Electronic Supporting Information

Carbazole appended *trans*-dicationic pyridinium porphyrin finds supremacy in DNA binding/photocleavage over non-carbazolyl analogue

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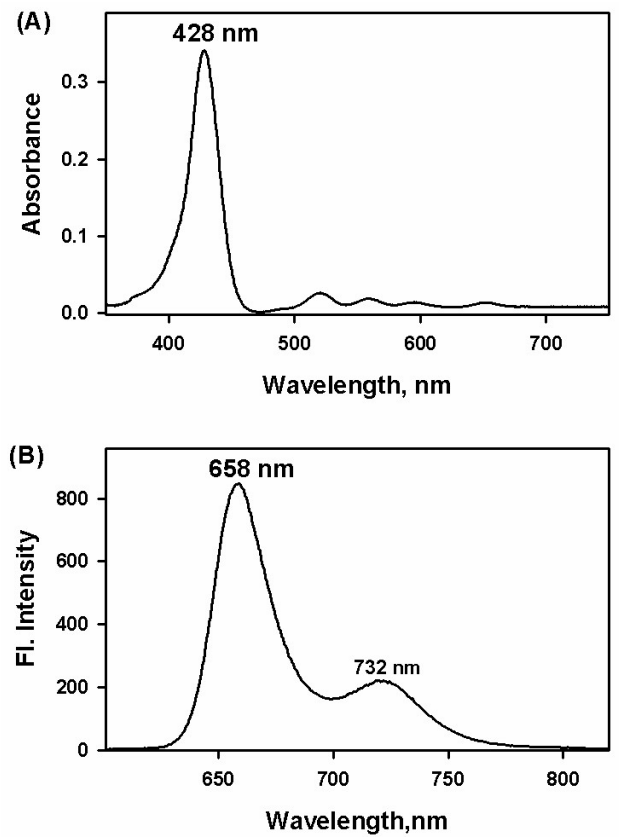

Fig. S1. (A) UV-visible absorption and (B) Fluorescence emission spectra of **1** recorded in $CHCl_3$ at 298 K.

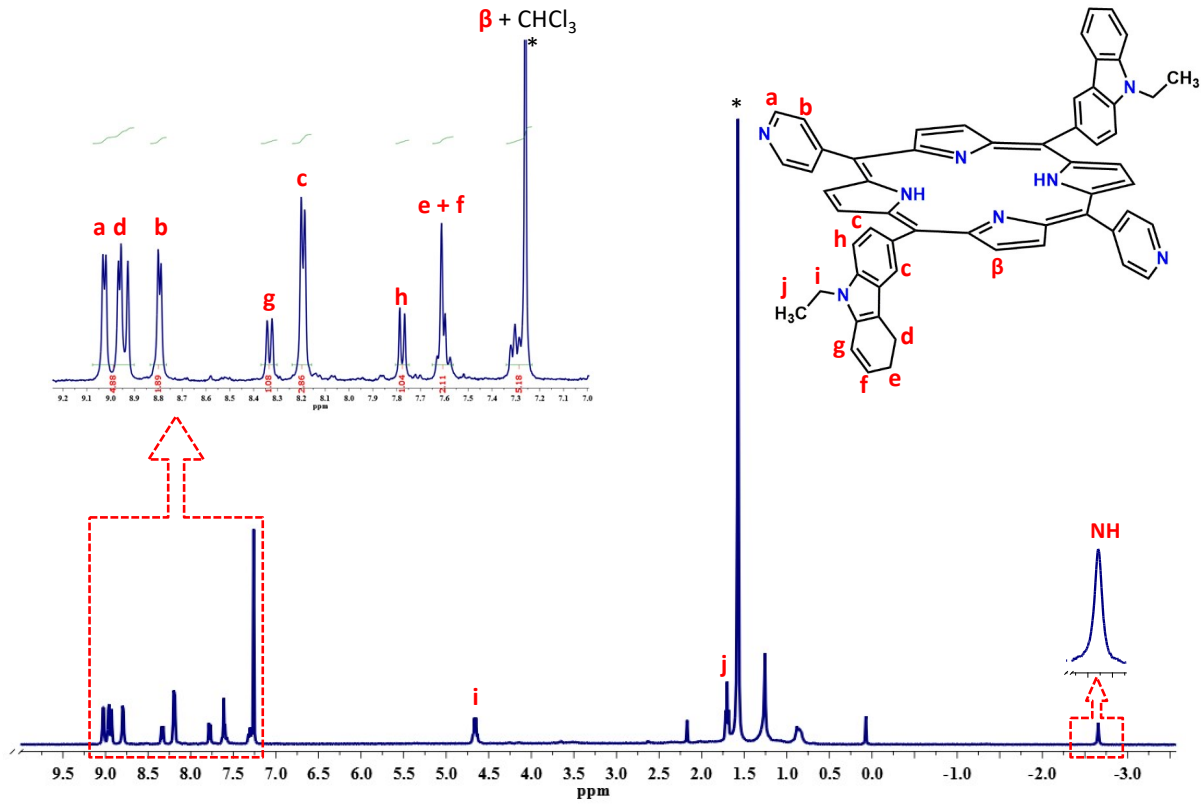

Fig. S2. ^{1}H NMR spectrum of **1** recorded in $CDCl_3$. Marked peak with an asterisk (*) at 1.56 and 7.26 ppm indicates residual $CDCl_3$ and water respectively.

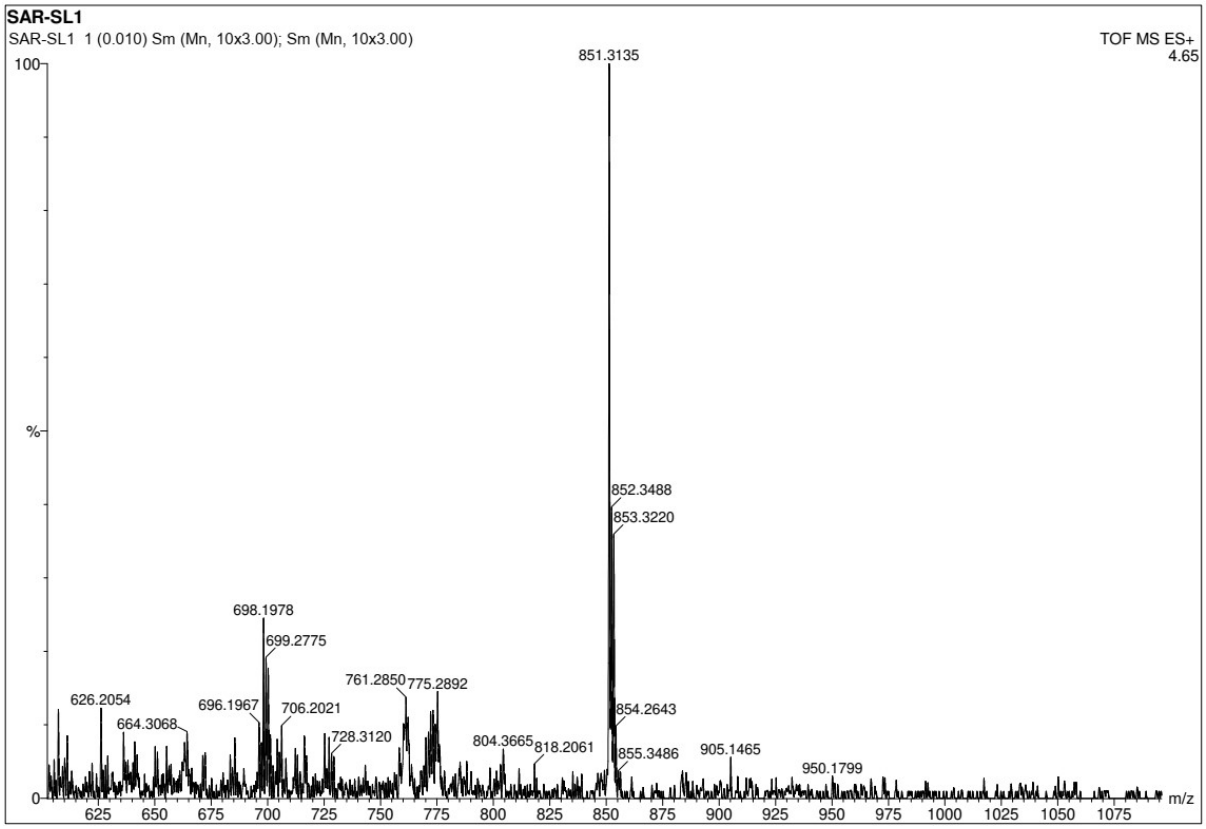

Fig. S3. Mass spectrum of **1** recorded in $CHCl_3$.

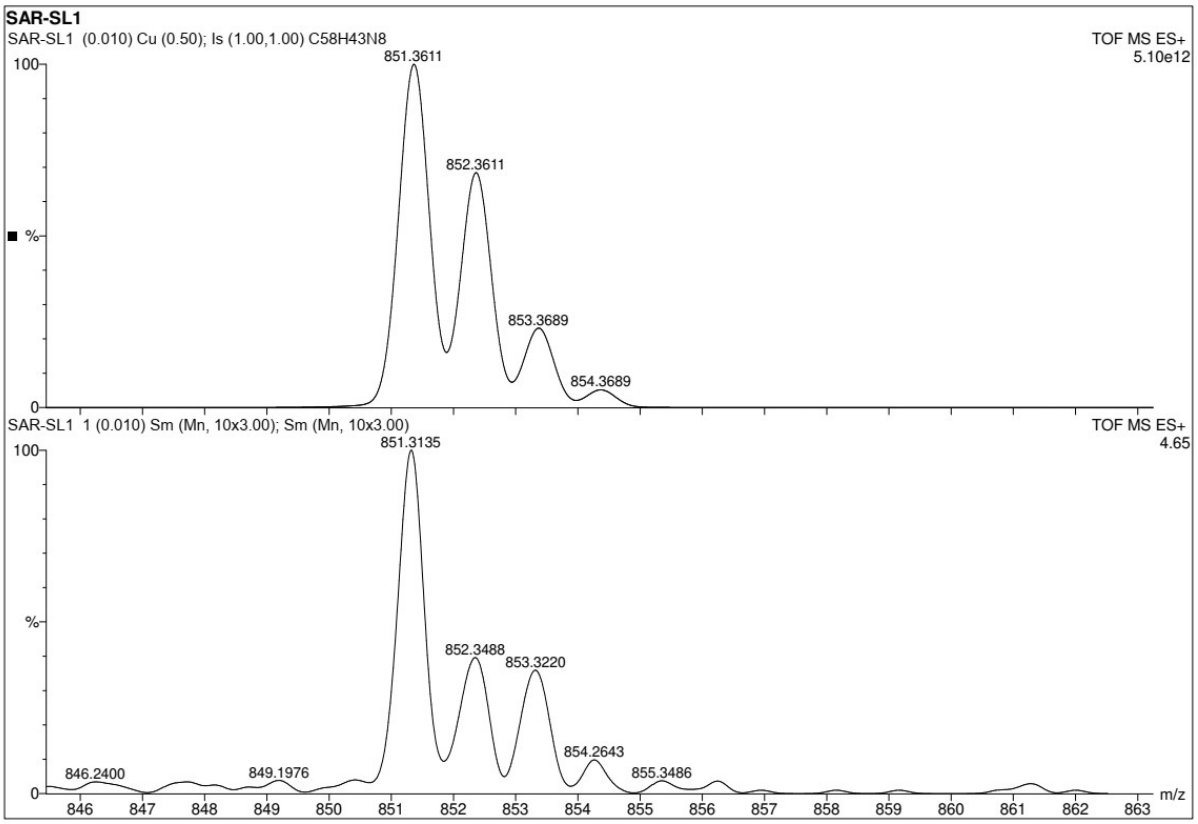

Fig. S4. Experimental (top) and theoretical (bottom) isotopic distribution of **1 was** recorded in $CHCl_3$.

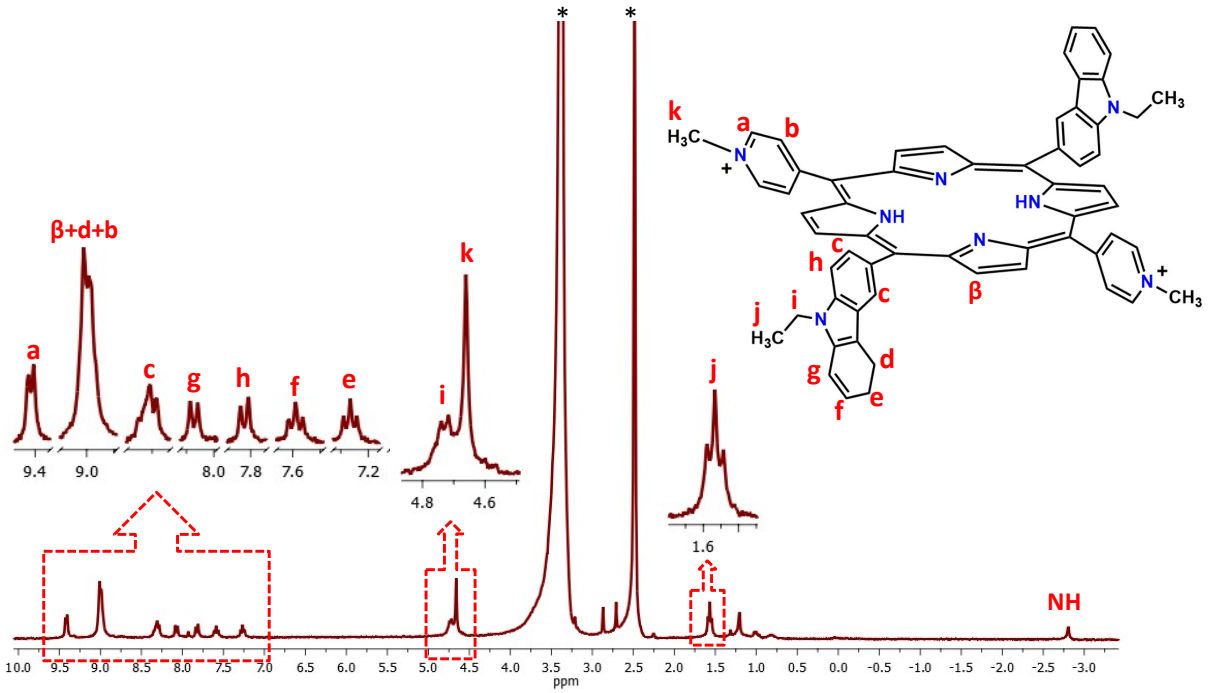

Fig. S5. [1]H NMR spectrum of **2** recorded in DMSO-d_6. Marked peak with an asterisk (*) at 2.5 and 3.5 ppm indicates residual DMSO and water, respectively.

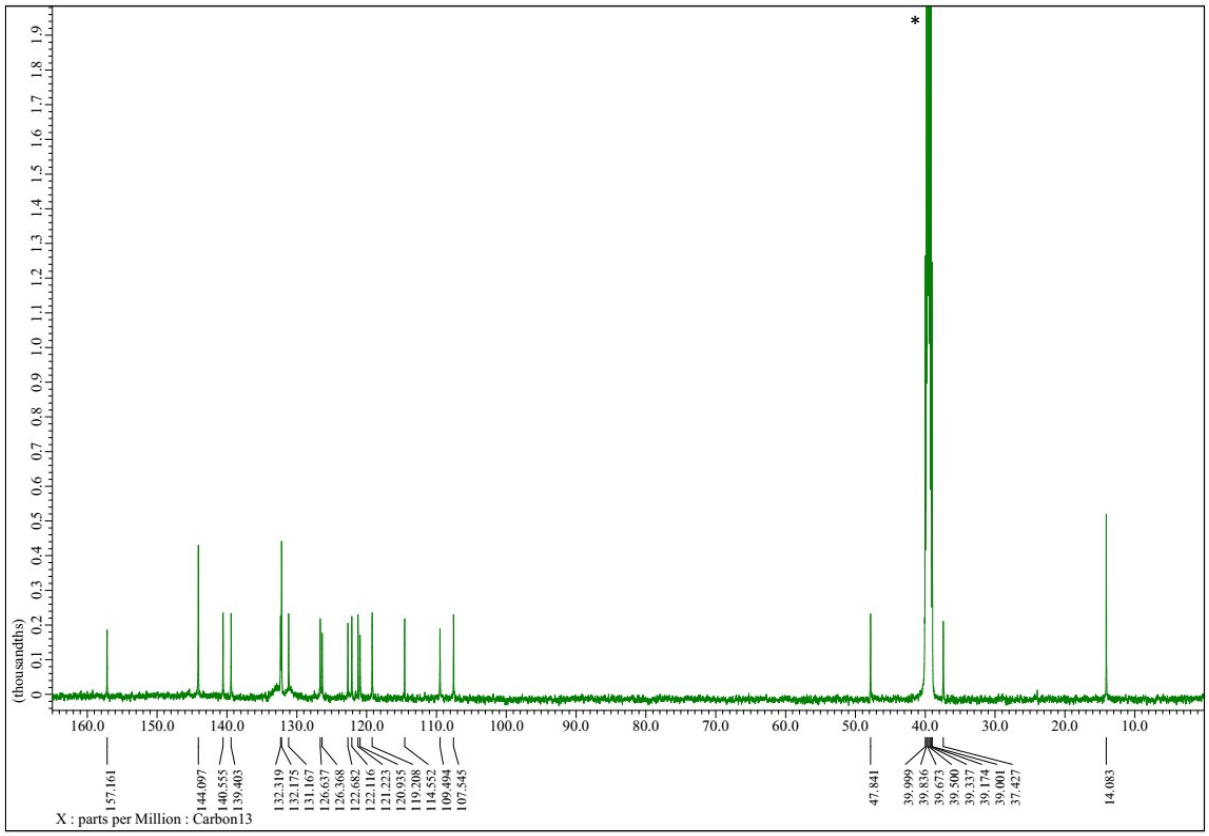

Fig. S6. [13]H NMR spectrum of **2** recorded in DMSO-d_6. Marked peak with an asterisk (*) at 39-39.9 ppm indicates residual DMSO.

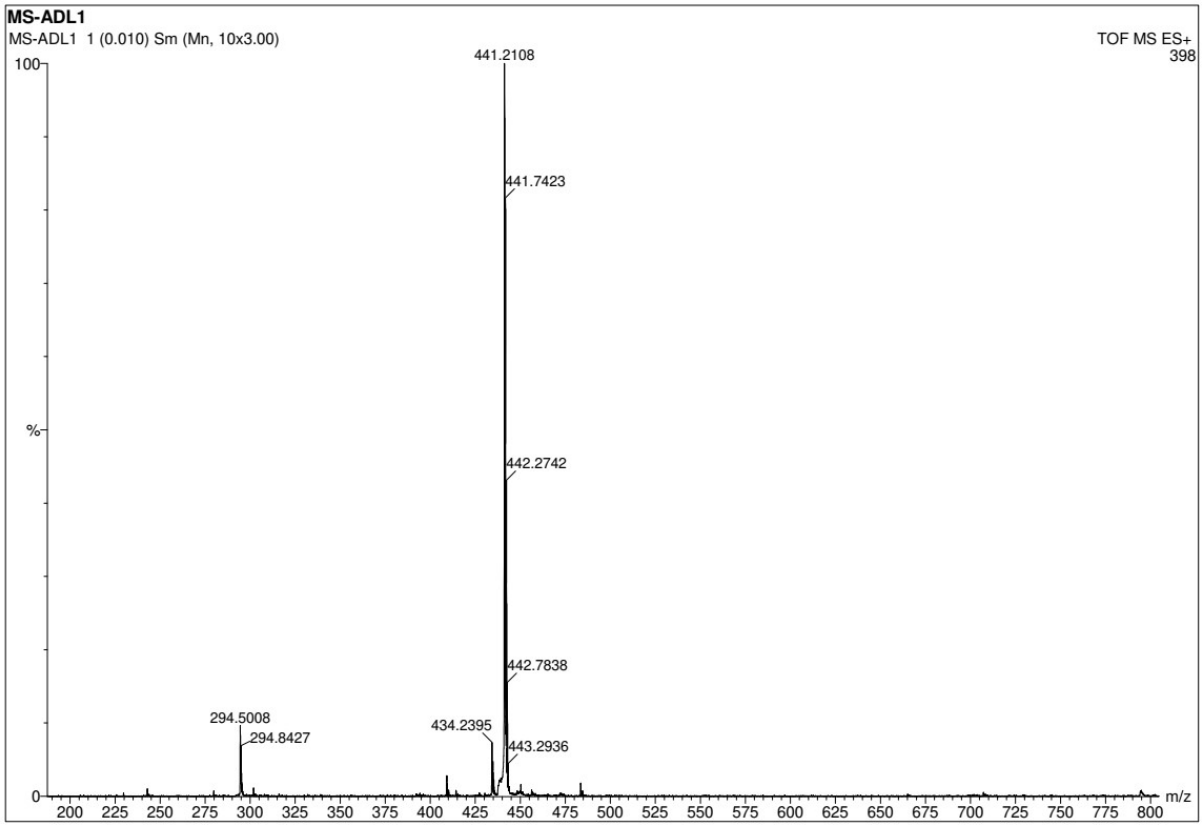

Fig. S7. Mass spectrum of **2** recorded in CH_3OH.

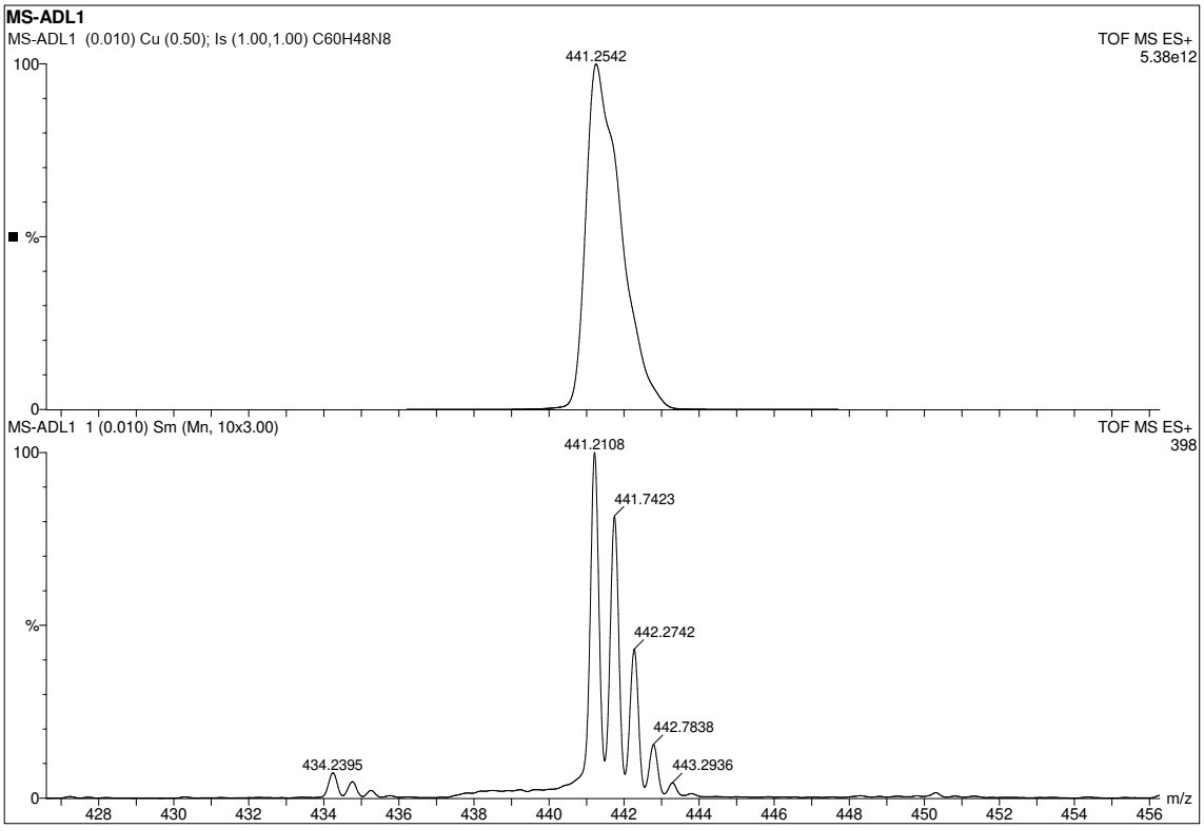

Fig. S8. Theoretical (top) experimental (bottom) isotopic distribution of **2** recorded in CH_3OH.

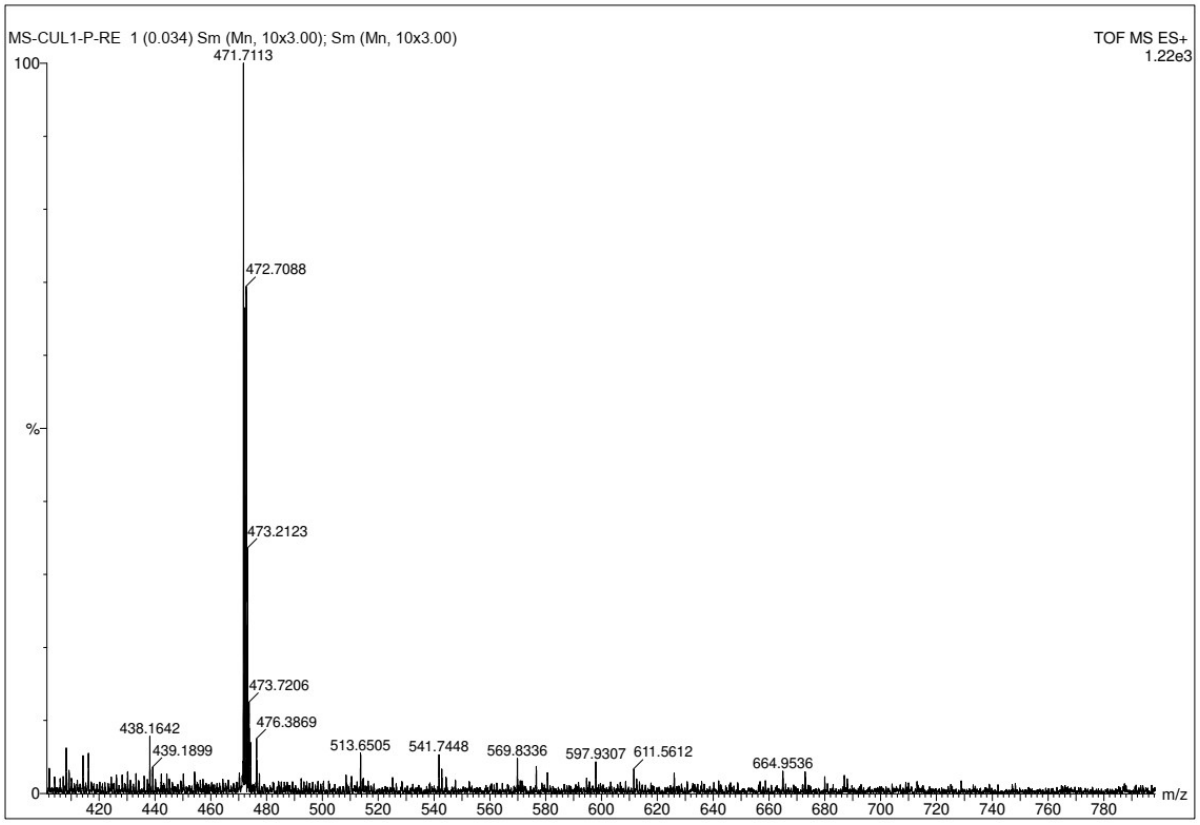

Fig. S9. Mass spectrum of **3** recorded in CH_3OH.

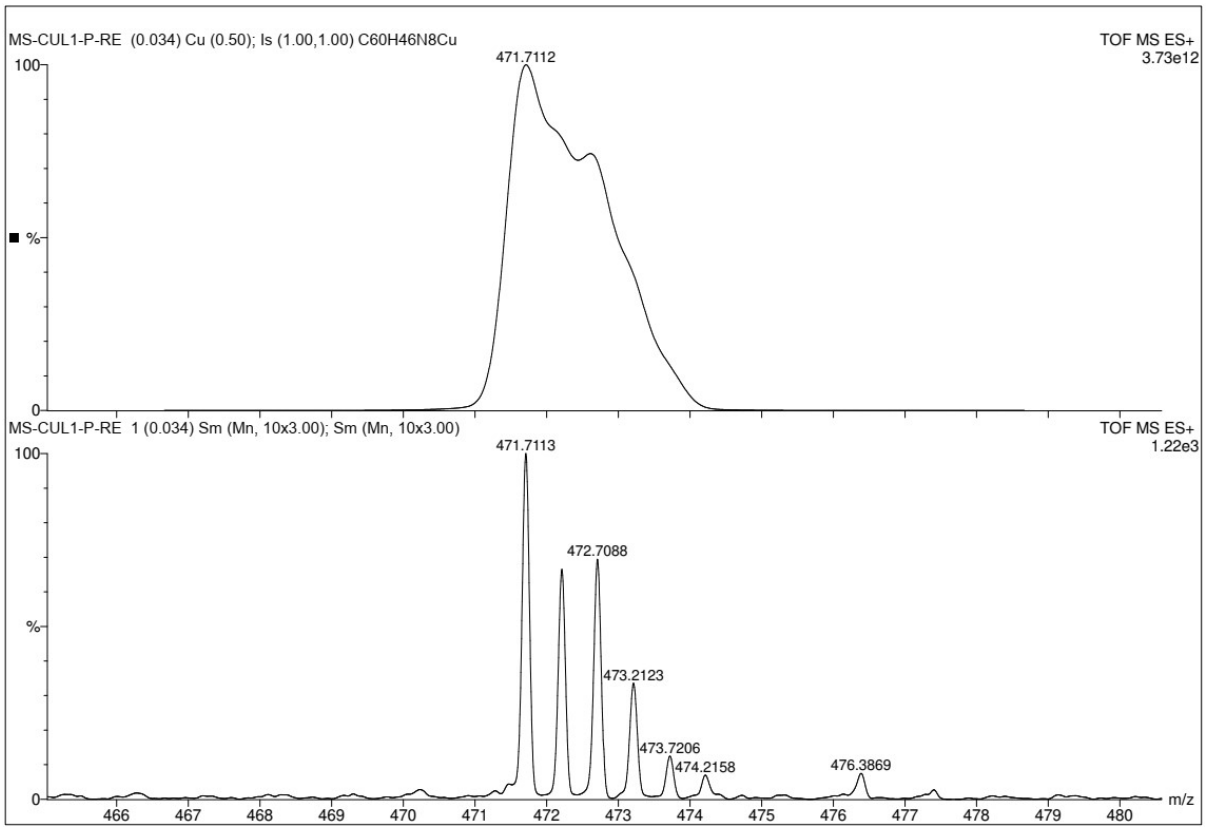

Fig. S10. Theoretical (top) experimental (bottom) isotopic distribution of **3** recorded in CH_3OH.

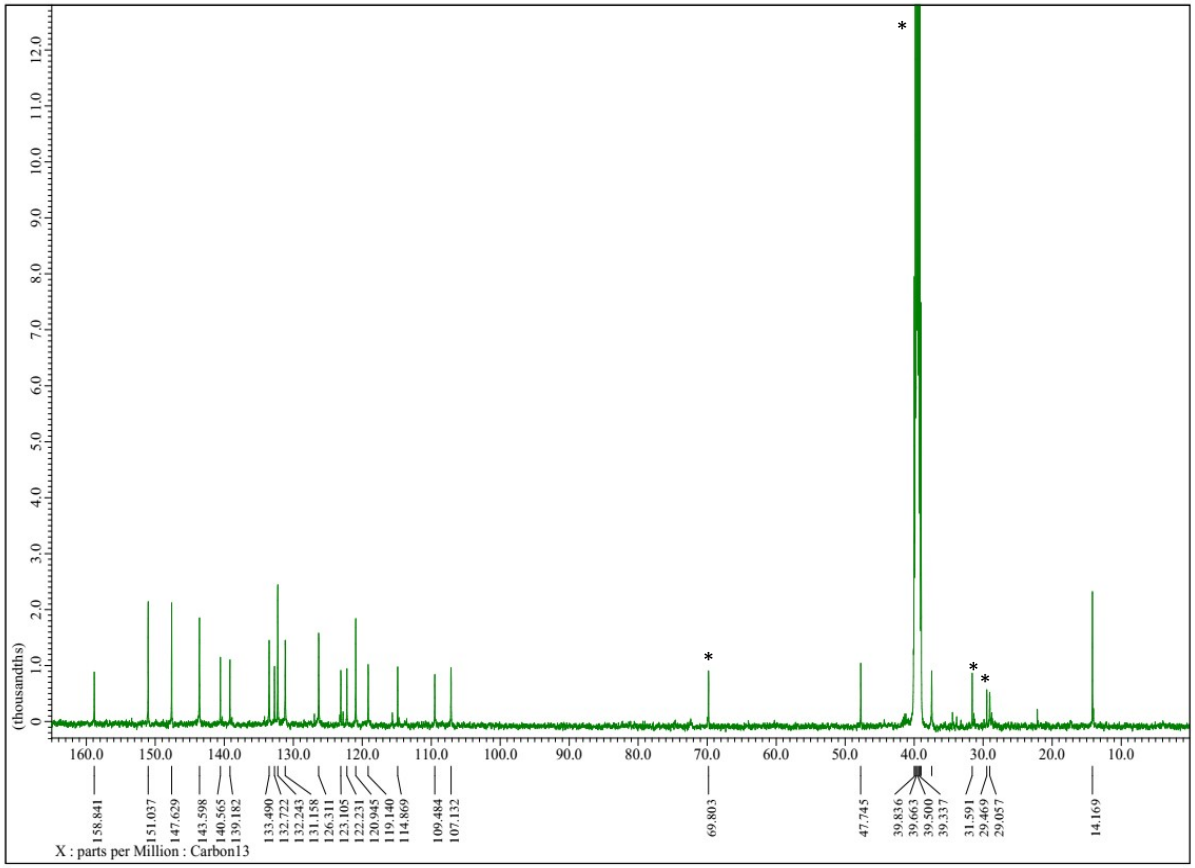

Fig. S11. ^{13}H NMR spectrum of **4** recorded in DMSO-d_6. Marked peak with an asterisk (*) at 39.1-39.8 ppm indicates residual DMSO, 29-31.5 ppm indicates hexane, and 69.8 ppm indicates chloroform.

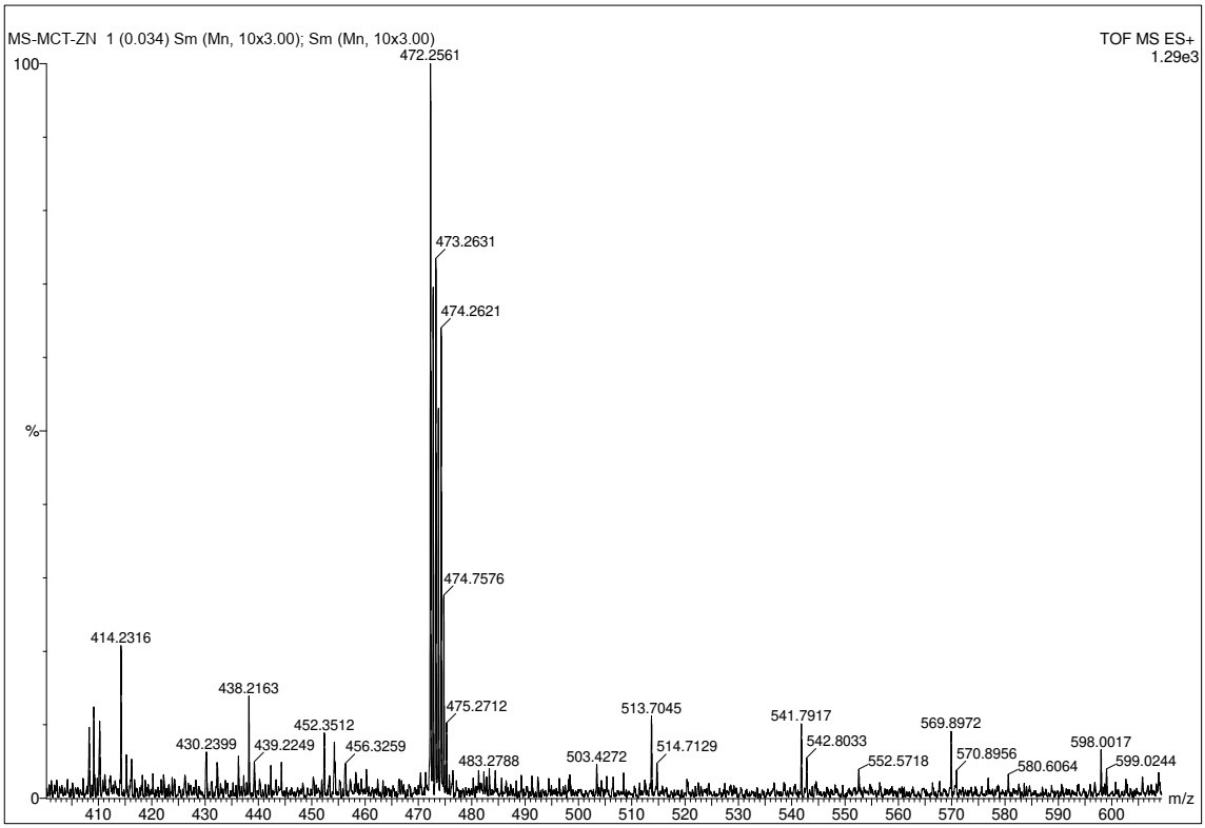

Fig. S12. Mass spectrum of **4** recorded in CH_3OH.

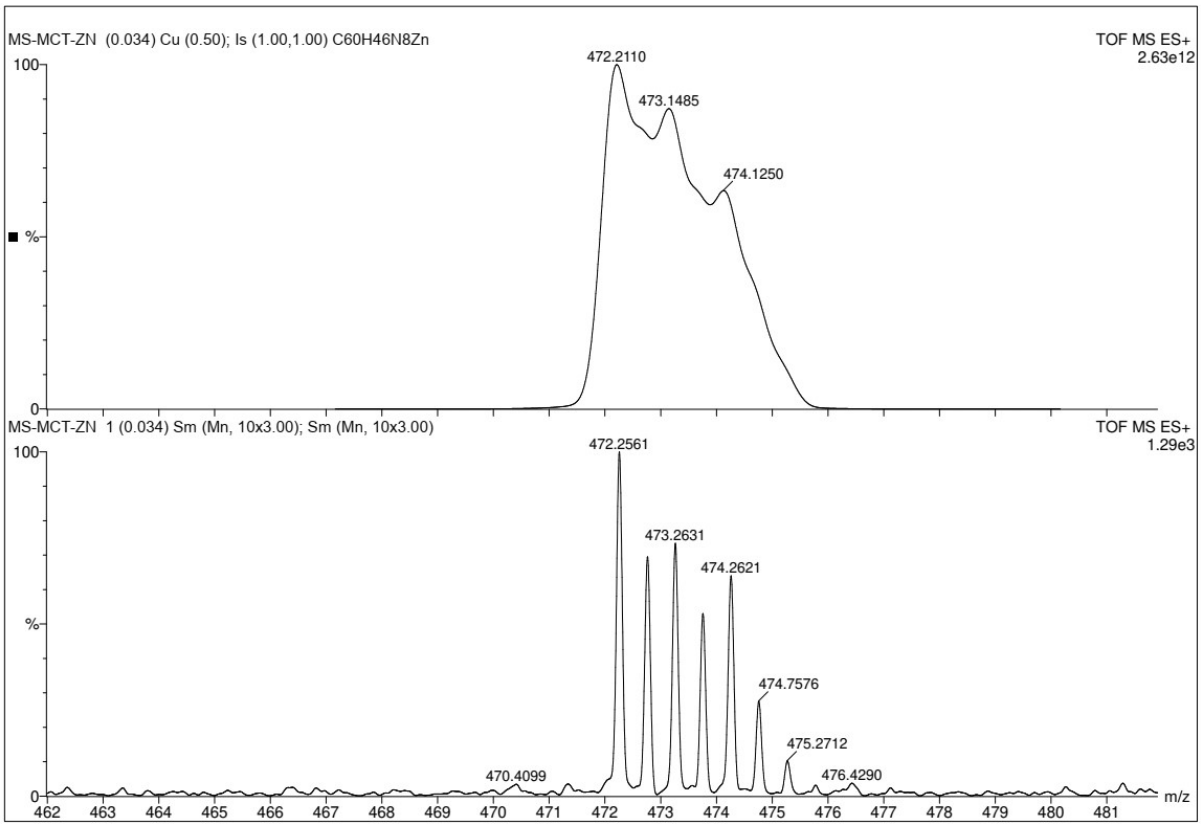

Fig. S13. Theoretical (top) experimental (bottom) isotopic distribution of **4** recorded in CH_3OH.

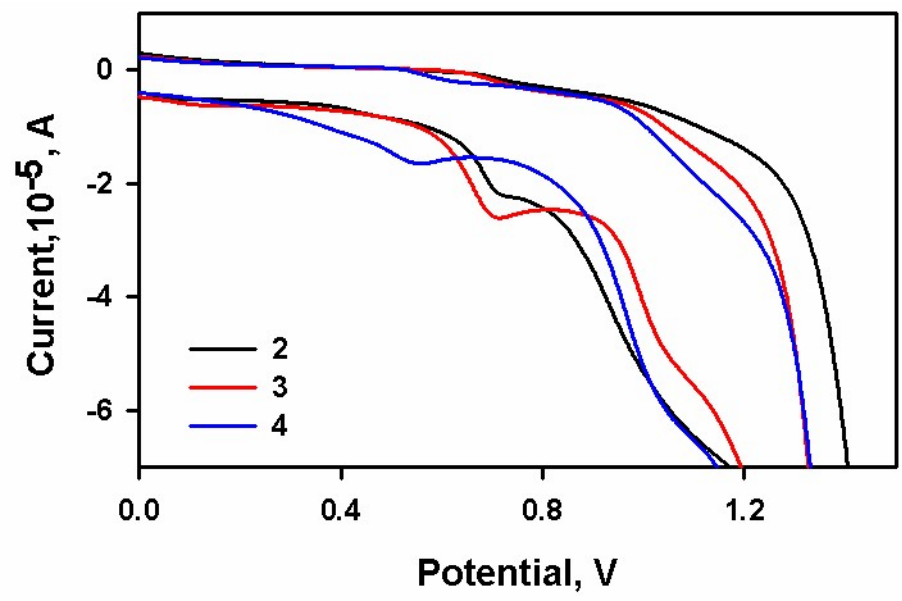

Fig. S14. Cyclic voltammograms (oxidation) of **2**, **3** and **4** in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte with a scan rate of 0.1 V/s.

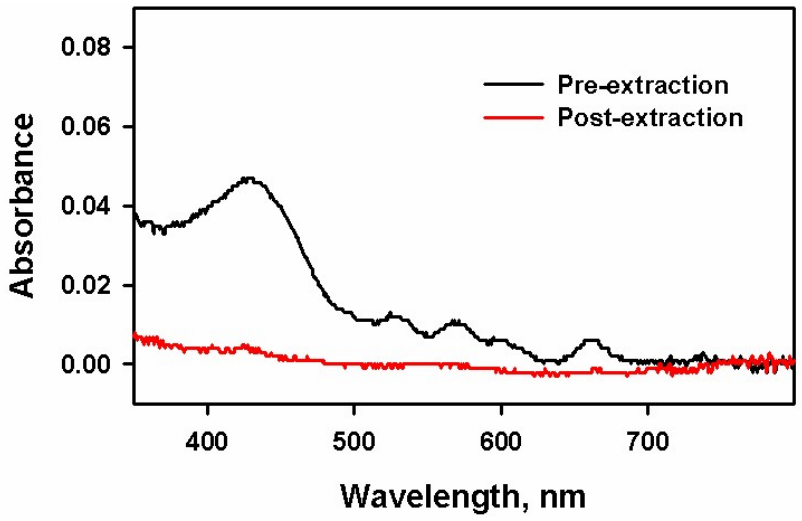

Fig. S15. UV-Visible spectra of compound **1** in aqueous phase before (black) and after (red) extraction with the water-saturated 1-octanol.

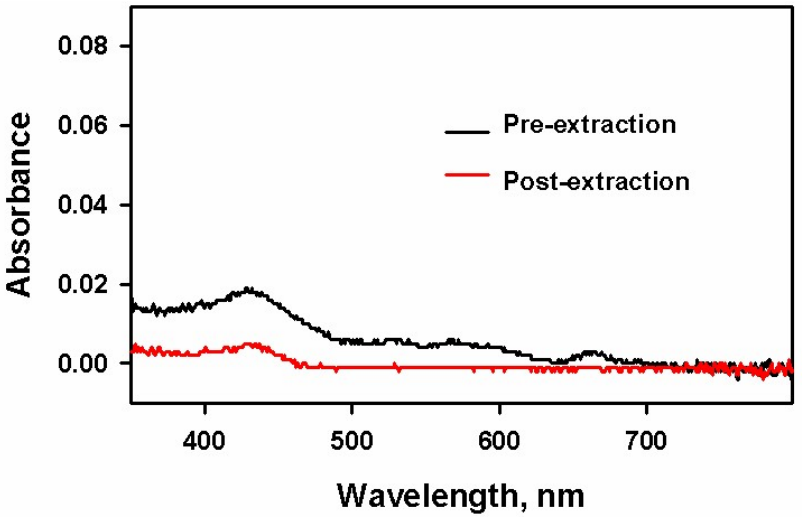

Fig. S16. UV-Visible spectra of compound **2** in aqueous phase before (black) and after (red) extraction with the water-saturated 1-octanol.

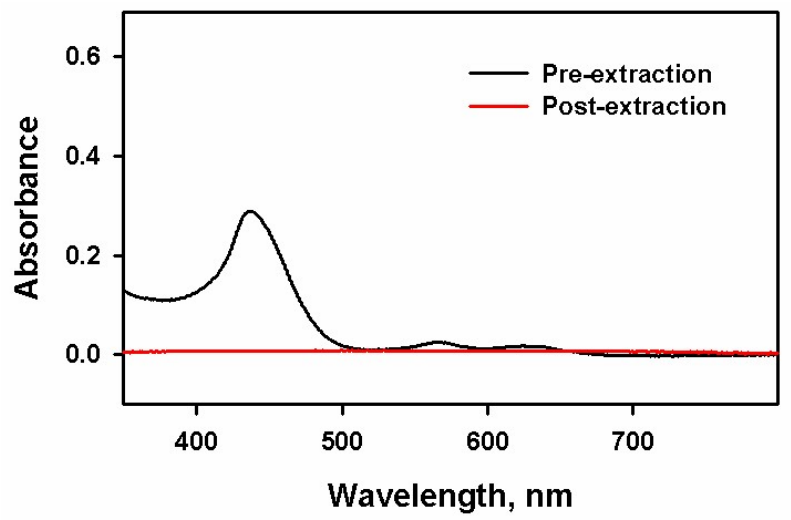

Fig. S17. UV-Visible spectra of compound **3** in aqueous phase before (black) and after (red) extraction with the water-saturated 1-octanol.

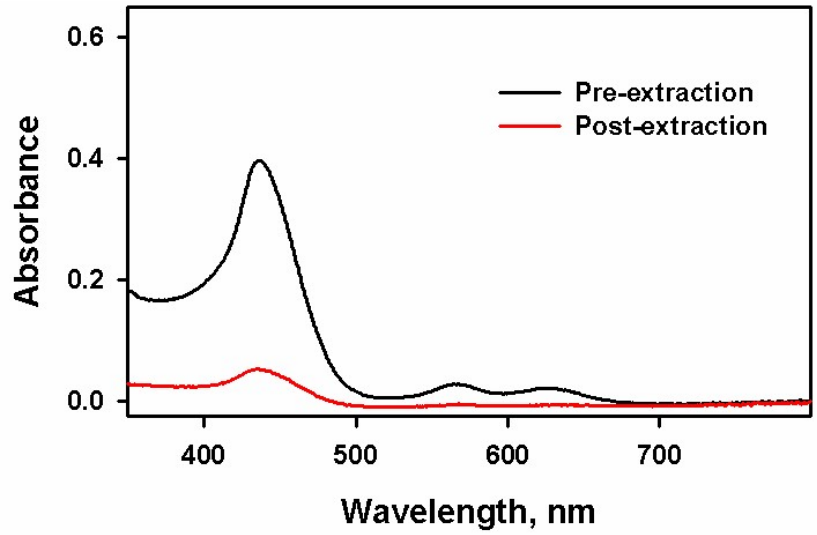

Fig. S18. UV-Visible spectra of compound **4** in aqueous phase before (black) and after (red) extraction with the water-saturated 1-octanol.

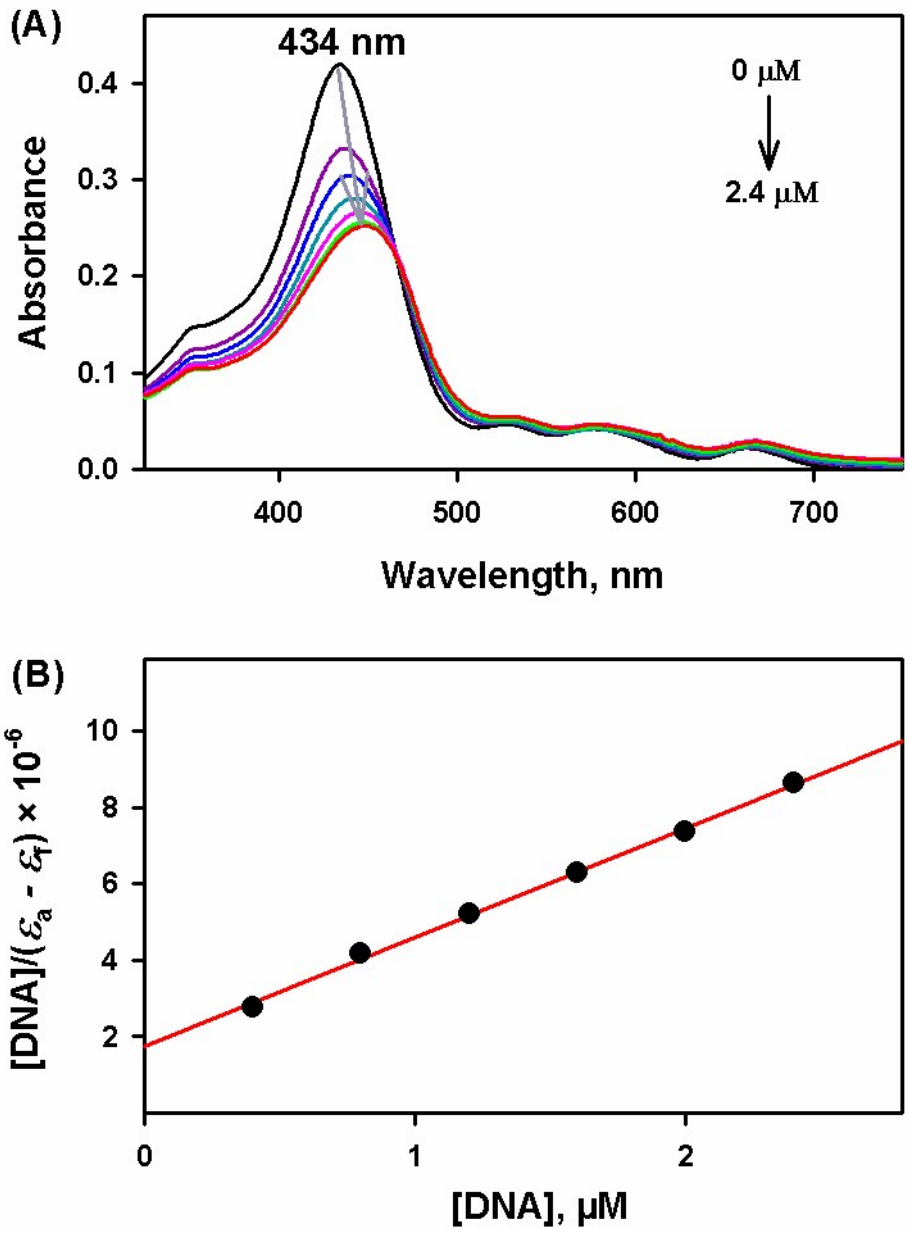

Fig. S19. **(A)** Absorption spectra of **2** in pH=7.2 buffer at 25 °C in the presence of the increasing amount of CT-DNA. [**2**] = 6 μM, [DNA] = Increment of 0.4 μM. The grey arrow indicates the change in absorption upon increasing the DNA concentration. **(B)** A plot of [DNA]/(Δε) *vs.*[DNA].

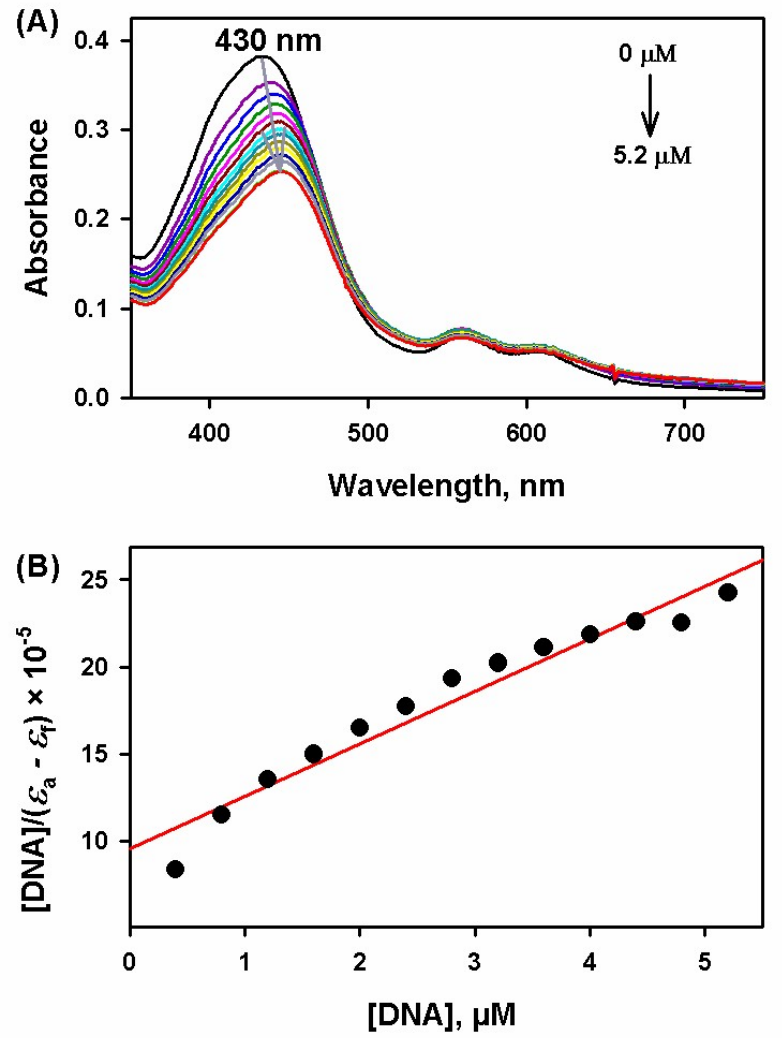

Fig. S20. **(A)** Absorption spectra of **3** in pH = 7.2 buffer at 25 °C in the presence of an increasing amount of CT-DNA. [**3**] = 6 μM, [DNA] = Increment of 0.4 μM. The grey arrow indicates the change in absorption upon increasing the DNA concentration. **(B)** A plot of [DNA]/(Δε) *vs.*[DNA].

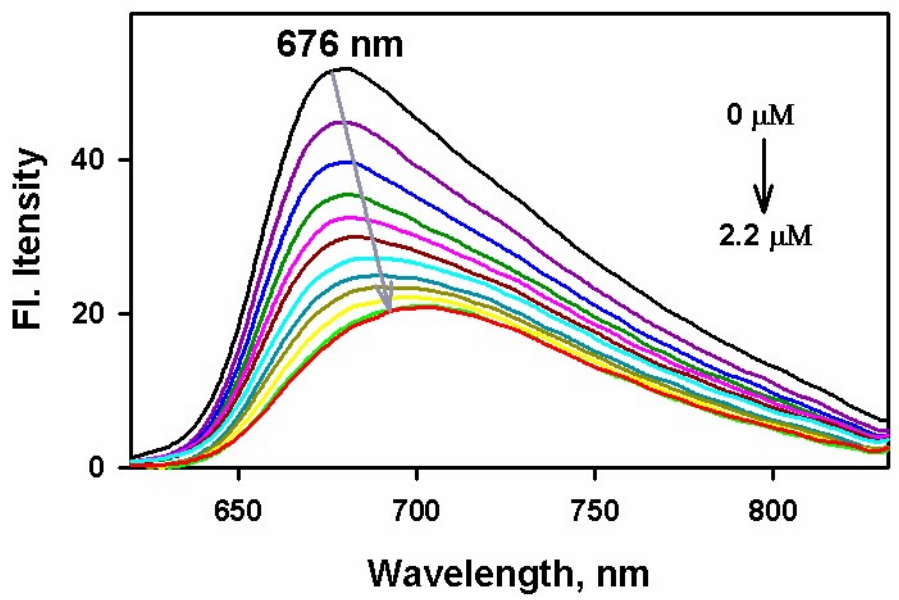

Fig. S21. Fluorescence emission spectra of **2** in pH = 7.2 buffer solution, with increasing concentration of CT-DNA. [**2**] = 6 μM, [DNA] = increment of 0.2 μM. The grey arrow indicates the change in emission intensity upon increasing the complex concentration.

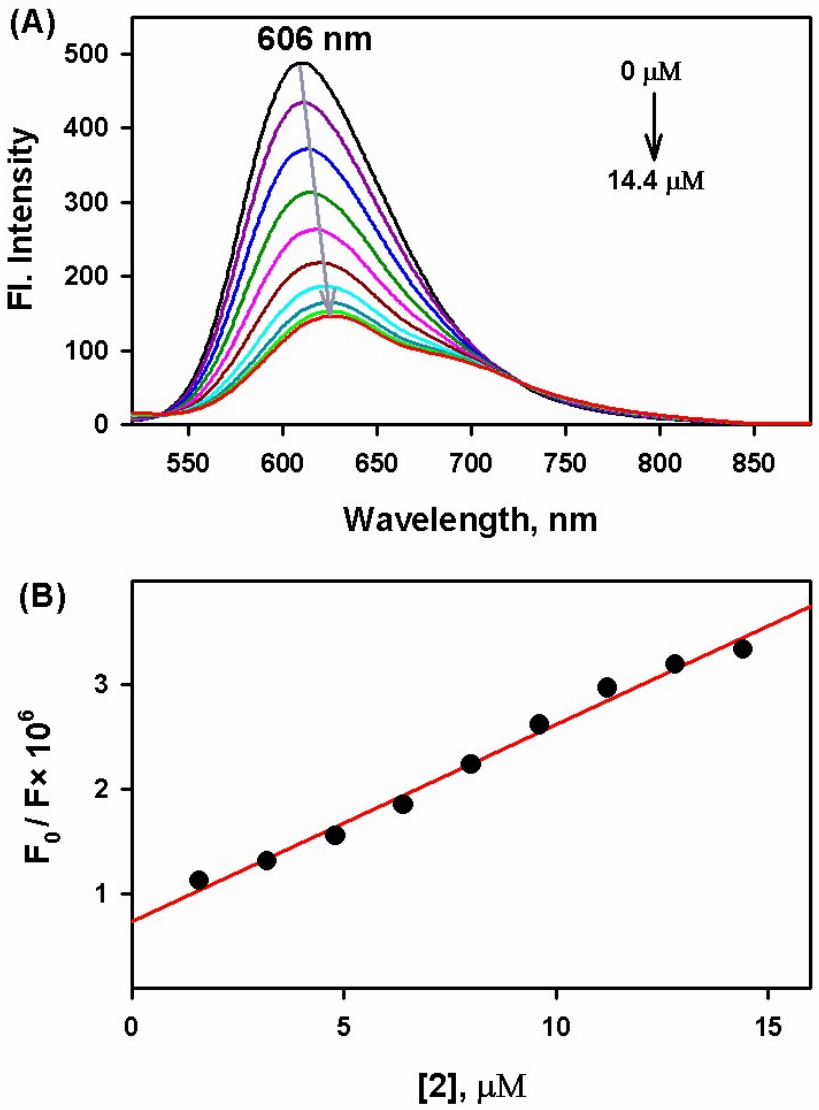

Fig. S22. (A) Emission spectra of EB bound to DNA in the presence of porphyrins, **(A) 2** with increasing concentration of CT DNA. [DNA] = 12 μM, [EB] = 5 μM, [**2**] = 1.6 μM increment. The grey arrow indicates the change in emission intensity upon increasing the concentration of [**2**]. **(B)** Fluorescence quenching curve of EB bound DNA by the porphyrins.

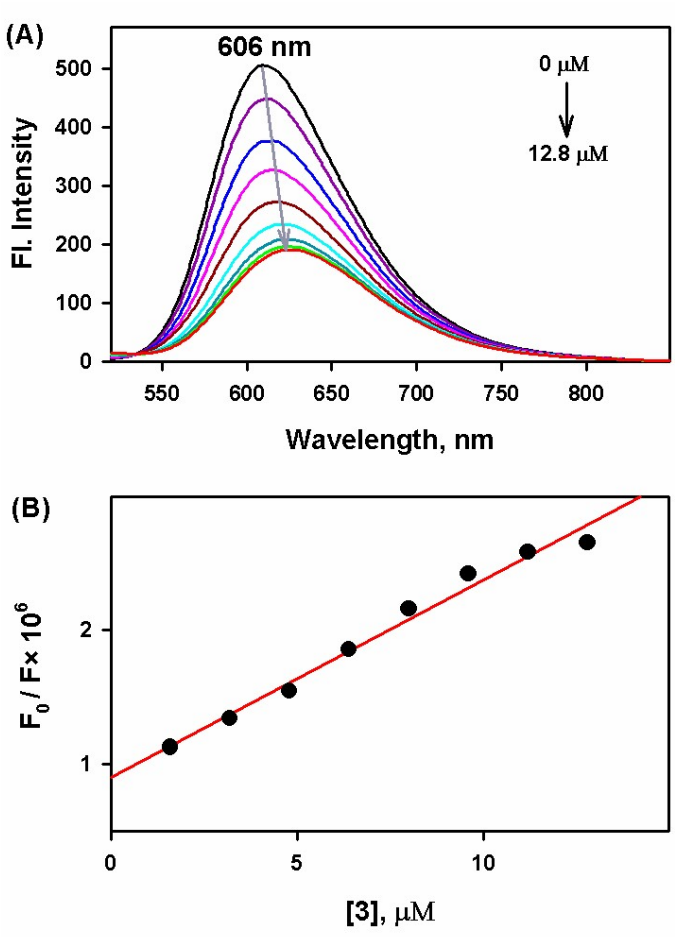

Fig. S23. Emission spectra of EB bound to DNA in the presence of porphyrins, **(A) 3** with increasing concentration of CT DNA. [DNA] = 12 μM, [EB] = 5 μM, [**3**] = 1.6 μM increment. The grey arrow indicates the change in emission intensity upon increasing the concentration of [**3**] **(B)** Fluorescence quenching curve of EB bound DNA by the porphyrins.

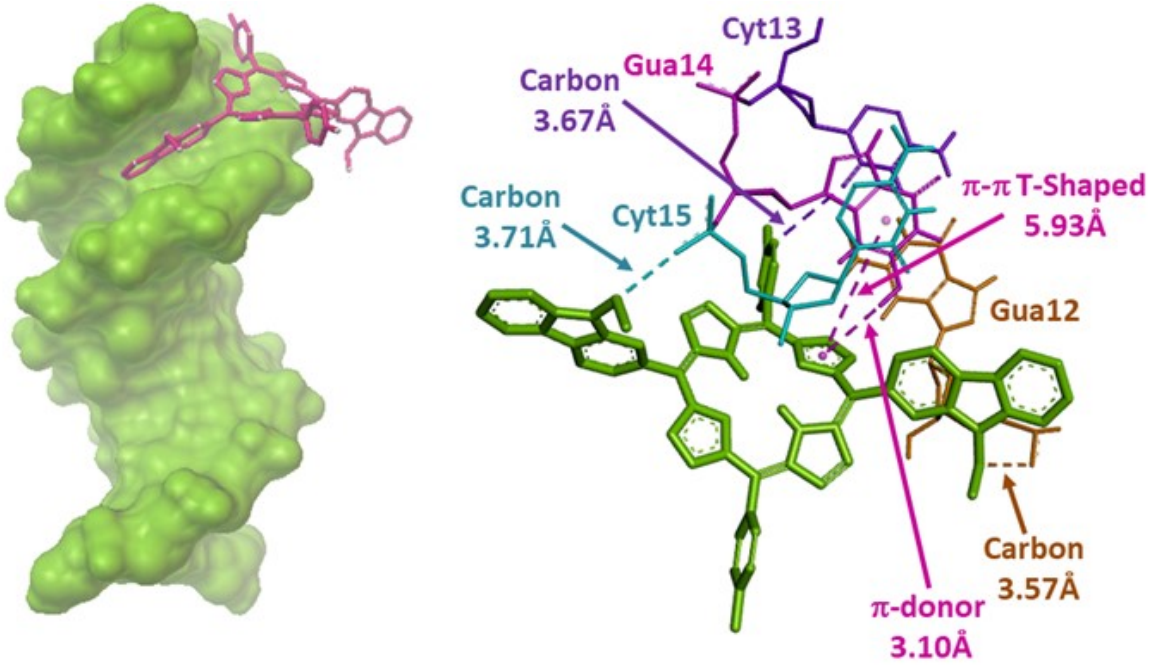

Fig. S24. Molecular docked structure and interactions of **2** with DNA.

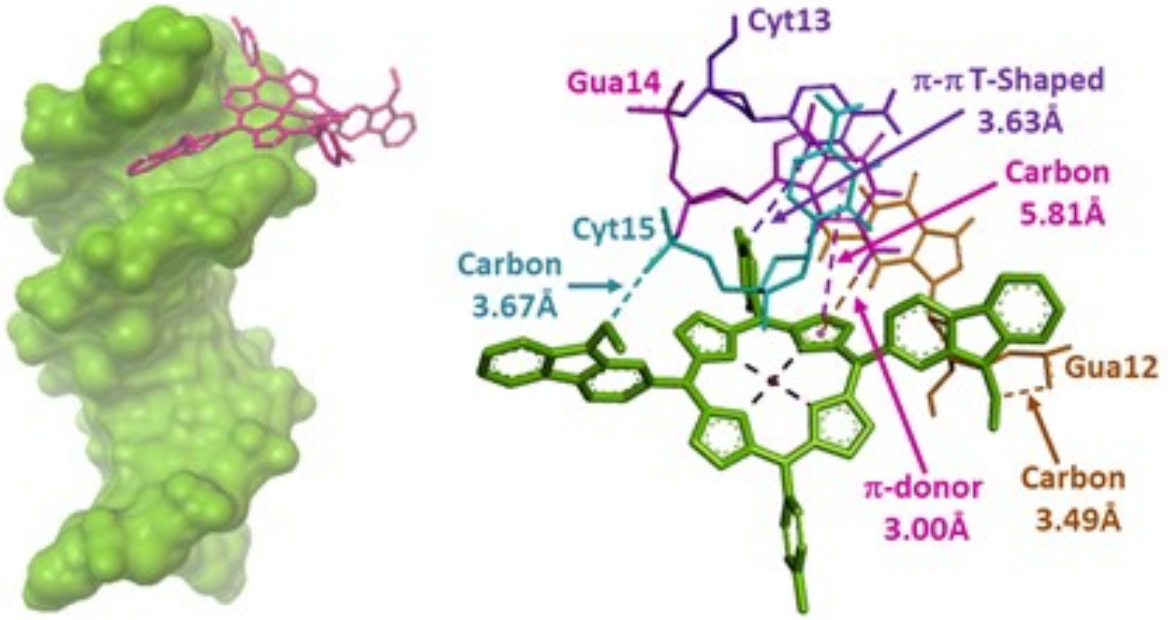

Fig. S25. Molecular docked structure and interactions of **3** with DNA.

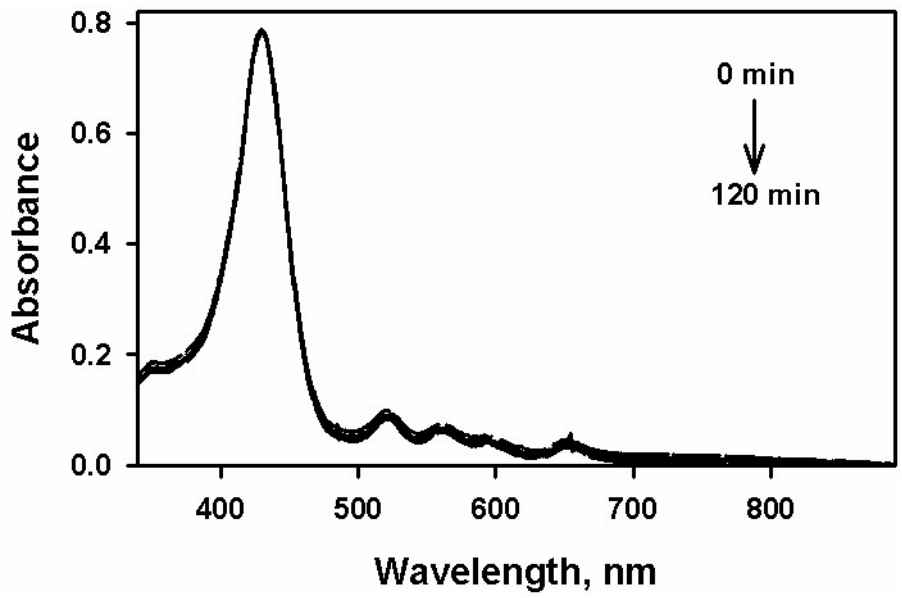

Fig. S26. The time-dependent absorption spectrum of compound **2** under the light source of λ = 450−750 nm, 15 J cm^{-2}.

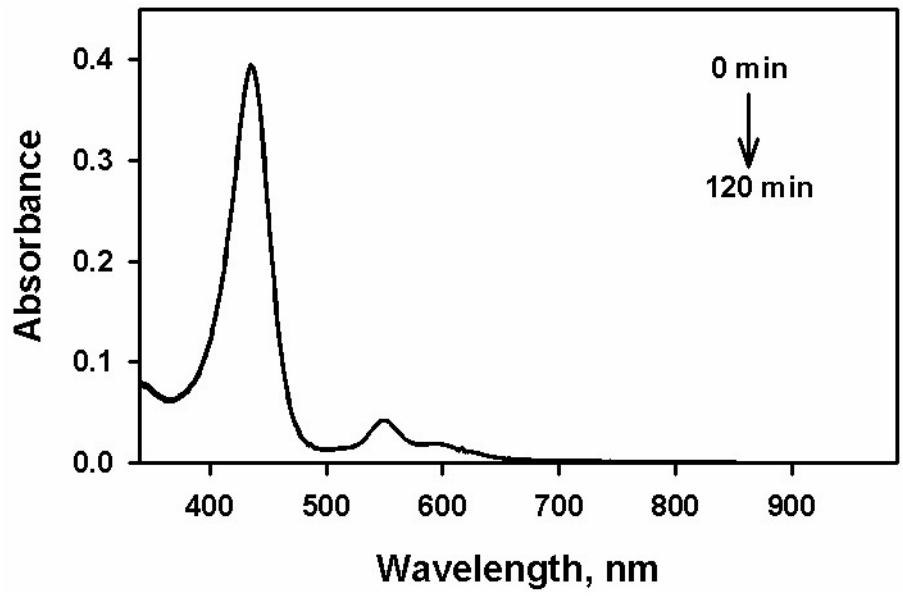

Fig. S27. The time-dependent absorption spectrum of compound **3** under the light source of λ = 450−750 nm, 15 J cm^{-2}.

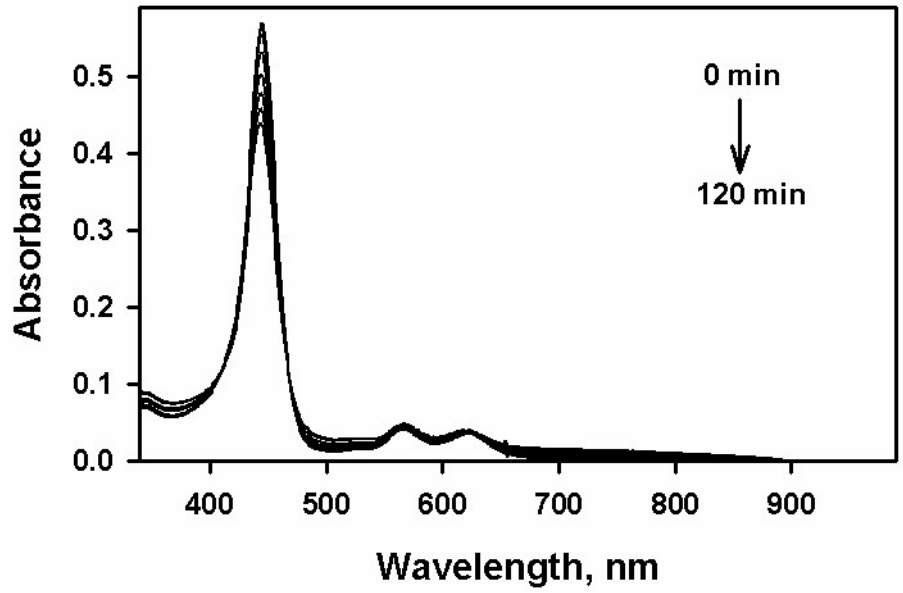

Fig. S28. The time-dependent absorption spectrum of compound **4** under the light source of λ = 450−750 nm, 15 J cm^{-2}.

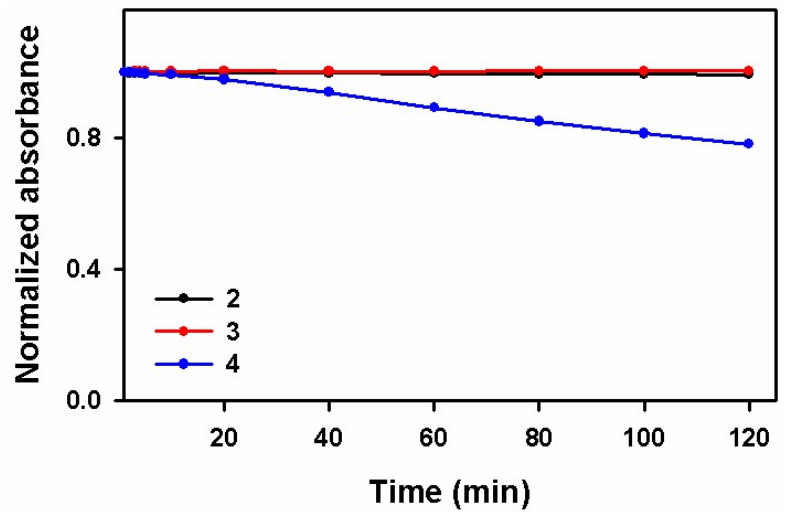

Fig. S29. Change in absorbance of compound **2-4** with an increase in time of irradiation under the light source of λ = 450−750 nm, 15 J cm^{-2}.

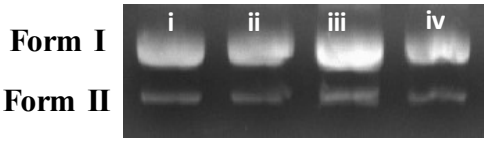

Fig. S30. Effect of NaN_3 on the cleavage in presence of compounds **2-4**. Lane (i): DNA alone; Lane (ii): DNA+10 μM **2**+ 50 μM NaN_3; Lane (iii): DNA+10 μM **3** + 50 μM NaN_3; Lane (iv): DNA+10 μM **4** + 50 μM NaN_3.

Table S1 Electrochemical data of **2-4** in DMF using 0.1 M TBAHFP at 25˚C.

Compound	$E_{1/2}$(oxd)/V		$E_{1/2}$(red)/V		Energy Level (eV)		Δ*E* (eV) (From CV)
					HOMO[a]	LUMO[a]	
H_2TPP[1]	1.08	-	-1.11	-1.53	-5.48	-3.29	2.19
CuTPP[1]	1.01	1.26	-1.19	-1.71	-5.41	-3.21	2.20
ZnTPP[1]	0.79	1.38	-1.34	-1.73	-5.19	-3.06	2.13
2	0.69	1.04	-1.00	-1.71	-5.09	-3.40	1.69
3	0.68	1.01	-1.09	-1.80	-5.08	-3.31	1.77
4	0.54	0.99	-1.14	-1.66	-4.94	-3.26	1.68

[a]E_{HOMO} = -(E_{oxd} + 4.4) eV; E_{LUMO} = -(E_{red} + 4.4) eV, [a]*Chem. Commun*, 48 (2012), 8377

[1] J. Ramesh, S. Sujatha and C. Arunkumar, *RSCAdv.*, 2016, **6**, 63271-63285.