

## Effect of methoxy group/s on D- $\pi$ -A porphyrin based DSSC: efficiency enhanced by co-sensitization

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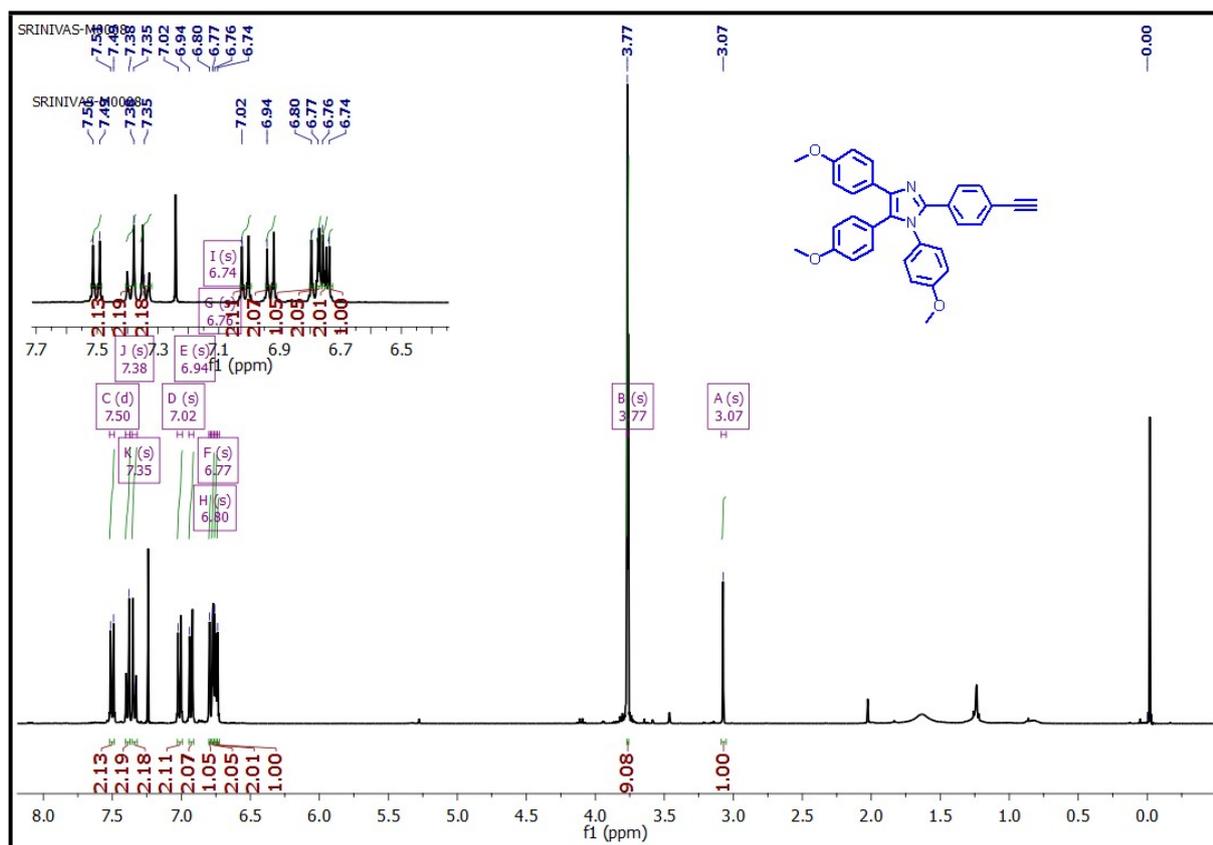


Figure S1.  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **D1**.

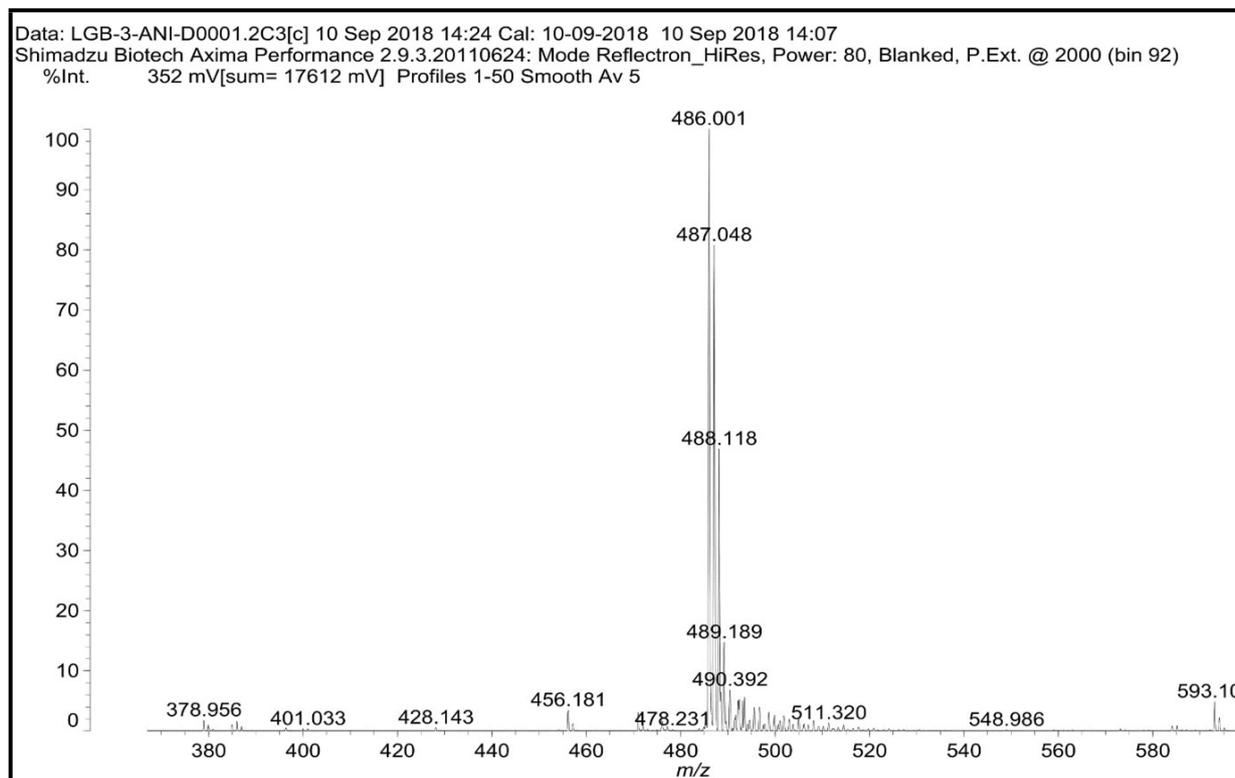


Figure S2. ESI-MS of **D1**

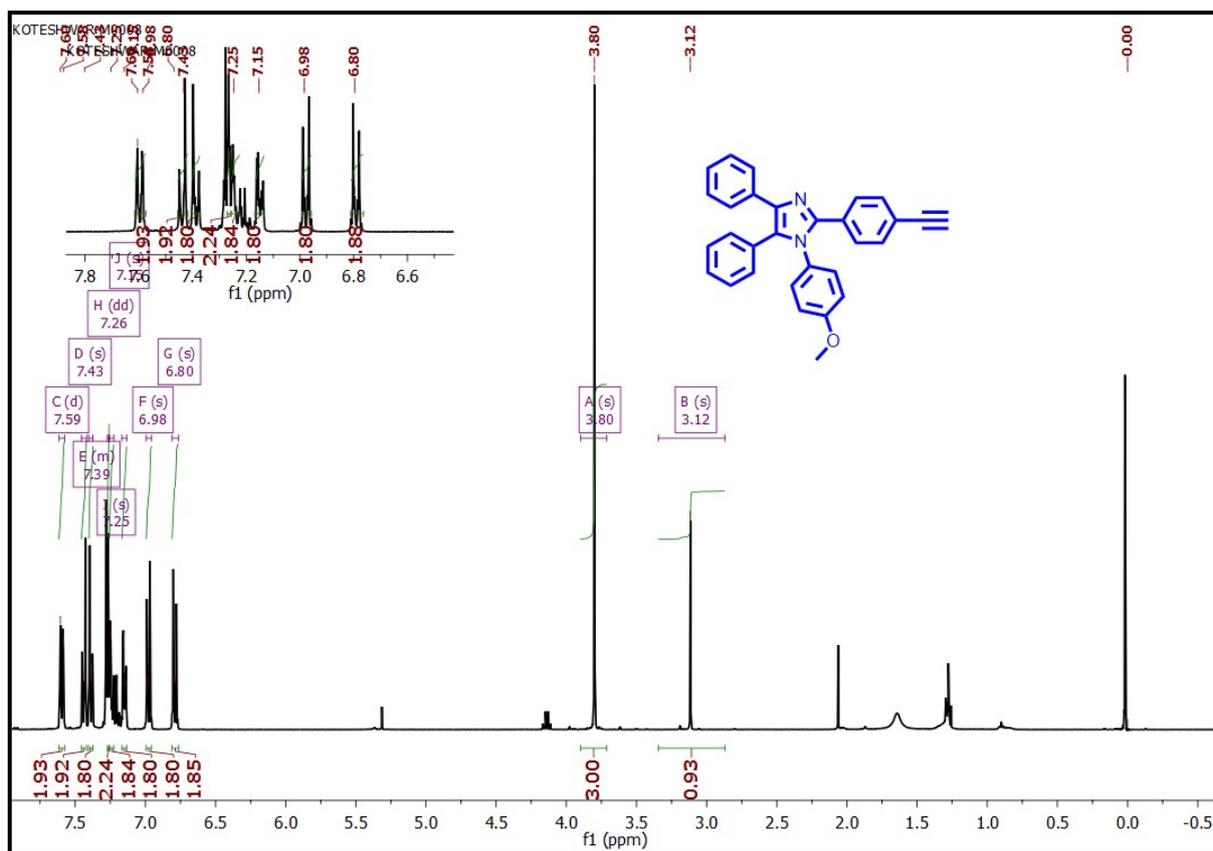


Figure S3.  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ ) of **D2**.

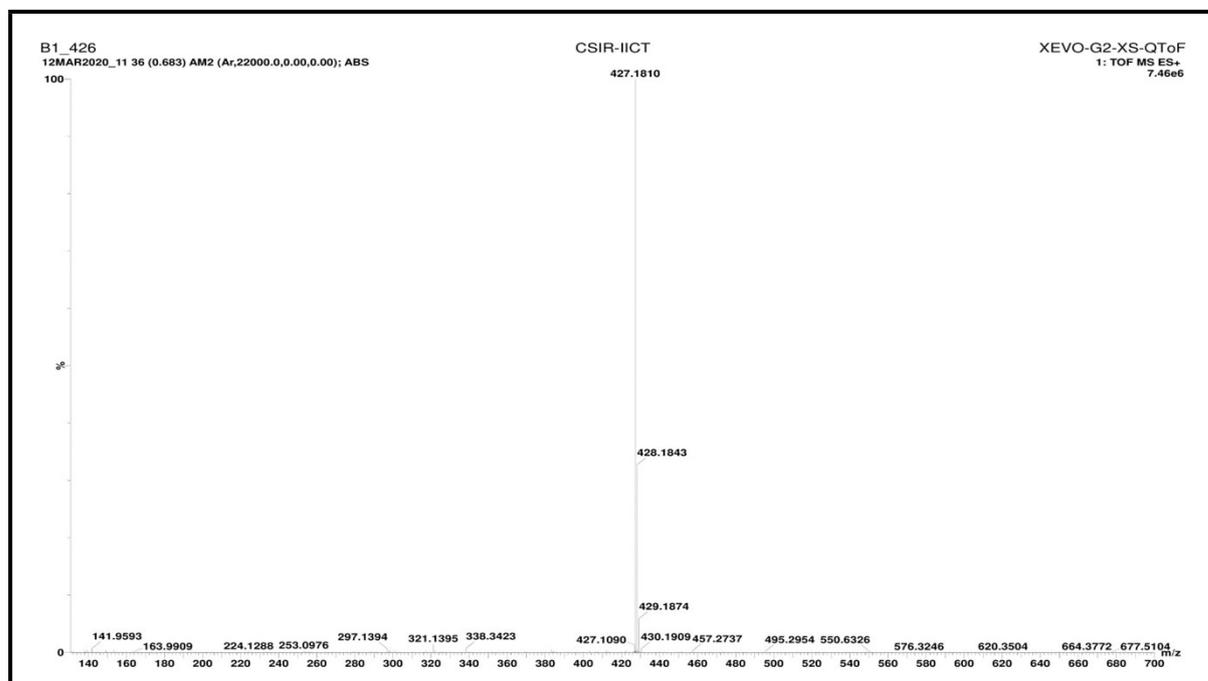


Figure S4. ESI-MS of **D2**.

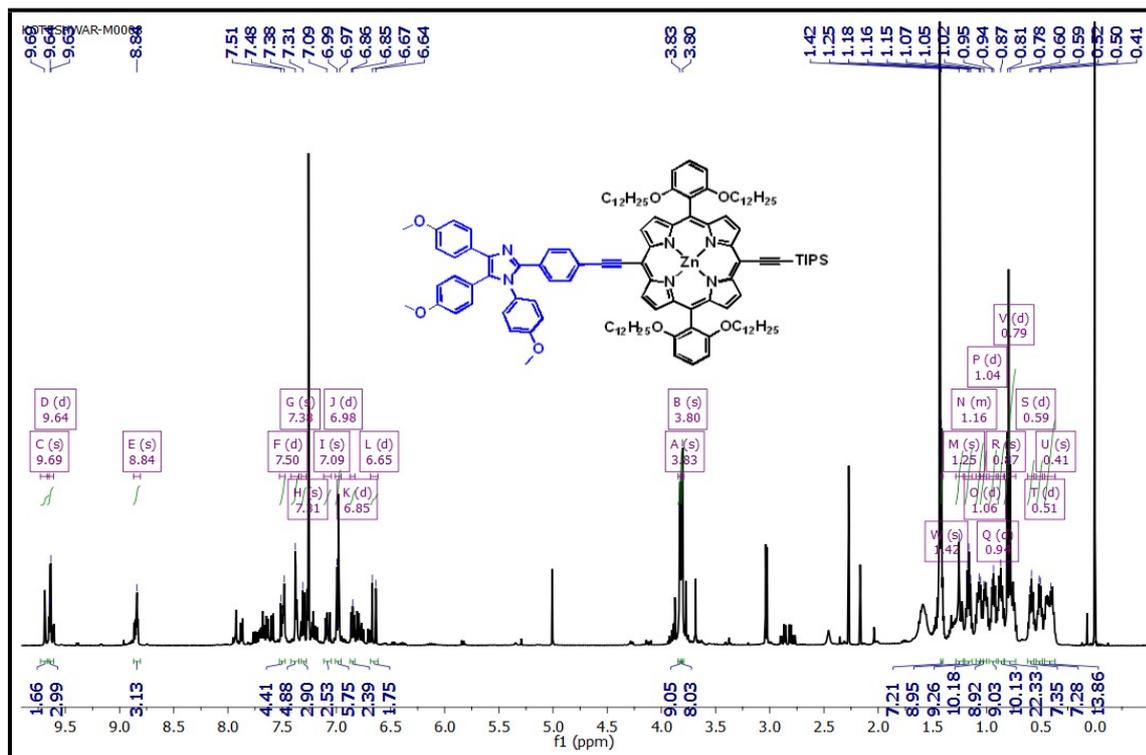


Figure S5. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) of 3.

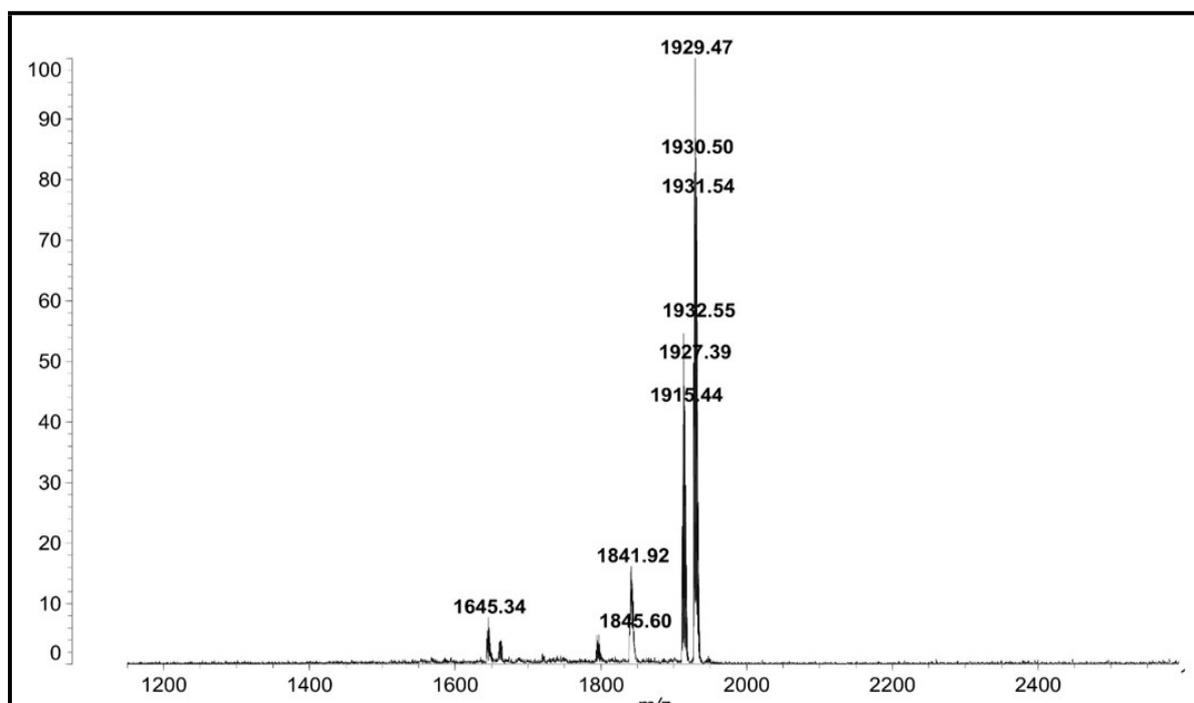


Figure S6. MALDI-TOF of 3.

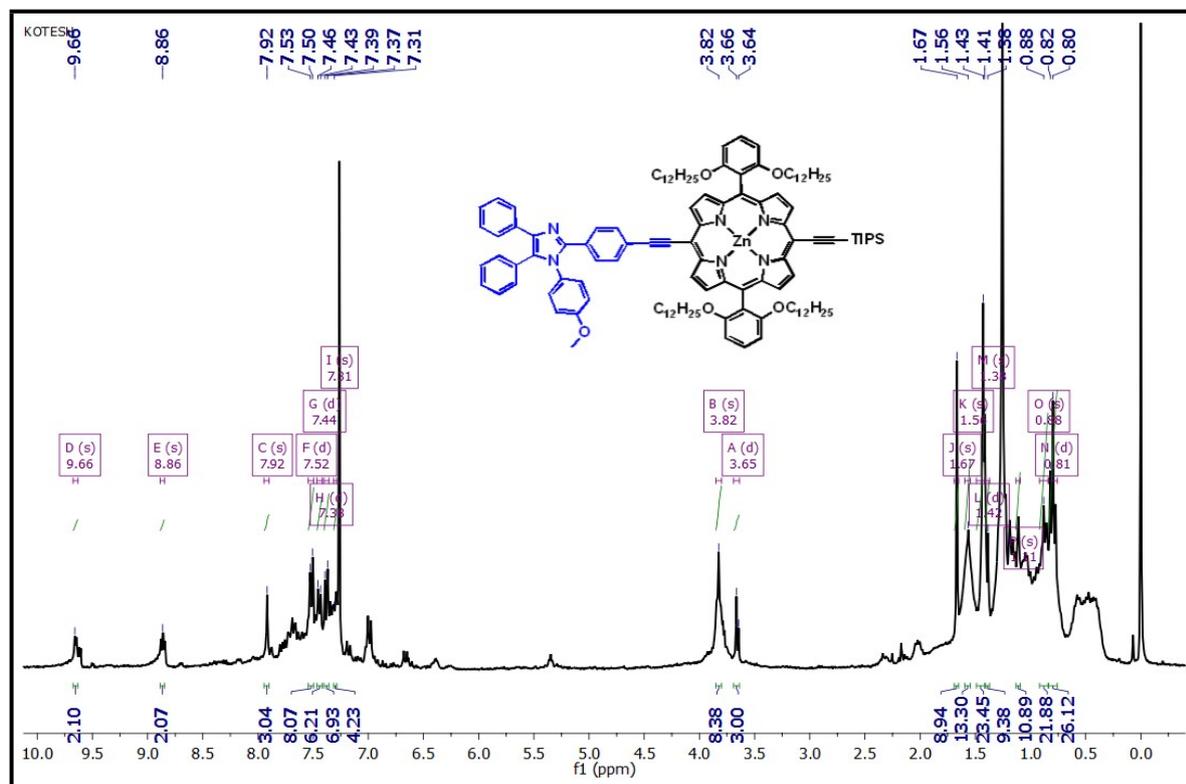


Figure S7.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ ) of 4.

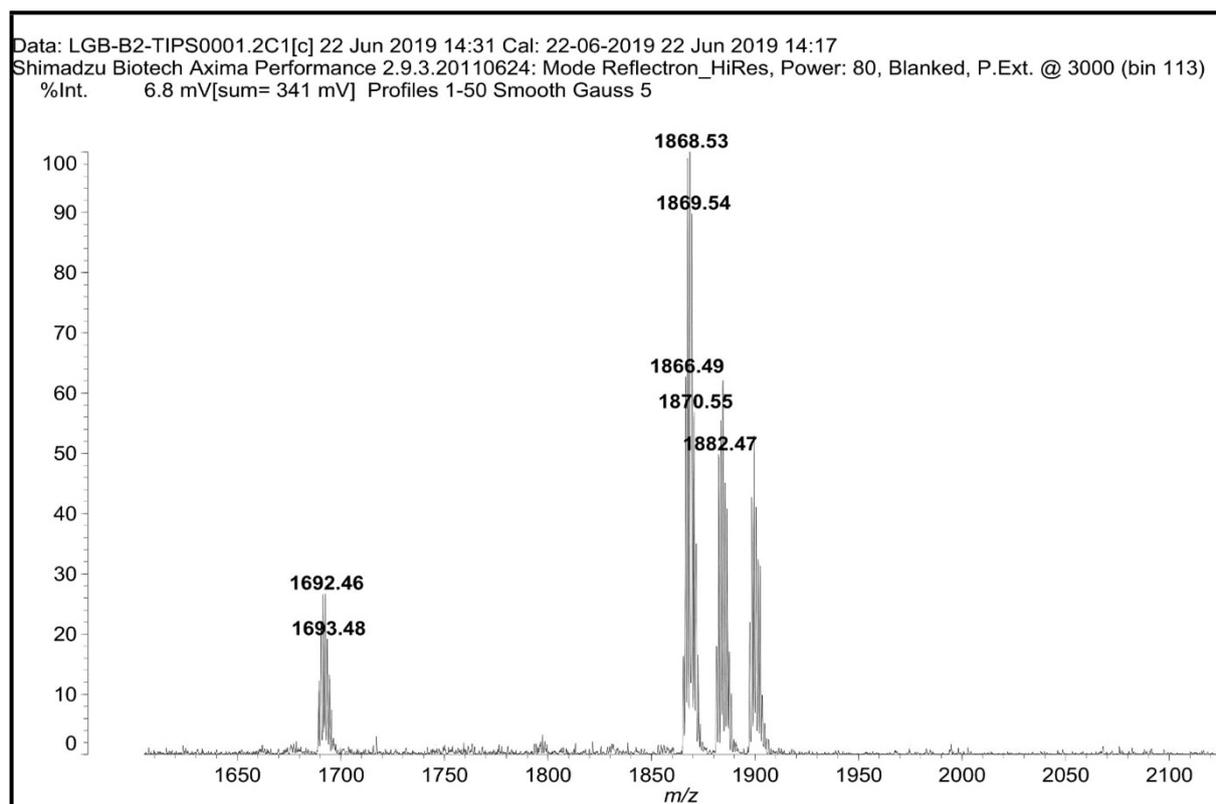


Figure S8. MALDI-TOF of 4.

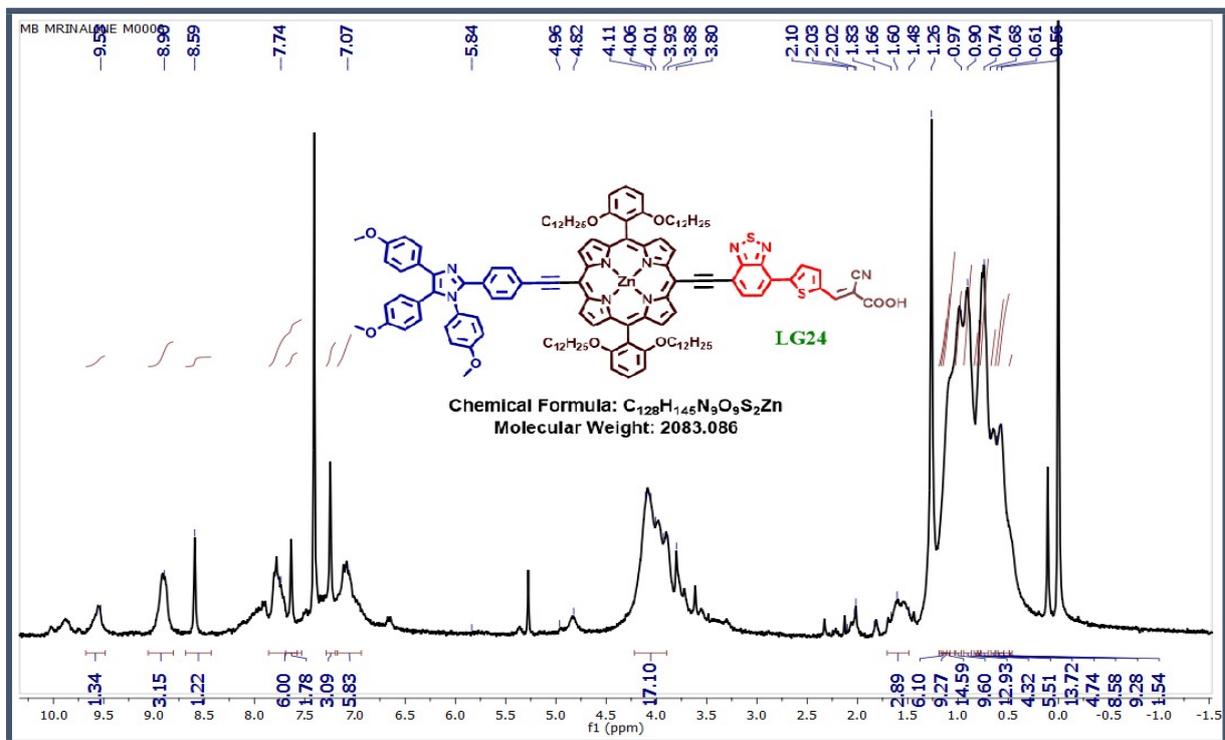


Figure S9.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ ) LG24

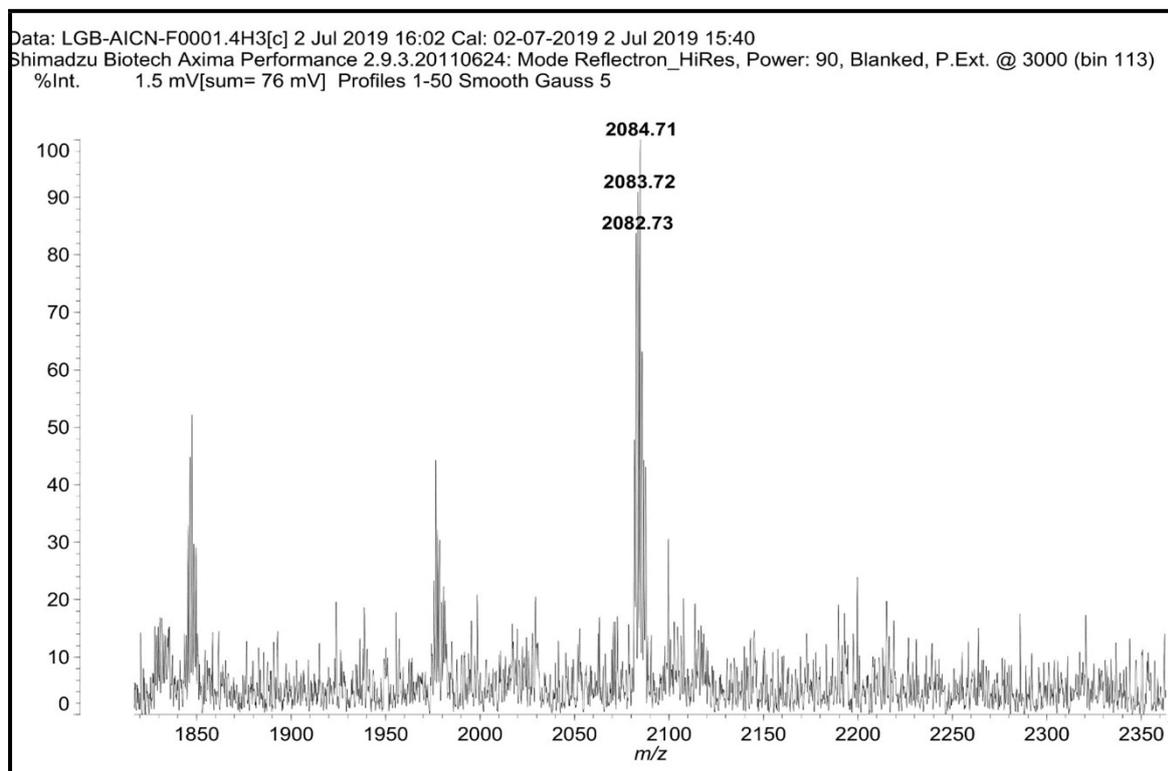


Figure S10. MALDI-TOF of LG24.

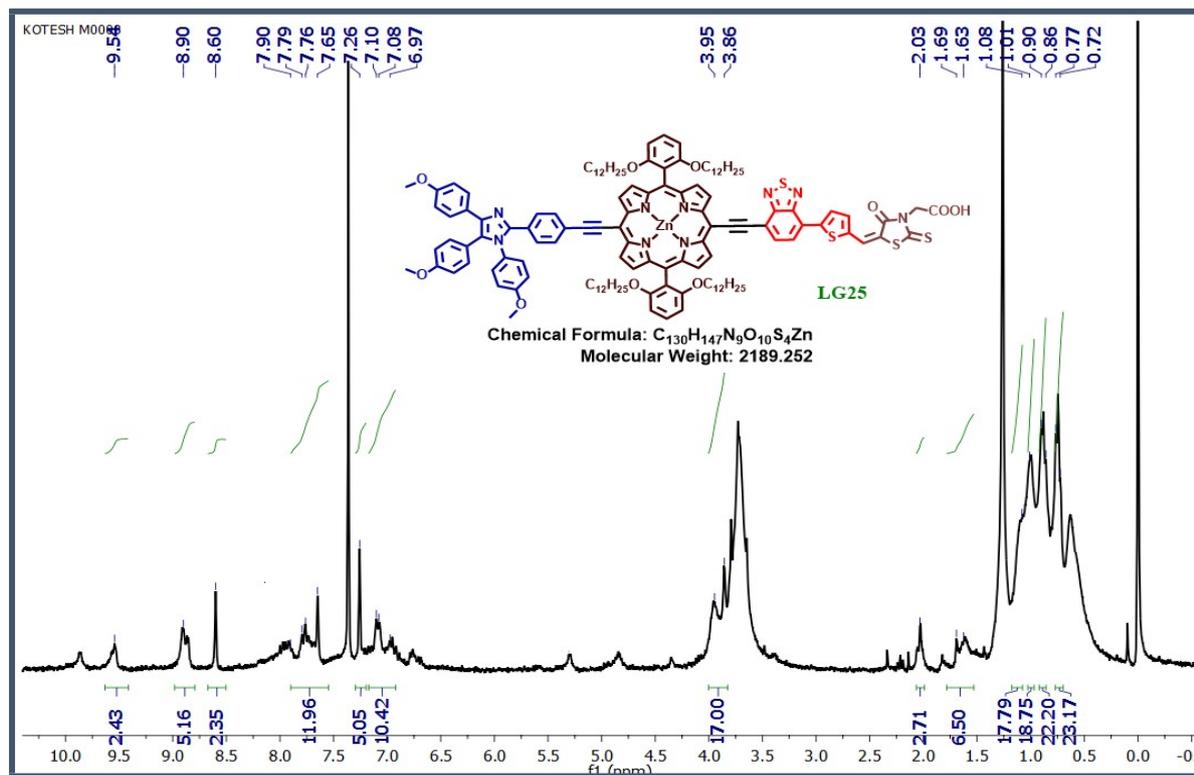


Figure S11.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ ) of LG25.

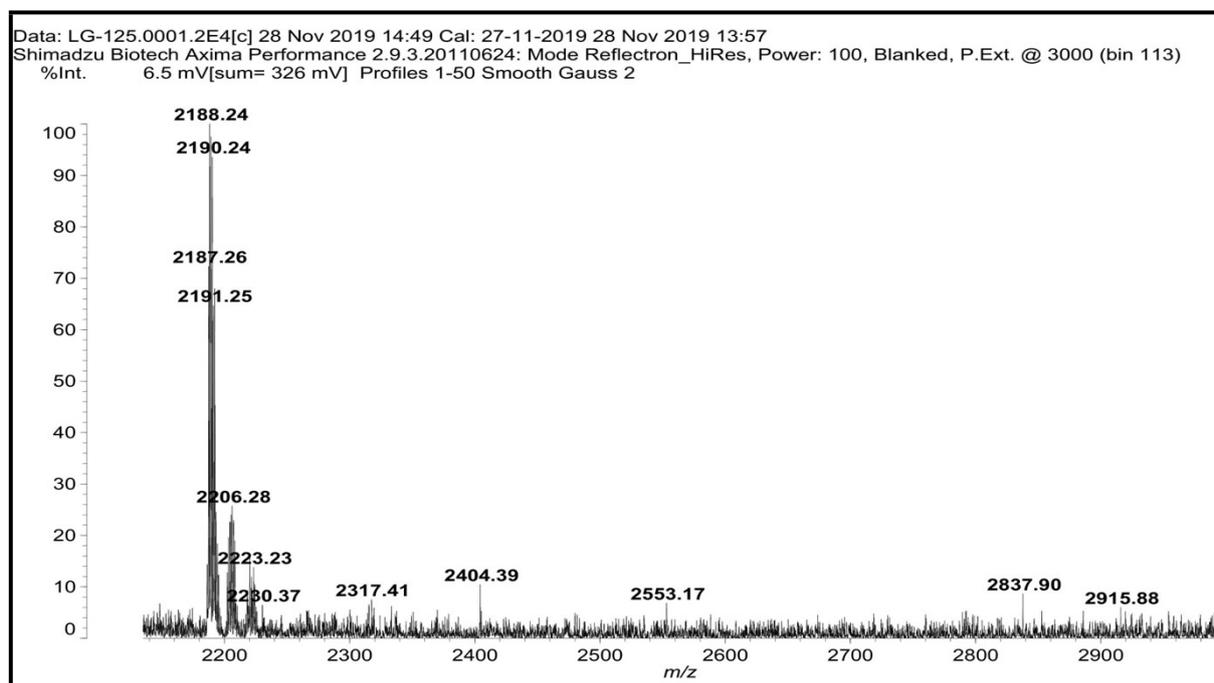


Figure S12. MALDI-TOF of LG25.

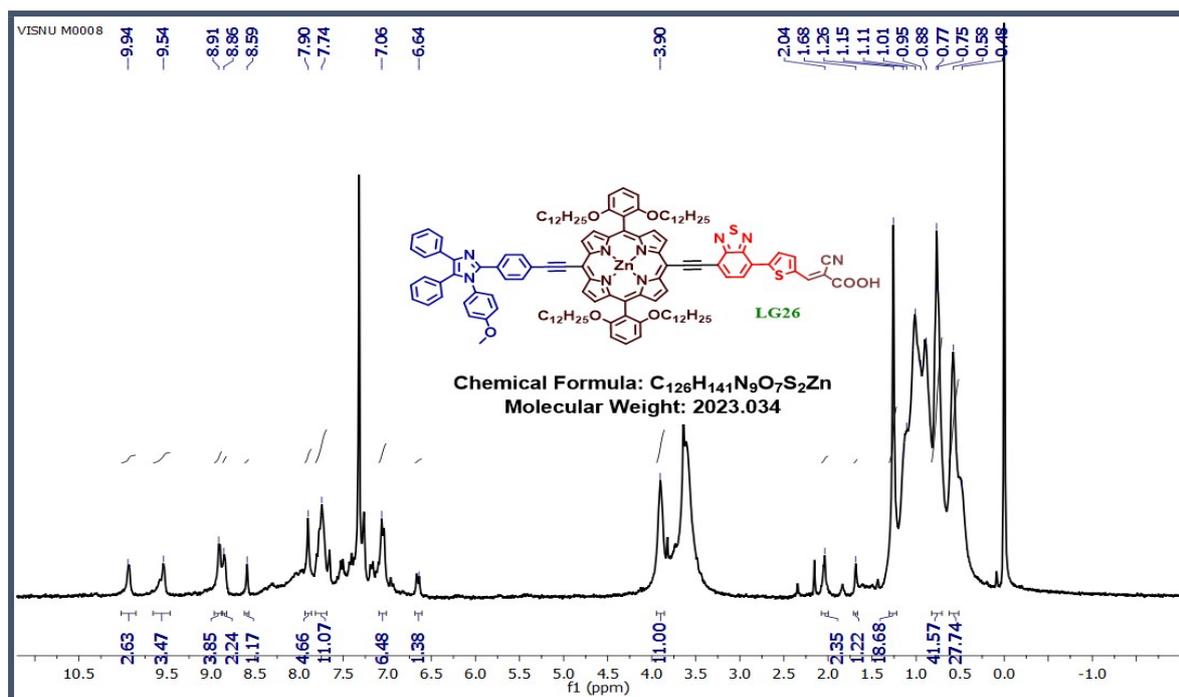


Figure S13.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ ) of LG26.

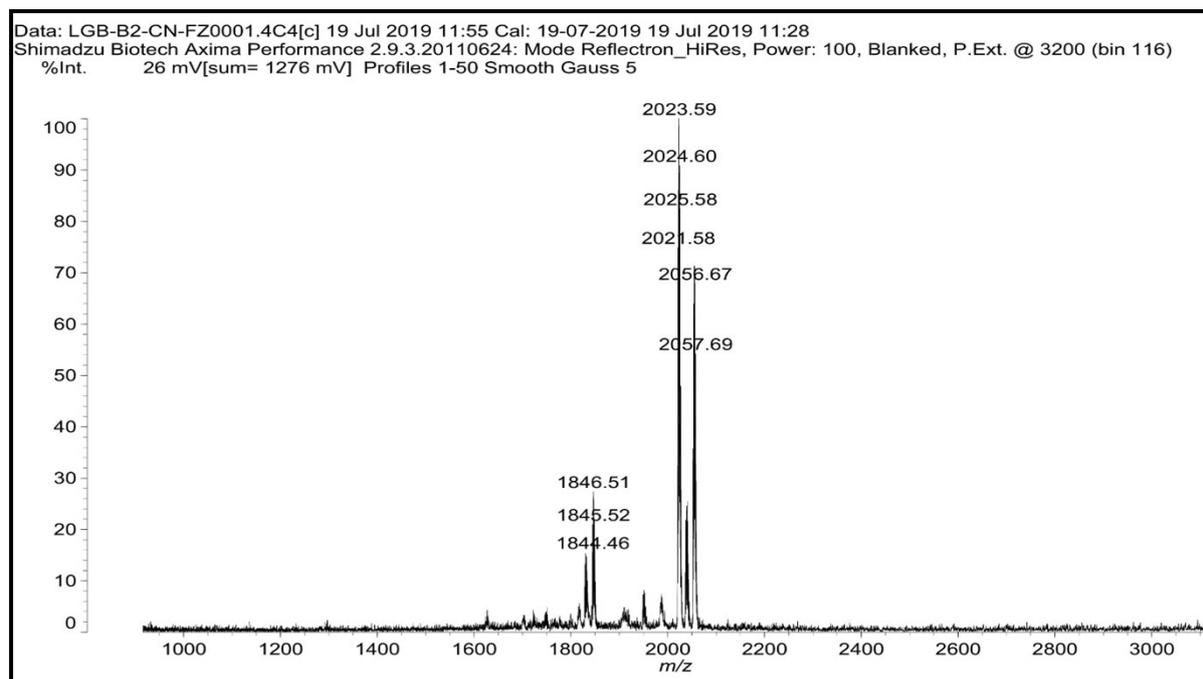


Figure S14. MALDI-TOF of LG26.

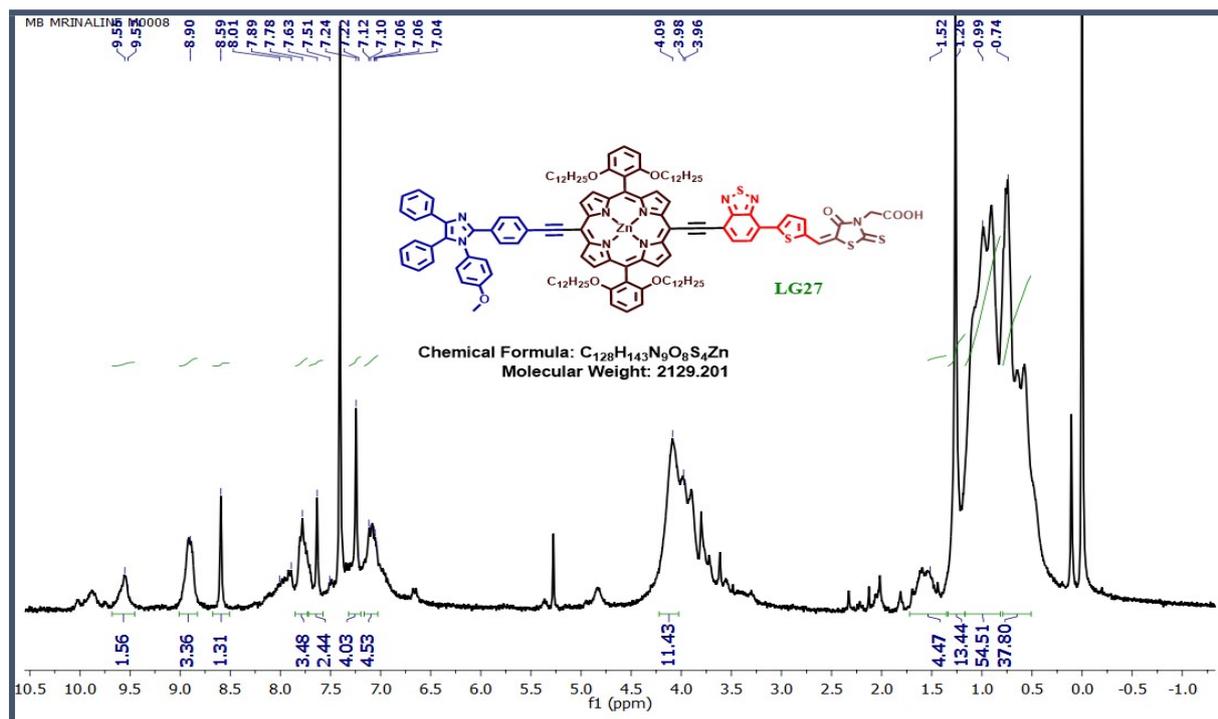


Figure S15.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ ) of LG27.

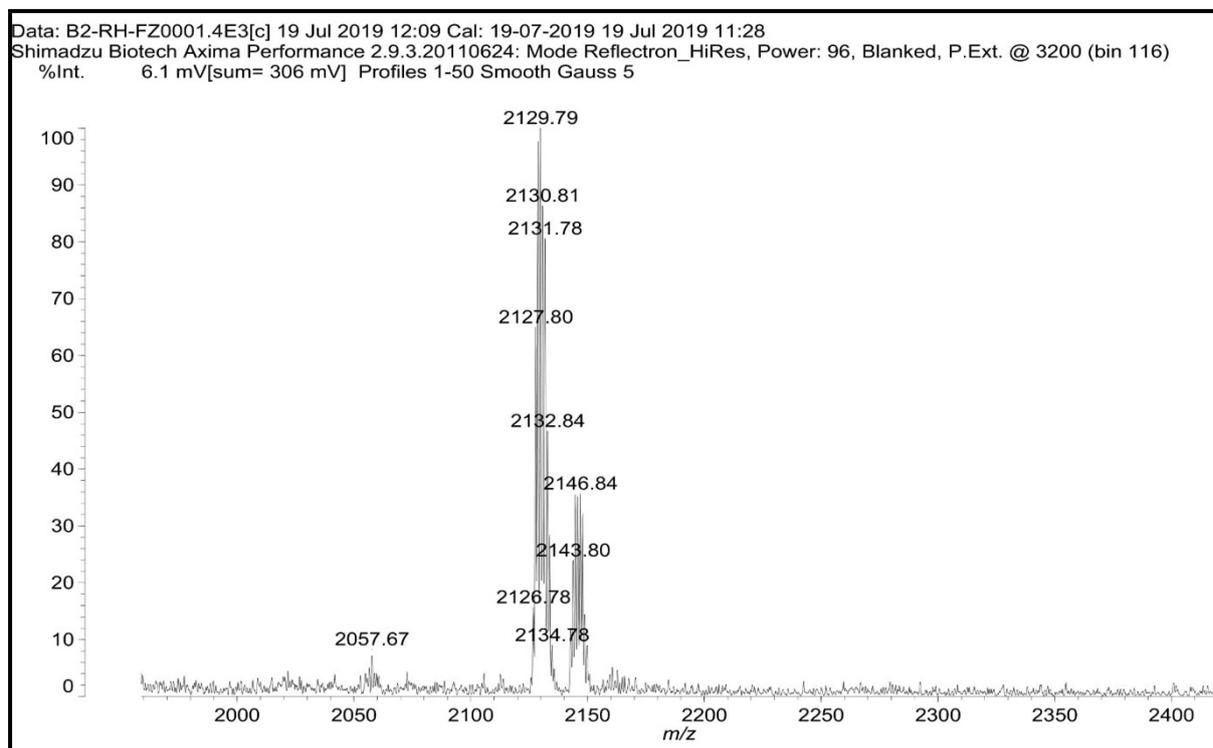
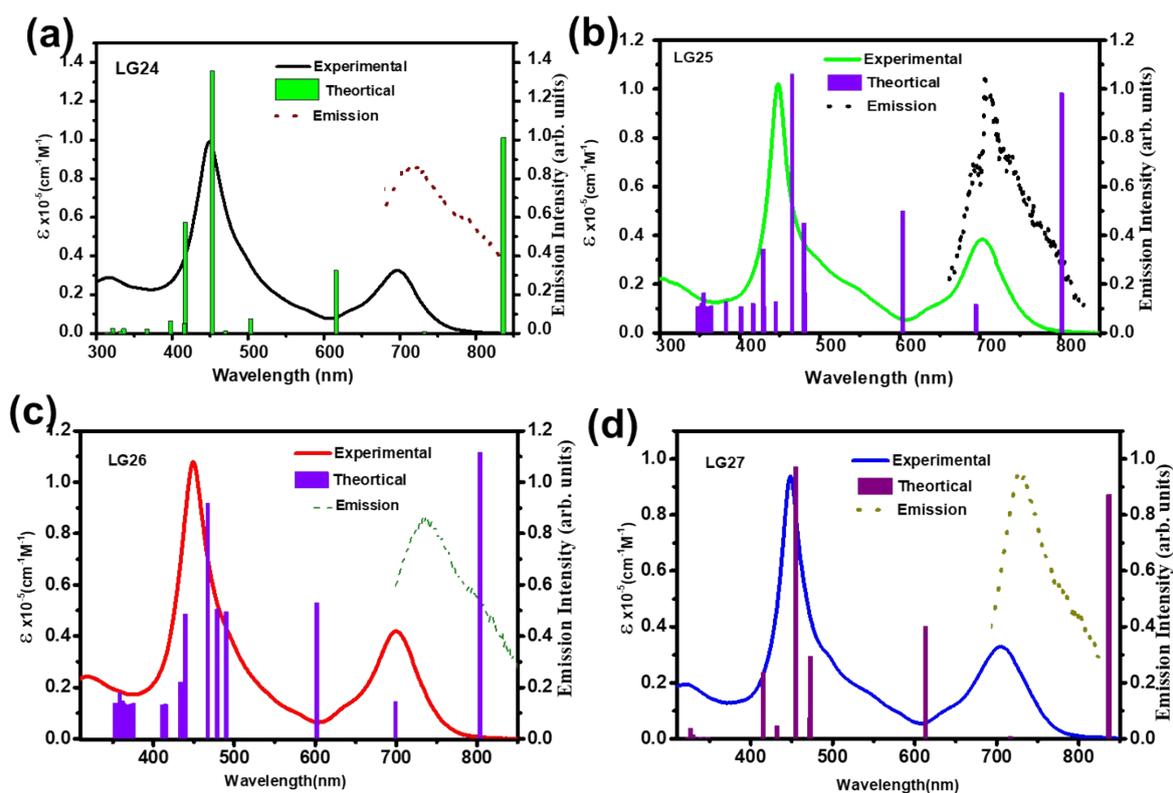


Figure S16. MALDI-TOF of LG27.



**Figure S17.** Theoretical absorption spectra of **LG24-LG27** Dyes by using B3LYP method PCM model in tetrahydrofuran solvent with B3LYP/6-31G(d,p) method.

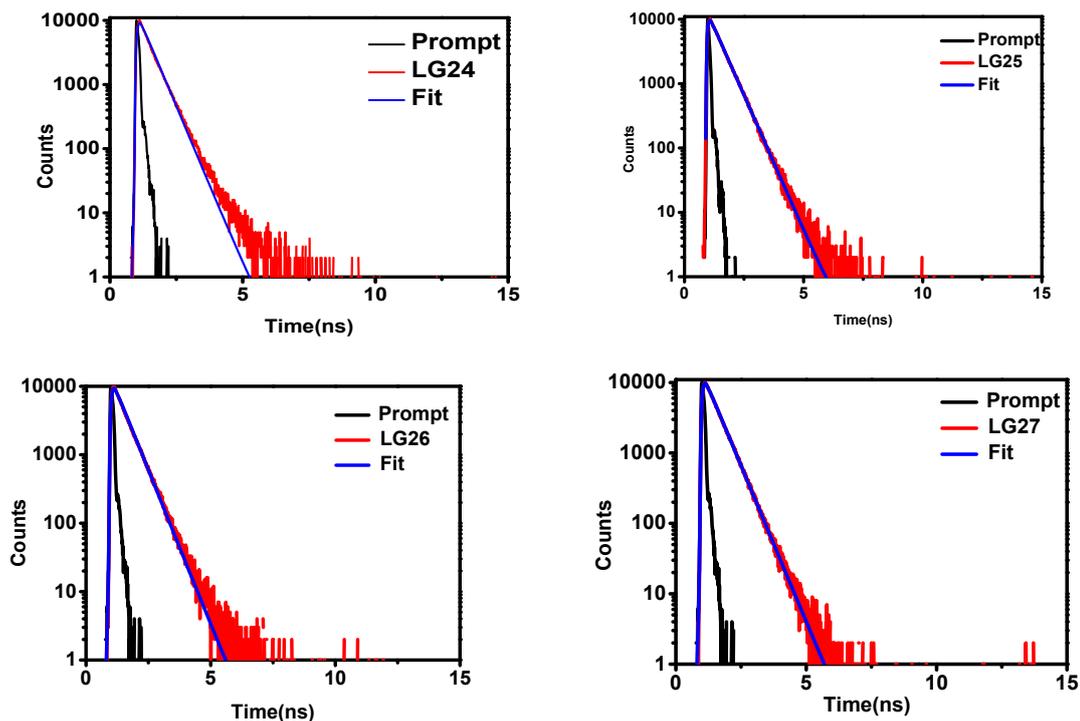


Figure S18. Singlet excited-state lifetimes of LG24, LG25, LG26 and LG27 in THF solution

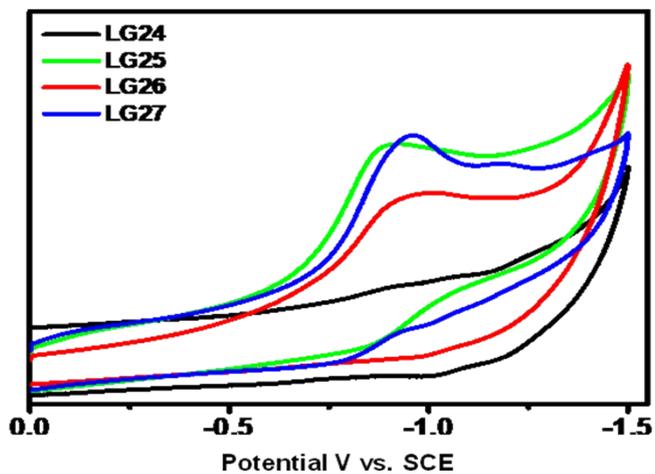
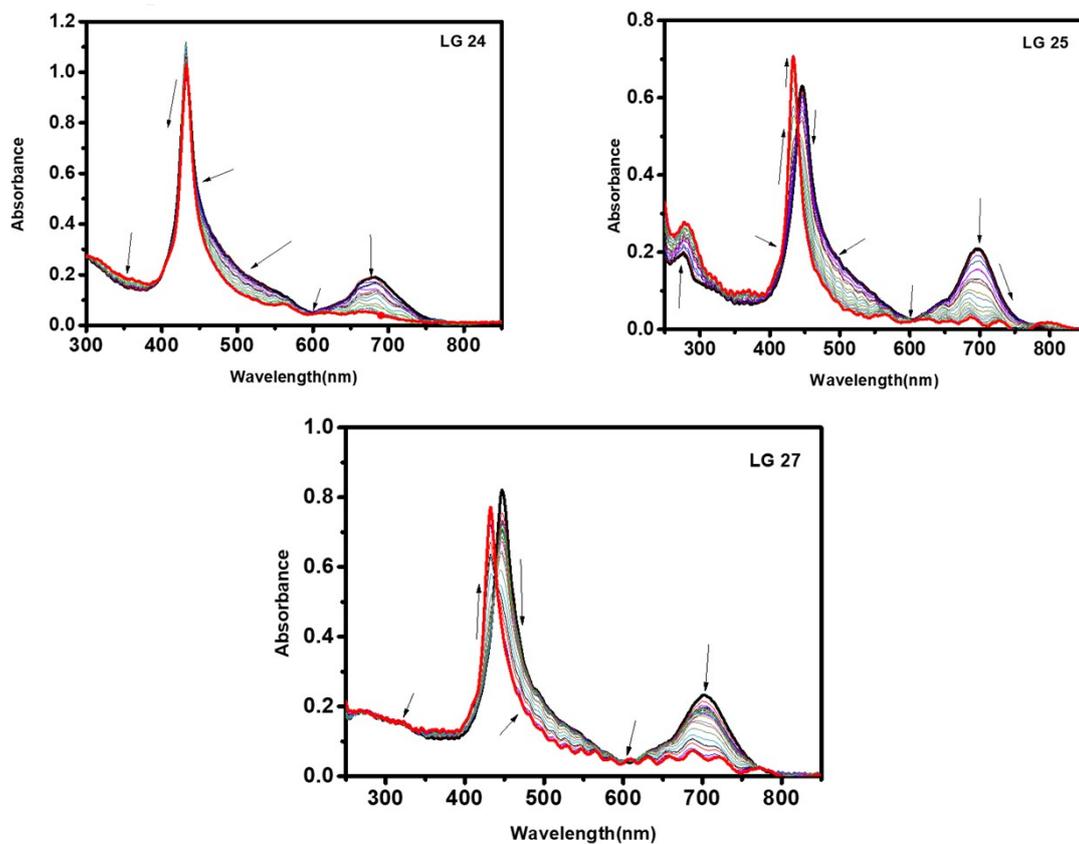
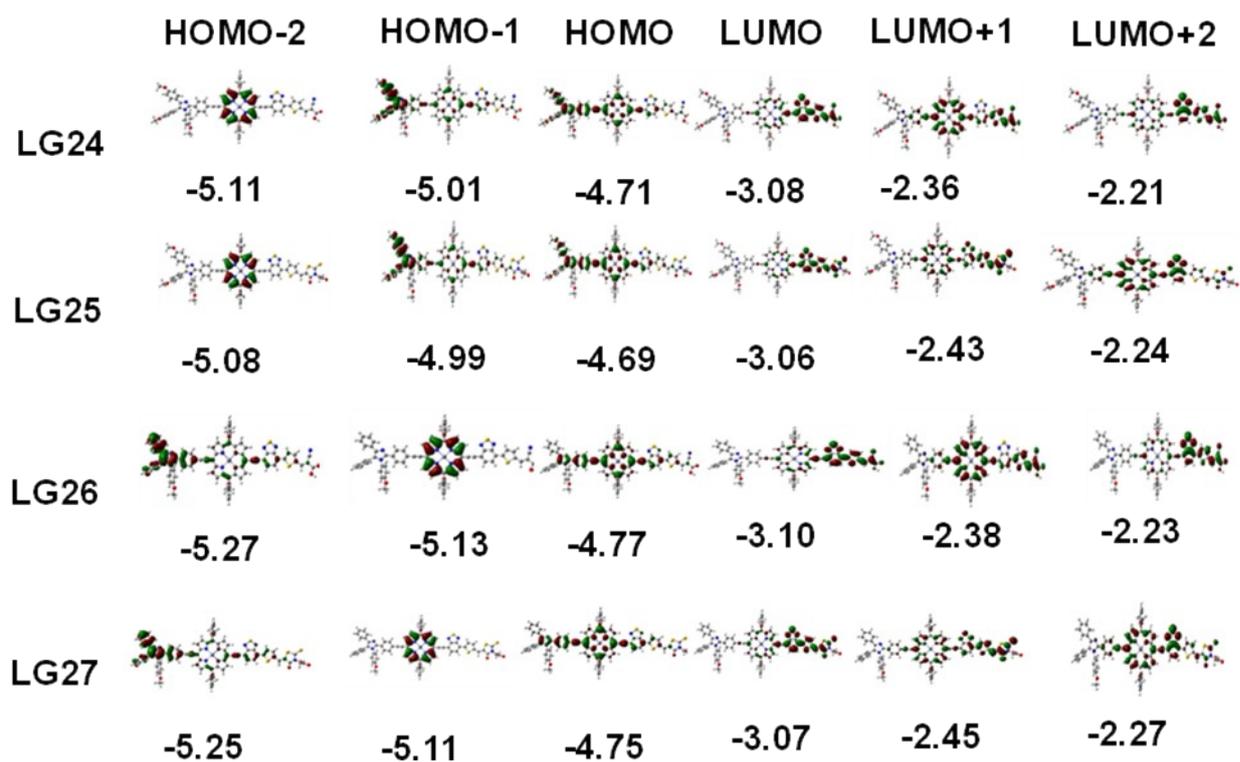


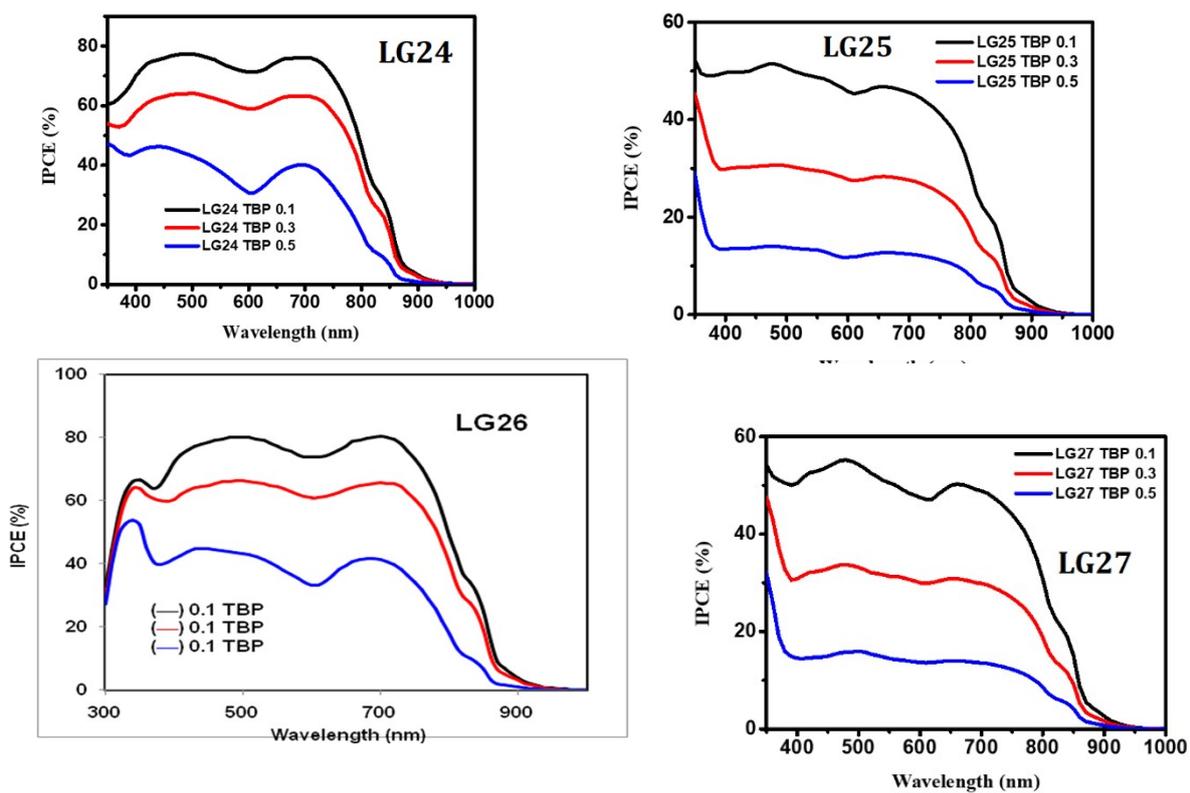
Figure S19. Reduction spectra of LG24, LG25, LG26 and LG27 in THF.



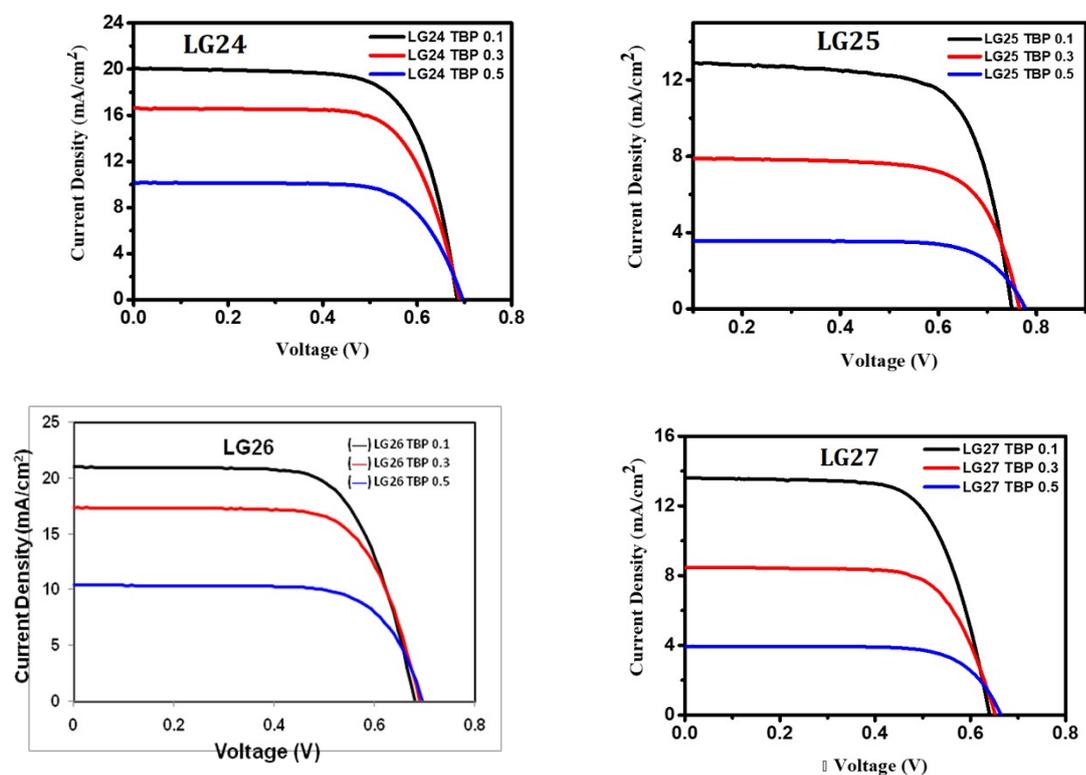
**Figure S20.** Oxidative OTTLE studies of **LG24**, **LG25**, **LG27** series sensitizers in 0.3M TBAP/THF with an applied potential of +0.95V (vs. SCE/KCl).



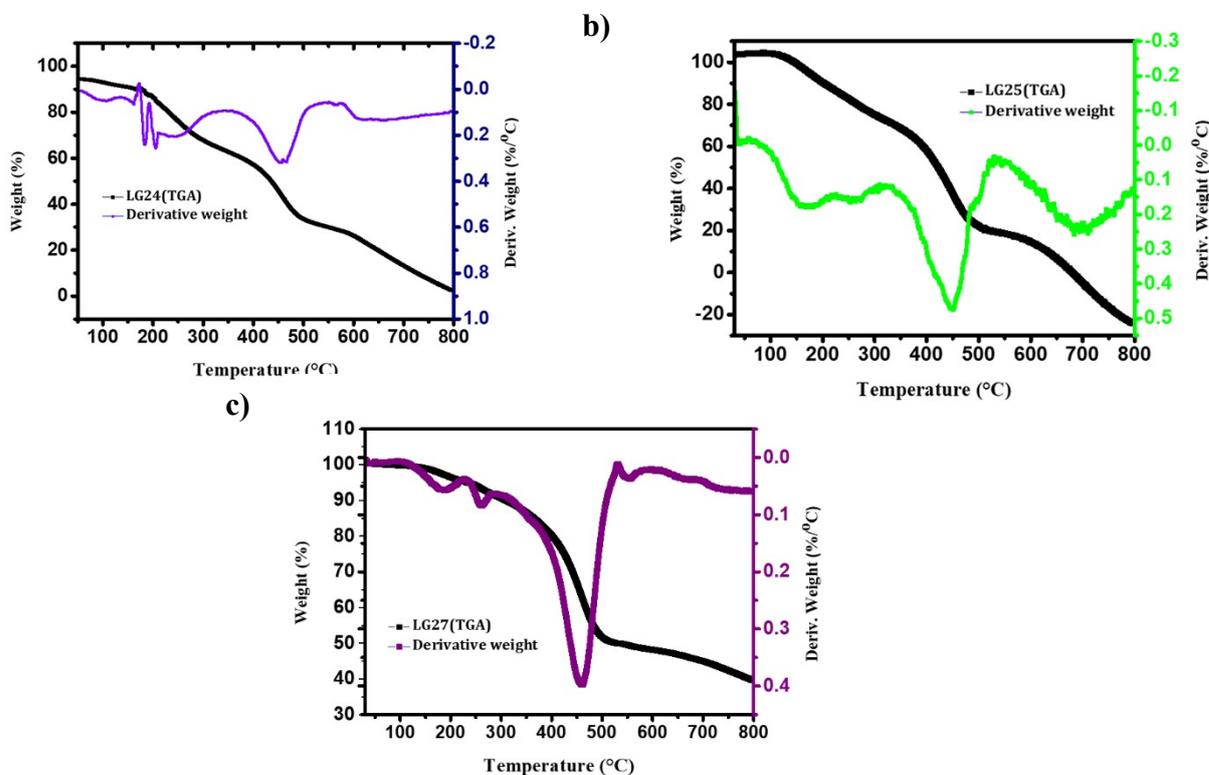
**Figure S21.** Isodensity (0.02) plots of FMOs and the energy values in eV by using the B3LYP method 6-31G(d,p).



**Figure S22.** Photocurrent action spectra porphyrin sensitizers using different concentrations of 4-tert butylpyridine.



**Figure S23.** Current–voltage characteristics of porphyrin sensitizers using different concentrations of 4-*tert* butylpyridine.



**Figure S24.** TG/DTG curves of **LG24**, **LG25** and **LG27** porphyrins with heating rate  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  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	<sup>a</sup> <i>E</i> , K.cal./mol	<sup>b</sup> HOMO (H),	<sup>b</sup> LUMO (L)	<sup>b</sup> H-Lgap	<sup>c</sup> μ
<b>LG24</b>	-4380303	-4.74	-3.08	1.66	17.517
<b>LG25</b>	-4975847	-4.69	-3.06	1.63	16.047
<b>LG26</b>	-4236628	-4.77	-3.10	1.67	15.372
<b>LG27</b>	-4832119	-4.75	-3.07	1.68	13.477

<sup>a</sup>Total minimum energy of **LG24-LG27**, <sup>b</sup>values in eV, <sup>c</sup>values in debye units.

**Table 2:** Singlet excited state properties of dyes by B3LYP method in tetrahydrofuran solvent in PCM model.

Dye	<sup>a</sup> $\lambda_{\max}$	<sup>b</sup> $f$	<sup>c</sup> E (eV)	% of Molecular Orbital Contribution
<b>LG24</b>	430	0.128	2.878	H-1->LUMO (59%), H-1->L+1 (11%), HOMO->L+3 (17%) H-1->L+2 (4%), HOMO->L+2 (5%)
	583	0.016	2.123	H-1->LUMO (38%), H-1->L+1 (27%), HOMO->L+3 (24%) HOMO->L+2 (7%)
	653	1.689	1.898	HOMO->LUMO (64%), HOMO->L+1 (16%) H-3->LUMO (3%), H-2->LUMO (3%), H-1->L+3 (8%)
<b>LG25</b>	415	0.131	2.986	H-3->LUMO (33%), H-1->L+2 (23%), HOMO->LUMO (13%)H-7->L+1 (4%), H-3->L+1 (3%), H-2->LUMO (9%), HOMO->L+3 (4%)
	580	0.018	2.136	H-1->LUMO (36%), H-1->L+1 (25%), HOMO->L+2 (34%)
	662	2.00	1.870	HOMO->LUMO (66%), HOMO->L+1 (15%)H-3->L+1 (3%), H-2->LUMO (3%), H-1->L+2 (9%)
<b>LG26</b>	416	0.679	2.977	H-1->LUMO (51%), HOMO->L+2 (46%)
	581	0.021	2.132	H-1->LUMO (38%), H-1->L+1 (25%), HOMO->L+2 (33%)
	663	1.845	1.869	HOMO->LUMO (69%), HOMO->L+1 (14%) H-3->L+1 (3%), H-2->LUMO (2%), H-1->L+2 (9%)
<b>LG27</b>	413	0.672	2.995	H-1->LUMO (44%), HOMO->L+2 (43%) H-3->LUMO (3%), H-1->L+2 (2%)
	580	0.041	2.196	H-1->LUMO (37%), H-1->L+1 (24%), HOMO->L+2 (34%)

<sup>a</sup>Theoretical absorbance in nm, <sup>b</sup>Oscillator strength, and <sup>c</sup>Excited state energy in eV.