Supplementary Information (SI) for Sustainable Energy & Fuels.

Rational Molecular Engineering of Porphyrins for Enhanced Performance in Dye-Sensitized Solar Cells.

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Experimental Procedures

Materials and instruments

All chemicals and solvents were purchased from commercial sources and used as received unless otherwise noted. THF and CH_2Cl_2 were dried over sodium/benzophenone and CaH_2, respectively, and freshly distilled before use. Tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized from absolute ethanol and dried under vacuum before use. Thin-layer chromatography (TLC) was performed with TLC silica GF254 (Agela Technologies). Column chromatography was performed on silica gel 45−75 μm (KM3 Scientific Corporation). UV-visible and emission spectra were recorded on Cary 50 (Varian) and FP-6000 spectrofluorometer (Jasco). ^1H and ^{13}C NMR are measured with Mercury-400 (Varian) or Unity Inova600 (Varian) NMR Spectrometer using $CDCl_3$ as solvent. Mass spectra were recorded on MALDI-TOF(thermos Finnigan) MAT 95XL.

Device fabrication

A 2.2 mm thick fluorine-doped tin oxide (FTO) glass (8 Ω/ square, Dyesol) was sequentially cleaned by dipping in detergent solution (PK-LCG46, Taiwan) at 70 °C for 30 min with ultrasonication, followed by rinsing with deionized (DI) water and ethanol. TiO_2 photoanode (0.16 cm^2) was prepared using screen printing. First, a 7 μm thick mesoporous TiO_2 layer with 30 nm particle size (G24) was deposited, followed by a 5 μm thick scattering layer of TiO_2 using PST400 (JGC C&C, Japan). The photoanode was then sintered in air at a ramped temperature profile (325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min). Subsequently, the photoanode was immersed in a 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, followed by annealing at 450 °C for 30 min. After cooling to 80 °C, the TiO_2 electrode was immediately immersed in a 0.1 mM solution (1:4 THF/EtOH) containing the dye and 0.2 mM CDCA as a co-adsorbent. A self-developed "two-step dip-coating method was used to fabricate the platinum counter electrode. [1,2] Briefly, FTO glass with pre-drilled holes (Advanced Optowave) was cleaned. The cleaned FTO glass was dipped in an aqueous solution containing 2 wt% surfactant (ML371, MacDiarmid, USA) at 70 °C for 5 min, followed by immersion in a 50 ppm PVP-Pt aqueous solution at 45 °C for 5 min. After rinsing with DI water and drying, the PVP-Pt-attached substrate was sintered at 325 °C for 30 min. The dye-sensitized TiO_2 electrode and a PVP-Pt counter electrode were sandwiched using a piece of 25 μm-thick thermoplastic film to control the gap. Electrolyte containing 0.25 M $[Co(bpy)_3(TFSI)_2]$, 0.06 M [Co(bpy)3(TFSI)2], 0.1 M LiTFSI, and 0.5 M tert-butylpyridine (tBP) in acetonitrile was injected into one hole on the counter electrode.

Photovoltaic performance characterization

Before measurement, a black mask was applied to the device, defining an active area of 0.16 cm^2. A solar simulator equipped with a 150 W xenon lamp and an AM 1.5G filter (PEC-L15, PECCELL, Japan) illuminated the device. The simulator was calibrated to 100 mW/cm^2 irradiance using a reference cell (KG4, ORIEL, USA) to ensure accurate measurements. Current-voltage (J-V) curves were obtained by scanning the device with a computer-controlled digital source meter (Keithley 2400C, USA) using commercial software (PEC-IV3.0, PECCELL, Japan). Incident photon to current efficiency (IPCE) spectra were measured using a commercial system (PEC-S20, PECCELL, Japan).

Electrochemical impedance spectroscopy (EIS) measurement:

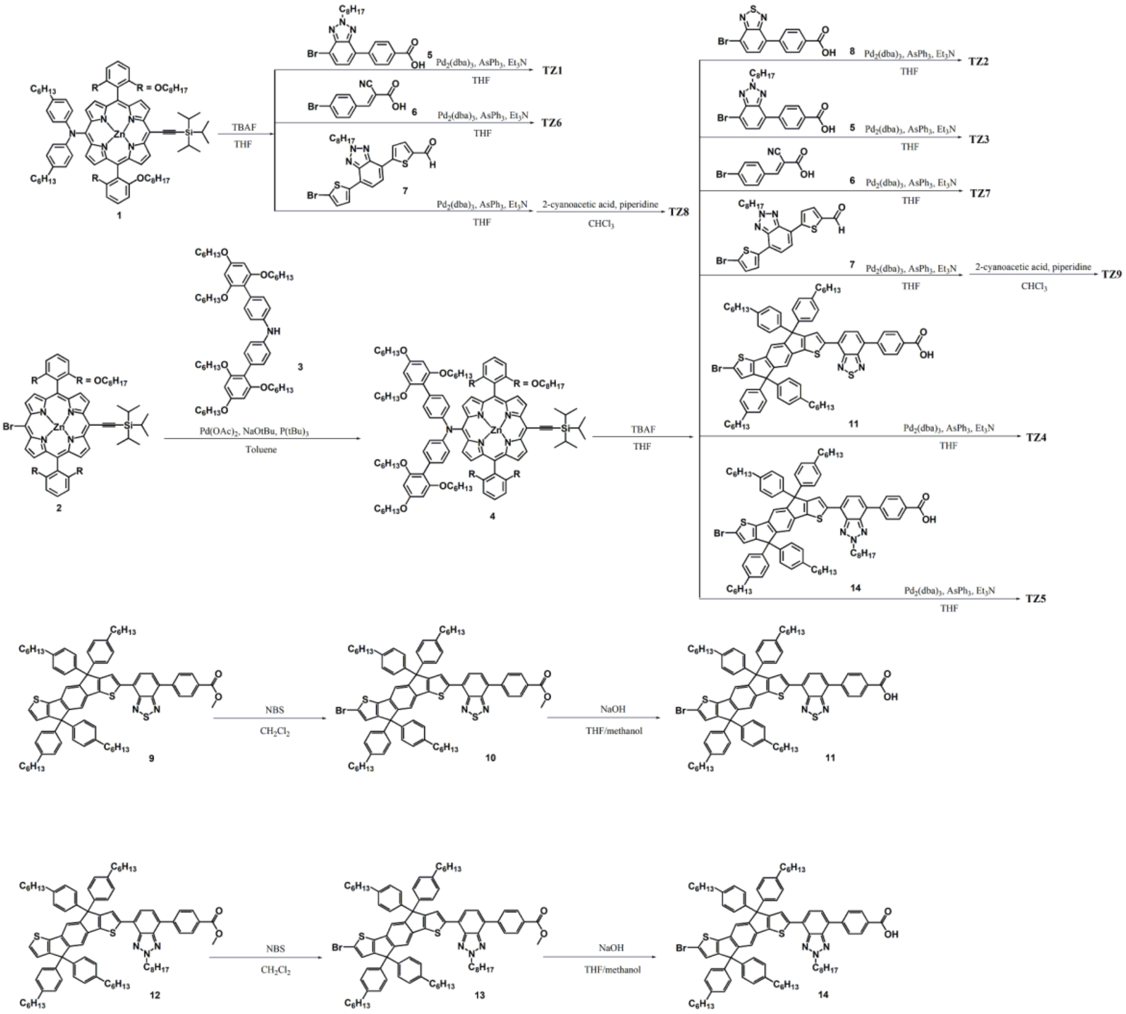
The EIS measurements were conducted by applying different biases in the dark using an electrochemical workstation (Schlumberger SI-1286) equipped with a frequency response analyzer (Schlumberger SI-1255). The impedance data of symmetric cells was recorded with frequencies ranging from 100 kHz to 0.1 Hz and an AC amplitude of 10 mV in two ways. The data were then fitted with an equivalent circuit of TLM by Z-View software.

Electrochemical measurements:

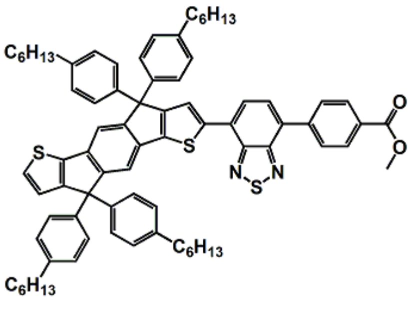
Electrochemistry was performed using a three-electrode potentiostat (Model 750A, CH Instruments) in THF deoxygenated by purging with high-purity nitrogen. Cyclic voltammetry was carried out with a three-electrode cell equipped with a glassy carbon working electrode (BAS, 0.07 cm^2 disc), a platinum wire auxiliary electrode, and a homemade saturated Ag/AgCl reference electrode. The reference electrode was separated from the bulk solution by a double junction filled with the same electrolyte solution as the bulk solution. Potentials are reported versus the saturated Ag/AgCl reference electrode and calibrated using the ferrocene/ferrocenium (Fc/Fc^+) couple, which exhibits a half-wave potential ($E_{1/2}$) of + 0.63 V versus saturated Ag/AgCl. The glassy carbon working electrode was polished with 0.03 μm alumina on Buehler felt pads, rinsed thoroughly with deionized water, and dried with THF before each experiment. The individual potential values exhibited reproducibility within ± 5 mV.

Time-resolved decay: Time-resolved decay traces were measured using the time-correlated single photon counting (TCSPC) technique. The samples were excited by a 405-nm CW/Pulse diode laser (LDH-D-C-400, Picoquant); the emissions were passed through a spectrometer (HORIBA Jobin Yvon; model: iHR550) equipped with a 550-mm focal-length achromatic flat field monochromator, then collected by a photosensor (PMT low-noise, AST Instrument).

Synthesis Procedures:



Scheme S1. Synthetic routes of **TZ** porphyrin dyes.

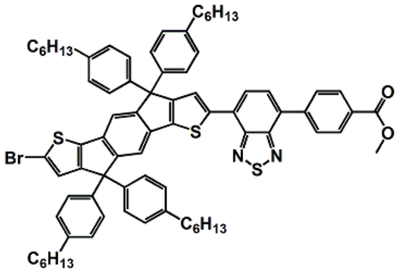


(9):

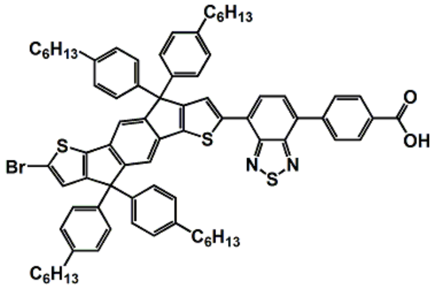
To a solution of 2-bromo-4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b’]dithiophene (0.2 g, 0.20 mmol), methyl-4-(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)benzoate (0.12 g, 0.30 mmol), and $Pd(PPh_3)_4$ (0.034 g, 0.029 mmol) in dry THF (10 mL) was followed by addition of 2 M

$K_2CO_{3(aq)}$ (1.00 mL, 1.01 mmol). Then the reaction mixture was reflux for 20 h under $N_{2(g)}$ atomosphere, and then extracted with CH_2Cl_2/H_2O. The crude product was purified by column chromatographyn (Silica gel) using EA/hexane = 1:50 as eluent to afford as red solid **9** (0.13 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.2 Hz, 2H), 8.06-8.02 (m, 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.44 (s, 1H), 7.26-7.23 (m, 10H), 7.16 (d, J = 8.1 Hz, 4H), 7.07 (dd, J = 10.2 Hz, J = 8.4 Hz, 8H), 7.01 (d, J = 4.8 Hz, 1H), 3.95 (s, 3H), 2.55 (t, J = 7.8 Hz, 8H), 1.61-1.57 (m, 4H), 1.34-1.26 (m, 28H), 0.89-0.83 (m, 12H).

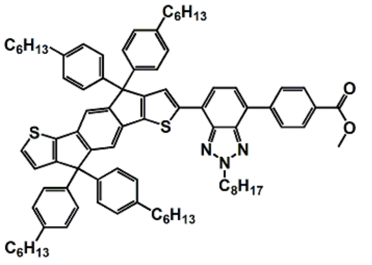
(10):



To a solution of **9** (0.68 g, 0.58 mmol) in CH_2Cl_2 (15 mL) was followed by addition of N-bromosuccinimide (0.12 g, 0.70 mmol) slowly, and then stirred for 12 h at room temperature. The mixture was quenched with acetone and removed solvent by rotavapor. Recrystallization of the crude with methanol/CH_2Cl_2 afford **10** (0.70 g, 96%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.5 Hz, 2H), 8.04-8.02 (m, 3H), 7.92 (d , J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.49 (s, 1H), 7.37 (s, 1H), 7.25-7.22 (m, 8H), 7.13 (d, J = 8.4 Hz, 4H), 7.07 (dd, J = 8.1 Hz, J = 6.6 Hz, 8H), 7.01 (s, 1H), 3.95 (s, 4H), 2.55 (t, J = 7.6 Hz, 8H), 1.61-1.54 (m, 4H), 1.34-1.27 (m, 28H), 0.88-0.84 (m, 12H).

(11): 

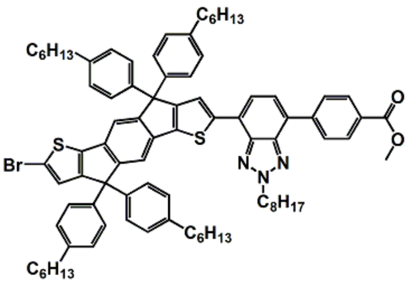
To a solution of **10** (0.69 g, 0.55 mmol) in THF/methanol = 3:1 (40 mL), was followed by addition of 5N $NaOH_{(aq)}$ (2.5 mL) slowly, and then stirred for 4 h at room temperature. The mixture was neutralized with 35% $HCl_{(aq)}$ to pH = 6-7, and then extracted with CH_2Cl_2/H_2O to afford red solid **11** (0.65 g, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.6 Hz, 2H), 8.07-8.05 (m, 3H), 7.92 (d , J = 7.4 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.48 (s, 1H), 7.36 (s, 1H), 7.24-7.21 (m, 7H), 7.13-7.05 (m, 11H), 7.00 (s, 1H), 2.55 (t, J = 7.8 Hz, 8H), 1.60-1.53 (m, 8H), 1.33-1.24 (m, 24H), 0.87-0.83 (m, 12H).

(12): 

To a solution of 2-bromo-4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (0.81 g, 0.82 mmol), methyl-4-(2-octyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-benzo[d][1,2,3]triazol-4-yl)benzoate (0.60 g, 1.22 mmol), and $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol) in dry THF (50 mL) was followed by addition of 2 M $K_2CO_{3(aq)}$ (5.00 mL, 5.01 mmol). Then the reaction mixture was refluxed for 20 h under $N_{2(g)}$ atmosphere and extracted with CH_2Cl_2/H_2O. The crude product was purified by column chromatography (Silica gel) using EA/hexane = 1:50 as eluent to afford as red solid **9** (0.97 g, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, J = 11.1 Hz, J = 8.5

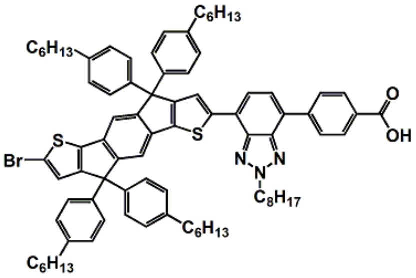
Hz, 4H), 7.98 (s, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.49 (s, 1H), 7.43 (s, 1H), 7.26-7.24 (m, 8H), 7.16 (d, J = 8.2 Hz, 4H), 7.06 (t, J = 7.9 Hz, 8H), 7.00 (d, J = 4.8 Hz, 1H), 4.78 (t, J = 7.2 Hz, 2H), 3.94 (s, 3H), 2.55 (t, J = 7.8 Hz, 8H), 2.16 (t, J = 7.0 Hz, 2H), 1.61-1.54 (m, 6H), 1.44-1.25 (m, 36H), 0.87-0.83 (m, 15H).

(13):

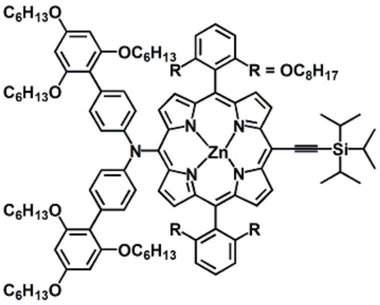


To a solution of **12** (0.95 g, 0.75 mmol) in CH_2Cl_2 (72 mL) was followed by addition of N-bromosuccinimide (0.15 g, 0.86 mmol) slowly, and then stirred for 12 h at room temperature. The mixture was quenched with acetone and removed solvent by rotavapor. Recrystallization of the crude with methanol/CH_2Cl_2 affords **13** (0.95 g, 94%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, J = 9.0 Hz, J = 2.5 Hz, 4H), 7.98 (d, J = 5.2 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 10.4 Hz, 1H), 7.44 (s, 1H), 7.26-7.22 (m, 8H), 7.18-7.12 (m, 4H), 7.07 (t, J = 7.8 Hz, 8H), 7.01-7.00 (m, 1H), 4.78 (t, J = 7.2 Hz, 2H), 3.94 (s, 3H), 2.55 (t, J = 7.8 Hz, 8H), 2.20-2.13 (m, 2H), 1.58 (dd, J = 14.4 Hz, J = 7.6 Hz, 6H),1.42-1.26 (m, 36H), 0.86-0.84 (m, 15H).

(14):



To a solution of **13** (0.92 g, 0.68 mmol) in THF/methanol = 3:1 (50 mL), was followed by addition of 5N $NaOH_{(aq)}$ (3.0 mL) slowly, and then stirred for 4 h at room temperature. The mixture was neutralized with 35% HCl $_{(aq)}$ to pH = 6-7, and then extracted with CH_2Cl_2/H_2O to afford red solid **14** (0.86 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.7 Hz, 2H), 8.17-8.14 (m, 2H), 7.70 (d , J = 7.6 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 3.6 Hz, 1H), 7.36 (s, 1H), 7.25-7.22 (m, 8H), 7.14-7.11 (m, 4H), 7.07 (q, J = 4.2 Hz, 8H), 7.00 (s, 1H), 4.79 (t, J = 7.3 Hz, 2H), 2.55 (t, J = 7.6 Hz, 8H), 2.18-2.14 (m, 8H), 1.61-1.53 (m, 6H), 1.42-1.25 (m, 36H), 0.87-0.82 (m, 15H).



(4):

To a solution of **3** (0.71 g, 0.75 mmol), **2** (0.20 g, 0.15 mmol), $Pd(OAc)_2$ (10 mg, 0.046 mmol), NaO*t*Bu (0.074 g, 0.75 mmol) in toluene (12 mL), added P(*t*Bu)$_3$ (0.1 mL) at 120 °C and refluxing for 4 h. The mixture was cooled to room temperature and was purified by column chromatography (Silica gel) using CH_2Cl_2/hexane = 1:3 as eluent to afford as green solid **4** (0.27 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (d, J = 4.5 Hz, 2H), 9.27 (d, J = 4.7 Hz, 2H), 8.84 (d, J = 4.7 Hz, 2H), 8.66 (d, J = 4.7 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.31 (d , J = 8.6 Hz, 4H), 7.14 (d, J = 8.6 Hz, 4H), 6.94 (d, J = 8.6 Hz, 4H), 6.13 (s, 4H), 3.91 (t , J = 6.7 Hz, 4H), 3.78 (t , J = 6.7 Hz, 8H), 1.74 (q , J = 7.2 Hz, 4H), 1.60-1.54 (m, 36H), 1.46-1.42 (m, 24H), 1.33-1.18 (m, 32H), 1.00-0.93 (m, 8H), 0.90-0.86 (m, 8H), 0.72 (qt, J = 18.9, 6.8 Hz, 20H), 0.54-0.40 (m, 46H).

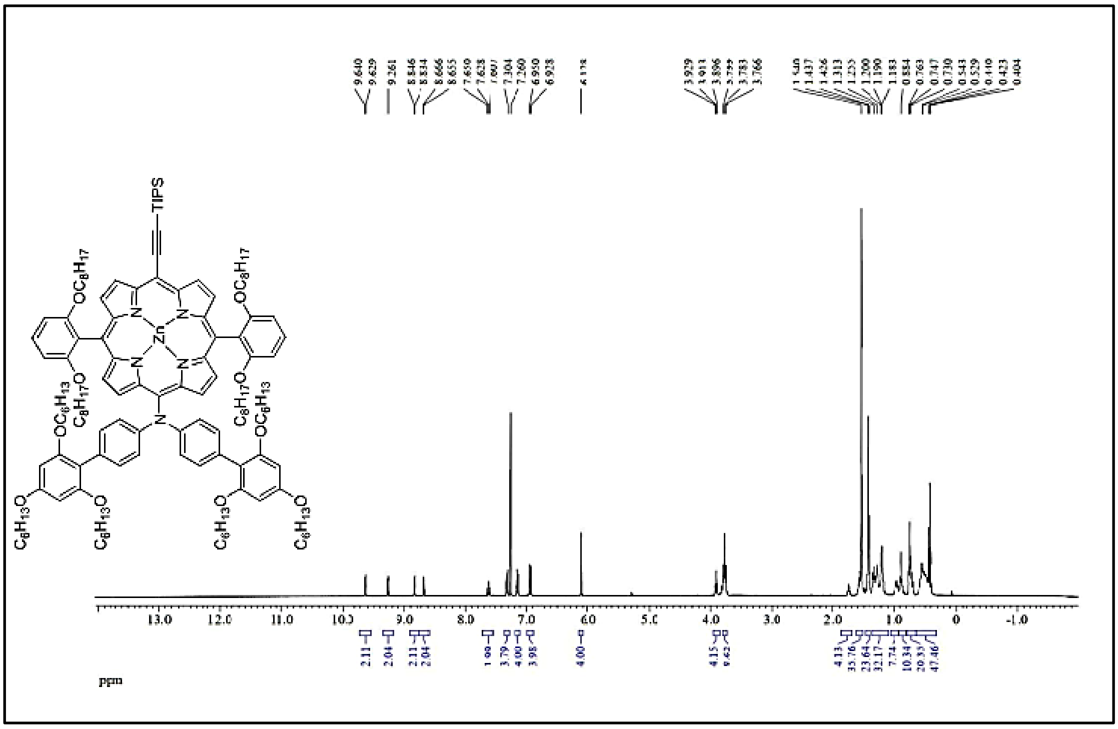


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4**.

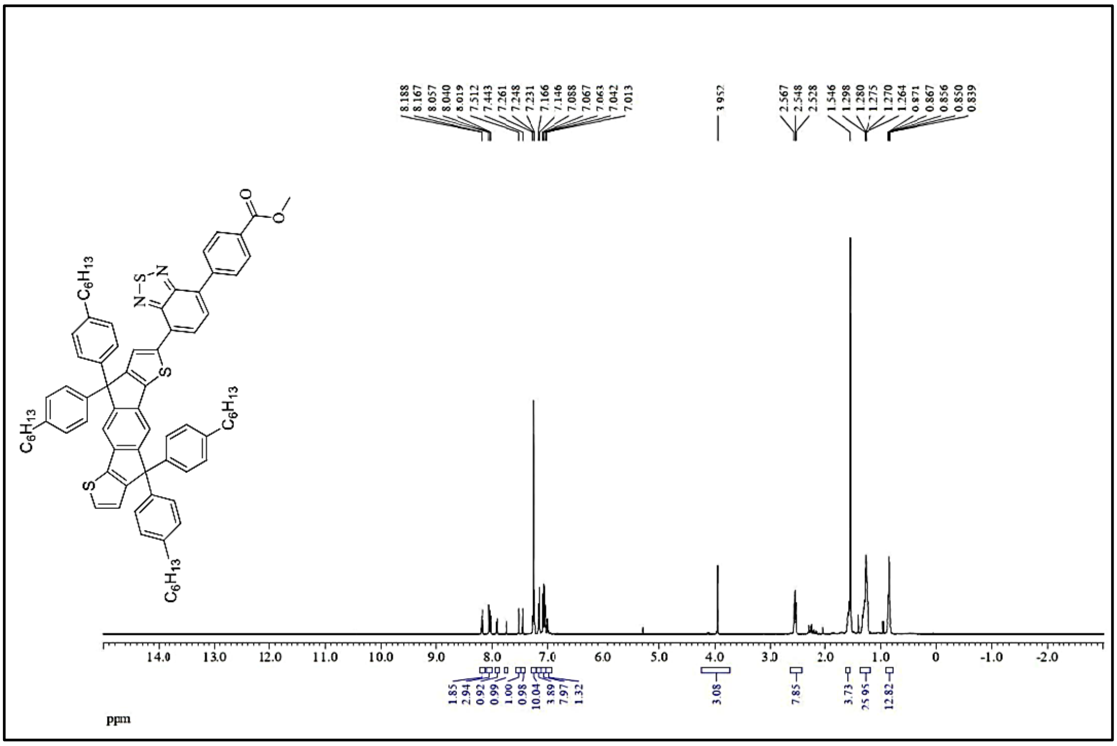


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **9**.

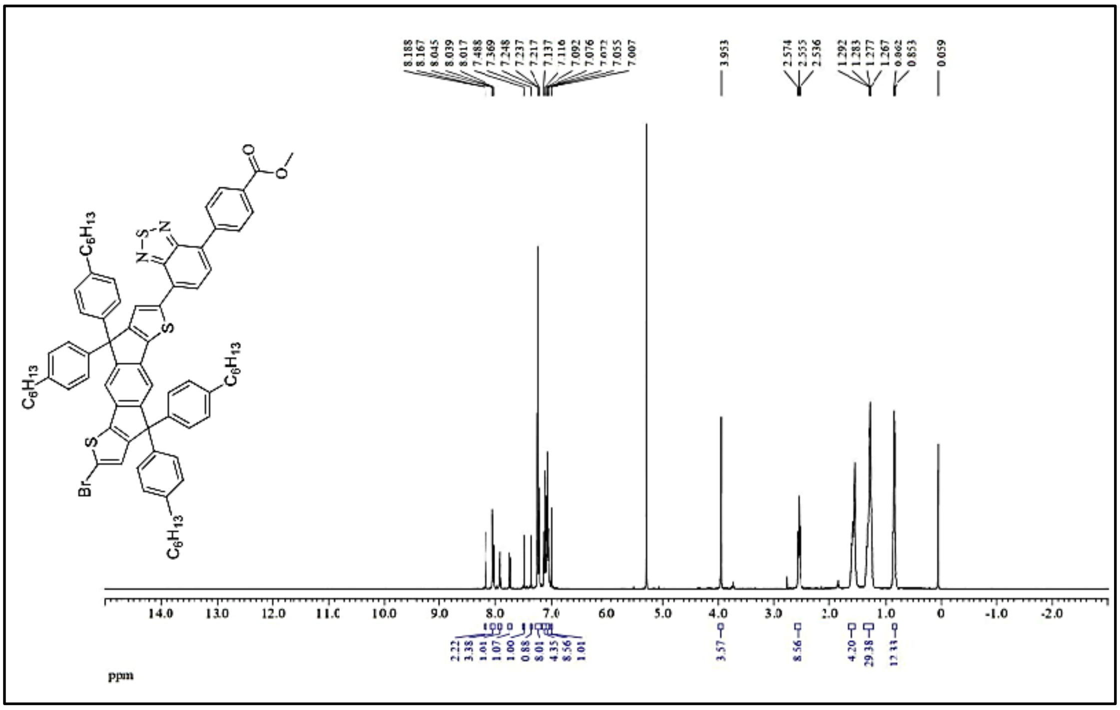


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**.

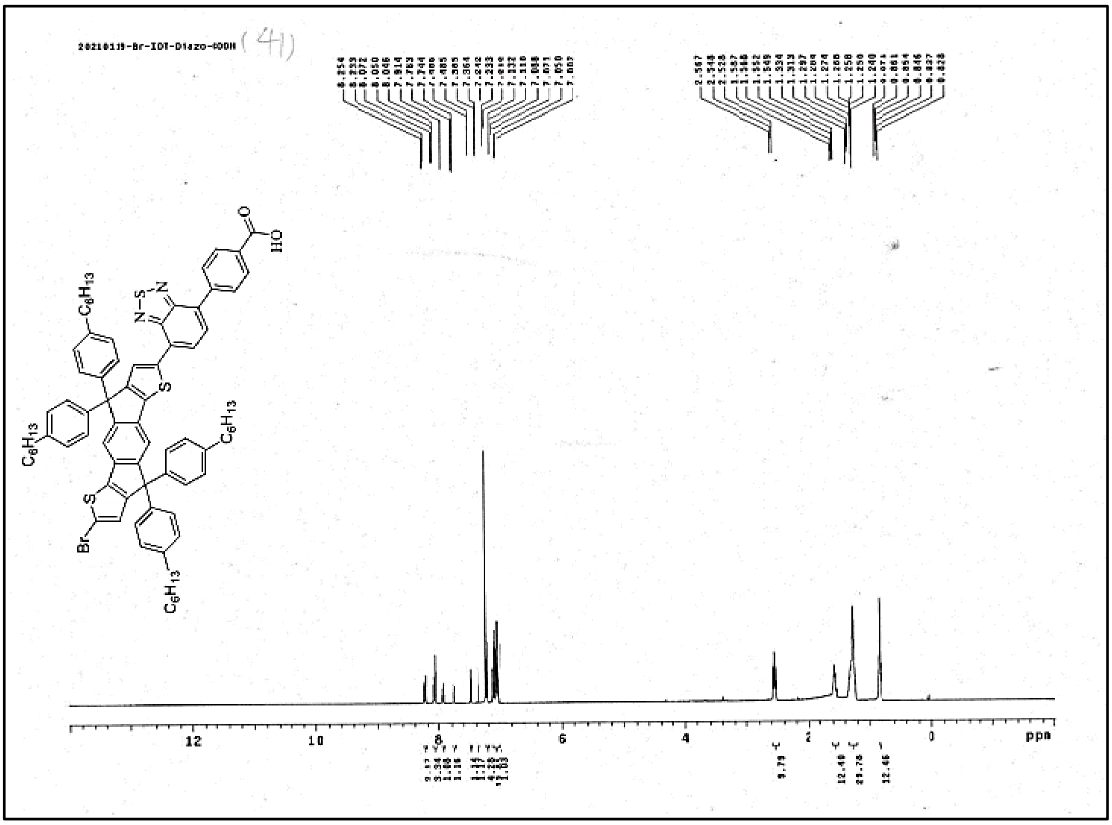


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **11**.

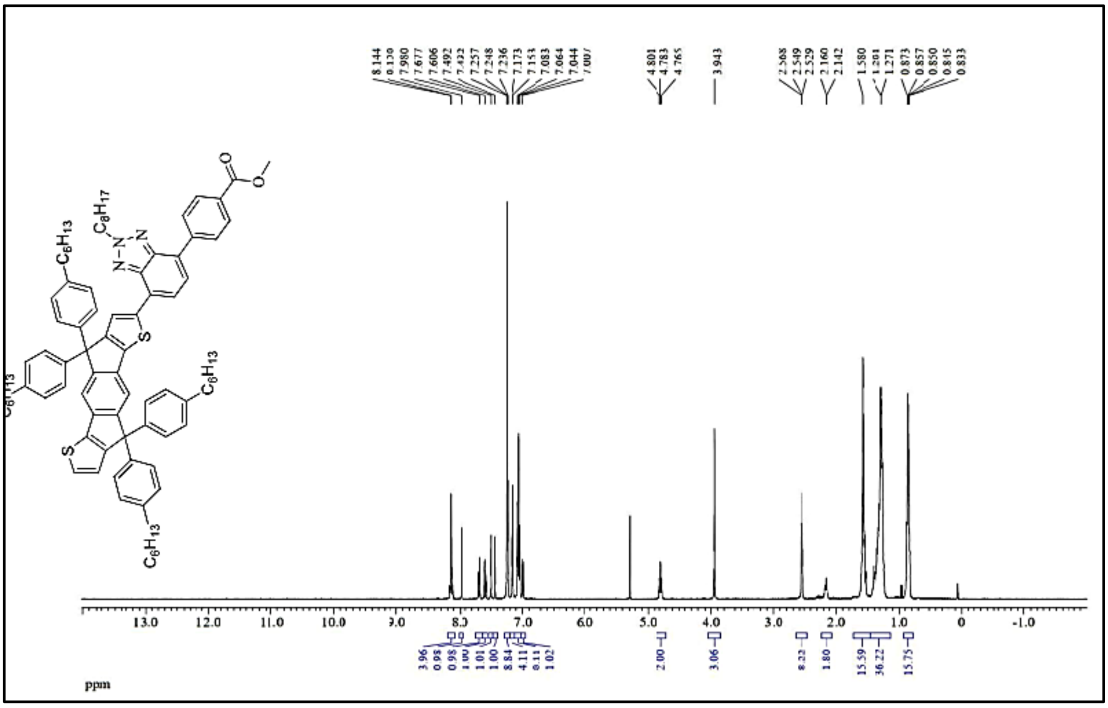


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **12.**

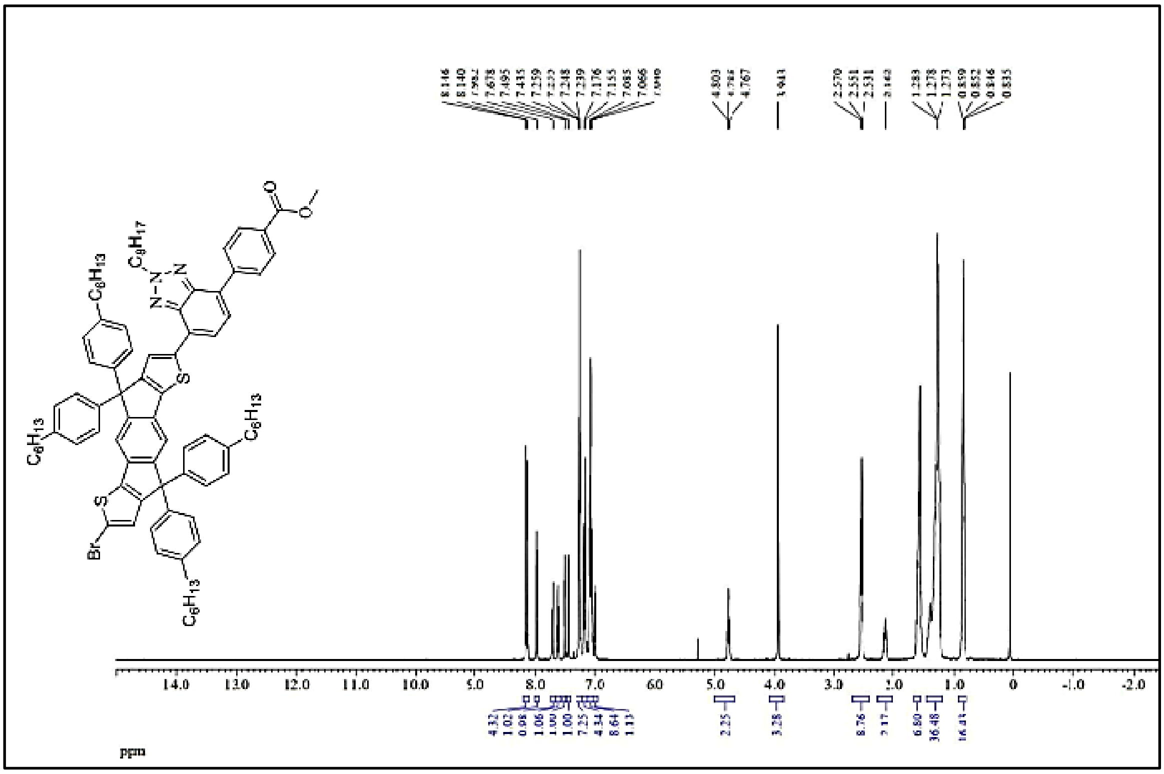


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **13**.

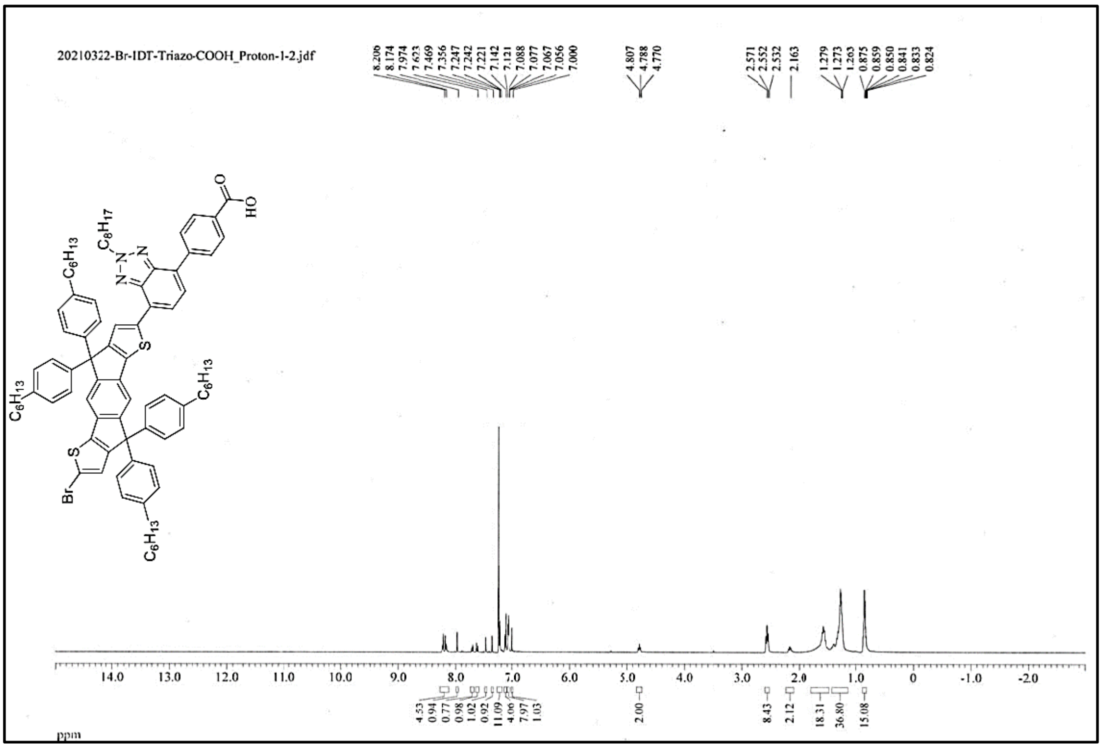


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **14**.

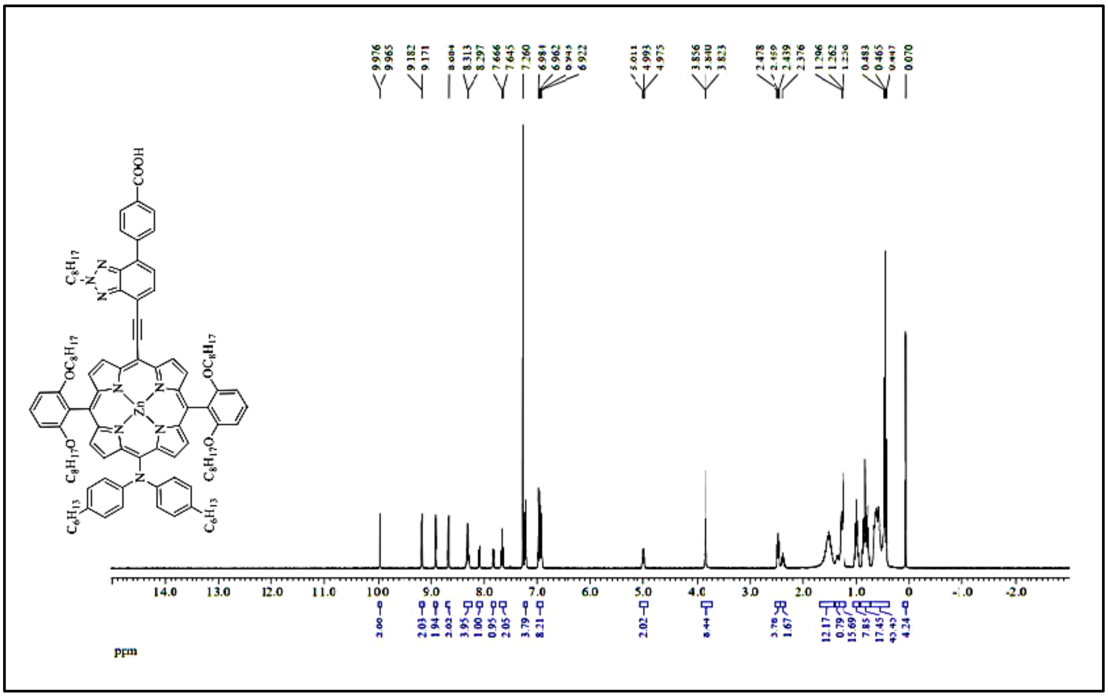


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **TZ1.**

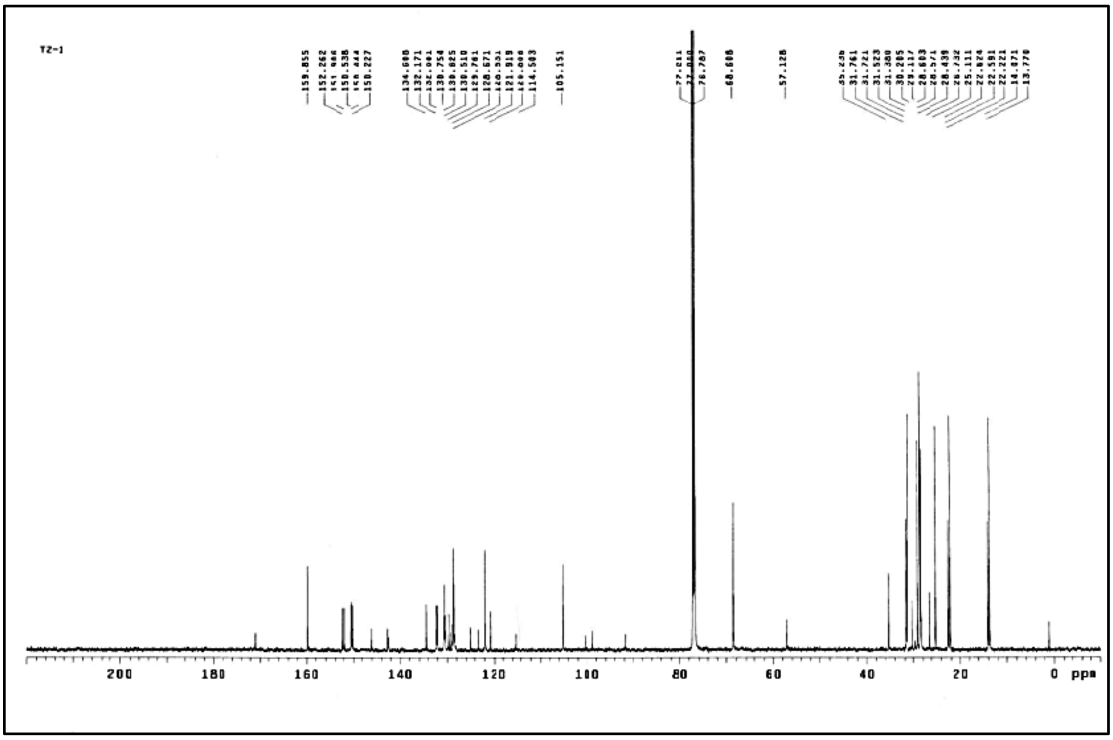


Figure S9. ^{13}C NMR spectrum (400 MHz, CDCl$_3$) of compound **TZ1**.

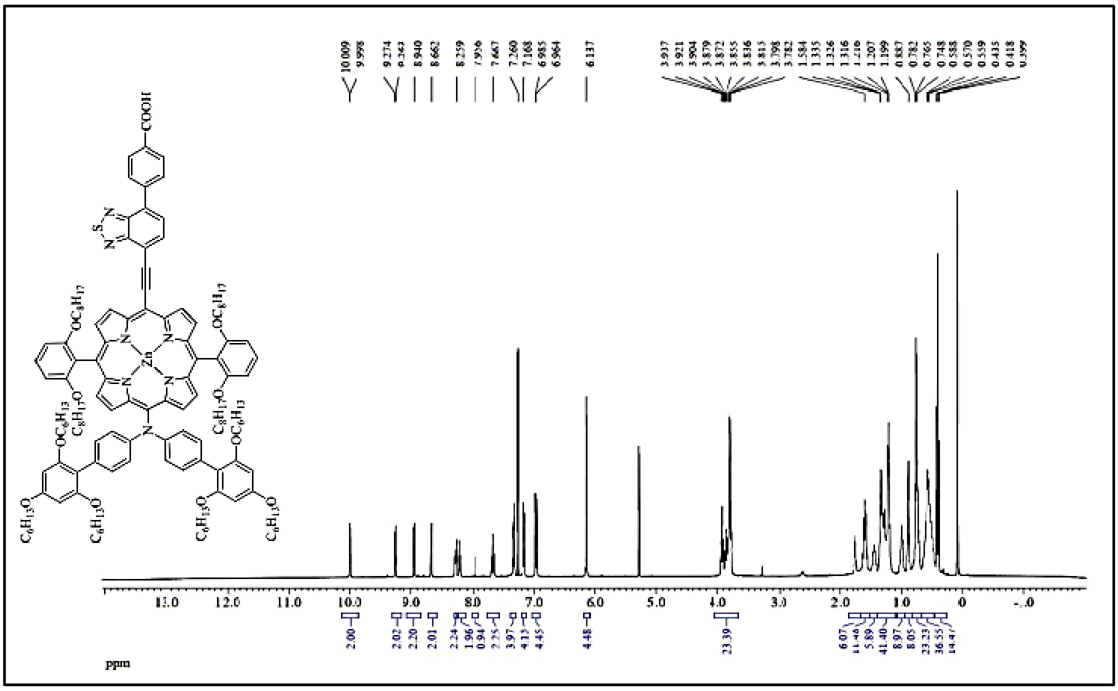


Figure S10. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **TZ2.**

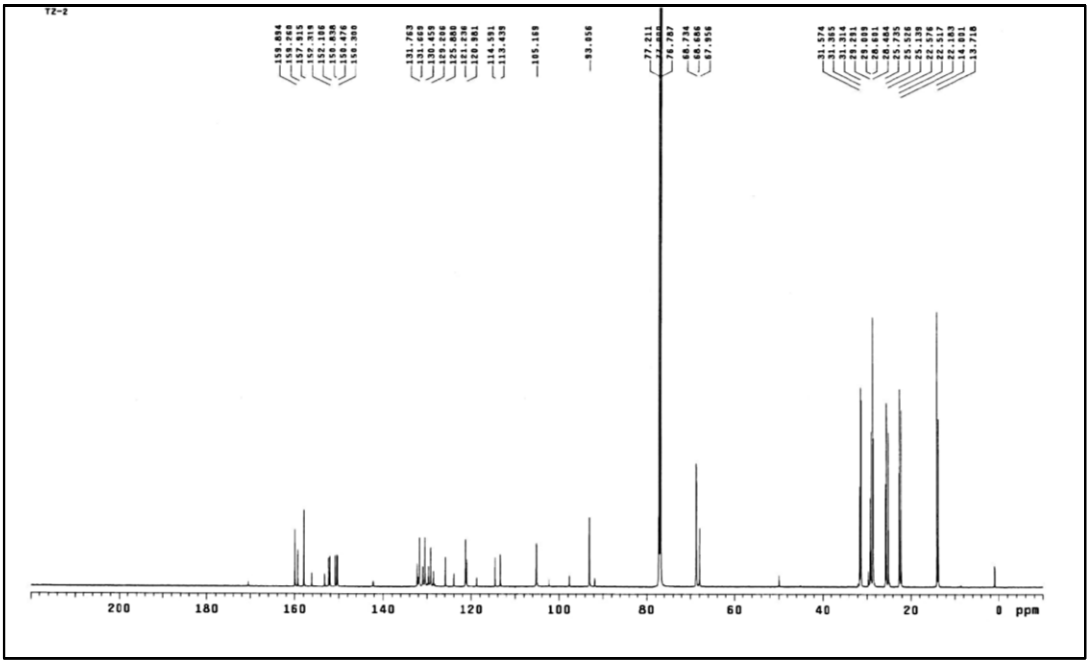


Figure S11. ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of compound **TZ2**.

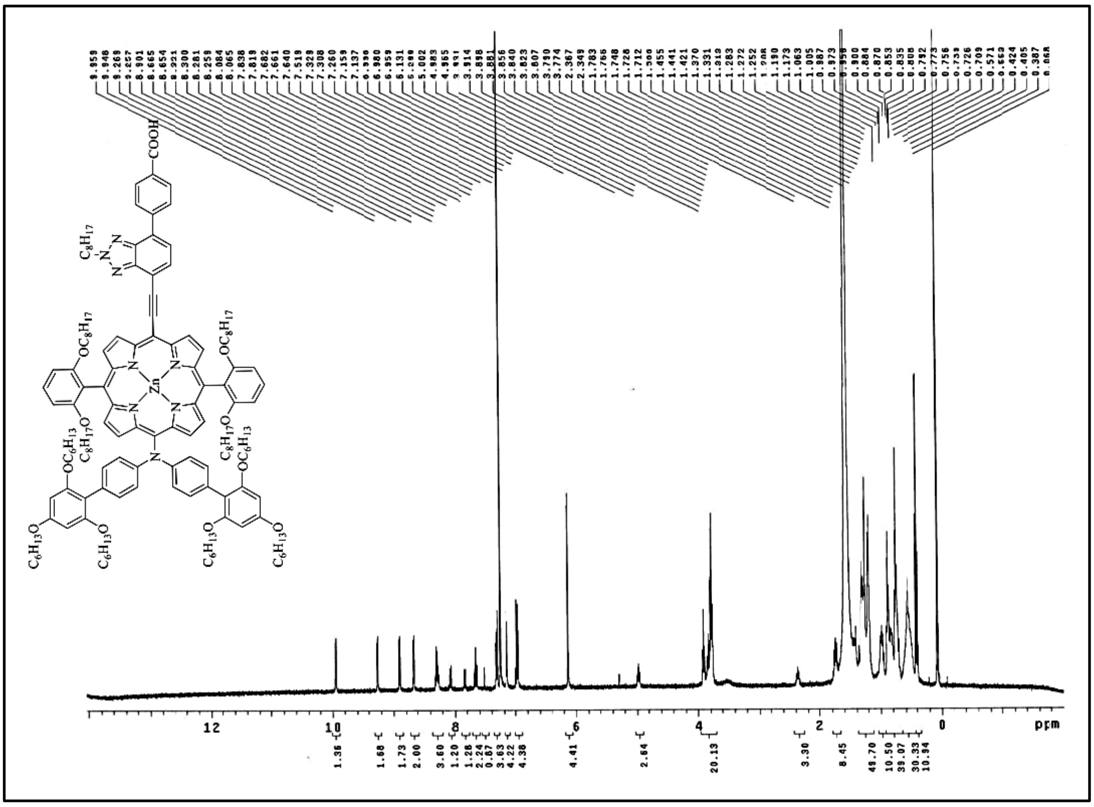


Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **TZ3.**

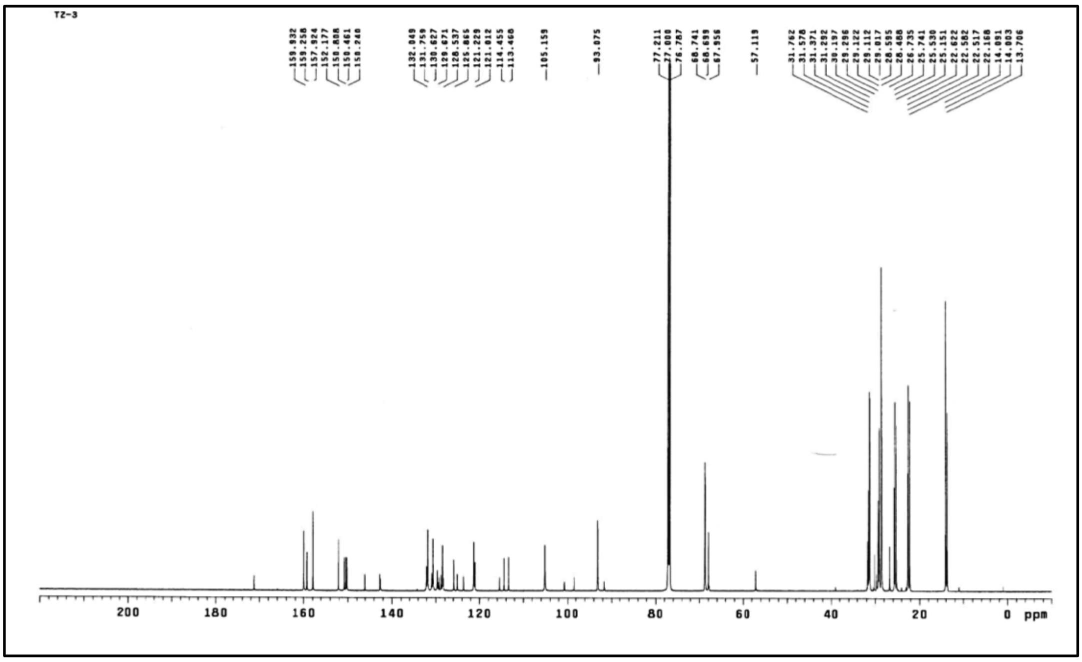


Figure S13. ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of compound **TZ3**.

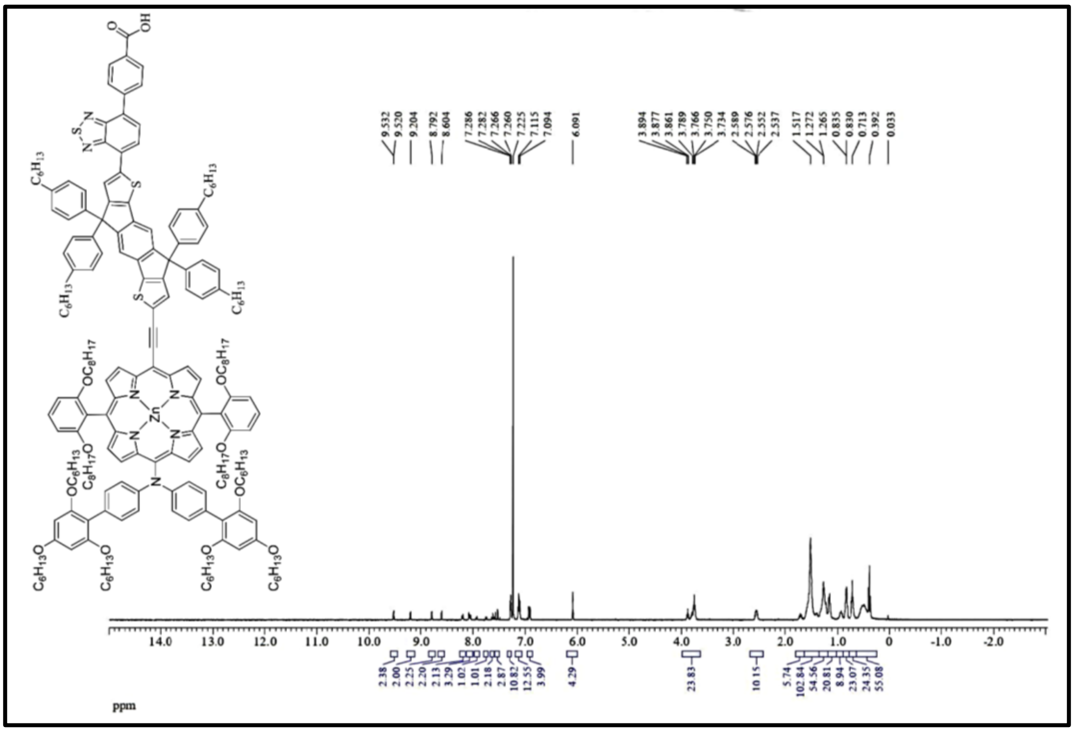


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **TZ4.**

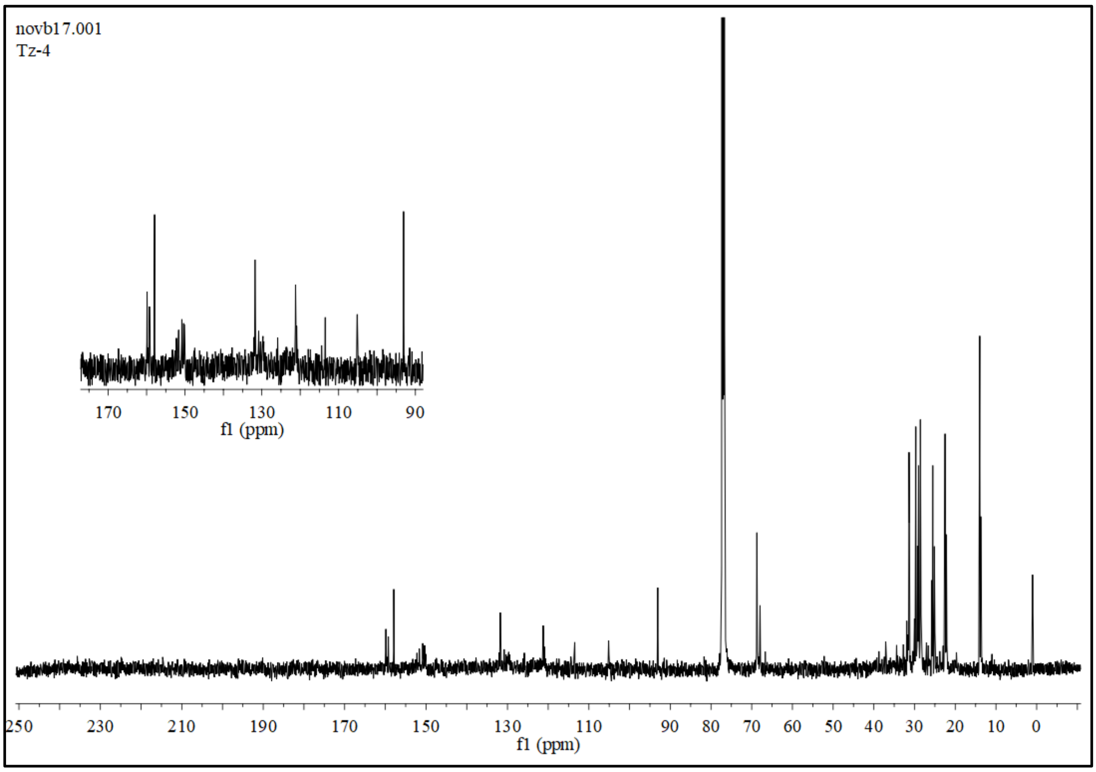


Figure S15. ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of compound **TZ4**.

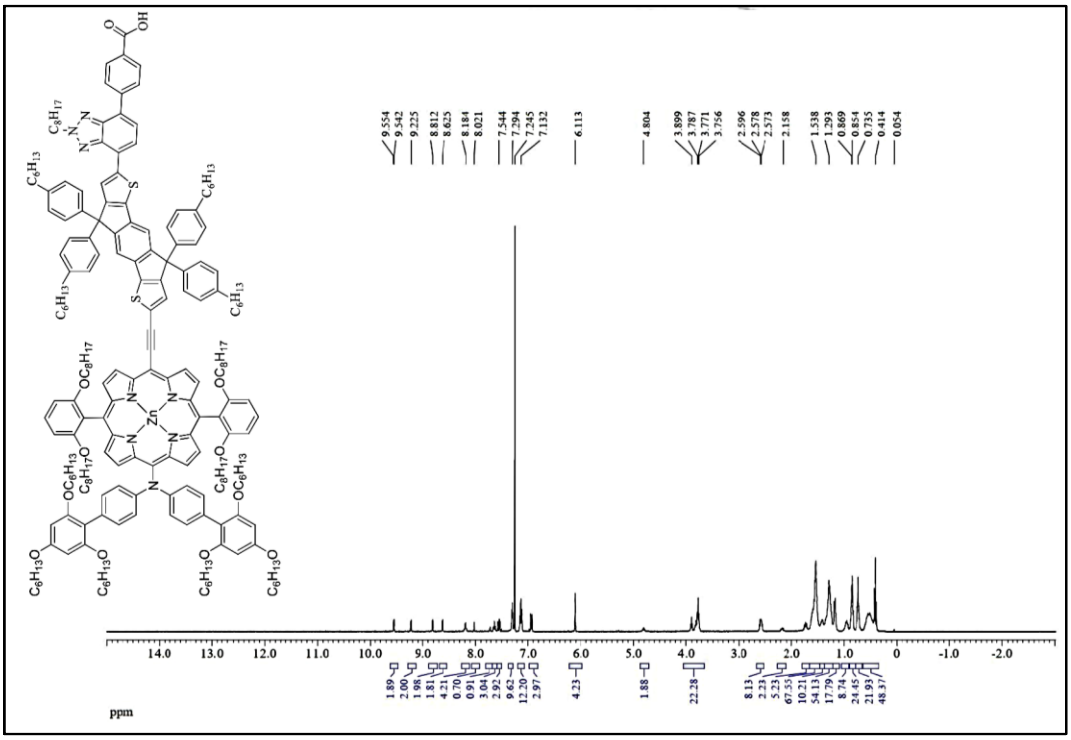


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **TZ5.**

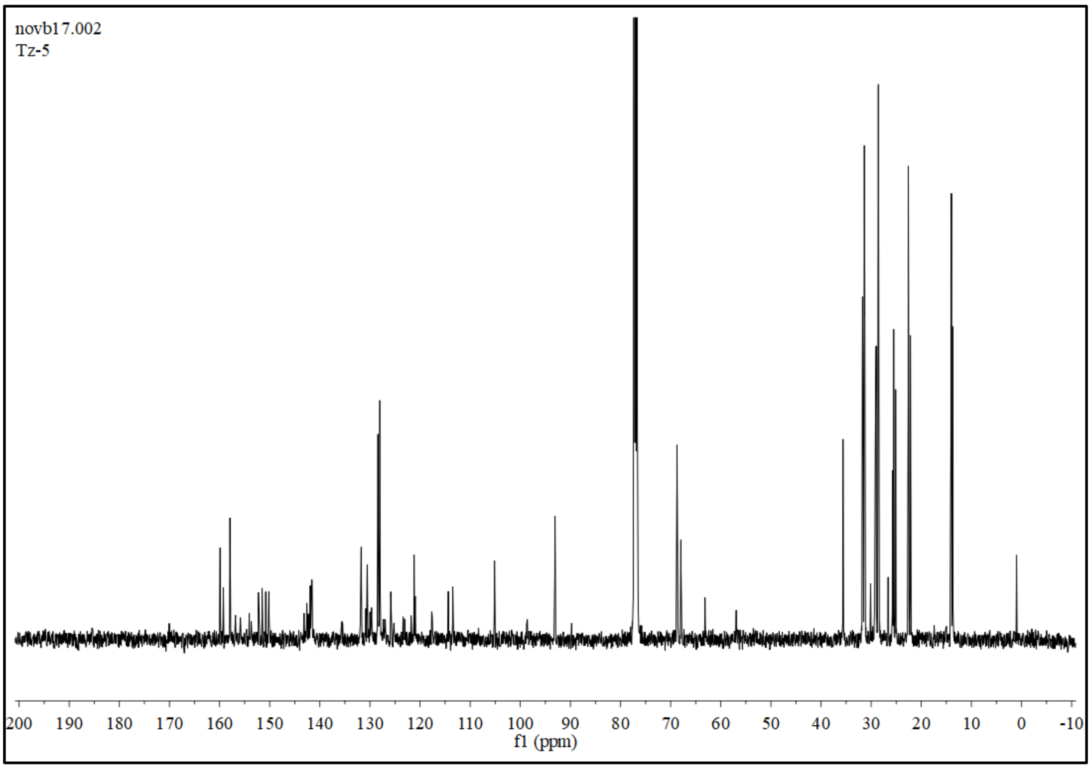


Figure S17. ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of compound **TZ5**.

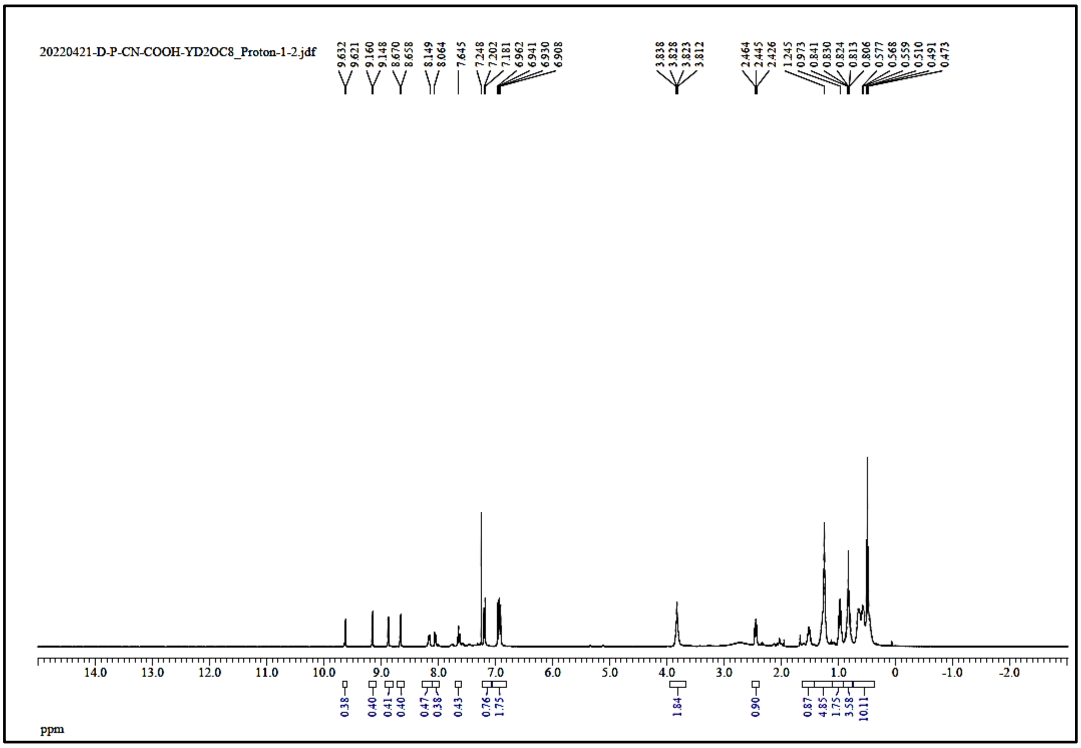


Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **TZ6.**

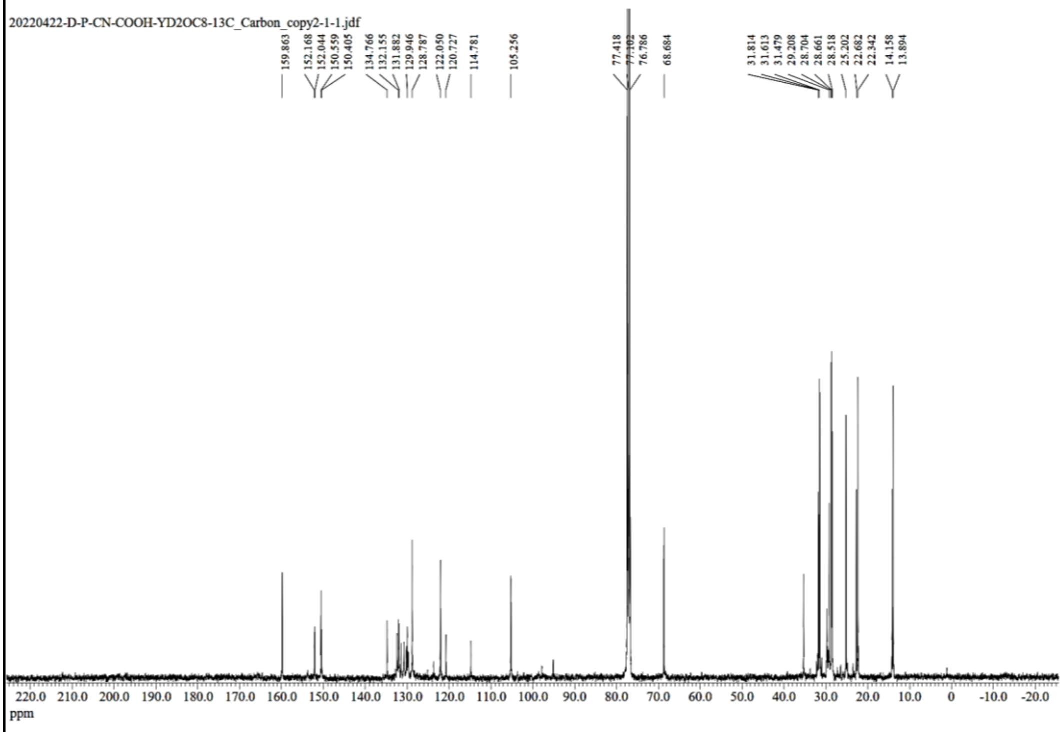


Figure S19. ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of compound **TZ6**.

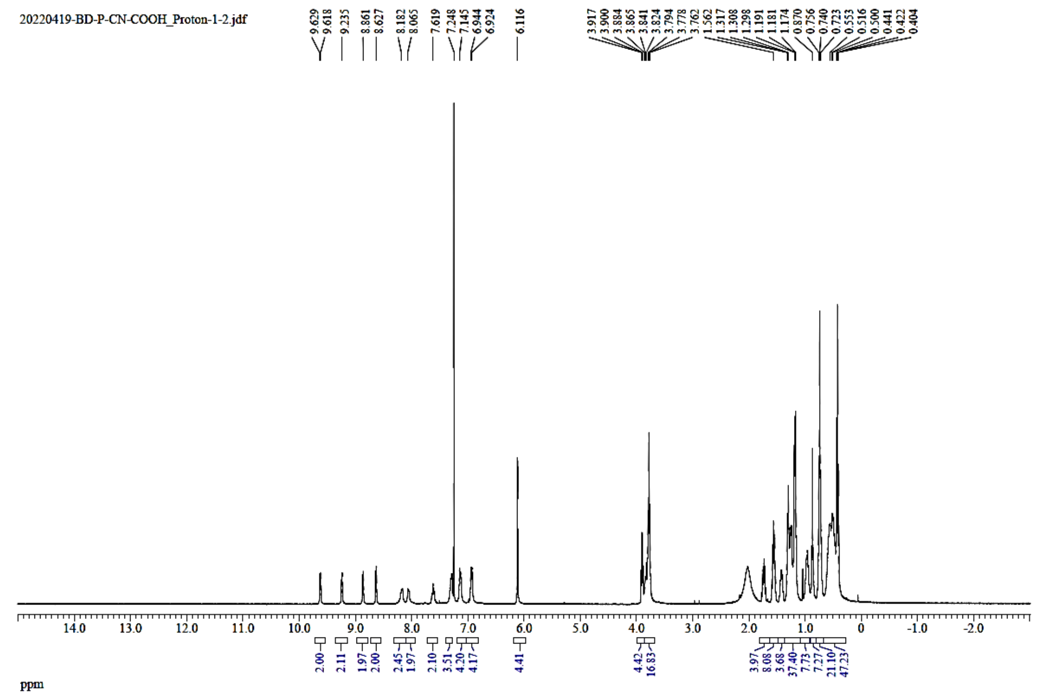


Figure S20. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **TZ7.**

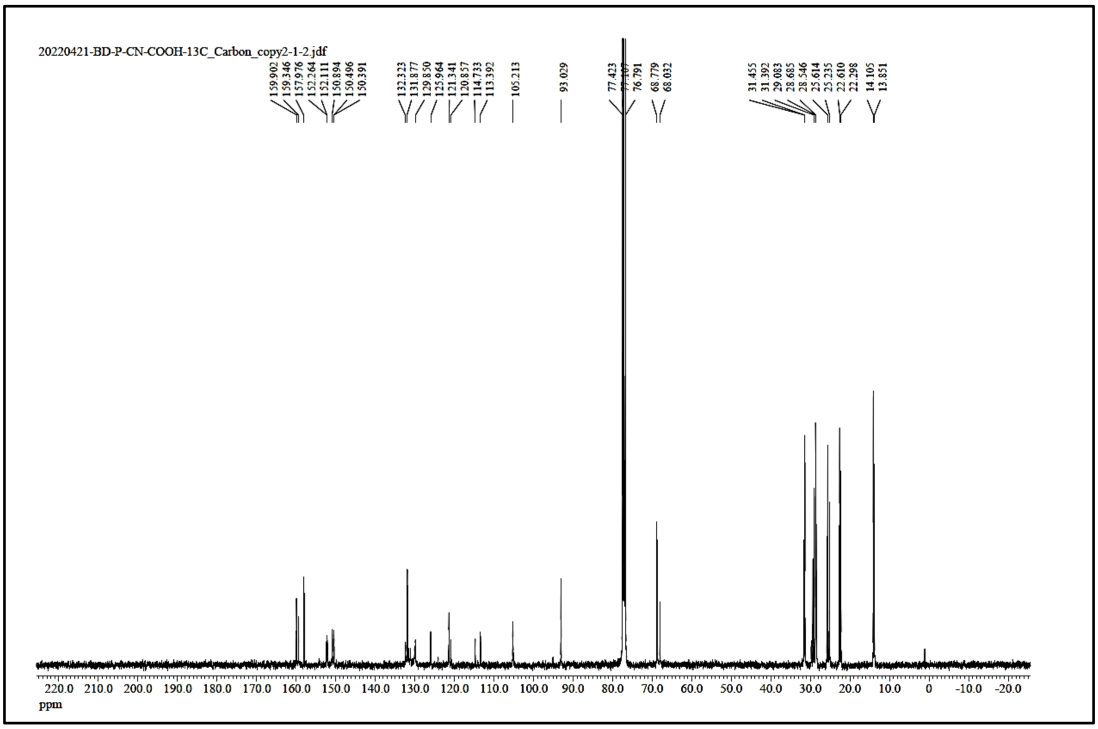


Figure S21. ^{13}C NMR spectrum (400 MHz, CDCl$_3$) of compound **TZ7**.

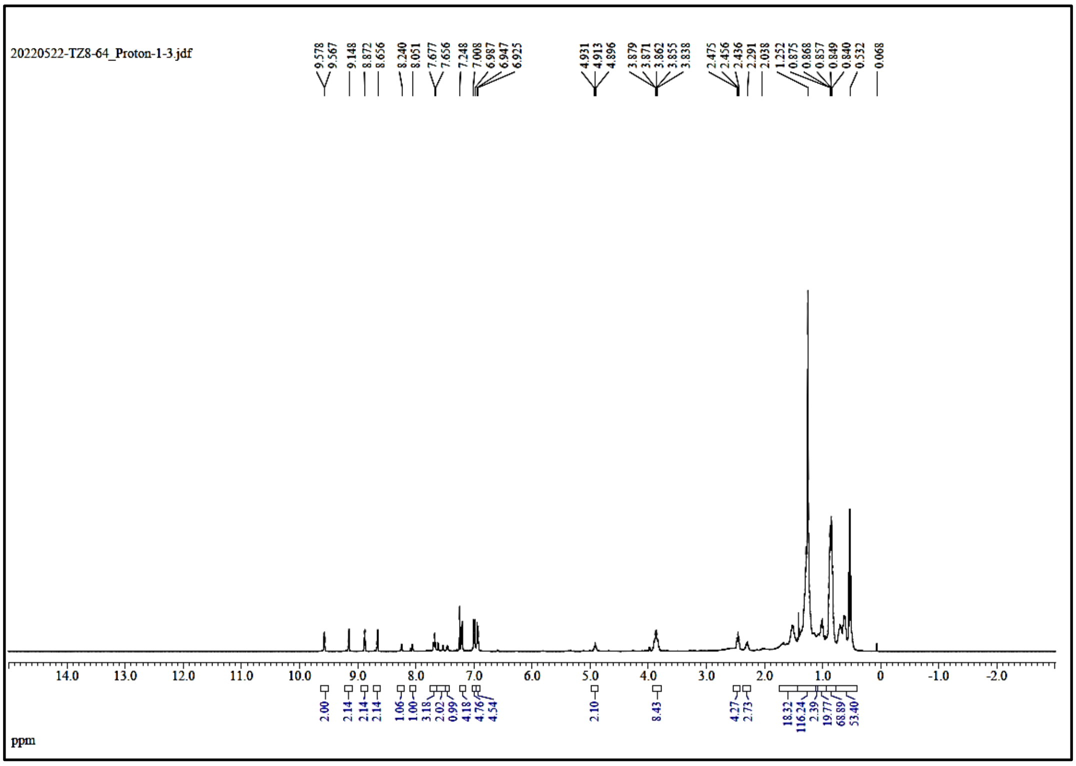


Figure S22. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **TZ8.**

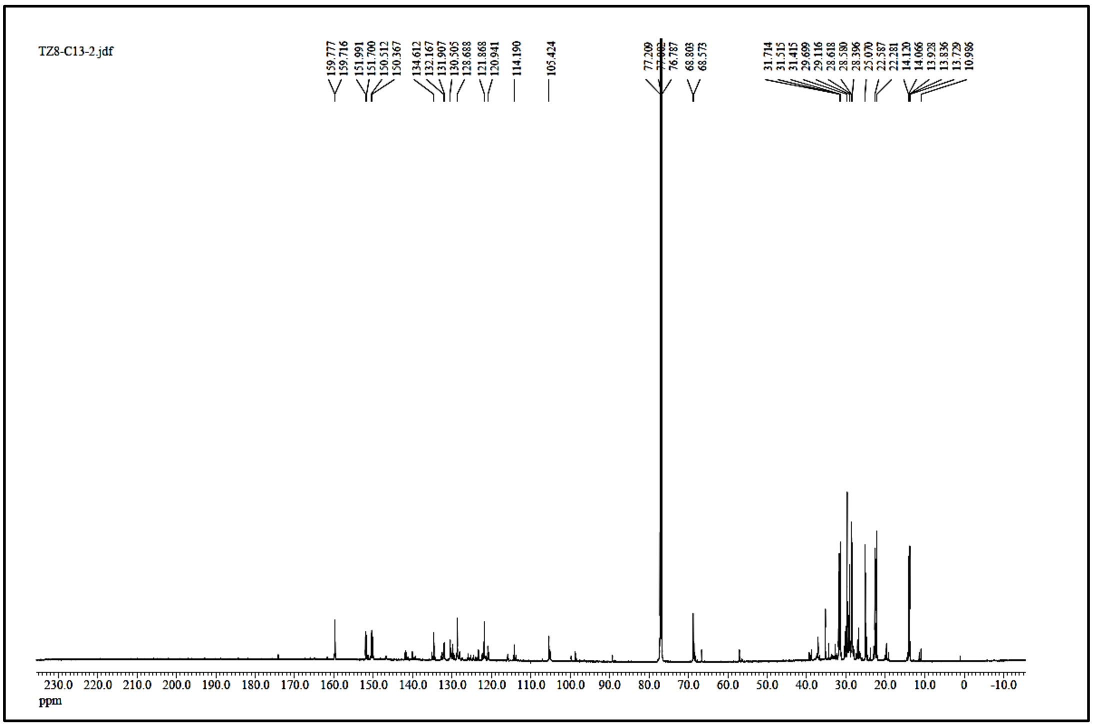


Figure S23. ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of compound **TZ8**.

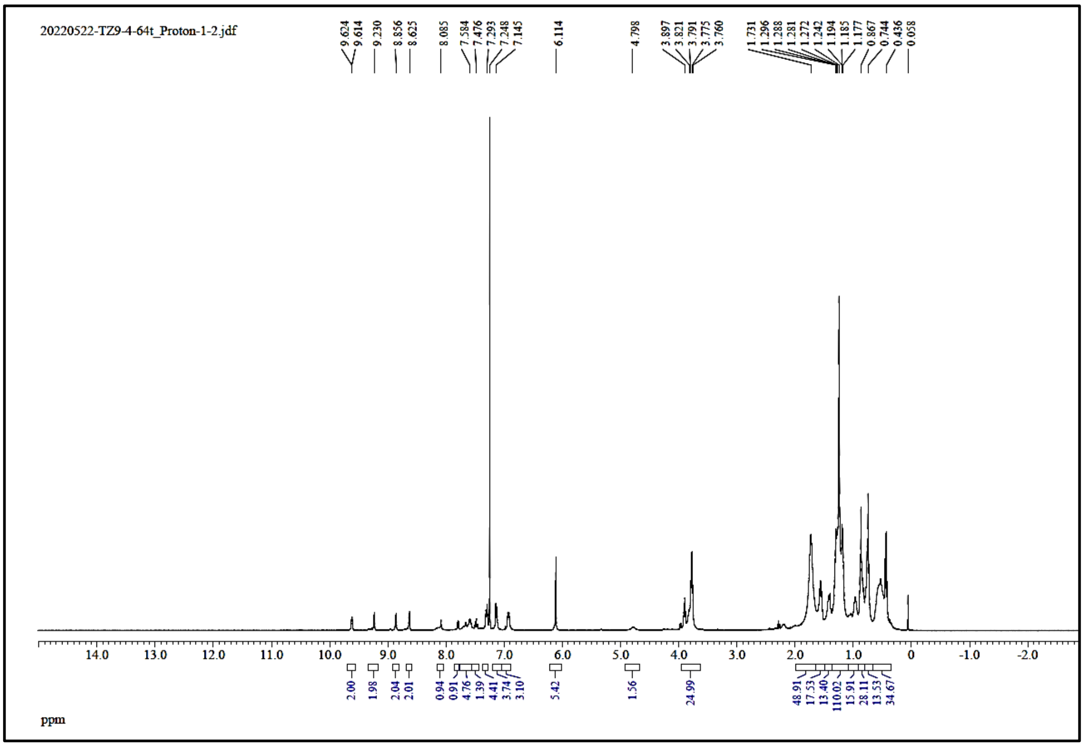


Figure S24. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **TZ9.**

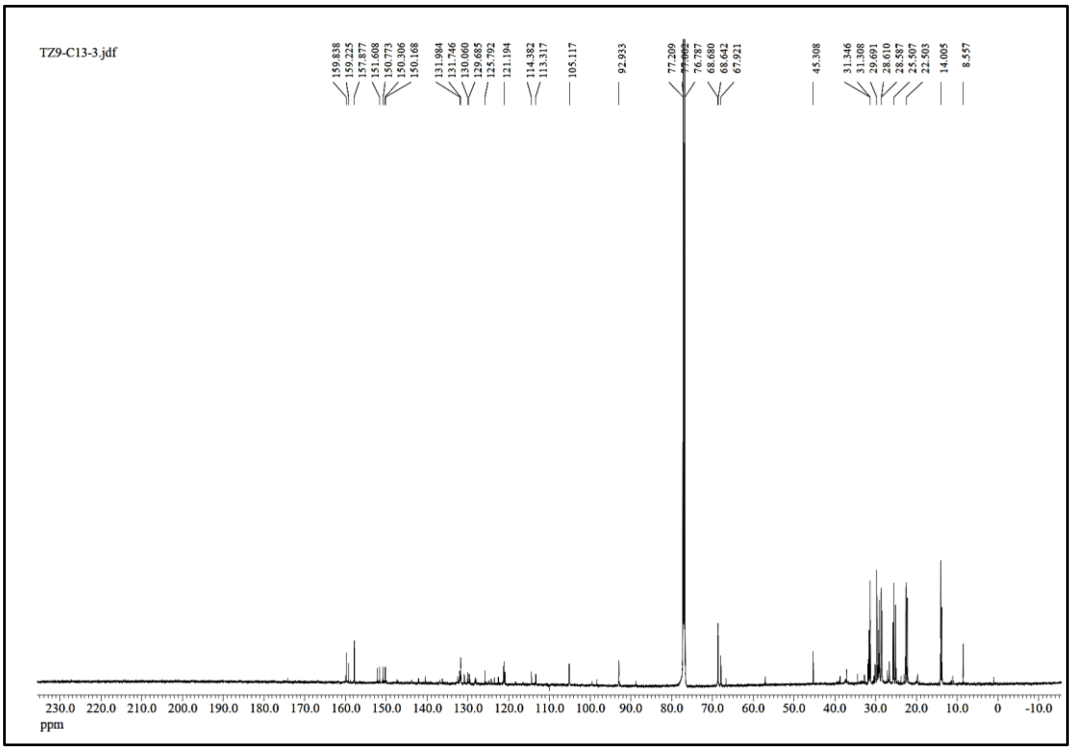


Figure S25. ^{13}C NMR spectrum (400 MHz, CDCl$_3$) of compound **TZ9**.

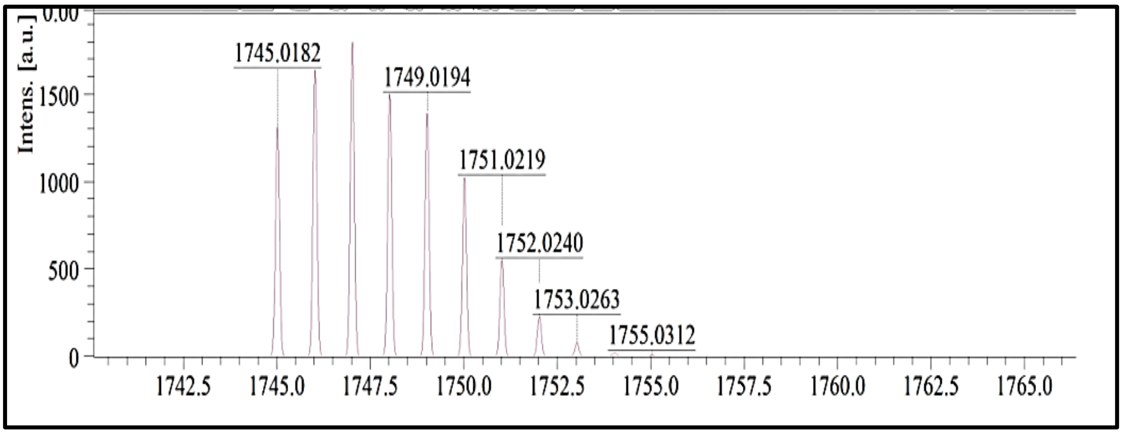


Figure S26. MALDI-TOF (HRMS) spectrum of **TZ1.**

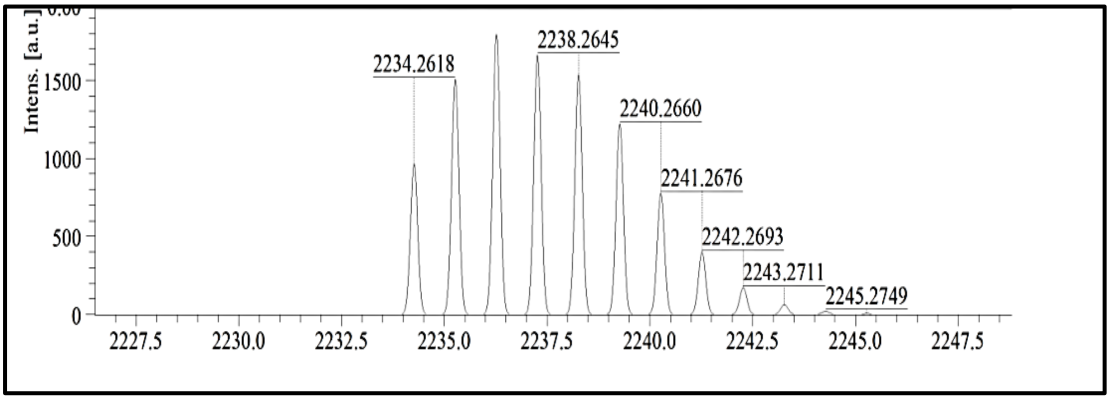


Figure S27. MALDI-TOF (HRMS) spectrum of **TZ2.**

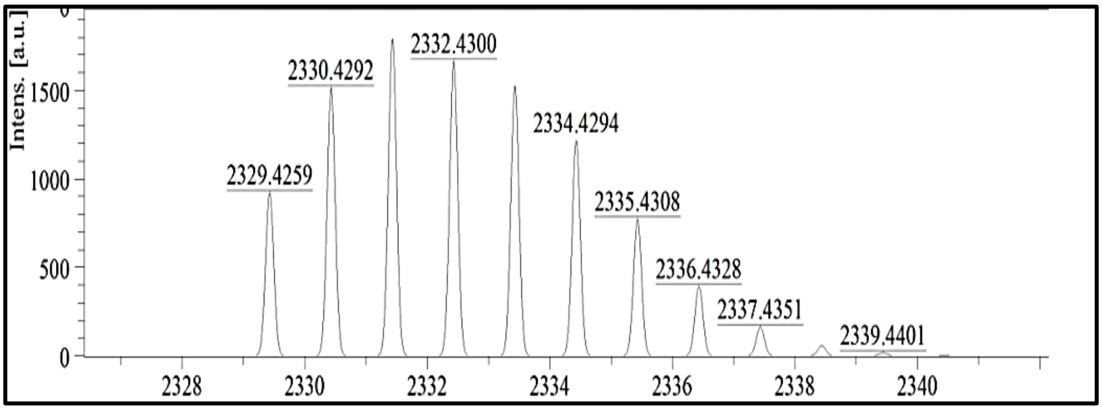


Figure S28. MALDI-TOF (HRMS) spectrum of **TZ3.**

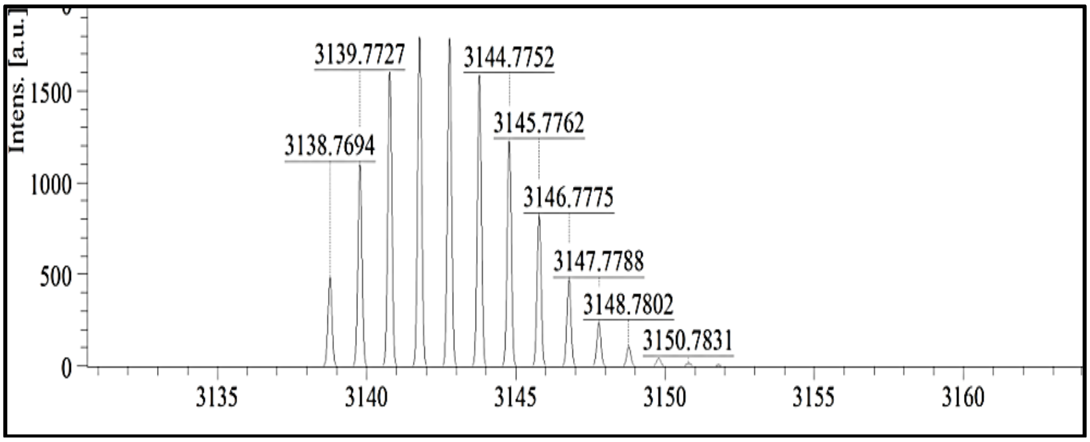


Figure S29. MALDI-TOF (HRMS) spectrum of **TZ4.**

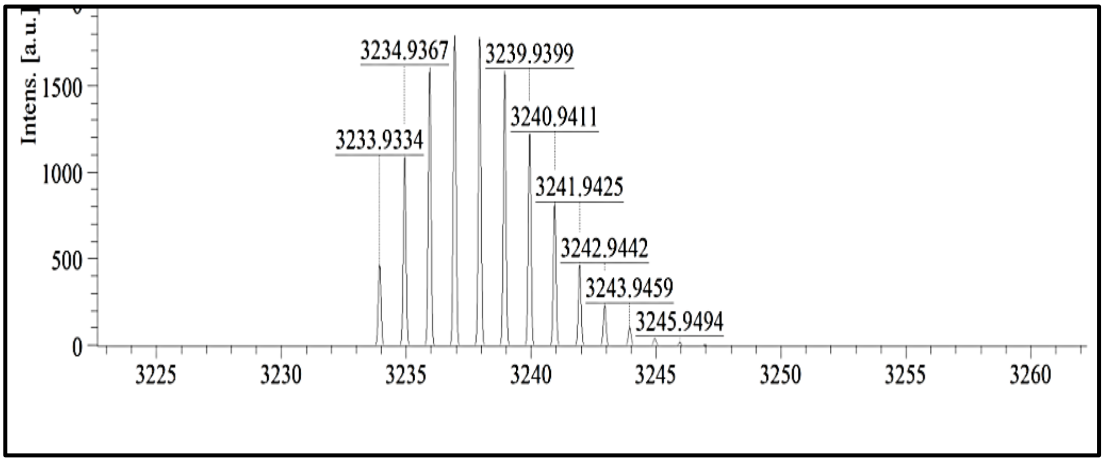
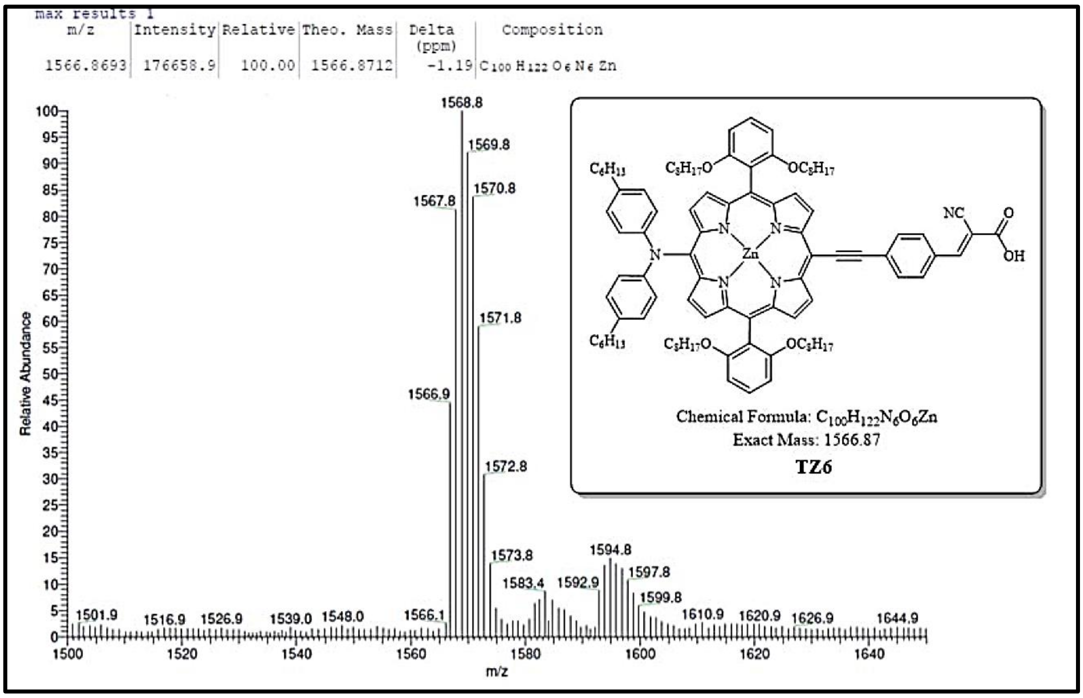


Figure S30. MALDI-TOF (HRMS) spectrum of **TZ5.**



```
max results 1
    m/z     |Intensity|Relative|Theo. Mass| Delta  |     Composition
            |         |        |          | (ppm)  |
 1566.8693  | 176658.9|  100.00| 1566.8712|   -1.19|C100 H122 O6 N6 Zn
```

Figure S31. ESI-MS spectrum of **TZ6.**

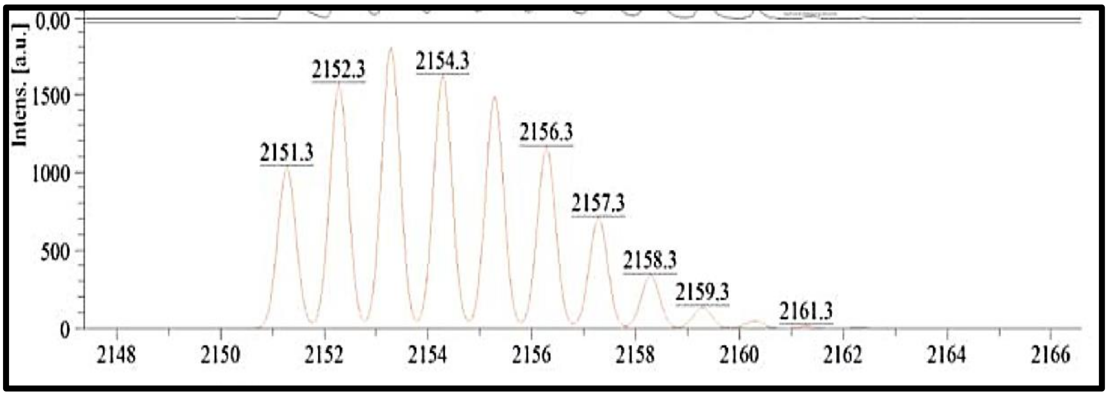


Figure S32. MALDI-TOF (HRMS) spectrum of **TZ7.**

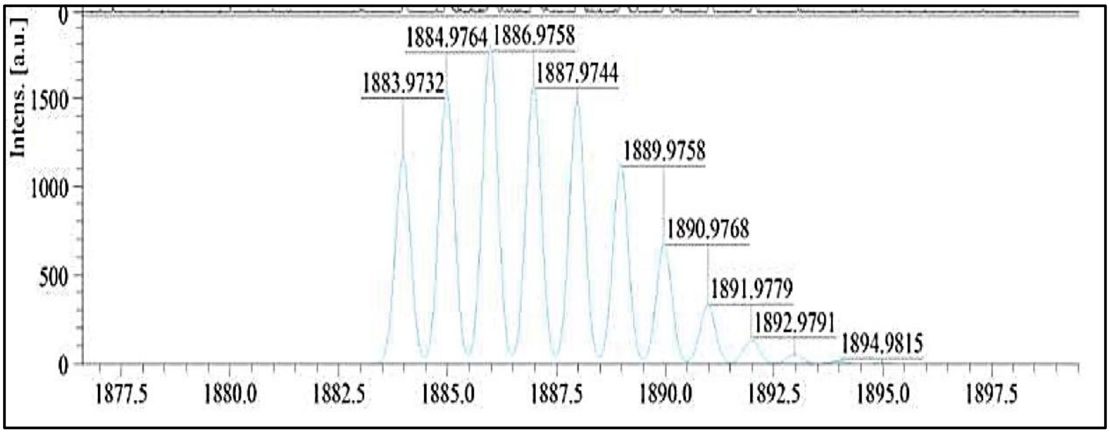


Figure S33. MALDI-TOF (HRMS) spectrum of **TZ8.**

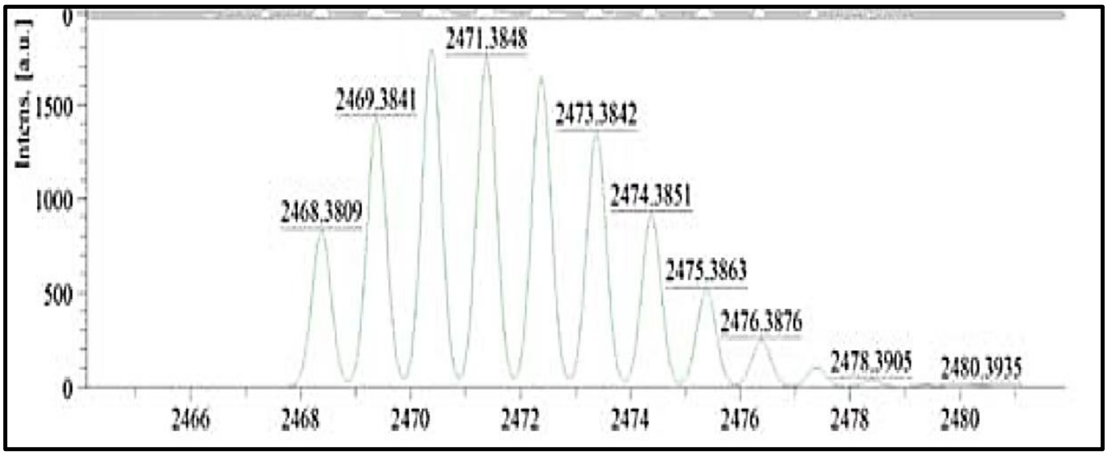


Figure S34. MALDI-TOF (HRMS) spectrum of **TZ9.**

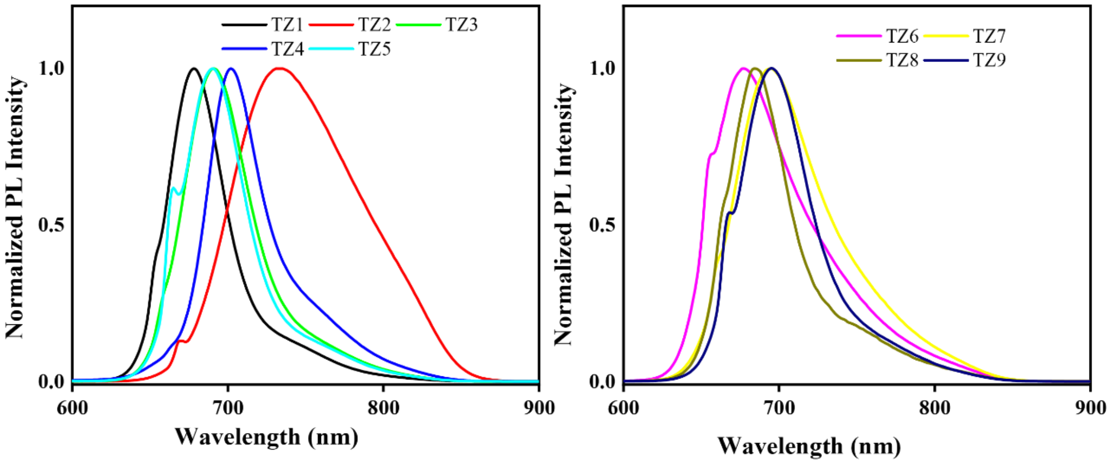


Figure S35. Normalized emission spectrum of TZ dyes in THF.

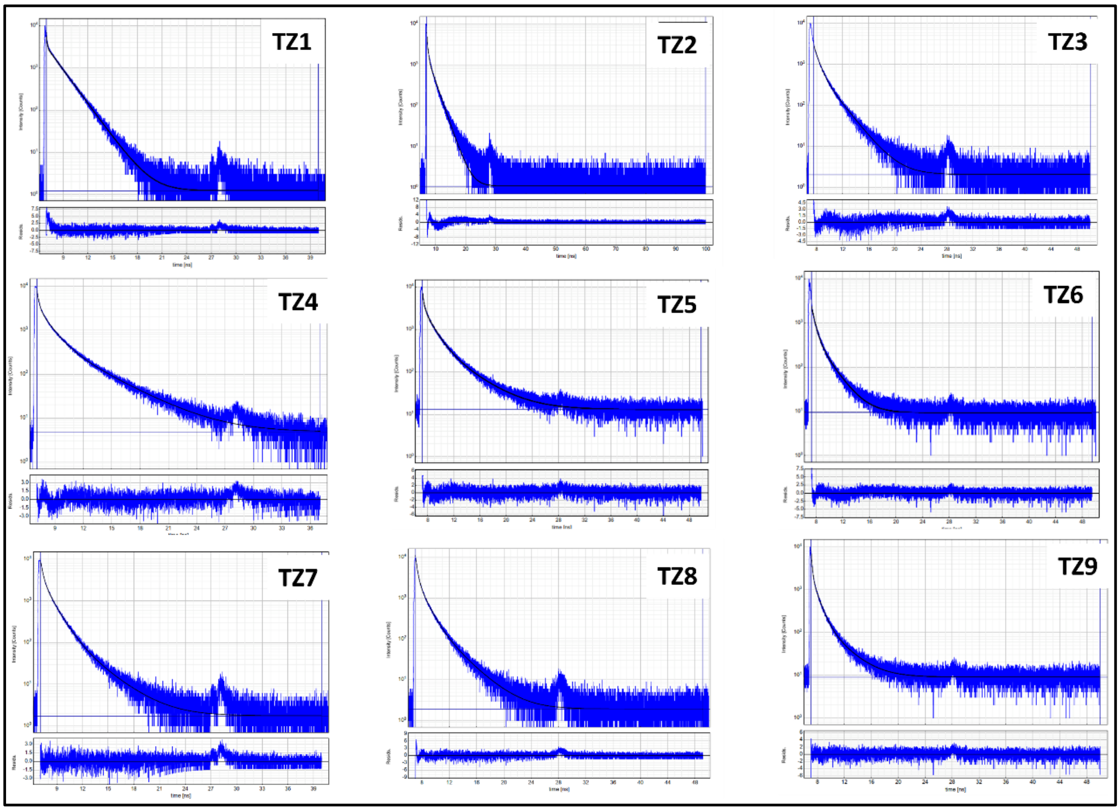


Figure S36. Fluorescence decays lifetimes of **TZ** days in THF solution (1x10^{-6} M).

Cyclic Voltammograms:

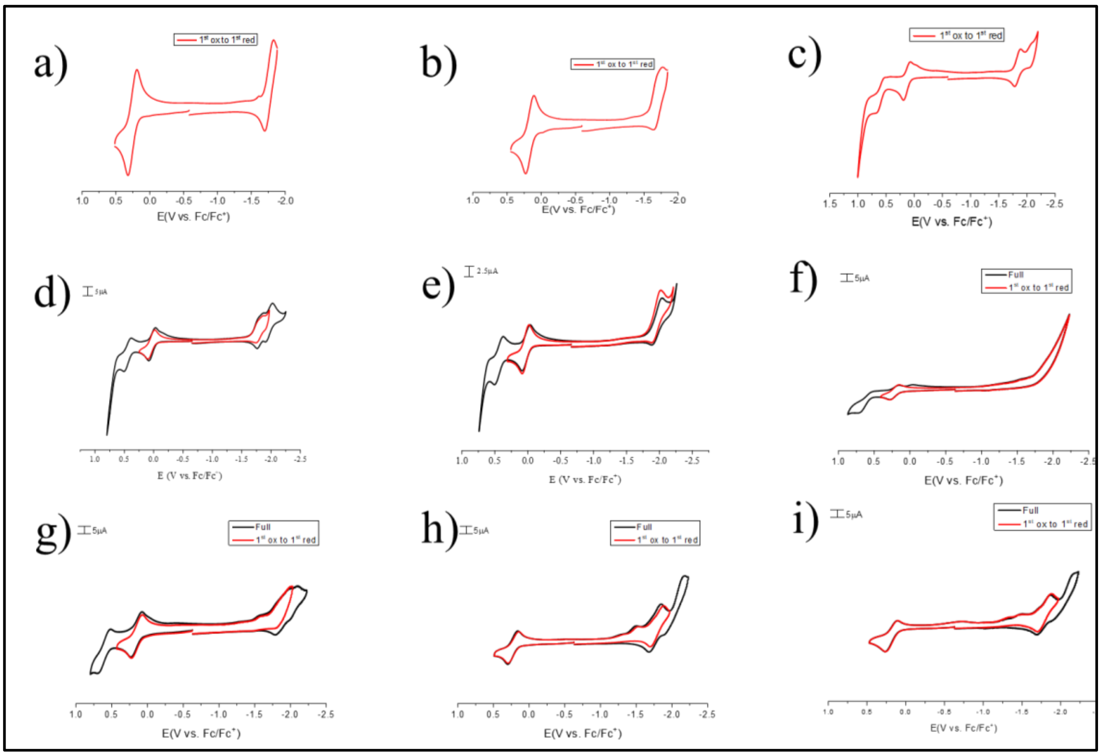


Figure S37. Cyclic Voltammetry of a) **TZ1**, b) **TZ2**, c) **TZ3**, d) **TZ4**, e) **TZ5**, f) **TZ6**, g) **TZ7**, h) **TZ8**, and i) **TZ9**.

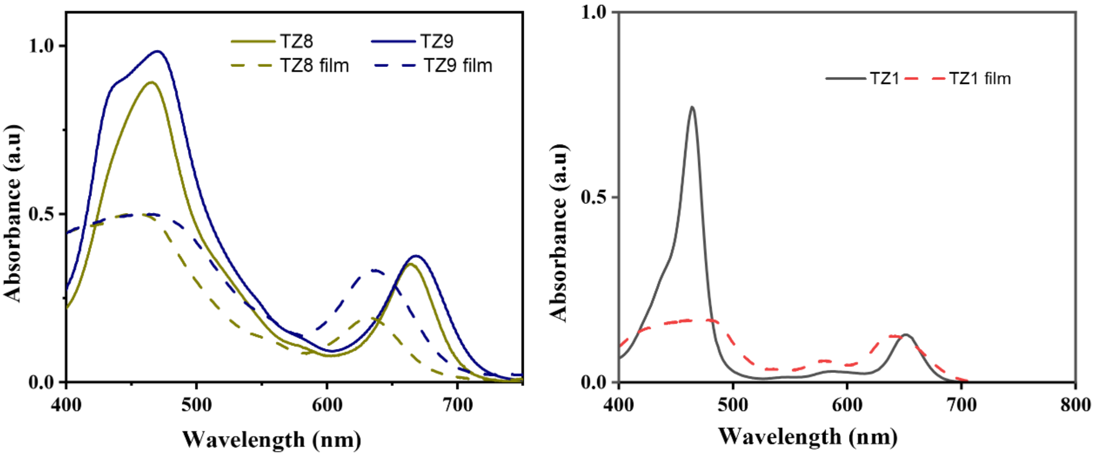


Figure S38. UV-vis absorption spectra of **TZ1**, **TZ8**, and **TZ9** dyes on TiO_2.

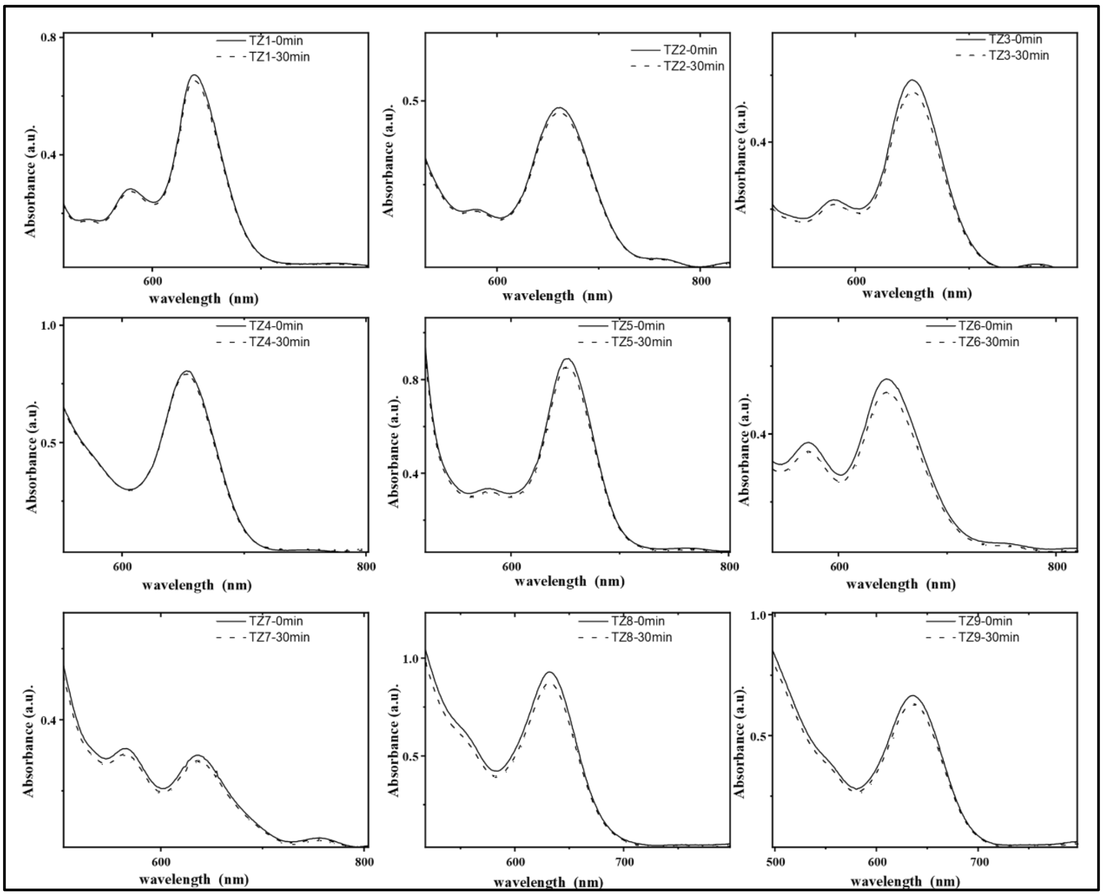


Figure S39. Absorption spectra of **TZ** dyes absorbed onto the TiO_2 films after 1 sun irradiation.

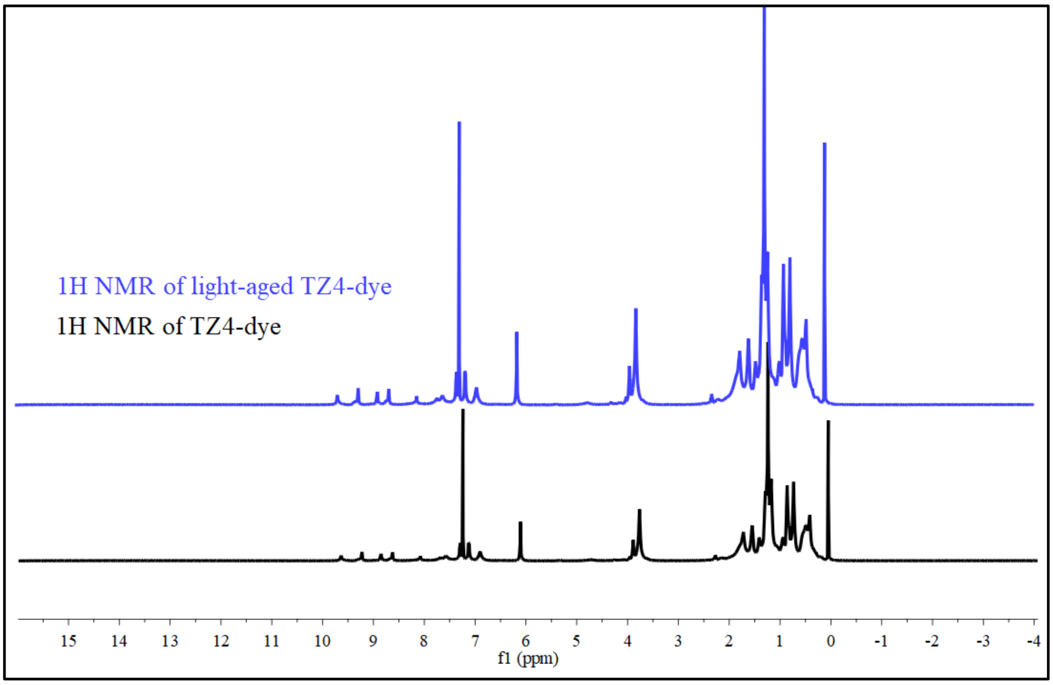


Figure S40.^{1}H NMR spectrum (400 MHz, $CDCl_3$) of fresh and light-aged **TZ4.**

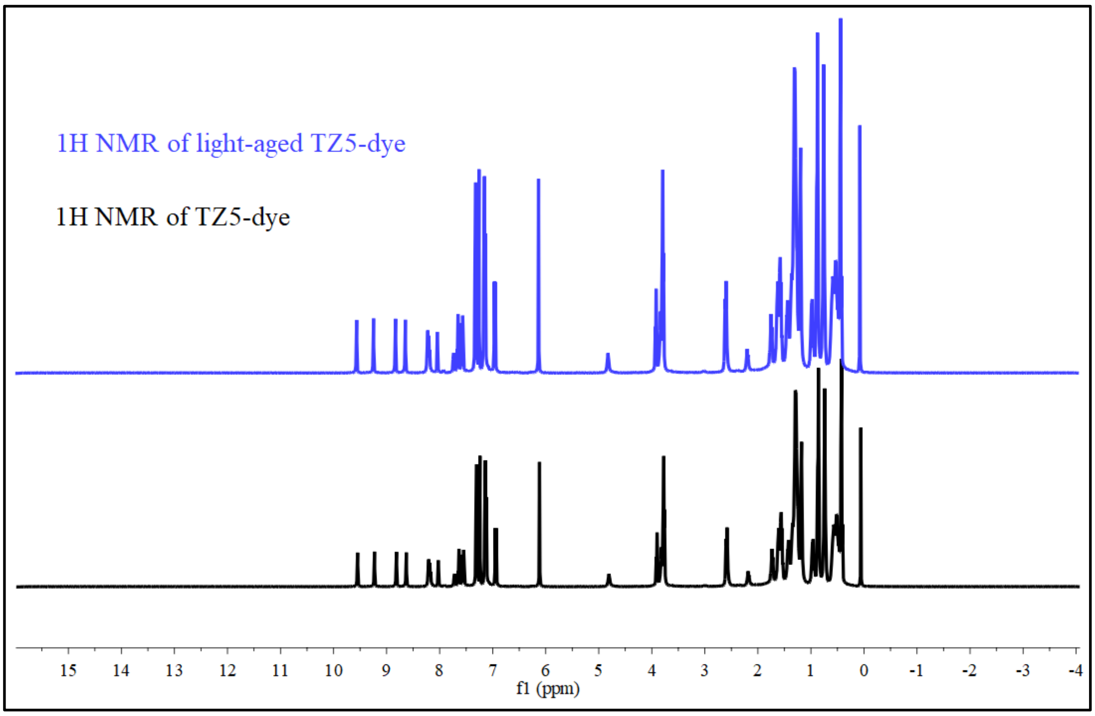


Figure S41. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of fresh and light-aged **TZ5.**

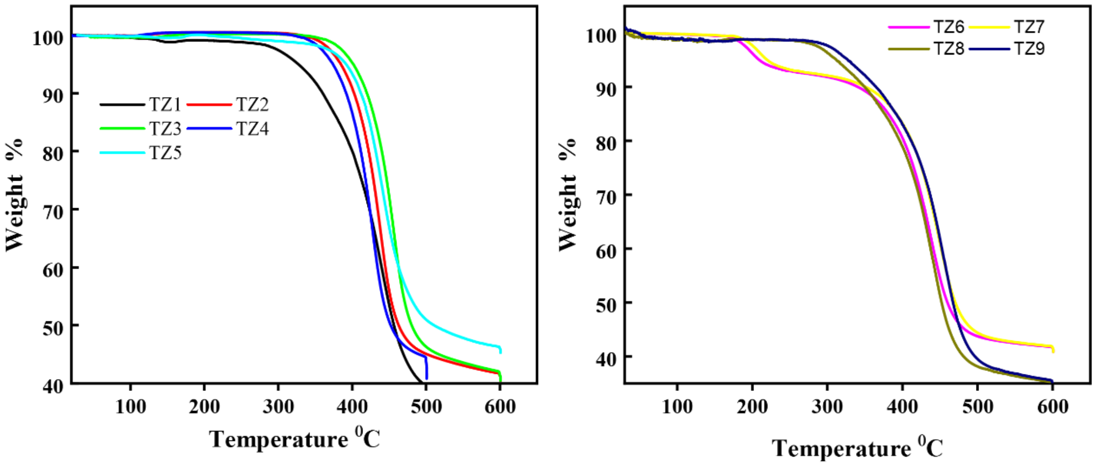


Figure S42. thermogravimetric analysis (TGA) of TZ dyes under nitrogen atmosphere at a heating rate of 10 ^{0}C min^{-1}.

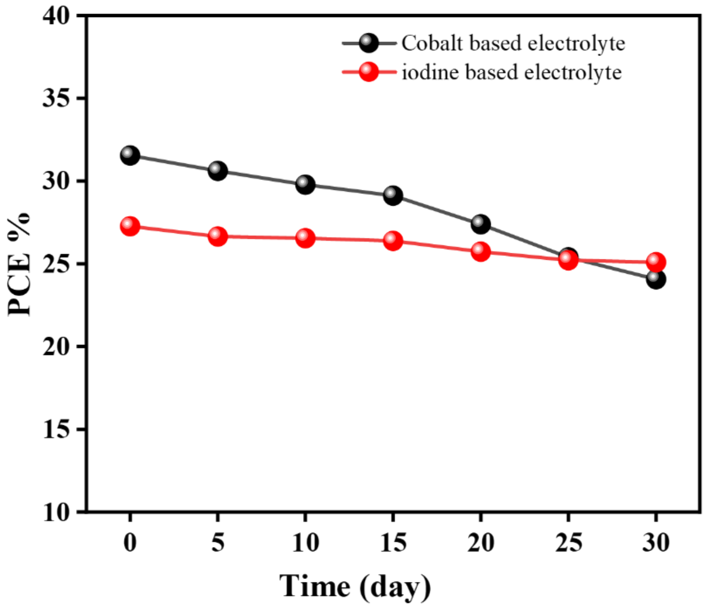


Figure S43. Stability of the **TZ1-based** DSSC over 30 days under 6000 lux illumination**.**

Table S1. Photovoltaic parameters of **TZ1**-based devices under different power of T5 illumination.

Illuminance	**Irradiance**	**J$_{SC}$ [uA cm^{-2}]**		**V$_{OC}$ [mV]**		**FF**		**PCE%**	
[lux]	**[mW cm^{2}]**	**Co-EL**	**I-EL**	**Co-EL**	**I-EL**	**Co-EL**	**I-EL**	**Co-EL**	**I-EL**
900	0.278	0.13	0.05	0.61	0.53	0.69	0.75	19.35	19.87
1800	0.558	0.313	0.28	0.653	0.60	0.74	0.73	22.38	22.35
3600	1.09	0.57	0.57	0.67	0.63	0.77	0.74	27.15	24.59
4800	1.456	0.74	0.78	0.72	0.64	0.77	0.74	28.54	25.89
6000	1.80	1.00	1.01	0.73	0.65	0.77	0.74	31.54	27.27

References

[1] T. C.Wei, C. C.Wan, Y. Y.Wang, *Appl. Phys. Lett.* **2006**, *88*

[2] J. L.Lan, Y. Y.Wang, C. C.Wan, T. C.Wei, H. P.Feng, C.Peng, H. P.Cheng, Y. H.Chang, W. C.Hsu, *Curr. Appl. Phys.* **2010**, *10*.