

Rationalization of Excited State Energy Transfer in D- π -A Porphyrin Sensitizers Enhancing Efficiency in Dye-Sensitized Solar Cells

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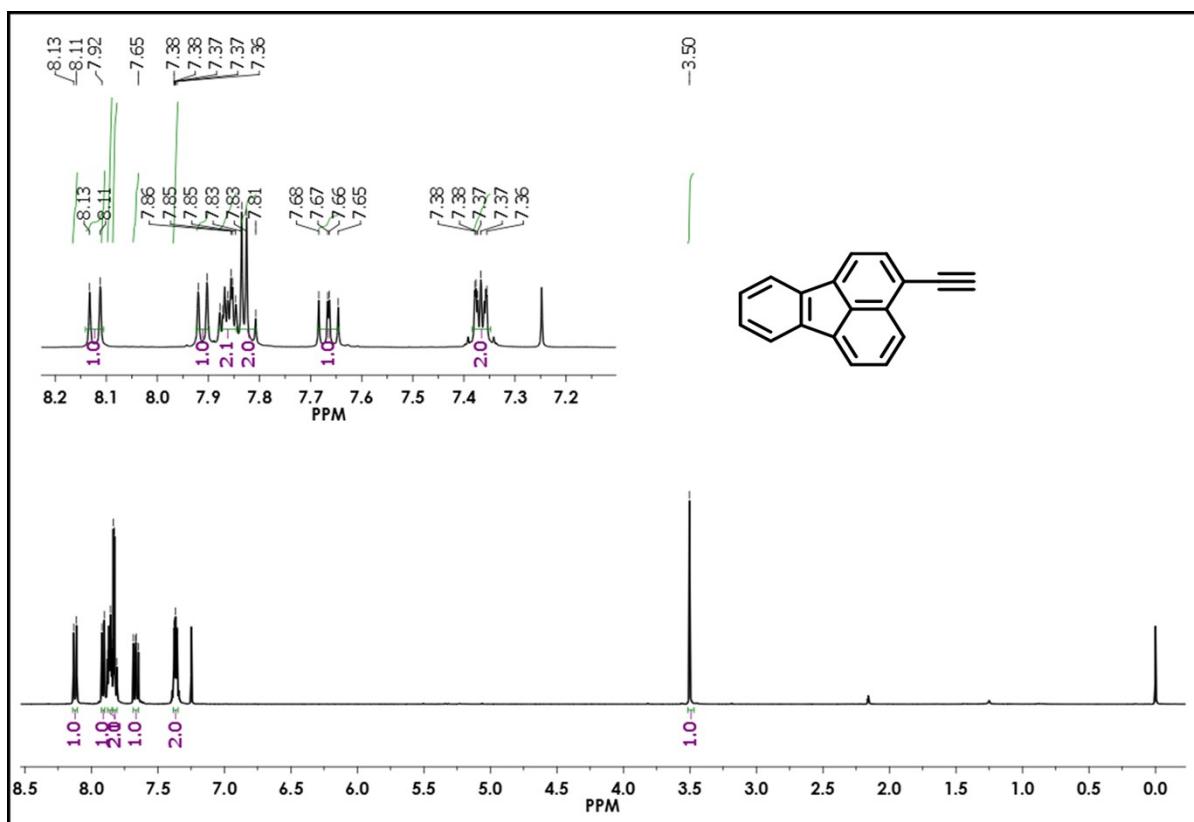


Figure S1. ^1H NMR spectrum (500 MHz, CDCl_3) of **1**.

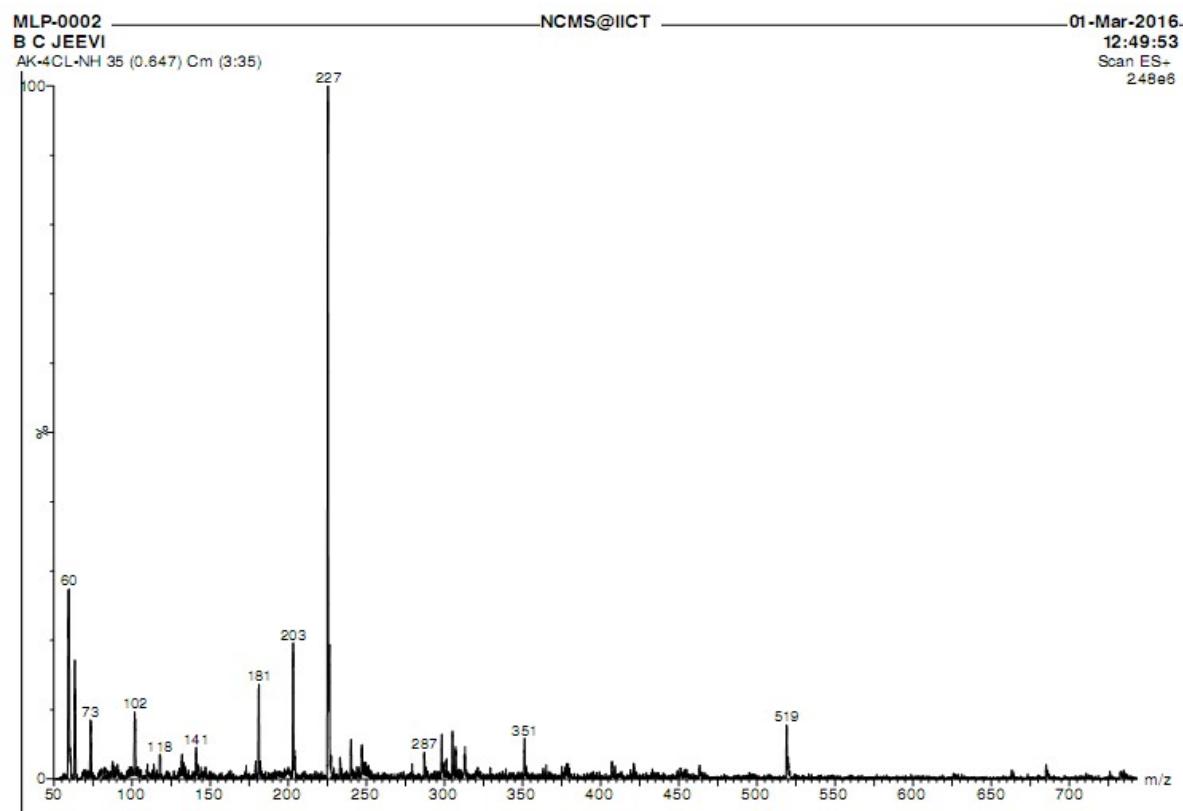
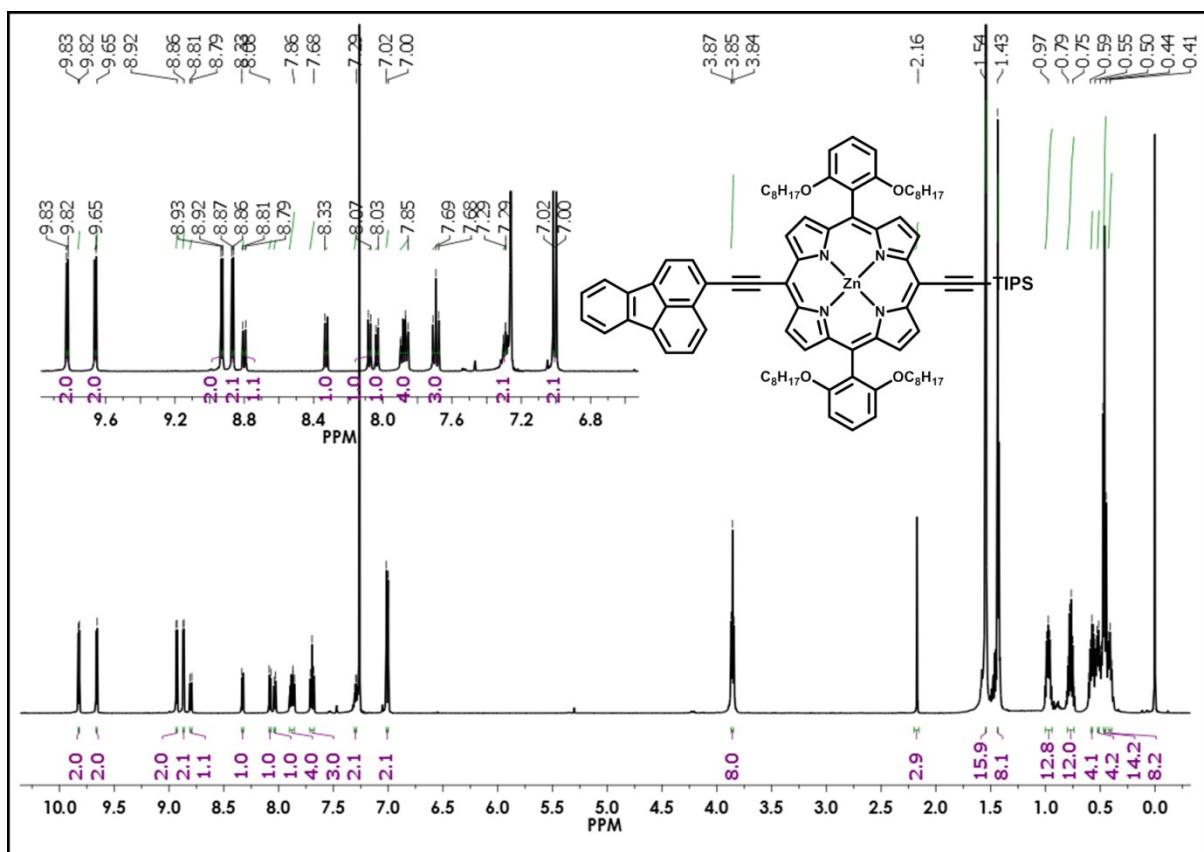


Figure S2. HRMS of **1** (APPI-FTMS).



Data: SK0043.4B4[c] 1 Feb 2016 14:56 Cal: NPR28DEC 28 Dec 2012 14:44
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 64, Blanked, P.Ext. @ 2000 (bin 66)
 %Int. 141 mV[sum= 2403 mV] Profiles 1-17 Smooth Gauss 5

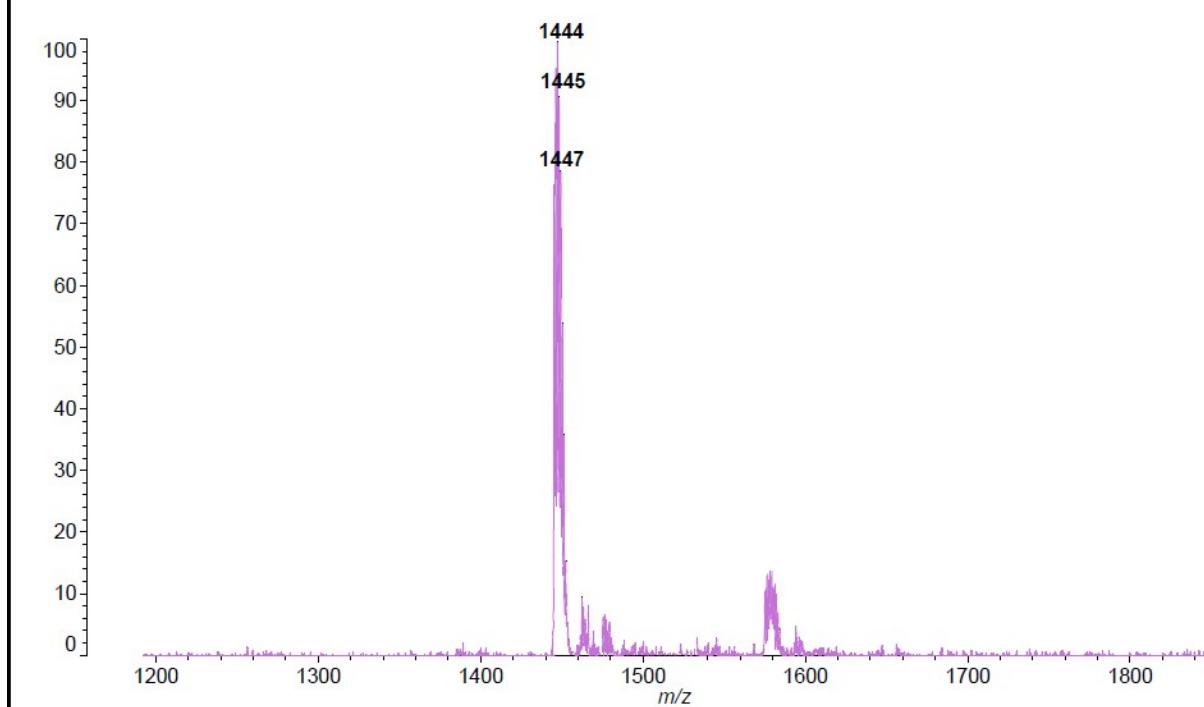


Figure S4. MALDI-TOF of 3.

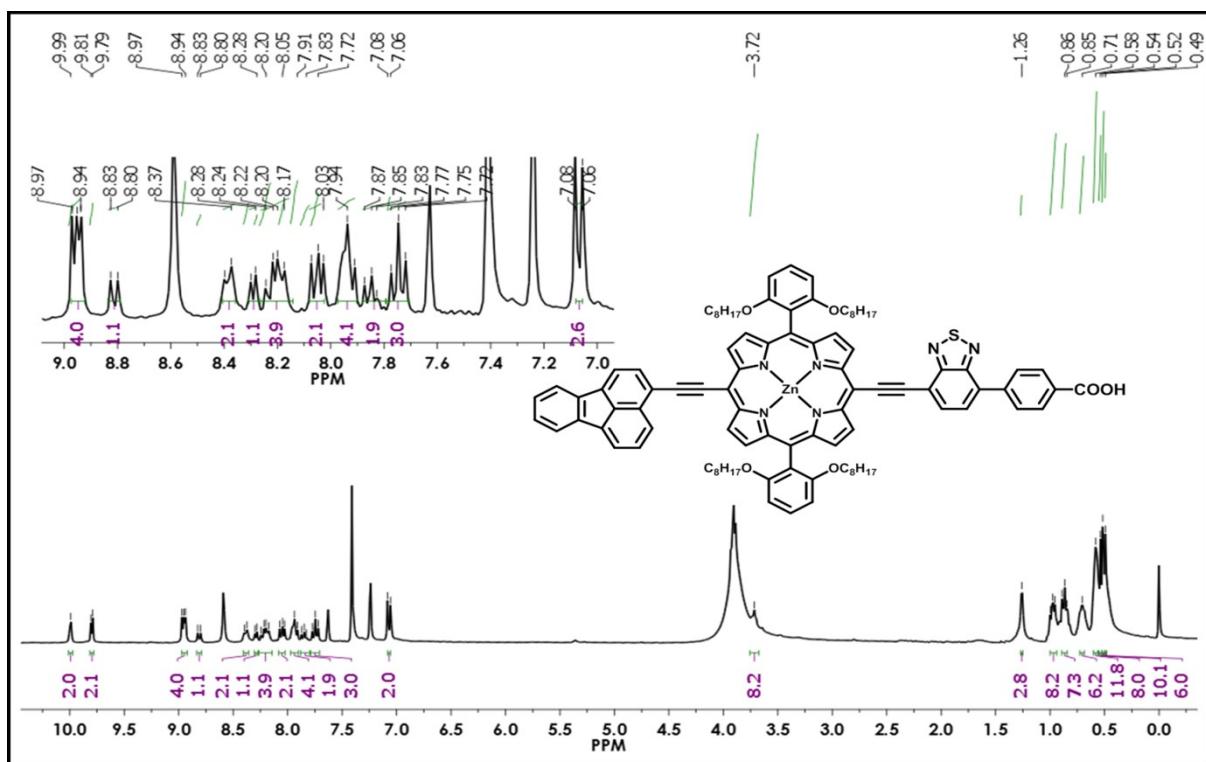


Figure S5. ^1H NMR spectrum (500 MHz, CDCl_3) of **LG8**.

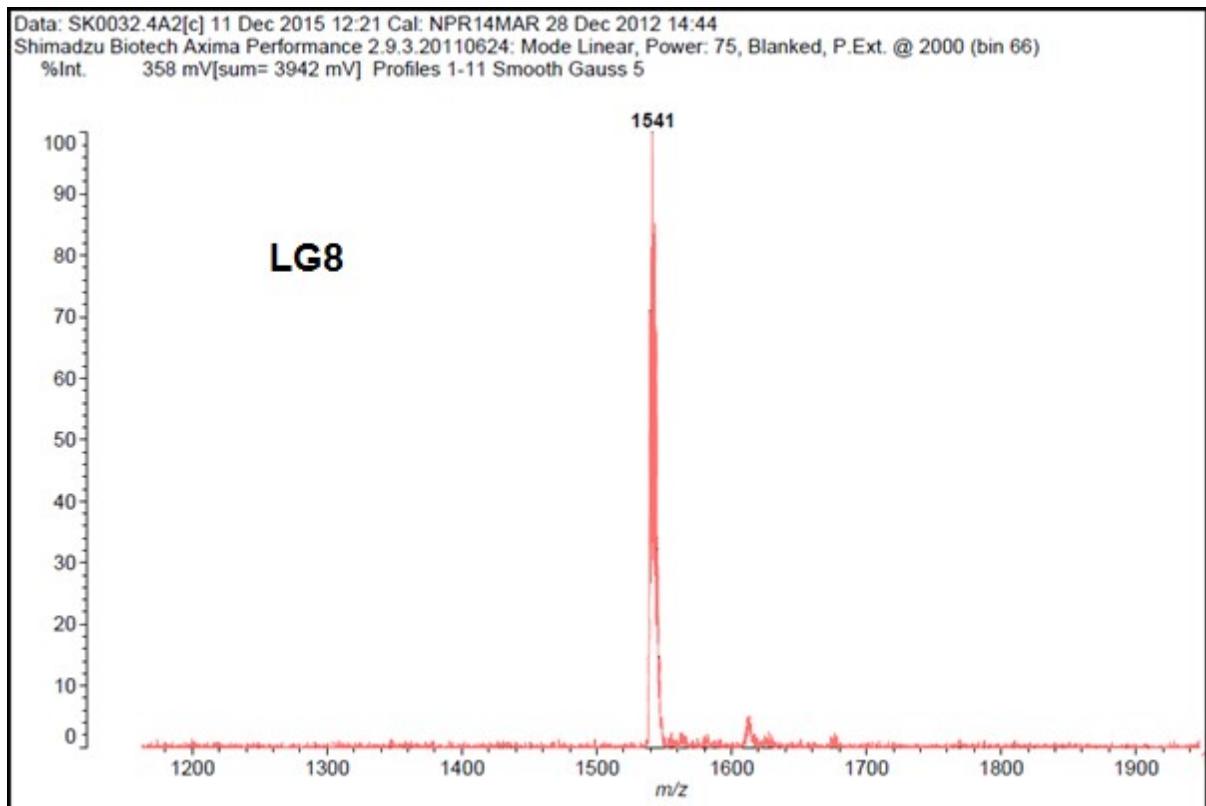


Figure S6. MALDI-TOF of **LG8**.

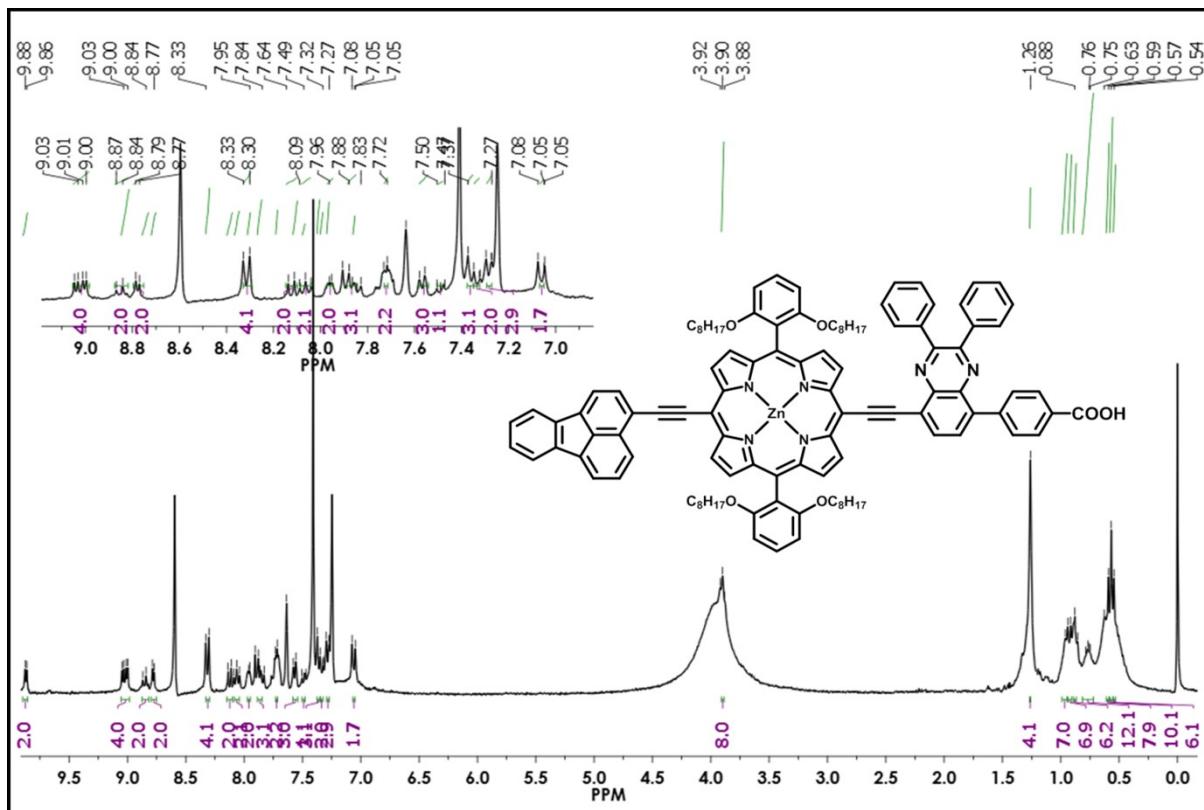


Figure S7. 1H NMR spectrum (500 MHz, $CDCl_3$) of LG9.

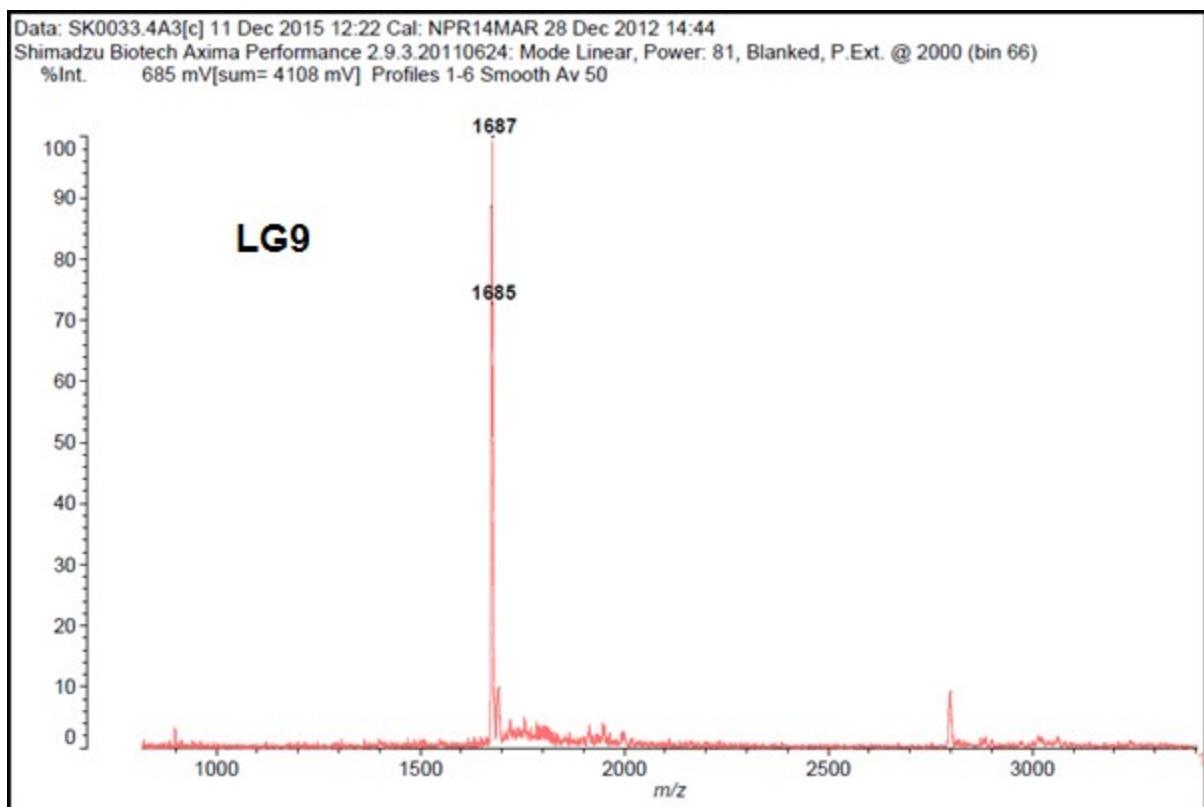


Figure S8. *MALDI-TOF of LG9.*

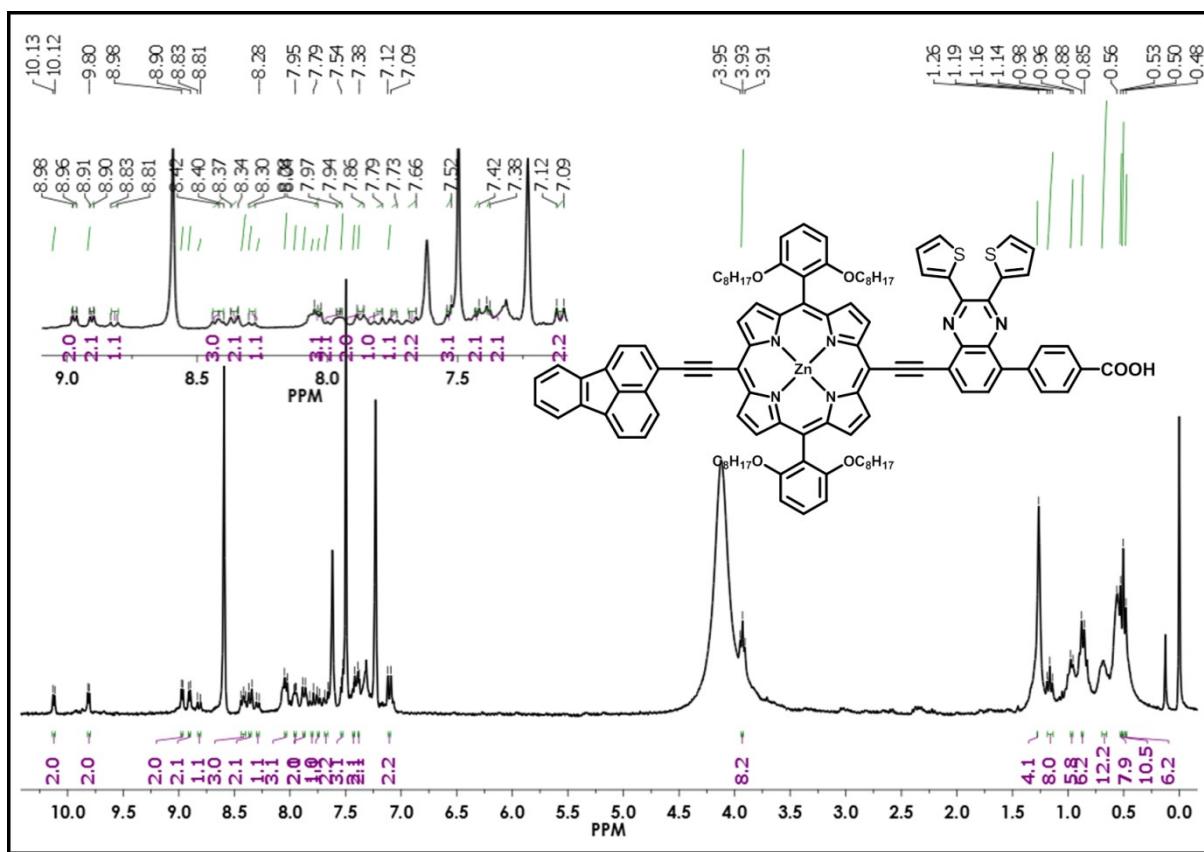


Figure S9. ^1H NMR spectrum (500 MHz, CDCl_3) of **LG10**.

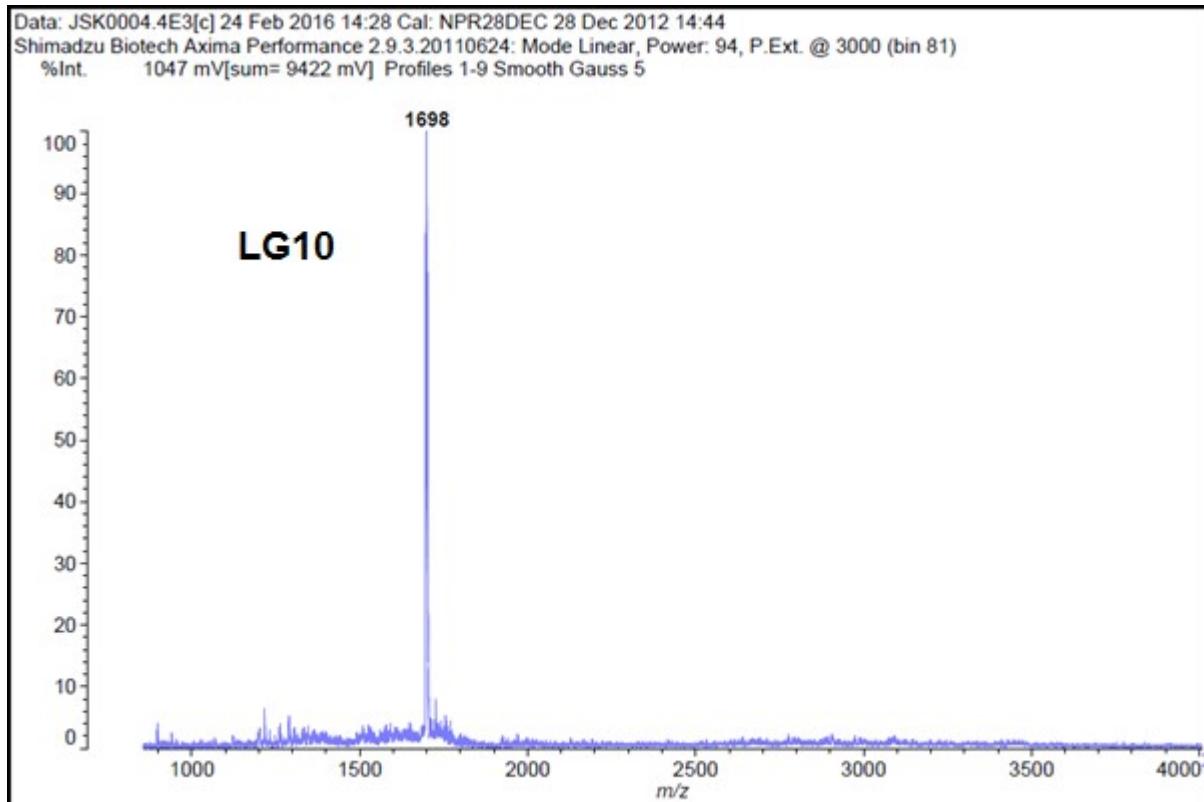


Figure S10. MALDI-TOF of **LG10**.

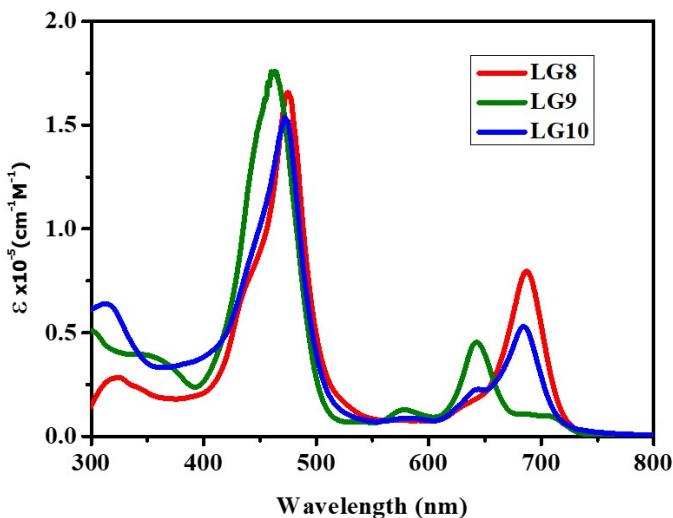


Figure S11. UV-visible absorption spectra of **LG8-LG10** in THF solvent.

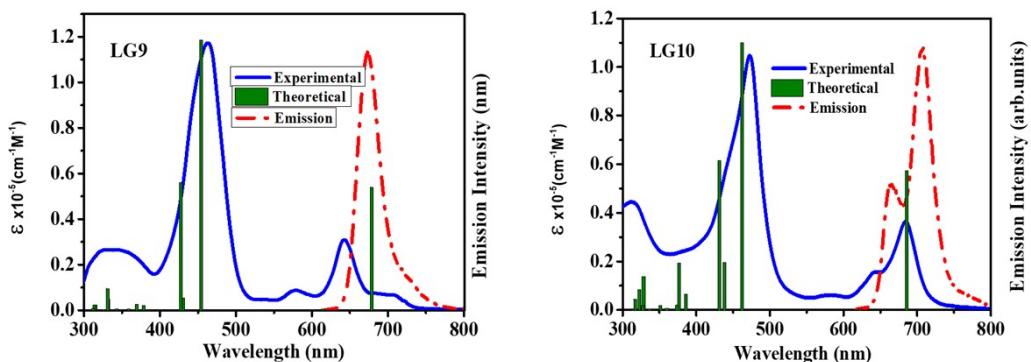


Figure S12. Theoretical absorption spectra of **LG9**, **LG10** Dyes by using B3LYP method PCM model in tetrahydrofuran solvent with M06-2X function.

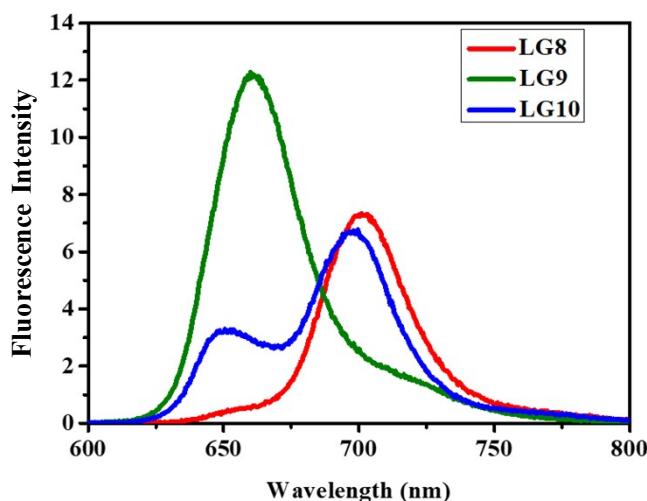


Figure S13. Fluorescence spectra of **LG8**, **LG9** and **LG10** in THF solution

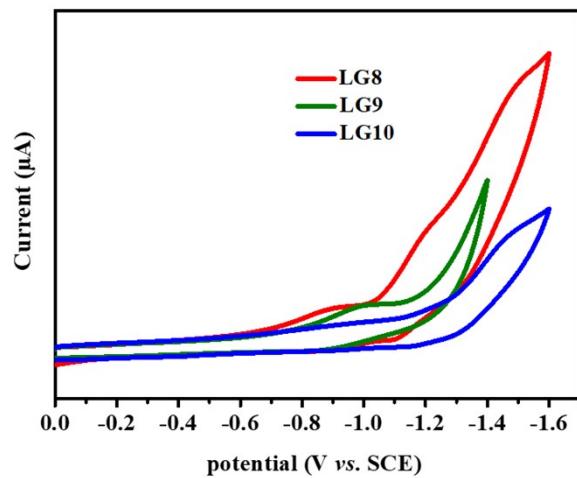


Figure S14. Reduction spectra of dyes **LG8**, **LG9** and **LG10** in THF.

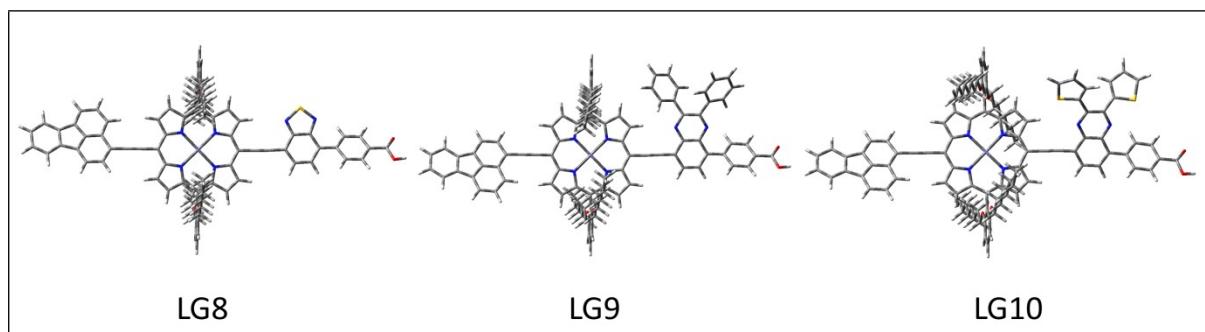


Figure. S15. Optimized structure of **LG8**, **LG9** and **LG10** dyes.

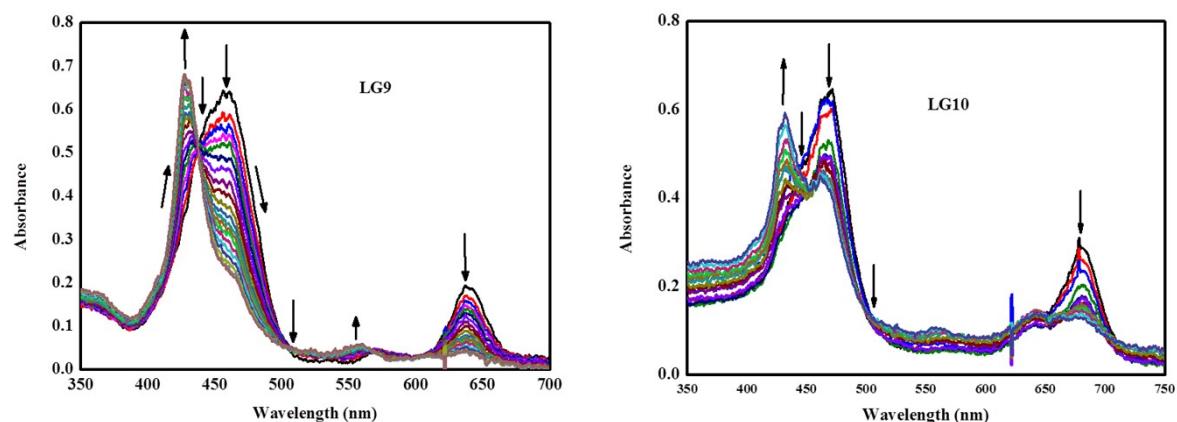


Figure S16. Oxidative OTTLE studies of **LG 9** and **LG10** sensitizers in 0.3M TBAP/THF with an applied potential of +0.90V (vs. SCE/KCl).

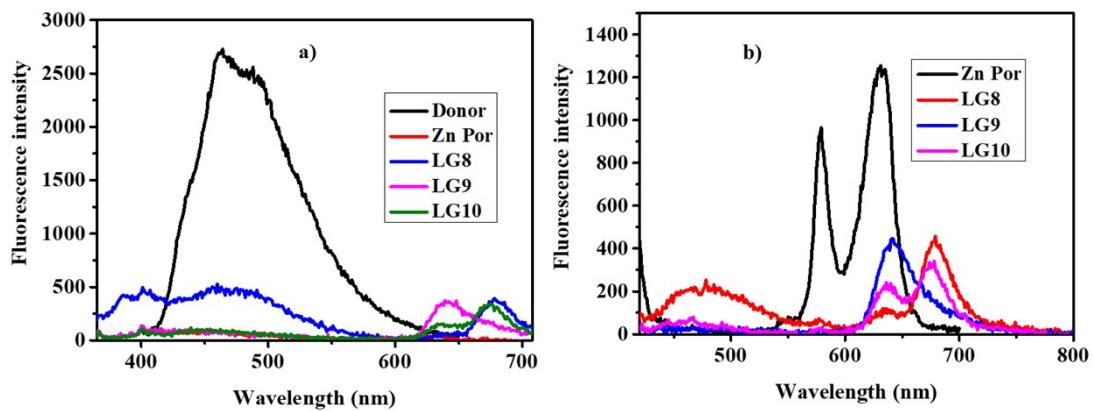


Figure S17. a) Emission spectra of equi-absorbing solutions of **Donor**, **Zn Por**, **LG8- LG10** ($OD_{lex} = 0.08$) in CH_2Cl_2 solvent at 357 nm. b) Emission spectra of equi-absorbing solutions of **Zn Por**, **LG8- LG10** ($OD_{lex} = 0.08$) in CH_2Cl_2 solvent at 410 nm.

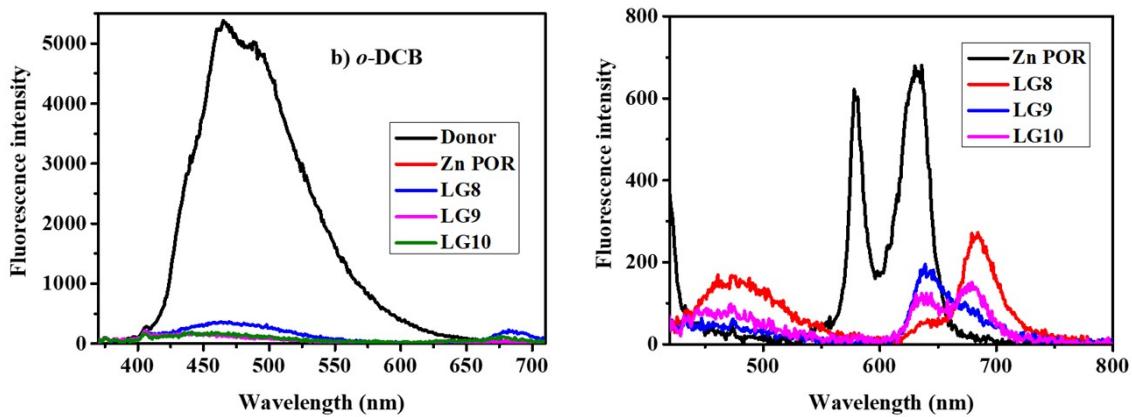


Figure S18. a) Emission spectra of equi-absorbing solutions of **Donor**, **Zn Por**, **LG8- LG10** ($OD_{lex} = 0.08$) in *o*-DCB solvent at 357 nm. b) Emission spectra of equi-absorbing solutions of **Zn Por**, **LG8- LG10** ($OD_{lex} = 0.08$) in *o*-DCB solvent at 410 nm.

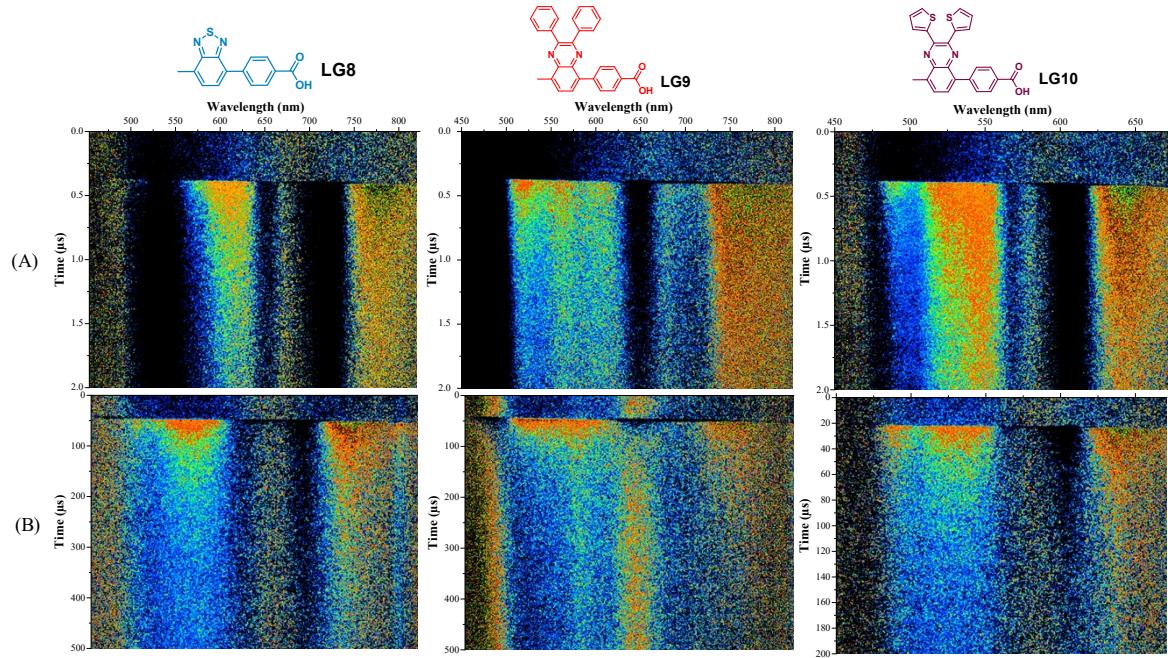


Figure S19. Streak images for **LG8**, **LG9** and **LG10** dyes with an electrolyte (a) containing I_3^-/I^- redox couple, (b) without redox mediator. The device was pump at 430 nm (10Hz) with an energy of $700\mu J/cm^2$.

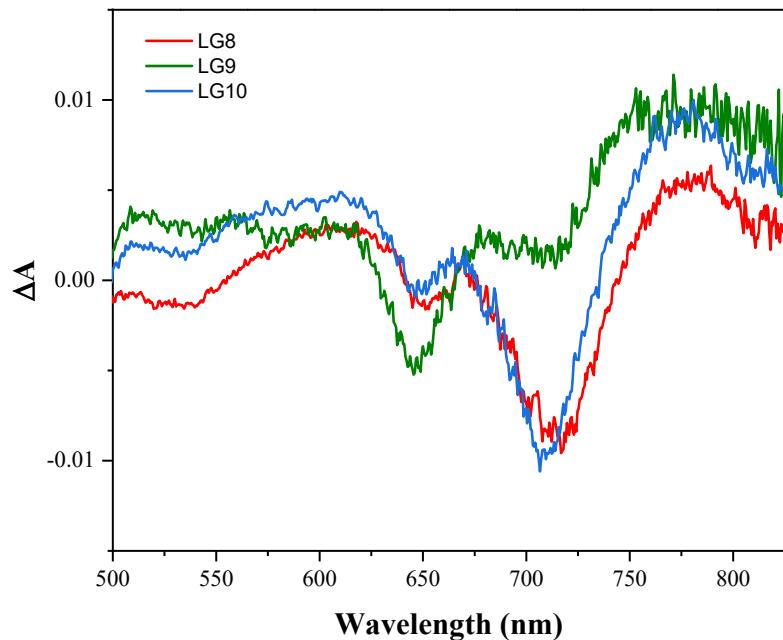


Figure S20. Comparison of transient absorption spectrum of **LG8** (red curve), **LG9** (green curve) and **LG10** (blue curve)-based DSSC after pump pulse at 430nm with an energy of $700\mu J/cm^2$.

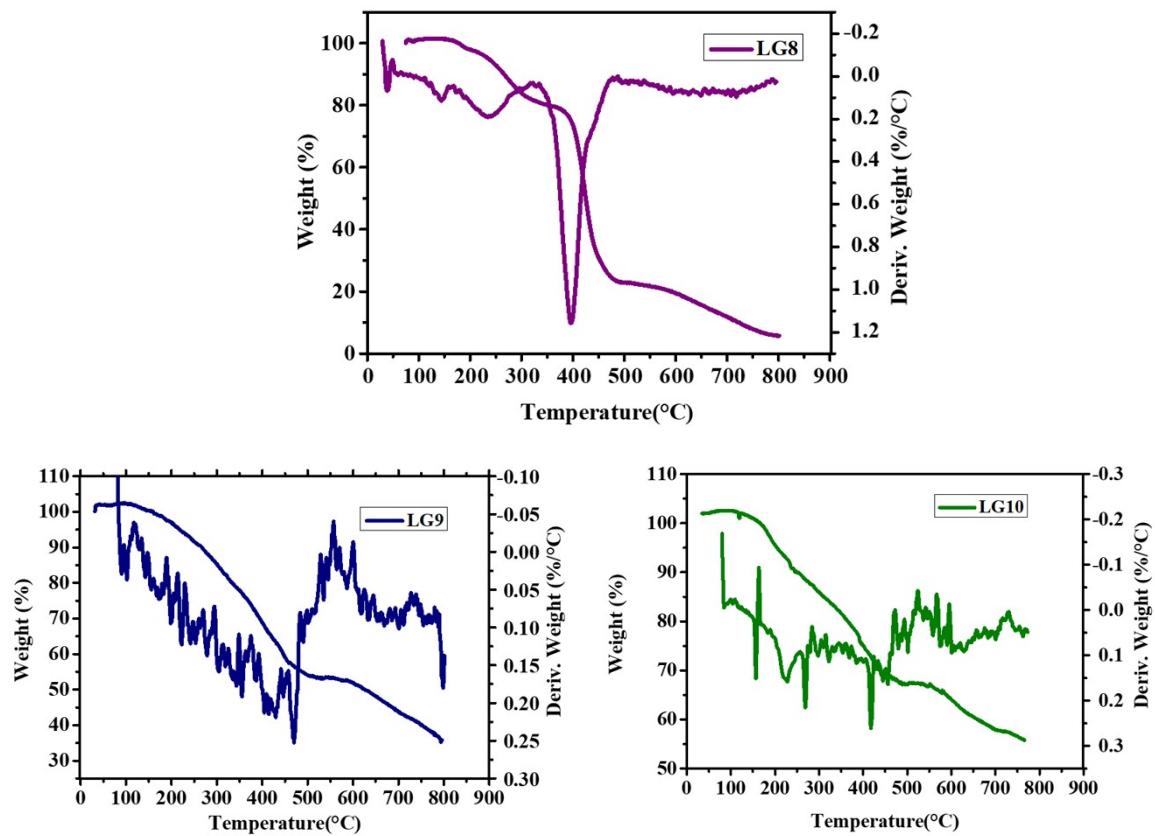


Figure S21. TG/DTG curves of **LG8**, **LG9**, and **LG10** porphyrins with heating rate $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$ under nitrogen using 10 mg of sample.

Table S1: Optimized energies, HOMO-LUMO energies and ground state dipolemoment by DFT studies by using B3LYP/6-31G (d, p) in vacuum.

Dye	^a <i>E</i> , K.cal./mol	^b HOMO (H),	^b LUMO (L)	^b H-L gap	^c μ
LG 8	-4703479	-4.666	-2.535	2.13	2.340
LG 9	-4300925	-4.664	-2.501	2.16	2.131
LG 10	-4212222	-4.732	-2.737	2.00	3.814

^aTotal minimum energy of **LG8-LG10**, ^bvalues in eV, ^cvalues in Debye units.

Table S2: Singlet excited state properties of dyes by B3LYP method and M06-2X function in tetrahydrofuran solvent in PCM model.

Dye	^a λ_{max}	^b f	^c E (eV)	% of Molecular Orbital Contribution
LG 8	470	1.083	2.764	H-1→L+2 (30%), HOMO→L+1 (44%)H-6→LUMO (3%), H-2→LUMO (4%), H-2→L+1 (4%), HOMO→LUMO (8%)
	636	1.293	2.982	H-2→LUMO (16%), H-1→L+2 (33%), HOMO→L+1 (25%), HOMO→L+3 (11%), H-2→L+3 (5%), HOMO→LUMO (3%)
	667	1.330	1.998	H-1→L+2 (11%), HOMO→LUMO (83%) HOMO→L+1 (2%)
LG 9	458	0.929	2.767	H-2→LUMO (45%), H-1→L+1 (28%), HOMO→L+2 (12%) H-5→LUMO (7%)
LG10	562	1.548	2.599	H-2→LUMO (28%), H-1→L+1 (46%), HOMO→LUMO (16%) H-2→L+2 (2%), HOMO→L+3 (2%)
	646	1.074		H-1→L+1 (13%), HOMO→LUMO (82%)
	663	1.156	3.062	H-1→L+1 (57%), HOMO→LUMO (11%), HOMO→L+2 (13%)
	619	1.473	2.604	H-2→LUMO (30%), H-1→L+1 (44%), HOMO→LUMO (16%) HOMO→L+3 (2%)
				H-1→L+1 (13%), HOMO→LUMO (82%)

^aTheoretical absorbance in nm, ^bOscillator strength, and ^cExcited state energy in eV.