Efficient near IR porphyrins containing triphenylamine substituted anthryl donating group for dye sensitized solar cells

Jonnadula Venkata Suman Krishna,[a,b] Devulapally Koteshwar,[a,b] Towhid H. Chowdhury,[c] Suryaprakash Singh, [a,b] Idriss Bedja,[d] Ashraful Islam*[,c] Lingamallu Giribabu*[a,b]

Polymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Habsiguda, Hyderabad-500007, (Telangana), India .Email: giribabu@iict.res.in. Phone: +91-40-27191724, Fax: +91-40-27160921

Academy of Scientific and Innovative Research, CSIR-Indian Institute of Chemical Technology, India.

Photovoltaic Materials Unit, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan.Email: slam.Asraful@nims.go.jp

Cornea Research Chair, Optometry Department, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia

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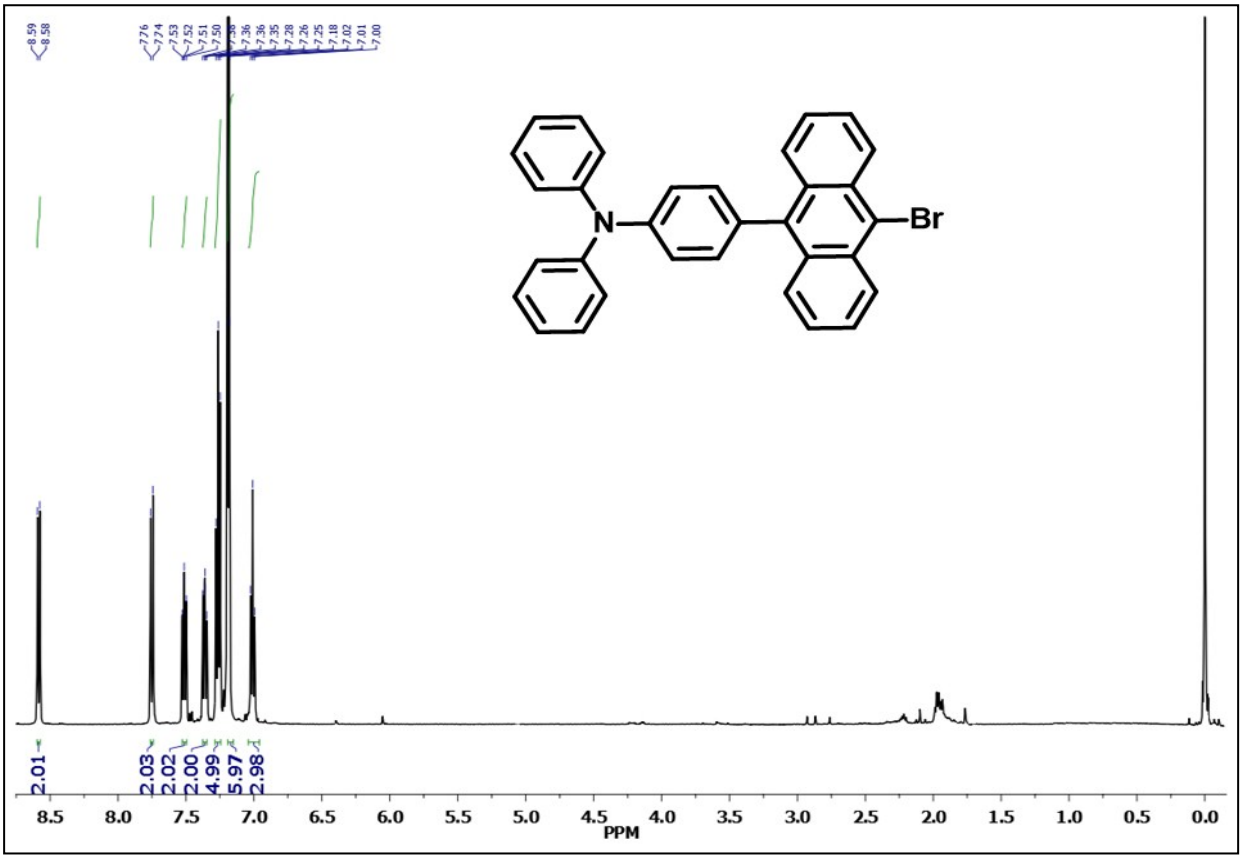

Figure S1. *^{1}H NMR spectrum (500 MHz, CDCl3) of **1**.*

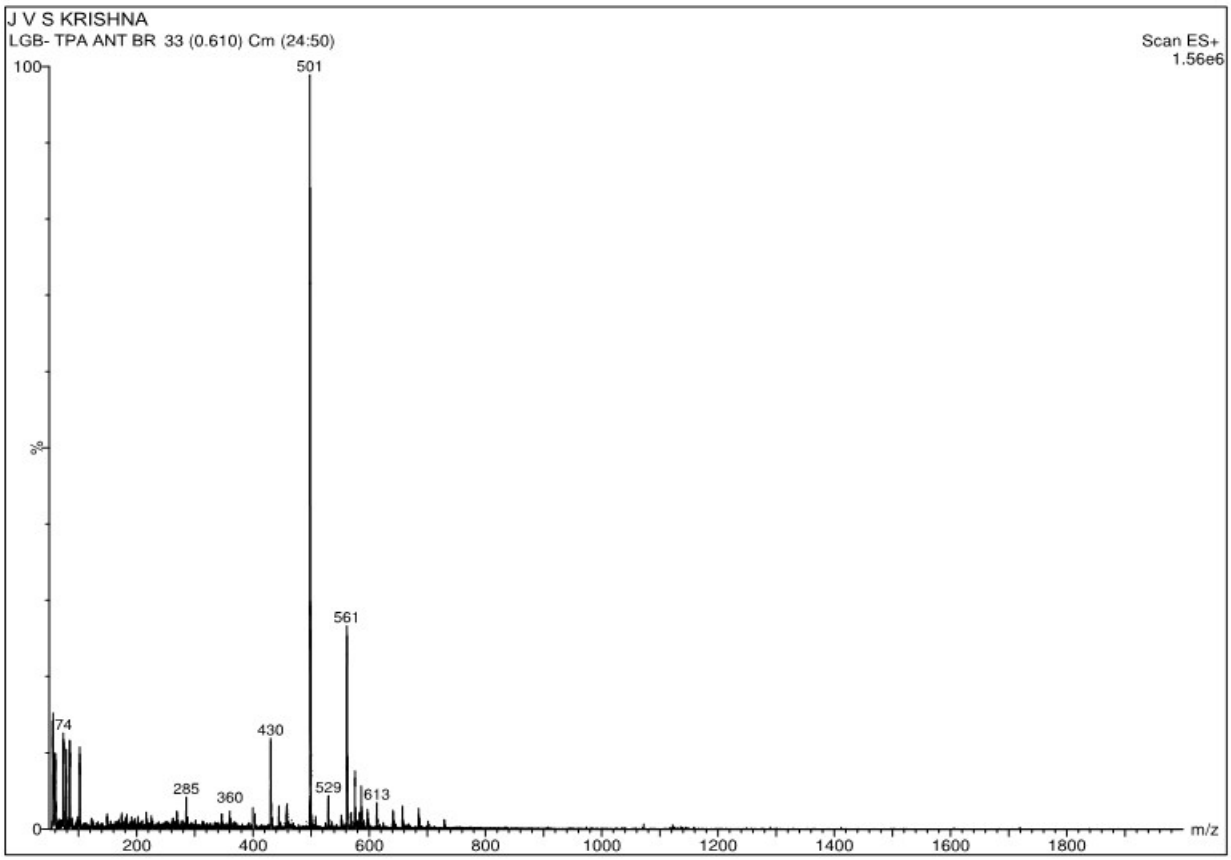

Figure S2. *HRMS of **1** (APPI-FTMS).*

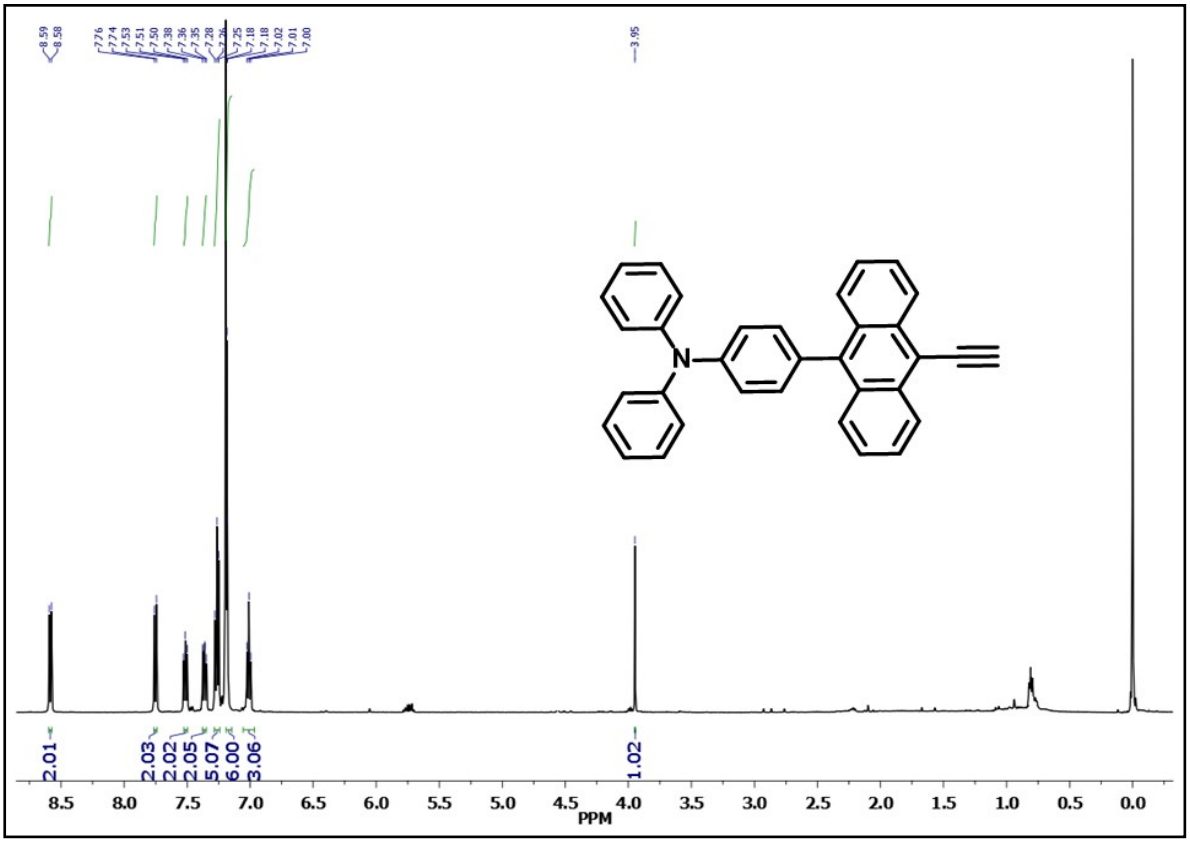

Figure S3. *[1]H NMR spectrum (500 MHz, CDCl3) of **2**.*

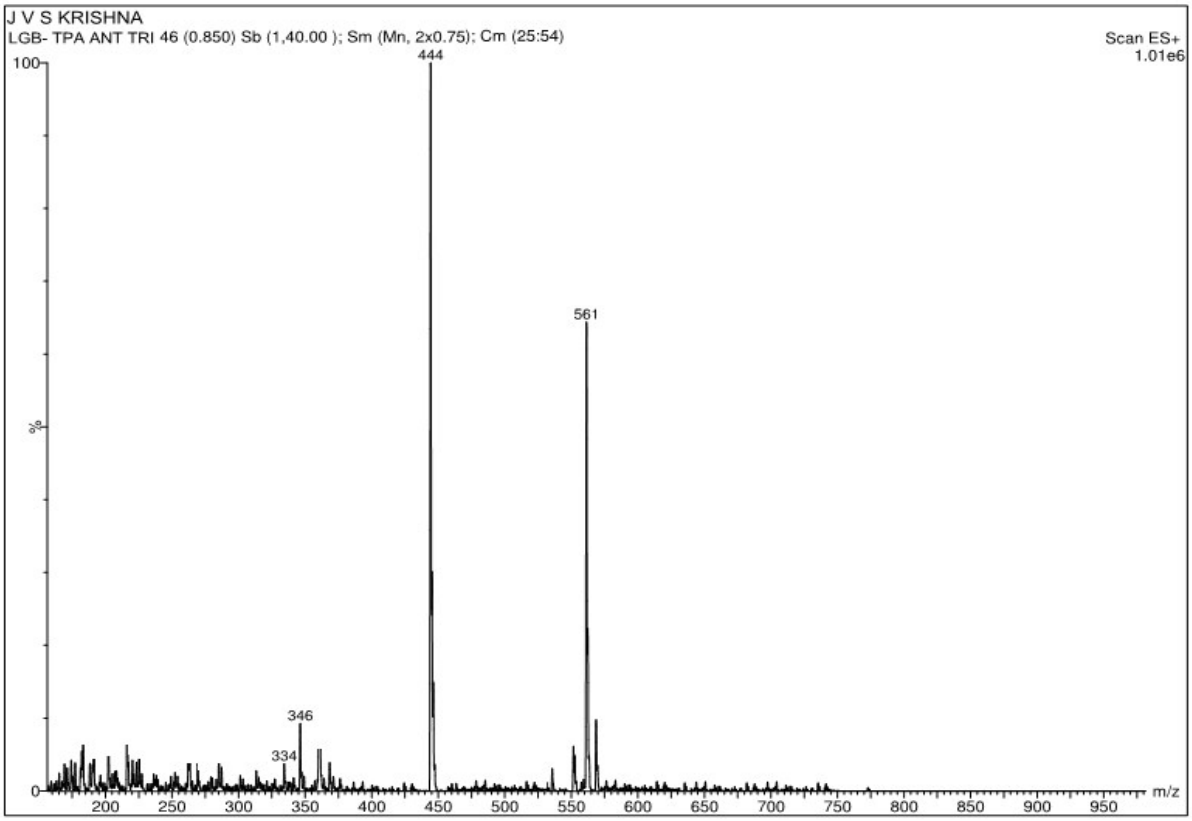

Figure S4. *HRMS of* ***2*** *(APPI-FTMS).*

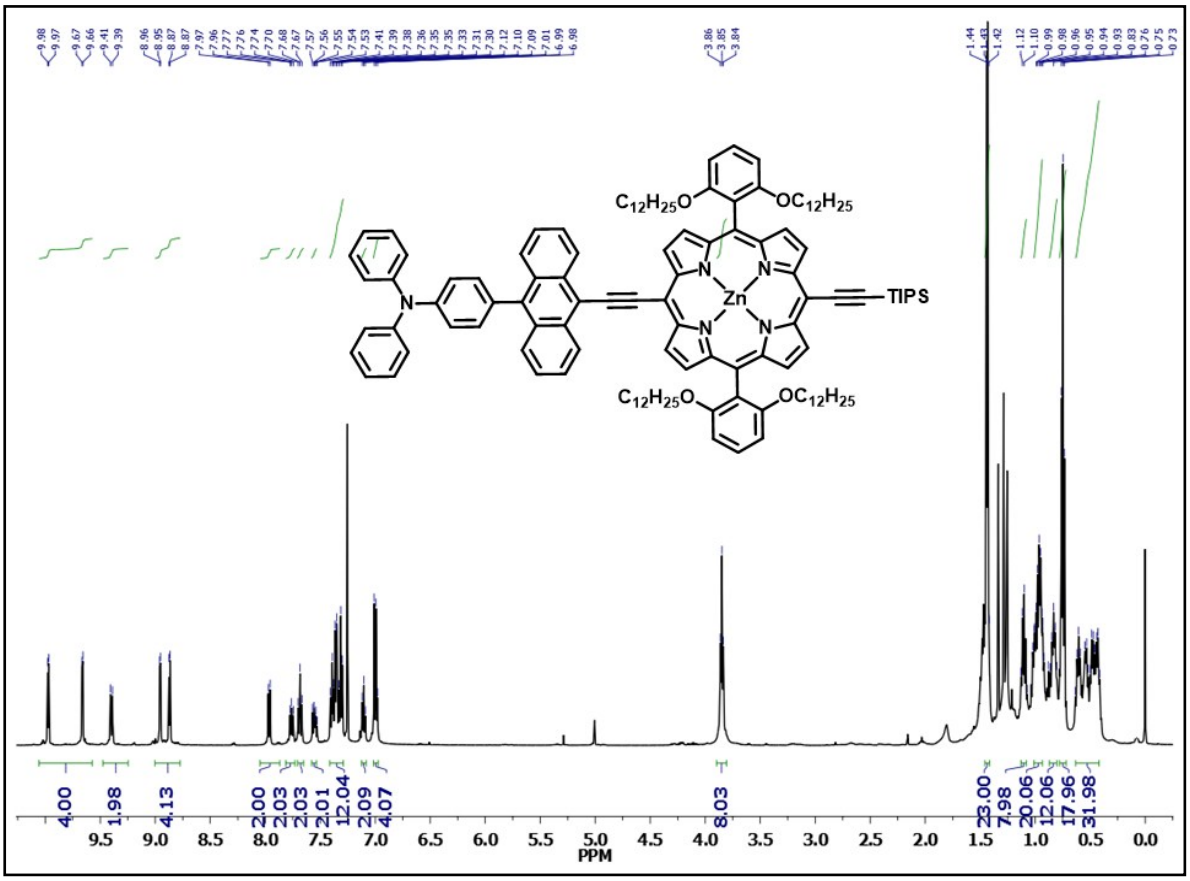

Figure S5. *[1]H NMR spectrum (500 MHz, CDCl3) of* ***4*****.**

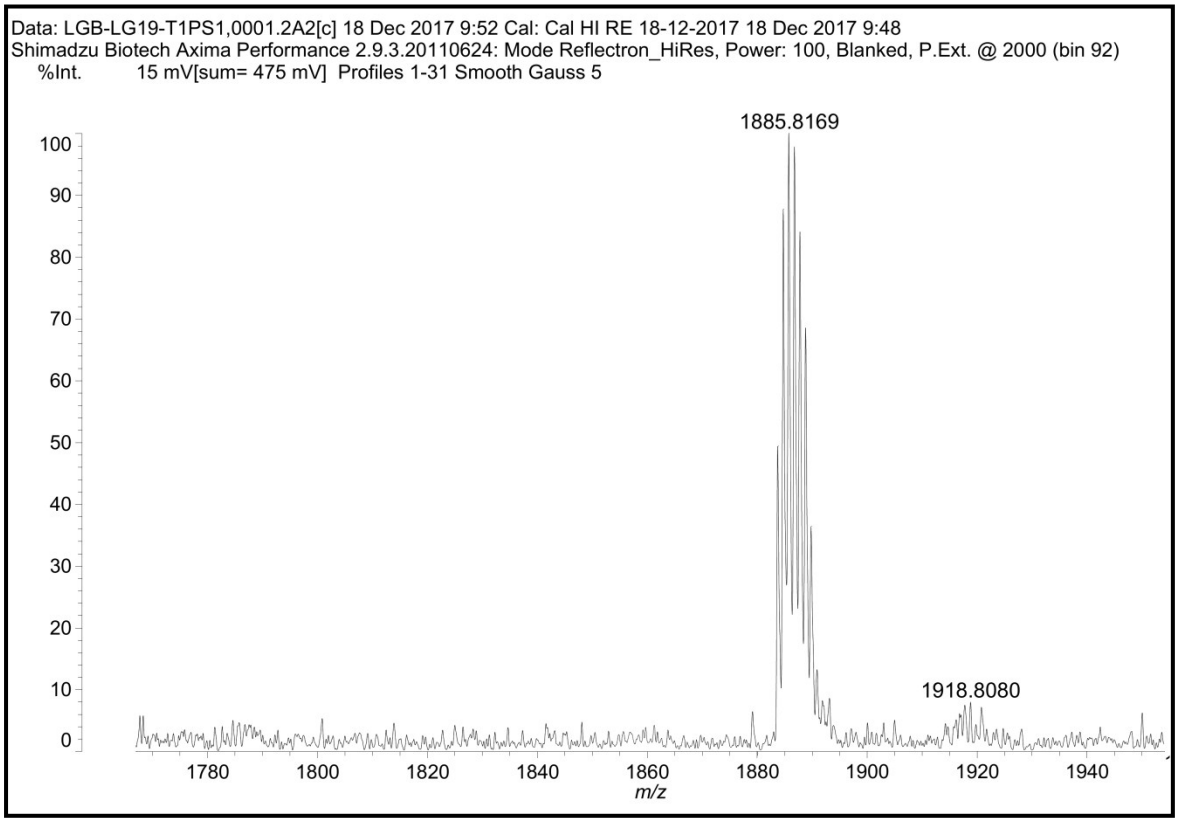

Figure S6. *MALDI-TOF of* ***4*****.**

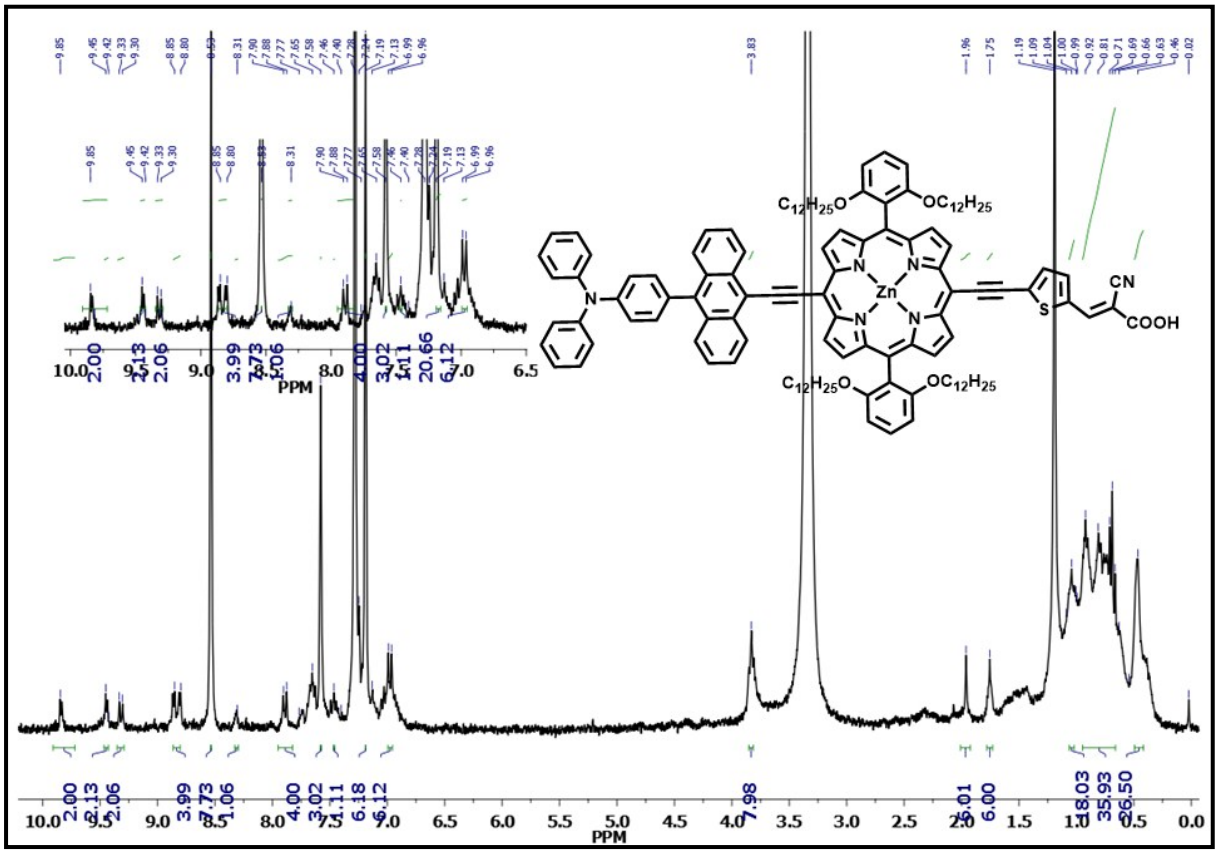

Figure S7. *[1]H NMR spectrum (500 MHz, CDCl3) of* ***LG19****.*

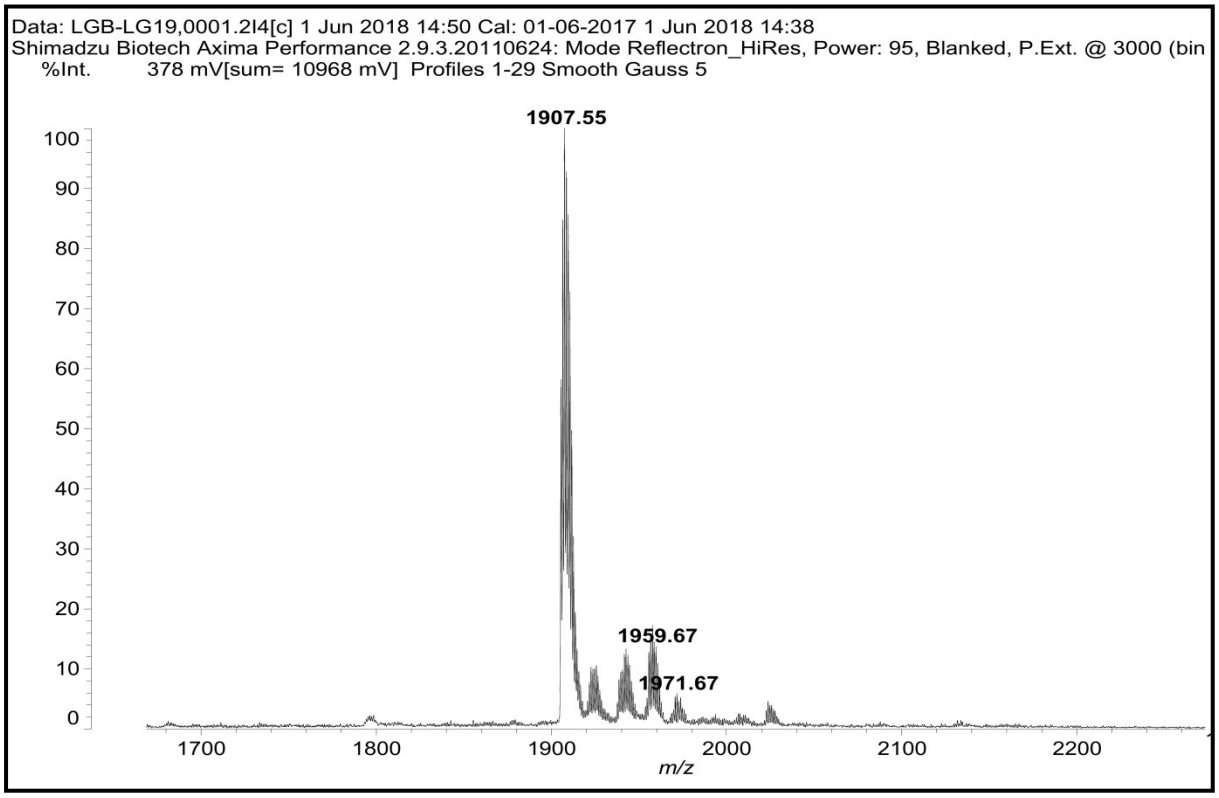

Figure S8. *MALDI-TOF of* ***LG19.***

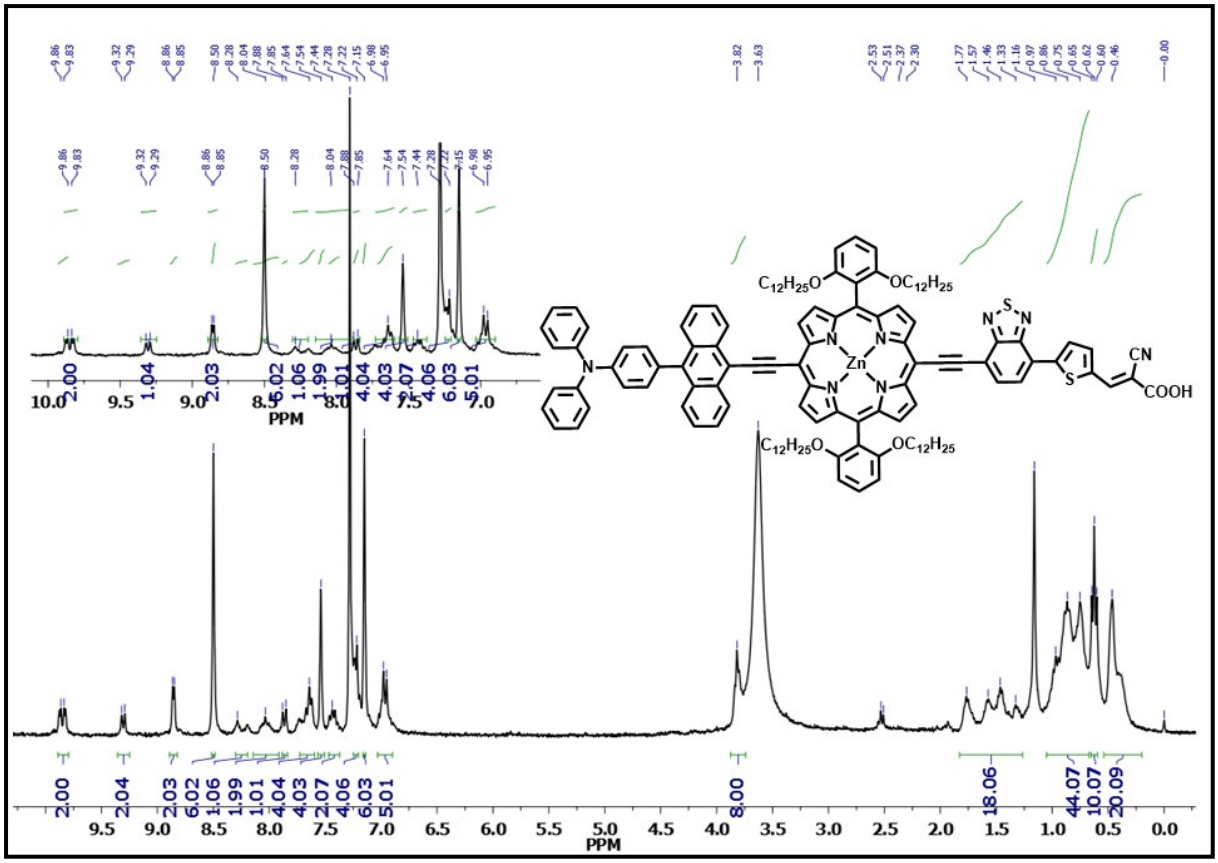

Figure S9. *[1]H NMR spectrum (500 MHz, CDCl3) of* ***LG20****.*

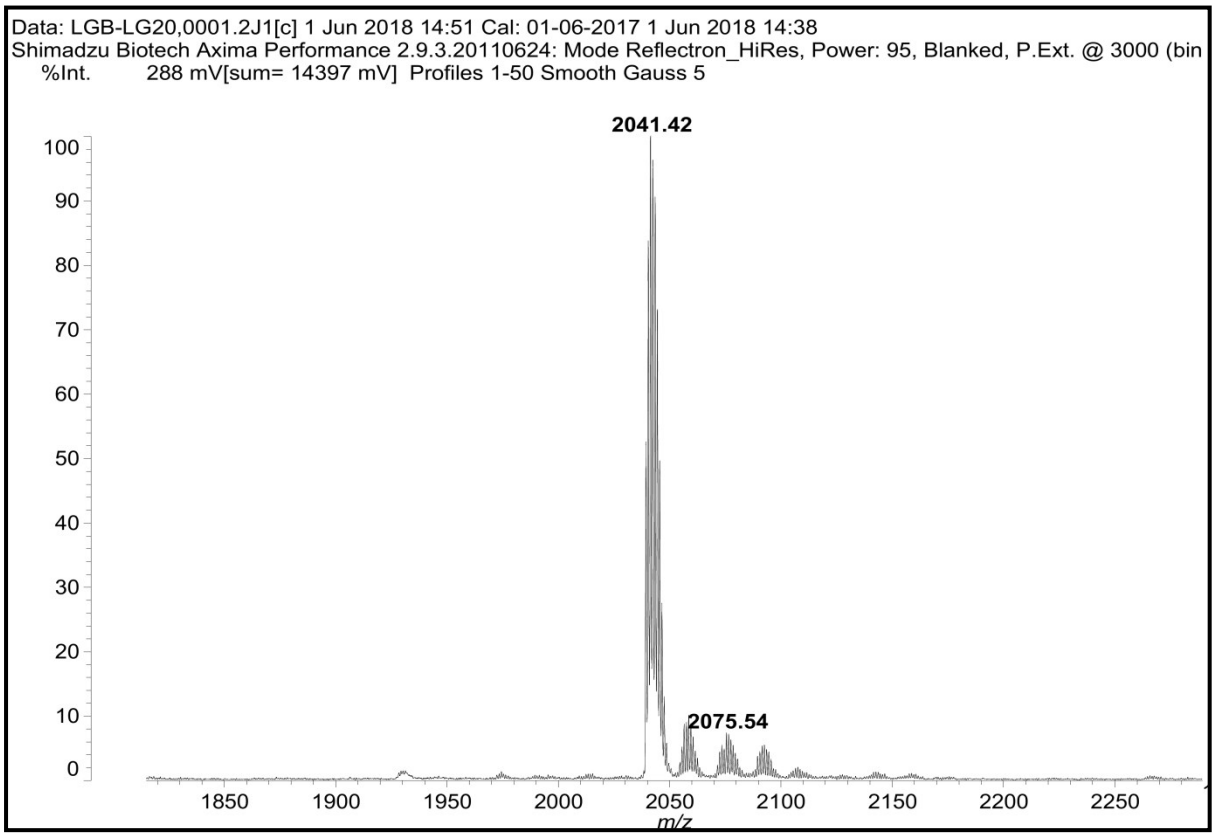

Figure S10. *MALDI-TOF of* ***LG20****.*

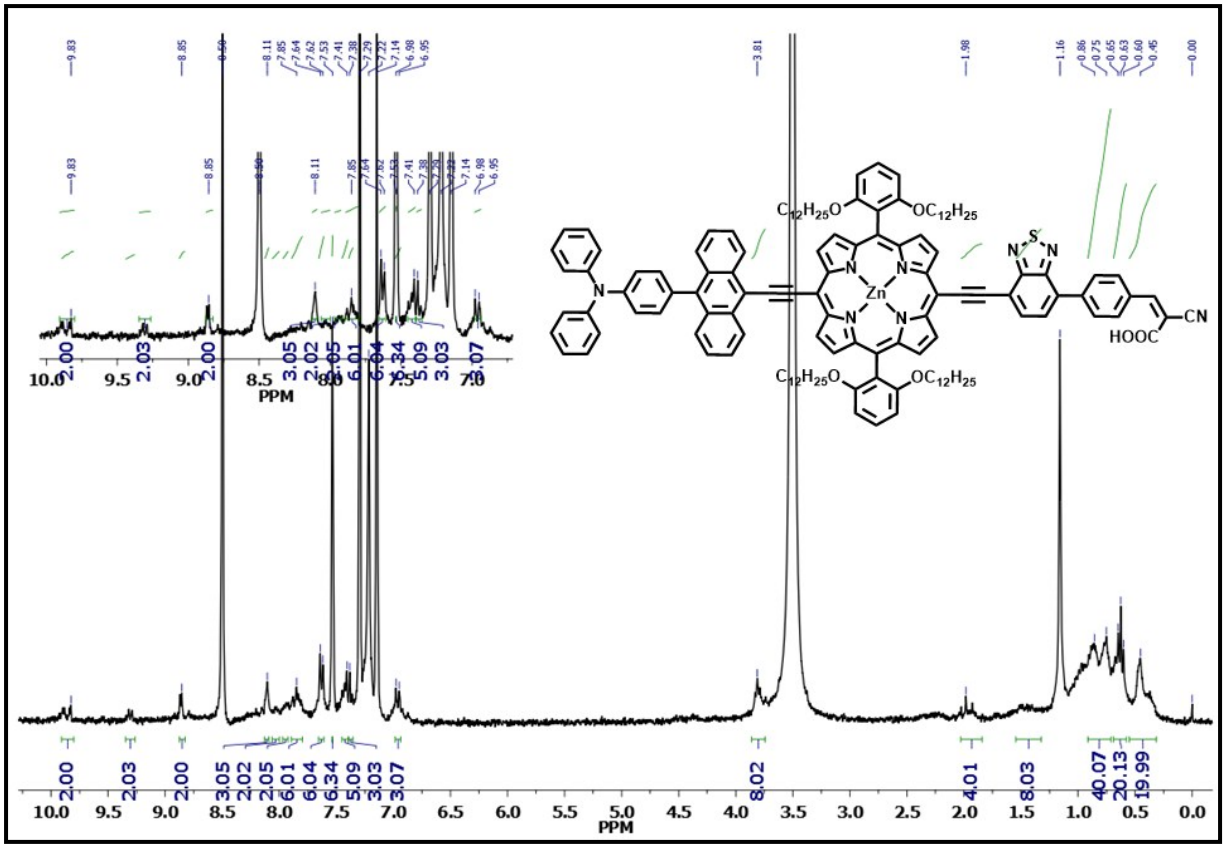

Figure S11. *[1]H NMR spectrum (500 MHz, CDCl3) of* ***LG21****.*

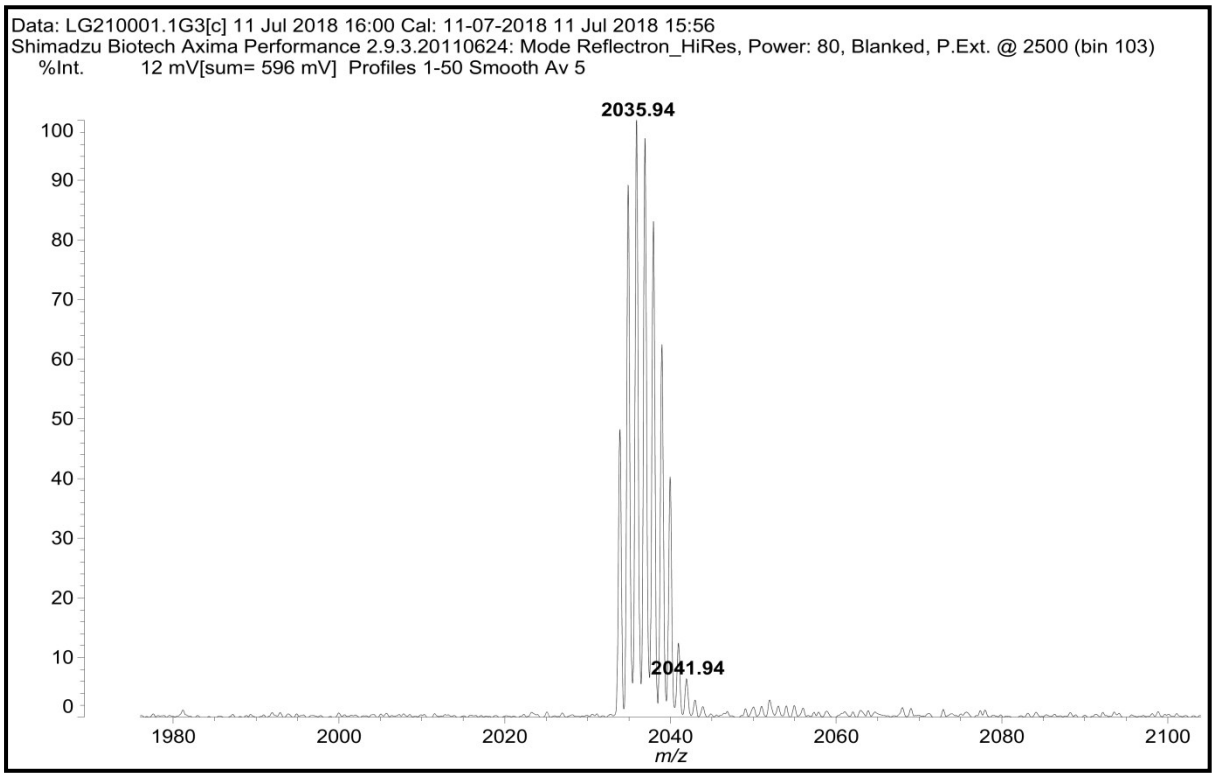

Figure S12. *MALDI-TOF of* ***LG21****.*

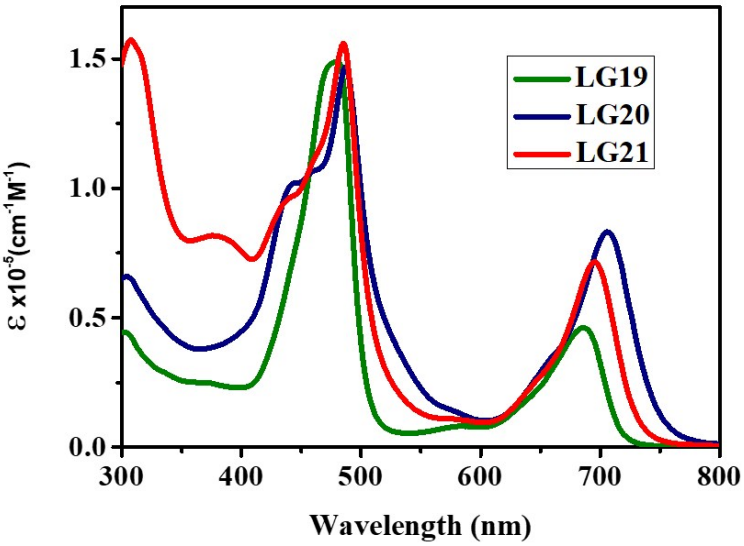

Figure S13. *UV–visible absorption spectra of **LG19, LG20** and **LG21** in THF solvent.*

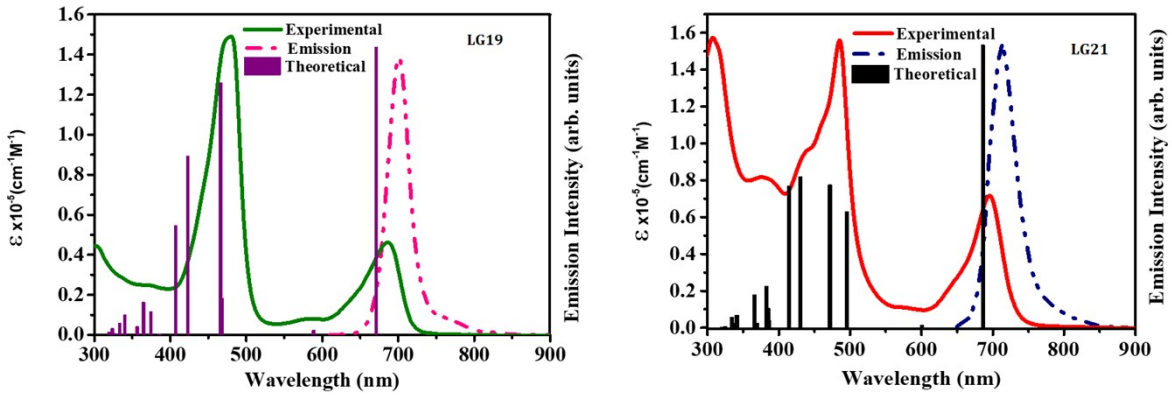

Figure S14. *Theoretical absorption spectra of **LG19**, **LG21** Dyes by using B3LYP method PCM model in tetrahydrofuran solvent with M06-2X function.*

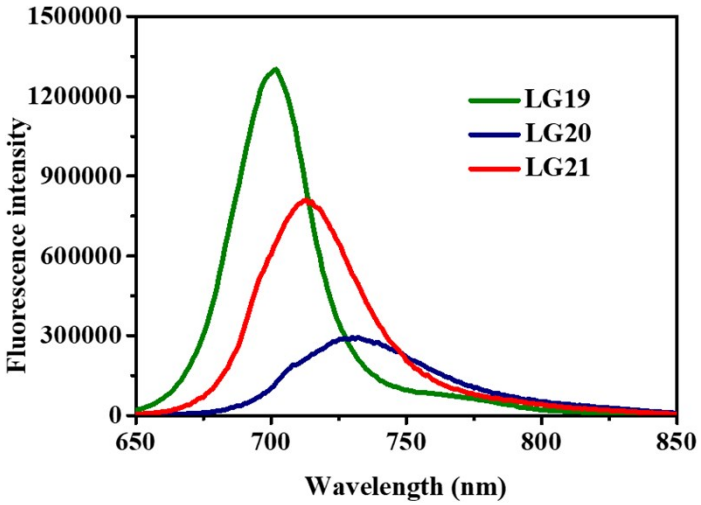

Figure S15. *Fluorescence spectra of **LG19, LG20** and **LG21** in THF solution.*

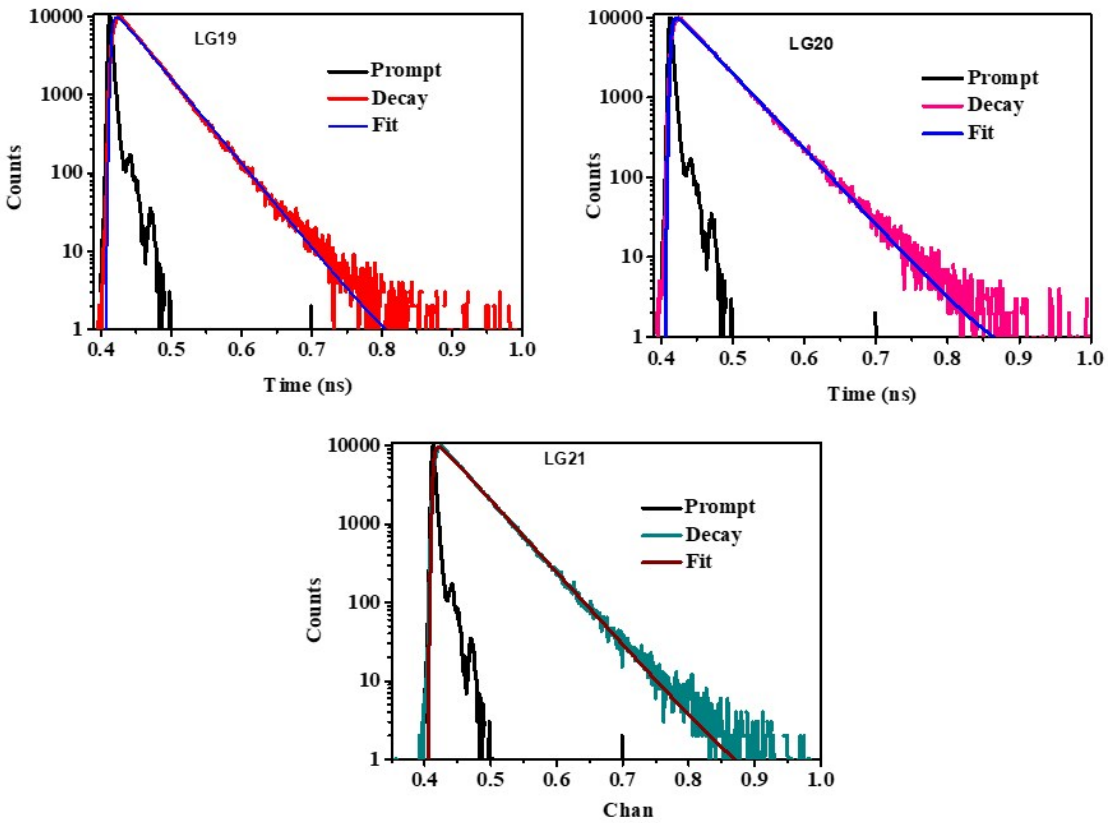

Figure S16. *Singlet excited-state lifetimes of **LG19, LG20** and **LG21** in THF solution.*

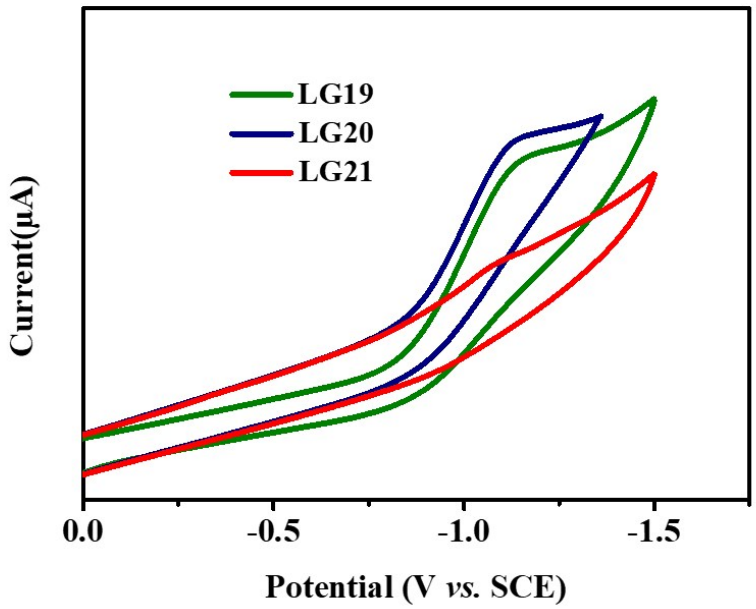

Figure S17. *Reduction spectra of dyes **LG19, LG20** and **LG21** in THF.*

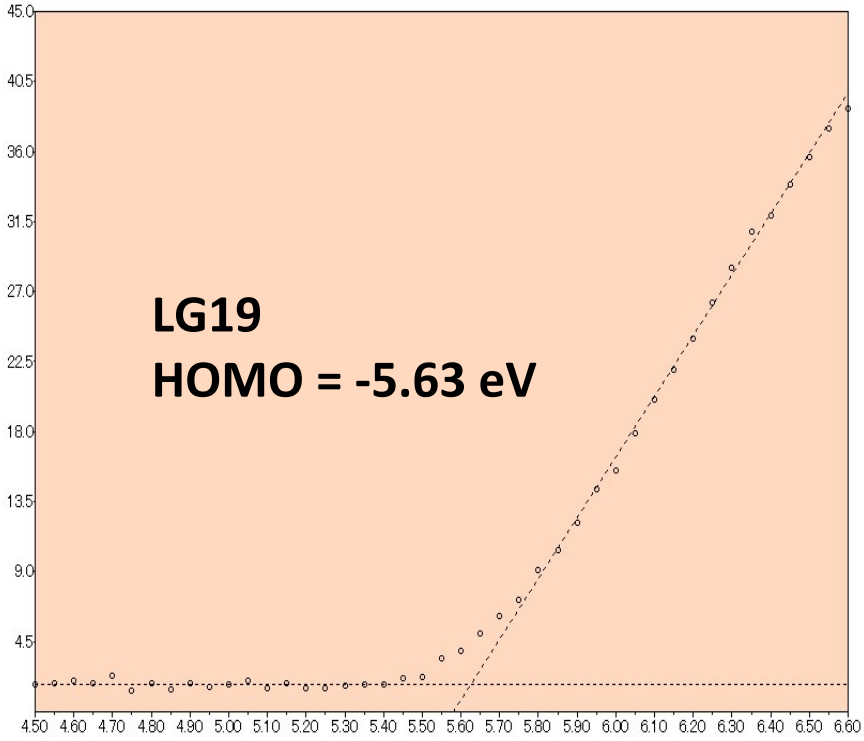

Figure S18. *Ionization potential (IP) of LG19 anchored to TiO_2 film*

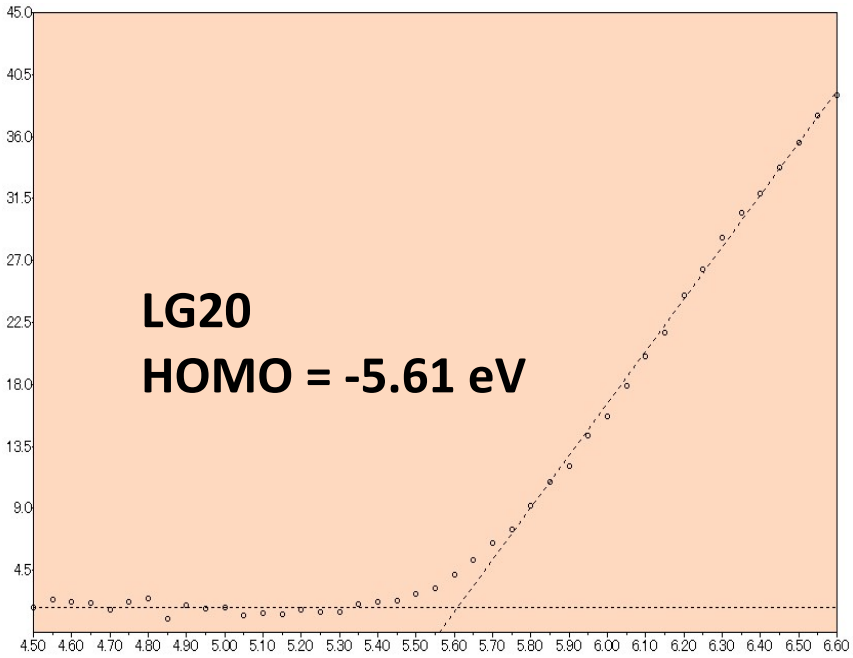

Figure S19. *Ionization potential (IP) of LG20 anchored to TiO_2 film*

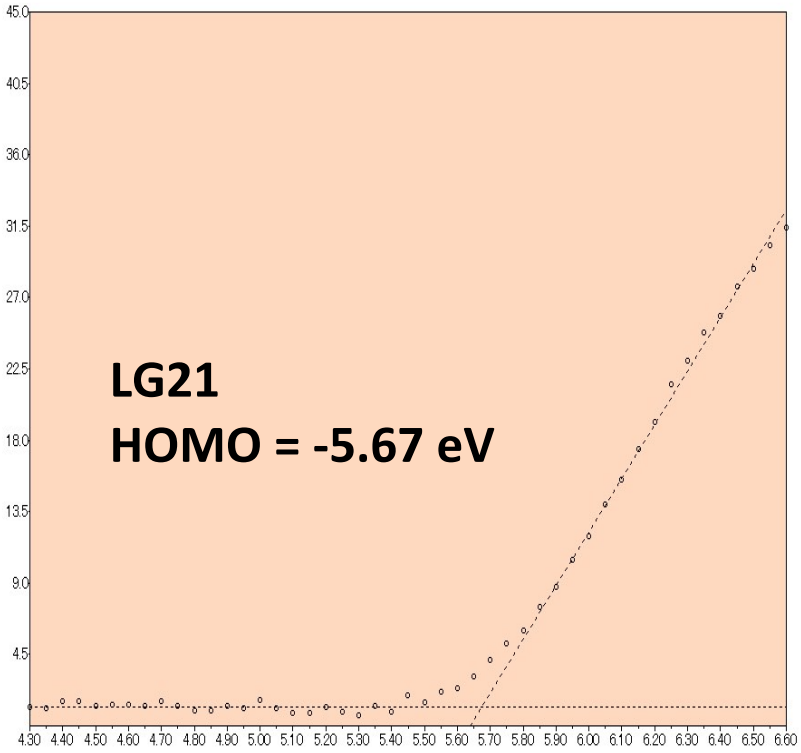

Figure S20. *Ionization potential (IP) of LG21 anchored to TiO_2 film*

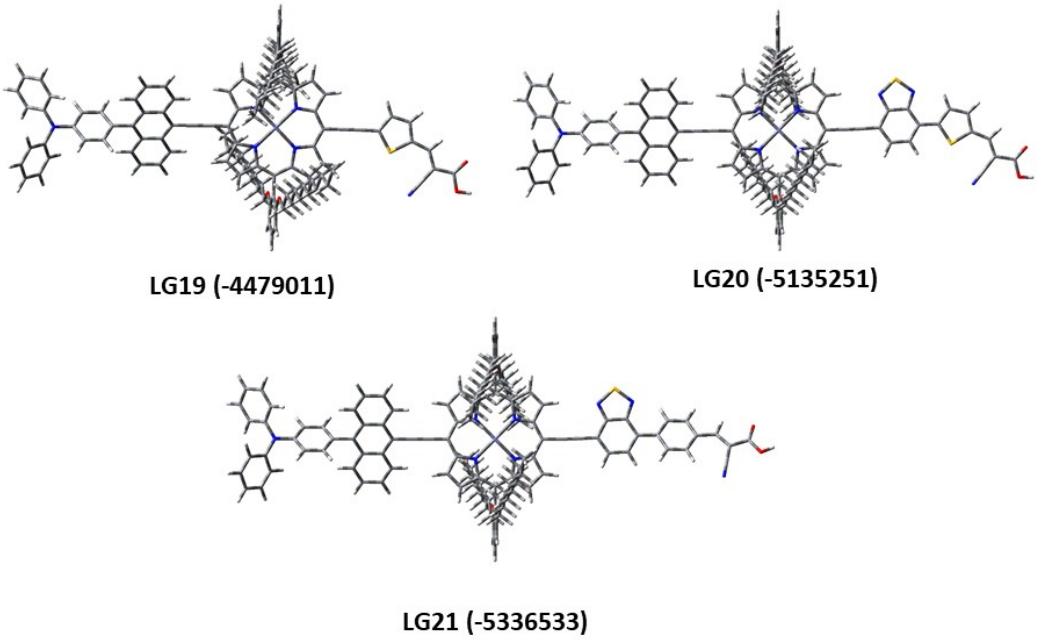

Figure S22. *Optimized structure of **LG19, LG20** and **LG21** dyes.*

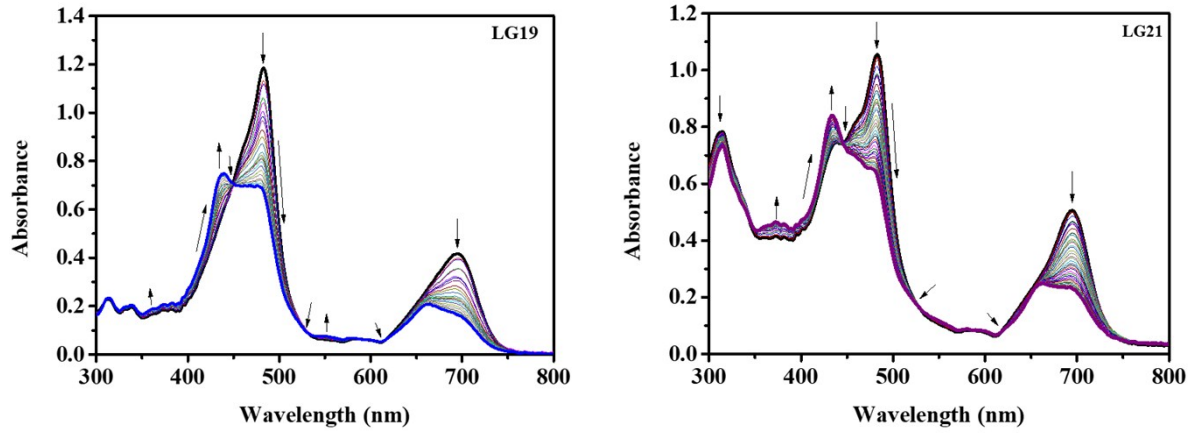

***Figure S21.** Oxidative OTTLE studies of **LG19** and **LG21** sensitizers in 0.3M TBAP/THF with an applied potential of +0.90V (vs. SCE/KCl).*

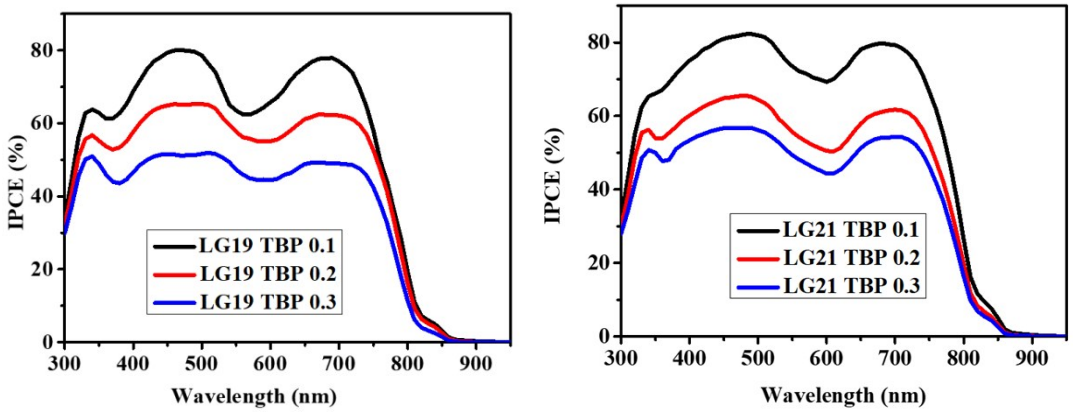

***Figure S23.** Photocurrent action spectra of **LG19** and **LG21** using different concentrations of TBP.*

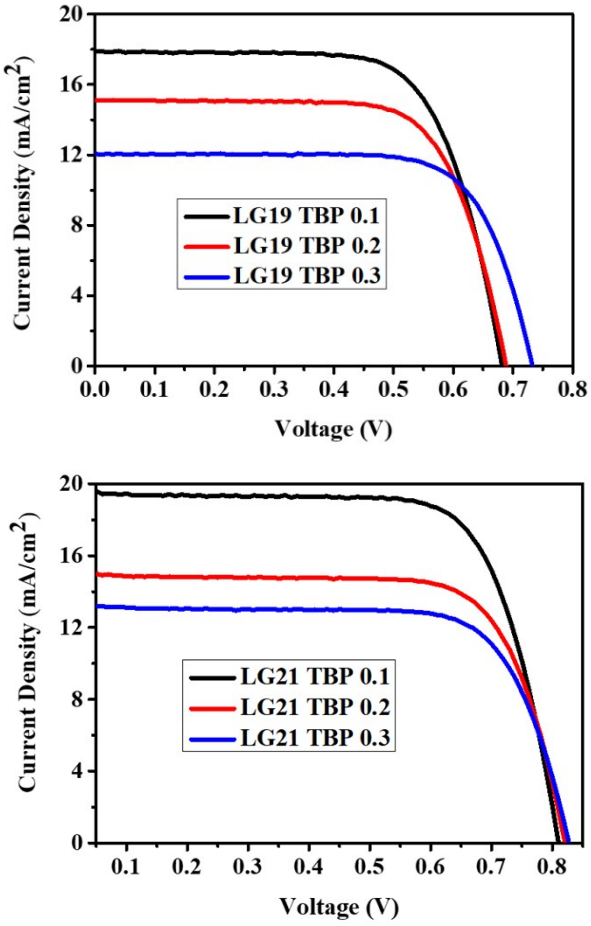

Figure S24. *Current–voltage characteristics of* ***LG19*** *and* ***LG21*** *using different concentrations of TBP.*

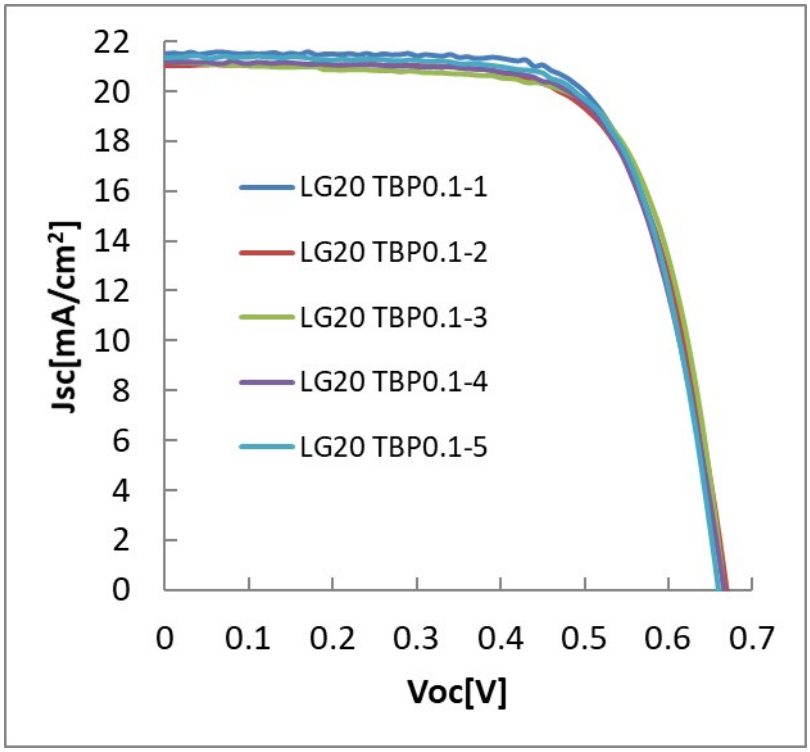

Figure S25. *Current–voltage characteristics of* ***LG20*** *based devices using 0.1M TBP.*

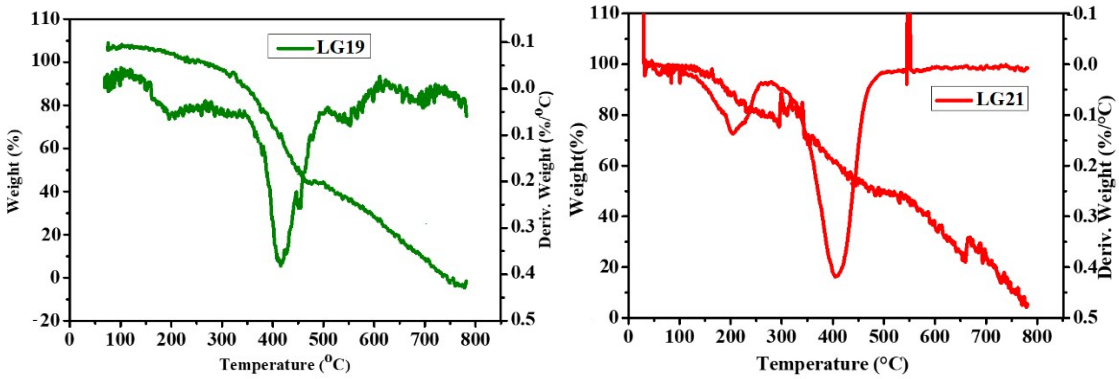

Figure S26. *TG/DTG curves of* ***LG19***, ***LG21*** *porphyrins with heating rate 10 °C.min^{-1} under nitrogen using 10 mg of sample.*

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]μ
LG19	-4479011	-4.735	-2.805	1.93	7.8143
LG20	-5135251	-4.709	-3.079	1.63	8.3739
LG21	-5336533	-4.687	-2.923	1.76	7.8459

[a]Total minimum energy of **LG19-LG21**, [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]λ_{max}	[b]f	[c]E (eV)	% of Molecular Orbital Contribution
LG19	454	0.195	2.727	H-3->LUMO (38%), H-2->LUMO (17%), HOMO->L+1 (19%) H-3->L+1 (4%), H-3->L+3 (2%), H-1->L+2 (5%), HOMO->L+3 (5%)
	565	0.024	2.192	H-1->LUMO (57%), HOMO->L+2 (31%) H-1->L+1 (6%)
	641	1.527	1.933	HOMO->LUMO (81%) H-2->LUMO (2%), H-1->L+2 (8%), HOMO->L+1 (4%)
LG20	468	0.595	2.727	H-3->LUMO (25%), H-3->L+1 (14%), H-2->LUMO (12%), H-1->L+2 (23%), H-2->L+1 (6%), HOMO->LUMO (6%), HOMO->L+4 (7%)
	567	0.022	2.185	H-1->LUMO (44%), H-1->L+1 (20%), HOMO->L+2 (31%)
	665	1.987	1.861	HOMO->LUMO (74%), HOMO->L+1 (11%)H-4->L+1 (2%), H-3->LUMO (3%), H-2->LUMO (2%), H-1->L+2 (5%)
LG21	470	0.667	2.634	HOMO->LUMO (74%), HOMO->L+1 (11%)H-4->L+1 (2%), H-3->LUMO (3%), H-2->LUMO (2%), H-1->L+2 (5%)
	562	0.017	2.203	H-1->LUMO (48%), H-1->L+1 (12%), HOMO->L+2 (34%)
	643	1.624	1.944	HOMO->LUMO (75%), H-1->L+2 (8%), HOMO->L+1 (9%)

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

Table S3: LG20 Devices data

Dye	LG20 TBP0.1-1	LG20 TBP0.1-2	LG20 TBP0.1-3	LG20 TBP0.1-4	LG20 TBP0.1-5

J_{sc}[mA/cm^2]	21.50	21.04	21.20	21.16	21.35
V_{oc}[V]	0.666	0.668	0.664	0.665	0.656
FF	0.698	0.708	0.693	0.698	0.709
η[%]	10.00	9.95	9.76	9.83	9.93