

-Electronic Supplementary Information-

On the Redox Stability of Phenothiazine Sensitizers on Semiconducting Surfaces

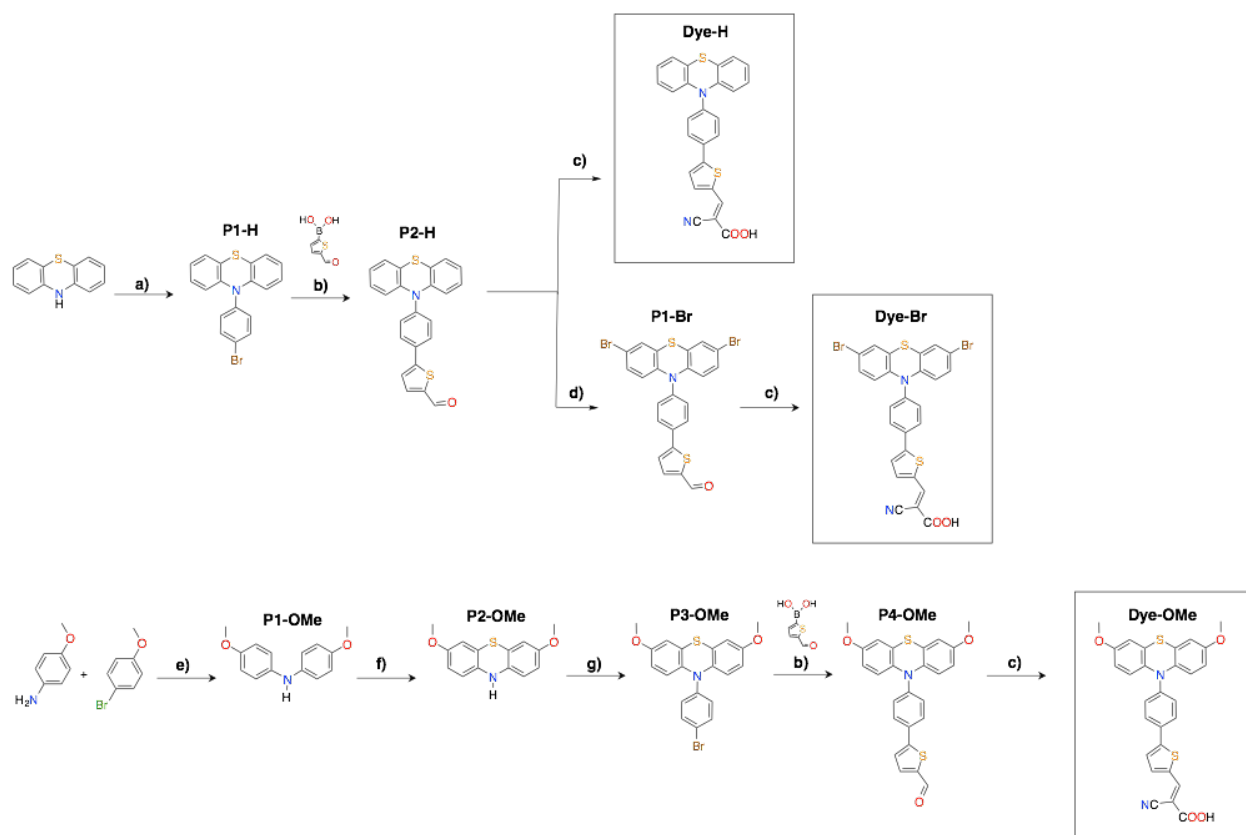
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Experimental Section

Preparation of compounds. All reagents were obtained from Sigma Aldrich, Alfa Aesar or Fisher Scientific and used as received. All reactions were performed using solvents that were passed through a solvent purification system prior to use except for water, toluene, 1,2-dichlorobenzene and dimethylsulfoxide (DMSO). Standard inert atmosphere and Schlenk techniques were carried out under nitrogen. All reactions and purification were carried out in the dark. Purification by column chromatography was performed using silica (Silicycle: Ultrapure Flash Silica). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed sheets pre-coated with silica 60 F-254 adsorbent (250 μm thick; Silicycle, QC, Canada) and visualized under UV light. Routine ^1H and ^{13}C NMR spectra were collected on a Bruker AV300 or Bruker AV400 inv/dir instrument at ambient temperatures, operating at 400 MHz and 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) using the residual signals δ 7.26 and 77.0 for CDCl_3 , δ 3.31 and 49.0 for MeOD and δ 2.50 and 39.4 for DMSO-d_6 as internal references for ^1H and ^{13}C , respectively. The synthesis for all intermediates and final products is outlined in the Supplementary Information.



Scheme S1. Reaction conditions for **Dye-H**, **Dye-Br** and **Dye-OMe**: (a) Cu powder, K₂CO₃, 1-bromo-4-iodobenzene, 1,2-dichlorobenzene, reflux, 48 h; (b) KOAc, Pd(PPh₃)₄, THF/H₂O (9:1 v/v), reflux, 16 h; (c) NCCH₂CO₂H, piperidine, MeCN, reflux, 20 h; (d) NBS, THF, 0 °C to room temperature, 16 h; (e) CuI, K₂CO₃, DMSO, 100 °C, 48 h; (f) S₈, I₂, 1,2-dichlorobenzene, 180 °C, 24 h; (g) Cu, K₂CO₃, 1,2-dichlorobenzene, 180 °C, 24 h

bis(4-methoxyphenyl)amine (P1-OMe): 4-aminoanisole (2.46 g, 20.1 mmol), 4-bromoanisole (3.00 g, 16.0 mmol), copper iodide (0.610 g, 3.20 mmol), potassium carbonate (7.36 g, 6.40 mmol) and L-proline (0.810 g, 6.40 mmol) were added to sparged DMSO (25 mL) under N₂. The reaction mixture was stirred at 100 °C for 48 h. The reaction mixture was quenched with distilled water (50 mL) and extracted with 3 × 20 mL of diethyl ether. The organic phase was collected, dried over MgSO₄ and solvent was removed *in vacuo*. Purification by silica column chromatography (SiO₂: hexanes/EtOAc, 4:1, R_f = 0.54) yielded 1.44 g (39.3%) of product as pale brown flakey crystals. ¹H NMR (300 MHz, MeOD): δ = 6.95 (d, 4H, ²J =

9.07 Hz), 6.82 (d, 4H, $^2J = 9.05$ Hz), 3.77 (s, 6H). ^{13}C NMR (100 MHz, DMSO- d_6): $\delta = 153.2, 138.5, 118.5, 115.0, 55.7$ ppm. HRMS (ESI) m/z : 230.1176 [(M+H) $^+$] calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ m/z : 230.1181.

3,7-dimethoxy-10H-phenothiazine (P2-OMe): P1-OMe (1.40 g, 6.11 mmol), sulfur (0.685 g, 21.4 mmol) and iodine (0.115 g, 6.90 mmol) were added to 1,2-dichlorobenzene (3 mL) under N_2 . The reaction mixture was stirred at reflux for 16 h. The reaction mixture was cooled to room temperature. Purification by silica column chromatography (SiO_2 : hexanes/EtOAc, 3:1, $R_f = 0.28$) yielded 0.320 g (20.1%) of an orange solid product. ^1H NMR (300 MHz, MeOD): $\delta = 6.60$ (d, 4H, $^2J = 1.55$ Hz), 6.57 (d, 2H, $^2J = 1.48$ Hz), 3.72 (s, 6H) ^{13}C NMR (100 MHz, DMSO- d_6): $\delta = 154.7, 136.8, 117.4, 115.3, 113.7, 112.0, 55.9$ ppm. HRMS (ESI) m/z : 259.0661 [(M+H) $^+$] calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$ m/z : 259.0667.

10-(4-bromophenyl)-3,7-dimethoxy-10H-phenothiazine (P3-OMe): P2-OMe (0.316 g, 1.20 mmol), 4-iodobromobenzene (0.416 g, 1.46 mmol), potassium carbonate (0.662 g, 4.80 mmol) and copper powder (0.154 g, 2.40 mmol) were added to 1,2-dichlorobenzene (5 mL) under N_2 . The reaction mixture was stirred at reflux for 16 h. The reaction mixture was cooled to room temperature. Purification by silica column chromatography (SiO_2 : hexanes/ CH_2Cl_2 , 4:1, $R_f = 0.19$) yielded 0.391 g (40.9%) of a pale yellow solid. ^1H NMR (300 MHz, MeOD): $\delta = 7.26$ (d, 2H, $^2J = 8.97$ Hz), 7.02 (m, 4H), 6.89 (d, 2H, $^2J = 8.90$ Hz), 6.85 (dd, 2H, $^2J = 8.85$ Hz), 3.75 (s, 6H) ^{13}C NMR (100 MHz, DMSO- d_6): $\delta = 156.9, 145.4, 135.7, 132.8, 131.0, 125.5, 121.9, 114.9, 113.9, 113.3, 56.0$ ppm. HRMS (ESI) m/z : 413.0070 [(M+H) $^+$] calcd for $\text{C}_{20}\text{H}_{16}\text{NO}_2\text{SBr}$ m/z : 413.0085.

(4-(3,7-dimethoxy-10H-phenothiazin-10-yl)phenyl)thiophene-2-carbaldehyde (P4-OMe): P3-OMe (0.340 g, 0.800 mmol), 5-formyl-2-thienylboronic acid (0.160 g, 1.00 mmol), palladium tetrakis(triphenylphosphine) (0.046 g, 0.040 mmol) and sodium carbonate (0.260 g, 2.60 mmol) were added sequentially to sparged THF/ H_2O (5:1, v/v, 25 mL) solution under N_2 . The reaction mixture was stirred and left at reflux for 16 h. The reaction mixture was then cooled to room temperature and THF was removed *in vacuo*. Crude mixture was extracted with 20 mL of distilled water and 3 \times 20 mL of CH_2Cl_2 . The organic phase was collected, dried over MgSO_4 and solvent was removed *in vacuo*.

Purification by silica column chromatography (SiO₂: hexanes/CH₂Cl₂, 4:1, R_f = 0.2) yielded 0.232 g (64.7%) of product as brown oil. ¹H NMR (300 MHz, MeOD): δ = 9.87 (s, 1H), 8.00 (d, 1H, ²J = 8.90 Hz), 7.68 (d, 2H, ²J = 8.89 Hz), 7.58 (d, 1H, ²J = 3.99 Hz), 7.30 (d, 2H, ²J = 3.99 Hz), 7.12 (d, 2H, ²J = 2.80 Hz), 6.95 (m, 4H), 3.80 (s, 6H). ¹³C NMR (100 MHz, DMSO-d₆): δ = 184.1, 157.4, 153.4, 147.9, 141.3, 139.9, 135.0, 133.4, 128.0, 126.0, 124.3, 117.4, 114.1, 113.6, 56.1 ppm. HRMS (ESI) *m/z*: 446.0490 [(M+H)⁺] calcd for 446.0885.

(E)-2-cyano-3-(5-(4-(3,7-dimethoxy-10H-phenothiazin-10-yl)phenyl)thiophen-2-yl)acrylic acid (Dye-OMe): P4-OMe (0.230 g, 0.500 mmol), cyanoacetic acid (0.130 g, 1.50 mmol) and piperidine (0.300 g, 3.50 mmol) were added to acetonitrile (20 mL) under N₂. The reaction mixture was stirred and left at reflux for 16 h. The reaction mixture was then cooled to room temperature and solvent was removed *in vacuo*. Purification by silica column chromatography (SiO₂: CH₂Cl₂/MeOH, 9:1, R_f = 0.3) yielded 0.190 g (73.8%) of product as a pale orange solid. ¹H NMR (300 MHz, MeOD): δ = 7.98 (s, 1H), 7.70 (s, 1H), 7.64 (d, 2H, ²J = 8.79 Hz), 7.47 (d, 1H, ²J = 3.94 Hz), 7.13 (d, 2H, ²J = 8.79 Hz), 7.04 (d, 2H, ²J = 2.81 Hz), 7.00 (d, 2, ²J = 8.80 Hz), 6.89 (dd, 2H, ²J = 8.80, 2.85 Hz), 3.77 (s, 6H) ¹³C NMR (100 MHz, DMSO-d₆): δ = 56.1, 107.6, 113.4, 113.5, 114.0, 118.9, 119.4, 123.9, 126.3, 127.0, 132.2, 135.4, 135.6, 137.6, 141.7, 141.7, 146.8, 149.4, 157.1, 164.2 ppm. HRMS (ESI) *m/z*: 467.0894 [(M+H)⁺] calcd for C₂₈H₂₀N₂O₄S₂ *m/z*: 467.0888.

10-(4-bromophenyl)-10H-phenothiazine (P1-H): Phenothiazine (0.100 g, 0.501 mmol), 1-bromo-4-iodobenzene (0.194 g, 0.620 mmol), potassium carbonate (0.275 g, 1.99 mmol) and copper powder (0.066 g, 1.0 mmol) were added to 1,2-dichloromethane (2.5 mL) under N₂. The reaction was left to stir at reflux for 48 h. The reaction mixture was then cooled to room temperature. Purification by silica column chromatography (SiO₂: hexanes/CH₂Cl₂, 5:1, R_f = 0.104) yielded 0.101 g (56.0%) of product as a white crystal. ¹H NMR (300 MHz, MeOD): δ = 7.77 (dd, 2H, ²J = 8.68 Hz) 7.30 (dd, 2H, ²J = 8.68 Hz) 7.07 (dd, 2H, ²J = 7.38 Hz) 6.91 (m, 4H) 6.36 (dd, 2H, ²J = 8.05 Hz) ¹³C NMR (100 MHz, DMSO): δ = 143.57, 140.55, 134.39, 132.09, 127.87, 127.35, 123.65, 121.23, 121.00, 117.39 ppm. HRMS (ESI) *m/z*: 352.9871 [(M)] calcd for C₁₈H₁₂BrNSH *m/z*: 352.9874).

5-(4-(10H-phenothiazin-10-yl)phenyl)thiophene-2-carbaldehyde (P2-H): P1-H (0.100 g, 0.280 mmol), 5-formyl-2-thienyl boronic acid (0.059 g, 0.38 mmol), palladium tetrakis(triphenylphosphine) (0.066 g, 0.057 mmol) and sodium carbonate (0.100 g, 0.920 mmol) were added sequentially to sparged THF/H₂O (5:1, v/v, 25 mL) solution under N₂. The reaction mixture was stirred and left at reflux for 16 h. The reaction mixture was then cooled to room temperature and THF was removed *in vacuo*. Crude mixture was extracted with 20 mL of distilled water and 3 × 20 mL of CH₂Cl₂. The organic phase was collected, dried over MgSO₄ and solvent was removed *in vacuo*. Purification by silica column chromatography (SiO₂: hexanes/CH₂Cl₂, 1:1, R_f = 0.30) yielded 0.065 g (60%) of product as a yellow crystal. ¹H NMR (300 MHz, MeOD): δ = 9.90 (s, 1H), 7.95 (m, 3H), 7.65 (d, 1H, ²J = 3.99 Hz), 7.39 (d, 2H, ²J = 8.70 Hz), 7.16 (dd, 2H, ²J = 7.47 Hz, ³J = 1.62 Hz), 7.01 (m, 4H), 6.62 (d, 2H, ²J = 8.13 Hz) ¹³C NMR (100 MHz, DMSO-d₆): δ = 184.6, 152.1, 143.3, 142.8, 142.6, 139.8, 131.4, 129.0, 128.7, 127.9, 127.6, 126.1, 124.122.7, 118.8 ppm. HRMS (ESI) *m/z*: 386.0681 [(M+H)⁺] calcd for C₂₃H₁₆NOS₂⁺ *m/z*: 386.0673.

(E)-3-(5-(4-(10H-phenothiazin-10-yl)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (Dye-H): P2-H (0.0601 g, 0.162 mmol), cyanoacetic acid (0.0341 g, 0.470 mmol), piperidine (0.0951 g, 1.10 mmol) were added to acetonitrile (10 mL) under N₂. The reaction mixture was stirred and left at reflux for 16 h. The reaction mixture was then cooled to room temperature and solvent was removed *in vacuo*. Purification by silica column chromatography (SiO₂: CH₂Cl₂/methanol, 9:1, R_f = 0.2) yielded 0.0670 g (93.0%) of product as an orange solid. ¹H NMR (300 MHz, MeOD): δ = 8.44 (s, 1H), 7.99 (d, 2H), 7.78 (s, 1H), 7.75 (d, 1H, ²J = 3.99 Hz), 7.45 (d, 2H, ²J = 8.55 Hz), 7.20 (dd, 2H, ²J = 7.50 Hz, ³J = 1.56 Hz), 7.02 (m, 4H), 6.50 (d, 2H, ²J = 8.09 Hz, ³J = 1.13 Hz) ¹³C NMR (100 MHz, DMSO): δ = 163.8, 148.0, 143.6, 141.7, 141.4, 137.4, 137.0, 132.4, 129.9, 128.7, 127.9, 127.5, 125.6, 123.8, 121.6, 119.3, 118.0, 99.9. HRMS (ESI) *m/z*: 407.0669 [(M-COOH)] calcd for C₂₅H₁₅N₂S₂ *m/z*: 407.0677.

5-(4-(3,7-dibromo-10H-phenothiazin-10-yl)phenyl)thiophene-2-carbaldehyde (P1-Br): P2-H (0.0510 g, 0.130 mmol) and N-bromosuccinimide (0.0530 g, 0.300 mmol) was added to dichloromethane (10 mL) under N₂. The reaction mixture was cooled to 0°C for 30 min before N-bromosuccinimide (0.0530 g,

0.300 mmol) was added. Reaction was brought to room temperature and was stirred for 16 h. The reaction mixture was quenched with distilled water (20 mL) and extracted with 3 × 20 mL of CH₂Cl₂. The organic phase was collected, dried over MgSO₄ and solvent was removed *in vacuo*. Purification by silica column chromatography (SiO₂: hexanes/CH₂Cl₂, 4:1, R_f = 0.25) yielded 0.0650 g (60.1%) of product as a orange crystal. ¹H NMR (300 MHz, MeOD): δ = 9.95 (s, 1H), 8.09 (m, 3H), 7.87 (d, 1H, ²J = 3.90 Hz), 7.53 (d, 2H, ²J = 8.54 Hz), 7.36 (d, 2H, ²J = 2.34 Hz), 7.16 (dd, 2H, ²J = 8.81 Hz, ³J = 2.33 Hz), 6.19 (d, 2H, ²J = 8.80 Hz) ¹³C NMR (100 MHz, DMSO-d₆): δ = 184.7, 151.7, 143.0, 142.7, 141.2, 139.8, 132.9, 130.9, 130.7, 129.5, 129.2, 126.6, 122.3, 118.7, 115.1 ppm. HRMS (ESI) *m/z*: 541.8870 [(M+H)⁺] calcd for C₂₃H₁₄NS₂Br₂ *m/z*: 541.8884.

(E)-2-cyano-3-(5-(4-(3,7-dibromo-10H-phenothiazin-10-yl)phenyl)thiophen-2-yl)acrylic acid (Dye-Br): P1-Br (0.0280 g, 0.0520 mmol), cyanoacetic acid (0.0132 g, 0.161 mmol) and piperidine (0.0311 g, 0.360 mmol) were added to acetonitrile (10 mL) under N₂. The reaction mixture was stirred and left at reflux for 16 h. The reaction mixture was then cooled to room temperature and solvent was removed *in vacuo*. Purification by silica column chromatography (SiO₂: CH₂Cl₂/methanol, 9:1, R_f = 0.18) yielded 0.0281 g (90.3%) of product as an yellow solid. ¹H NMR (300 MHz, MeOD): δ = 8.17 (s, 1H), 8.02 (d, 2H, ²J = 8.48 Hz), 7.79 (dd, 2H, ²J = 15.57 Hz, ³J = 4.00 Hz), 7.50 (d, 2H, ²J = 8.51 Hz), 7.32 (d, 2H, ³J = 2.31 Hz), 7.13 (dd, 2H, ²J = 8.82 Hz, ³J = 2.34 Hz), 6.159 (d, 2H, ²J = 8.81 Hz). ¹³C NMR (100 MHz, DMSO): δ = 164.2, 147.7, 142.8, 141.4, 140.4, 137.4, 137.3, 133.5, 131.2, 130.6, 129.1, 129.1, 125.9, 122.0, 119.3, 118.4, 114.9, 109.1 ppm. HRMS (ESI) *m/z*: 562.8887 [(M-COOH)⁻] calcd for C₂₅H₁₃N₂S₂Br₂ *m/z*: 562.8887.

Physical Methods.

DFT Calculations. The Gaussian 03 computational package was used to perform ground-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr nonlocal correlation functional B3LYP23–25 a 6-31G* basis set was used for S, C, N, O, Br and H atoms. Optimized geometry and frequency calculations carried out in the gas phase.

Spectroelectrochemistry. Spectroelectrochemical cells were assembled with sensitized nanocrystalline TiO₂ (18-nm average particle size) as the working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode with degassed 0.1 mM *n*-NBu₄PF₆ in MeCN. A potential that was 100 mV more positive than the first $E_{p,a}$ of the dye was applied for 1 min. The absorptivity at wavelengths characteristic of phenothiazinium cations was recorded every second until nominal changes were observed for half-life curves and entire spectra (196-1100 nm) were collected every 3 min for full spectra spectroelectrochemistry experiments.

Electrochemistry. Solution-phase electrochemical data was recorded with a CHI660D potentiostat using a platinum wire counter electrode, Ag/AgCl reference electrode, and a platinum working electrode. A 0.1 M *n*-NBu₄BF₄ electrolyte solution in MeCN at ambient temperature was used for all dyes. Ag/AgCl in saturated KCl was used as the reference electrode and was calibrated versus the normal hydrogen electrode (NHE) by addition of 0.235 mV. Cyclic voltammograms (CVs) were acquired for 0.5 mM solutions of **Dye-Br**, **Dye-H** and **Dye-OMe** or sensitized nanocrystalline TiO₂ (18-nm average particle size) at a scan rate of 50 mV s⁻¹.

Cell Fabrication. Photoanodes were fabricated following previously reported methods (Ito, 2005) by screen-printing TiO₂ pastes (2 layers of 18-NRT and 1 layer of WER4-0, Dyesol). (Ito, 2007) The active area of the TiO₂ electrodes was 0.128 cm² and the thickness was 13-15 μm on fluorine-doped tin-oxide [FTO; TEC7 (7 Ω cm⁻²)]. The TiO₂ substrates (anodes) were treated with TiCl_{4(aq)} (0.05 M) at 70 °C for 30 min followed by rinsing with H₂O and EtOH and then dried prior to heating. Anodes were heated to 450 °C for 20 min in an ambient atmosphere and left to cool to 80 °C prior to immersing into an MeCN solution containing the dye (~0.5 mM) and deoxycholic acid (~5.0 mM) for 16 h. The stained anodes were then rinsed with copious amounts of MeCN and dried. The cathodes were prepared by pre-washing the [FTO TEC7 (7 Ω cm⁻²)] substrates in a 0.1 M HCl/EtOH solution, sonicated in acetone for 10 min, rinsed with EtOH and dried prior to heating. Cathodes were heated to 400 °C for 15 min in ambient atmosphere and left to cool to room temperature. A drop of PtH₂Cl₆ in EtOH was placed on the cathodes and substrate was heated to 400 °C for 15 min in ambient atmosphere and left to cool to room temperature. The cells were fabricated by sealing the cathode and the anode with a 30 μm Surlyn (Dupont) gasket via a mechanical hot press. Iodide electrolyte was used for this study, where 1.0 M 1,3-dimethylimidazolium

iodide (DMII), 60 mM I₂, 0.5 M *tert*-butylpyridine, 0.05 M NaI, and 0.1 M guanidinium thiocyanate was in a mixed solvent system of acetonitrile and valeronitrile (85:15, v/v) was used as the liquid electrolyte. The electrolyte was introduced via syringe into the cavity between the sandwiched electrodes through holes in the cathode. The holes were sealed with Bynel and a glass microscope slide; aluminum foil was then taped to the back of the cell. Silver bus bars were added to all cells after sealing.

Cell Characterization. Photovoltaic measurements were recorded with a TriSOL solar simulator equipped with a 300 W xenon light source powered by a Newport power supply (model 69911). The light output (area = 5 cm × 5 cm) was calibrated to AM 1.5 using a Newport Oriel correction filter to reduce the spectral mismatch in the region of 350-700 nm to less than 1.5%. The power output of the lamp was measured to 1 Sun (100 mW cm⁻²) using a certified Si reference cell. The current–voltage (*I*–*V*) characteristic of each cell was obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley digital source meter (model 2400).

Light-Soaking Studies. Assembled cells were subjected to constant 1 Sun illumination using a 1 kW metal-halide lamp in a custom-built chamber where the temperature was controlled at 45°C by fan speed and monitored with a thermocouple.

Dye Desorption Studies. The UV-vis spectra of sensitized nanocrystalline TiO₂ (18-nm average particle size) on FTO were collected prior to substrates being soaked in a dilute electrolyte solution (0.1 M 1,3-dimethylimidazolium iodide (DMII), 0.60 mM I₂, 0.05 M *tert*-butylpyridine, 5 mM NaI, and 0.01 M guanidinium thiocyanate in acetonitrile) in the dark. UV-Vis spectra were then collected every couple hours for 5 days.

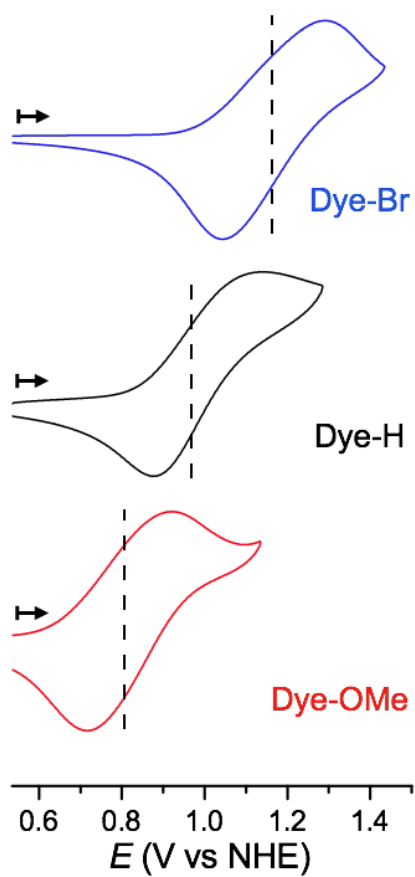


Fig. S1 Cyclic voltammograms of **Dye-Br**, **Dye-H** and **Dye-OMe** on mesoporous TiO_2 in 0.1 M *n*- NBu_4PF_6 MeCN solutions recorded at room temperature. Dashed lines indicate $E_{1/2}$.

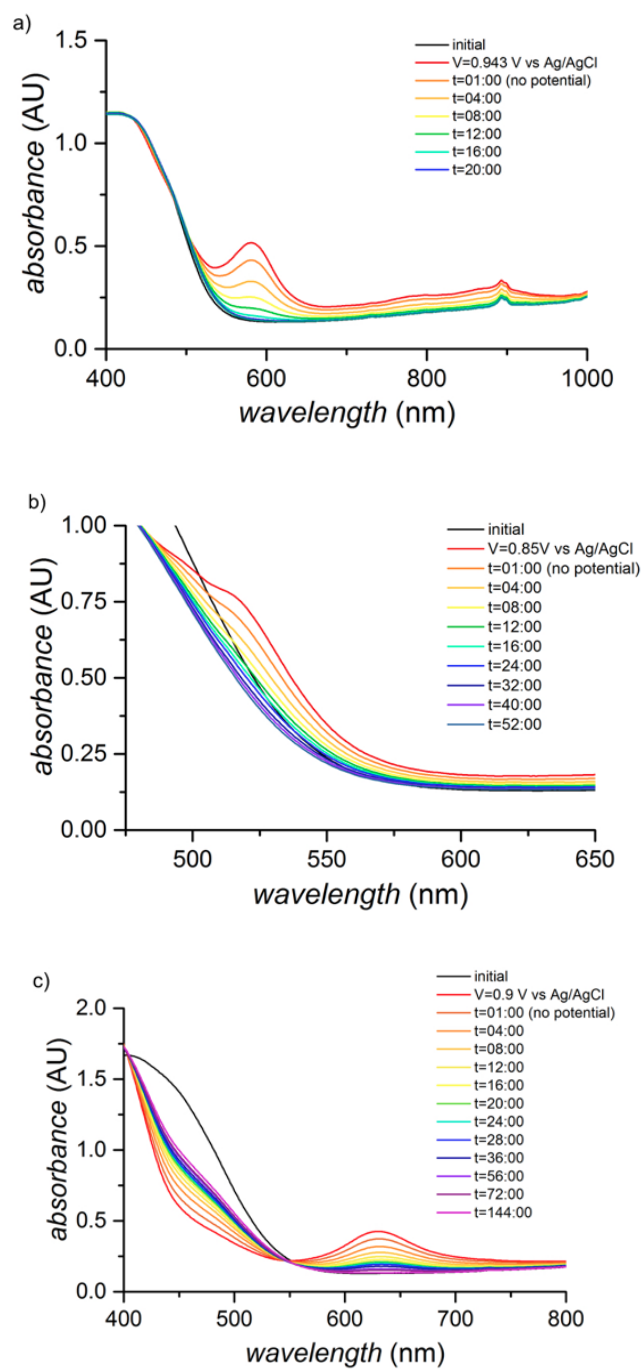


Fig. S2 UV-vis spectra for (a) **Dye-Br**/TiO₂, (b) **Dye-H**/TiO₂ and (c) **Dye-OMe**/TiO₂ collected following 1 min at potential 0.1 mV more positive than the **Dye-R⁺**/Dye-R⁺ redox potential in 0.1 M *n*-NBu₄PF₆ MeCN solution.

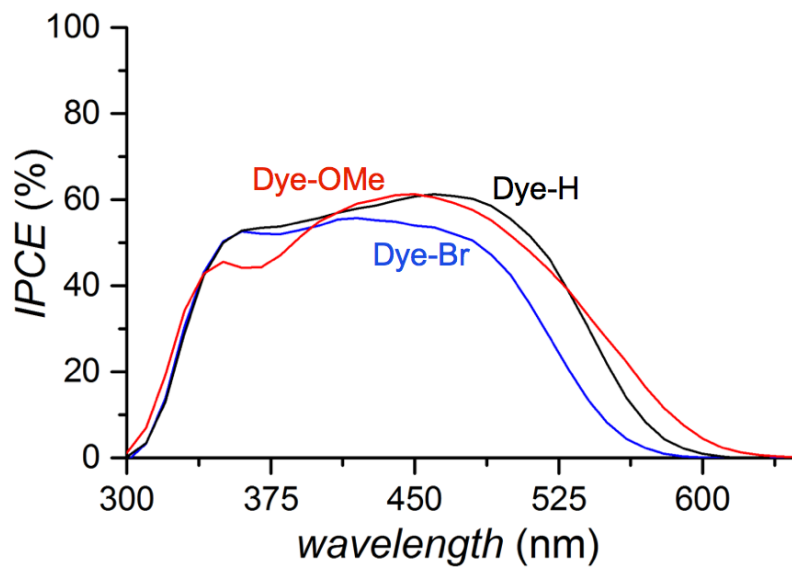


Fig. S3 Incident photon-to-current efficiencies (IPCE) for **Dye-Br**, **Dye-H** and **Dye-OMe** DSSCs fabricated with Γ/I_3^- electrolyte.

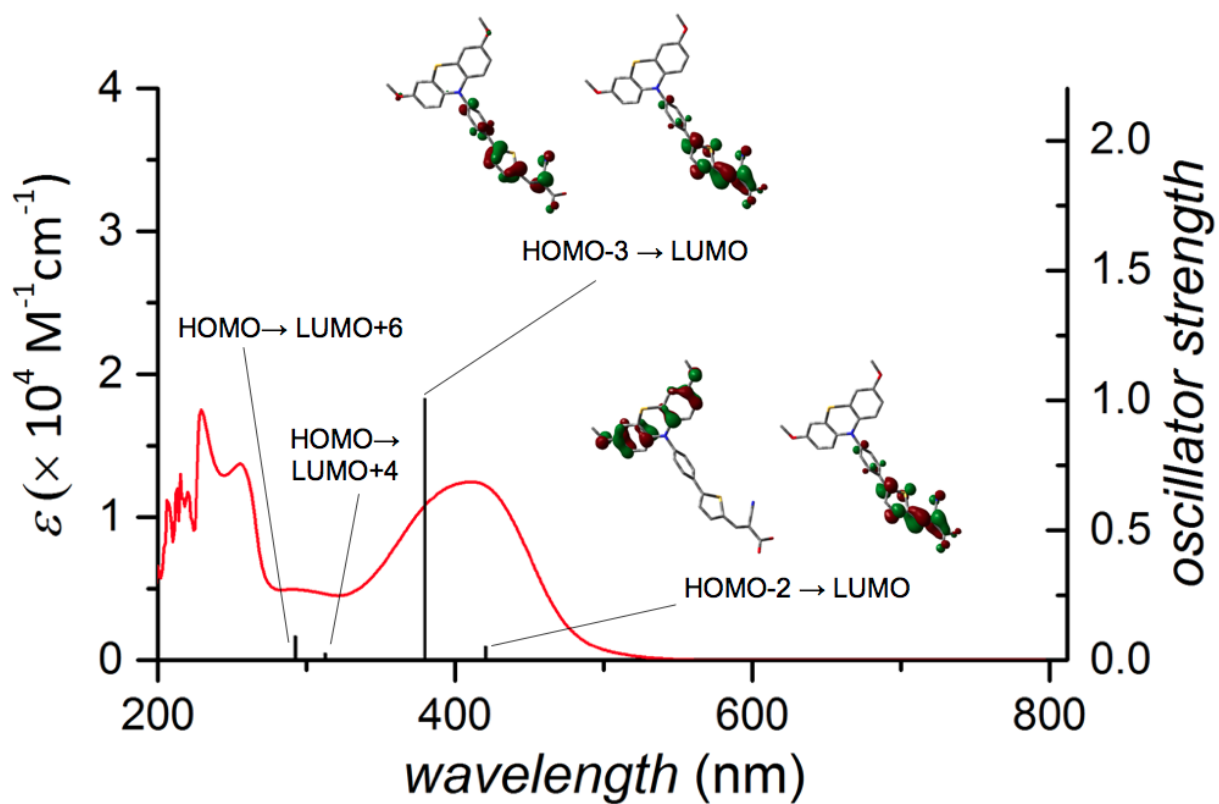


Fig. S4 UV-Vis absorption spectra (red) and TD-DFT calculated transitions (black) for **Dye-OMe**. The orbital diagrams are shown.

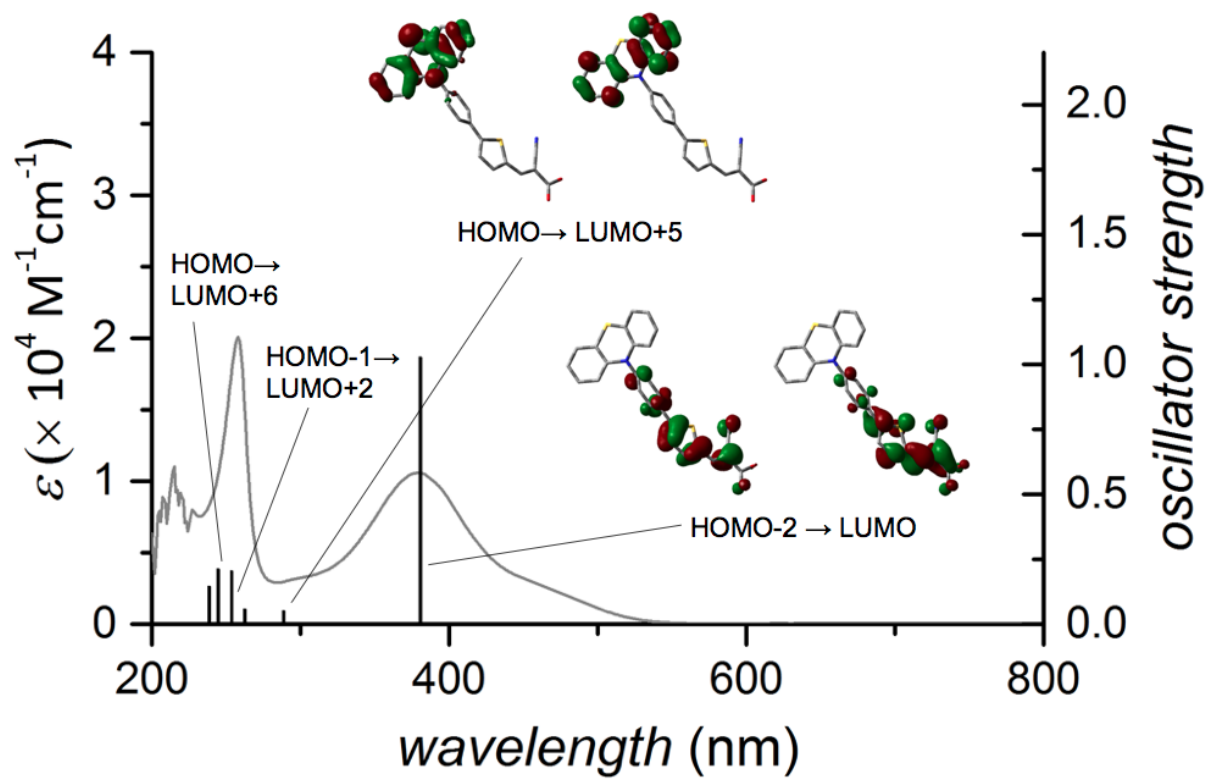


Fig. S5 UV-Vis absorption spectra (grey) and TD-DFT calculated transitions (black) for **Dye-H**. The orbital diagrams are shown.

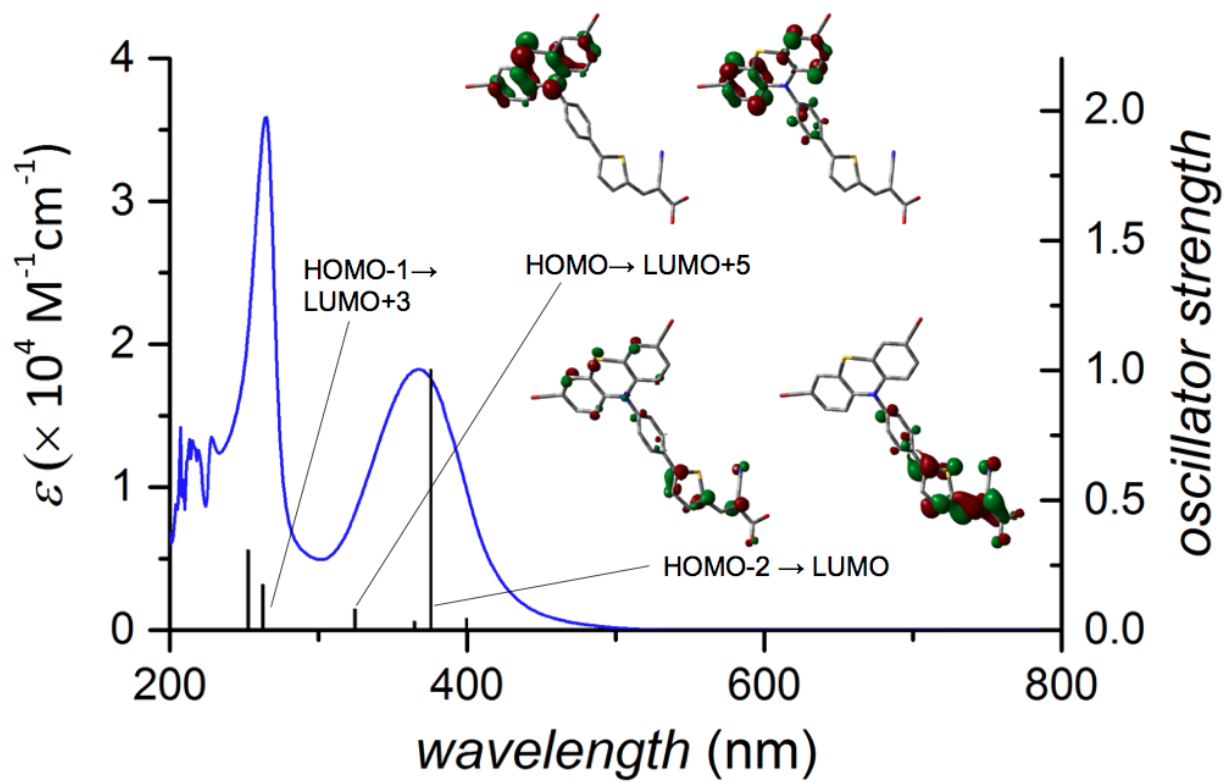


Fig. S6 UV-Vis absorption spectra (blue) and TD-DFT calculated transitions (black) for **Dye-Br**. The orbital diagrams are shown.

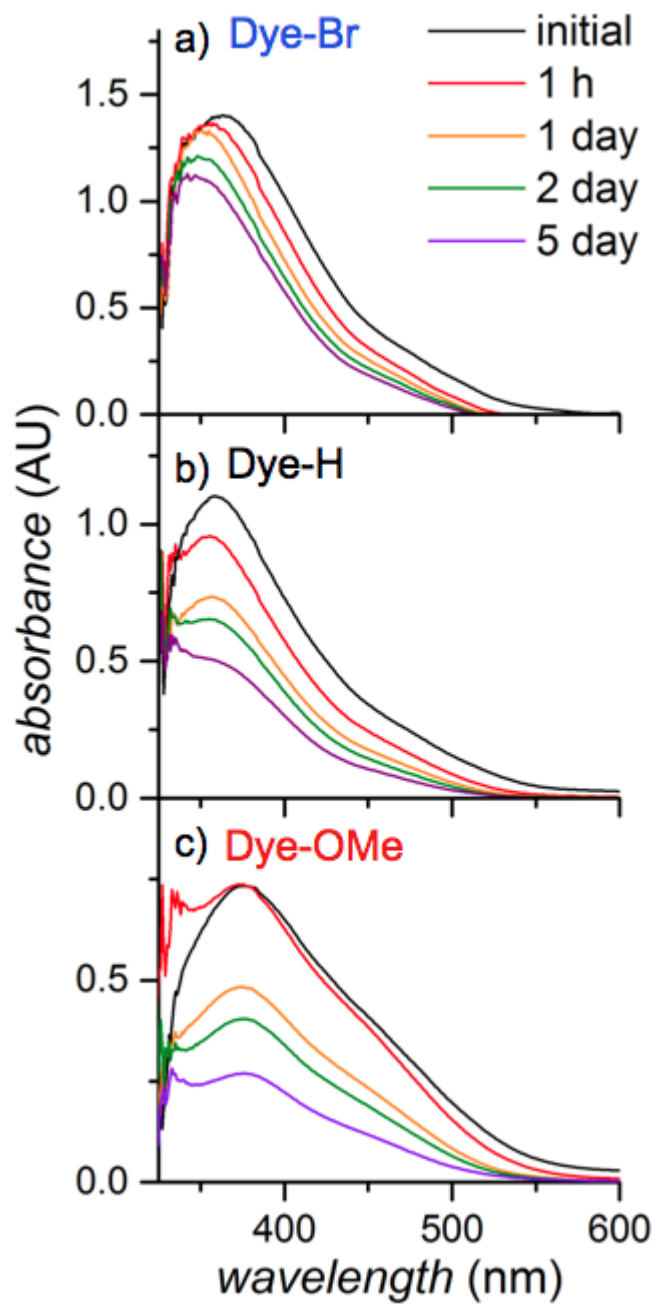


Fig. S7 Spectrophotometric record of dye coverage by UV-Vis absorption spectra of (a) **Dye-Br**, (b) **Dye-H** and (c) **Dye-OMe** on TiO_2 over 5 days of soaking in an electrolyte solution (0.1 M 1,3-dimethylimidazolium iodide (DMII), 0.60 mM I_2 , 0.05 M *tert*-butylpyridine, 5 mM NaI, and 0.01 M guanidinium thiocyanate in MeCN) in the dark.

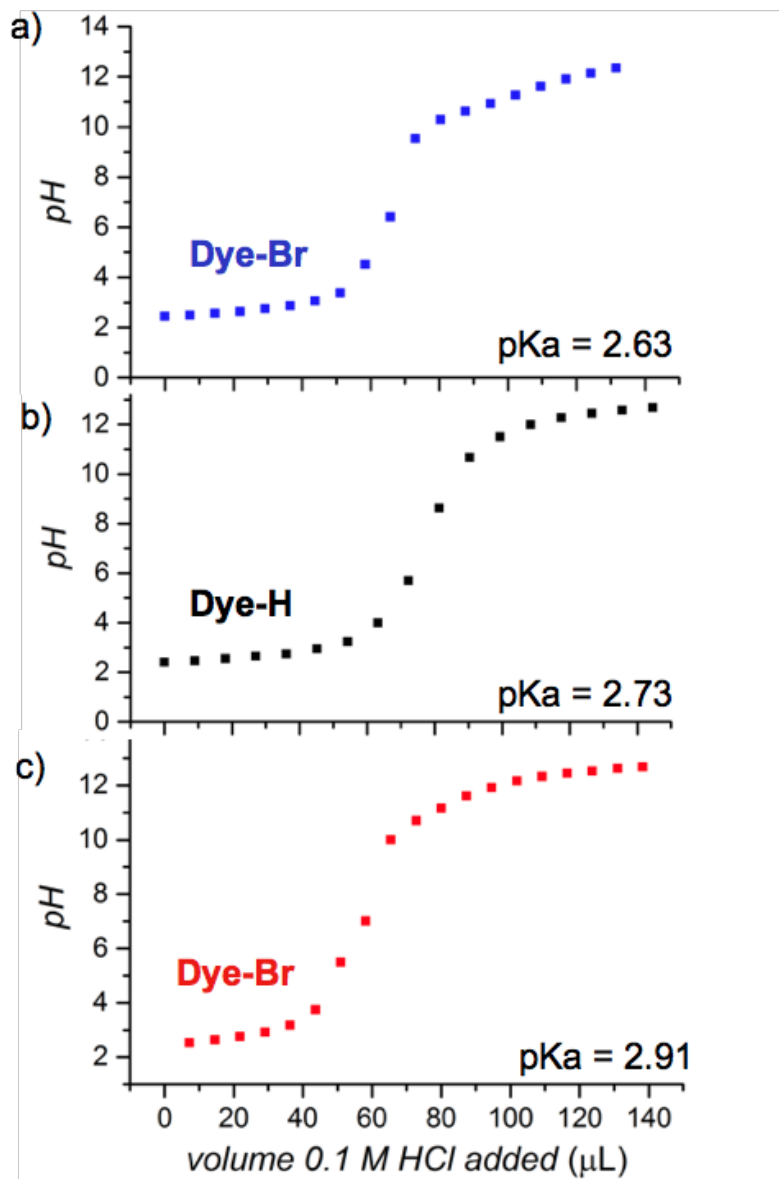


Fig. S8 Titration curves where 0.1 M HCl is added to (a) **Dye-Br** (blue), (b) **Dye-H** (black) and (c) **Dye-OMe** (red) in DMSO.

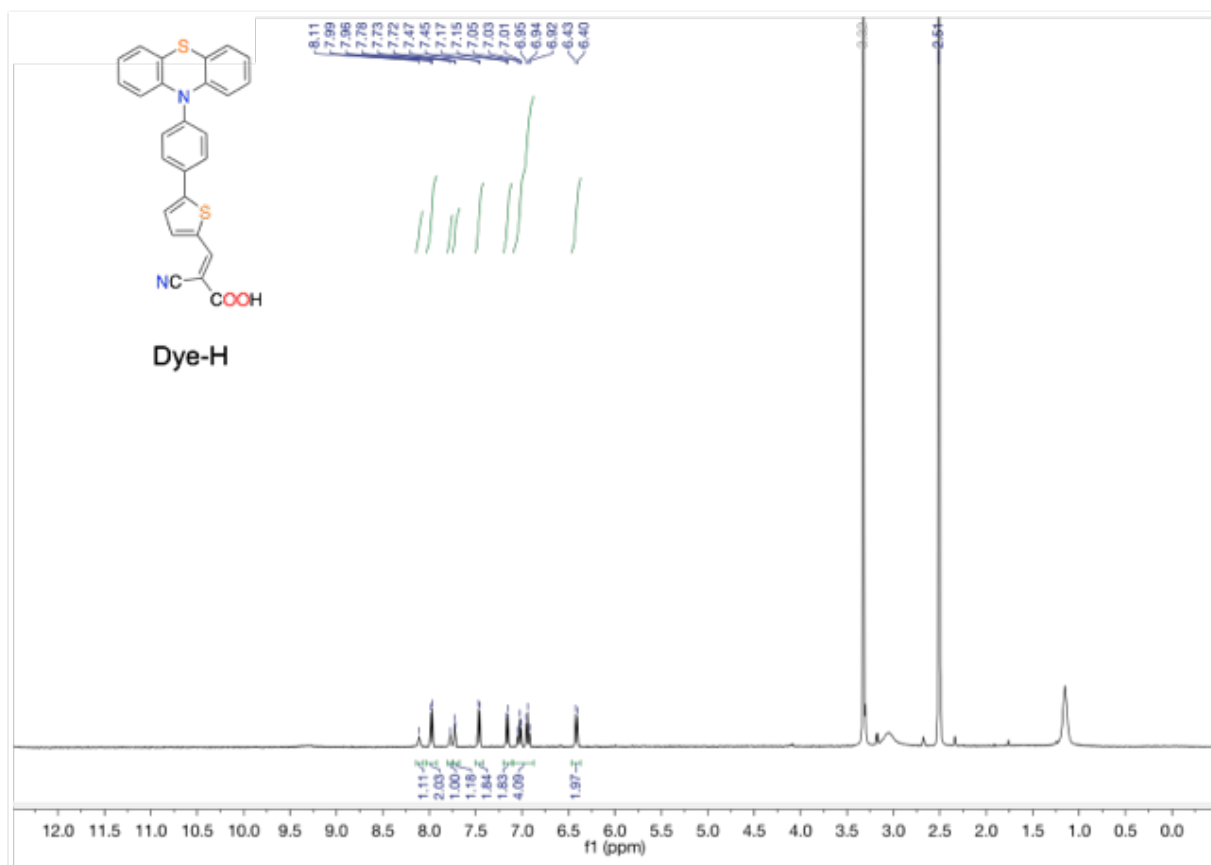


Fig. S9 ¹H NMR spectrum of **Dye-H** in MeOD at ambient temperature.

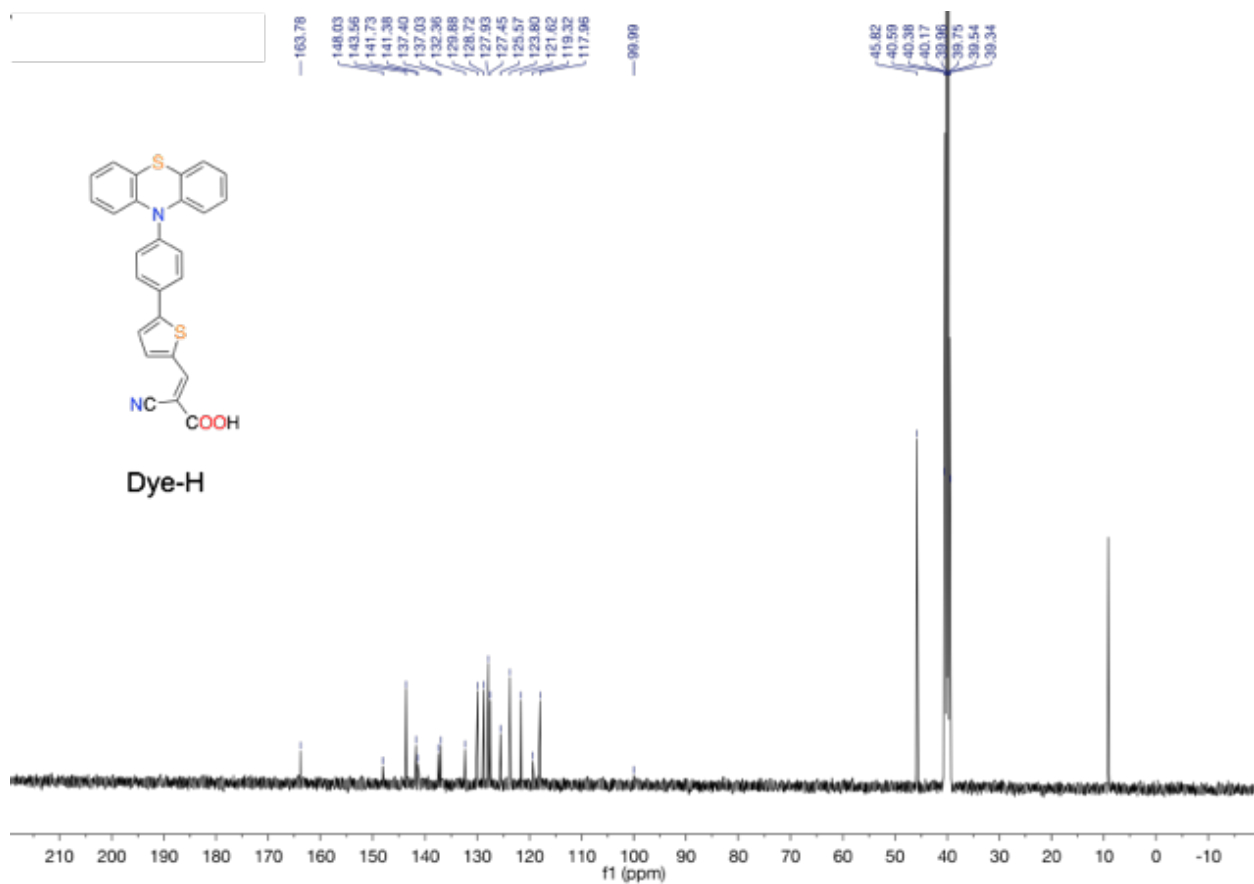


Fig. S10 ^{13}C NMR spectrum of **Dye-H** in DMSO-d_6 at ambient temperature.

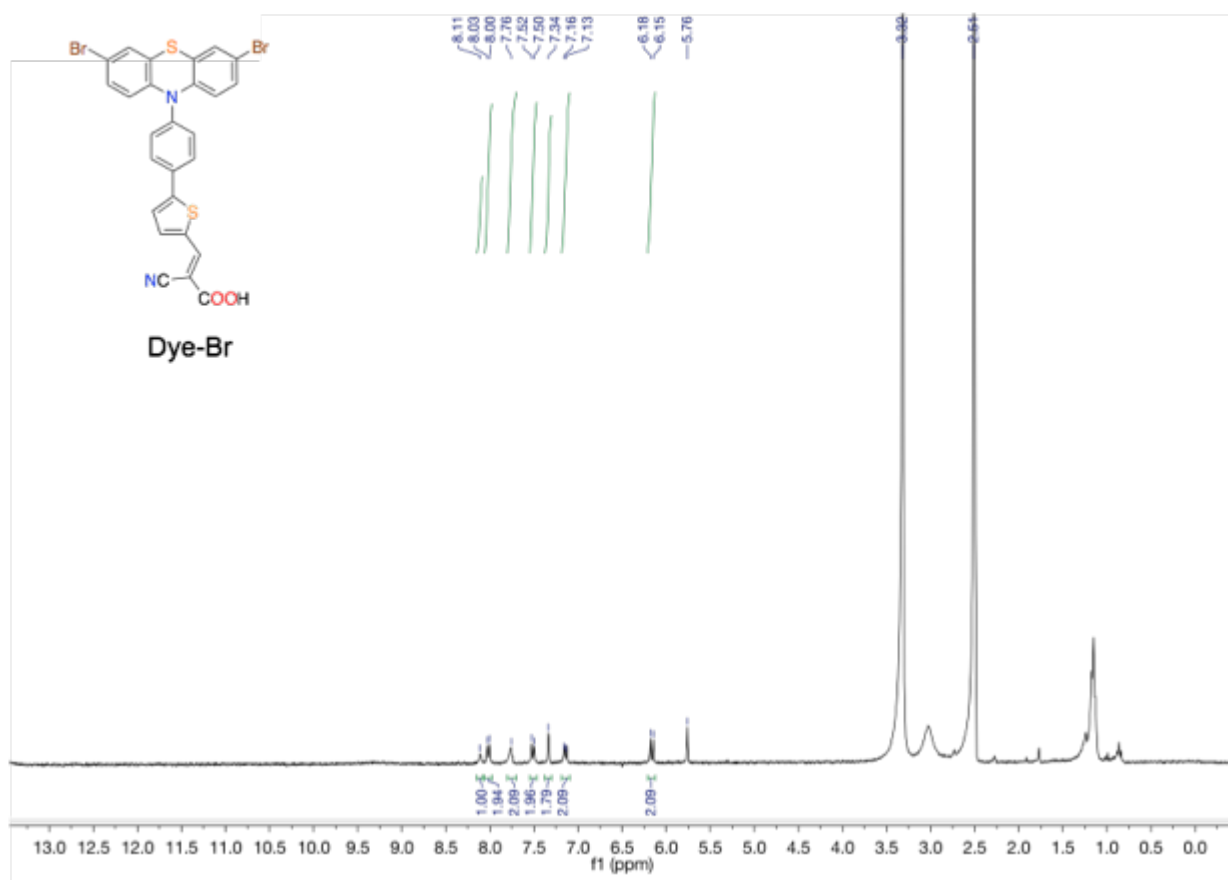


Fig. S11 ¹H NMR spectrum of **Dye-Br** in MeOD at ambient temperature

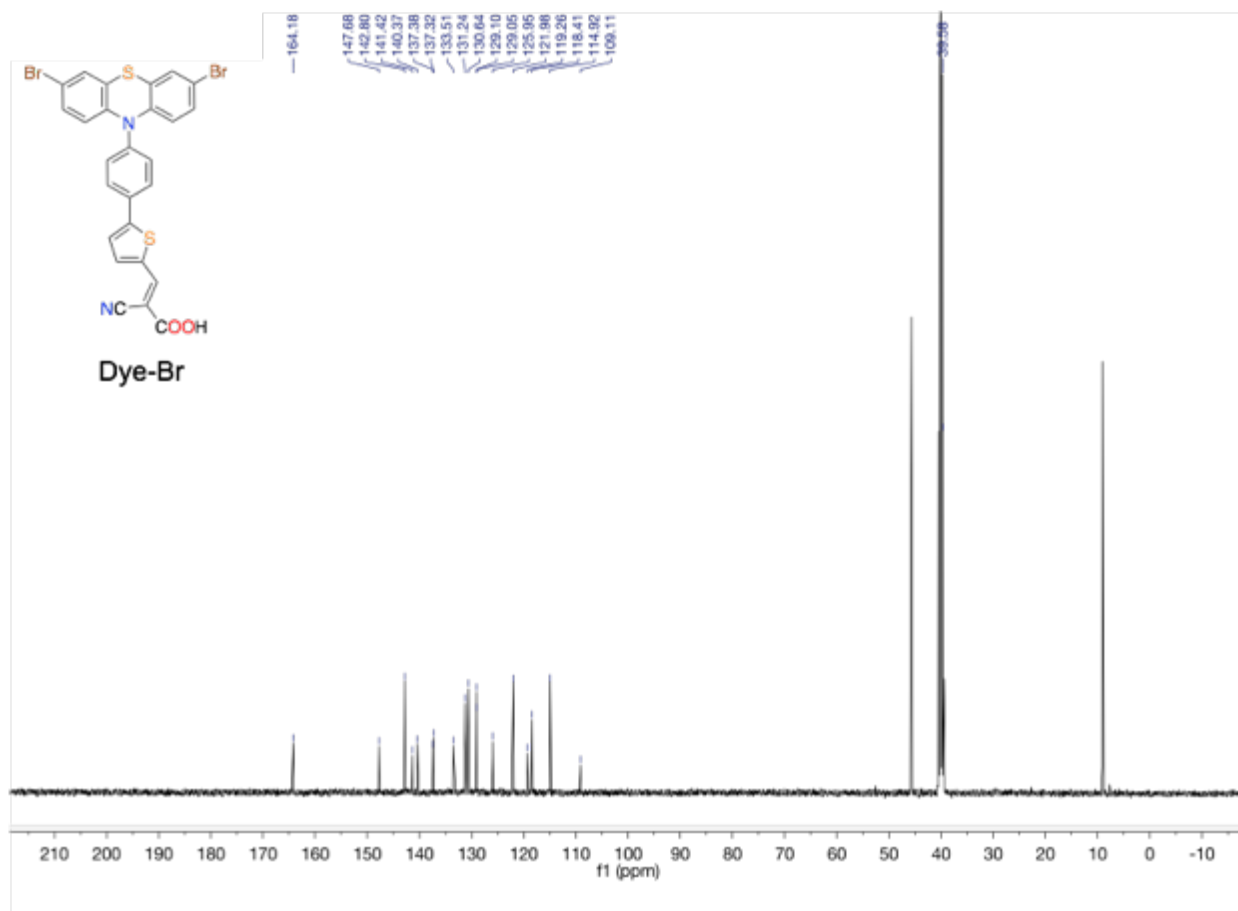


Fig. S12 ^{13}C NMR spectrum of **Dye-Br** in DMSO at ambient temperature

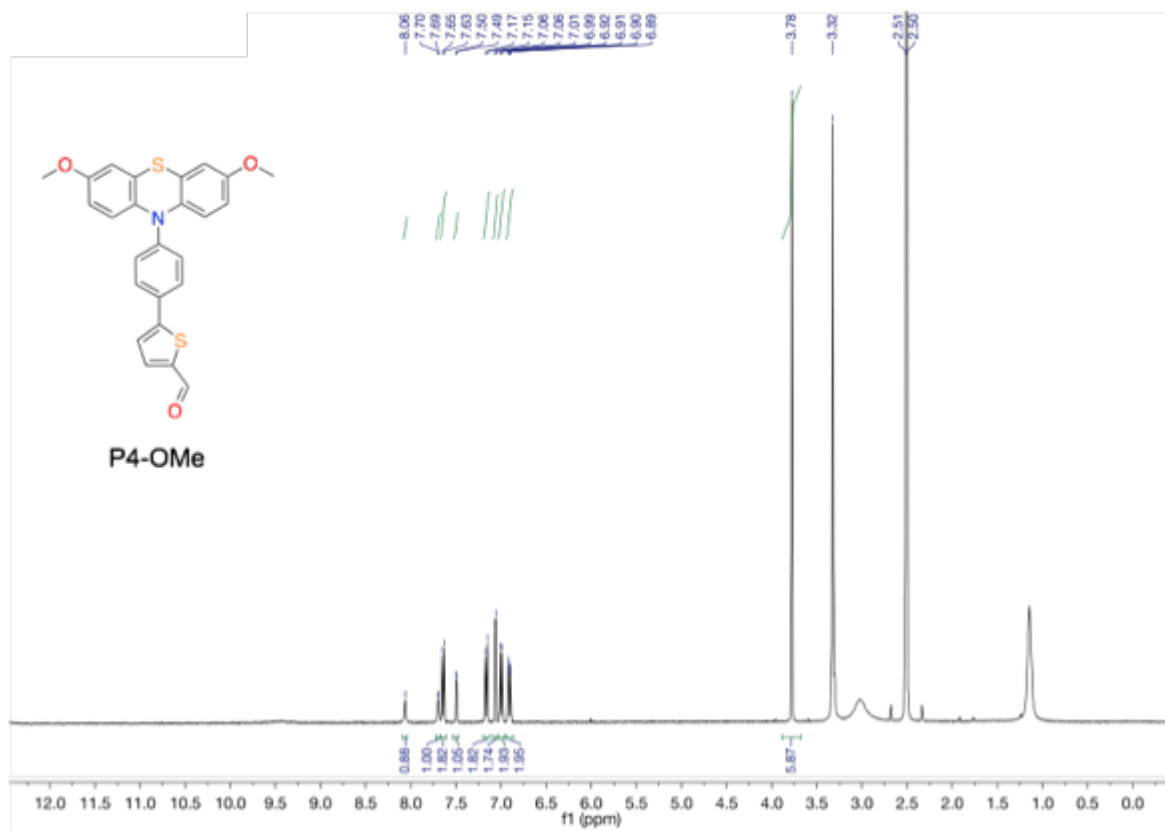


Fig. S13 ¹H NMR spectrum of **P4-OMe** in MeOD at ambient temperature

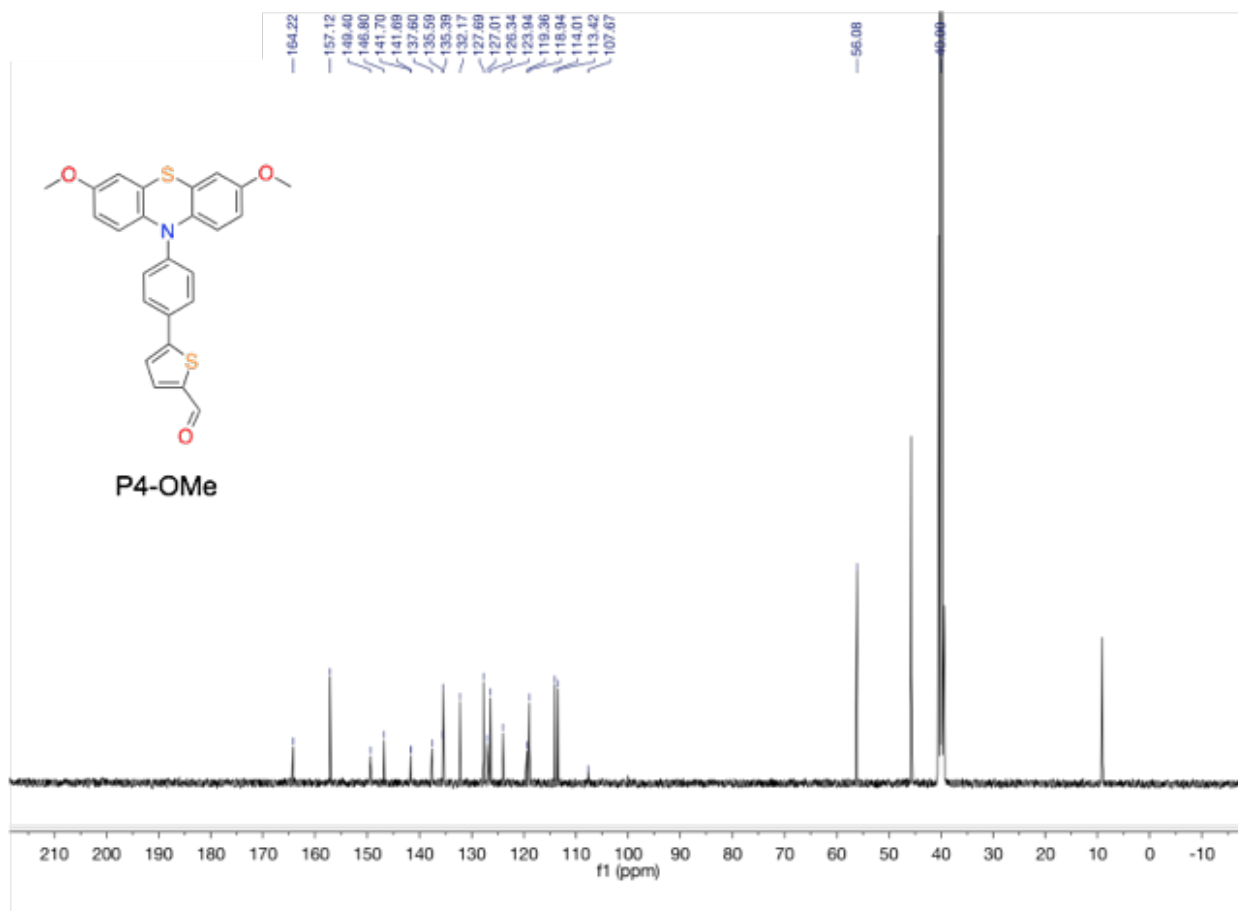


Fig. S14 ^{13}C NMR spectrum of **P4-OMe** in DMSO-d_6 at ambient temperature

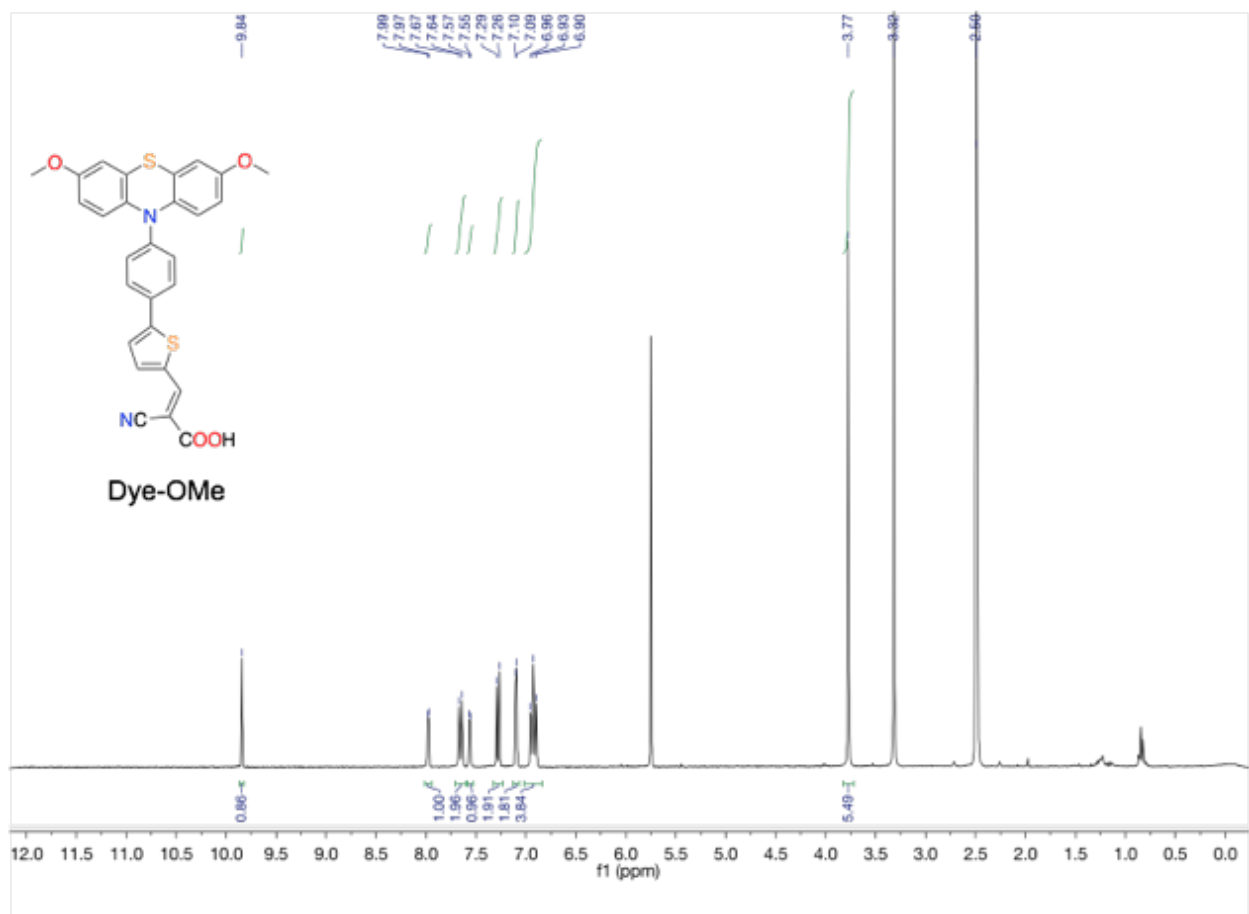


Fig. S15 ¹H NMR spectrum of **Dye-OMe** in MeOD at ambient temperature

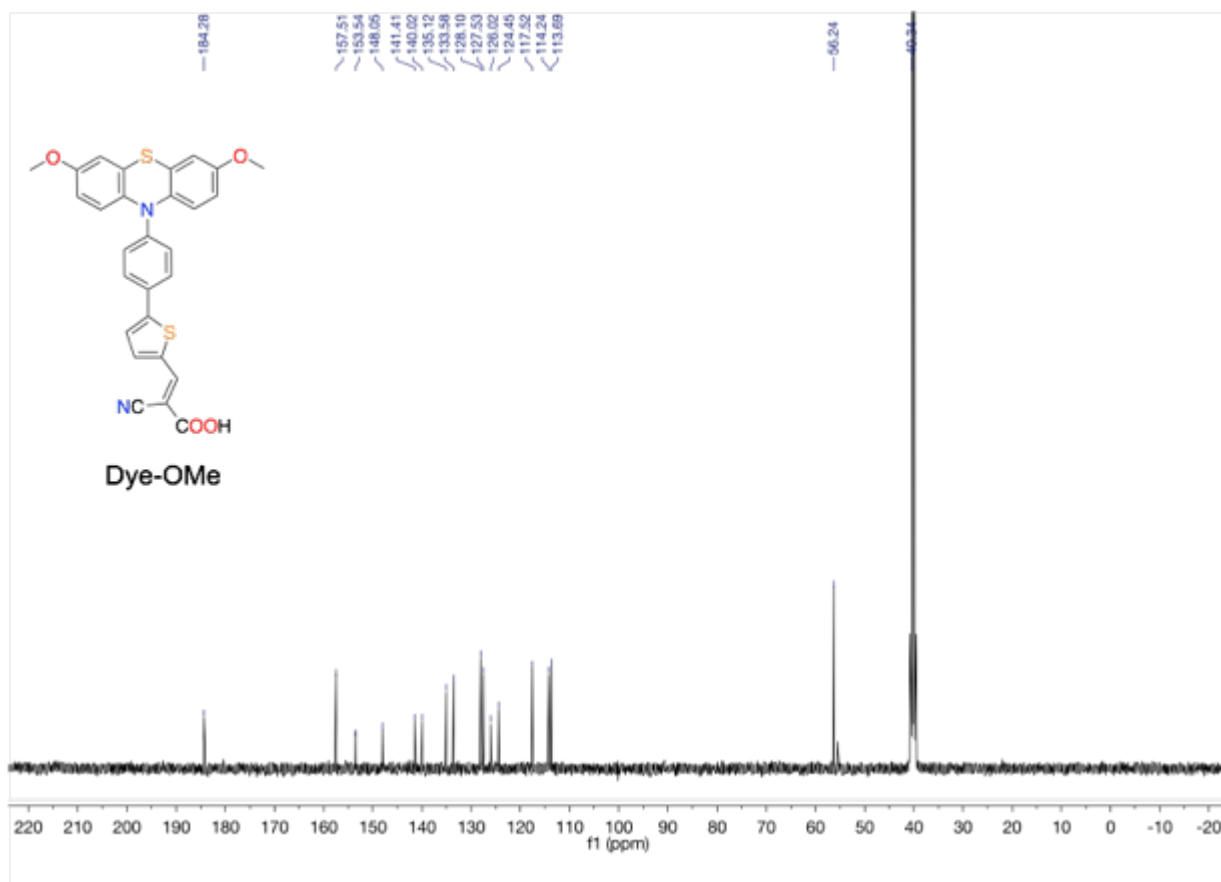


Fig. S16 ^{13}C NMR spectrum of **Dye-OMe** in DMSO at ambient temperature