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

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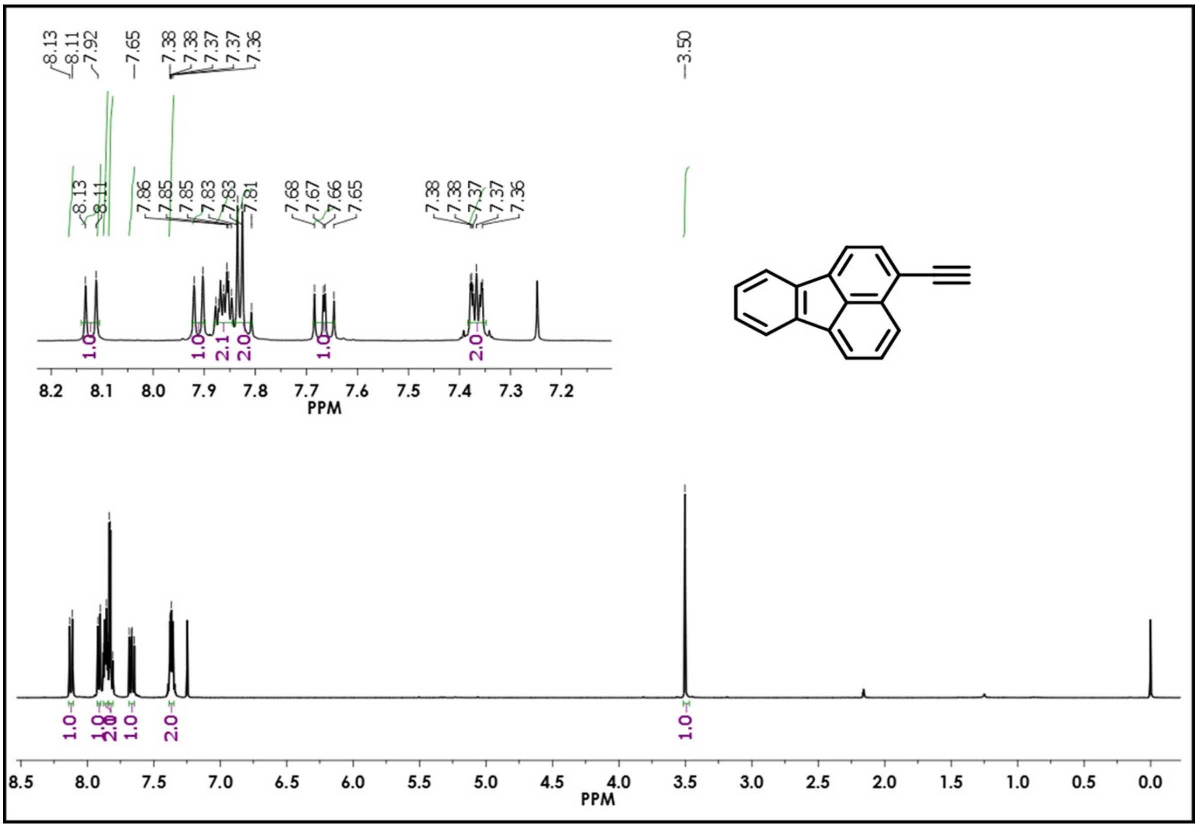


Figure S1. *[1]H NMR spectrum (500 MHz, CDCl3) of **1**.*

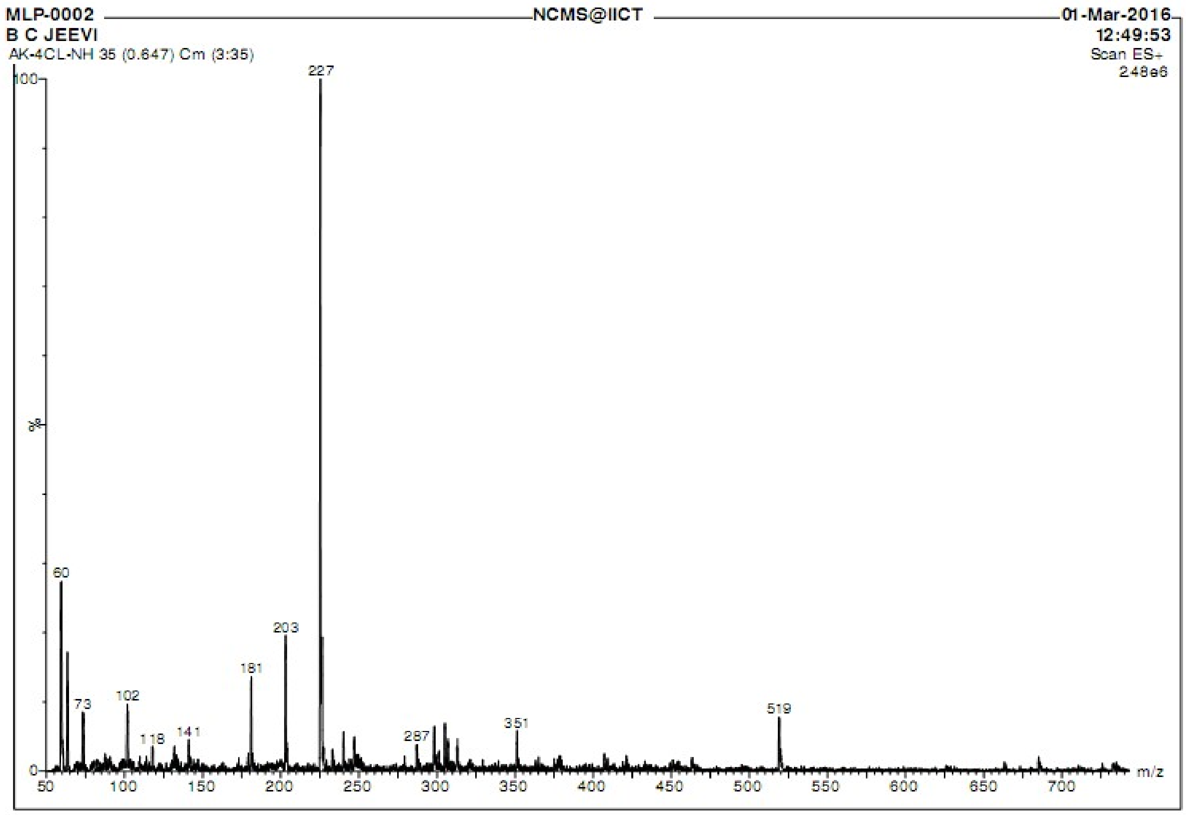


Figure S2. *HRMS of **1** (APPI-FTMS).*

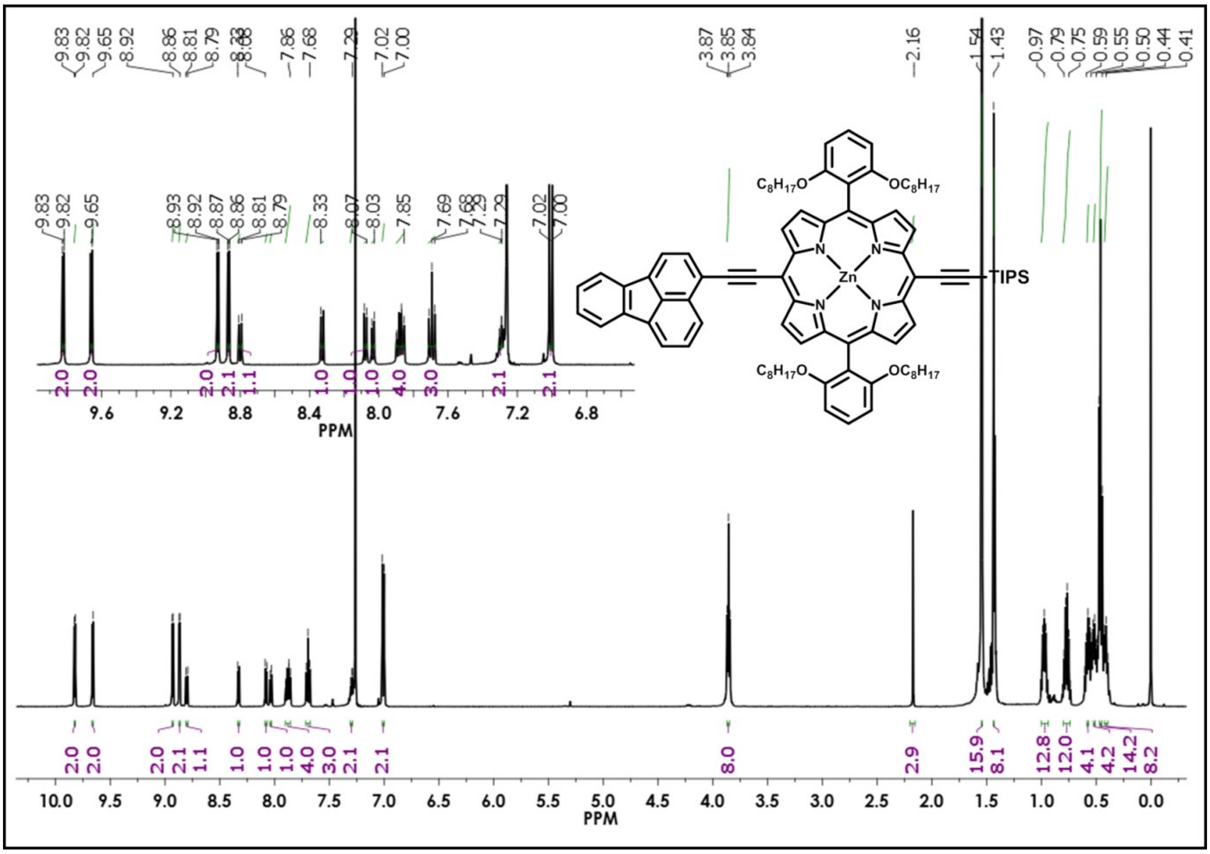


Figure S3. *¹H NMR spectrum (500 MHz, CDCl3) of **3**.*

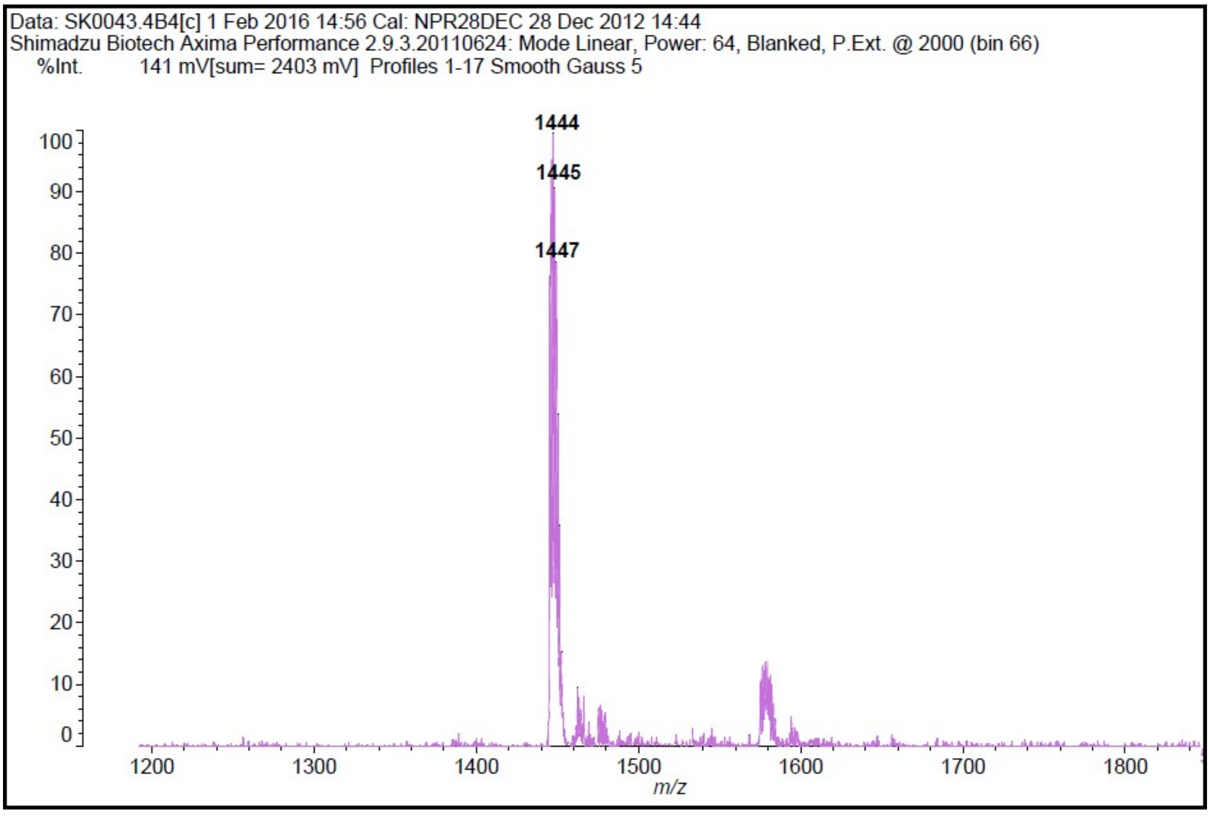


Figure S4. *MALDI-TOF of **3**.*

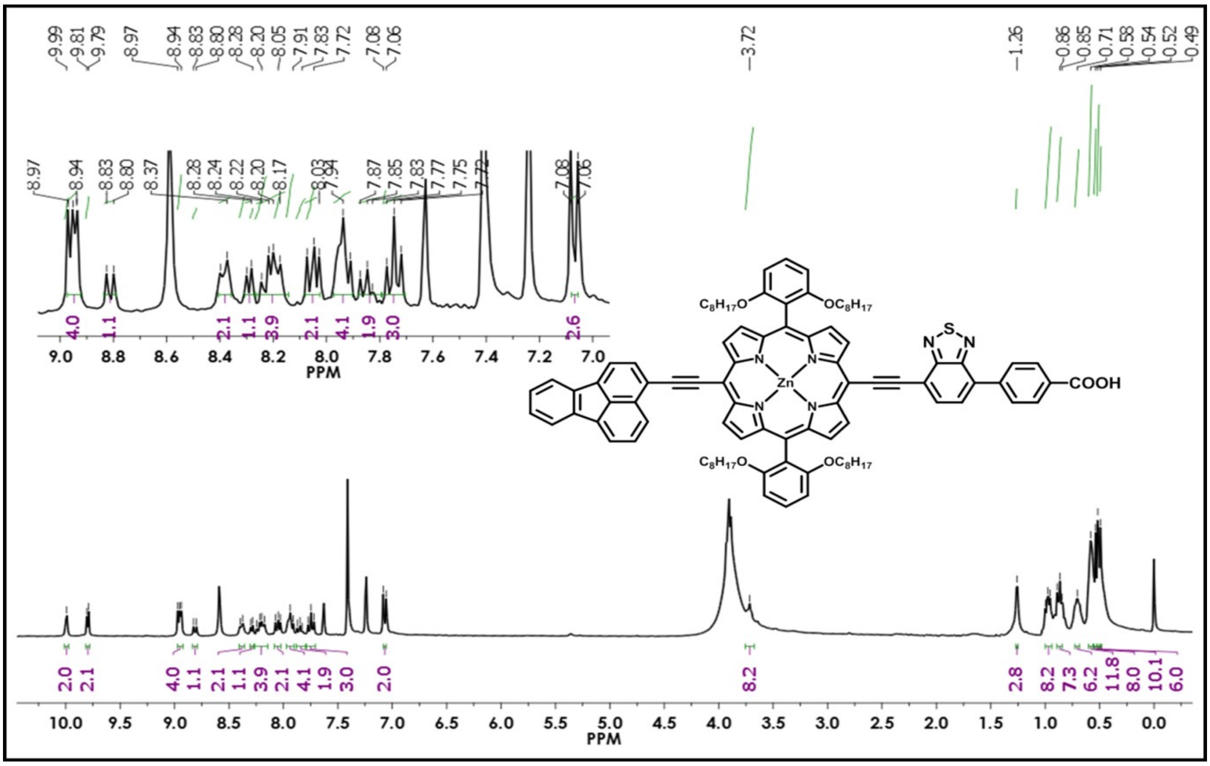


Figure S5. *[1]H NMR spectrum (500 MHz, CDCl3) of* ***LG8***.

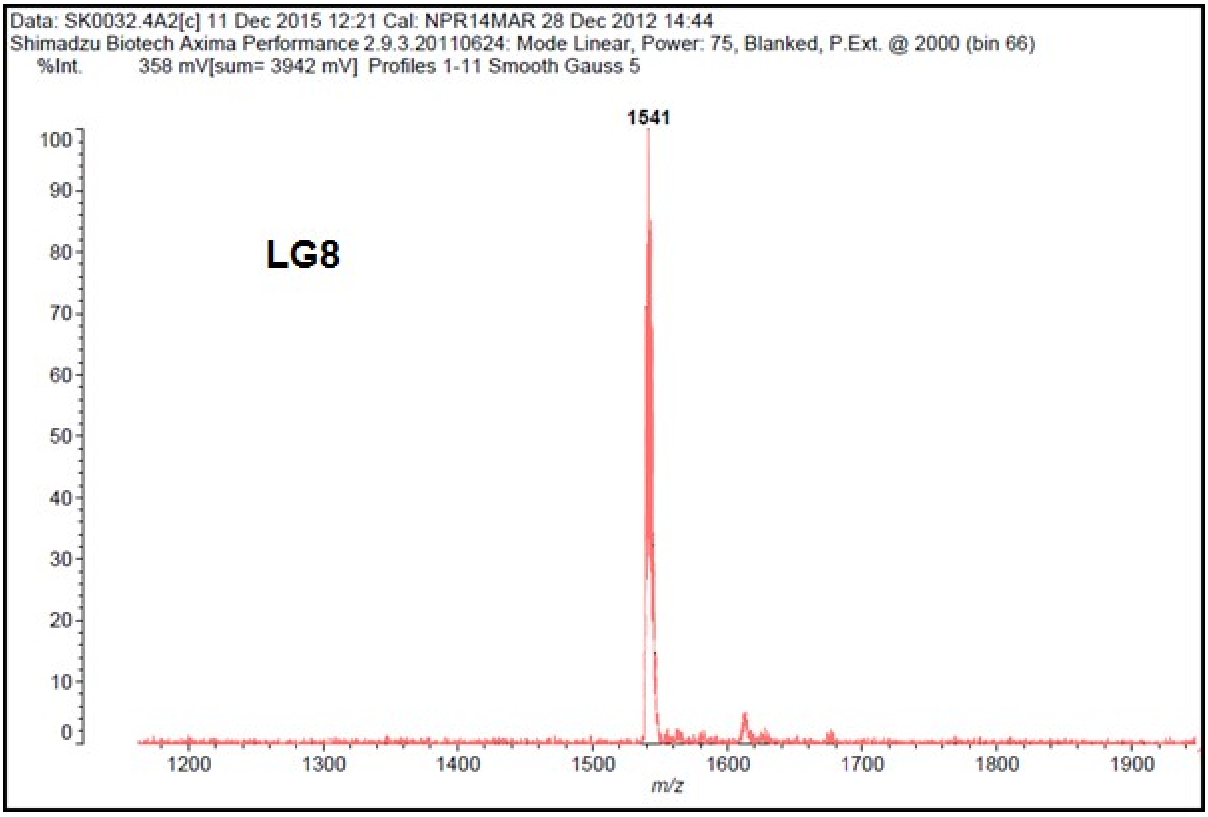


Figure S6. *MALDI-TOF of* ***LG8.***

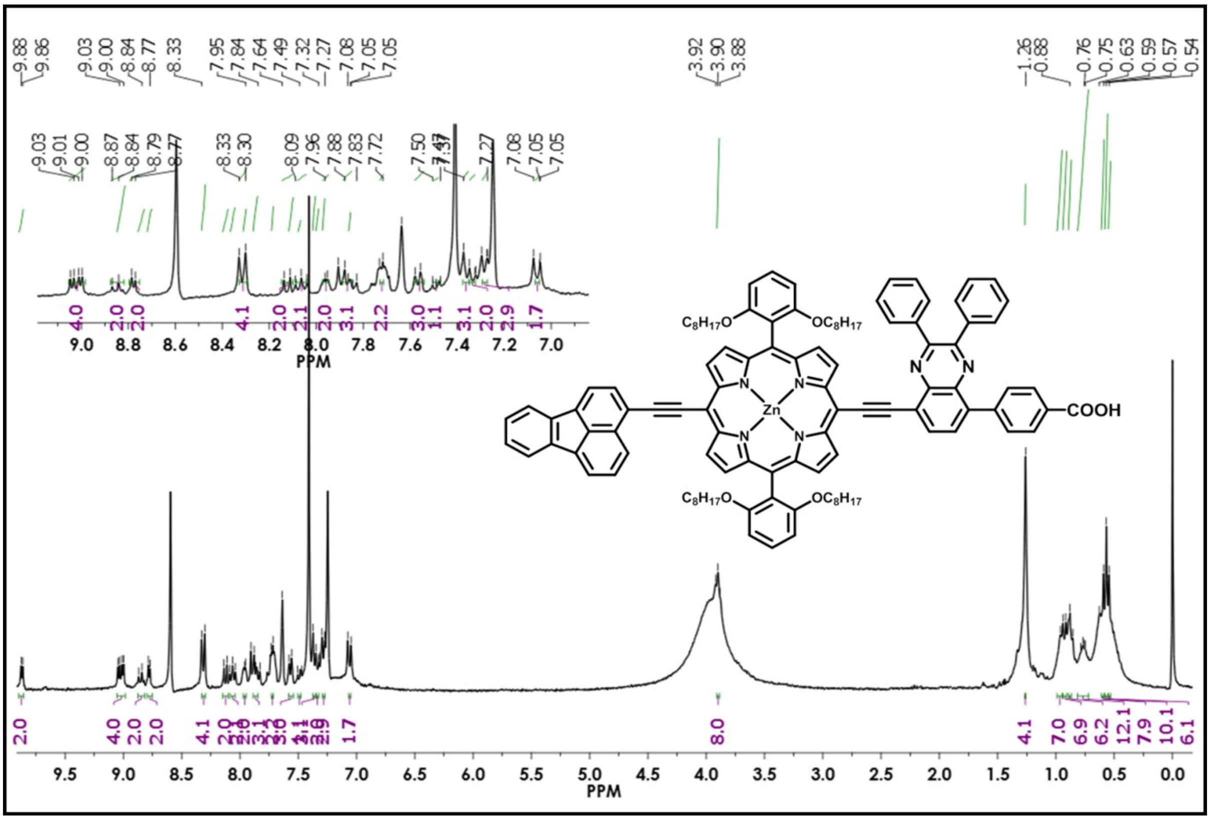


Figure S7. ^{1}H NMR spectrum (500 MHz, CDCl3) of **LG9**.

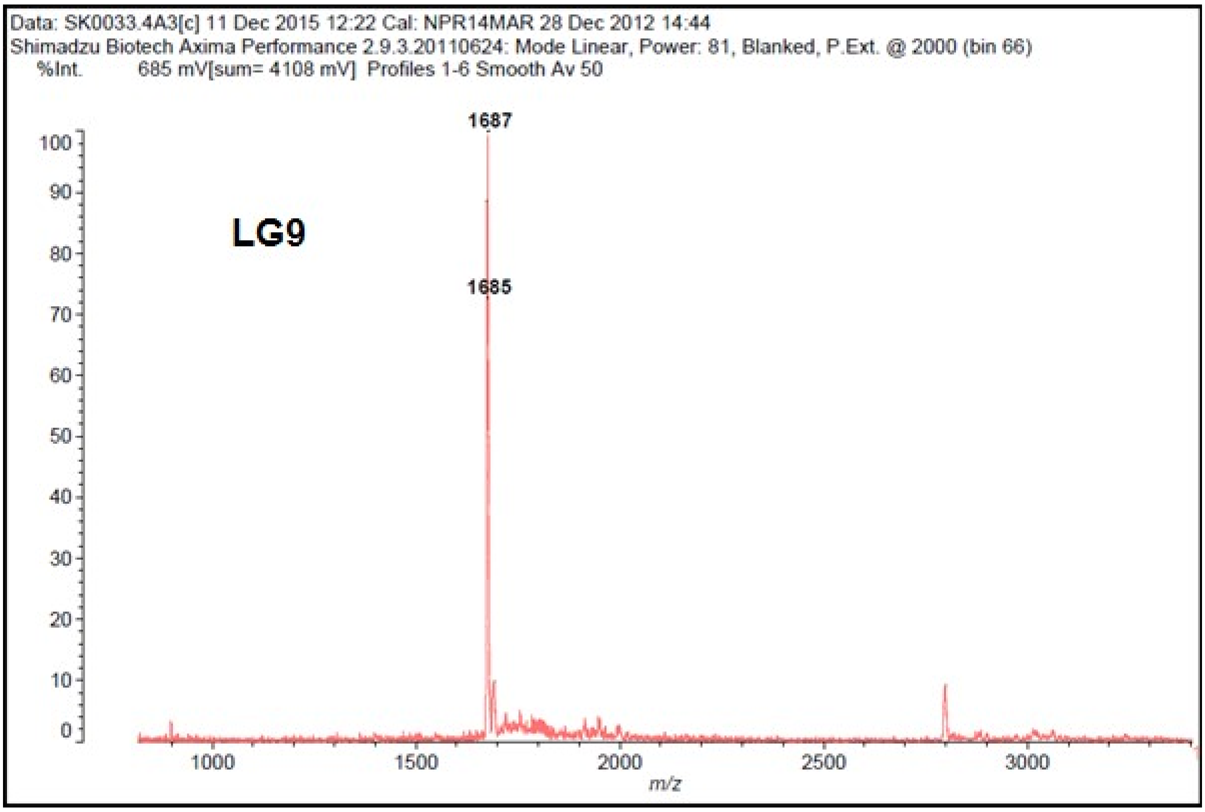


Figure S8. *MALDI-TOF of* ***LG9***.

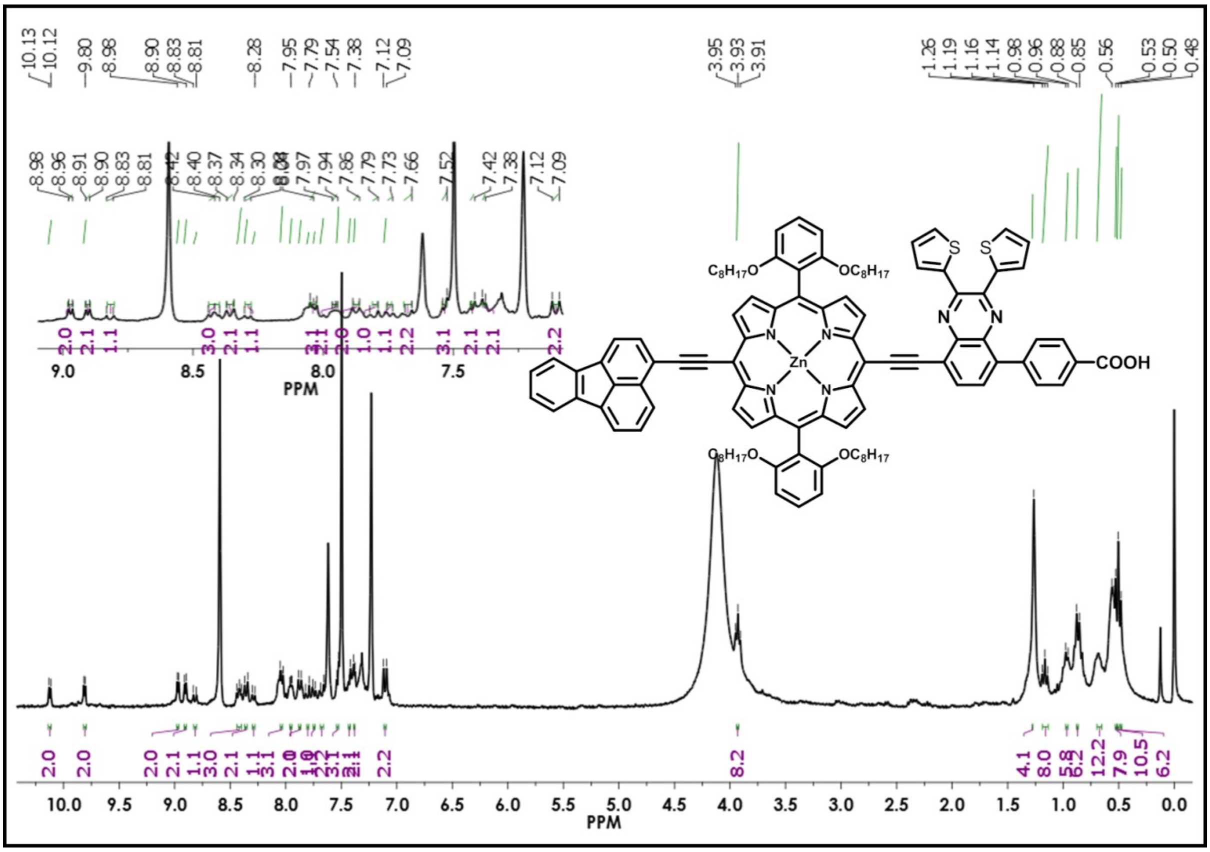


Figure S9. *[1]H NMR spectrum (500 MHz, CDCl3) of* ***LG10***.

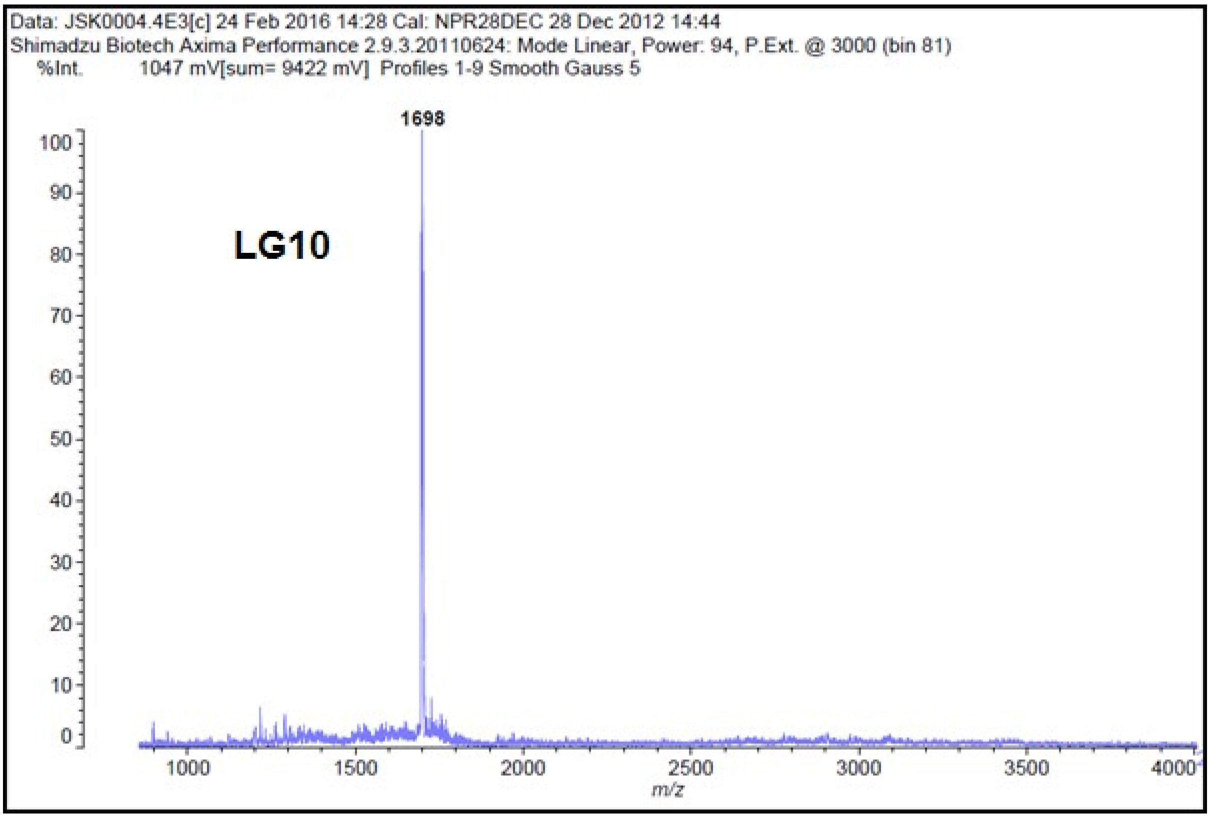


Figure S10. *MALDI-TOF of* ***LG10***.

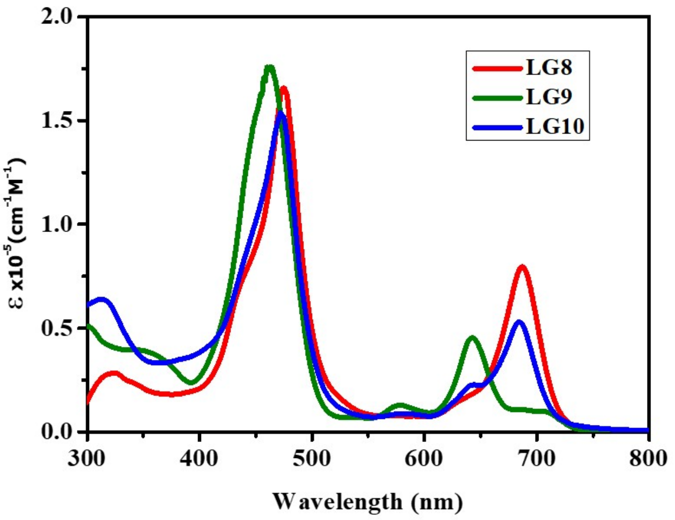


Figure S11. *UV–visible absorption spectra of* ***LG8-LG10*** *in THF solvent.*

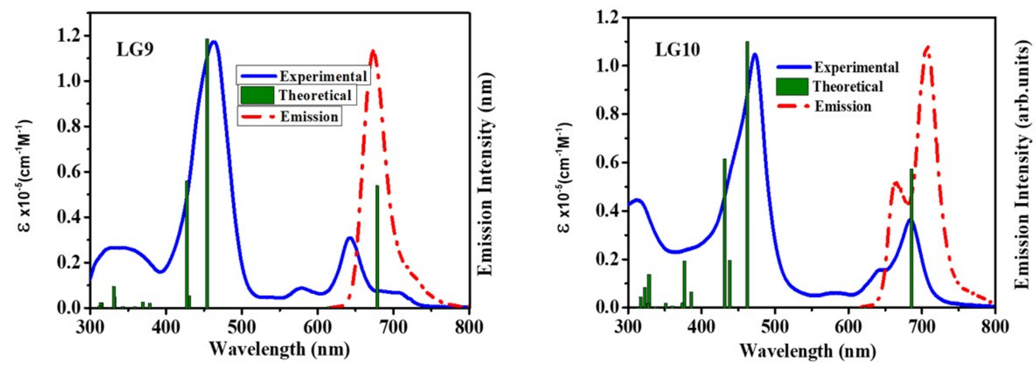


Figure S12. *Theoretical absorption spectra of* ***LG9***, ***LG10*** *Dyes by using B3LYP method PCM model in tetrahydrofuran solvent with M06-2X function.*

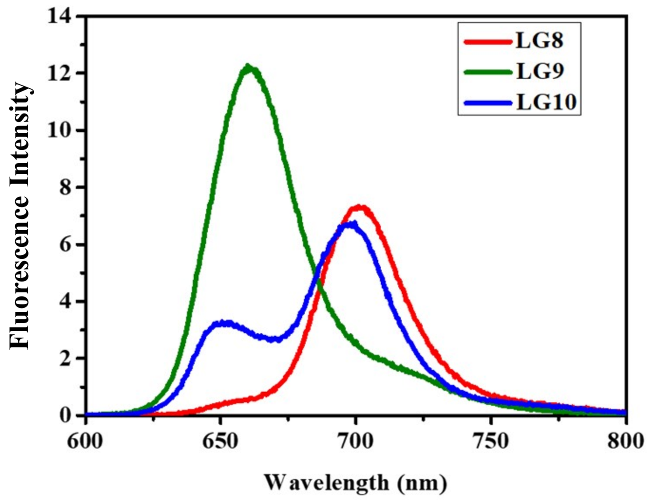


Figure S13. *Fluorescence spectra of* ***LG8***, ***LG9*** *and* ***LG10*** *in THF solution*

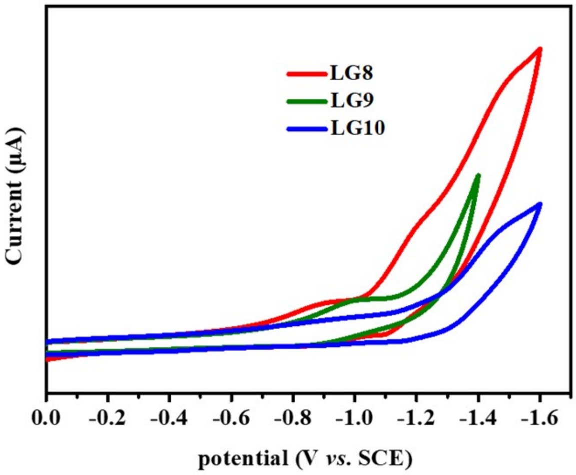


Figure S14. *Reduction spectra of dyes **LG8, LG9 and LG10** in THF*.

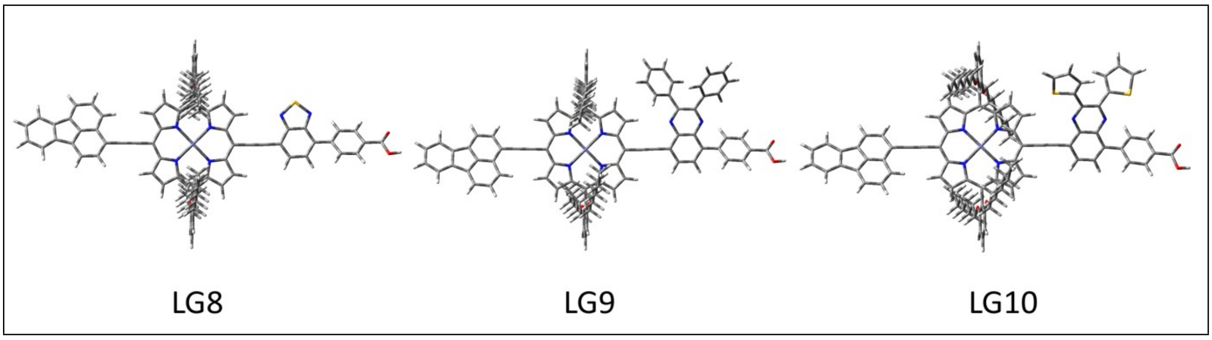


Figure. S15. *Optimized structure of **LG8**, **LG9** and **LG10** dyes*.

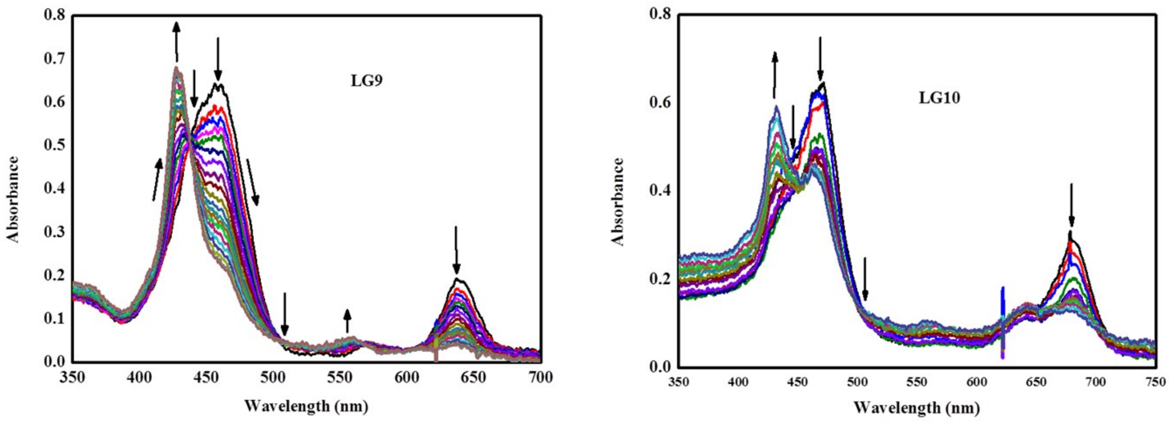


Figure S16. *Oxidative OTTLE studies of **LG 9** and **LG10** sensitizers in 0.3M TBAP/THF with an applied potential of +0.90V (vs. SCE/KCl).*

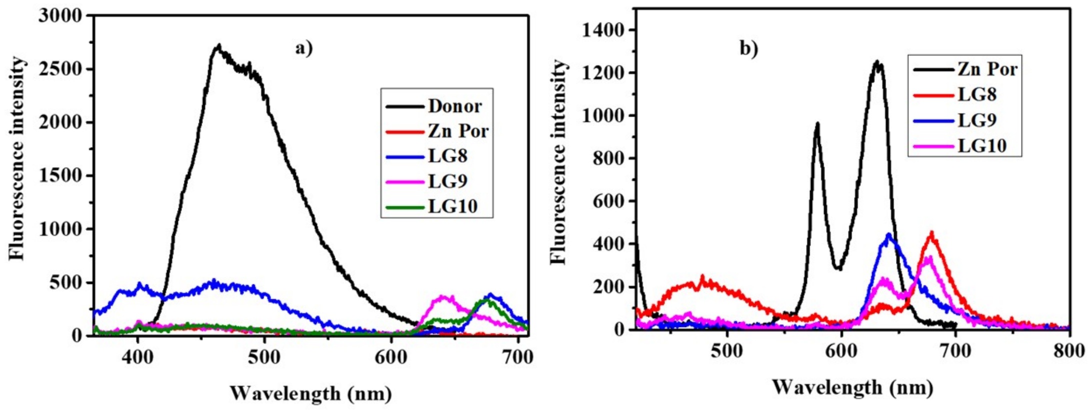


Figure S17. *a) Emission spectra of equi-absorbing solutions of* ***Donor****,* ***Zn Por****,* ***LG8****-* ***LG10*** *(OD lex = 0.08) in* CH_2Cl_2 *solvent at 357 nm. b) Emission spectra of equi-absorbing solutions of* ***Zn Por****,* ***LG8****-* ***LG10*** *(OD lex = 0.08) in* CH_2Cl_2 *solvent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

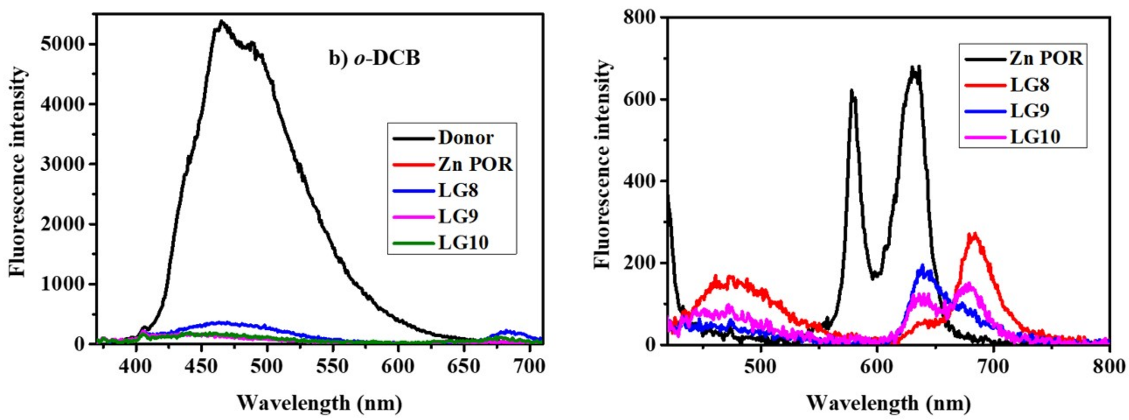


Figure S18. *a) Emission spectra of equi-absorbing solutions of* ***Donor****,* ***Zn Por****,* ***LG8- LG10*** *(OD lex = 0.08) in o-DCB solvent at 357 nm. b) Emission spectra of equi-absorbing solutions of* ***Zn Por****,* ***LG8- LG10*** *(OD lex = 0.08) in o-DCB solvent at 410 nm.*

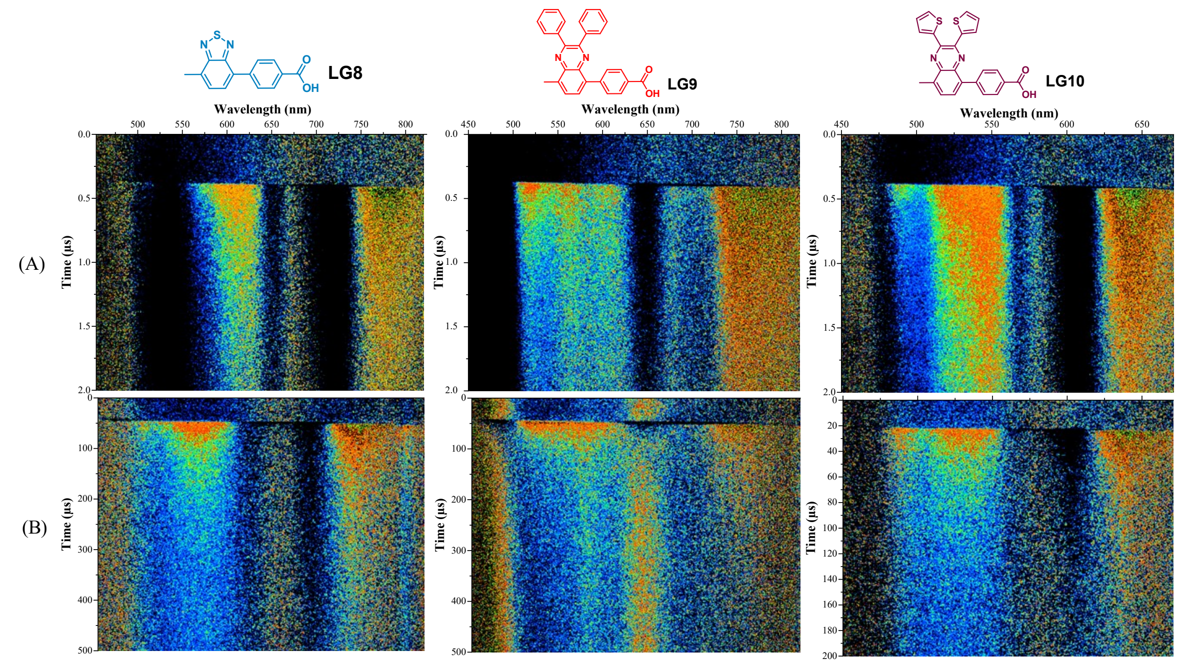


Figure S19. *Streak images for* ***LG8****,* ***LG9*** *and* ***LG10*** *dyes with an electrolyte (a) containing* I_3^-/I^- *redox couple, (b) without redox mediator. The device was pump at 430 nm (10Hz) with an energy of 700μJ/cm*^{2}.

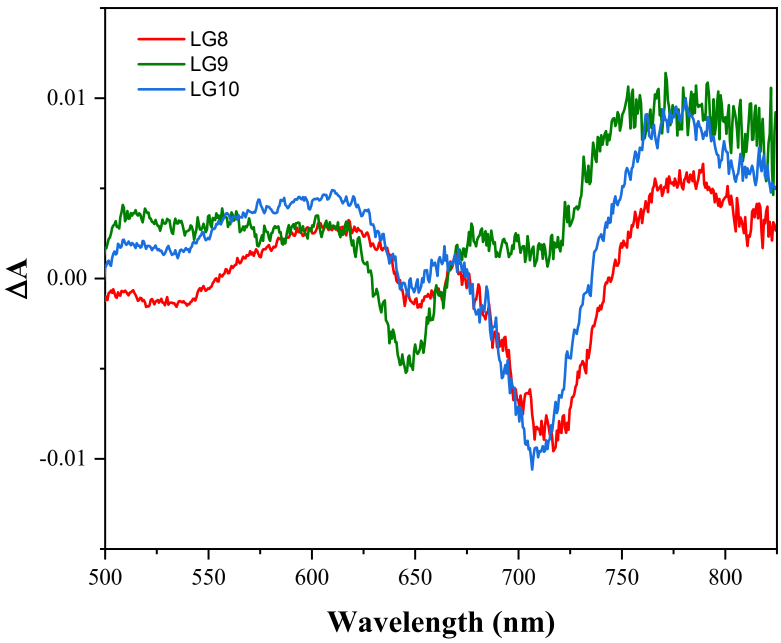
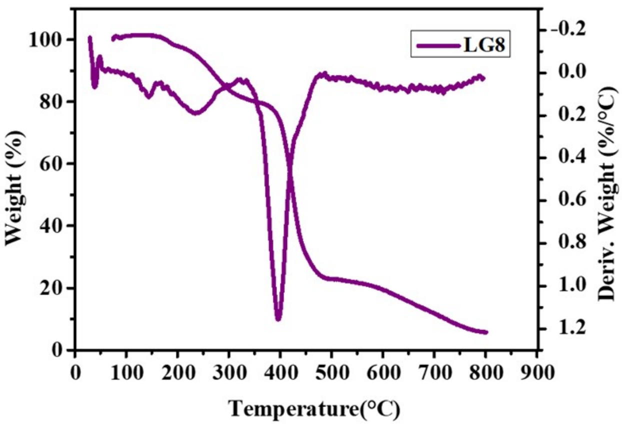
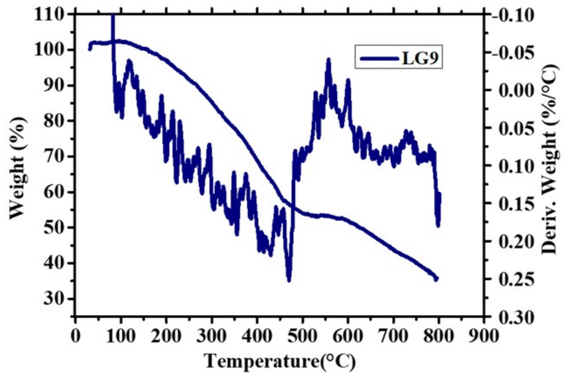


Figure S20. *Comparison of transient absorption spectrum of* ***LG8*** *(red curve),* ***LG9*** *(green curve) and* ***LG10*** *(blue curve)-based DSSC after pump pulse at 430nm with an energy of 700μJ/cm*^{2}.





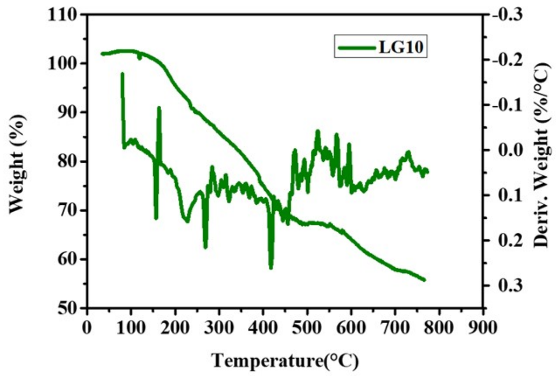


Figure S21. *TG/DTG curves of **LG8**,**LG9**, and **LG10** porphyrins with heating rate 10 °C.min^{-1} under nitrogen using 10 mg of sample.*

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}*E*, K.cal./mol	^{b}HOMO (H),	^{b}LUMO (L)	^{b}H-L gap	$^{c}\mu$
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

^{a}Total minimum energy of **LG8-LG10**, ^{b}values in eV, ^{c}values 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	$^{a}\lambda_{max}$	^{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%)
	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%)
LG10	467	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%)
	663	1.074	2.037	H-1→L+1 (13%), HOMO→LUMO (82%)

[a]Theoretical absorbance in nm, [b]Oscillator strength, and [c]Excited state energy in eV.