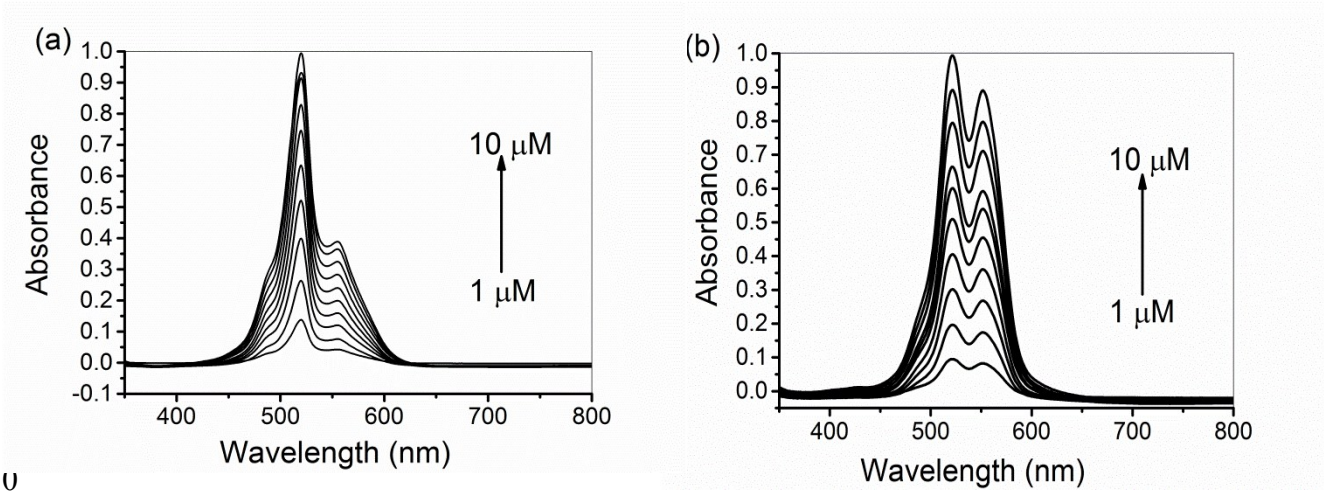

Figure S2. UV-vis absorption spectra of (a) **5a** and (b) **5b** in 100% MeOH. Samples were prepared as described in Experimental.

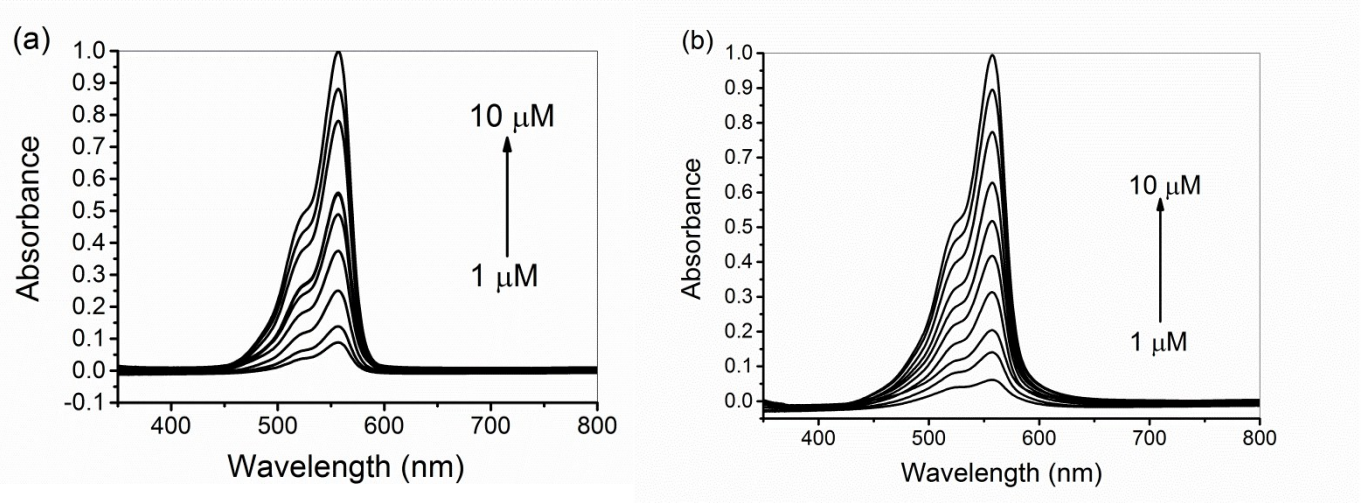

Figure S3. UV-vis absorption spectra of (a) **8a** and (b) **8b** in water, 10% MeOH. Samples were prepared as described in Experimental.

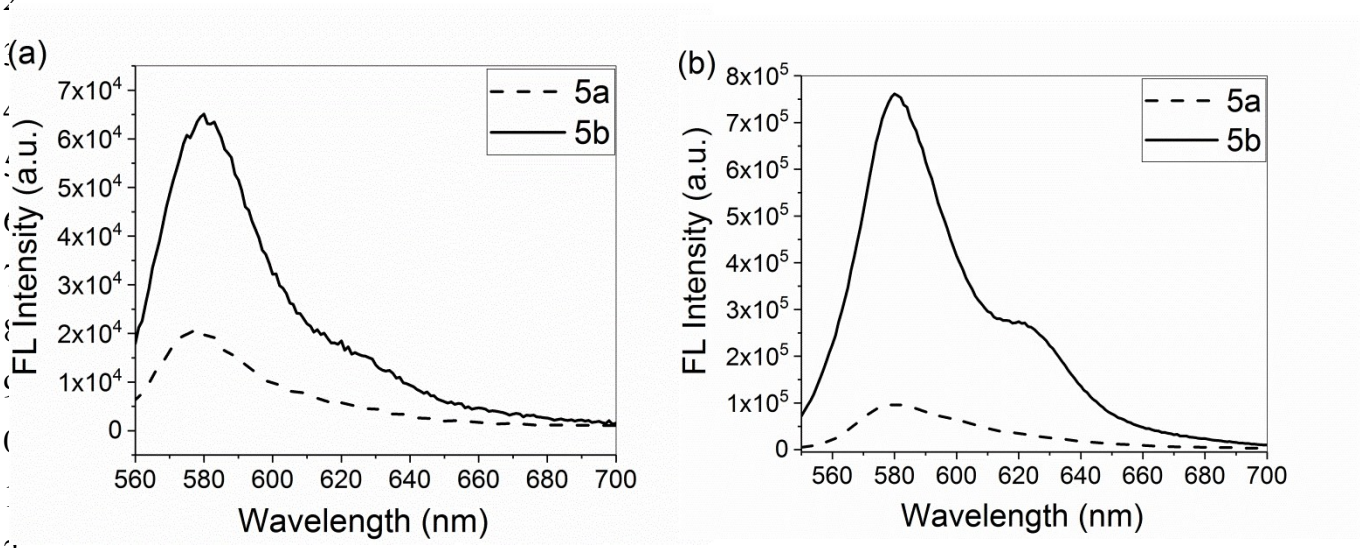

Figure S4. Relative fluorescence spectra of **5a-b** in (a) 10% MeOH, water (b) 100% MeOH (5 μM dye concentration).

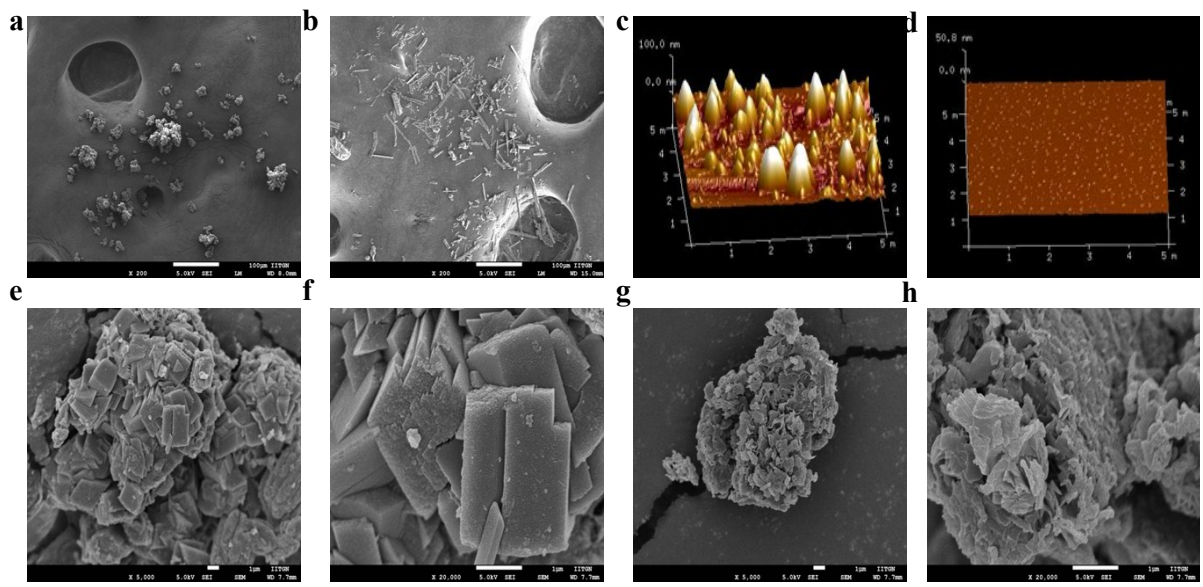

Figure S5. SEM images of (a) **5a** (100 μm) (b) **8a** (100 μm), 3D-AFM images of (c) **5a** and (d) **8a.** (e and f) SEM images of **5a** (1 μm) **(**g-h) SEM images of **5b** (1 μm). (sample preparation details provided in experimental section).

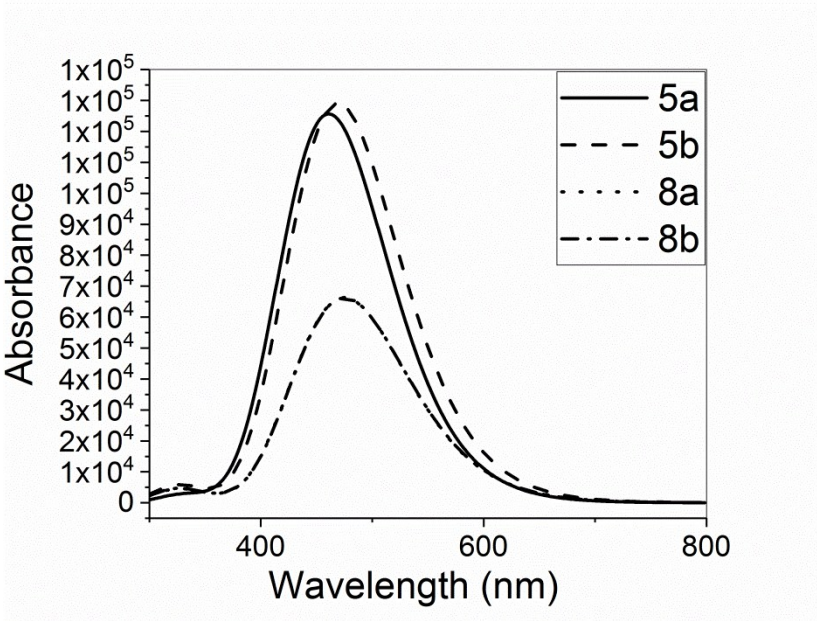

Figure S6. Comparative UV-Visible spectra obtained from TD-DFT calculations for monomers **8a**-**b** and dimers **5a**-**b** in gas phase at B3LYP level using 6-31G basis set and a total of 6 states were used to estimate the vertical excitations.

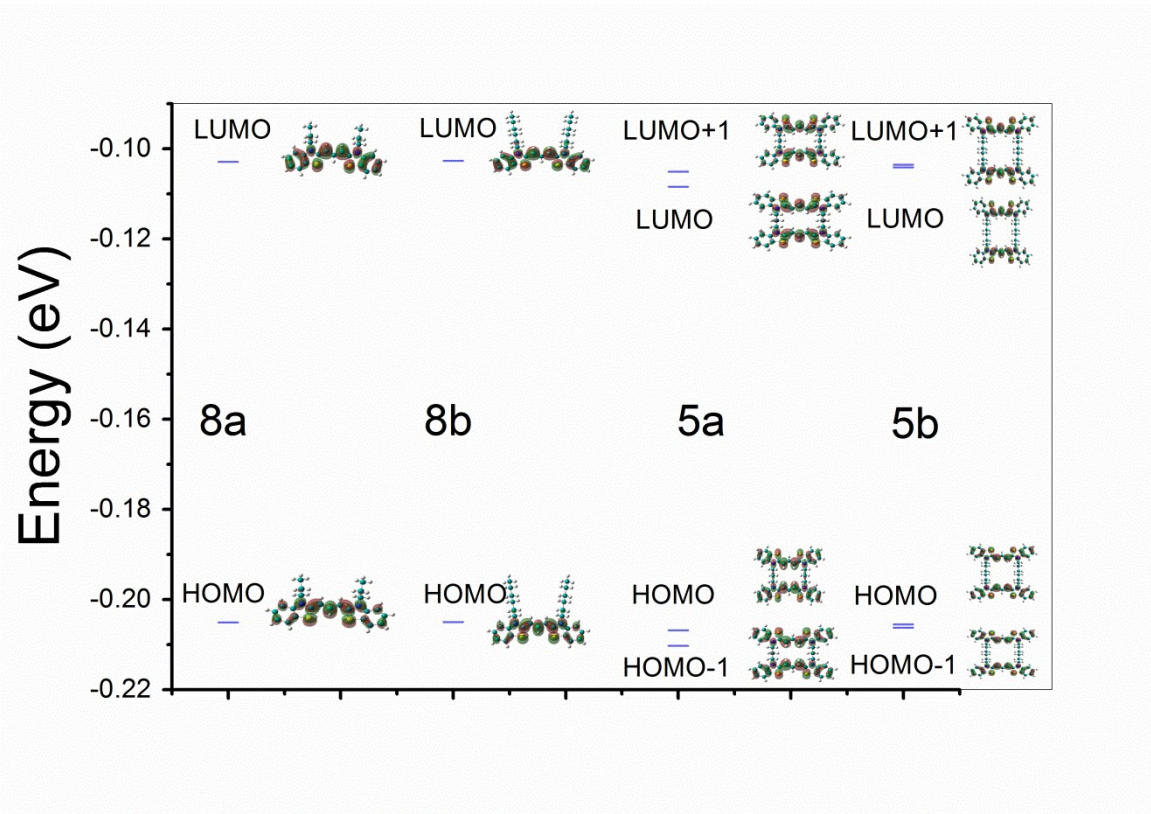

Figure S7. Energy level diagram for monomers and dimers. Orbitals corresponding to the non-degenerate and degenerate HOMO and LUMO are leveled also.

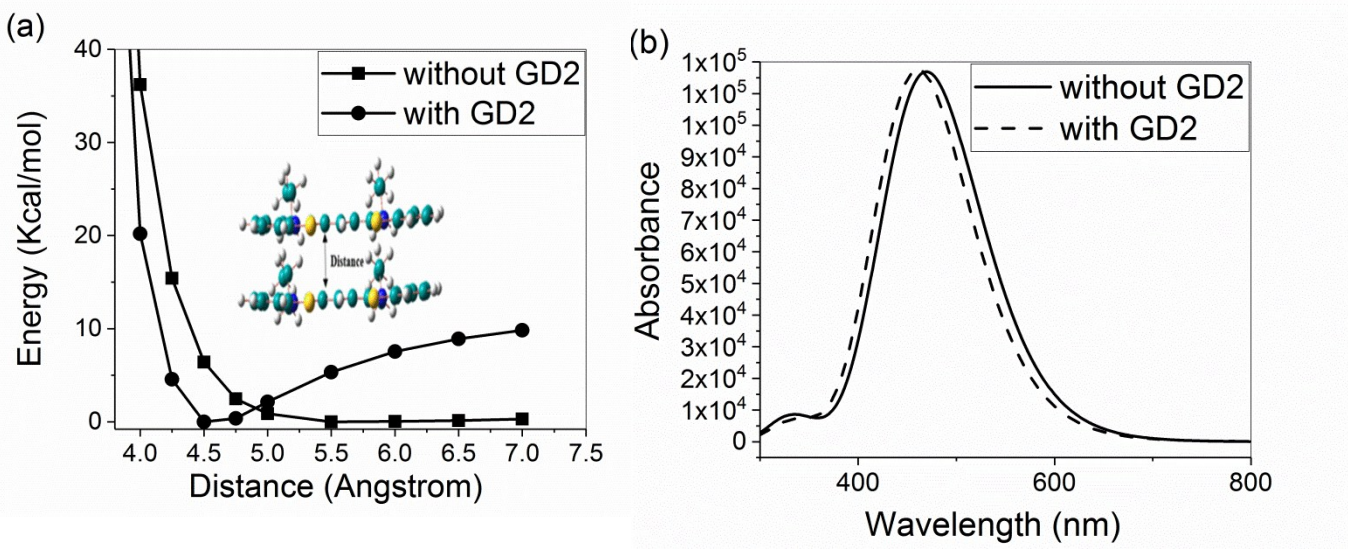

Figure S8. (a) Energy profile corresponding to potential energy scan as a function of distance between two monomers from DFT with empirical dispersion=GD2 and without empirical dispersion=GD2 (b) UV-Visible spectra obtained from DFT calculations with and without empirical dispersion = GD2.

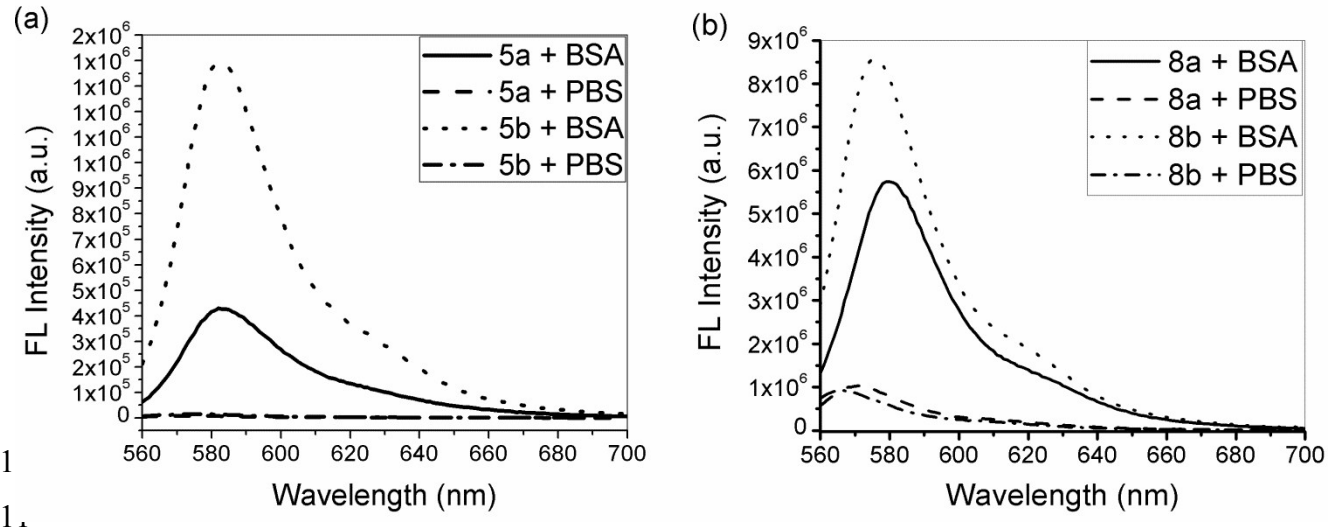

Figure S9. Fluorescence spectra of (a) **5a** and **5b** (b) **8a** and **8b** with BSA (30 μM) or without BSA (5 μM dye concentration at 550 nm excitation).

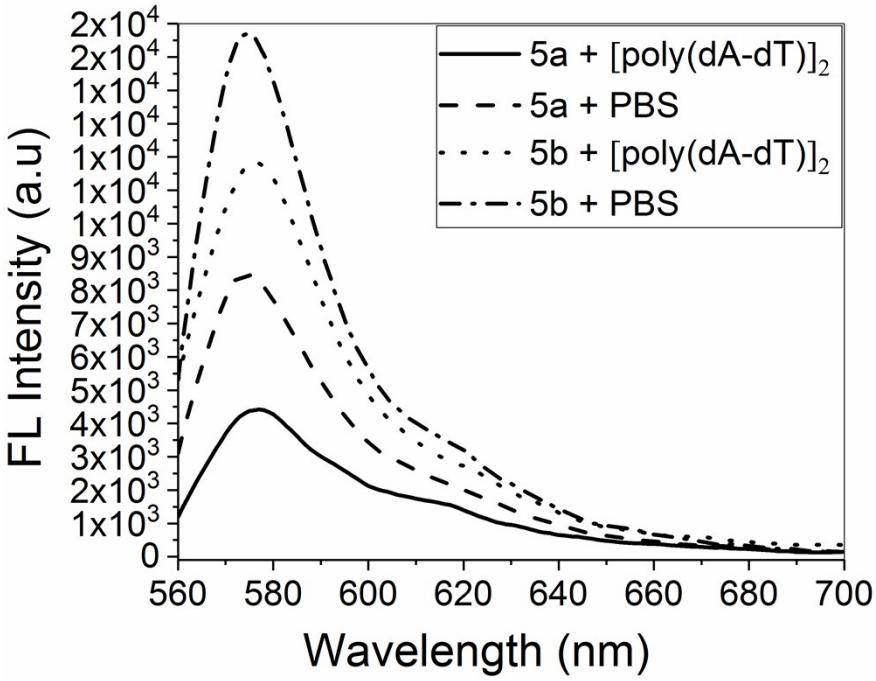

Figure S10. Fluorescence spectra of **5a, 5b** in the presence of poly $(dA\text{-}dT)_2$ (5 μM) and in PBS buffer (5 μM dye concentration at 550 nm excitation).

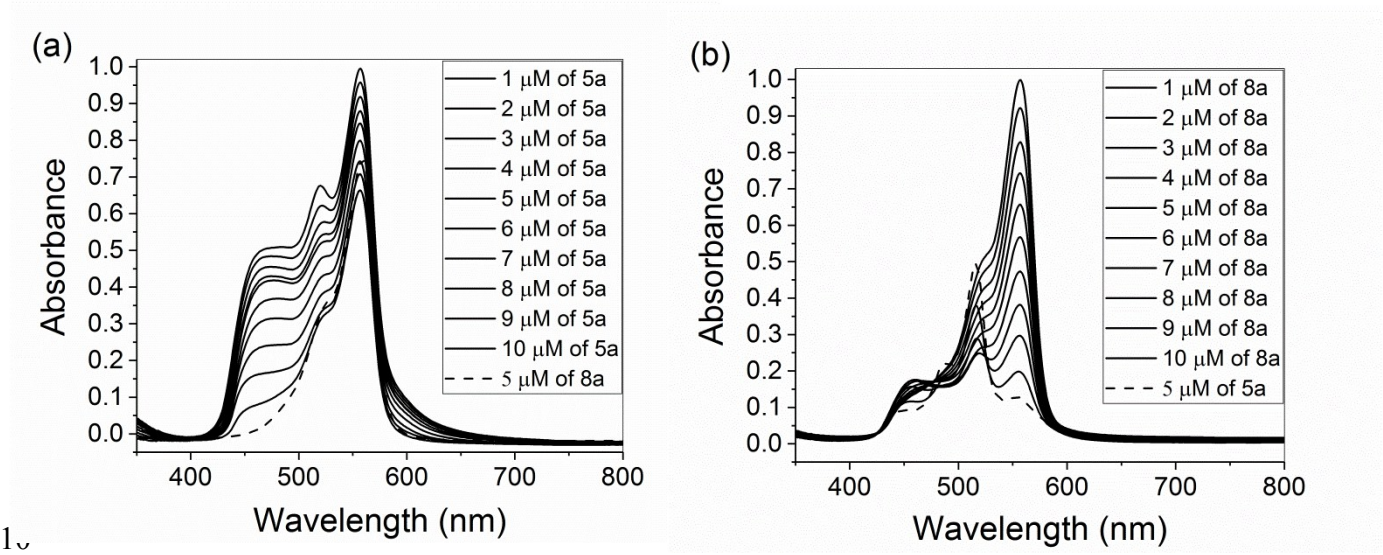

Figure S11. UV-visible analysis of titration of (a) **5a** into **8a** (5 μM) and (b) **8a** into **5a** (5 μM) in water with 10% methanol. Dyes were added in 1 μM aliquots and spectra were recorded at 25 °C.

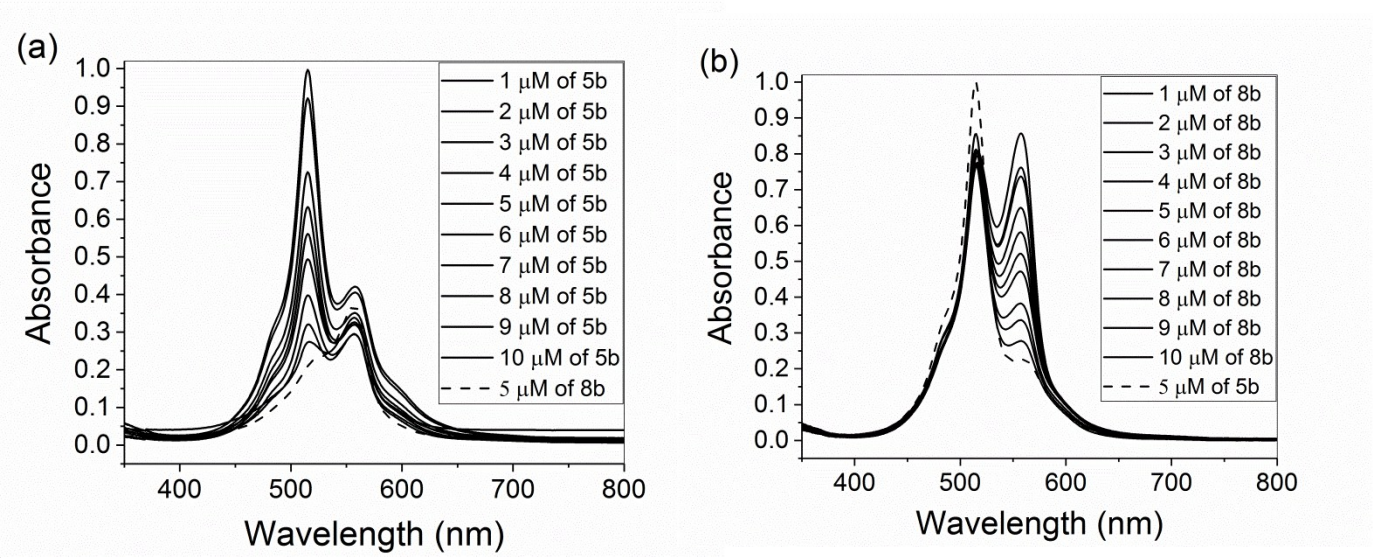

Figure S12. UV-visible analysis of titration of (a) **5b** into **8b** (5 μM) and (b) **8b** into **5b** (5 μM) in water with 10% methanol. Dyes were added in 1 μM aliquots and spectra were recorded at 25 °C.

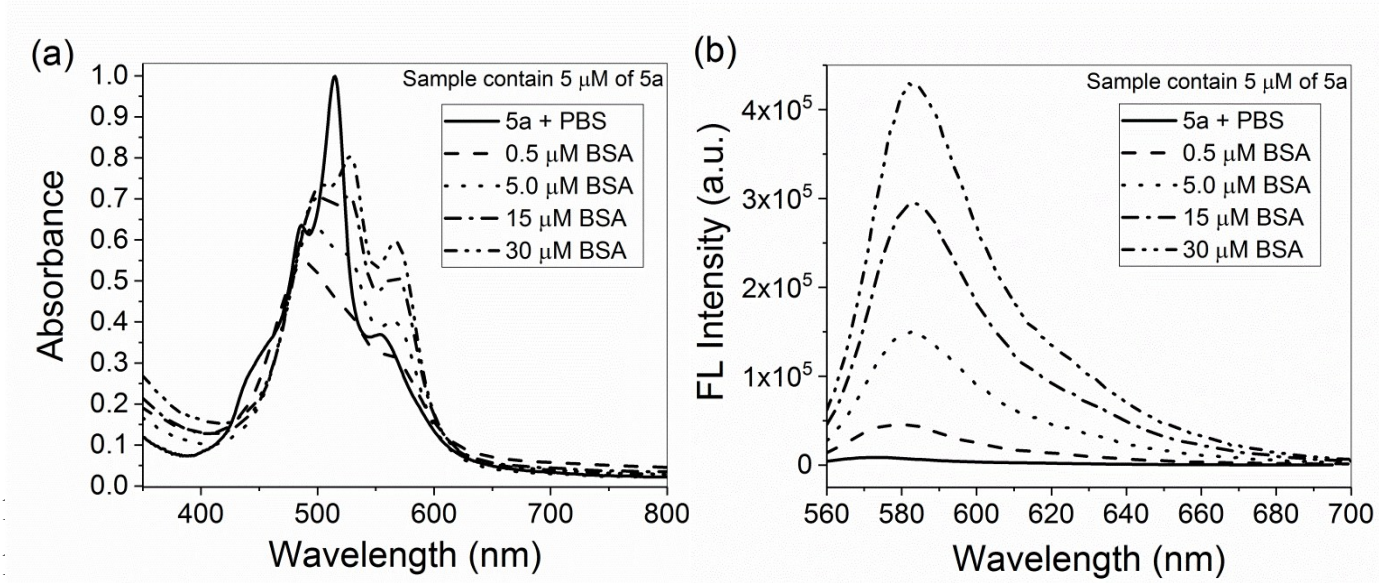

Figure S13. (a) UV-visible (b) fluorescence analysis of the interaction of **5a** with BSA. Spectra were recorded of 5 μM dye **5a** alone and with different concentration of BSA (0.5 μM, 5.0 μM, 15 μM and 30 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

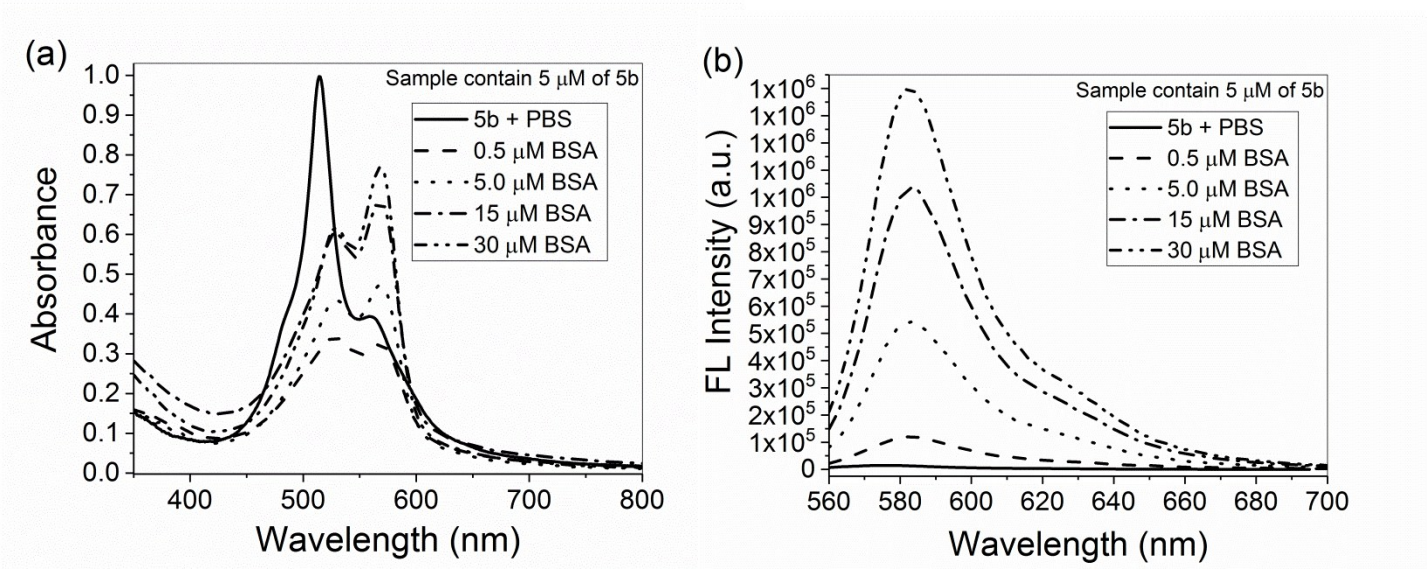

Figure S14. (a) UV-visible (b) fluorescence analysis of the interaction of **5b** with BSA. Spectra were recorded of 5 μM dye **5b** alone and with different concentration of BSA (0.5 μM, 5.0 μM, 15 μM and 30 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

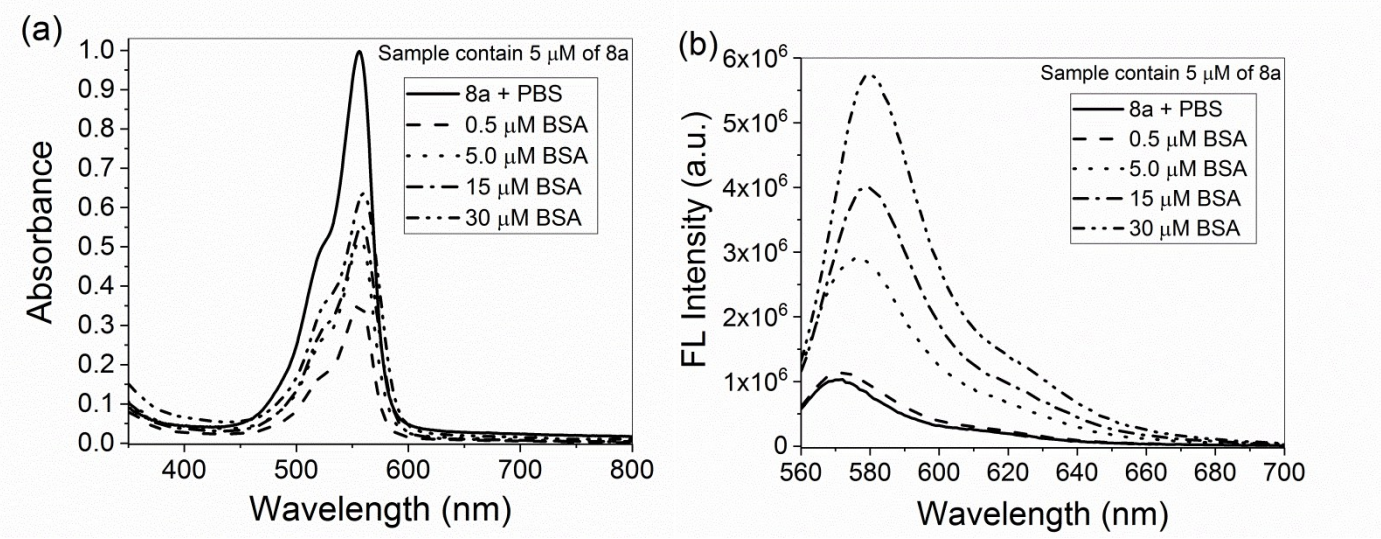

Figure S15. (a) UV-visible (b) fluorescence analysis of the interaction of **8a** with BSA. Spectra were recorded of 5 μM dye **8a** alone and with different concentration of BSA (0.5 μM, 5.0 μM, 15 μM and 30 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

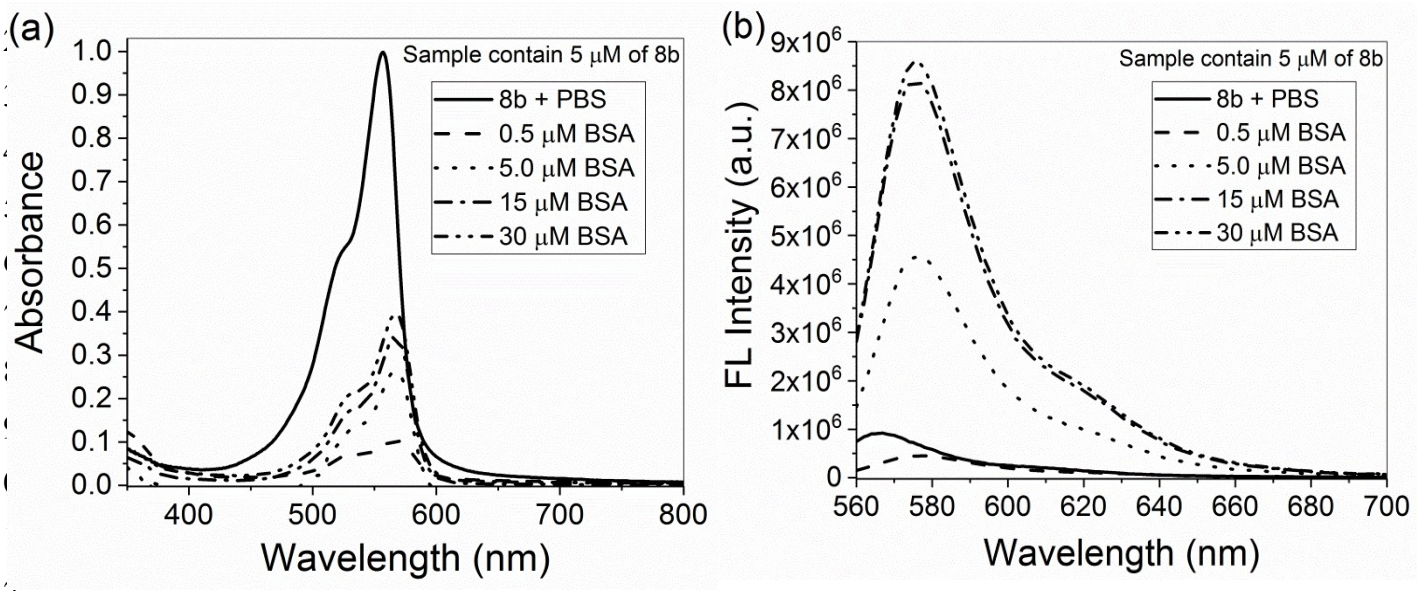

Figure S16. (a) UV-visible (b) fluorescence analysis of the interaction of **8b** with BSA. Spectra were recorded of 5 μM dye **8b** alone and with different concentration of BSA (0.5 μM, 5.0 μM, 15 μM and 30 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

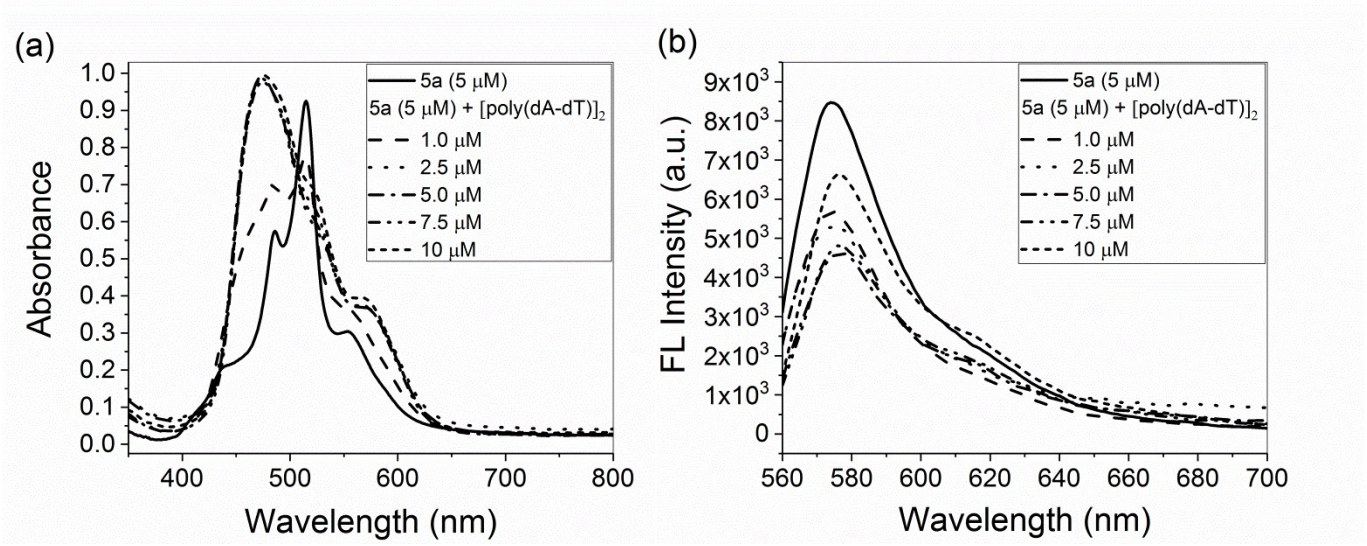

Figure S17. (a) UV-visible (b) fluorescence analysis of the interaction of **5a** with [poly(dA-dT)]$_2$. Spectra were recorded of 5 μM dye **5a** alone and with different concentration of [poly(dA-dT)]$_2$ (1.0 μM, 2.5 μM, 5 μM, 7.5 μM and 10 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

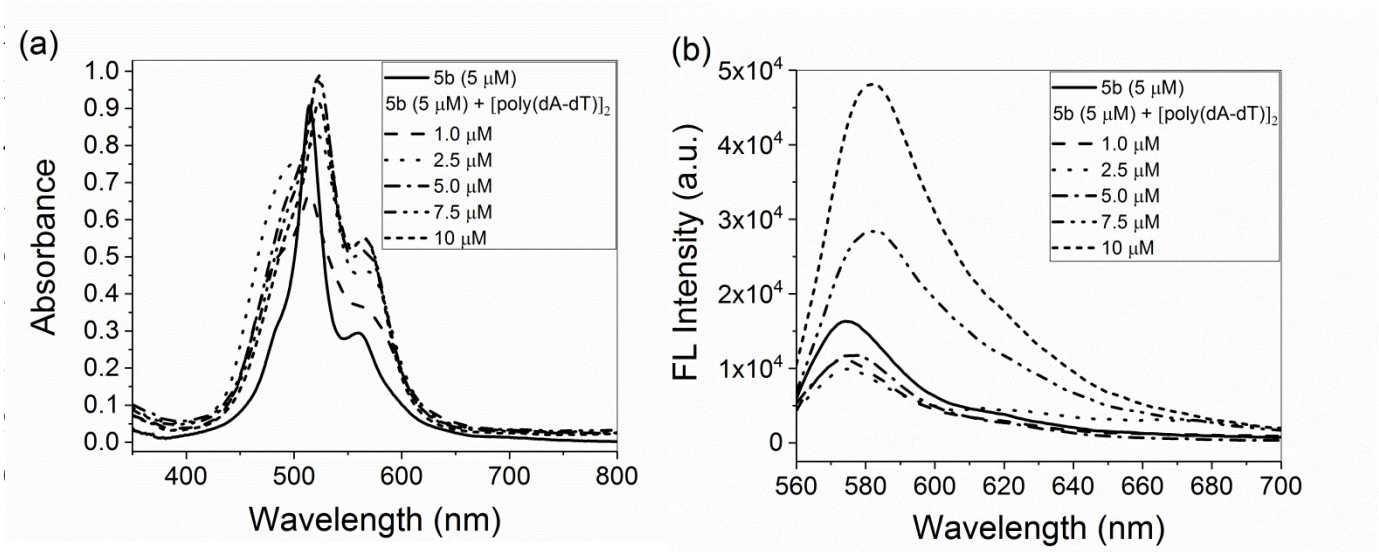

Figure S18. (a) UV-visible (b) fluorescence analysis of the interaction of **5b** with [poly(dA-dT)]$_2$. Spectra were recorded of 5 μM dye **5b** alone and with different concentration of [poly(dA-dT)]$_2$ (1.0 μM, 2.5 μM, 5 μM, 7.5 μM and 10 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

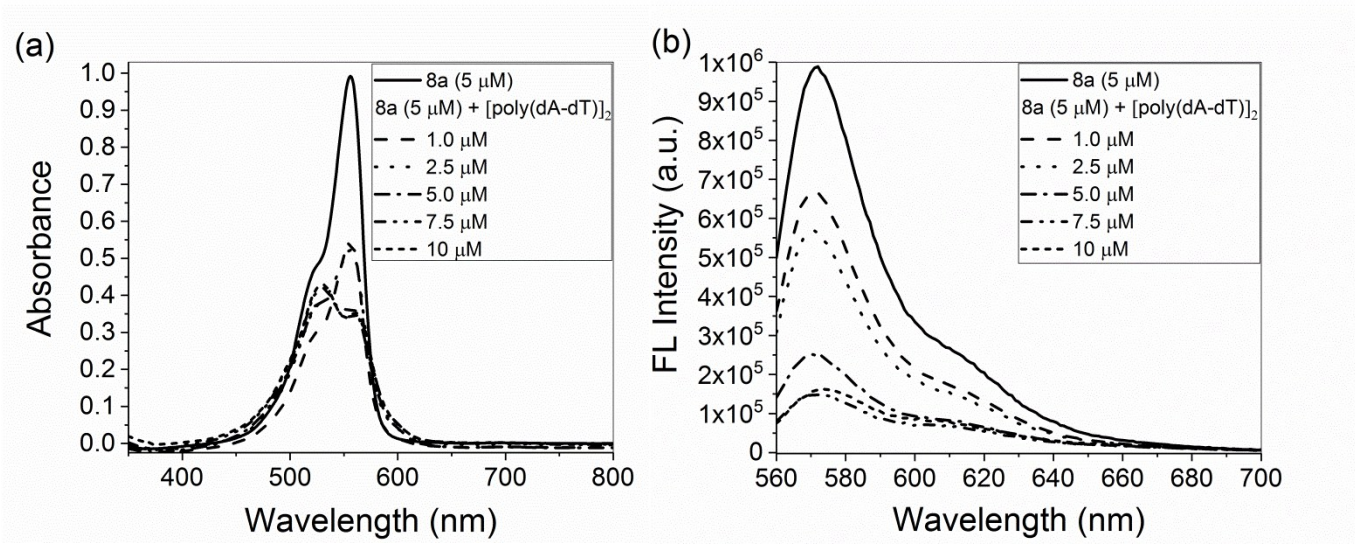

Figure S19. (a) UV-visible (b) fluorescence analysis of the interaction of **8a** with [poly(dA-dT)]$_2$. Spectra were recorded of 5 μM dye **8a** alone and with different concentration of [poly(dA-dT)]$_2$ (1.0 μM, 2.5 μM, 5 μM, 7.5 μM and 10 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

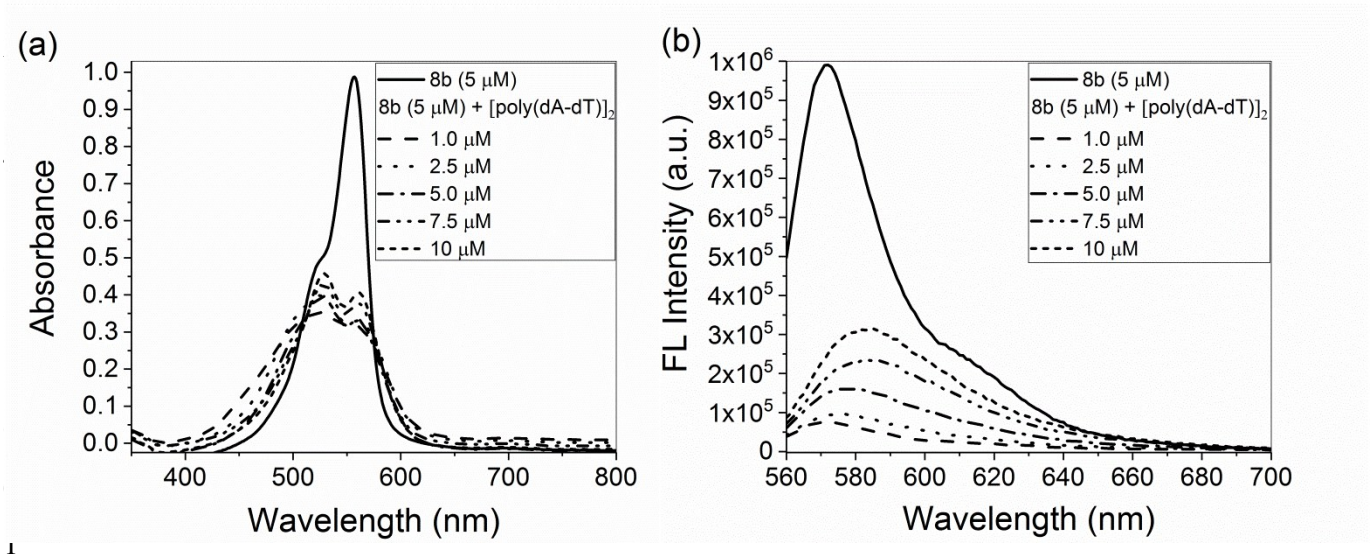

Figure S20. (a) UV-visible (b) fluorescence analysis of the interaction of **8b** with [poly(dA-dT)]$_2$. Spectra were recorded of 5 μM dye **8b** alone and with different concentration of [poly(dA-dT)]$_2$ (1.0 μM, 2.5 μM, 5 μM, 7.5 μM and 10 μM), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

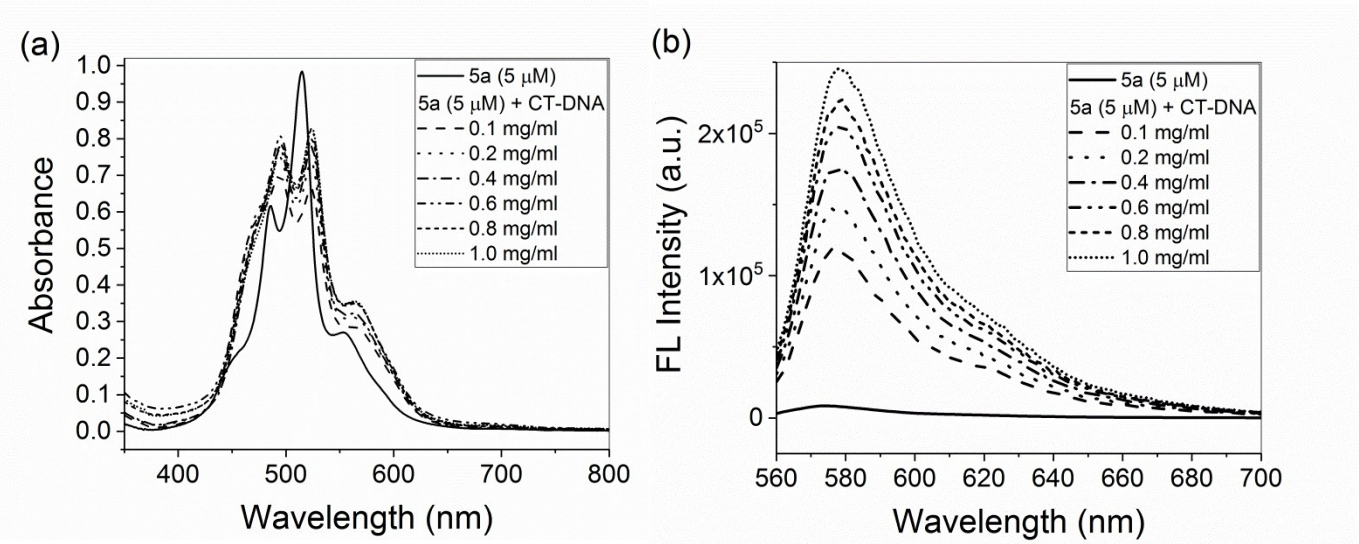

Figure S21. (a) UV-visible (b) fluorescence analysis of the interaction of **5a** with CT-DNA. Spectra were recorded of 5 μM dye **5a** alone and with different concentration of CT-DNA (0.1 mg/ml, 0.2 mg/ml, 0.4 mg/ml, 0.6 mg/ml, 0.8 mg/ml, and 1.0 mg/ml), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

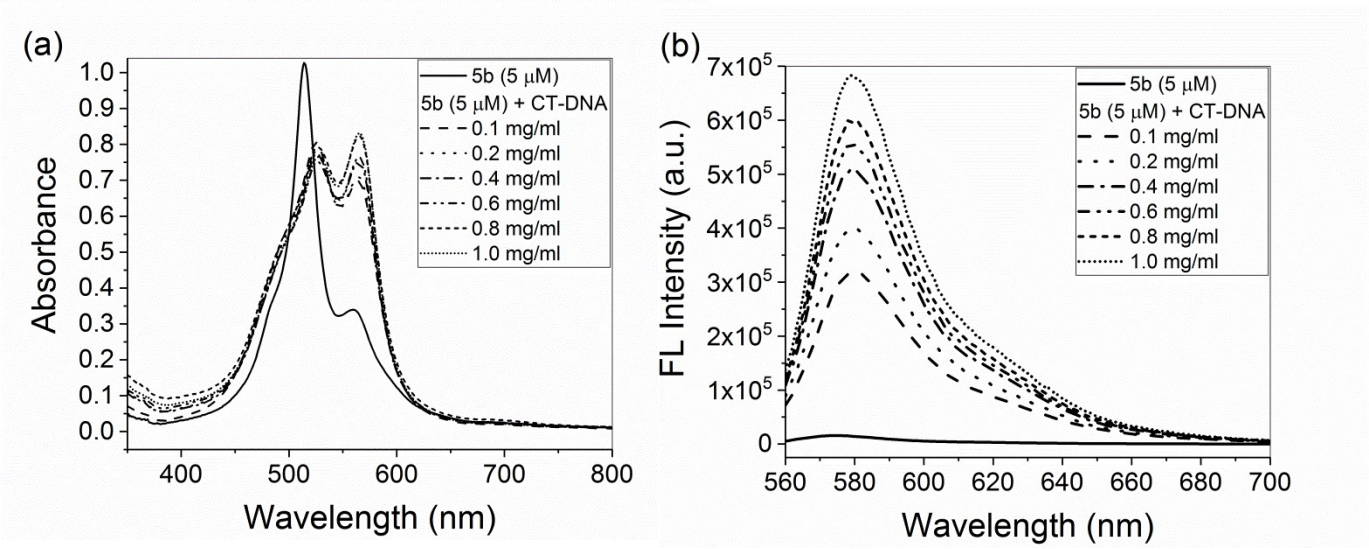

Figure S22. (a) UV-visible (b) fluorescence analysis of the interaction of **5b** with CT-DNA. Spectra were recorded of 5 μM dye **5b** alone and with different concentration of CT-DNA (0.1 mg/ml, 0.2 mg/ml, 0.4 mg/ml, 0.6 mg/ml, 0.8 mg/ml, and 1.0 mg/ml), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

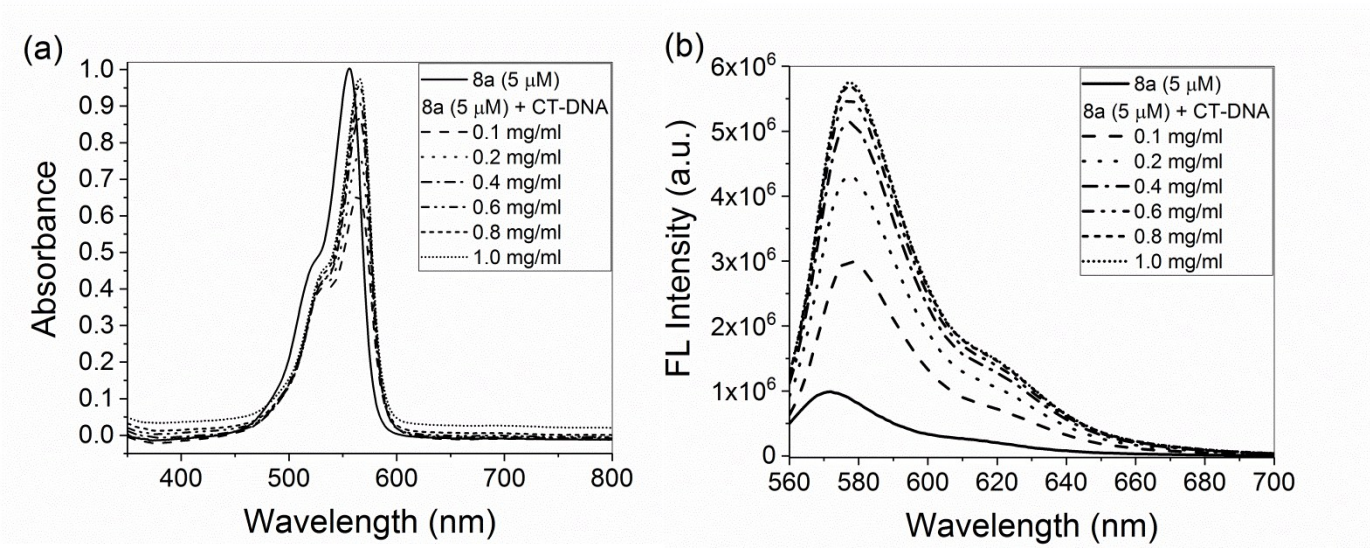

Figure S23. (a) UV-visible (b) fluorescence analysis of the interaction of **8a** with CT-DNA. Spectra were recorded of 5 μM dye **8a** alone and with different concentration of CT-DNA (0.1 mg/ml, 0.2 mg/ml, 0.4 mg/ml, 0.6 mg/ml, 0.8 mg/ml, and 1.0 mg/ml), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

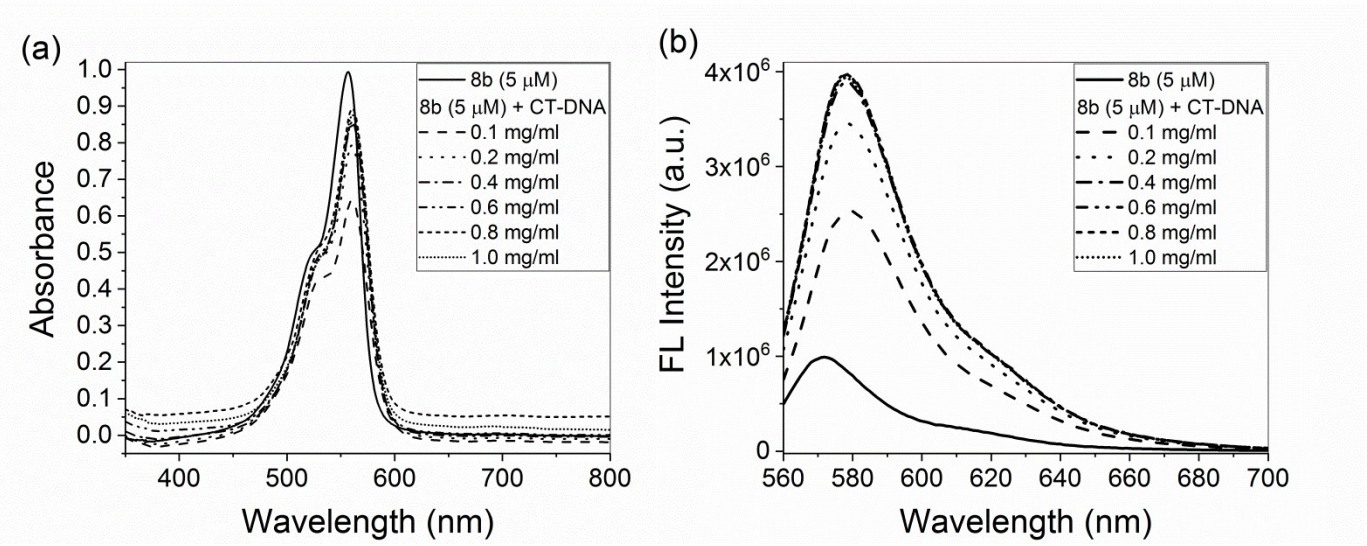

Figure S24. (a) UV-visible (b) fluorescence analysis of the interaction of **8b** with CT-DNA. Spectra were recorded of 5 μM dye **8b** alone and with different concentration of CT-DNA (0.1 mg/ml, 0.2 mg/ml, 0.4 mg/ml, 0.6 mg/ml, 0.8 mg/ml, and 1.0 mg/ml), in 10 mM sodium phosphate buffer (pH = 7.0) at 25 ^{o}C. Fluorescence spectra were recorded by exciting samples at 550 nm.

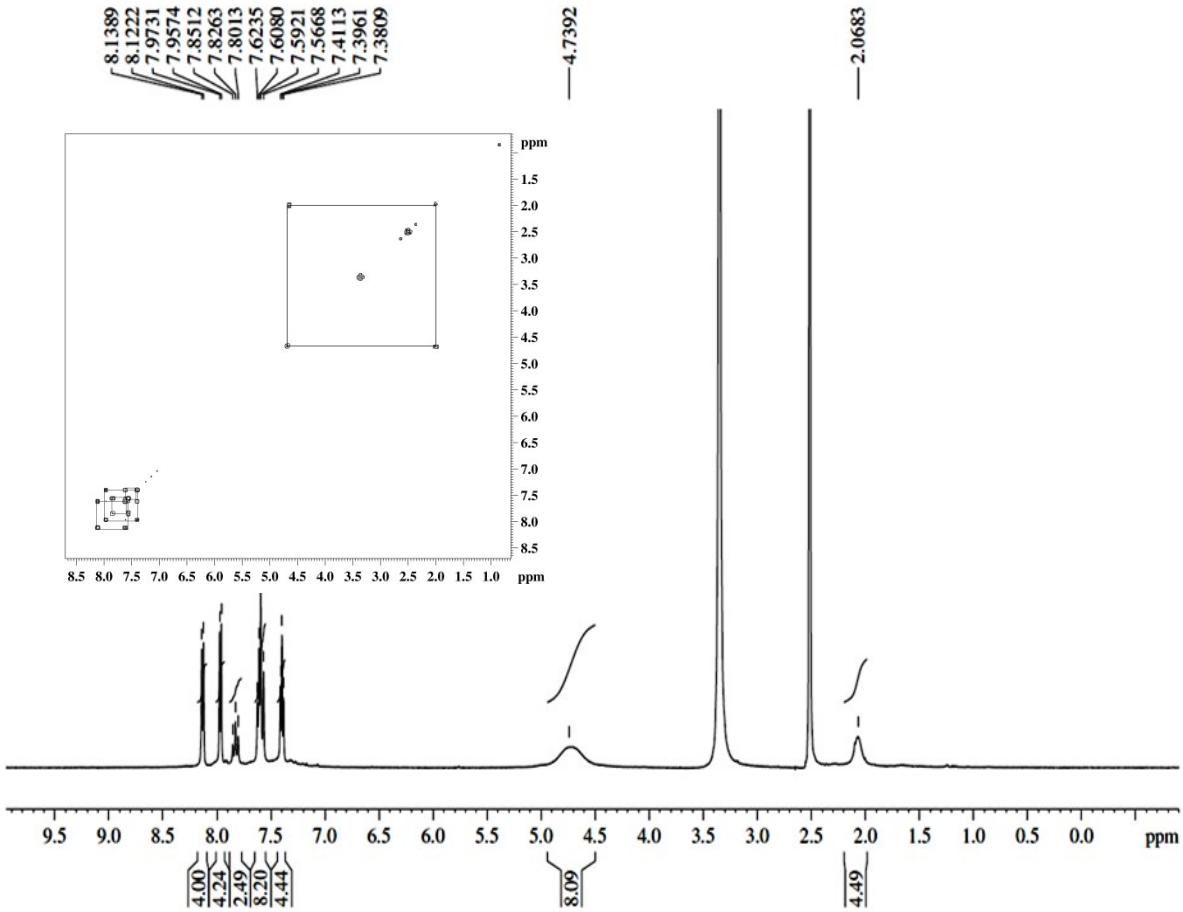

Figure S25. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of compound 5**a** (inset 2D homo cosy).

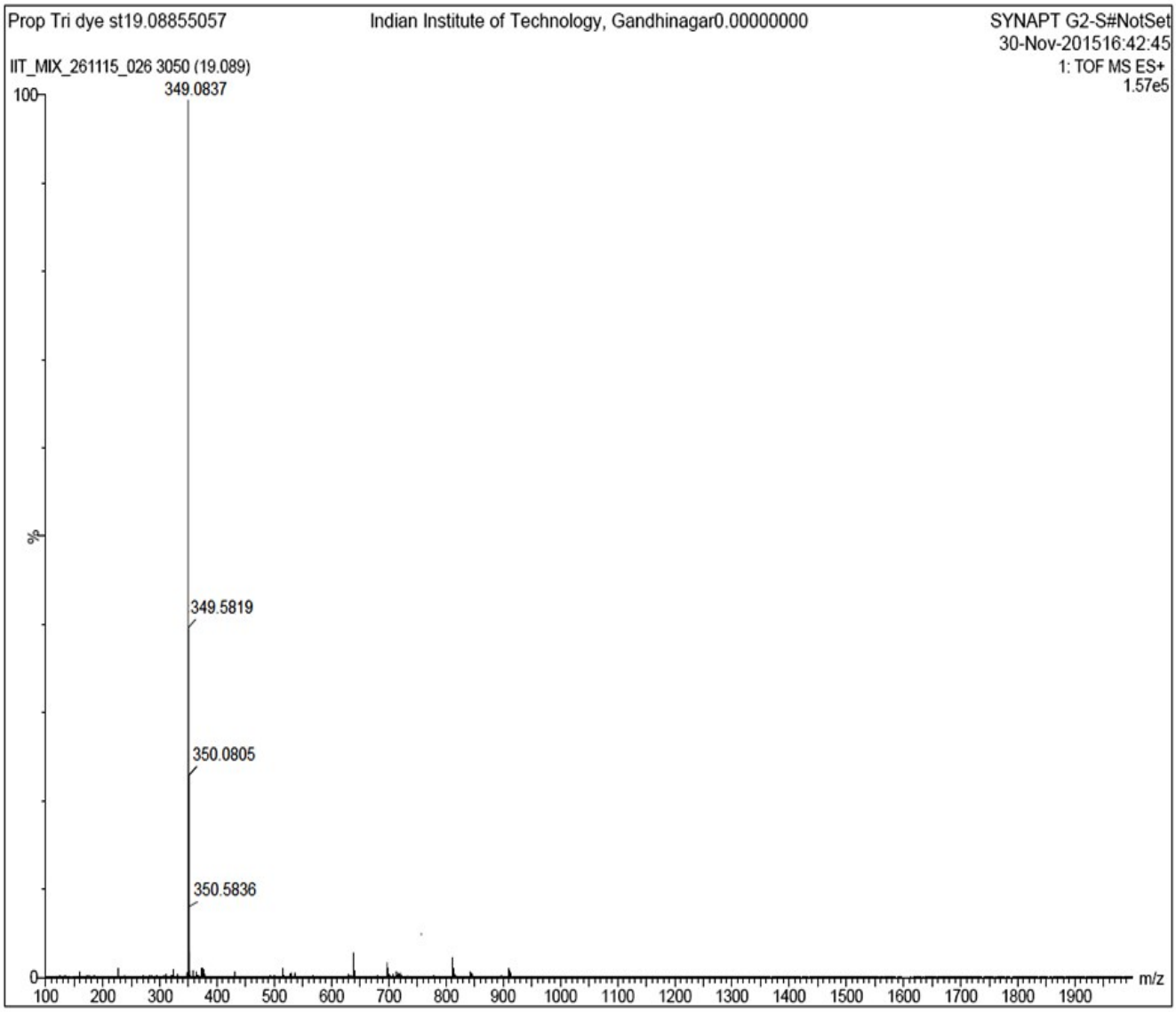

Figure S26. ESI-MS of 5**a**.

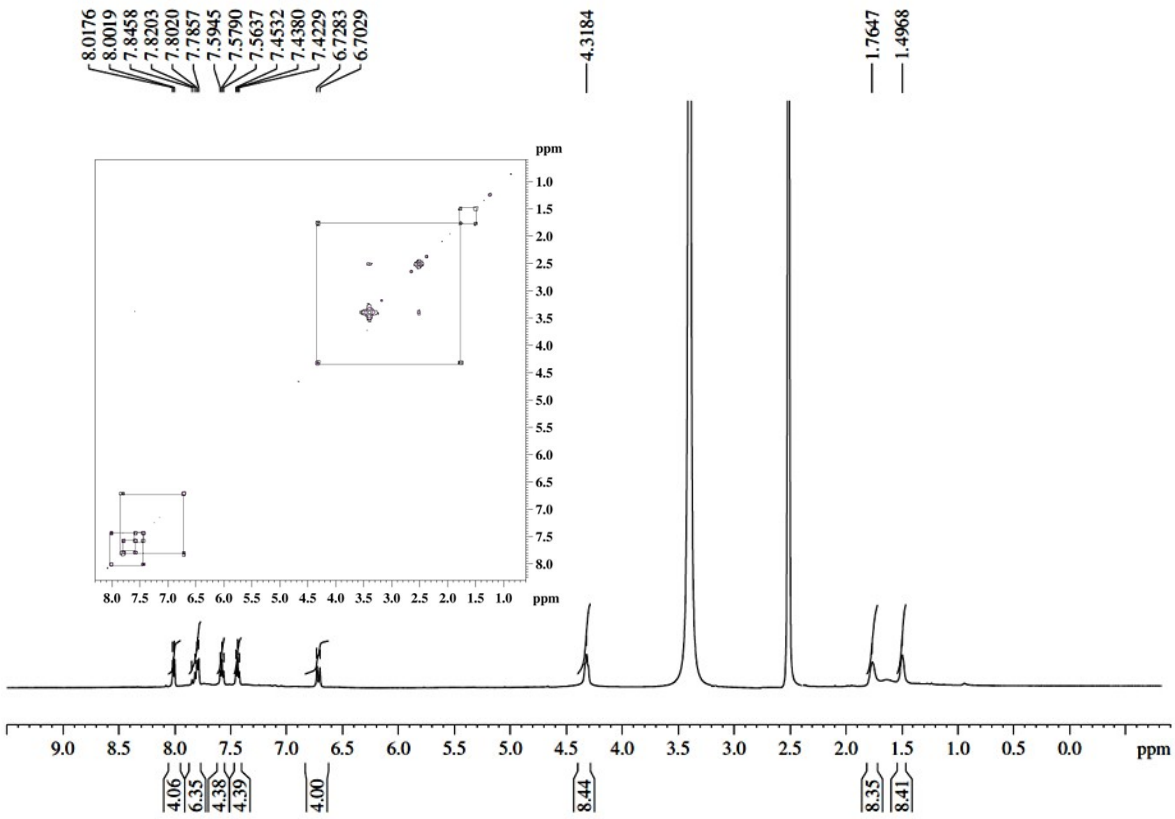

Figure S27. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of compound **5b**. (inset 2D homo cosy).

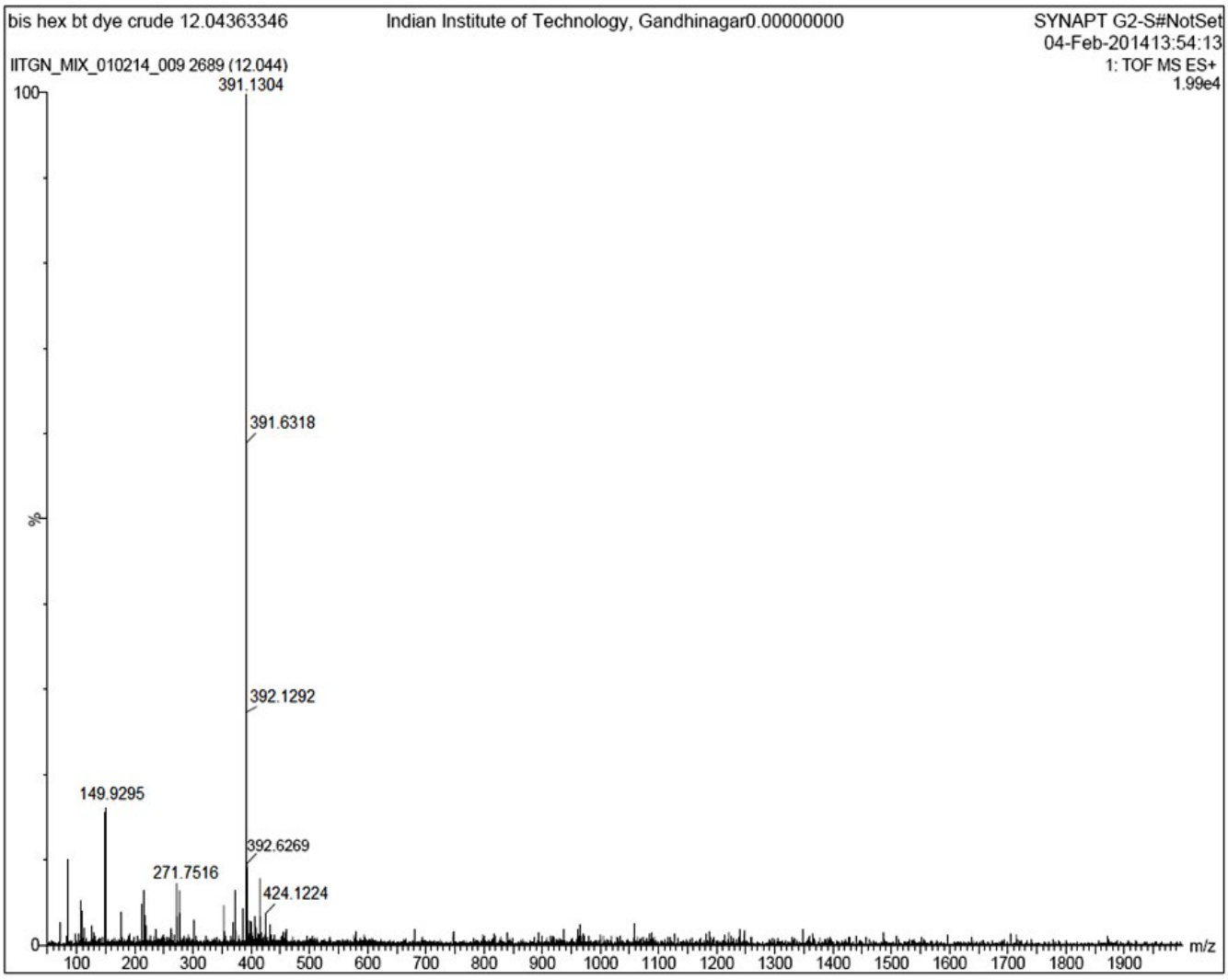

Figure S28. ESI-MS of **5b**.

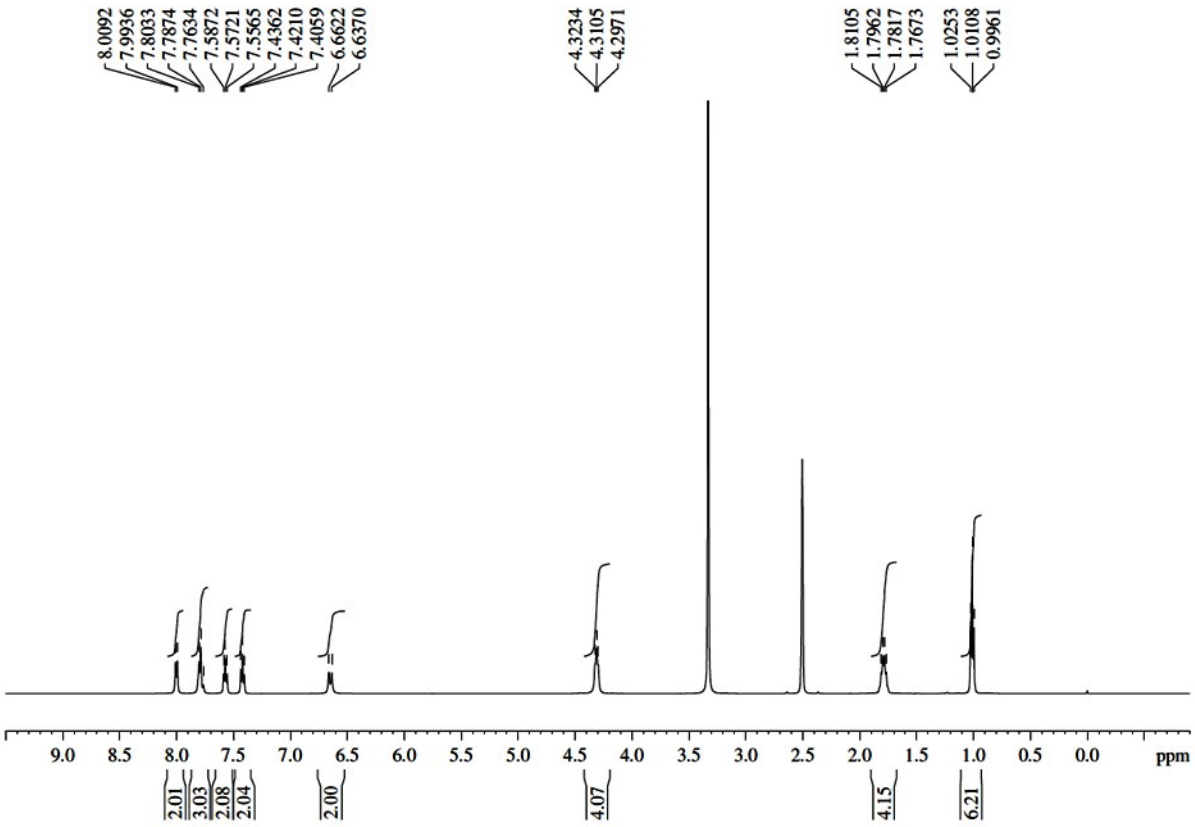

Figure S29. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of compound **8a**.

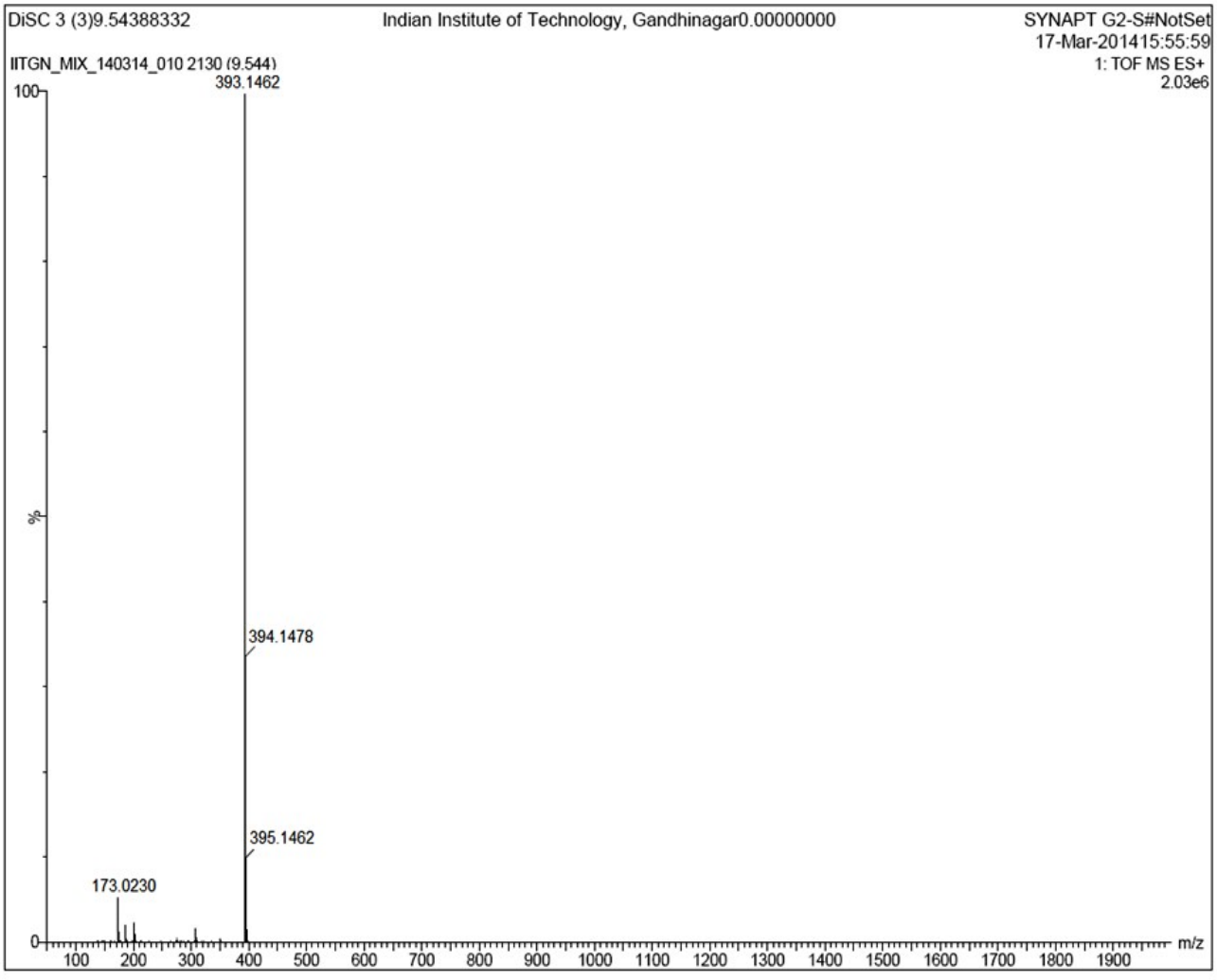

Figure S30. ESI-MS of **8a**.

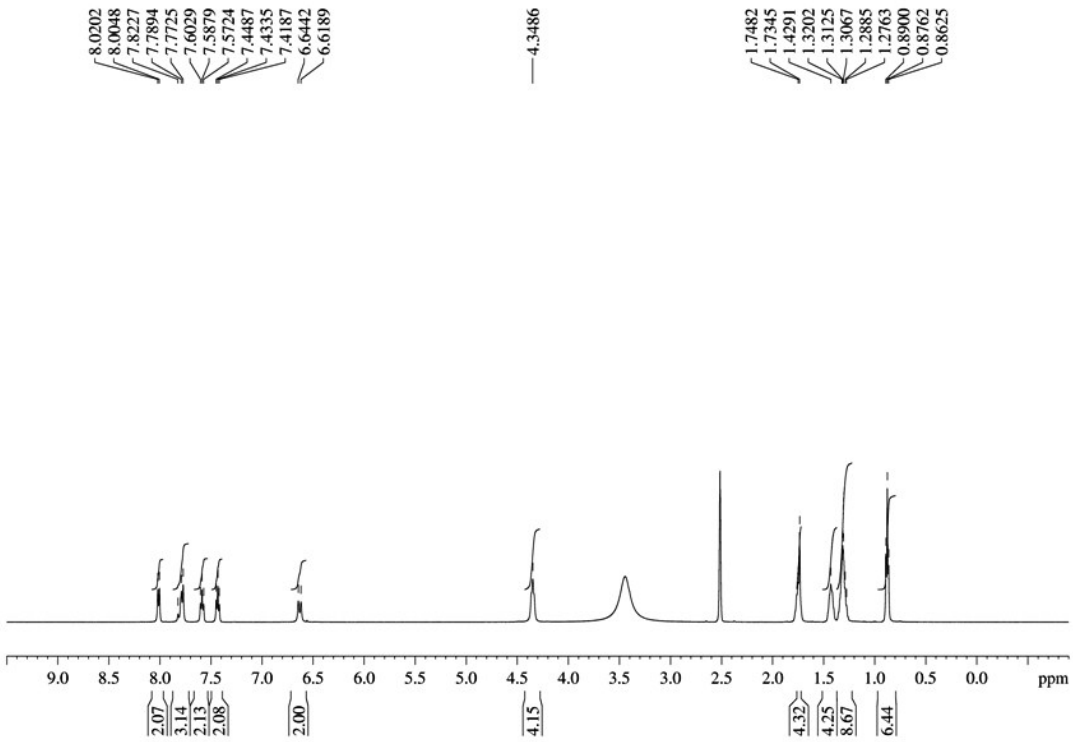

Figure S31. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of compound **8b**.

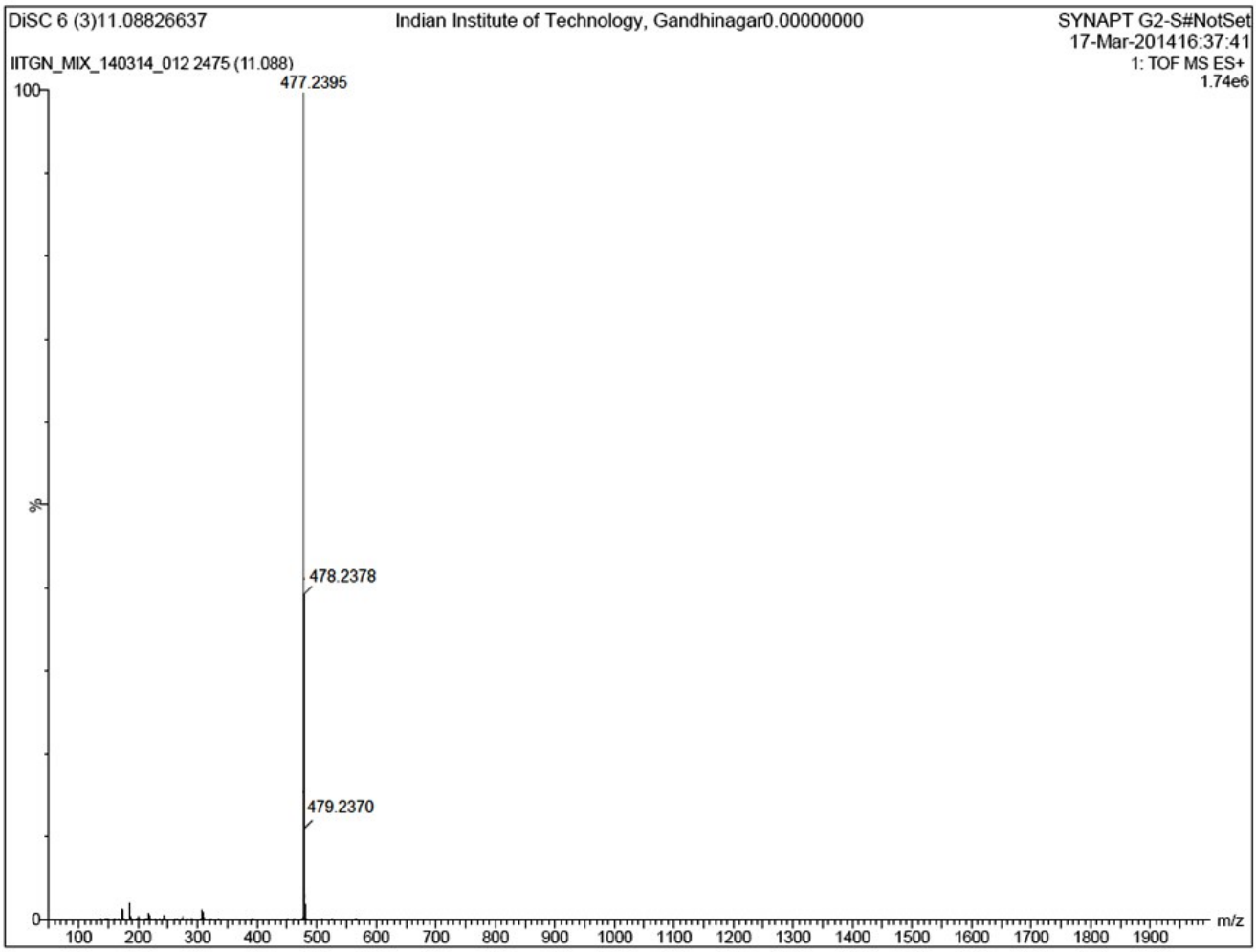

Figure S32. ESI-MS of **8b**.