Kinetics of Dye Regeneration in Liquid Electrolyte Unveils Efficiency of 10.5% in Dye-Sensitized Solar Cells

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Table of Contents		Page No.
Figure S1	*^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***1***	S3
Figure S2	*ESI-MS of 1 (APPI--FTMS)* ***1***	S3
Figure S3	*^{1}H NMR spectrum (500 MHz, CDCl3) of 3.*	S4
Figure S4	*MALDI-TOF of* ***3.***	S4
Figure S5	*^{1}H NMR spectrum (300 MHz, CDCl3+C5D5N) of LG15.*	S5
Figure S6	*MALDI-TOF of* ***LG15***	S5
Figure S7	*^{1}H NMR spectrum (300 MHz, CDCl3+C5D5N) of LG16.*	S6
Figure S8	*MALDI-TOF of* ***LG16.***	S6
Figure S9	*^{1}H NMR spectrum (300 MHz, CDCl3+C5D5N) of LG17.*	S7
Figure S10	*MALDI-TOF of* ***LG17.***	S7
Figure S11	*^{1}H NMR spectrum (300 MHz, CDCl3+C5D5N) of LG18.*	S8
Figure S12	*MALDI-TOF of* ***LG18.***	S8
Figure S13	*UV–visible absorption spectra of* ***LG15, LG16, LG17*** *and* ***LG18*** *in THF solvent.*	S9
Figure S14	*Theoretical absorption spectra of* ***LG15*** *and* ***LG16*** *Dyes by using B3LYP method PCM model in tetrahydrofuran solvent with M06-2X function.*	S9
Figure S15	*Fluorescence spectra of* **LG15, LG16, LG17** and **LG18** *in THF solution.*	S9
Figure S16	*Singlet excited-state lifetimes of* **LG15, LG16, LG17** and **LG18** *in THF solution*	S10
Figure S17	*Cyclic Voltammogramme of* **LG15, LG16, LG17** *and* **LG18**.	S10
Figure S18	*Optimized structure of LG15***, LG16, LG17 and LG18** *sensitizers and minimum energy in kcal/molby using B3LYP method6-31G (d,p).*	S11
Figure S19	*Oxidative OTTLE studies porphyrin sensitizers in 0.3M TBAP/THF with an applied potential of +0.90V (vs. SCE/KCl)*	S11
Figure S20	*Photocurrent action spectra porphyrin sensitizers using different concentrations of* 4-*tert* butylpyridine.	S12

Figure S21	*Current–voltage characteristics of porphyrin sensitizers using different concentrations of 4-tert butylpyridine.*	S12
Figure S22	*TG/DTG curves of **LG15, LG16, LG17** and **LG18** porphyrins with heating rate 10 °C.min^{-1} under nitrogen*	S13
Table S1	Optimized energies, HOMO-LUMO energies and ground state dipole moment by DFT studies by using B3LYP/6-31G (d,p) in vacuum.	S13
Table S2	Singlet excited state properties of dyes by B3LYP method and M06-2X function in tetrahydrofuran solvent in PCM model. [a] Total minimum energy of dyads and triad, [b]values in eV, [c]values in debye units.	S14

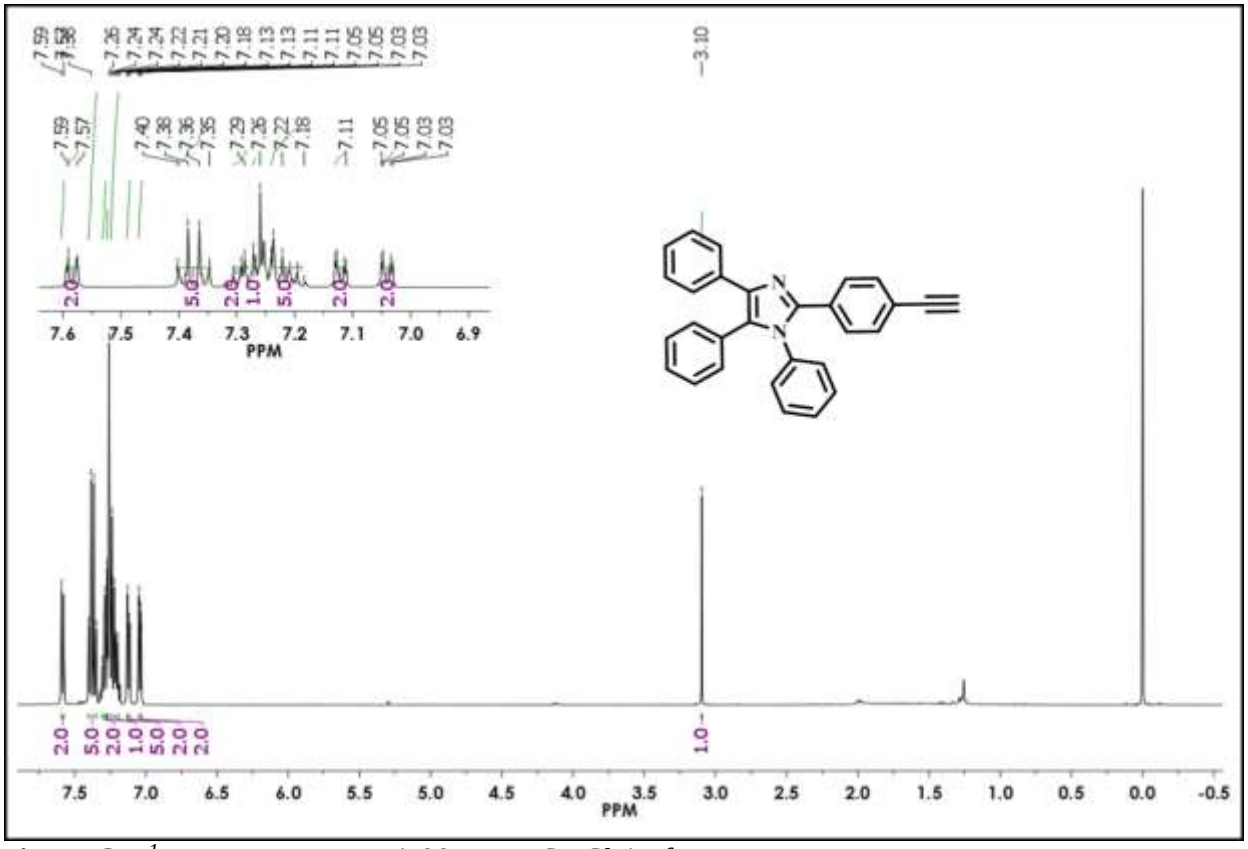

Figure S1. *^{1}H NMR spectrum (500 MHz, CDCl3) of 1a.*

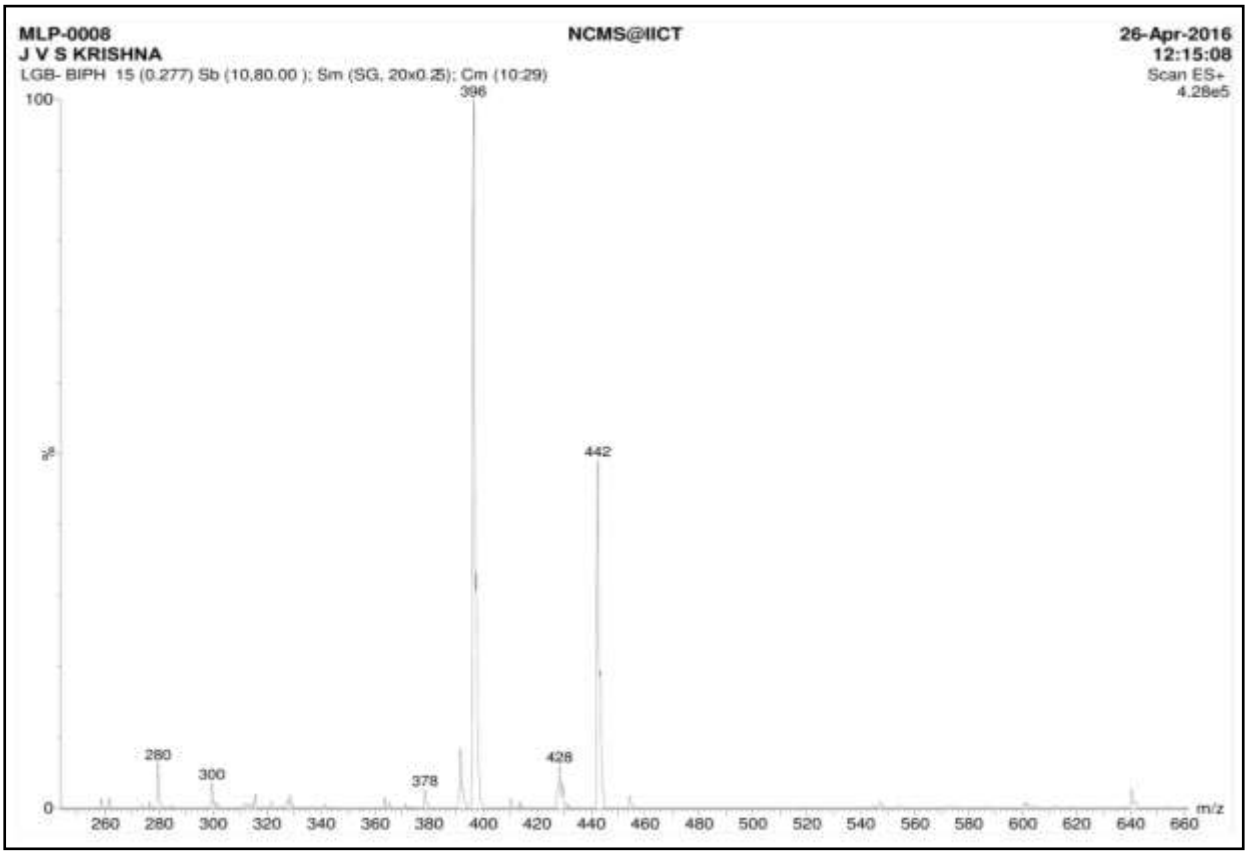

Figure S2. *ESI-MS of 1.*

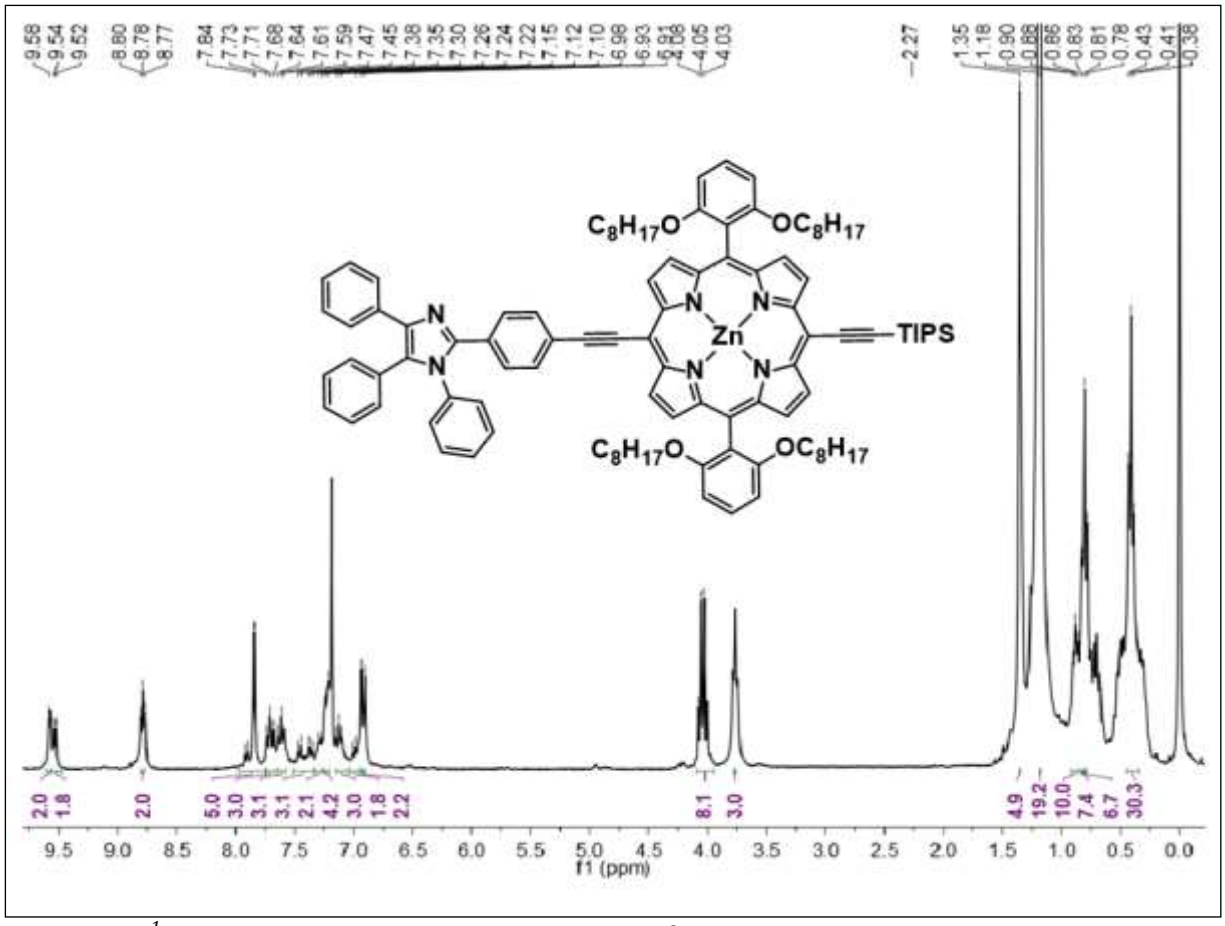

Figure S3. *^{1}H NMR spectrum (500 MHz, CDCl3) of 3.*

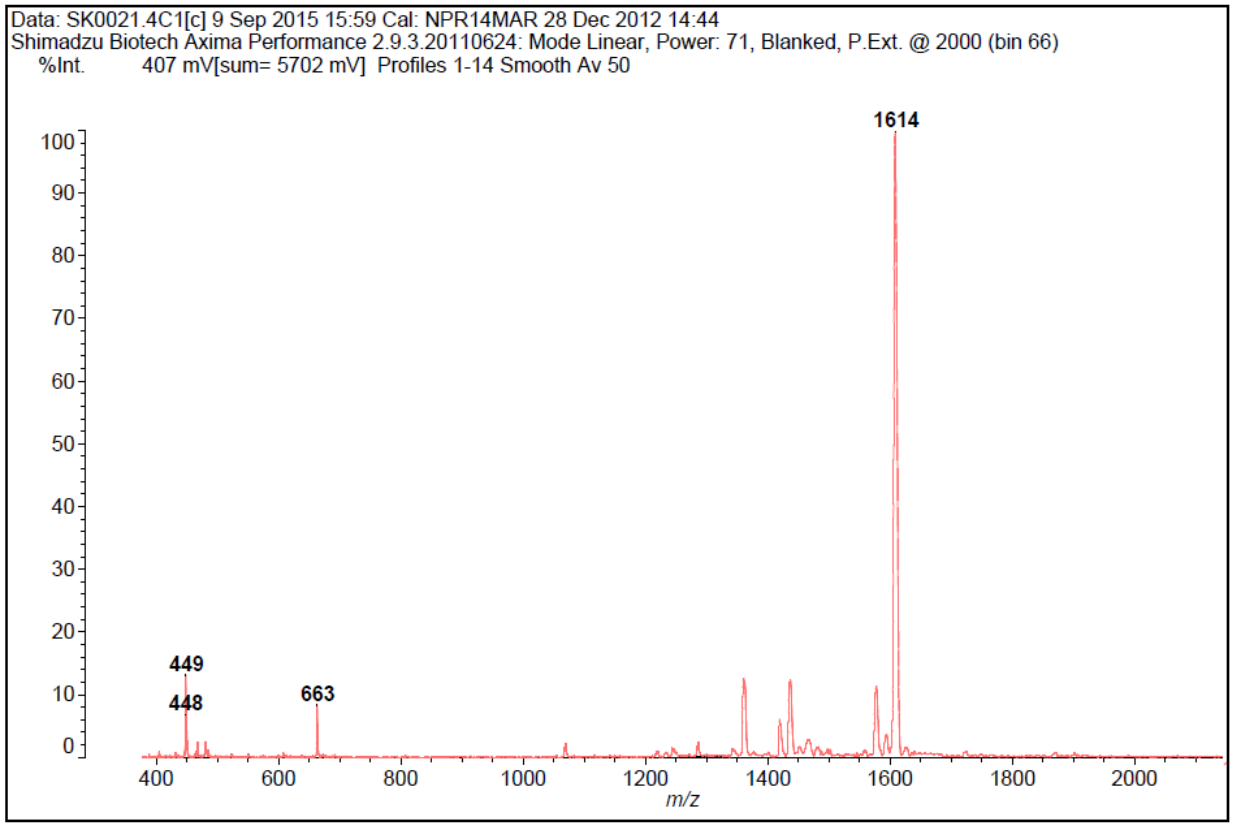

Figure S4. *MALDI-TOF of **3**.*

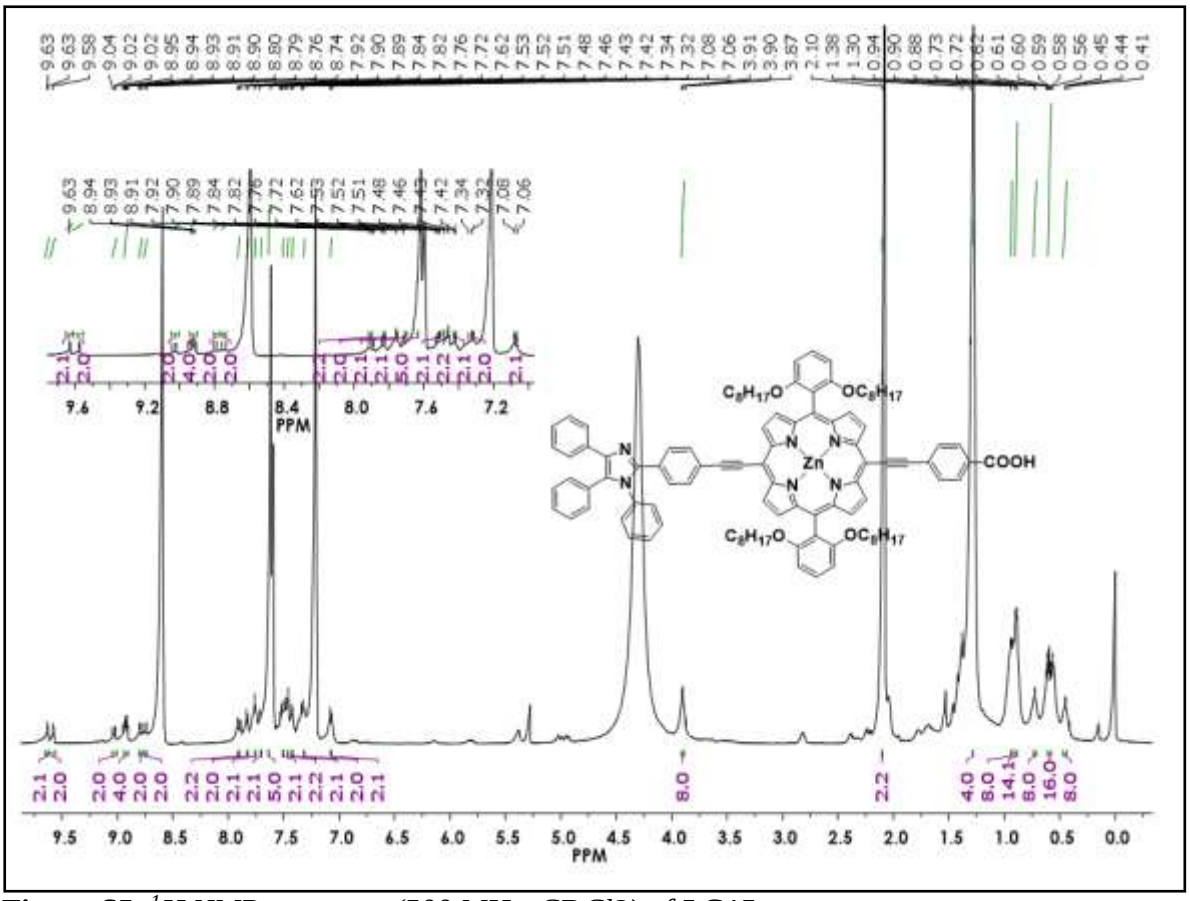

Figure S5. *^{1}H NMR spectrum (500 MHz, CDCl3) of* ***LG15***.

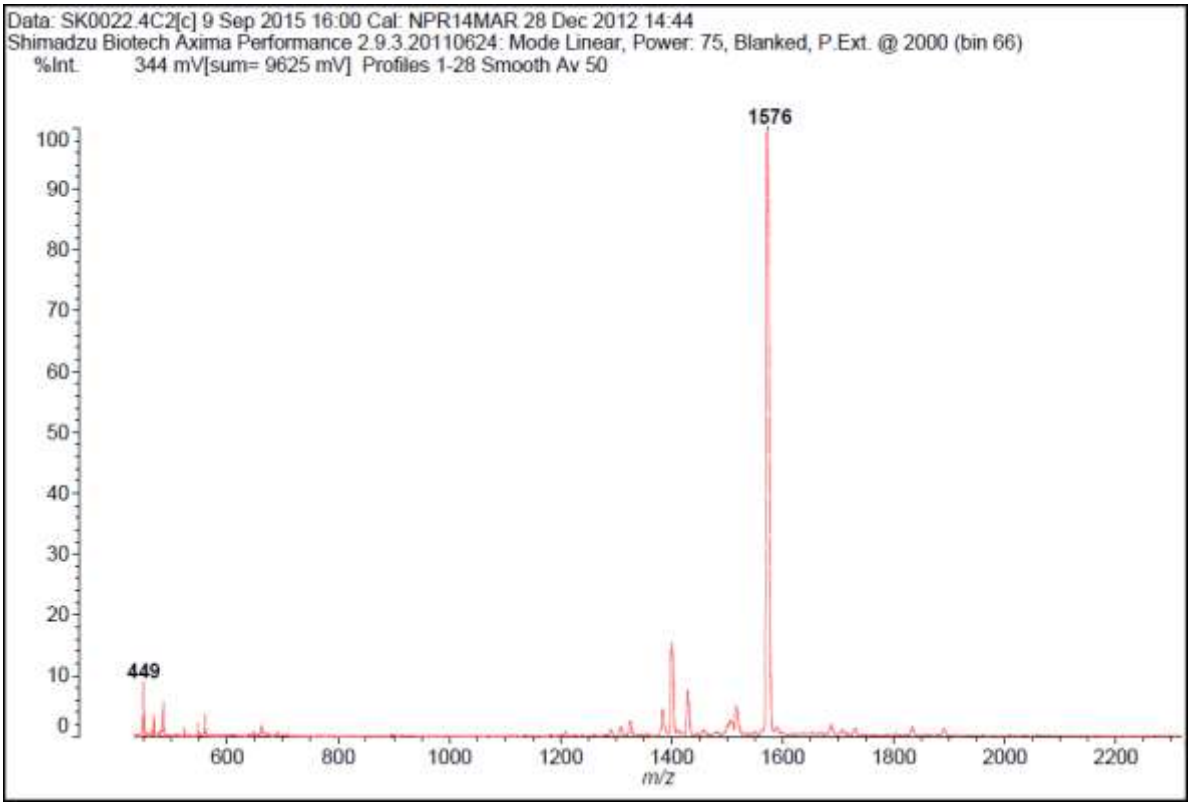

Figure S6. *MALDI-TOF of* ***LG15.***

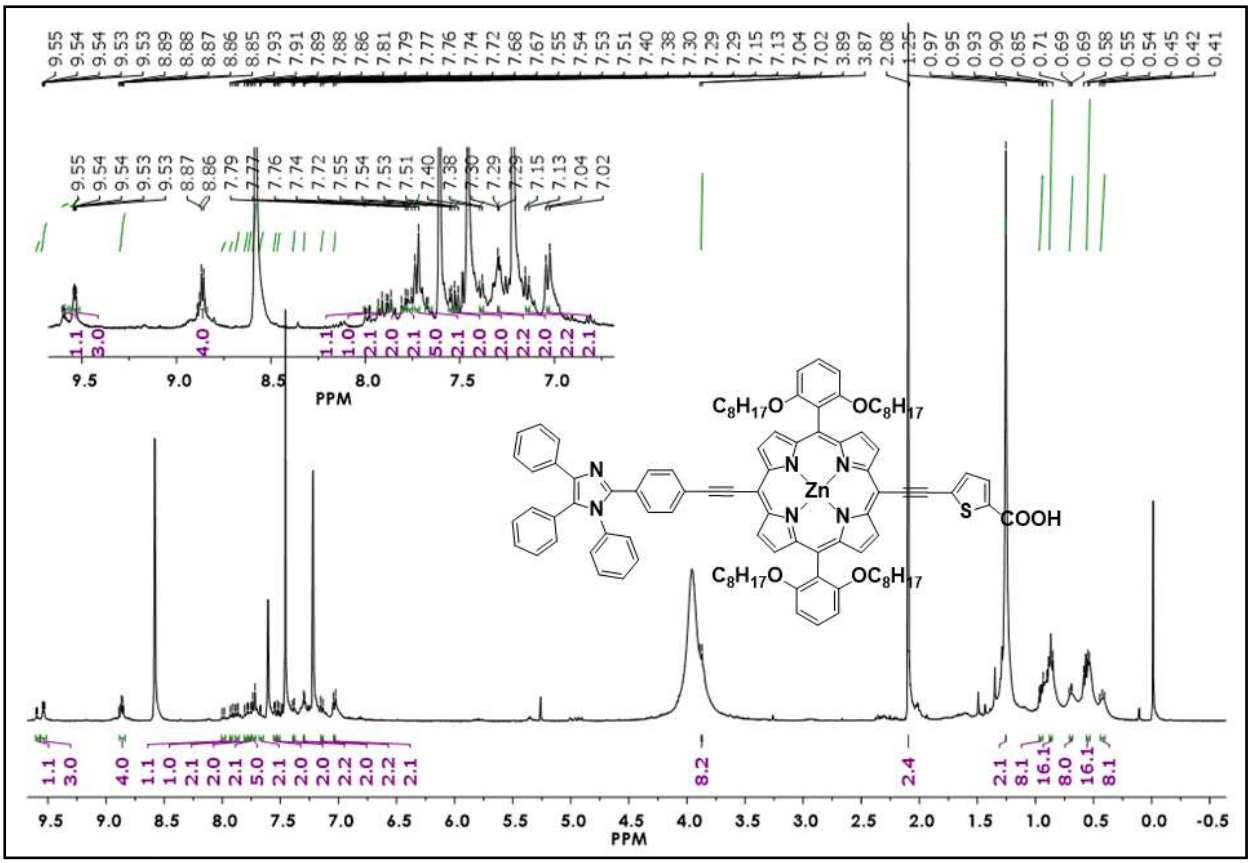

Figure S7. *^{1}H NMR spectrum (500 MHz, CDCl3) of* ***LG16***.

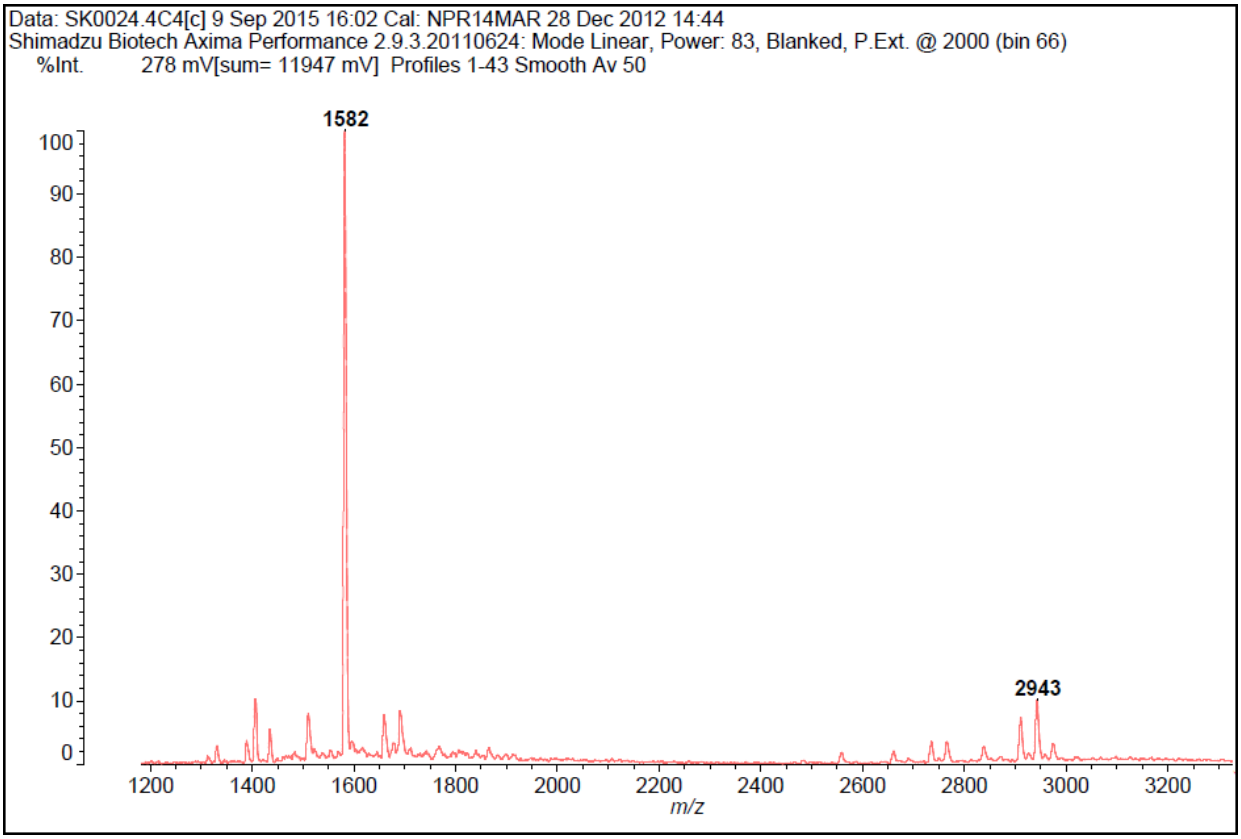

Figure S8. *MALDI-TOF of* ***LG16.***

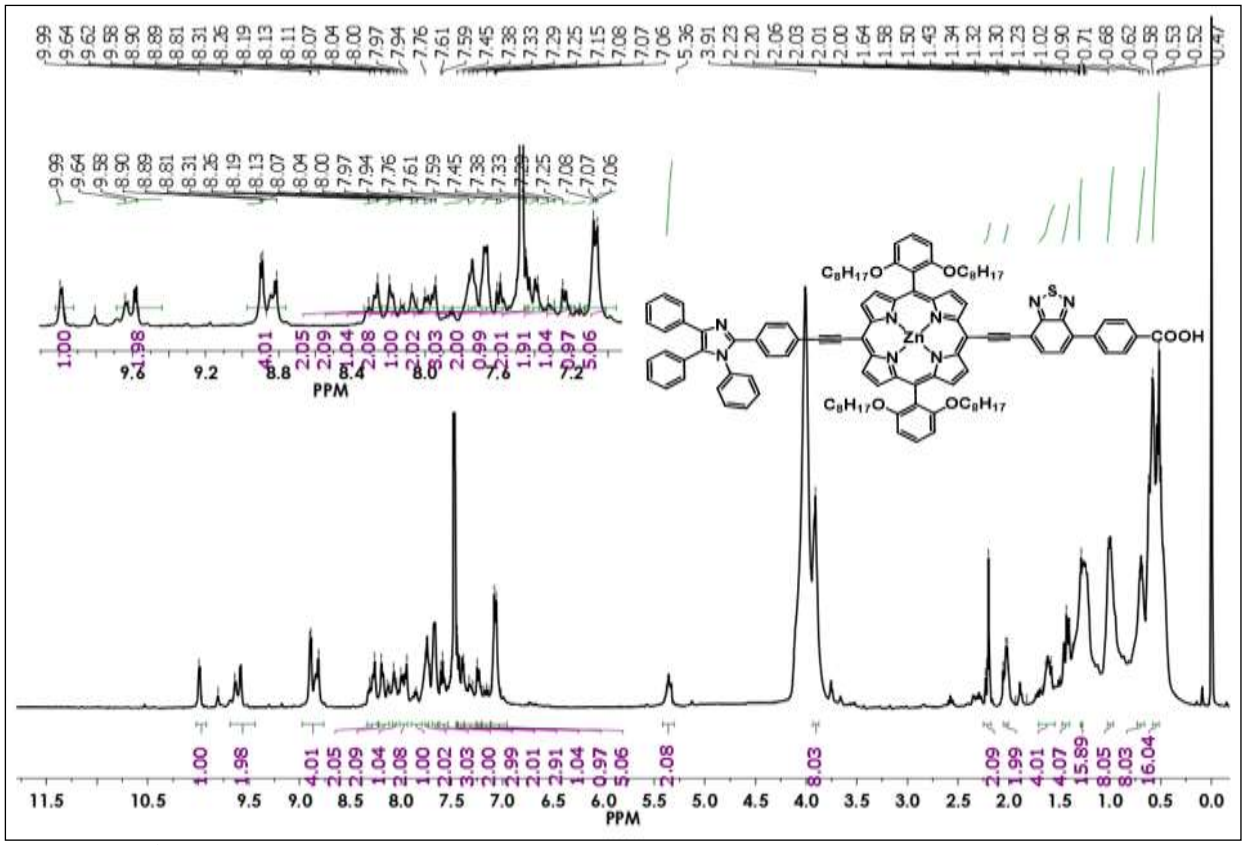

Figure S9. *^{1}H NMR spectrum (500 MHz, CDCl3) of* ***LG17****.*

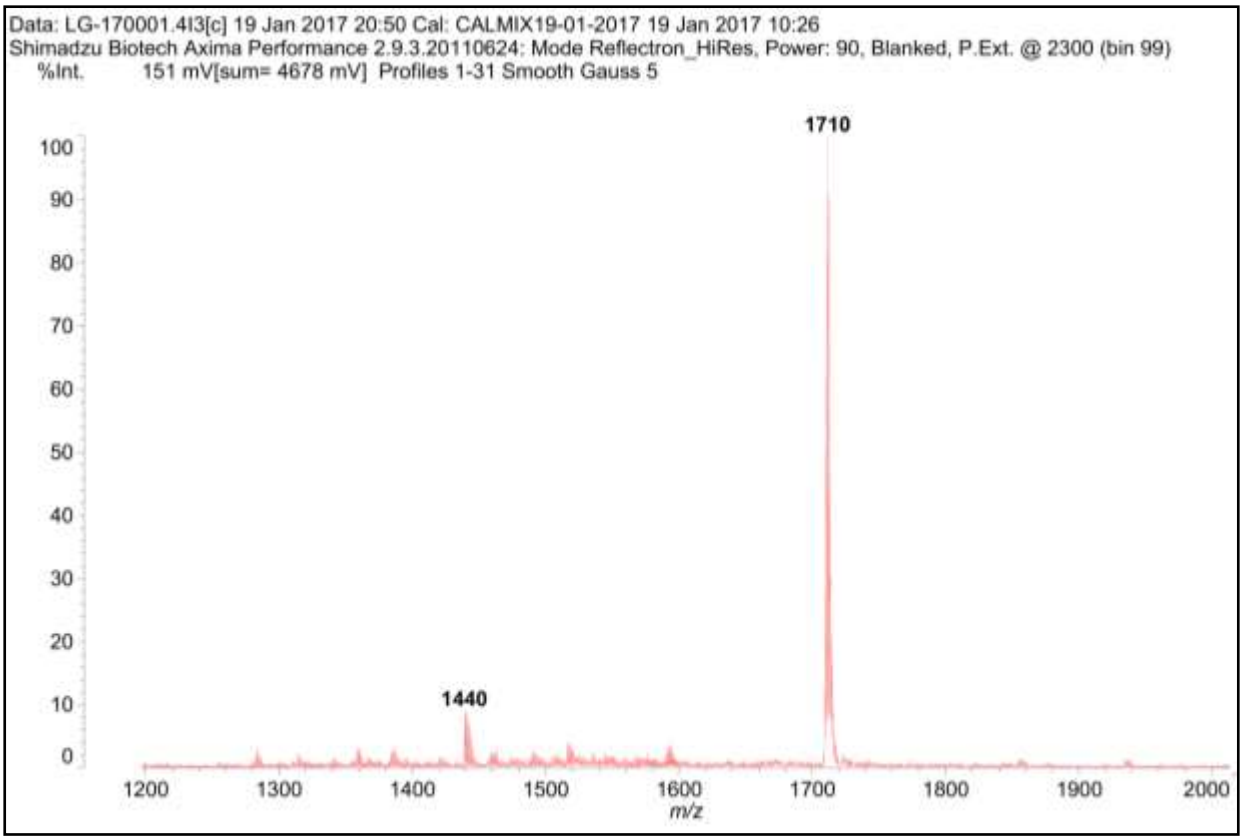

Figure S10. *MALDI-TOF of* ***LG17.***

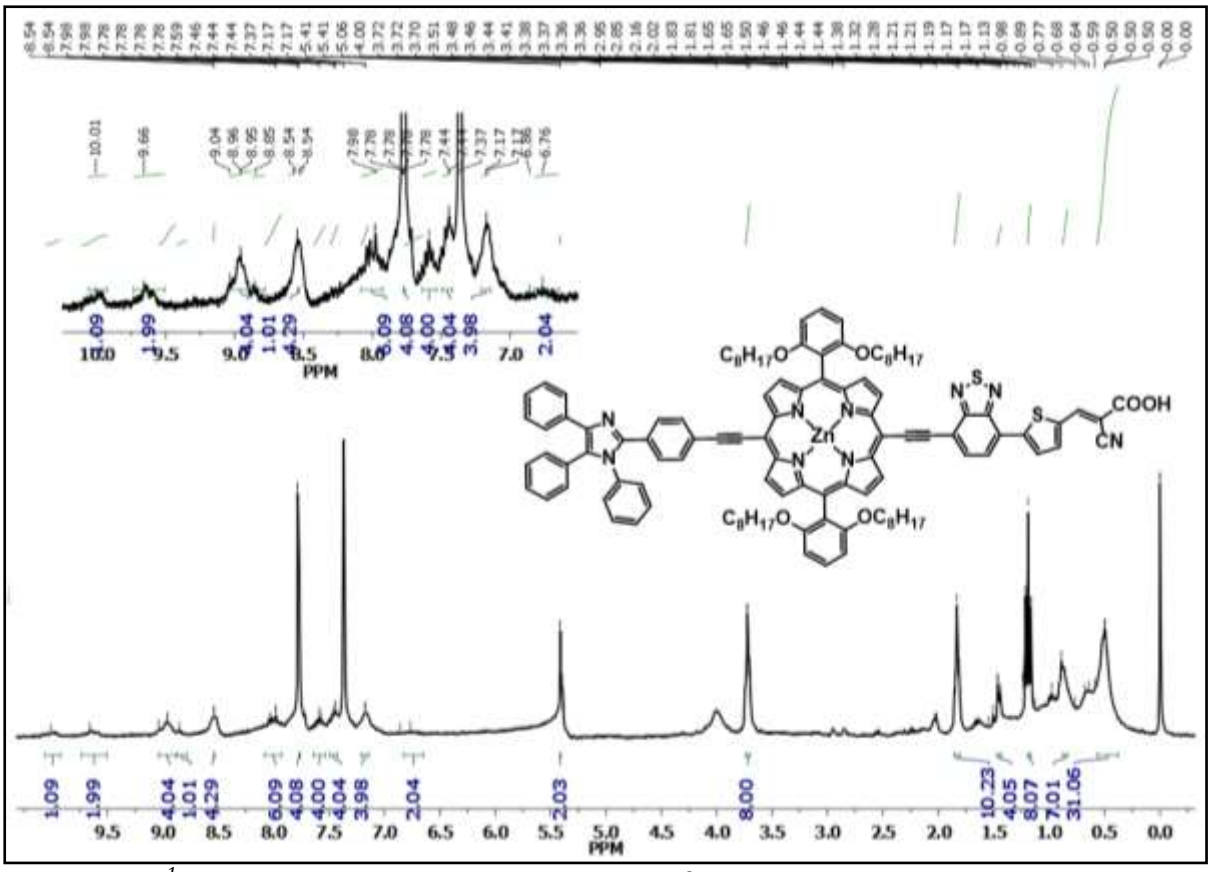

Figure S11. *^{1}H NMR spectrum (500 MHz, CDCl3) of* ***LG18****.*

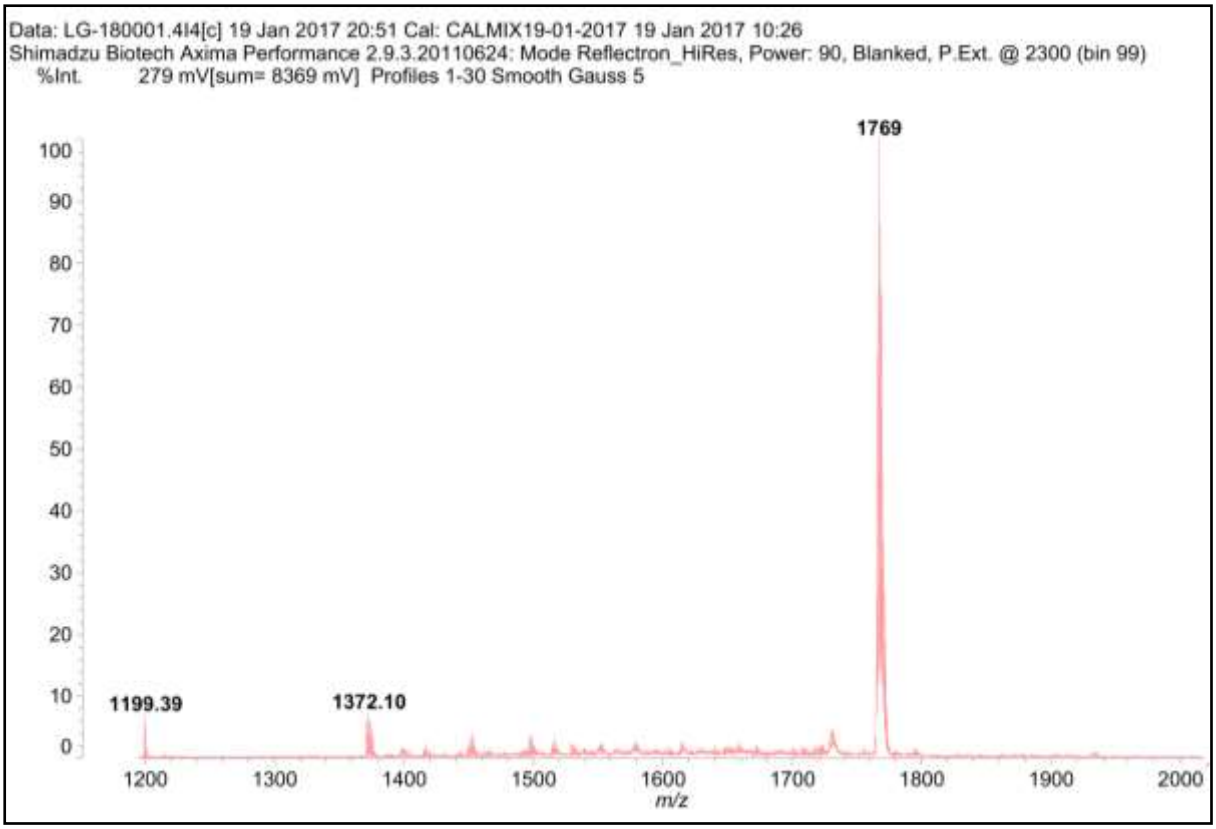

Figure S12. *MALDI-TOF of* ***LG18.***

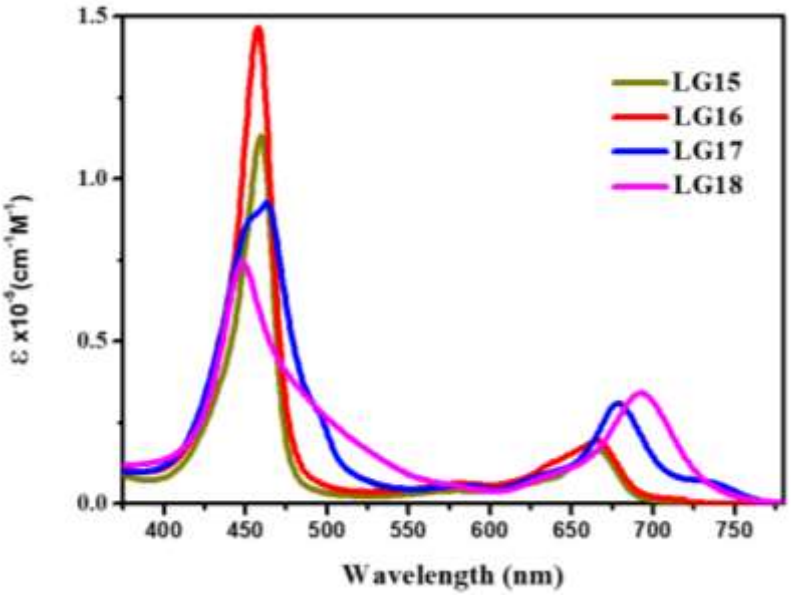

Figure S13. *UV–visible absorption spectra of LG15-LG18 in THF solvent.*

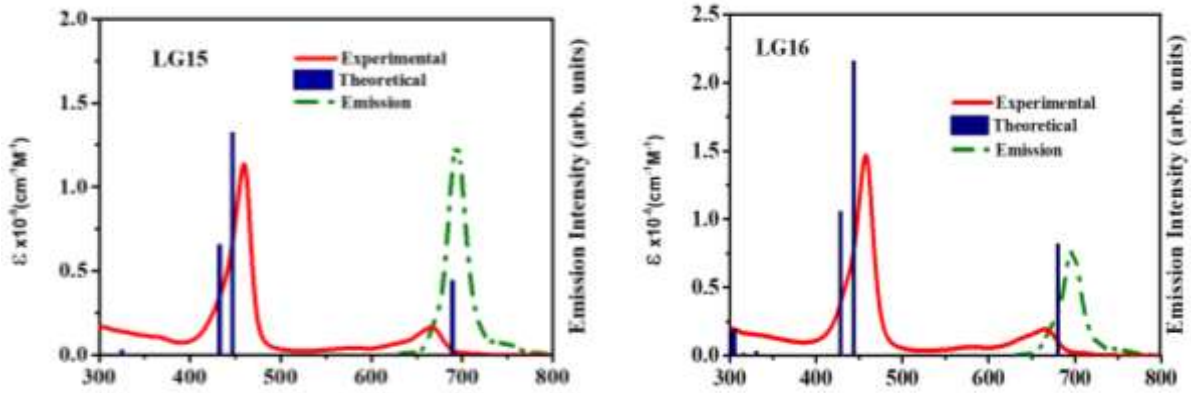

Figure S14. *Theoretical absorption spectra of LG15, LG16 Dyes by using B3LYP method PCM model in tetrahydrofuran solvent with M06-2X function.*

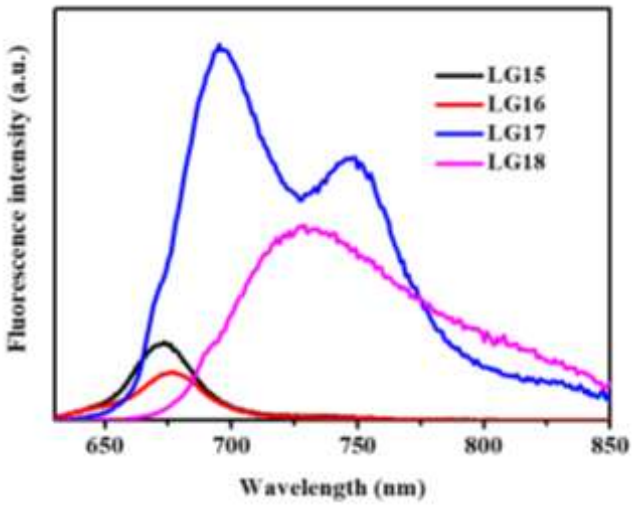

Figure S15. *Fluorescence spectra of **LG15**, **LG16**, **LG17 and LG18** in THF solution.*

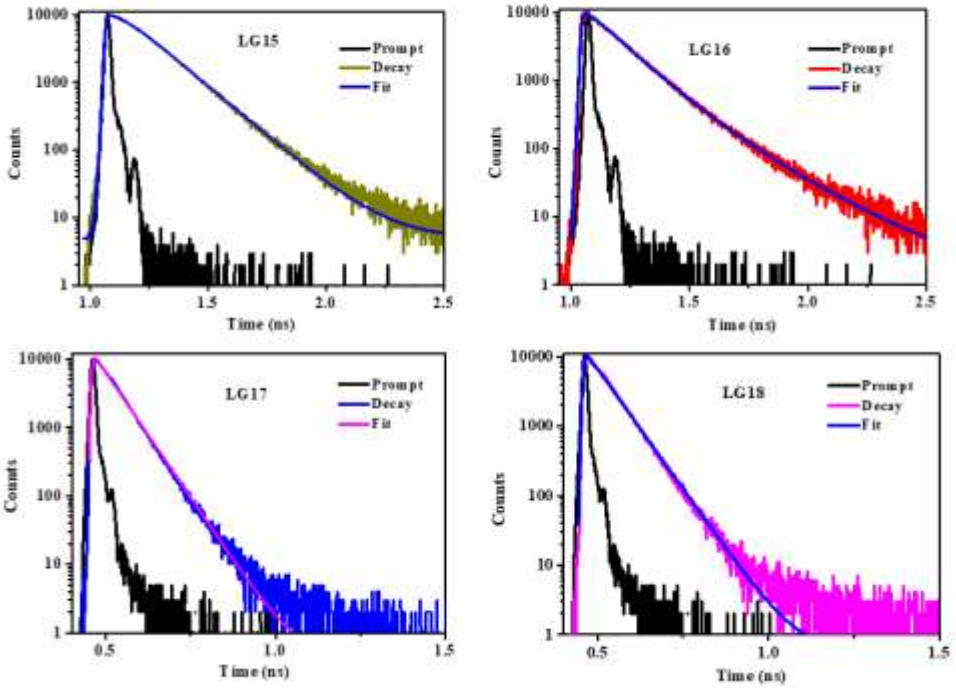

Figure S16. *Singlet excited-state lifetimes of* ***LG15****,* ***LG16, LG17 and LG18*** *in THF solution.*

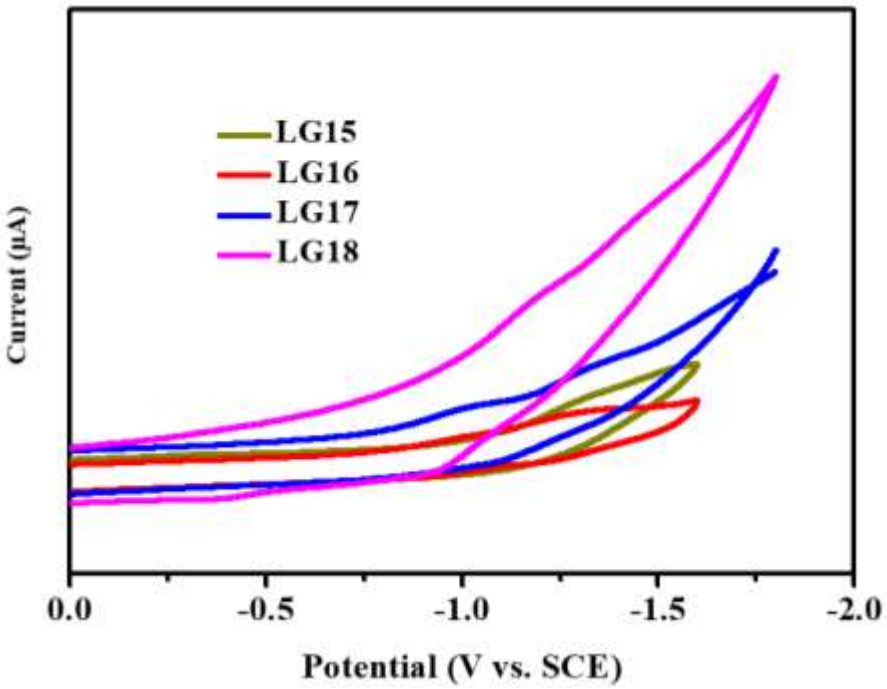

Figure S17. *Cyclic Voltammorgraame of* ***LG15, LG16, LG17 and LG18*** *in* ***THF.***

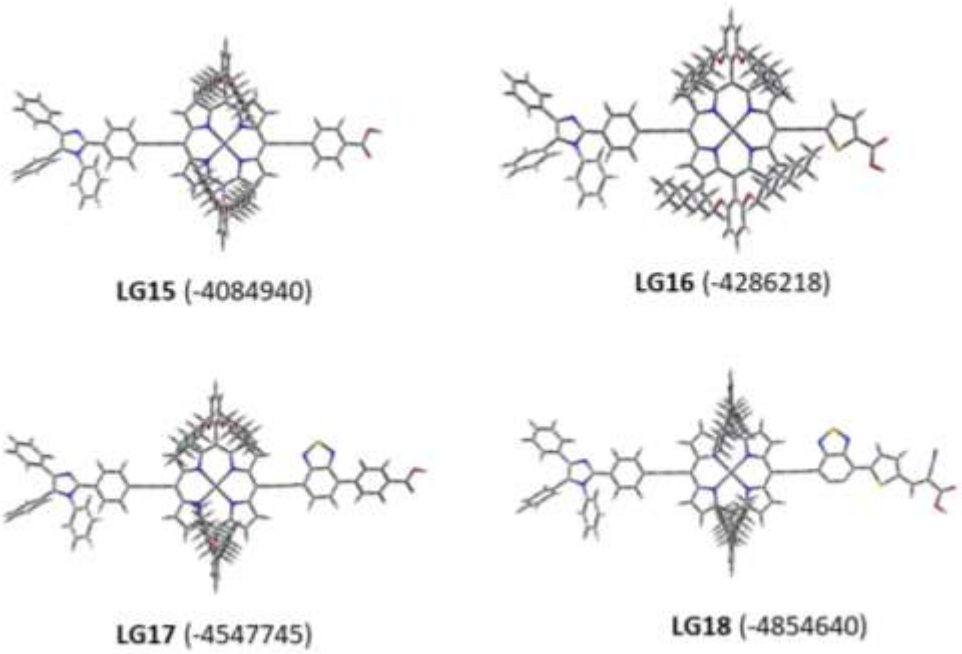

Figure S18. *Optimized structure of **LG15, LG16, LG17** and **LG18** dyes.*

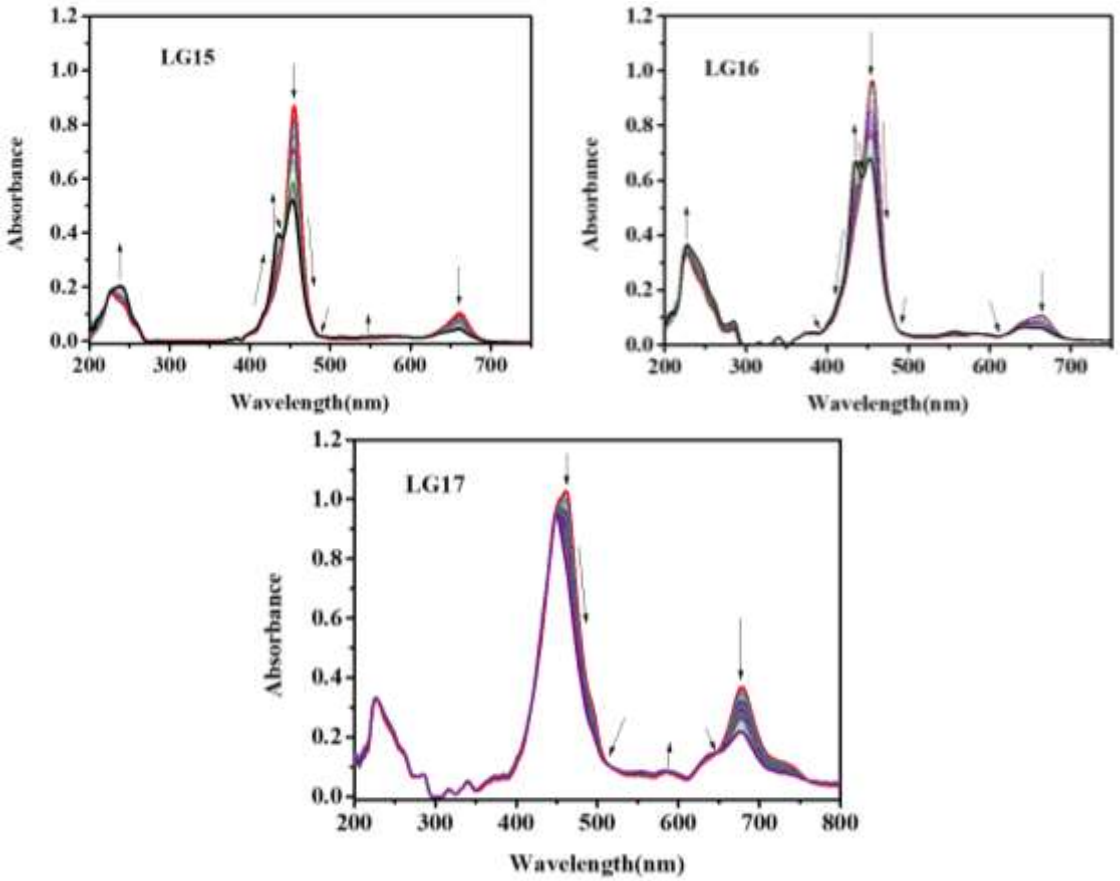

Figure S19. *Oxidative OTTLE studies of LG15, LG16, LG17 series sensitizers in 0.3M TBAP/THF with an applied potential of +0.90V (vs. SCE/KCl).*

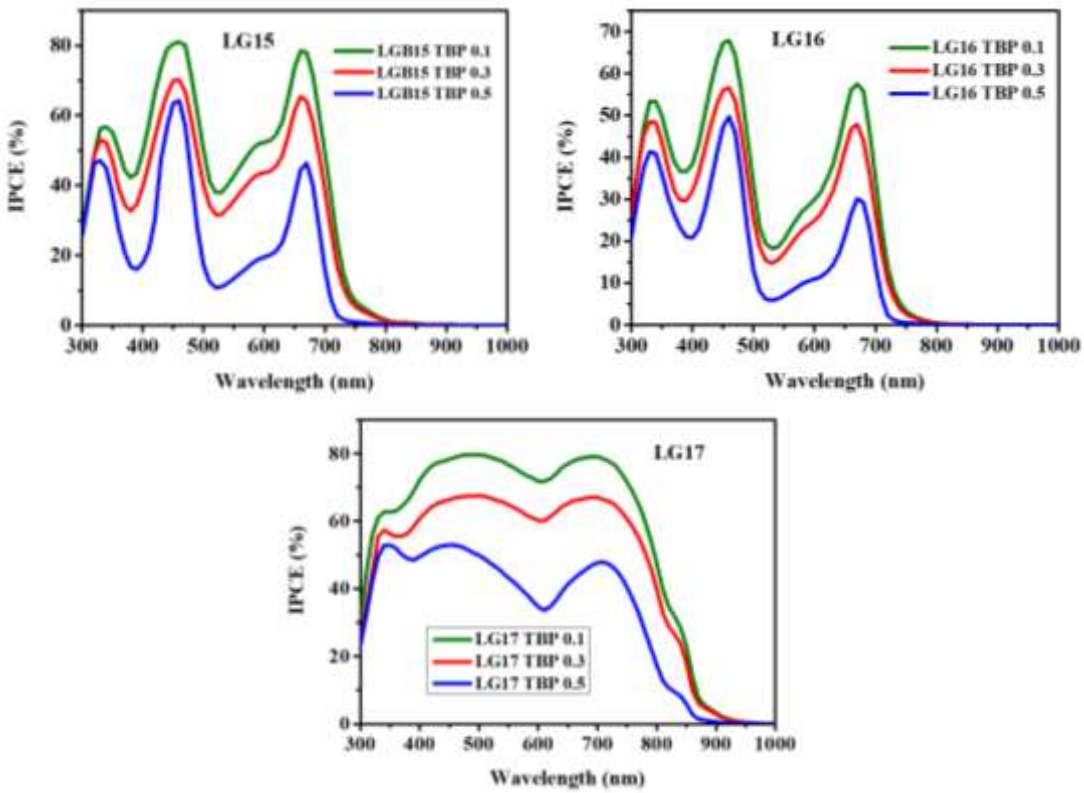

Figure S20. *Photocurrent action spectra porphyrin sensitizers using different concentrations of* 4-*tert* butylpyridine.

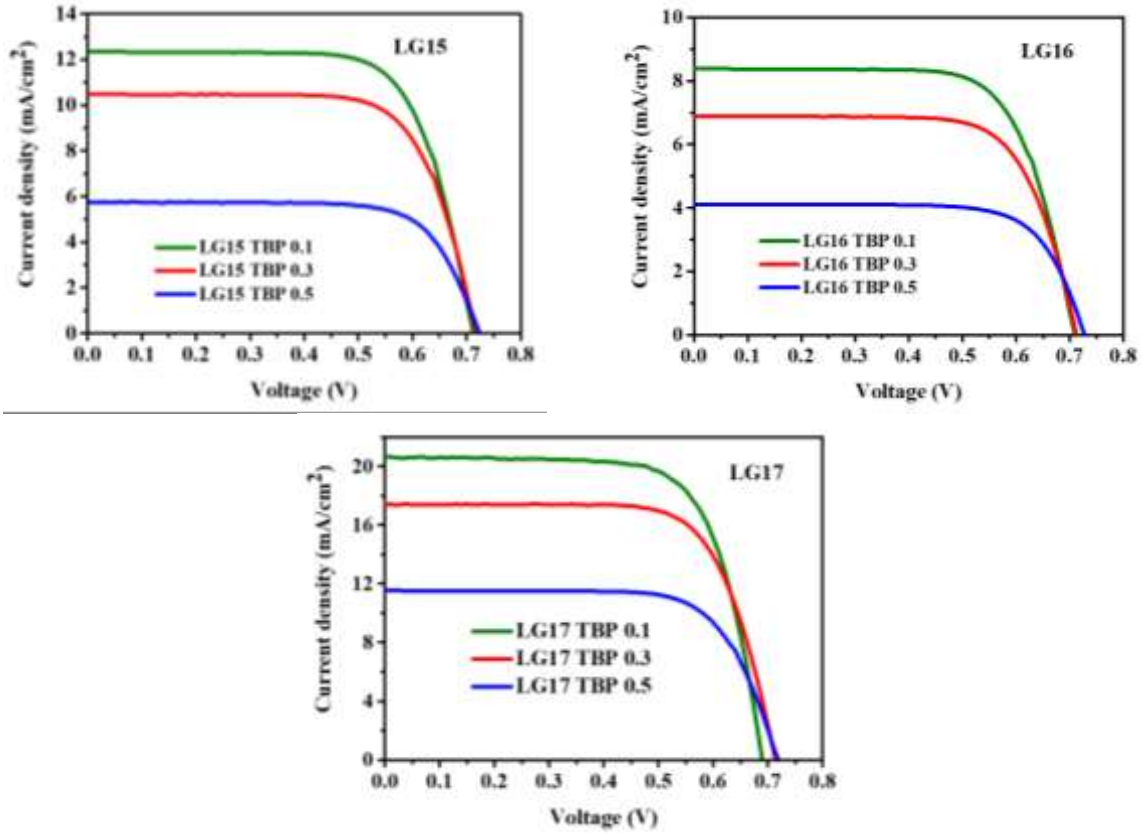

Figure S21. *Current–voltage characteristics of porphyrin sensitizers using different concentrations of 4-tert butylpyridine***.**

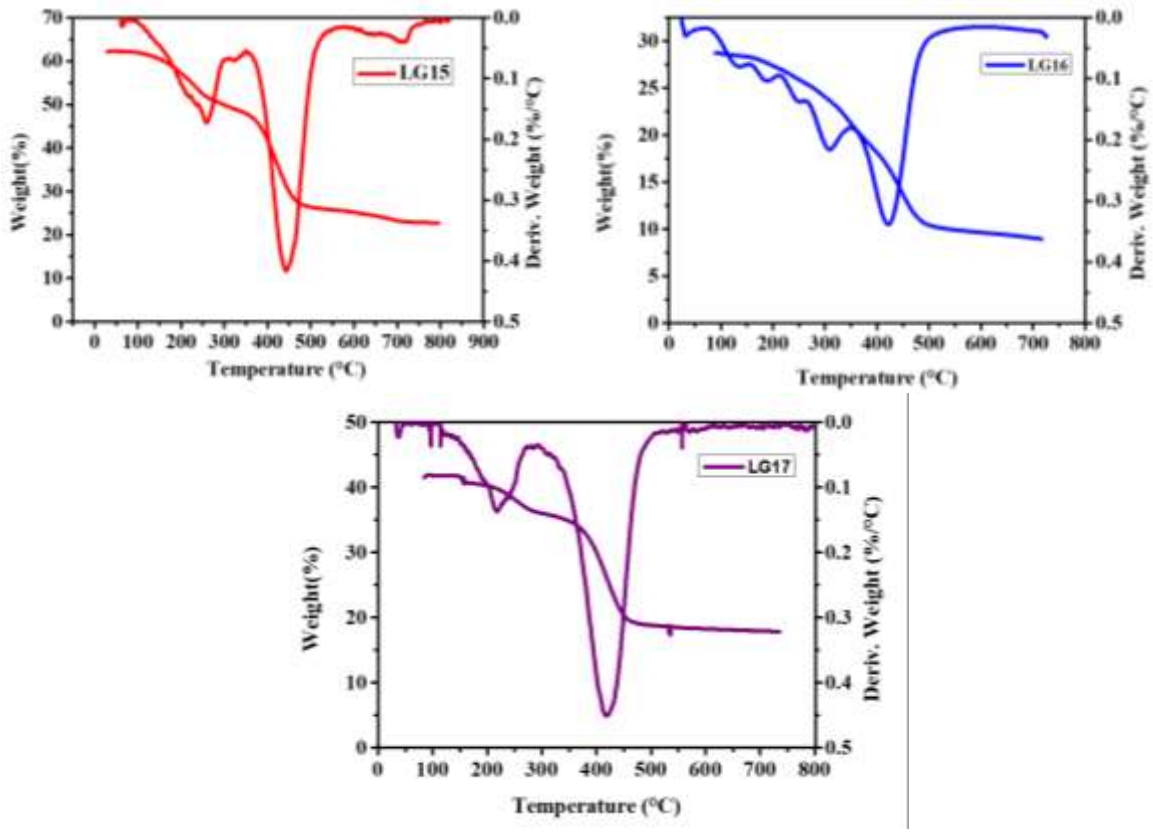

Figure S22. *TG/DTG curves of **LG15, LG16 and LG17** porphyrins with heating rate 10 °C.min-1 under nitrogen.*

Table 1: Optimized energies, HOMO-LUMO energies and ground state dipole moment 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-Lgap	[c] μ
LG15	-4084940)	-4.689	-2.431	2.25	4.785
LG16	-4286218	-4.698	-2.498	2.20	6.193
LG17	-4547745	-4.678	-2.701	1.97	6.284
LG18	-4854640	-4.849	-3.222	1.62	15.281

[a]Total minimum energy of **LG15-LG18**, [b]values in eV, [c]values in debye units.

Table 2: 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 15	441	2.652	3.014	H-1→L+1 (74%), HOMO→LUMO (17%) H-2→LUMO (3%), HOMO→L+3 (2%)
	555	0.014	2.231	H-1→LUMO (59%), HOMO→L+1 (39%)
	595	0.886	2.081	H-1→L+1 (16%), HOMO→LUMO (81%)
LG 16	440	2.592	2.991	H-1→L+1 (75%), HOMO→LUMO (15%) H-2→LUMO (2%)
	557	0.016	2.223	H-1→LUMO (59%), HOMO→L+1 (38%)
	603	0.987	2.052	H-1→L+1 (15%), HOMO→LUMO (82%)
LG 17	450	1.049	2.754	H-1→L+2 (30%), HOMO→L+1 (44%) H-3→LUMO (7%), H-3→L+1 (3%), H-2→L+1 (2%), HOMO→LUMO (9%)
	559	0.017	2.215	H-1→LUMO (54%), HOMO→L+2 (37%) H-1→L+1 (7%)
	616	1.273	2.011	H-1→L+2 (12%), HOMO→LUMO (81%), HOMO→L+1 (3%)
LG 18	441	0.226	2.807	H-1→LUMO (44%), H-1→L+1 (14%), HOMO→L+2 (37%), H-1→L+4 (3%)
	578	0.041	2.143	H-1→LUMO (54%), H-1→L+1 (19%), HOMO→L+2 (25%)
	692	2.384	1.789	HOMO→LUMO (83%) H-3→L+1 (2%), H-2→LUMO (3%), H-1→L+2 (4%), HOMO→L+1 (6%)

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