Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Comparative Analysis of Triarylamine and Phenothiazine Sensitizer Donor Units in the Dye-Sensitized Solar Cell

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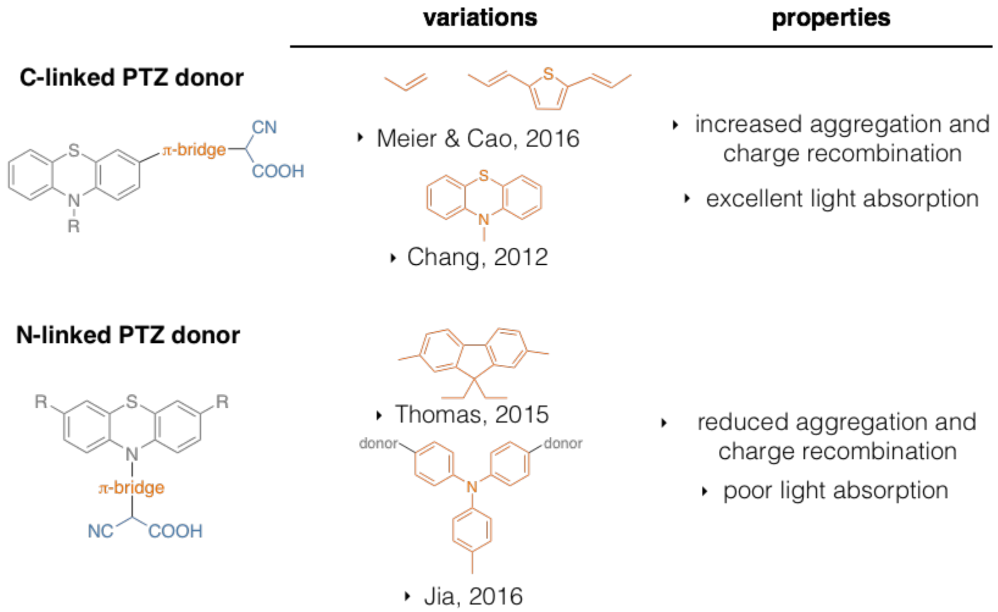
Supplementary Information



Scheme S1. Summary of key **PTZ** dye literature comparing properties of C- and N-linked donor molecules

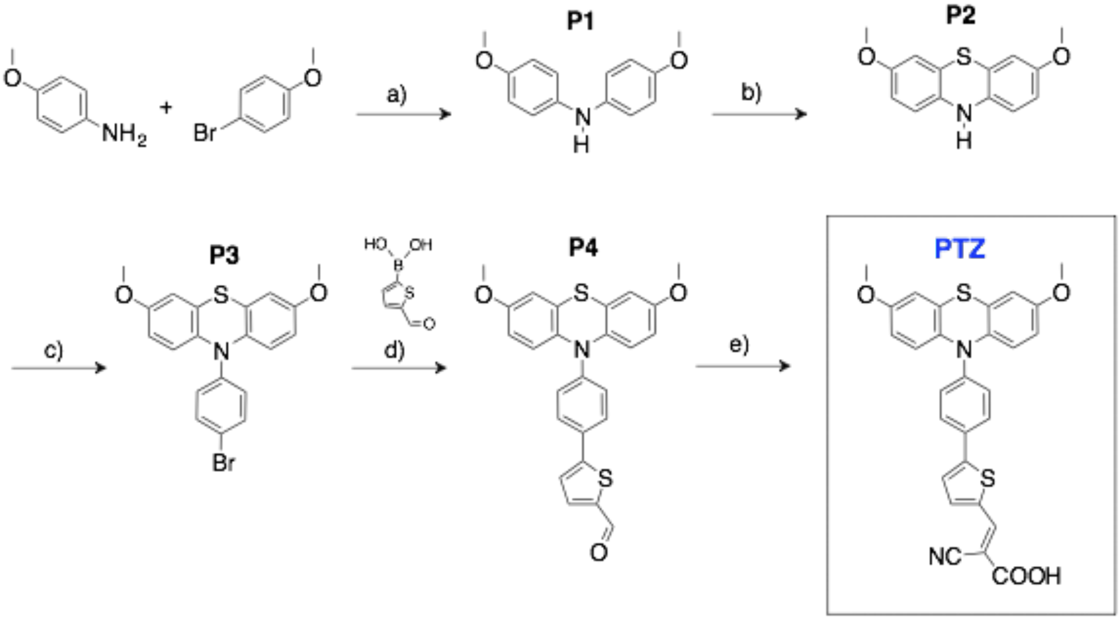


Fig. S1 Reaction conditions for **PTZ** dye: (a) CuI, K_2CO_3, DMSO, 100 °C, 48 h; (b) S_8, I_2, 1,2-dichlorobenzene, 180 °C, 24 h; (c) Cu, K_2CO_3, 1,2-dichlorobenzene, 180 °C, 24 h; (d) KOAc, $Pd(PPh_3)_4$, THF/H_2O (9:1 v/v), reflux, 16 h; (e) $NCCH_2CO_2H$, piperidine, MeCN, reflux, 20 hr.

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 steps 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 temperature, 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 d_6-DMSO as internal references for ^1H and ^{13}C, respectively. The synthesis for all intermediates and final products is outlined in the Supplementary Information.

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 functional B3LYP. 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. All calculations carried out with the Gaussian 03W software package.[1]

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-NBu_4BF_4 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 0.197 V. Cyclic voltammograms (CVs) were acquired for ~0.5 mM solutions of **TPA** and **PTZ** or sensitized nanocrystalline TiO_2 (18-nm average particle size) at a scan rate of 50 mV s^{-1}.

Cell Fabrication. Photoanodes were fabricated following previously reported methods by screen-printing TiO_2 pastes (2 layers of 18-NRT and 1 layer of WER4-0, Dyesol).[2] The active area of the TiO_2

electrodes was 0.128 cm and the thickness was 13-15 μm on fluorine-doped tin-oxide [FTO; TEC7 (7 Ω cm^{-2})].[2] The TiO_2 substrates (anodes) were treated with $TiCl_{4\ (aq)}$ (0.05 M) at 70 °C for 30 min followed by rinsing with H_2O 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 a MeCN solution containing the dye (~0.5 mM) and deoxychenocholic 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 PtH_2Cl_6 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 I_2, 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). 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. The power output of the lamp was measured to 1 Sun (100 mW cm^{-2}) using a certified Si reference cell. The current–voltage (*J*–*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).

Dye-Loading Studies. The TiO_2 substrates were treated with $TiCl_{4\ (aq)}$ (0.05 M) at 70°C for 30 min followed by rinsing with H_2O 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 acetonitrile solution containing the dye (~0.5 mM) and deoxychenocholic acid (~5.0 mM) for 16 h. Substrates were soaked in dry acetonitrile solution for 30 minutes to remove any dye aggregates before being submerged in 8 mL of 1 mM tetrabutylammonium hydroxide (TBAOH) in ethanol. Substrates were removed four hours later after full dye desorption. UV-visible light spectra were collected for basic solution and concentration of solution was determined against Beer-Lambert calibration plots.

Synthesis and Characterization

bis(4-methoxyphenyl)amine (P1): 4-aminoanisole (2.46 g, 20.1 mmol), 4-bromoanisole (3.00 g, 16.0 mmol), copper iodide (0.61 g, 3.2 mmol), potassium carbonate (7.36 g, 6.40 mmol) and L-proline (0.81 g, 6.4 mmol) were added to DMSO (25 mL) under N_2. The reaction mixture was stirred at 100 °C for 48 h, then quenched with distilled water (50 mL) and extracted with 3 × 20 mL of diethyl ether. The organic phase was collected, dried over $MgSO_4$ and reduced under pressure. Purification by silica column chromatography (SiO_2: hexanes/EtOAc, 4:1, R_f = 0.54) yielded 1.44 g (39.3%) of product as thin pale brown crystals. ^{1}H 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 (400 MHz, DMSO): δ = 153.2, 138.5, 118.5, 115.0, 55.7 ppm. HRMS (ESI) *m/z:* 230.1176 [$(M+H)^+$] calcd for $C_{14}H_{15}NO_2$ *m/z:* 230.1181.

3,7-dimethoxy-10*H*-phenothiazine (P2): P1 (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 and submitted directly to column. Purification by silica column chromatography (SiO_2: hexanes/EtOAc, 3:1, R_f =0.28) yielded 0.32 g (20%) of product as an orange solid. ^{1}H NMR (300 MHz, MeOD): δ = 6.60 (d, 4H, ^2J = 1.55 Hz), 6.57 (d, 2H, ^2J = 1.48 Hz), 3.72 (s, 6H) ^{13}C NMR (400 MHz, DMSO): δ = 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 $C_{14}H_{13}NO_2S$ *m/z:* 259.0667.

10-(4-bromophenyl)-3,7-dimethoxy-10*H*-phenothiazine (P3): P2 (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, then cooled to room temperature and submitted directly to column. Purification by silica column chromatography (SiO_2: hexanes/CH_2Cl_2, 4:1, R_f = 0.19) yielded 0.39 g (40.9%) of pale yellow tacky solid. ^{1}H NMR (300 MHz, MeOD): δ = 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 (400 MHz, DMSO): δ = 156.9, 145.4, 135.7, 132.8, 131.0, 125.5, 121.9, 114.9, 113.9, 113.3, 56.0xs ppm. HRMS (ESI) *m/z:* 413.0070 [$(M+H)^+$] calcd for $C_{20}H_{16}NO_2SBr$ *m/z*: 413.0085.

(4-(3,7-dimethoxy-10*H*-phenothiazin-10-yl)phenyl)thiophene-2-carbaldehyde (P4): P3 (0.34 g, 0.80 mmol), 5-formyl-2-thienylboronic acid (0.16 g, 1.0 mmol), palladium tetrakis(triphenylphosphine) (0.046 g, 0.040 mmol) and sodium carbonate (0.260 g, 2.64 mmol) were added sequentially to 25 mL of sparged THF/H_2O (5:1, *v/v*) under N_2. The reaction mixture was stirred and left at reflux for 16 h, then cooled to room temperature. THF was then removed *in vacuo.* A crude mixture was extracted with 20 mL of distilled water and 3 × 20 mL of CH_2Cl_2. The organic phase was collected, dried over $MgSO_4$ and reduced under pressure. Purification by silica column chromatography (SiO_2: hexanes/CH_2Cl_2, 4:1, R_f = 0.2) yielded 0.230 g (64.7%) of product as a brown oil. ^{1}H 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). ^{13}C NMR (400 MHz, DMSO): 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-10*H*-phenothiazin-10-yl)phenyl)thiophen-2-yl)acrylic acid (PTZ): P4 (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 N_2. The reaction mixture was stirred and left at reflux for 16 h, then cooled to room temperature and solvent was removed *in vacuo*. Purification by silica column chromatography (SiO_2: CH_2Cl_2/MeOH, 9:1, R_f = 0.3) yielded 0.190 g (73.8%) of product as a pale orange solid. ^{1}H 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) ^{13}C NMR (400 MHz, DMSO): 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 $C_{28}H_{20}N_2O_4S_2$ *m/z:* 467.0888.

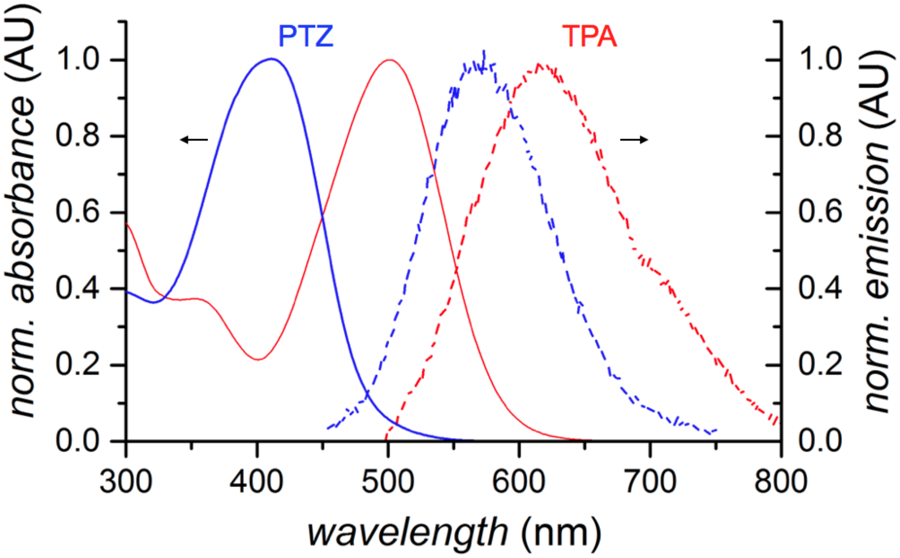


Fig. S2 Absorption and emission (dashed) spectra for **PTZ** and **TPA** in MeCN.

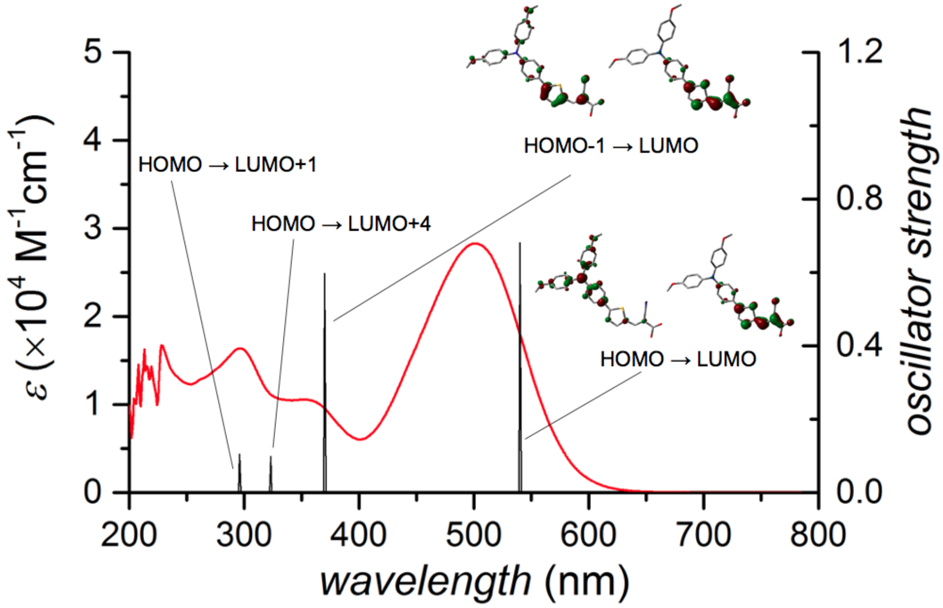


Fig. S3 UV-vis absorption spectra (red) and TD-DFT calculated transitions (black) for **TPA** and corresponding orbital diagrams.

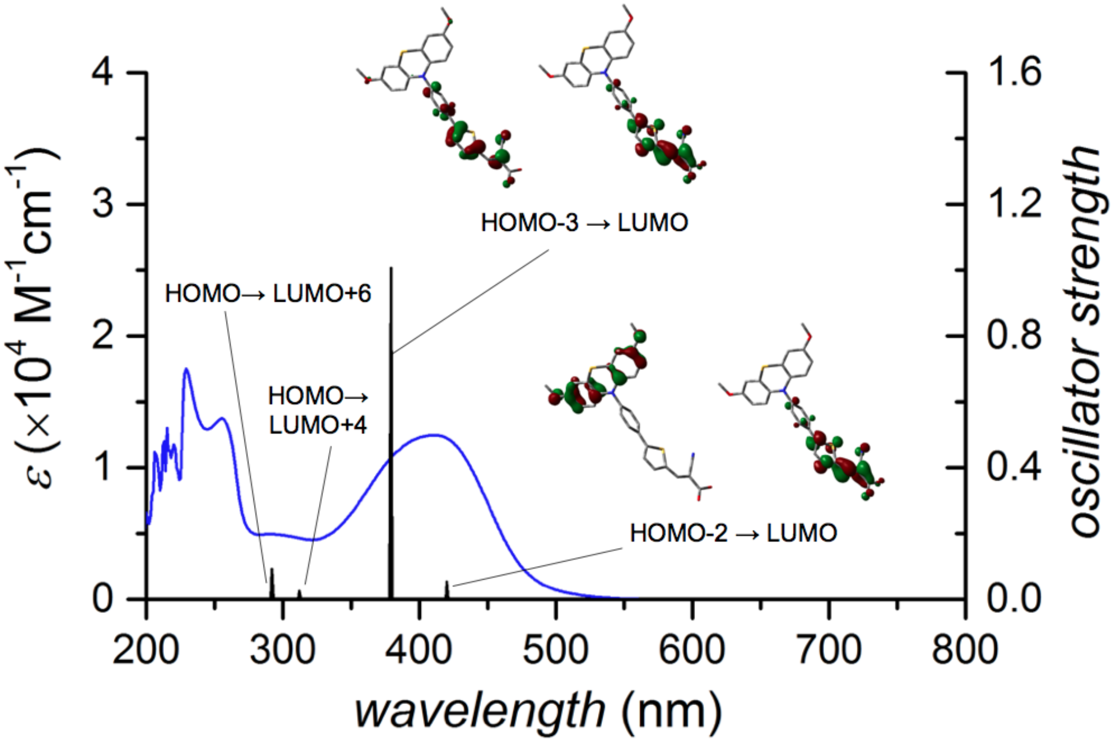


Fig. S4 UV-Vis absorption spectra (blue) and TD-DFT calculated transitions (black) for **PTZ**. The orbital diagrams are shown.

Table S1. Dye loading on mesoporous nanocrystalline TiO_2[a] for **TPA** and **PTZ**

Dye loading solution	χ_{TPA} (x 10^{-7} mol/cm^2)	χ_{PTZ} (x 10^{-7} mol/cm^2)
0.25 mM dye	4.85 ± 0.01	10.00 ± 0.01
0.25 mM dye and 0.25 mM CDCA	4.25 ± 0.08	7.76 ± 0.07
0.25 mM dye 2.5 mM CDCA	2.96 ± 0.09	6.30 ± 0.14

[a] Dye loading on TiO_2 (2 layers of 18-NRT and 1 layer of WER4-0) with an active area of 0.128 cm^2 and thickness of 13-15 μm on fluorine-doped tin oxide. Data corresponds to averaged dye loading values with standard deviations derived from no fewer than two desorption studies.

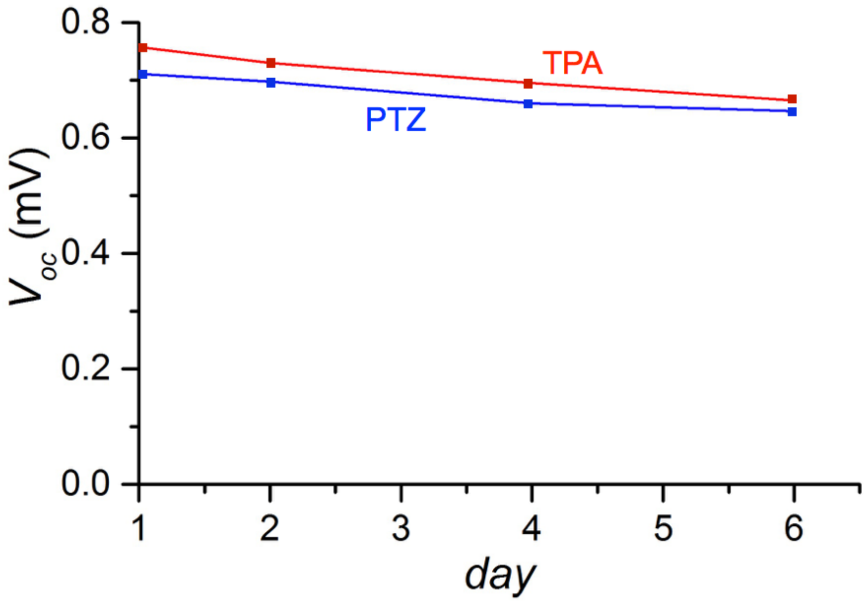


Fig. S5 Open-circuit potential (V_{oc}) for dyes **TPA** and **PTZ** in a DSSC under constant illumination at AM 1.5 (1 Sun) and 45 °C for 150 h.

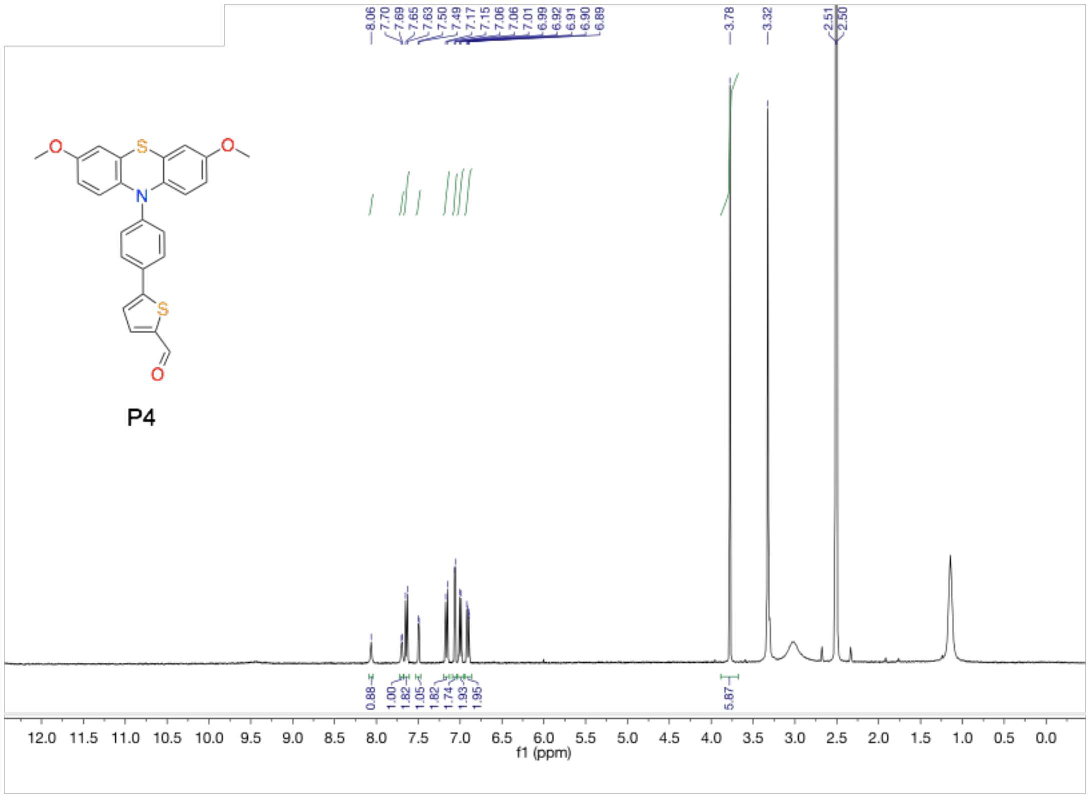


Fig. S6 ^{1}H NMR spectrum of **P4** in MeOD at ambient temperatures.

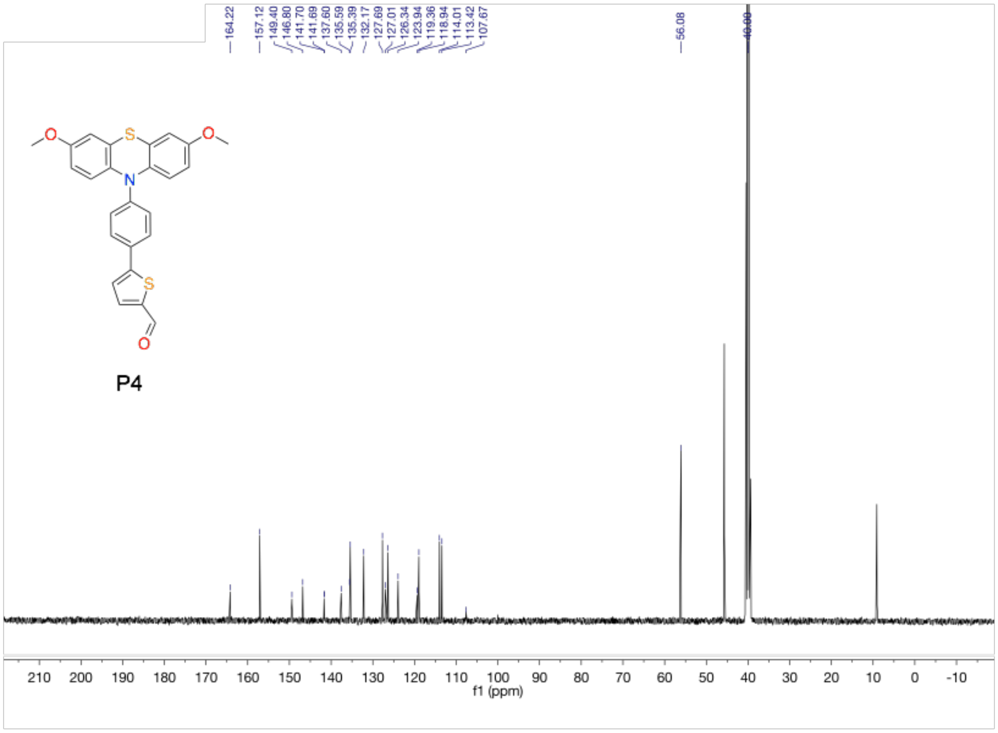


Fig. S7 ^{13}C NMR spectrum of **P4** in DMSO at ambient temperatures.

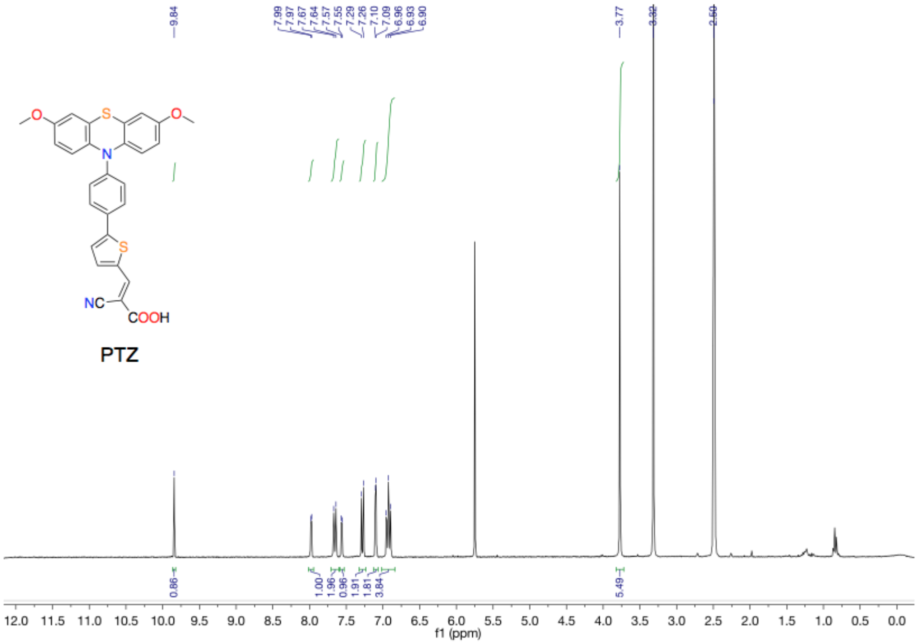


Fig. S8 ^{1}H NMR spectrum of **PTZ** in MeOD at ambient temperatures.

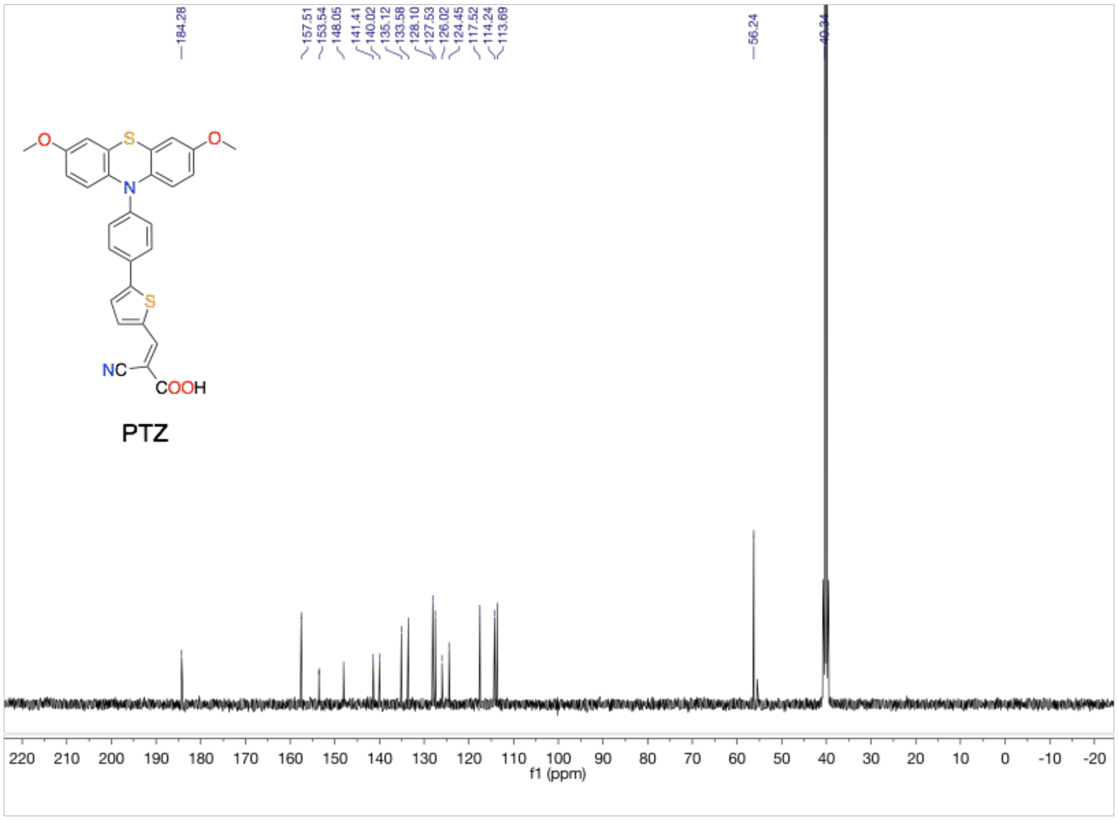


Fig. S9 ^{13}C NMR spectrum of **PTZ** in DMSO at ambient temperatures.

Notes and References

1. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
2. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel, *Prog. Photovolt: Res. Appl.*, 2007, **15**, 603–612.