

## Supporting Information

### Elucidating the non-radiative losses encountered in intramolecular charge transfer compounds with benzodithiophene-4,8-dione acceptors

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## General methods

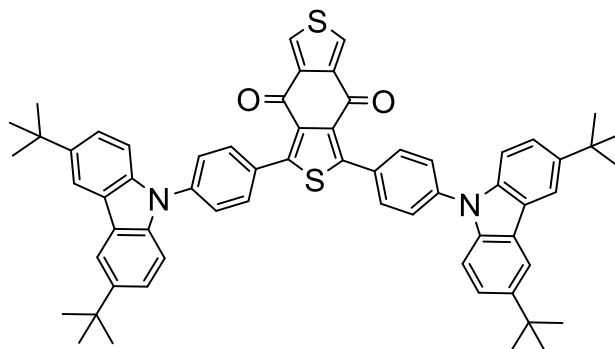
All reactants and reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. Column chromatography was carried out using silica gel 60, 40–60  $\mu\text{m}$  mesh (Fluorochem). Analytical thin-layer chromatography was performed on precoated aluminum silica gel 60 F254 plates (Merck), which were approximately 2 cm  $\times$  6 cm in size, and visualized using ultraviolet light (254/365 nm).

NMR spectra were recorded on Jeol ECS 400 MHz and Jeol ECZ 500 MHz spectrometers. Chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) using TMS or the residual solvent as an internal reference. NMR spectra were processed using MestReNova. Multiplicities are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). Melting points were determined in open-ended capillaries using a Stuart Scientific SMP10 melting point apparatus at a ramping rate of 1  $^{\circ}\text{C}/\text{min}$ . They are recorded to the nearest 1  $^{\circ}\text{C}$  and are uncorrected. IR spectra were collected on a Thermo Scientific Nicolet FTIR spectrometer. Atmospheric solids analysis probe (ASAP) mass spectra were recorded on a ThermoFisher LTQ Orbitrap XL spectrometer. The sample was introduced as a solid, applied directly to a glass probe tip. Elemental analyses were obtained on an Exeter Analytical CE440 Elemental analyser.

Cyclic voltammetry was recorded using a Princeton Applied Research VersaSTAT 3. A glassy carbon disk, Pt wire, and Ag/Ag<sup>+</sup> (AgNO<sub>3</sub> in acetonitrile) were used as the working, counter, and reference electrodes, respectively. Measurements were corrected to the ferrocene/ferrocenium redox couple as an internal standard. 1,2-Dichlorobenzene was used as the solvent with an analyte molarity of ca.  $10^{-5}$  M in the presence of  $10^{-1}$  M (*n*-Bu<sub>4</sub>N)(PF<sub>6</sub>) as a supporting electrolyte. Solutions were degassed with Ar and experiments run under a blanket of Ar.

## Synthetic Methods

### 1,3-Bis(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (Compound 1)



An oven dried two-neck flask fitted with a condenser was placed under a N<sub>2</sub> atmosphere. Dibromide **8** (100 mg, 0.26 mmol) and K<sub>2</sub>CO<sub>3</sub> (109 mg, 0.78 mmol) were added to the flask followed by THF (15 mL) and water (5 mL). The mixture was thoroughly degassed by bubbling with N<sub>2</sub> for 45 min. Boronic acid **9** (232 mg, 0.57 mmol) was added and the mixture degassed for a further 5 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mg, 3 μmol) was added before the mixture was heated to 55 °C for 24 hr. Water (25 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic portions dried over MgSO<sub>4</sub>, and the solvent removed under reduced pressure. The crude product was purified by column chromatography on SiO<sub>2</sub> (0-20% EtOAc/hexane) to yield 233 mg (97%) of **1** as a yellow solid. mp. > 300 °C

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*, ppm) δ = 8.32 (s, 2H, H<sup>Th</sup>), 8.16 (d, *J* = 1.3 Hz, 4H, H<sup>Cz</sup>), 7.93 (d, *J* = 8.6 Hz, 4H, H<sup>Ph</sup>), 7.72 (d, *J* = 8.6 Hz, 4H, H<sup>Ph</sup>), 7.54 (dd, *J* = 8.6, 0.4 Hz, 4H, H<sup>Cz</sup>), 7.50 (dd, *J* = 8.7, 1.9 Hz, 4H, H<sup>Cz</sup>), 1.49 (s, 36H, H<sup>tBu</sup>).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*, ppm) δ = 176.0, 151.7, 143.4, 139.7, 139.5, 139.0, 133.1, 132.7, 131.5, 130.3, 126.1, 123.9, 123.8, 116.5, 109.6, 34.9, 32.2

HRMS (ASAP, *m/z*) 927.4025 [M+H<sup>+</sup>], requires 927.4012 for [C<sub>62</sub>H<sub>59</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>]

IR (*v*<sub>max</sub>/cm<sup>-1</sup>) 2954, 2902, 2865, 1669 (C=O, s), 1603, 1526, 1471, 1448, 1362, 1232, 811, 611

Elemental analysis: Calculated for C<sub>62</sub>H<sub>58</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 80.31; H, 6.30; N 3.02. Found C, 80.09; H, 6.06; N, 3.19

# $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

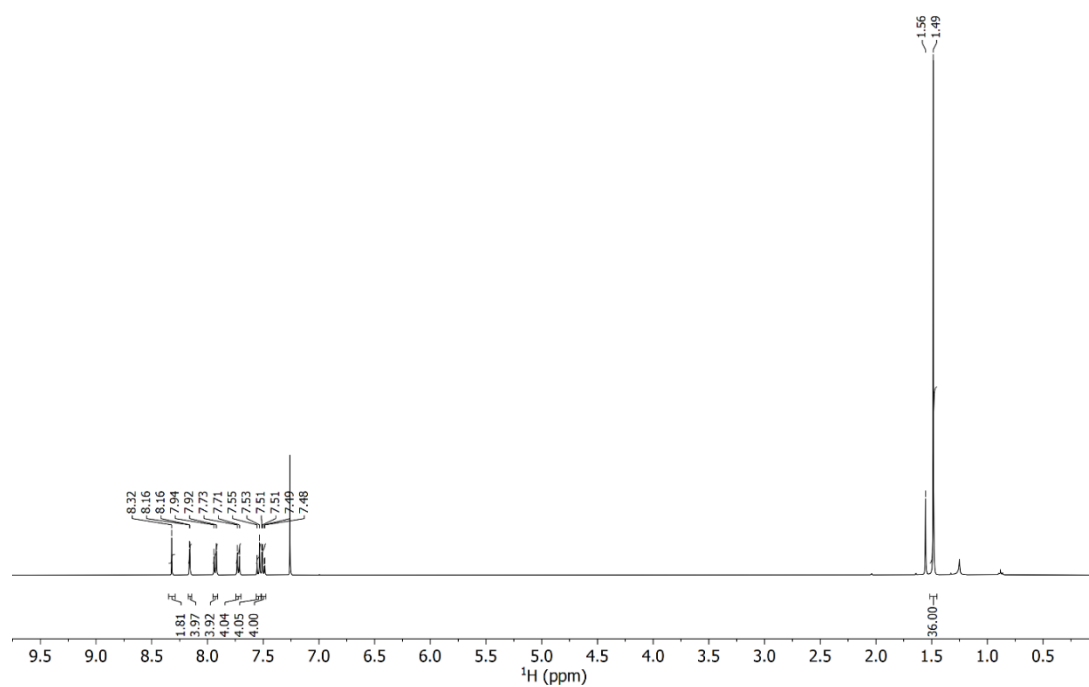


Figure S1.  $^1\text{H}$  NMR spectrum of **1**.

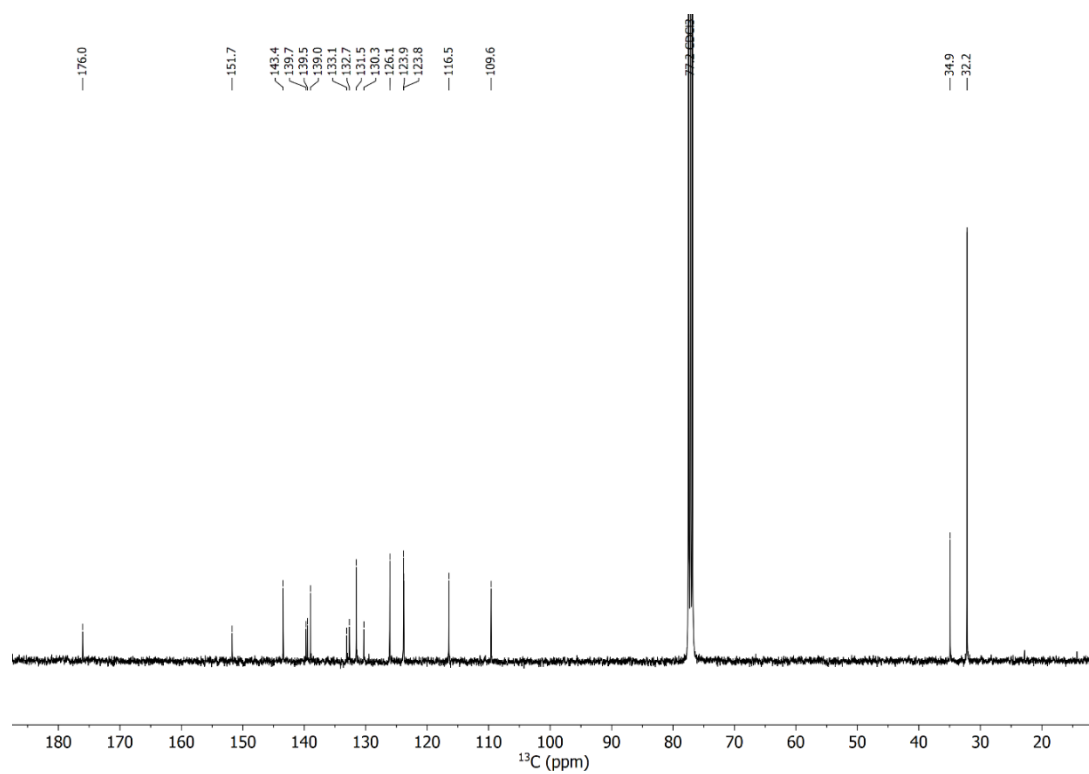


Figure S2.  $^{13}\text{C}$  NMR Spectrum of **1**.

# Photophysics

## Experimental Details

### Sample fabrication

Solutions of **1** and polystyrene were created in toluene with a total concentration of 100 mg/mL, consisting of 2 wt % **1**. These solutions were then drop cast onto substrates warmed to 80 °C. All films were deposited onto Spectrosil fused silica substrates that were first cleaned by sonicating in acetone and isopropanol for 10 minutes each. Films for optical studies were encapsulated under glass in an inert N<sub>2</sub> atmosphere prior to use.

### Transient absorption spectroscopy

The TA experiments were performed using a commercially available Ti:sapphire amplifier (Spectra Physics Solstice Ace). The amplifier operates at 1 kHz and generates 100 fs pulses centered at 800 nm. For the ultrafast measurements, the 400 nm pump is generated by frequency doubling the 800 nm output of the Ti:sapphire in a beta barium borate (BBO) crystal. The residual 800 nm was removed from the pulse using a BG39 coloured glass filter. For the long-time TA, a 1 ns duration pump pulse is provided by the third harmonic (355 nm) of an electronically triggered Q-switched Nd:YVO<sub>4</sub> laser (Advanced Optical Technologies Ltd AOT-YVO-25QSPX). For both the ultrafast and long-time TA, the probe pulses used in our experiments were provided by NOPAs operating in the visible (510 – 780 nm) and NIR (830 – 1025 nm) regions. The transmitted probe pulses were then collected with a silicon dual-line array detector (Hamamatsu S8381-1024Q) driven and read out by a custom-built board from Stresing Entwicklungsbüro.

### Time-resolved photoluminescence

Time-resolved PL spectra were recorded using an electrically-gated intensified CCD camera (Andor iStar DH740 CCI-010) connected to a calibrated grating spectrometer (Andor SR303i). Sample excitation with a 400 nm pump pulse was provided by frequency doubling a small portion of the Ti:sapphire 800 nm output in a BBO crystal. The residual 800 nm was removed from the pulse using a BG39 coloured glass filter. Temporal evolution of the photoluminescence emission was obtained by electrically stepping the ICCD gate delay with respect to the excitation pulse.

### **Steady-state absorption**

Steady-state absorption spectra were measured using an HP 8453 spectrometer.

### **Steady-state photoluminescence and photoluminescence quantum efficiency**

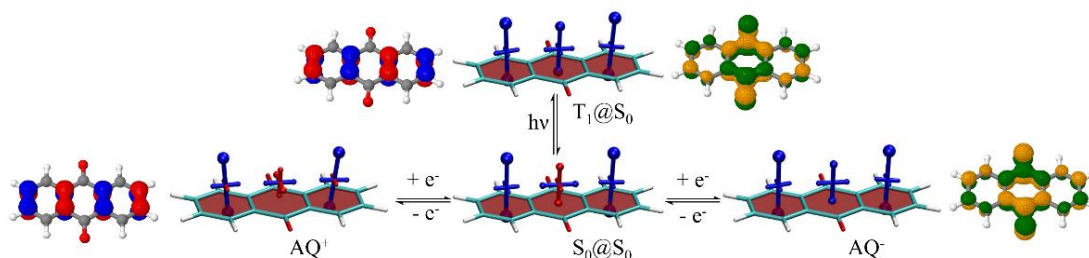
The PLQE was determined using method previously described by De Mello *et al.*<sup>1</sup> The steady-state PL was measured simultaneously. Samples were placed in an integrating sphere and were photoexcited using 405 and 520 nm continuous-wave lasers. The laser and the emission signals were measured and quantified using a calibrated Andor iDus DU420A BVF Si detector.

### **Rate Constant Equations**

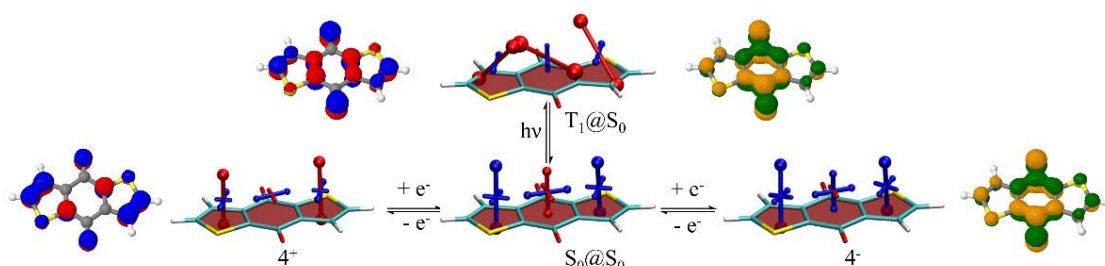
$$k_r^S = \Phi_F k_p \quad (\text{S1})$$

$$k_{ISC} = (1 - \Phi_F) k_p \quad (\text{S2})$$

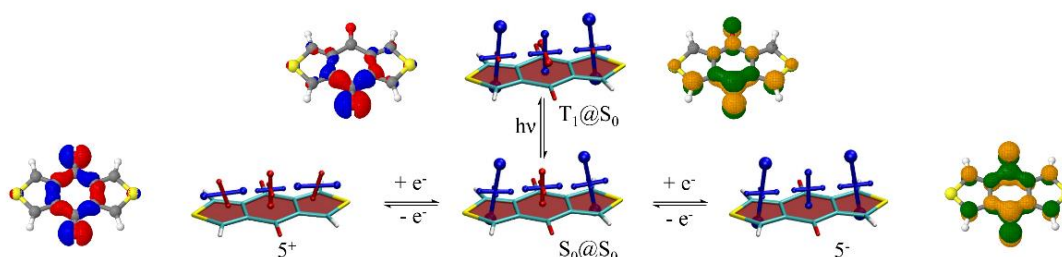
## Additional VIST Plots and NDOs



**Figure S3.** Analysis of charged and excited states of **AQ** showing VIST plots and NDOs (blue/red for electron detachment; green/orange for attachment). Top, left and right is for  $T_1$ , cationic and anionic state, respectively.

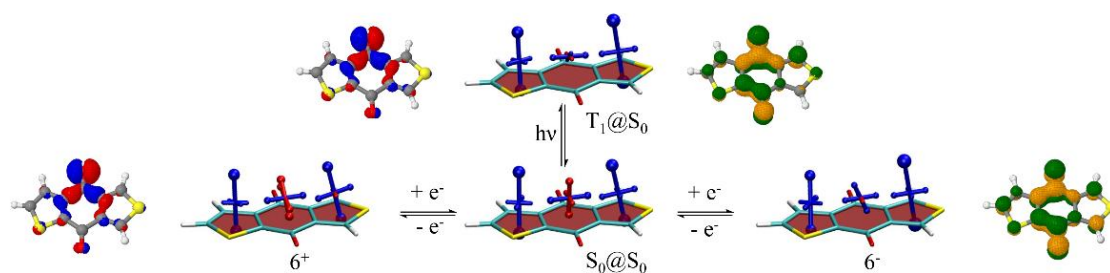


**Figure S4.** Analysis of charged and excited states of compound **4** showing VIST plots and NDOs (blue/red for electron detachment; green/orange for attachment). Top, left and right is for  $T_1$ , cationic and anionic state, respectively.

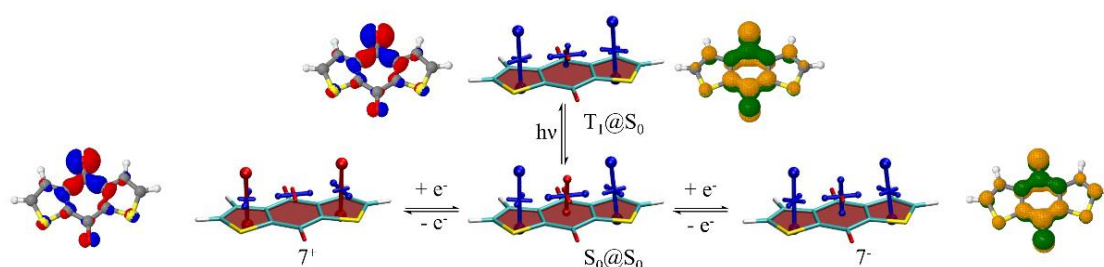


**Figure S5.** Analysis of charged and excited states of compound **5** showing VIST plots and NDOs (blue/red for electron detachment; green/orange for attachment). Top, left and right is for  $T_1$ , cationic and anionic state, respectively.





**Figure S6.** Analysis of charged and excited states of compound **6** showing VIST plots and NDOs (blue/red for electron detachment; green/orange for attachment). Top, left and right is for  $T_1$ , cationic and anionic state, respectively.



**Figure S7.** Analysis of charged and excited states of compound **7** showing VIST plots and NDOs (blue/red for electron detachment; green/orange for attachment). Top, left and right is for  $T_1$ , cationic and anionic state, respectively.

## References

S1 J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230–232