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Supplemental Information for

An Intermediate Band Dye-sensitized Solar Cell Using Triplet-Triplet Annihilation

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Section S1. Detailed operation of IBDSC (and TTA-UC)

A step-by-step schematic of the process of charge generation in an IBDSC is shown below.

1.	Excitation	$2\ Por(S_0) + 2\ h\upsilon \rightarrow 2\ Por(S_1)$
2.	Intersystem crossing	$2Por(S_1) \rightarrow 2\ Por\ (T_1)$
3.	Triplet energy transfer	$Por\ (T_1) + 2\ BDCA(S_0) \rightarrow 2\ Por(S_0) + 2\ BDCA(T_1)$
4.	Triplet-triplet annihilation	$BDCA(T_1) \rightarrow BDCA(S_0) + BDCA(S_1)$
5.	Electron injection	$BDCA(S_1) \rightarrow TiO2(e^-) + BDCA^+$
5a.	Photon emission	$BDCA(S_1) \rightarrow BDCA(S_0) + h\upsilon$
6.	Dye regeneration	$BDCA^+ + RedOx(e^-) \rightarrow BDCA(S_0)$

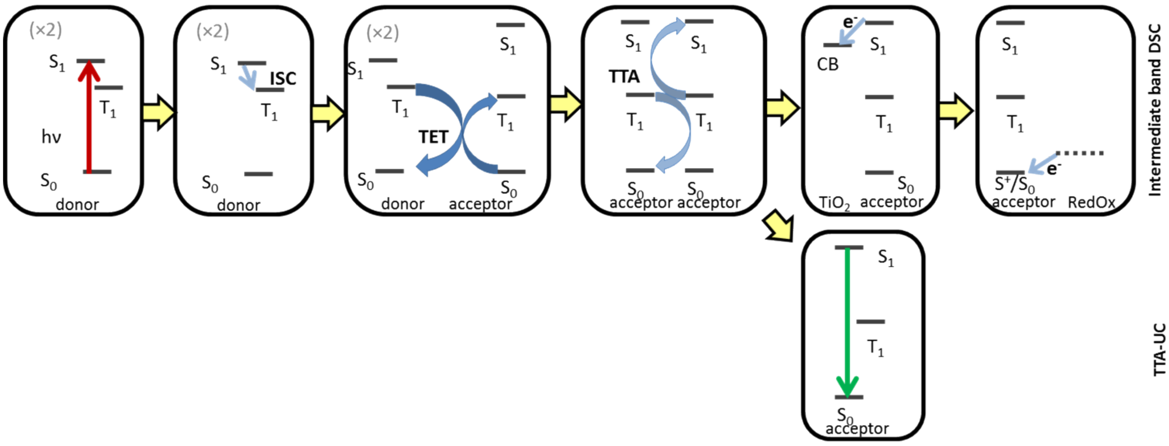


Fig S1 – Schematic operation of IBDSC (and TTA-UC) systems

The first four steps above are common for both the TTA-IB mechanism and TTA-UC. It should also be noted in cases where the second triplet excited state (T_2) of the acceptor is accessible after TTA it is a loss channel for TTA-UC [1], as T_2 decays non-radiatively to T_1 with little probability of ISC to an emissive state. On the other hand, this is not necessarily problematic for an IBDSC, provided that injection can occur from this higher energy triplet. The issue of emitted light being reabsorbed is also overcome in this system.

Section S2. Preliminary measurements of candidate acceptors

A number of small molecule emitters were identified as possible acceptors in this system, having being used previously in TTA-UC applications. Preliminary electrochemical experiments showed BPEA and BPA-Cl to be the most promising as they can be expected to provide a reasonable driving force for S_1 injection, while prohibiting T_1 injection.

Per = Perylene
DMP-PDI = N,N'-Bis(2,6-dimethylphenyl)perylene-3,4,9,10-tetracarboxylic diimide
BPEA-Cl = 2-chloro-9,10-Bis(phenylethynyl)anthracene
BPEA = 9,10-Bis(phenylethynyl)anthracene

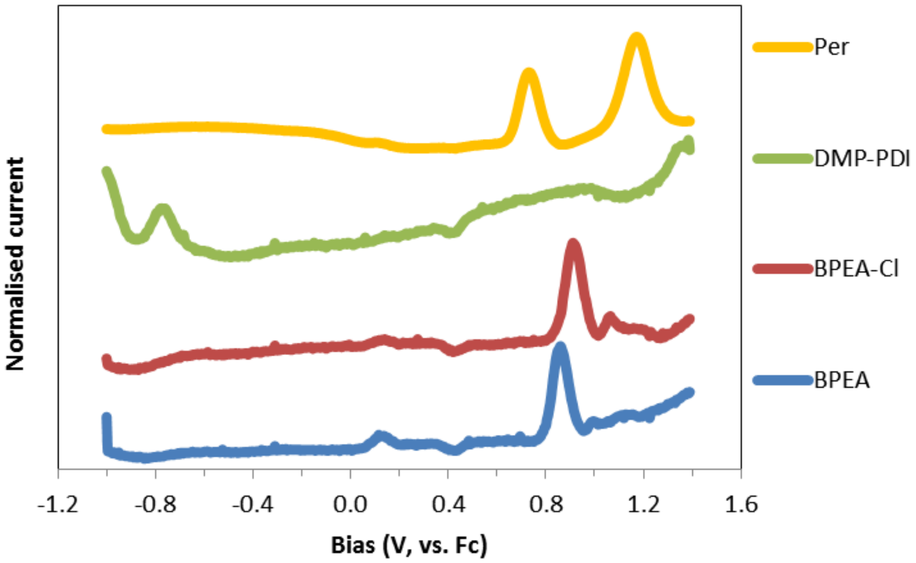


Fig S2. Square wave electrochemical measurements of various small molecule dyes with 0.1 M TBAP supporting electrolyte in acetonitrile, measured using glass carbon working, platinum mesh counter and silver/silver nitrate (acetonitrile) reference electrode. These potentials were confirmed using 1 mM Ferrocene in acetonitrile (with 0.1 M TBAP supporting electrolyte).

Section S3. Synthesis and characterisation of BDCA

The synthesis of BDCA was based on previously published methods [2]. The reaction steps are illustrated in Figure S3.1.

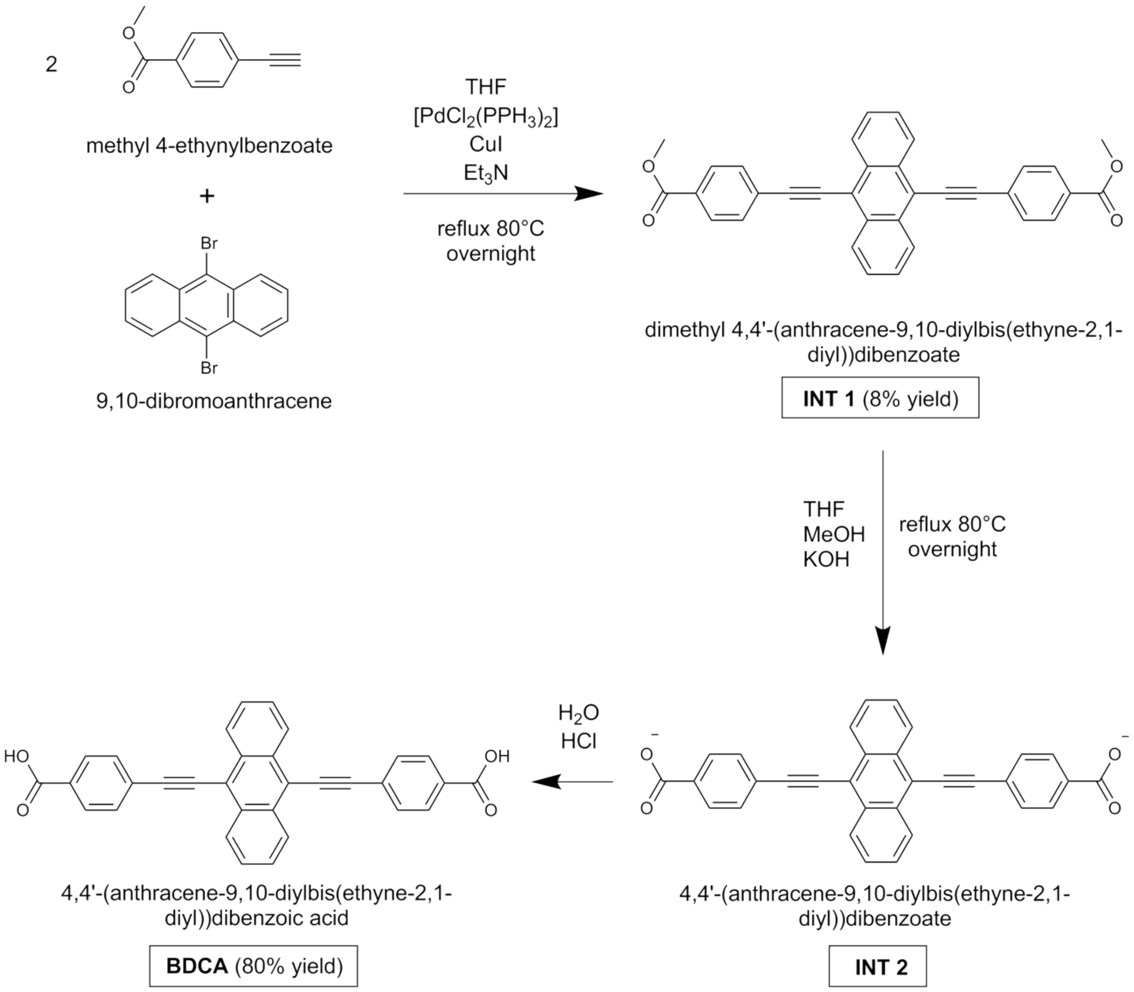


Fig S3.1. BDCA synthesis method. Step one is a Sonogashira reaction, which forms intermediate product 1 (INT 1). Step two is hydrolysis of the ester group, which forms intermediate product 2 (INT 2). The final step is protonation of the carboxylate group, producing BDCA.

9,10-dibromoanthracene (0.2056 g) was added to dry tetrahydrofuran (THF, Honeywell) (5 mL) and degassed with argon for 30 mins. Copper(I) iodide (8.5 mg, Aldrich) and dichlorobis(triphenylphosphine) palladium(II) (5.1 mg, Aldrich) in triethylamine (5 mL) was added and stirred for 20 min. Methyl-4-ethynyl benzoate (0.2010 g, Sigma) in dry THF (10 mL) was added dropwise. The solution was heated to 80 °C and stirred overnight, then evaporated. The remainder was separated with distilled water and dichloromethane, (DCM, Sigma). The organic layer was then washed with distilled water and then with brine (Sodium Chloride from Ajax FineChem), dried with sodium sulphate (Sigma), then evaporated to dryness. The solid product was purified via silica column chromatography, with 50:50 DCM:hexane (Chem-Supply). 24.0 mg of purified product (**INT 1**) was produced (8 % yield). **INT 1:** MALDI-MS: m/*z* 493 $[M-H]^-$. ^{1}H-NMR (400 MHz, $CDCl_3$ - Cambridge Isotope Laboratories, TMS, **assignment labels A to E** shown in figure S3.2a): δ 8.7 (m, 4H, **A**), 8.1 (d, 4H, J = 8.4 Hz, **B**), 7.8 (d, 4H, J = 8.4 Hz, **C**), 7.7 (m, 4H, **D**), 3.97 (s, 2H, methyl-H, **E**).

INT 1 was dissolved in THF (10 mL). Methanol (20 mL, Sigma-Aldrich) with saturated potassium hydroxide (Ajax FineChem) was added and the solution was refluxed overnight at 80 °C, to produce **INT 2**, and then evaporated. Distilled water (10 mL) was added. Conc. hydrochloric acid (Ajax FineChem) was added dropwise until the pH reached 2 – 3 (indicated by pH paper). The product was extracted via filtration with a glass, fritted filter and washed with water. The orange product – **BDCA –** was left to dry in a vacuum oven at 50 °C for 2 days (18.2 mg, 80 % yield). **BDCA:** MALDI-MS: m/*z* 466 [M-H]$^-$. ^{1}H-NMR (400MHz, DMSO-d_6 - Cambridge Isotope Laboratories, TMS, **assignment labels A to D** shown in figure S3.2b): δ 8.7 (m, 4H, **A**), 8.1 (d, 4H, J = 8.6 Hz, **B**), 8.0 (d, 4H, J = 8.6 Hz, **C**), 7.8 (m, 4H, **D**).

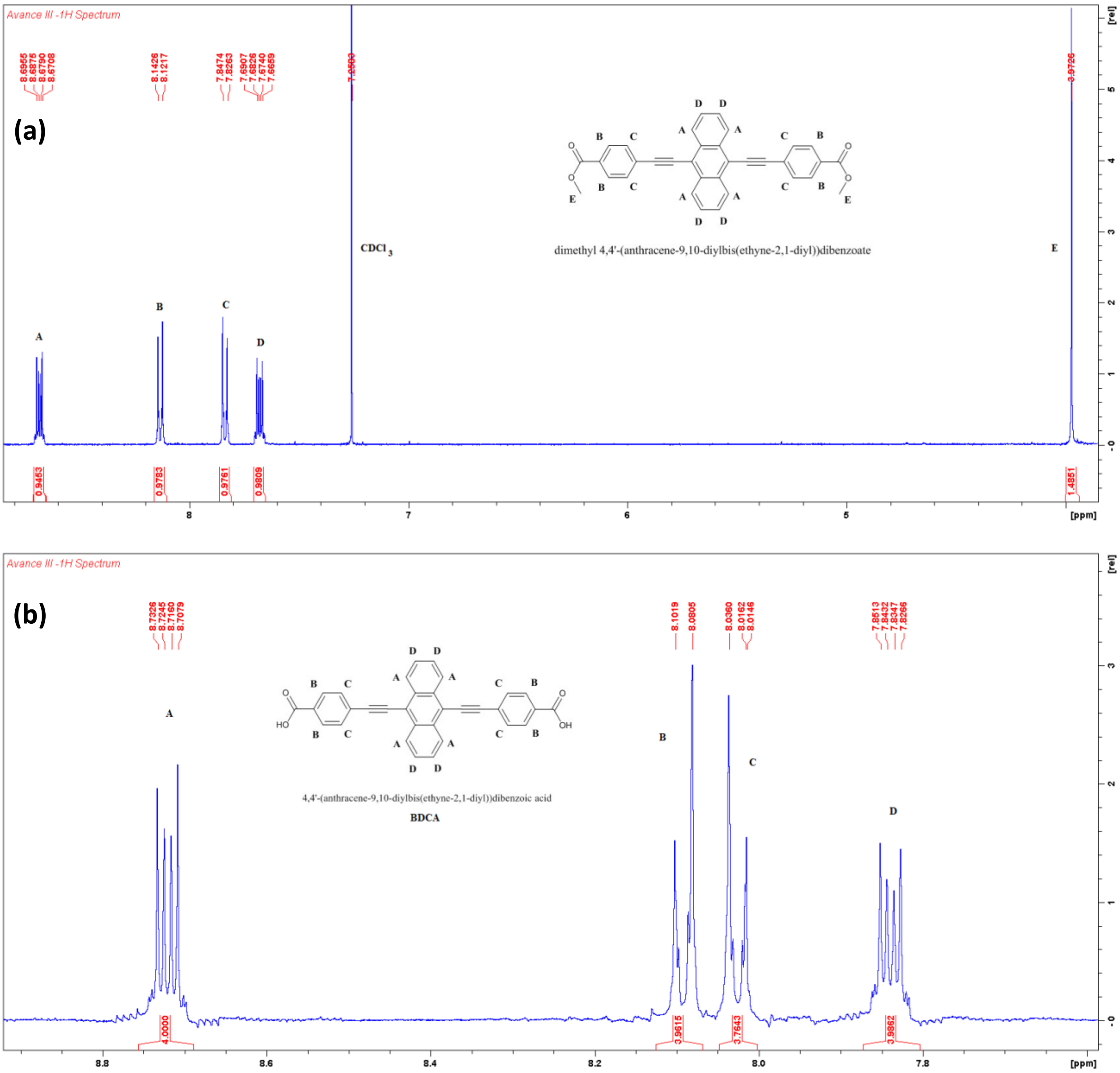


Fig S3.2. ^{1} **H NMR Spectrum of (a) INT1 and (b) BDCA**

Section S4. Electrochemistry of BDCA

Squarewave voltammetry using a glassy carbon working, platinum mesh counter and silver wire pseudo reference electrode was performed on BDCA and referenced against ferrocene.

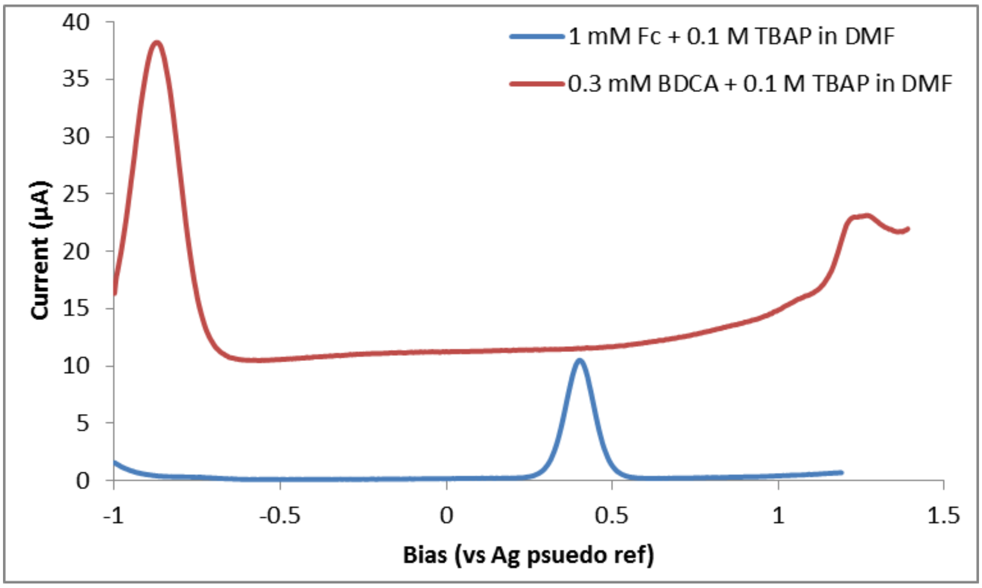


Fig S4. Square wave voltammogram of 0.3 mM BDCA in DMF (with 0.1 M tetrabutylammonium perchlorate support) and 1 mM Fc in DMF (with 0.1 M tetrabutylammonium perchlorate support).

Section S5. Absorption and PL spectrophotometry

Solution absorption measurements were taken using a Shimadzu UV-1800. Luminescence measurements were taken with a Horiba Fluorolog FL3-221 (see Fig S5.1 below).

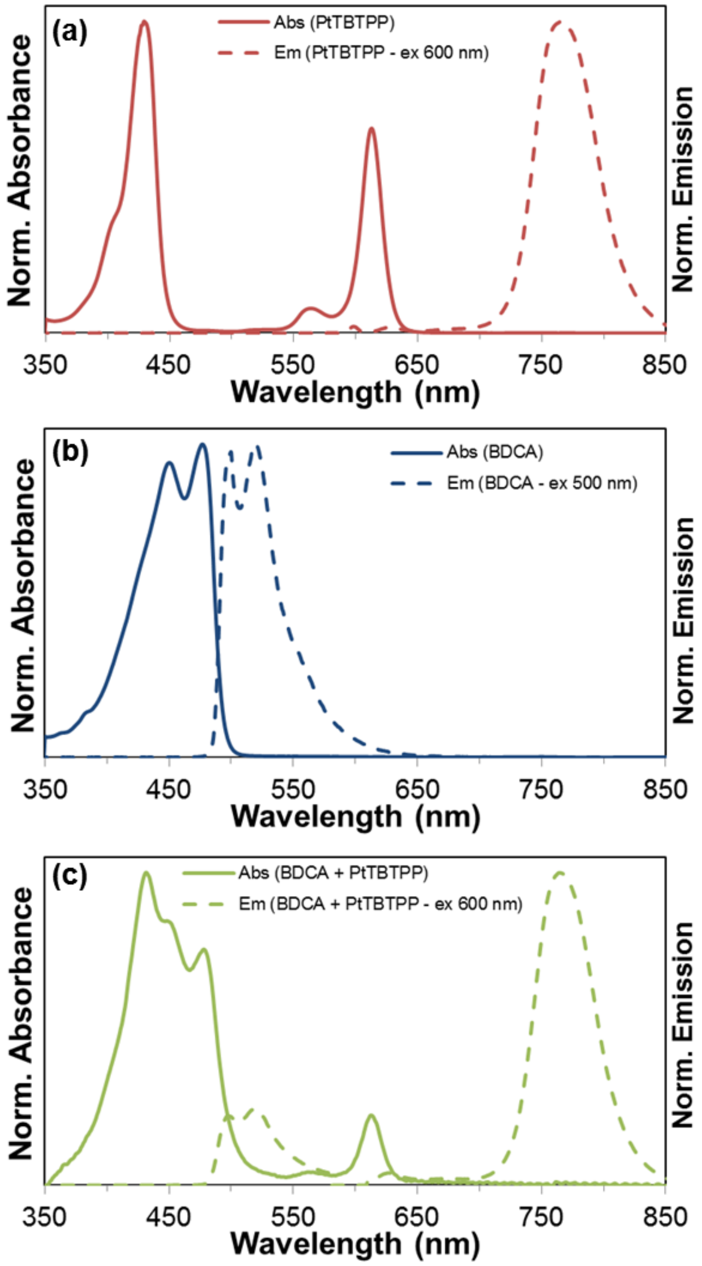


Fig S5.1 –Abs and emission spectra of solutions of (a) BDCA, (b) PtTBTPP and (c) mixed system. BDCA emission taken with excitation at 500 nm, PtTBTPP and mixed system excited at 610 nm. All solution measurements use DMF.

Additionally, PL measurements were made on the BDCA, to confirm no emission was obtained after 600 nm excitation. The figure below (Fig S5.2) shows excitation of the dye at 500 nm, with slits on both the excitation source and emission detector set to 1 nm, revealing a strong fluorescence signal, which was not present upon 610 nm excitation even after opening the slits to 5 nm.

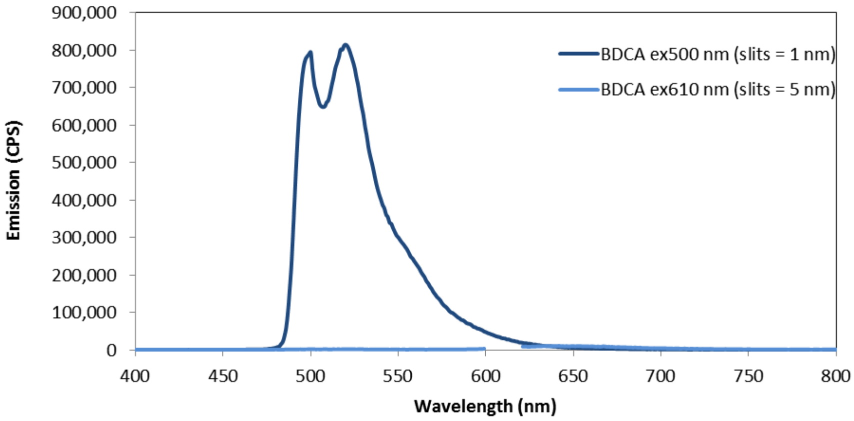


Fig S5.2 – Emission of BDCA after excitation at either 500 nm or 610 nm. Monochromator slits were opened up substantially wider with 610 nm illumination. Scatter from excitation beam masked at ± 10 nm.

Digital images of UC on an Al_2O_3 substrate were taken (Fig S5.3) with a Canon EOS 100D camera with 30 second exposure time, using a 500 ± 40 nm bandpass filter from Andover (500FS40-50), while the device was being illuminated with 5 mJ/mm^2 610 nm light from a 10 Hz Nd:YAG OPO laser.

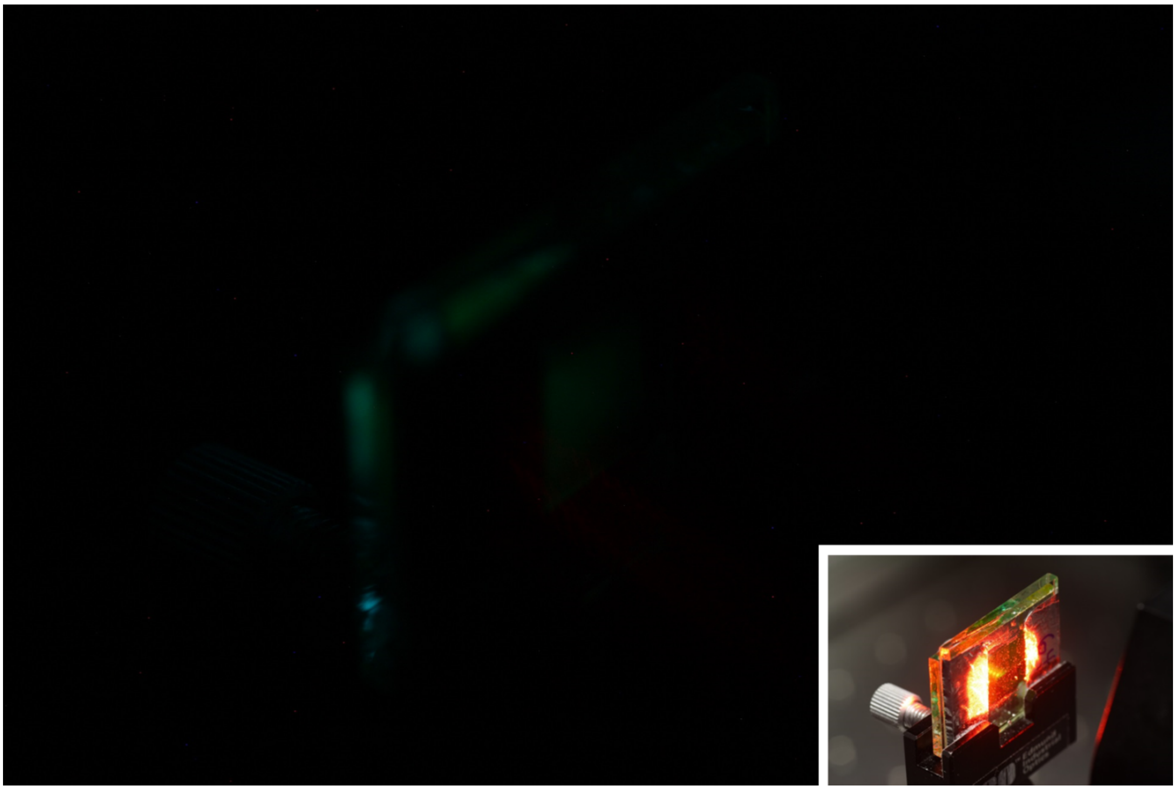


Fig S5.3 - Long exposure photograph of a device containing BDCA tethered to Al_2O_3, with PtTBTPP in solution (DMF), excited with 610 nm laser shot with a 500 ± 40 nm band-pass filter and no room lights and (inset) the same, with room lights, no filter and short exposure time.

PL quenching was observed by comparison of BDCA PL on TiO_2 versus that on Al_2O_3, highlighting that BDCA can successfully perform charge transfer into a TiO_2 substrate. Fig S5.4 shows that the absorption peak of BDCA is broadened compared to BDCA in solution.

This is expected and is due to the multiple bonding states that the BDCA can have with the substrates, i.e. unidentate, bidentate chelating and bidentate bridging. BDCA also has two carboxylic acid groups which increases the number of possible bonding coordination. The absorbance of the two substrates differed slightly, possibly due to differing extents of dye aggregation.

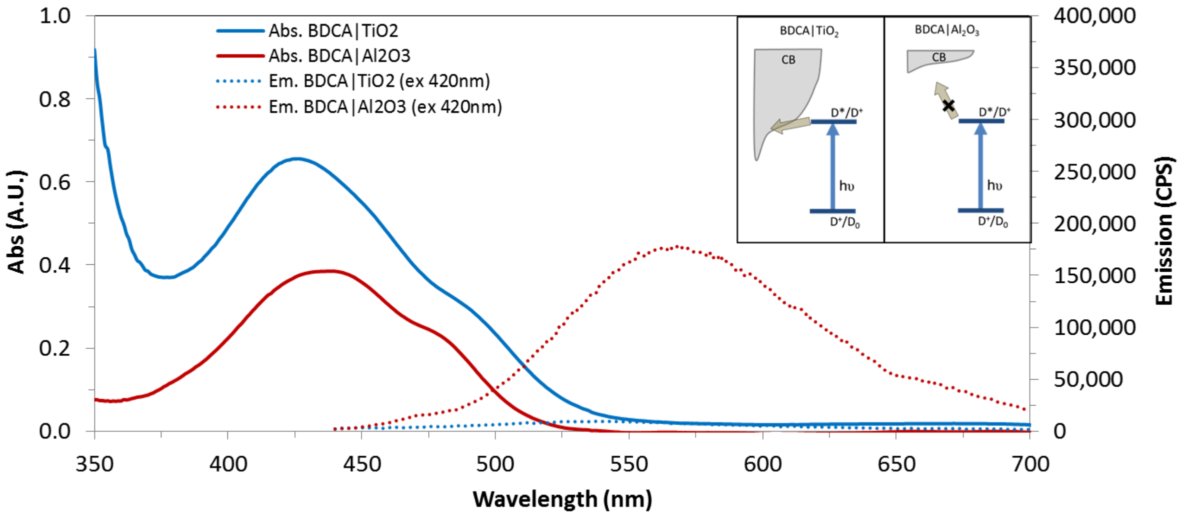
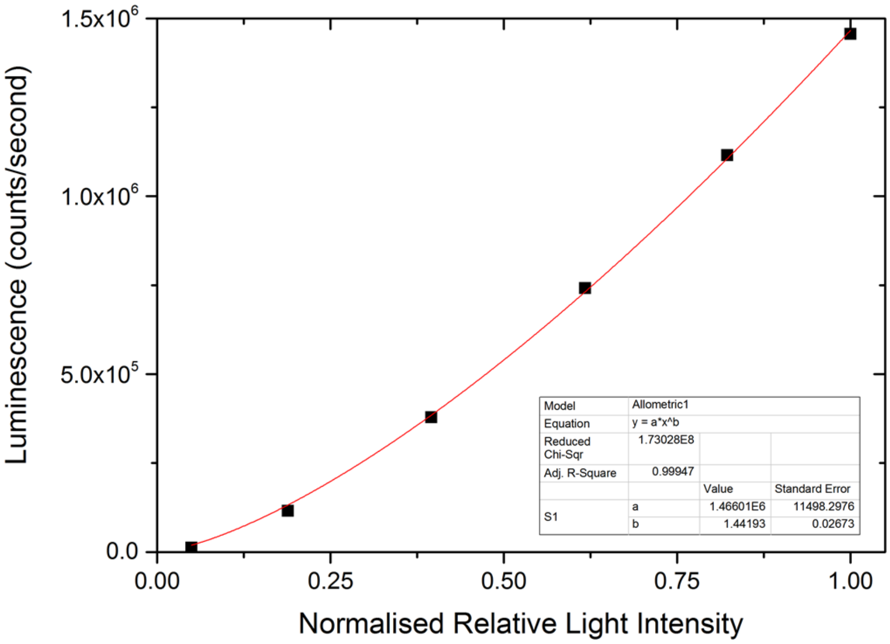


Fig S5.4. Absorbance of BDCA on Al_2O_3, TiO_2 and PL spectra of BDCA on TiO_2 and Al_2O_3. Inset demonstrates the pathway for electron injection from the photoexcited dye to the conduction band of TiO_2, while this is not energetically favourable when Al2O3 is used.

To investigate the relationship between light intensity and upconversion, the luminescence of the BDCA with PtTPTBP solution was measured at different excitation intensities (controlled by emission slit width). A photodetector monitors the intensity of this light, which is then normalised and plotted against the measured fluorescence (counts per second) at the 517 nm peak in Figure S5.5. The relationship was found to follow a power function of $y = 1.5x^{1.44}$. This non-linear relationship once again indicates a multimolecular process, in line with photocurrent measurements in Fig 1c and Fig S7.2.



Model	Allometric1		
Equation	y = a*x^b		
Reduced Chi-Sqr	1.73028E8		
Adj. R-Square	0.99947		
		Value	Standard Error
S1	a	1.46601E6	11498.2976
	b	1.44193	0.02673

Fig S5.5. Measured PL as a function of light intensity. Emission slit widths held at 10 nm.

Section S6. Detailed device assembly procedures

Along with the actual IBDSC devices a number of conventional DSC devices and TA specimens were produced.

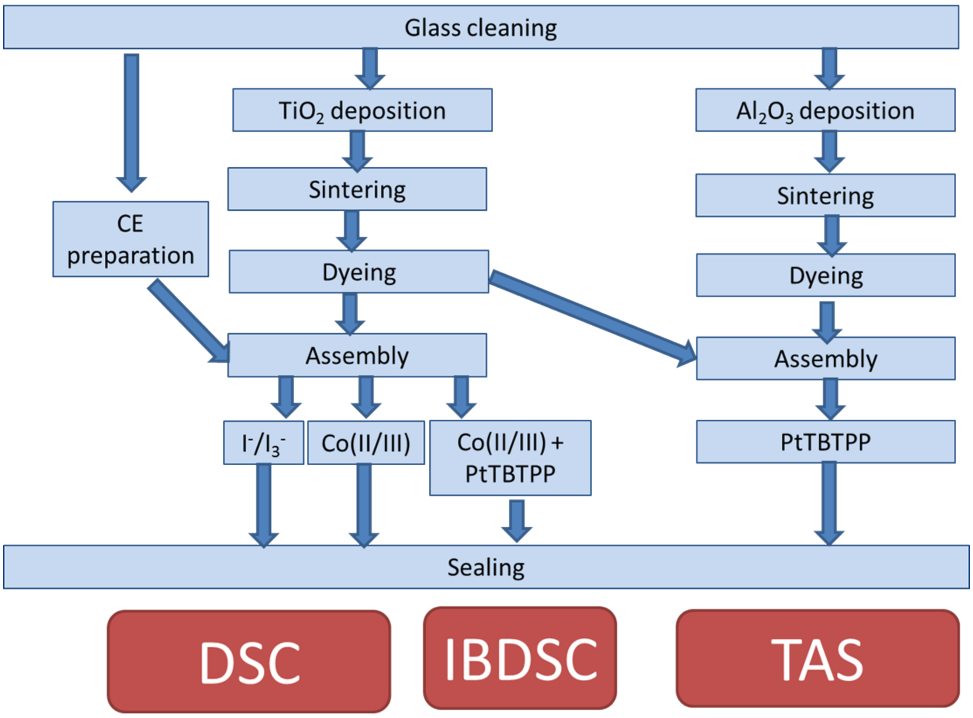


Fig S6.1. Schematic of various devices produced and steps involved in their manufacture.

Glass Cleaning:

F:SnO_2 (Hartford, 2.3 mm, 110 × 110 mm, > 10 Ω/□) and plain soda-lime glass was cleaned by a three stage ultrasonicsation process, with 20 minutes spent in each of (1) soapy water (2) acetone and (3) ethanol, prior to being dried using compressed nitrogen.

TiO_2 deposition:

Two types of TiO_2 films were produced, one for PL and TAS and one for IBDSC/DSC devices. Both these used commercial TiO_2 paste (Dyesol, NR 18T) and were screen printed. The PL & TAS samples were thinner (~1 µm) 8 × 8 mm and on plain glass, while 4 × 4 mm films (~3 µm) were produced using a 90T mesh on F:SnO_2 glass with and a dense TiO2 layer, created by spray pyrolysis of diisopropoxy Titanium (bis acetylacetonate) (Aldrich)[3].

Al_2O_3 deposition:

The Al_2O_3 paste was prepared using 1 mL 0.05µm particles of Al_2O_3 in colloidal suspension in water (Alfar Aesar) with a drop of Triton-X100 surfactant (Sigma). This was doctor bladed onto plain glass, resulting in films ~2 µm thick.

Sintering:

Films were sintered on a Harry Gestigkeit hotplate and controller (PZ28-3T / PR 5 3T) according to the program in Table S6.1.

Table S6.1. Sintering heating schedule for TiO_2 and Al_2O_3 substrates

Step	Ramp time (min)	Temperature (°C)	Duration (min)
1	10	150	10
2	15	325	5
3	5	375	5
4	7	450	30
5	5	500	15

Dyeing:

The slides were placed into a BDCA dye bath (0.2mM in 50:50 acetonitrile:ethanol) overnight. These were rinsed thoroughly to ensure all unbound dye was removed.

Counter electrodes:

$F:SnO_2$ glass was cut into approximately 2 cm x 1.5 cm slides. Counter electrodes were prepared by drilling two holes in opposite corners. After cleaning (as per above) a drop of 10mM H_2PtCl_6 in ethanol was cast onto the $F:SnO_2$ side and the slide heated to 400 °C for 30 mins with a heat gun.

Assembly:

Assembly of devices was completed inside an argon filled glovebox, so as to avoid oxygen. All solvents were deoxygenated by at least three freeze-pump-thaw cycles prior to introduction into the glovebox.

Devices were sealed with 25 µm thick Surlyn^{TM} (Solaronix), which was cut to size, placed between two pieces of glass, and pressed with a hydraulic press over a heating element at 120°C. IBDSCs were filled using an electrolyte comprised of 220 mM $Co^{2+}(bpy)_3(NTF)_2$ plus PtTBTPP (saturation) in DMF. Conventional DSCs were made with either the above cobalt electrolyte, in the absence of PtTBTPP, or an I^-/I_3^- based electrolyte (0.03 M I_2, 0.5 M 4-tertbutylpyridine, 0.6 M 1-butyl-3-methylimidazolium iodide, 0.1 M Guanidinium thiocyanate in 85:15 acetonitrile:valeronitrile). Devices for TA used either dyed or undyed TiO_2 films and were filled using pure DMF or PtTBTPP in DMF. Filling ports were then sealed with Surlyn backed aluminium foil.

Section S7. DSC characterisation

The overhanging edges of the F:SnO$_2$ were cleaned with ethanol, and connections made using Cerasolzer CS186 and an ultrasonic soldering iron (MBR USS-9200). The device was measured using a PV measurements EQE system (QEX10).

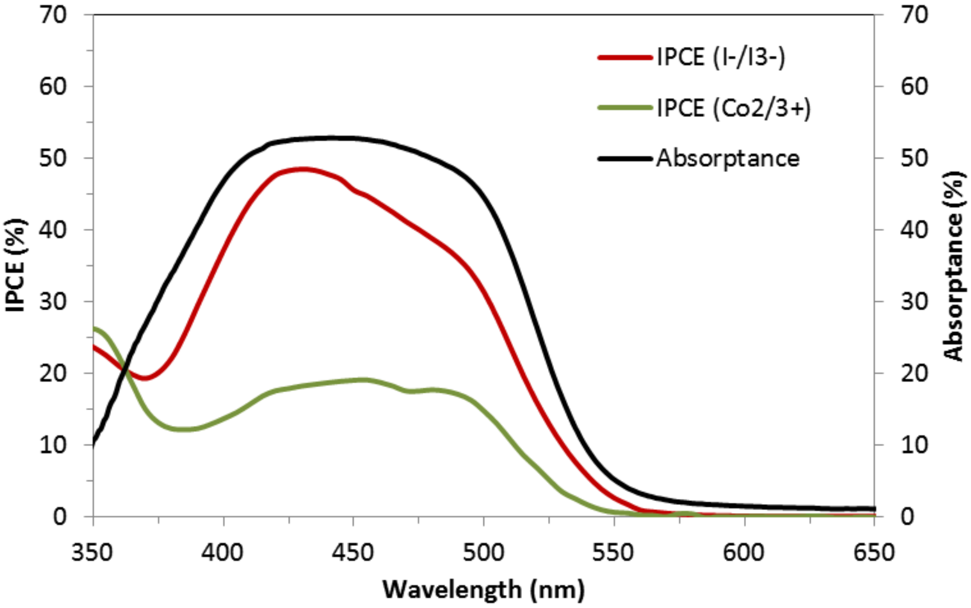


Fig S7.1. IPCE % of the BDCA DSC device (with I^-/I_3^- based electrolyte in green and Co($^{2/3+}$) in red) and the absorption % of BDCA on TiO$_2$ (black).

PtTBTPP 'supersensitized' (also using the cobalt electrolyte) device showed no photoresponse under 560 - 640 nm illumination. A photoresponse under white light (simulated sunlight, AM1.5G) was explained by direct excitation of TiO$_2$ (IPCE).

The linearity of the photoresponse of a BDCA device with currents comparable to those produced by TTA-IB mechanism in PtTBTPP+BDCA device was measured, with the results shown below (Fig S7.2). In order to achieve similar currents a 460-540 nm bandpass filter and neutral density gauze filters were used. The gauze filters used for direct BDCA excitation had a much higher attenuation than those for indirect excitation.

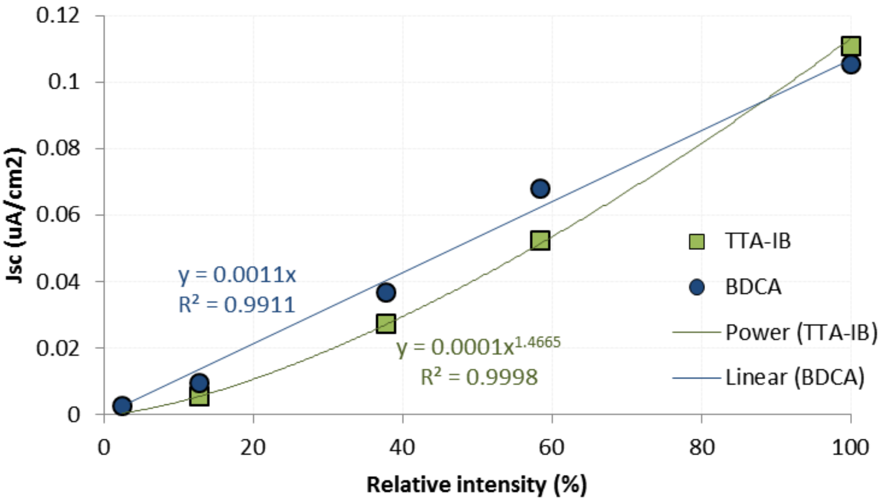


Fig S7.2 – Photocurrent response of BDCA + PtTBTPP device at various illumination intensities (560 – 640 nm light) alongside photoresponse of a directly excited (460 – 540 nm) BDCA device producing similar short circuit current densities.

J-V results were recorded (Fig S7.3, below). The devices had shunt resistances of ~30 kΩ Ohm, which meant that under (560-640 nm illumination) where the J_{SC} was slight above 0.1 µA/cm2 the J-V curve was dominated by this comparatively low shunt. J-V curves were also recorded for the device under 1 sun broadband illumination, where the vast majority of current was produced by direct excitation of the BDCA.

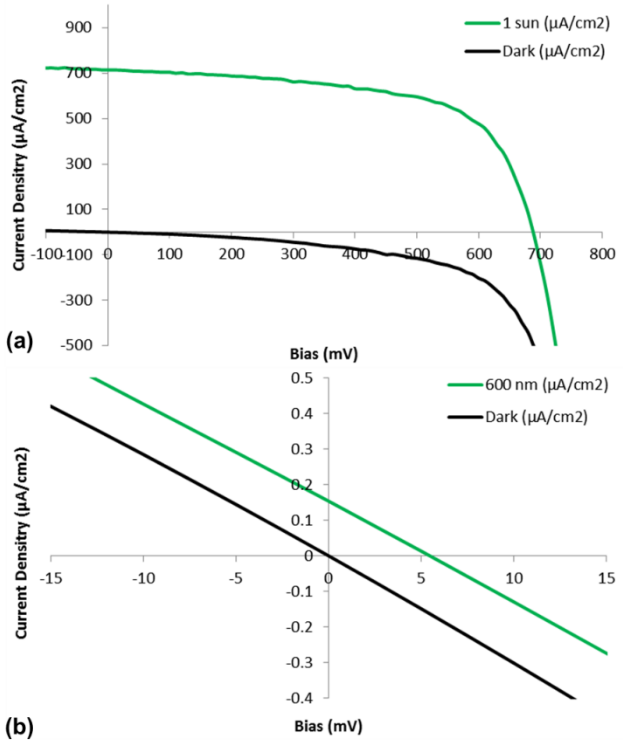


Fig S7.3 – Current density-voltage responses of IB DSC under (a) 1 sun illumination and (b) 560-640 nm monochromated light.

Section S8. Transient Absorption Spectroscopy

A schematic illustration of the devices produced for TA spectroscopy is shown below in Fig S8.1a. In this example both BDCA and PtTBTPP are present. Fig S8.1b shows the actual devices used.

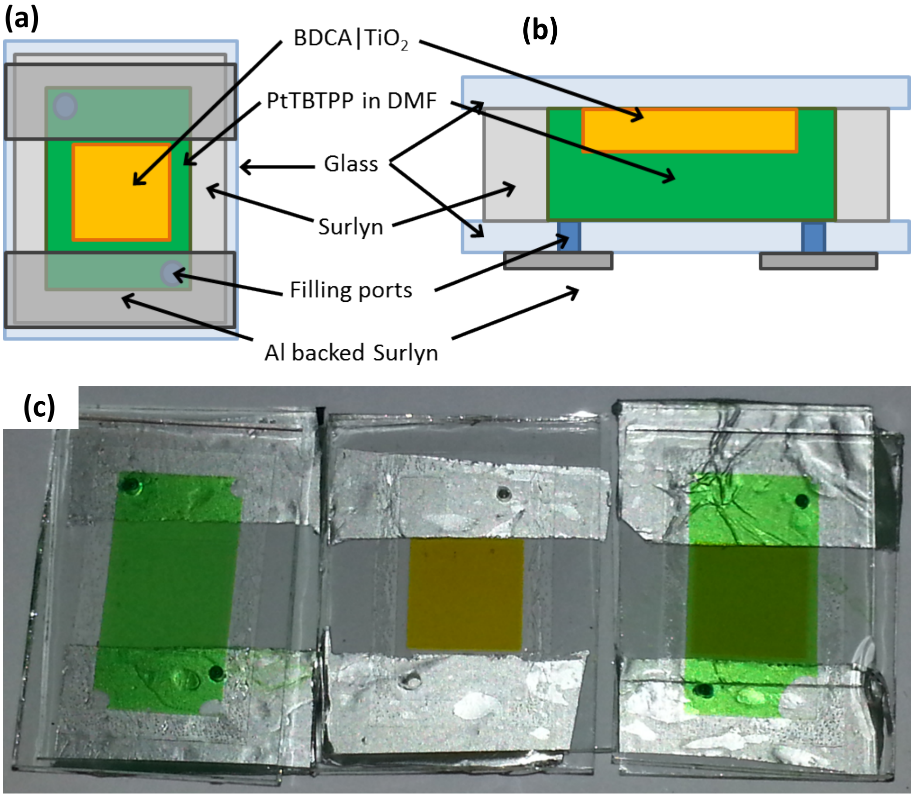
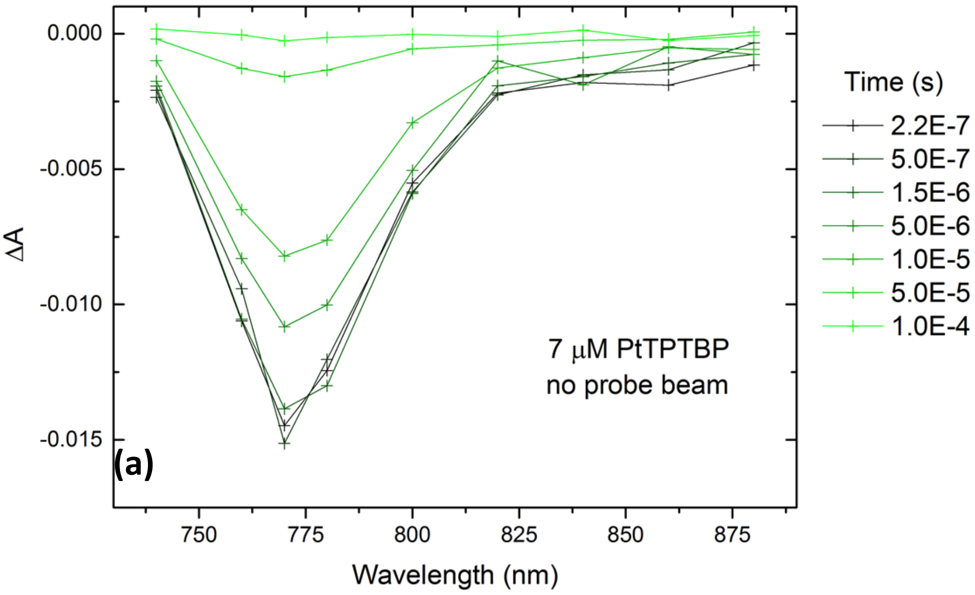


Fig S8.1. TAS chamber schematic (a) Top down view (b) cross sectional view. (c) image of TAS chamber with (left) PtTBTPP and an undyed TiO2 film (middle) pure DMF and a BDCA dyed film and (right) PtTBTPP and a BDCA dyed TiO_2 film. PtTBTPP at saturation in DMF.

The pump beam was provided by a Spectra Physics Quanta-Ray Nd:YAG OPO laser, which was aligned at an angle (approx. 45°) from the face of the sample and was pulsed at 10Hz. The pump beam passed through various neutral density (ND) filters, which controlled the intensity of the beam. The probe beam was provided by a Bertham ILI 100 W Illuminator xenon lamp. This light passed through various long pass (LP) filters. A Thor Labs shutter was used to protect or expose the sample to the probe beam. Transmitted probe light was collected by a FEMTO photoreceiver HCA-S 200m-SI detector after passing through a Spectral Products CM110 1/8m monochromators. A Tektronix DPO 4054 digital phosphor oscilloscope with custom Labview software then collected and processed the signal.

Negative values for ΔA were also observed with samples containing PtTBTPP between 740 nm and 820 nm, close to where phosphorescence is observed in steady-state PL (Fig S5.1). To confirm that the observed peak was phosphorescence, the probe beam was blocked, and the measurements were taken again (Fig S8.2).



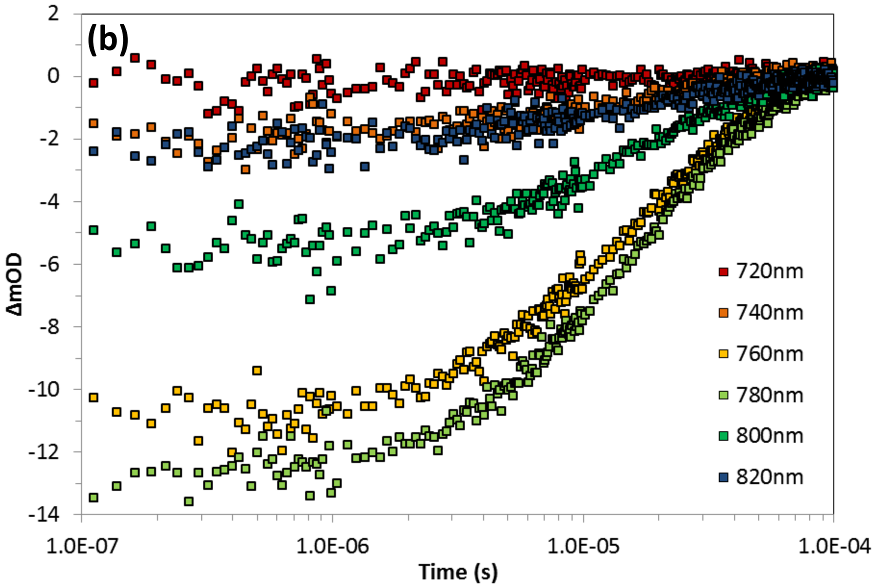


Fig S8.2. Phosphorescence of PtTBTPP with probe blocked (a) spectral response (b) kinetic traces.

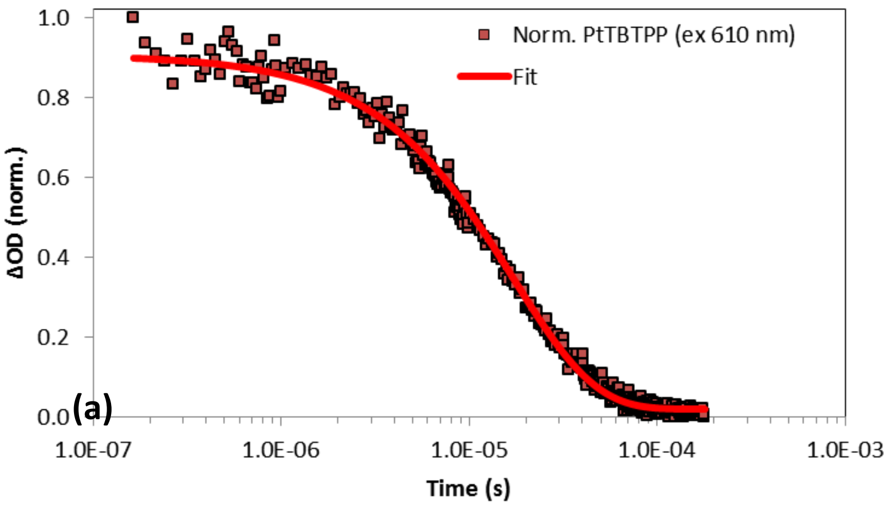
In order to avoid complications resulting from this signal kinetic analysis of pump-probe measurements was done at 720 nm, with Fig S8.2b illustrating the absence of PL response at this wavelength. This wavelength is also clear of ground state absorbance, meaning that complications resulting from ground state bleaching are also avoided.

The PtTBTPP sample was fitted with a single exponential, with a time constant of 17.2 ± 1.7 μs, typical of phosphorescence decay, while the BDCA alone was fitted as a stretched exponential with time constants of 4.49 ± 0.77 μs stretching factor (β) of 0.318 ± 0.002. The combination of the two materials resulted in a more complex response, which was fitted with a simple exponential decay, one rise and a stretched exponential decay (using the same parameters as for the BDCA (500 nm excitation) decay. The first decay (2.00 ± 0.07 μs) was ascribed to PtTBTPP, which was more rapid due to opening the quenching channel of triplet energy transfer from PtTBTPP(T_1) to BDCA(S_0). The rise (8.11 μs) is caused by the gradual creation of BDCA$^+$, as BDCA(T_1) meet, annihilate and the resultant BDCA(S_1) molecule injects an electron to TiO_2. These then decay slowly, in line with what was observed for direct excitation of BDCA. This multi-component fit was achieved by first fitting a single exponential decay to short timescales, followed by modelling the residual (see Fig S9c below for component models). A time offset was applied to the rise and stretched exponential decay to account for the slow onset, which results from slow, dark processes (including triplet migration).

It should be noted that the shape of the TA spectrum of BDCA+PtTBPP (ex 610 nm) before and after ~10 μs bares similarity to PtTBTPP (ex 610 nm) and BDCA (ex 500 nm) respectively. Fittings are shown in Table S9.1 and Fig S9.3.

Table S8.1 – Fitting parameters for TA spectra

	PtTBTPP	**BDCA**	**BDCA + PtTBTPP**
A_1	0.886 ± 0.001	1.248 ± 0.07	0.784 ± 0.024
τ_1 (μs)	17.2 ± 0.2	4.49 ± 0.77	2.00 ± 0.07
β_1	-	0.318 ± 0.002	-
A_2	-	-	9.53
τ_2 (μs)	-	-	8.11
A_3	-	-	2.12
τ_3 (μs)	-	-	4.49
β_3	-	-	0.318
C	0.0209 ± 0.0016	0.0202 ± 0.0054	-0.006
t_0 (μs)	-	-	26.2



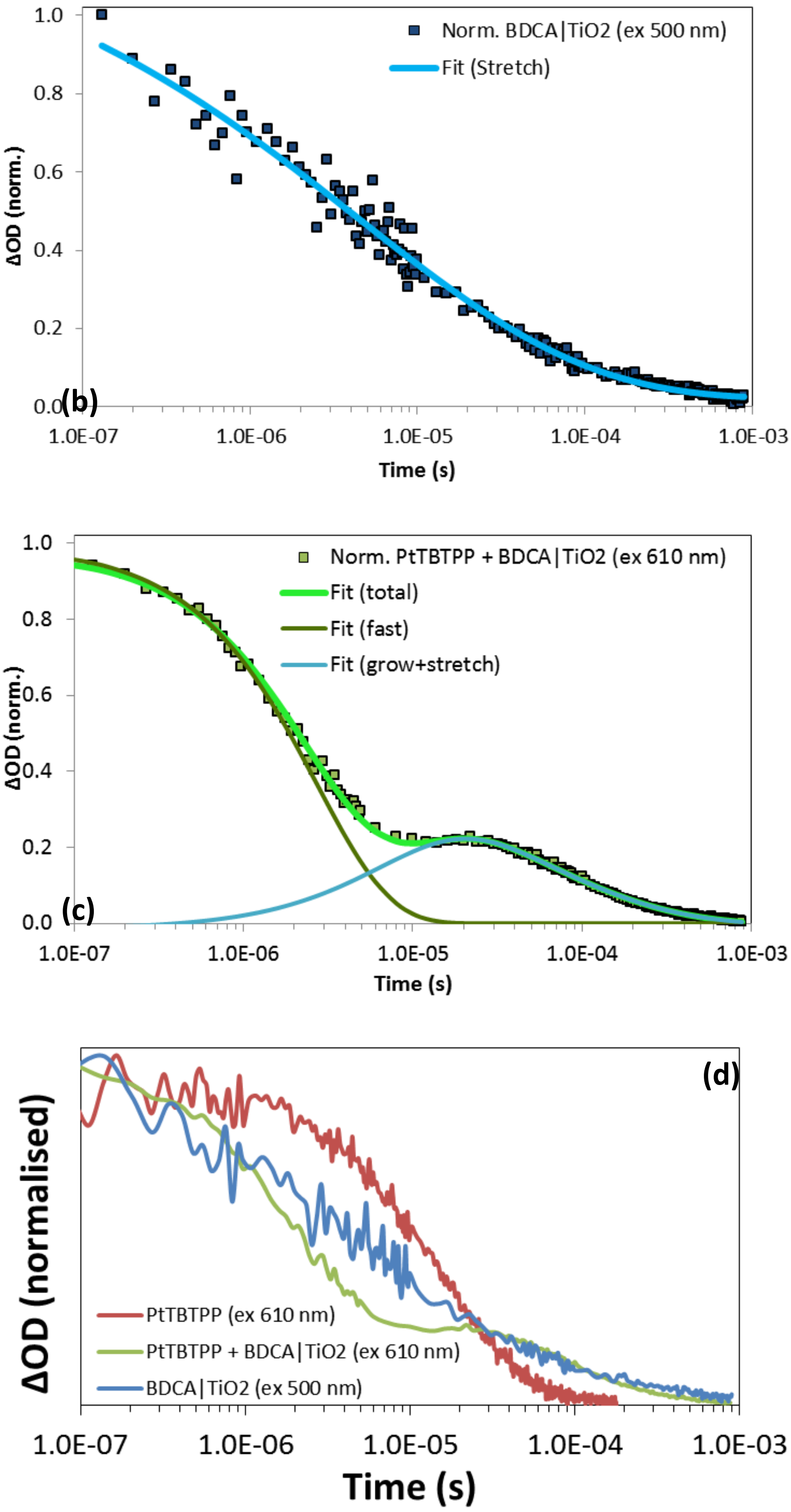


Fig S8.3. Fittings of ΔA for (a) PtTBTPP (b) BDCA on TiO_2 and (c) PtTBTPP and BDCA on TiO_2 (d) Overlaid spectra of the three systems

Section S9. Spectroelectochemistry

The cationic spectra of the molecules in solution were acquired using an Optically Transparent Thin Layer Electrochemical (OTTLE, University of Reading) cell, an EDAQ potentiostat (model 466) and a Shimadzu UV-3600 spectrophotometer. A schematic of an OTTLE cell is shown in Fig S9.1. The OTTLE cell consists of two transparent windows, sandwiched together with an approximately 0.2 mm polyethylene spacer between them, creating a thin chamber where the electrochemical reaction can take place.

The solutions being studied were de-oxygenated by bubbling with argon for 30 mins, followed by injection into the chamber via filling ports. Within the chamber there is a working electrode and counter electrode (both made from platinum wire mesh) and a silver wire pseudo reference electrode. Various voltages were applied to the electrodes with the potentiostat in order to induce the electrochemical reactions. The majority of the cell was masked except for a small window (approx. 4 mm x 5 mm) over the working electrode. The cell was placed into the spectrophotometer, and absorption measurements were taken through the unmasked region at various voltages.

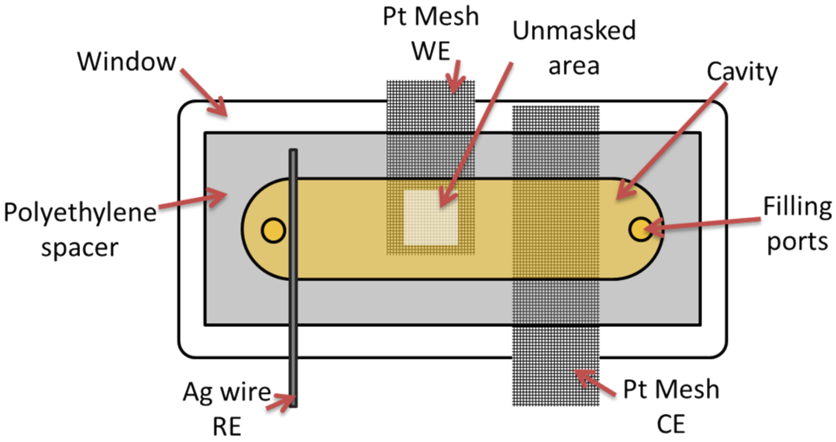


Fig S9.1 - Schematic of the cross section of the Optically Transparent Thin Layer Electrochemical (OTTLE) cell

Solutions of 200µM BDCA and 200µM PtTBTPP, each with 0.1M tetrabutylammonium perchlorate supporting electrolyte, in DMF were tested with the OTTLE cell. Absorption spectra were taken of each solution, initially with no voltage applied. The voltage was then increased in small increments (300 – 500 mV) and a spectra was taken each time until a change in the spectrum was observed, which signified the oxidation potential had been reached and the cation had been formed. For BDCA this voltage was 1.15 V, and for PtTBTPP the voltage was 1.85 V. The voltage was then kept constant and multiple spectra were taken until the cationic spectrum remained stable. The voltage was then returned to 0 V and spectra were taken until the original ground state spectrum was observed again to ensure the reaction was reversible.

In the cationic spectrum of BDCA a broad peak is present at 650 nm, with a notable shoulder around 700 nm. There was also a peak at 430 nm with a shoulder at 400 nm. The small peak a 475 nm could have been caused by remnants of ground state BDCA in the cell. It is expected that the observed redshift and broadening in BDCA absorption when attached to an oxide substrate will translate to a similar shift in the cationic spectra.

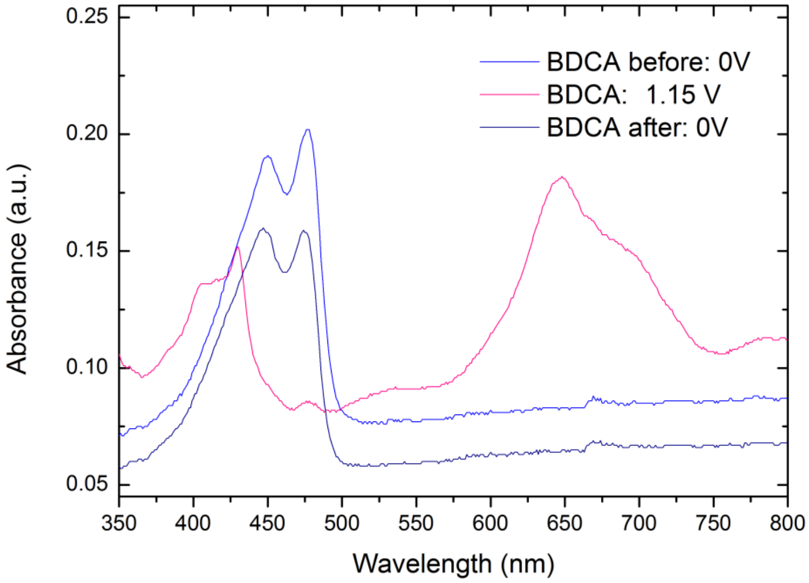


Fig S9.2 - Ground state (blue) and cationic (pink) absorption spectra of BDCA. Measurements were taken through the OTTLE cell at 0 V, 1.15 V, and 0 V again.

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