Supplementary Information

Promoting Charge-separation in p-Type Dye-sensitized Solar Cells using Bodipy.

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Contents:

1) Experimental

General Methods

All reagents and solvents (analytical grade) were purchased from Sigma-Aldrich or Fisher Scientific and used without further purification unless stated. Dichloromethane was dried over calcium hydride and distilled under argon. Methanol was dried over magnesium turnings and iodine and distilled under argon. Silica gel 60 and Alumina were purchased from Sigma-Aldrich.

Physical Methods.

All products were characterized by ^{1}H NMR and ^{13}C NMR using a Bruker 300MHz (dpx300) or 400 (av3400) MHz spectrometer; chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to residual non-deuterated solvent (δ = 7.29 ppm for chloroform). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; m = multiplet. All proton assignments are provided in the supporting information.

High resolution mass spectrometry (HRMS) was carried out on a high-throughput MS system, based on a Bruker MicroTOF (Time of Flight) mass spectrometer using ElectroSpray Ionisation (ESI). HRMS for **1** were obtained by direct injection in the spectrometer.

Absorption measurements were carried out using an Ocean Optics USB2000 spectrometer. The steady state emission spectra were recorded using an Edinburgh Instruments FL900 combined fluorimeter and lifetime spectrometer. An Edinburgh Instruments EPL-405 pulsed laser emitting at 405 nm was used to measure the lifetimes.

Electrochemical measurements were performed under N_2 using dry solvents using an IVIUM CompactStat potentiostat, a glassy carbon working electrode, Pt counter electrode and a $Ag/AgNO_3$ reference electrode, and 0.5 M NBu_4ClO_4 dichloromethane solutions. Spectroelectrochemical measurements were performed on sensitized NiO films using a platinum reference electrode and an $Ag/AgNO_3$ reference electrode and the supporting electrolyte was 0.1 M $LiClO_4$ in acetonitrile, which was degassed by bubbling with nitrogen. In both cases the cells were calibrated against ferrocene/ferrocenium using a glassy carbon working electrode.

Samples for transient absorption spectroscopy were prepared by adsorbing the dye on a mesoporous NiO film deposited on a CaF_2 window (Crystran). The NiO films were prepared by spraying a saturated solution of $NiCl_2$ in acetylacetone onto the surface of the CaF_2 window which was pre-heated to 450 °C on a hotplate; this was then allowed to cool slowly to room temperature to give a compact film of NiO. The mesoporous layer was then deposited on top of the compact layer using an F108–templated precursor solution containing $NiCl_2$ (1 g), Pluronic® co-polymer F108 (1 g), Milli-Q water (3 g) and ethanol (6 g) and the excess was removed by doctor blade. The film was sintered at 450 °C for 30 minutes and an additional layer of precursor solution was applied and sintered to increase the film thickness. For the samples measured in the presence of electrolyte 0.1 M $LiClO_4$ in propylene carbonate or 0.1M LiI and 3mM I_2 in propylene carbonate were introduced to the Harrick cell and a path length of 0.1 mm was used to ensure a sufficiently low optical density for the electrolyte that did not interfere with the signal for **1**/NiO.

The transient absorption spectroscopy measurement (λ_{ex} = 532 nm) is based on the pump-probe method described in detail elsewhere.[1] In brief, the probe beam of white light continuum, is generated by focusing small amount of 800 nm (~300 nJ) laser beam into a 3mm thick CaF_2 disk. The picoseconds 532 nm pump beam is obtained from a commercial Ti:sapphire oscillator / regenerative amplifier system (Spectra Physics, USA) and a TOPAS-C OPA (Light Conversion, Lithuania) and the time difference (up to 3 ns) between the pump and probe pulses is controlled by an optical delay line. The nanosecond 532 nm pump beam is produced with a Q-switched Nd:YVO laser (ACE-25QSPXHP/MOPA, Advanced Optical Technology, UK) which is electronically synchronised to the Spitfire Pro amplifier. Therefore, the delay between pump and probe pulses can be controlled with a pulse generator (DG535, Stanford Research System, USA) from 0.5 ns to 100 μs. The white light beam is split into two parts. One part passes through the sample and spatially overlapped with the pump beam. Another part serves as a reference to the probe beam fluctuations. The polarization of the pump pulse is set at the magic angle (54.7 degree) relative to the probe pulse to recover the isotropic absorption spectrum of solution. Both parts of probe beam are monitored by a duel array detector (512

pixels) (Cronin Camera, Spectronic device Ltd, UK). The detector is mounted in the focal plane of a 303 mm Acton spectrograph (Acton, USA) with 150 g/mm and 75 g/mm gratings. The pump beam size (~400 μm diameter) is larger than the probe spot (~200 μm diameter). A Harrick sample cell with 2-mm-thick CaF_2 windows is mounted on a motorized cell mount, which moves the cell in x and y dimensions rapidly and continuously.

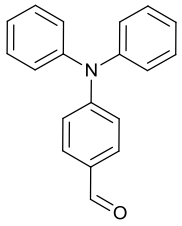
p-DSCs were made by depositing the precursor solution [$NiCl_2$ (1 g), Pluronic® co-polymer F108 (1 g), Milli-Q water (3 g) and ethanol (6 g)] by doctor blade onto conducting glass substrates (Pilkington TEC15, sheet resistance 15 Ω/square) using Scotch tape as a spacer (0.2 cm^2 active area), followed by sintering in an oven at 450 °C for 30 min. This process was repeated to add a second layer. The NiO electrodes were soaked in an acetonitrile solution of the dye (0.3 mM) for 16 h at room temperature. The dyed NiO electrode was assembled face-to-face with a platinized counter electrode (Pilkington TEC8, sheet resistance 8 Ω/square) using a 30 mm thick thermoplastic frame (Surlyn 1702, Dyesol). The electrolyte, containing LiI (1.0 M) and I_2 (0.5 M) in acetonitrile, was introduced through the pre-drilled hole in the counter electrode, which was sealed afterwards. The UV-visible absorption spectra of the dyes adsorbed on NiO films were recorded using an Ocean Optics USB2000+VIS-NIR fibre-optic spectrophotometer. Current-voltage measurements were measured using an Ivium CompactStat potentiostat under simulated sunlight from an Oriel 150 W solar simulator, giving light with an intensity of 100 mW cm^{-2}. Incident photon-to-current conversion efficiencies were recorded using monochromatic light from the solar simulator using a Cornerstone monochromator and appropriate filters and calibrated against a certified reference Si photodiode.

Theoretical studies were carried out using Gaussian g03 software on the University of Nottingham HPC facility (Minerva). All calculations for optimised geometry and the subsequent energies and plots of the principle molecular orbitals were performed using density functional theory (DFT) using a B3LYP hybrid functional and a 6-31+G (d) basis set. Principle electronic transitions and subsequent UV/Visible and IR spectra were predicted using time dependent density functional theory (TDDFT) using the same functional and basis sets as above. These calculations were performed for the compounds in dichloromethane.

[1] Q. Cao, C. M. Creely, E. S. Davies, J. Dyer, T. L. Easun, D. C. Grills, D. A. McGovern, J. McMaster, J. Pitchford, J. A. Smith, X.-Z. Sun, J. M. Kelly and M. W. George, *Photochemical & Photobiological Sciences*, 2011, **10**, 1355

Synthesis

4-formyltriphenylamine



Chemical Formula: $C_{19}H_{15}NO$
Exact Mass: 273.11536
Molecular Weight: 273.32850

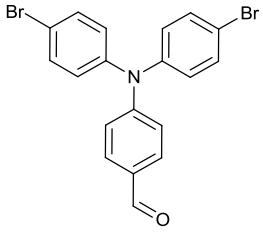
Triphenylamine (10 g, 40 mmol) was dissolved in dry N,N-Dimethylformamide DMF (100 mL) under argon in a three-necked flask and the solution was cooled at 0°C with stirring. Phosphoryl chloride $POCl_3$ (19.5 mL, 0.210 mol, 5.25 eq.) was added slowly to the mixture and then the reaction mixture was warmed to 100°C and stirred for 5 hours under argon. After cooling at room temperature, the mixture was neutralized slowly with a 2 M sodium hydroxide solution. After stirring for further 30 minutes, the mixture was extracted with 3 × 200 mL of ethylacetate. The organic layer was then dried with Na_2SO_4 and evaporated. The different products were separated by silica gel column chromatography (eluent: heptane/chloroform 2/1) to afford the 4-formyltriphenylamine in 79% yield (8.75 g) as a beige solid.

^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.82 (s, 1H, H_{CHO}), 7.69 (d, J = 8.7 Hz, 2H, H_{Ar}), 7.41-7.30 (m, 4H, H_{Ar}), 7.24-7.13 (m, 6H, H_{Ar}), 7.03 (d, J = 8.7 Hz, 2H, H_{Ar}) ppm.

^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C): δ 190.45 (C_{CHO}), 153.4, 146.2, 131.3, 129.7, 129.1, 126.3, 125.1, 119.4 ppm.

MS (ESI^+): calcd. for $C_{19}H_{16}NO$: 274.12, found: 274.12 ($[M+H]^+$).

4,4'-dibromo-4''-formyltriphenylamine



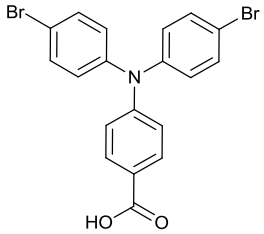
Chemical Formula: $C_{19}H_{13}Br_2NO$
Exact Mass: 428.93639
Molecular Weight: 431.12062

4-formyltriphenylamine (936 mg, 3.425×10^{-3} mol) was dissolved in dry THF (40 mL) under argon. N-bromosuccinimide NBS (1.58 g, 8.88×10^{-3} mol, 2.6 eq.) was added under argon at room temperature. The mixture was heated to reflux for 5 hours. The completion of the reaction was monitored by TLC. The solvent was then evaporated and chloroform (40 mL) was added to the residue. The solid was filtered and washed with chloroform. The filtrate was washed with a 10% $NaHCO_3$ aqueous solution and with water. After drying on magnesium sulphate and evaporation of the solvent, the residue was directly reused for the oxidation reaction.

^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.84 (s, 1H, H_{CHO}), 7.71 (d, J = 8.7 Hz, 2H, H_{Ar}), 7.44 (d, J = 8.7 Hz, 4H, H_{Ar}), 7.04 (d, J = 8.7 Hz, 2H, H_{Ar}), 7.01 (d, J = 8.7Hz, 4H, H_{Ar}) ppm.

MS (ESI^+): calcd. for $C_{19}H_{14}Br_2NO$: 429.94, found: 429.94 ($[M+H]^+$).

4-[bis-(4-bromo-phenyl)-amino]-benzoic acid



Chemical Formula: $C_{19}H_{13}Br_2NO_2$
Exact Mass: 444.93130
Molecular Weight: 447.12002

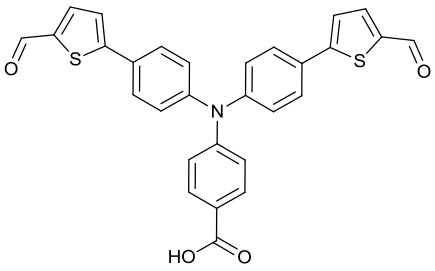
The residue was suspended in an acetone water (*v/v* 45/15 mL) mixture and heated to reflux. Potassium permanganate (2 g, 12.66×10^{-3} mol) was added portion wise to the mixture during 1h and the mixture was heated to reflux for 4 hours. Acetone was then evaporated and water (40 mL) was added to the mixture. The solid was filtered and washed with water. The filtrate was then acidified with concentrated hydrochloric acid until precipitation. The white solid was filtered, washed with water and dried. The compound was purified by column chromatography on silica gel using a gradient of acetic acid in chloroform as eluent to afford 1.88 g of 4-[bis-(4-bromo-phenyl)-amino]-benzoic acid as a white solid in 88% yield.

^{1}H NMR ($CDCl_3$, 300 MHz, 25°C): δ 7.94 (d, J = 8.7 Hz, 2H, H_{Ar}), 7.43 (d, J = 8.7 Hz, 4H, H_{Ar}), 7.04-6.98 (m, 6H, H_{Ar}) ppm.

^{13}C NMR ($CDCl_3$, 300 MHz, 25°C): δ 171.33 (C_{COOH}), 152.0, 145.4, 133.0, 131.9, 127.3, 122.3, 120.7, 117.8 ppm.

MS (ESI^-): calcd for $C_{19}H_{12}Br_2NO_2$: 443.92, found: 443.93 ($[M-H]^-$).

4-Carboxy-4',4''-di(5-formyl-2-thienyl)triphenylamine



Chemical Formula: $C_{29}H_{19}NO_4S_2$
Exact Mass: 509.07555
Molecular Weight: 509.59546

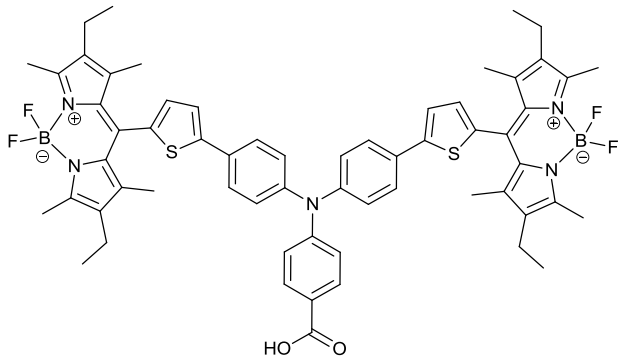
4,4'-dibromo-4''-formyltriphenylamine (100 mg, 2.24×10^{-4} mol), 5-formyl-2-thienylboronic acid (92 mg, 5.90×10^{-4} mol, 2.6 eq), bis-triphenylphosphinepalladium(II) chloride (8 mg, 1.12×10^{-5} mol, 0.05 eq.) and sodium carbonate (118 mg, 1.12×10^{-3} mol, 5 eq.) were loaded in a Schlenk tube purged with nitrogen. H_2O (1 mL) and then 1,2-dimethoxyethane DME (3 mL) were added and the mixture was heated to 90 °C overnight under nitrogen. After cooling, water (3 mL) was added and the mixture was acidified with diluted 0.1 M hydrochloric acid until slightly acidic pH. The organic phase was extracted with Ethyl acetate (3 × 20 mL) and washed with water (3 × 5 mL), dried on $MgSO_4$ and evaporated. The product was purified by silica gel column chromatography with a gradient of methanol in DCM as eluent to afford 90 mg of 4-carboxy-4',4''-di(5-formyl-2-thienyl)triphenylamine as a yellow solid in 79% yield. **Note**: the same reaction carried under microwave irradiation for one hour afforded 100 mg of product in 90% yield

^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.89 (s, 1H, H_{CHO}), 7.99 (d, J = 6.6 Hz, 2H, H_{Ar}), 7.75 (d, J = 3.0 Hz, 2H, $H_{thiophene}$), 7.63 (d, J = 6.6 Hz, 4H, H_{Ar}), 7.37 (d, J = 3.0 Hz, 2H, $H_{thiophene}$), 7.20 (d, J = 6.6Hz, 4H, H_{Ar}), 7.15 (d, J = 6.6Hz, 4H, H_{Ar}) ppm.

^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C): δ 182.9, 171.2, 153.6, 151.5, 147.3, 142.3, 137.7, 132.0, 129.3, 127.9, 125.7, 123.9, 123.3, 122.2 ppm.

MS (ESI^-): calcd. for $C_{29}H_{18}NO_4S_2$: 508.07, found: 508.07 ($[M-H]^-$).

4-carboxy- 4',4''-di-[2-(5-boron dipyrrene)thienyl]triphenylamine 1



Chemical Formula: $C_{61}H_{61}B_2F_4N_5O_2S_2$
Exact Mass: 1057.43889
Molecular Weight: 1057.91495

4-carboxy- 4',4''-di(5-formyl-2-thienyl)triphenylamine (50 mg, 9.81×10^{-5} mol) was dissolved in dry dichloromethane (2 mL) in a Schlenk tube purged with nitrogen. 2,4-dimethyl-3-ethylpyrrole (66 µL, 4.89×10^{-4} mol, 5 eq.) and then trifluoroacetic acid (1 drop) were added to the solution. The mixture was stirred for 3 hours under nitrogen. *p*-chloranil (50 mg, 2.03×10^{-4} mol, 2.07 eq.) was added under a flux of nitrogen and the mixture was stirred under nitrogen for another 30 minutes. Diisopropylethylamine (0.205 mL, 1.18×10^{-3} mol, 12 eq.) was added and the mixture was stirred under nitrogen for another 10 minutes. Finally, boron trifluoride etherate (0.24 mL, 1.94×10^{-3} mol, 20 eq.) was added and the mixture was stirred under nitrogen overnight. Dichloromethane (10 mL) was added to the mixture and the organic layer was washed with water (3 × 5 mL), dried on $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography with a dichloromethane / methanol mixture (*v/v* 99.5/0.5). Crystallisation from dichloromethane with addition of pentane afforded 35 mg of pure 4-carboxy- 4',4''-di-[2-(5-boron dipyrrene)thienyl]triphenylamine **1** in 34% yield.

^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.97 (d, J = 8.7 Hz, 2H, H_{Ar}), 7.61 (d, J = 8.7 Hz, 4H, H_{Ar}), 7.32 (d, J = 3.6 Hz, 2H, $H_{thiophene}$), 7.21 (d, J = 8.7 Hz, 4H, H_{Ar}), 7.13 (d, J = 8.7 Hz, 2H, H_{Ar}), 6.95 (d, J = 3.6 Hz, 2H, $H_{thiophene}$), 2.54 (s, 12H, H_{Me}), 2.34 (q, J = 7.5Hz, 8H, H_{CH2CH3}), 1.65 (s, 12H, H_{Me}), 1.01 (t, J = 7.5Hz, 12H, H_{CH2CH3}) ppm.

^{13}C NMR ($CDCl_3$, 300 MHz, 25°C): δ 154.7, 152.0, 146.1, 145.7, 138.7, 134.9, 133.3, 131.9, 130.2, 129.2, 127.2, 126.1, 123.1, 121.0, 17.3, 14.7, 12.7, 11.4 ppm.

HRMS (TOF-ESI^+): calcd. for $C_{61}H_{61}B_2F_4N_5NaO_2S_2$: 1080.4300, found: 1080.4303 ($[M+Na]^+$).

UV/Vis (DCM): λ (ε, L mol^{-1} cm^{-1}) = 365 (56 000), 412 (sh, 16 000), 507 (sh, 43 000), 540 (112 000) nm.
(CH_3CN): λ (ε, L mol^{-1} cm^{-1}) = 363 (60 000), 411 (sh, 16 200), 512 (sh, 40 000), 536 (112 000) nm.

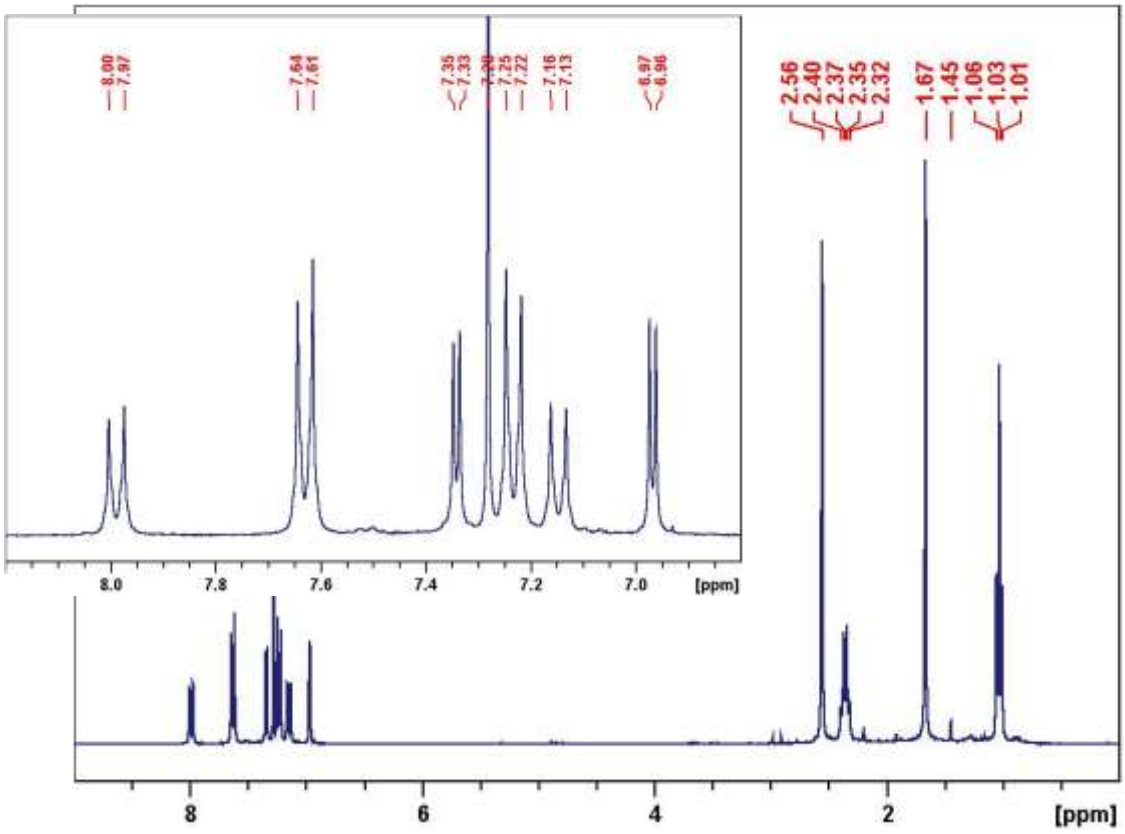


Figure S1. ^{1}H NMR spectrum of **1** (CDCl3, 300 MHz, 25°C).

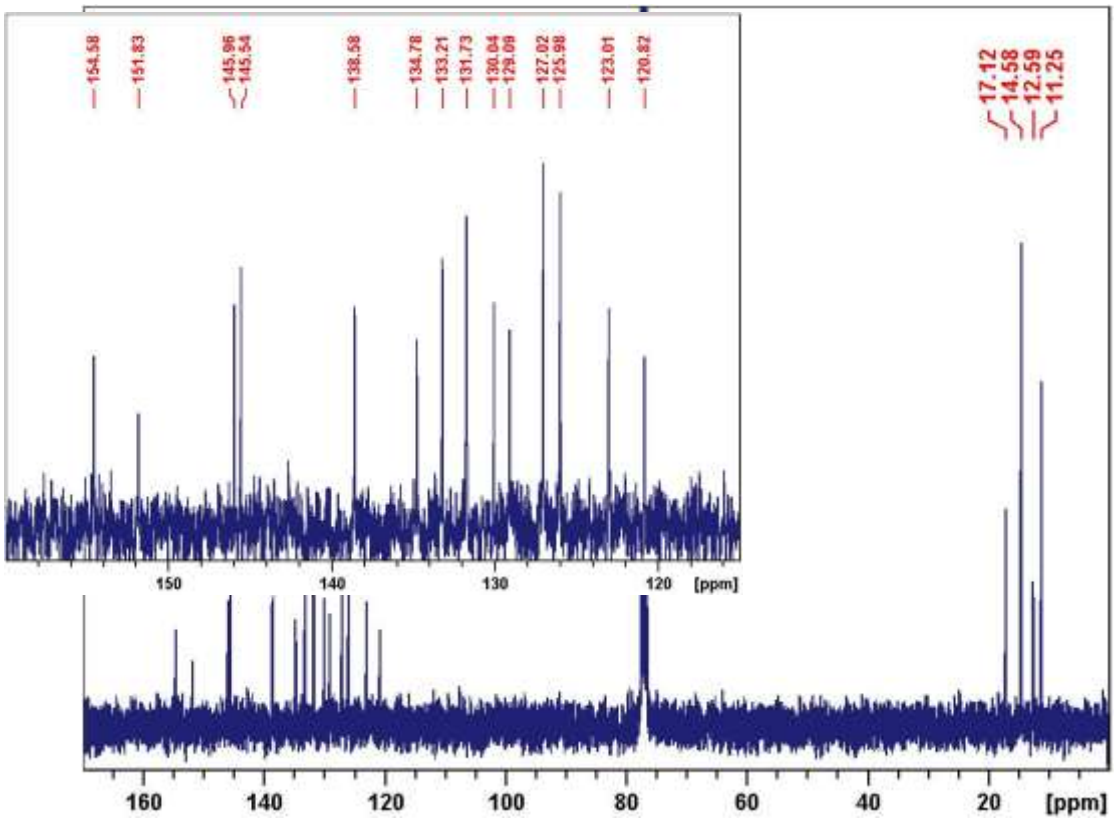


Figure S2. ^{13}C NMR spectrum of **1** (CDCl3, 300 MHz, 25°C).

2) Electronic Spectra

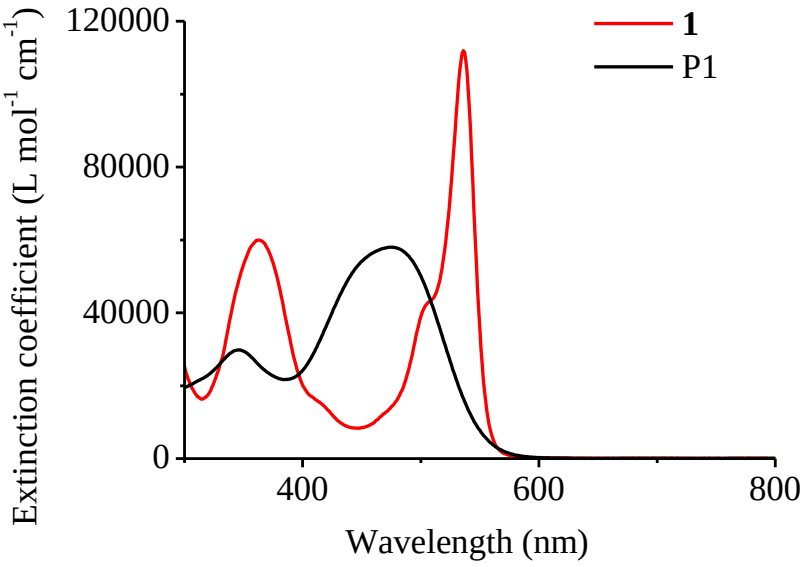


Figure S3. Absorption spectra of **1** (red) and **P1** (black) in acetonitrile

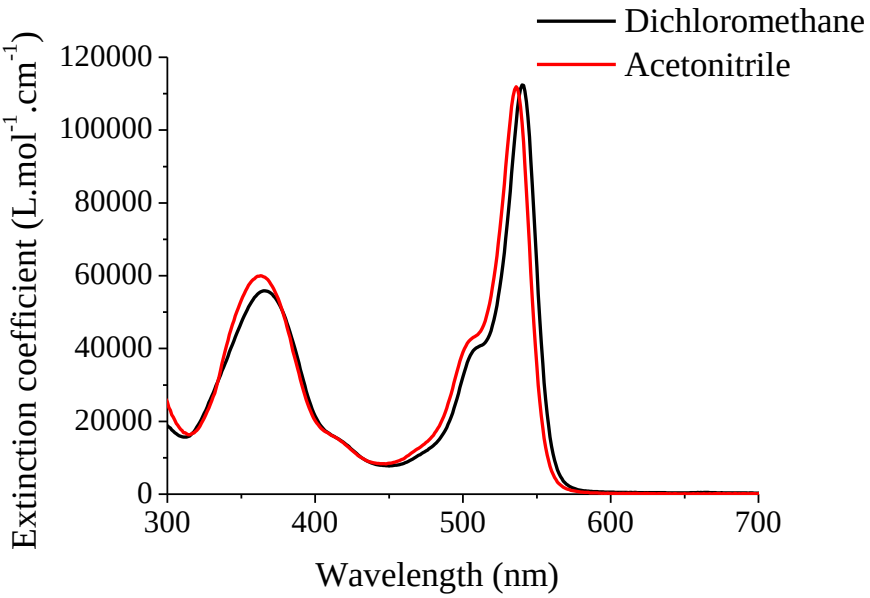


Figure S4. Absorption spectra of **1** in acetonitrile (red) and dichloromethane (black)

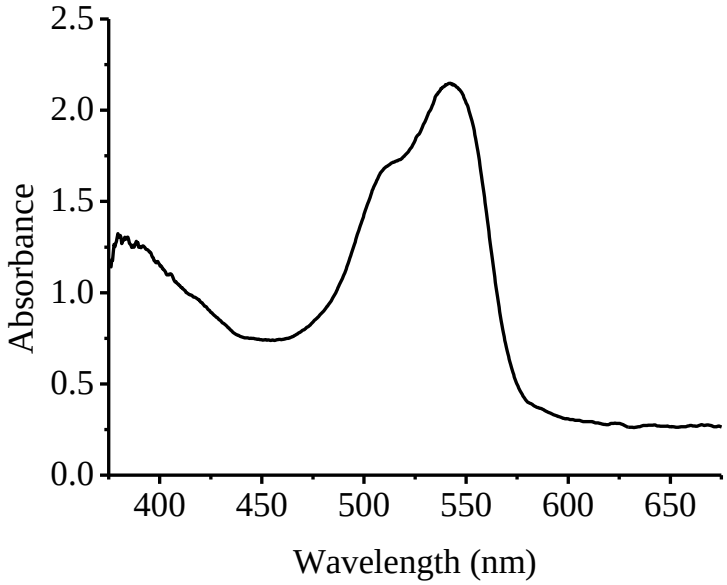


Figure S5. The UV-visible absorption spectra of the dyes adsorbed on NiO electrodes.

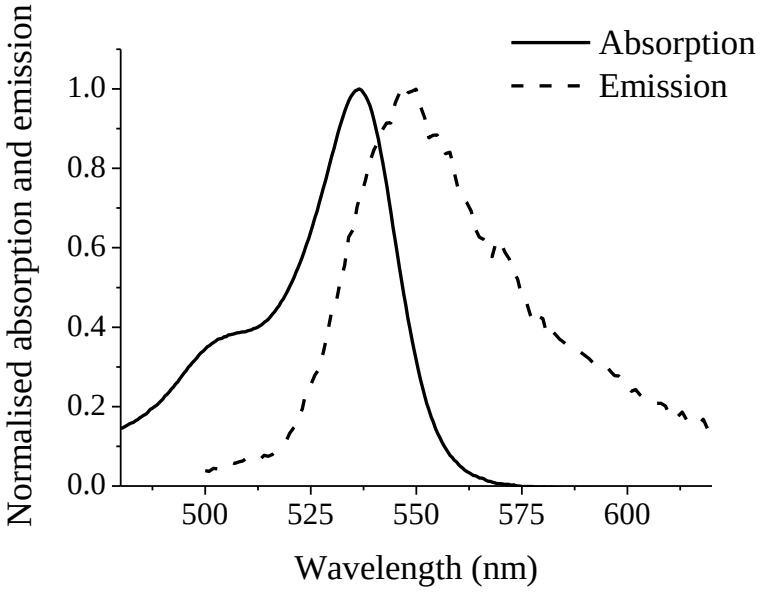


Figure S6. Normalised absorption (solid line) and emission (dashed line) of **1** in acetonitrile (excitation at 488 nm, crossing at 541nm)

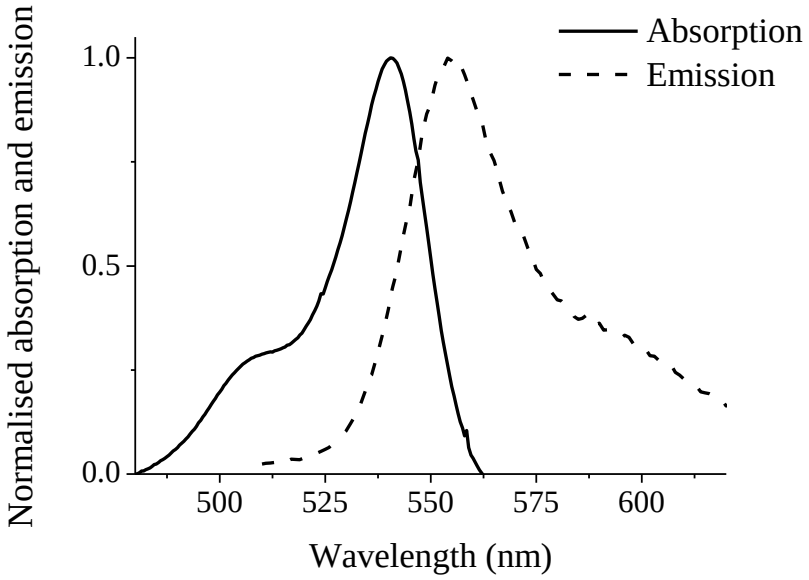


Figure S7. Normalised absorption (solid line) and emission (dashed line) of **1** in dichloromethane (excitation at 488 nm, crossing at 547nm)

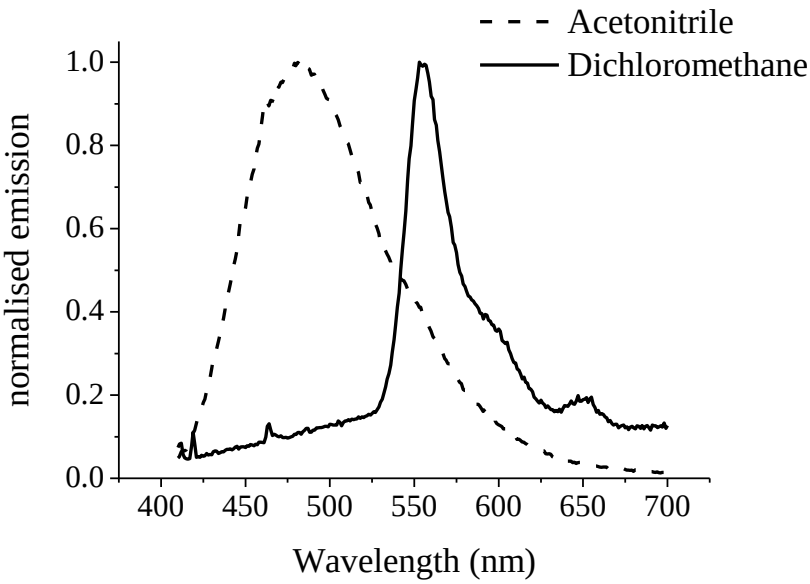


Figure S8. Normalised emission of **1** in acetonitrile (dashed line) and dichloromethane (solid line) (excitation at 406 nm).

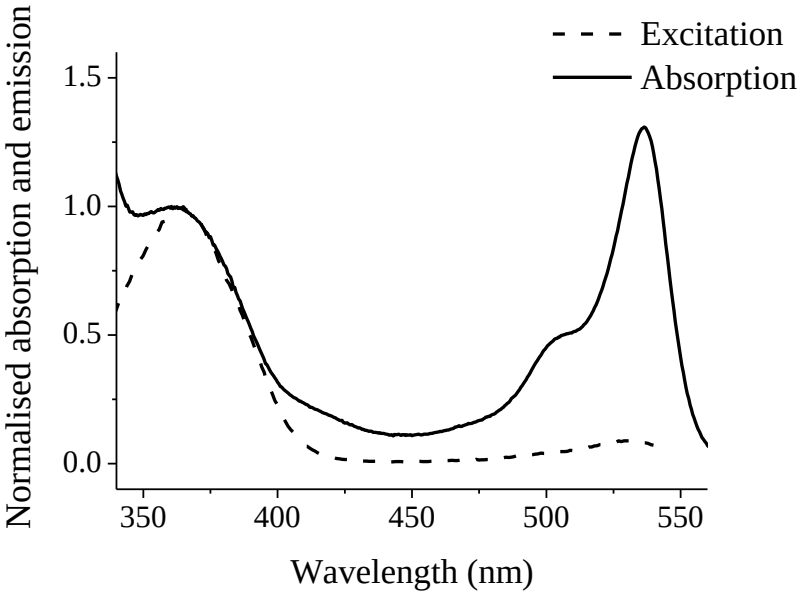


Figure S9. Normalised absorption (solid line) and excitation (dashed line) spectra of **1** in acetonitrile (emission at 550 nm, normalised at 363 nm)

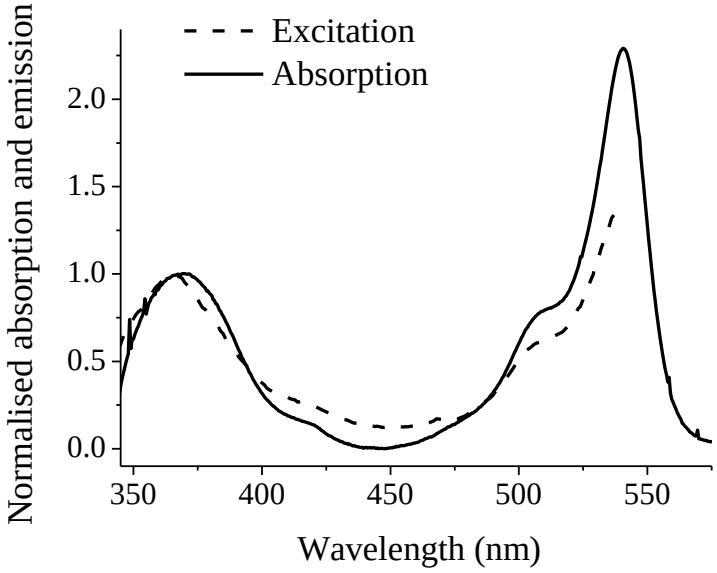


Figure S10. Normalised absorption (solid line) and excitation (dashed line) spectra of **1** in dichloromethane (emission at 550 nm, normalised at 363 nm).

3) Electrochemical Characterisation

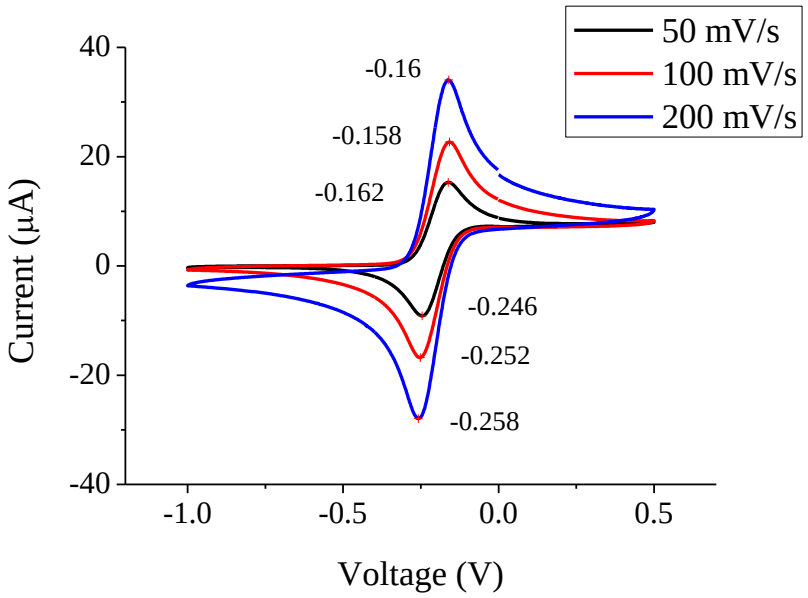


Figure S11. Cyclic voltammetry of ferrocene (1 mM) in dichloromethane with tetrabutylammonium perchlorate (0.5 M).

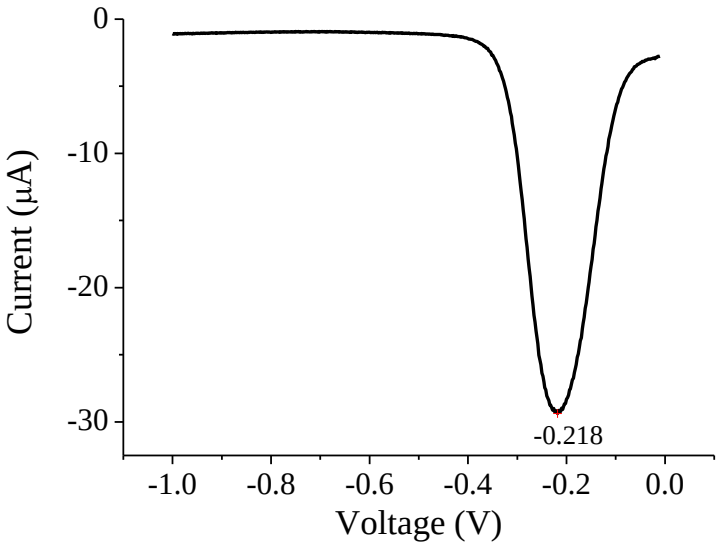


Figure S12. Square wave voltammetry of ferrocene (1 mM) in dichloromethane with tetrabutylammonium perchlorate (0.5 M).

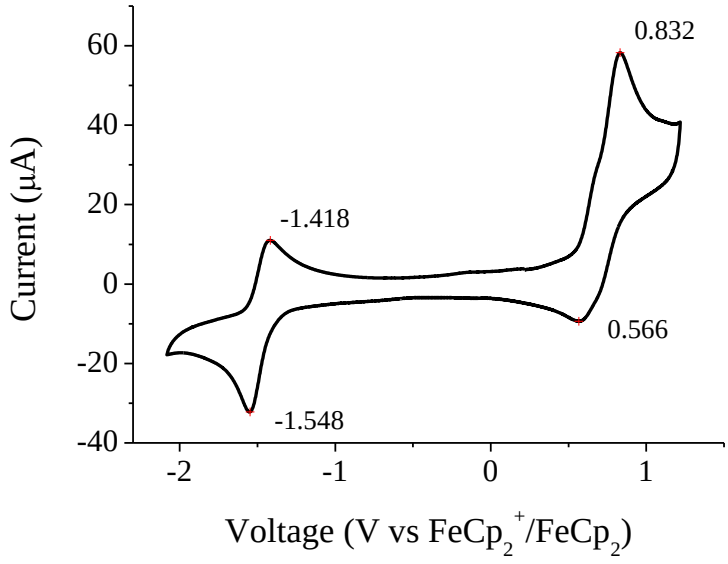
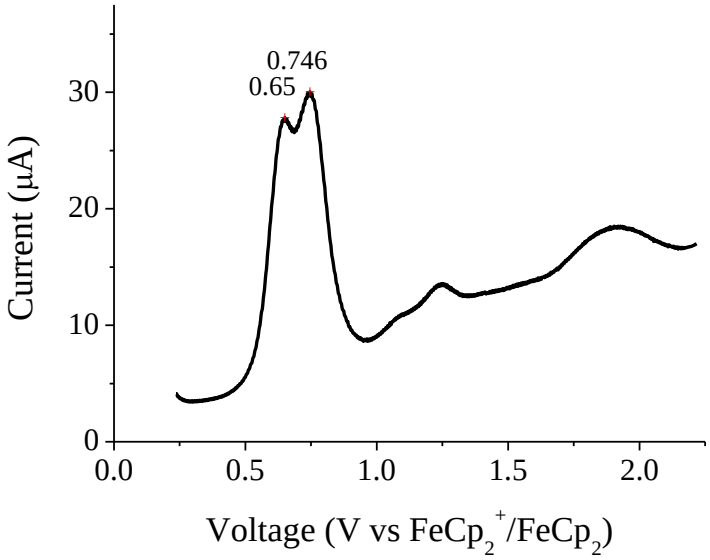


Figure S13. Cyclic voltammetry of **1** (1 mM) in dichloromethane with tetrabutylammonium perchlorate (0.5 M), at a scan rate of 200 mV s^{-1}.



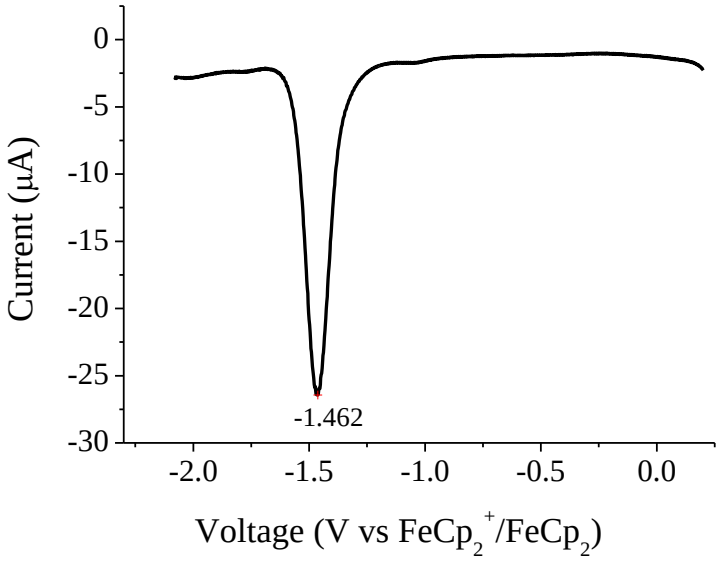


Figure S14. Square wave voltammetry of **1** (1 mM) in dichloromethane with tetrabutylammonium perchlorate (0.5 M), at a scan rate of 200 mV s^{-1}.

Table S1. Optical and Electronic properties of **1**.

Dye	**Absorption**[a]		**Emission**[b]			
	λ_{max} (nm)	**ε at λ_{max} (L mol^{-1} cm^{-1})**	**λ_{max} (nm)**	**$E_{0\text{-}0}$ (eV)**[b]	**$E_{(D/D+)}$**[c] **(V vs. $FeCp_2^+/FeCp_2$)**	**$E_{(D/D-)}$**[c] **(V vs. $FeCp_2^+/FeCp_2$)**
P1	481	57900	618	2.25	0.69	-1.46
1	540	112000	560	2.27	0.65	-1.46

[a]In dichloromethane solution. [b]E_{0-0} was estimated from the point of intercept of the normalized absorbtion and emission curves. [c]The oxidation and reduction potential of the dye was measured in dichloromethane with 0.5 M tetrabutylammonium perchlorate ($TBAClO_4$) as electrolyte (working electrode: glassy carbon; reference electrode: Ag^+/Ag; calibrated with ferrocene/ferrocenium ($FeCp_2^+/FeCp_2$) as an internal reference, counter electrode: Pt). P1 is in acetonitrile and $TBAPF_6$

4) TD DFT Calculations

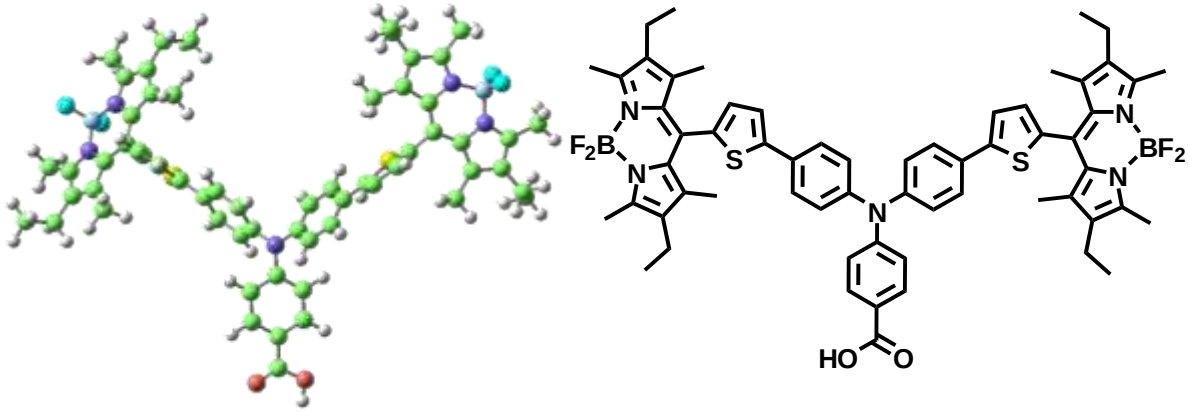


Figure S15. Optimised geometry of **1**. Colours correspond to atom types.

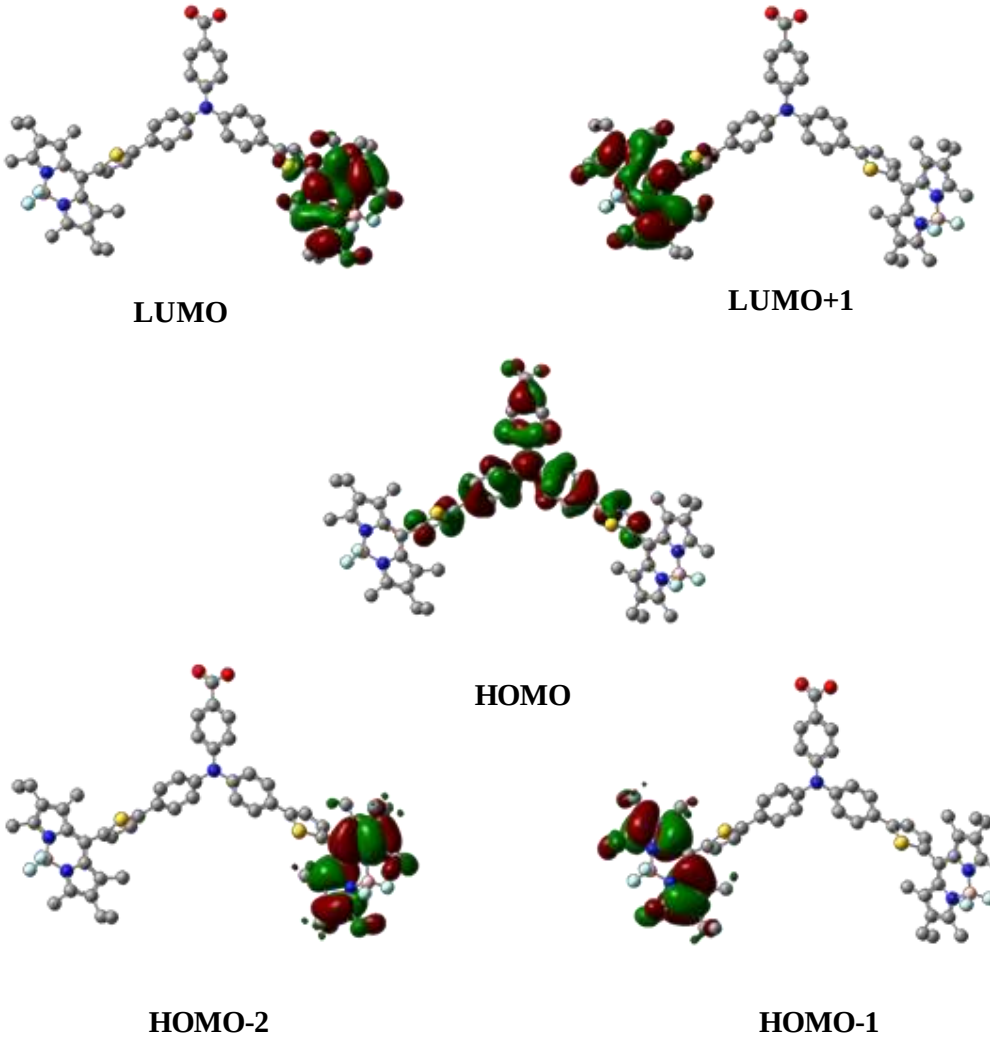


Figure S16. Calculated frontier orbitals for **1** in dichloromethane (B3LYP, 6-31G(d), CPCM solvent model).

Table S2. Computed vertical excitation energies of **P1**. The excitation energies were calculated using time dependent DFT with B3LYP/6-31+G (d).

λ (nm)	*E* (eV)	*f* [a]	excitation [b]
464.1	2.6717	0.696	HOMO-4 → LUMO (0.10632) HOMO-1 → LUMO (0.46539)
567.3	2.1856	0.032	HOMO-2 → LUMO (-0.12791) HOMO → LUMO (0.68914)

[a] Computed oscillator strengths, [b] Only the excitations with an oscillator strength higher than 0.05 are included. The contribution together with the parity of the transition is given in the parenthesis

5) Solar cell data

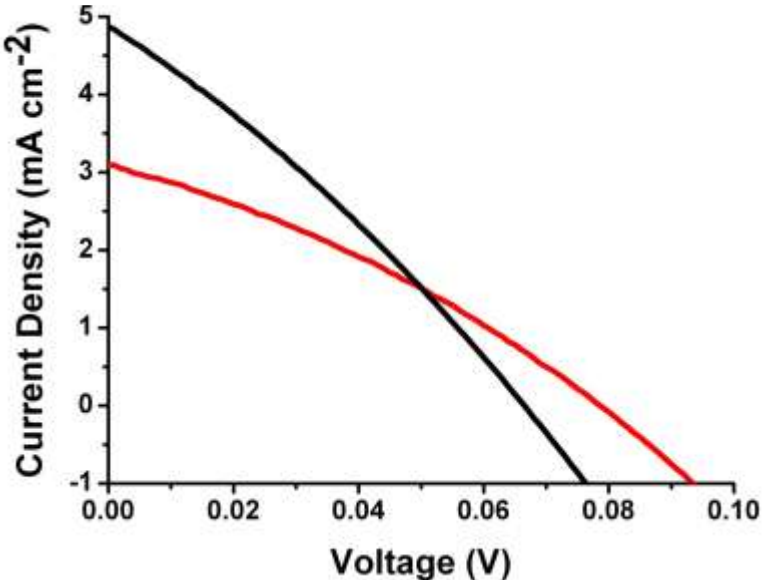


Figure S17. J-V curve of **1**-sensitized NiO (red) and **P1**-sensitized NiO (black) solar cells. The values for **P1** are slightly lower than usually obtained in our group because the electrolyte is not optimum for this dye.

6) Transient absorption spectroscopy

Excitation at 532 nm generated an excited state which absorbed between 400-500 nm which then decayed over *ca.* 400 ps to form a new intermediate with narrower absorption bands at 425 and 650 nm which decayed much more slowly ($\tau \approx 300$ (+/- 10) ns) to the ground state. When the dye solution was purged with Ar these bands decayed even slower ($\tau_{425} \approx 860$ ns, $\tau_{650} \approx 730$ ns) suggesting that a triplet bodipy (^{3}**1***) state had formed. Although triplet bodipy excited states are reasonably rare, the transient spectrum for the long-lived photoproduct of **1** matches extremely well with the transient spectra of the bodipy $^3\pi$-π* excited state reported by both Galletta *et al*. and by Harriman *et al*.[1, 2] We assign our transient to a triplet following their rational that it is possible that, after the bodipy S_1 excited state (^{1}**1***) is formed upon excitation, charge transfer occurs from the triphenylamine donor followed by rapid recombination to generate ^{3}**1*** which should lie *ca.* 0.5 eV lower in energy than **1**$^-$.

1. A. Harriman, J. P. Rostron, M. Cesario, G. Ulrich, and R. Ziessel, *J Phys. Chem. A*, 2006, **110**, 7994–8002.
2. M. Galletta, S. Campagna, M. Quesada, G. Ulrich, and R. Ziessel, *Chem. Comm.*, 2005, 4222–4.

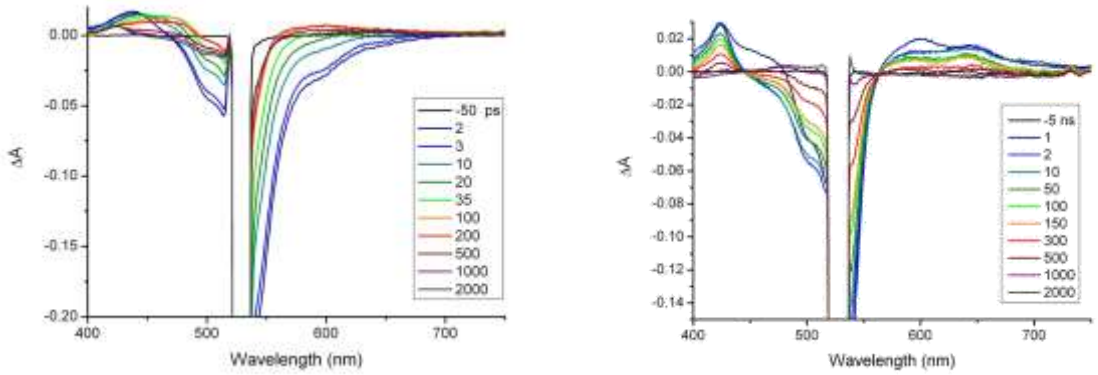


Figure S18. Transient absorption spectra of **1** in dichloromethane (air) (1.2 μJ ps, 1.6 μJ ns)

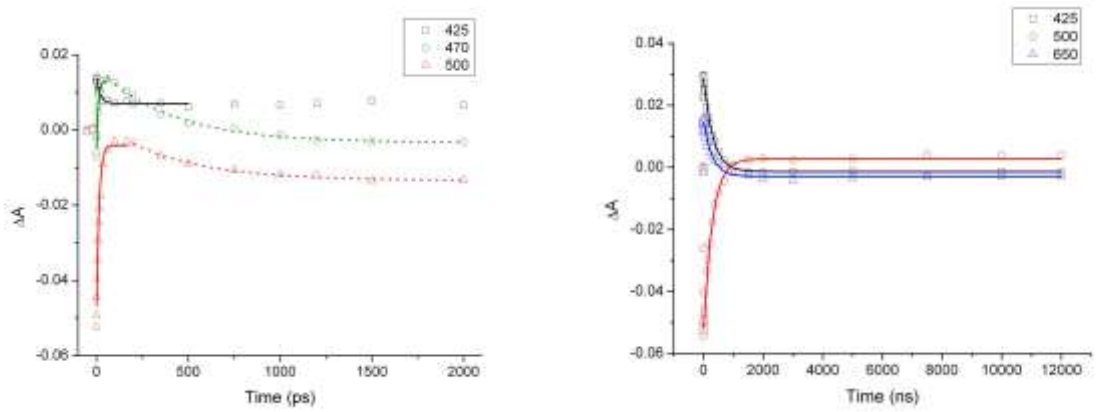


Figure S19. Kinetic traces of **1** in dichloromethane (Air) (1.2 μJ ps, 1.6 μJ ns). Symbols represent data, lines represent fit of single exponential rise/decay.

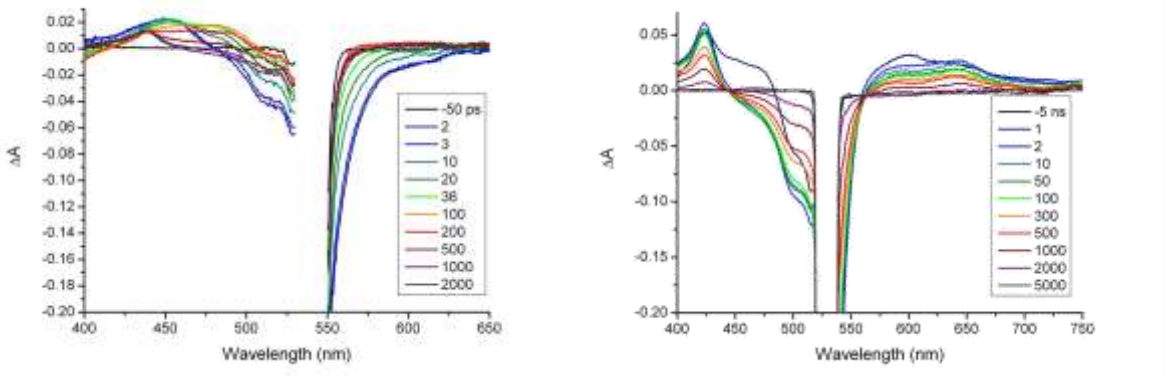


Figure S20. Transient absorption spectra of **1** in dichloromethane (Ar) (1.2 μJ ps, 1.6 μJ ns)

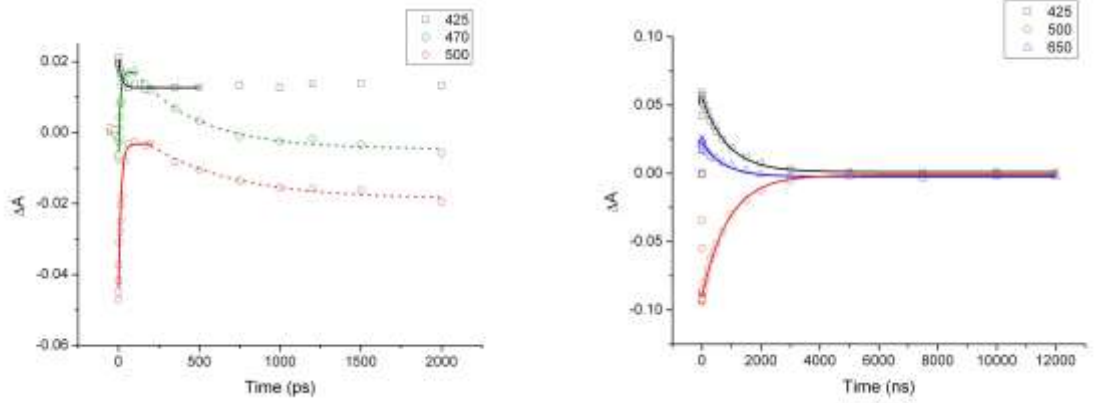


Figure S21. Kinetic traces of **1** in dichloromethane (Ar) (1.2 μJ ps, 1.6 μJ ns). Symbols represent data, lines represent fit of single exponential rise/decay.

λ (nm)	τ_{rise} (ps)	A_1 (× 10^3)	τ_1 (ps)	A_2 (× 10^3)	τ_2 (ns)	A_3 (× 10^3)
425 (Ar)			20.7 ±2.9	6.8 ±0.3	864 ±28	54 ±0.6
425 (air)			18. 3 ±2.1	8.4 ±0.3	311 ±13	30 ±0.3
470 (Ar)	9.52 ±0.91	20 ±7	396 ±33	20.2 ±0.6		
470 (air)	11.3 ±0.94	24 ±0.8	398 ±43	27.7 ±1.1		
500 (Ar)	14.1 ±1.2	45.7 ±15	413 ±50	22.1 ±1.9	896 ± 26	89 ±0.8
500 (air)	15.4 ±1.5	43 ±1.6	524 ±112	22.1 ±2.0	292 ± 11	55 ±0.6
650 (Ar)					729 ± 62	25 ±0.7
650 (air)					292 ± 31	17 ±0.5

Table S3. Time constants for **1** in dichloromethane (1.2 μJ ps, 1.6 μJ ns).

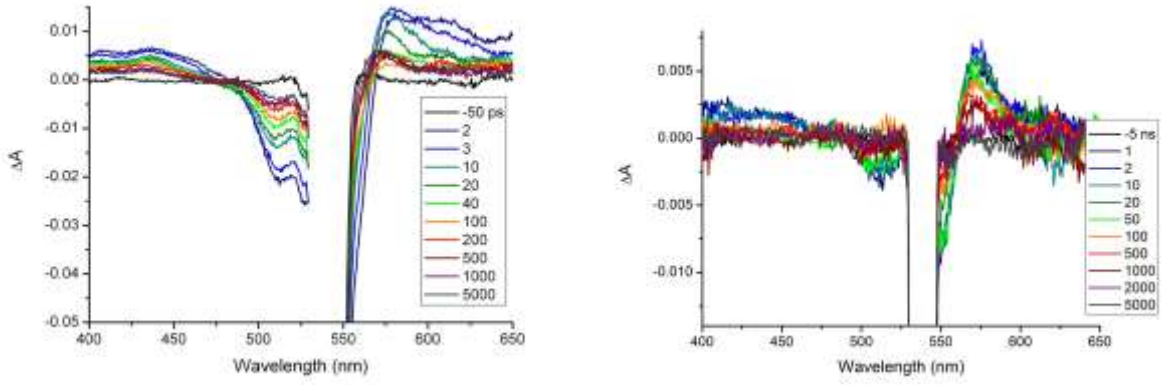


Figure S22. Transient absorption spectra of **1** adsorbed on NiO (Air) (1.2 μJ ps, 1.6 μJ ns).

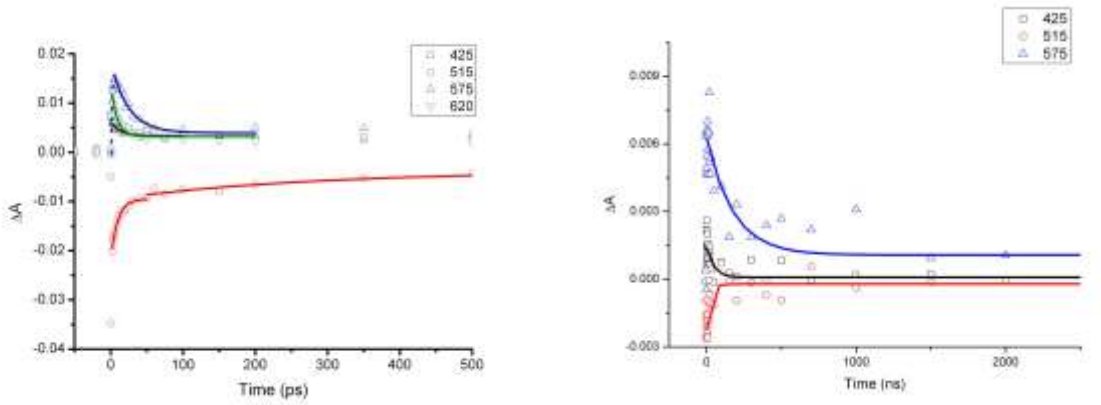


Figure S23. Kinetic traces of **1** adsorbed on NiO (Air) (1.2 μJ ps, 1.6 μJ ns). Symbols represent data, lines represent fit of single exponential rise/decay

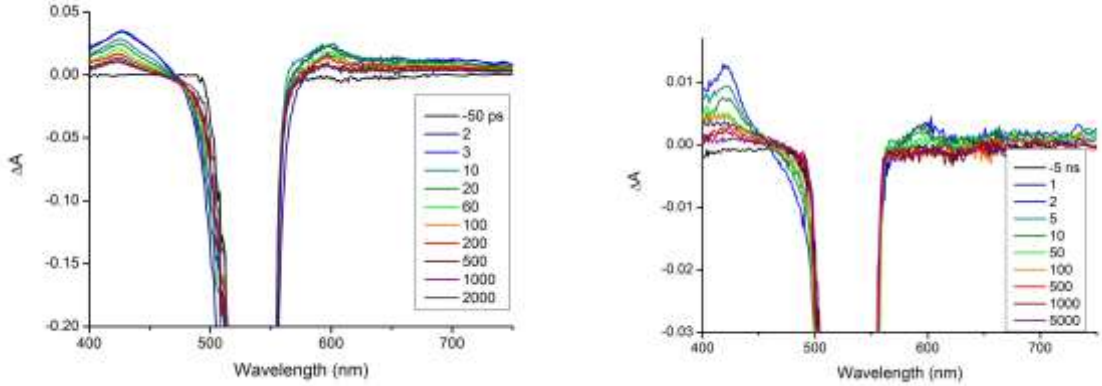


Figure S24. Transient absorption spectra of **1** adsorbed on NiO in the presence of LiI/I_2 in propylene carbonate (Ar) (1.2 μJ ps, 1.6 μJ ns).

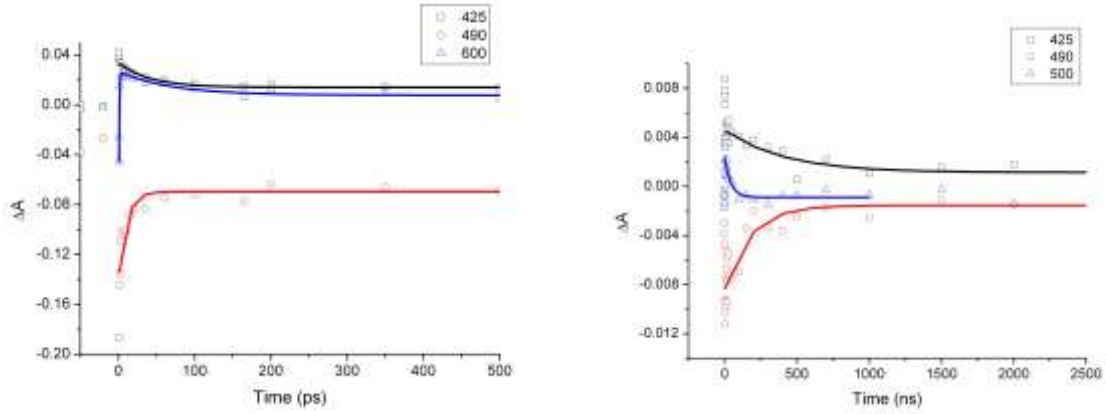


Figure S25. Kinetic traces of **1** adsorbed on NiO in the presence of LiI/I_2 in propylene carbonate (Ar) (1.2 μJ ps, 1.6 μJ ns). Symbols represent data, lines represent fit of single exponential rise/decay

λ (nm)	τ_1 (ps)	A_1 ($\times 10^3$)	τ_2 (ns)	A_2 ($\times 10^3$)
425 Film	12.5 ±2.9	2.96 ±0.29	49 ±28	1.31 ±0.3
425 LiI/I_2	41.1 ±6.6	19.65 ±0.10	466 ±168	3.67 ±0.38
515 Film	9.76 ±1.1	-12.3 ± 0.55	23 ±10	-2.07 ± 0.42
490 LiI/I_2	10.5 ±2.4	-71.1 ± 7.3	140 ±48	-6.79 ± 0.66
*575 Film	24.1 ±3.0	14.5 ±0.80	177 ±59	4.18 ±0.56
*600 LiI/I_2	70.2 ±19.1	19.0 ±1.8	23 ±5	3.25 ±0.60

*Rise time ca. 1 ps

Table S4. Time constants for **1** on NiO (1.2 μJ ps, 1.6 μJ ns).

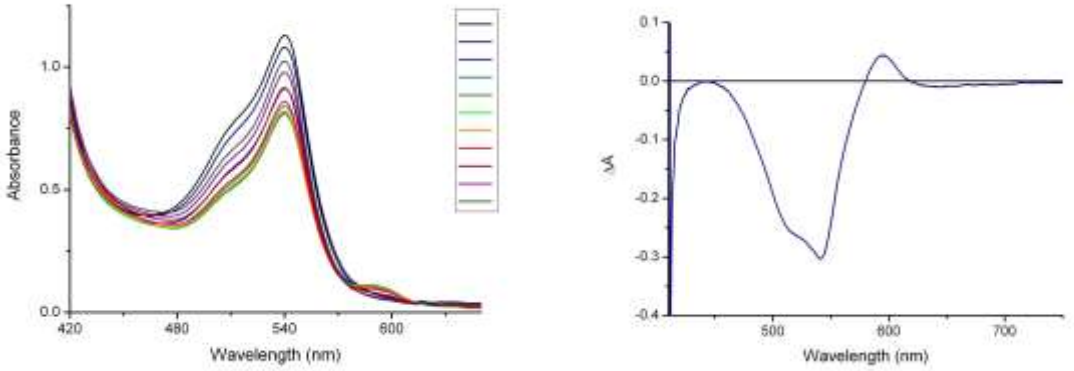


Figure S26. Change in absorbance (left) during a potential sweep to -1.5 V vs. $FeCp_2^+/FeCp_2$ and difference spectrum (right) for electrochemically reduced **1**-sensitized NiO. The supporting electrolyte was 0.1M $LiClO_4$ in acetonitrile.