Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Highly Efficient Electrogenerated Chemiluminescence of an Oligofluorene-Truxene Star-Shaped Compound Incorporating 2,1,3-Benzothiadiazole Units

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Supplementary Information

General experimental

For all electrochemical measurements a standard cell with a working volume 5-10 mL was used. The electrodes were: 2 mm platinum disk, platinum wire, and silver wire as the working, counter, and reference electrodes, respectively. All solutions were degassed (Ar) and contained monomer substrates in concentrations *ca.* 10^{-4} – 10^{-3} M, together with $TBAPF_6$ (0.1 M) as the supporting electrolyte. All measurements are referenced against the $E_{1/2}$of the Fc/Fc^+ redox couple. For ECL measurements, the cell was equipped with a holder which had a hole and outlet for attaching fiber optics at the bottom.

Dry solvents used for electrochemical measurements were either purchased from Aldrich (acetonitrile, benzene) or obtained (toluene, CH_2Cl_2) from a solvent purification system (SPS 400, innovative technologies) using alumina as the drying agent. The solvent used for recrystallisation and column chromatography was purchased commercially from Sigma Aldrich or Alfa Aesar and were used without any purification.

T4BT-B was synthesised and purified using the literature procedure (reference 17 in the main paper). 9,10-Diphenylanthracene (97%) was purchased from Aldrich and purified on a silica gel column using hexane as an eluent. The yield after column purification was 83%. Ferrocene and tetrabutylammonium hexafluorophosphate were purchased from Aldrich and re-crystallised twice from methanol and an ethyl acetate / cyclohexane mixture, respectively.

UV absorption measurements were performed on a UV-2600 Shimadzu spectrometer. PL spectra were run on an FP-6500 Spectrofluorometer.

CV measurements, including the scan rate experiment, were performed using a CH instrument electrochemical analyser, CHi602e. ECL transient and co-reactant ECL were measured on a CH instrument electrochemical analyser, CHi760e, HAMAMATSU H10723-20 PMT and HAMAMATSU C10709 power supply. ECL spectra were recorded on an Ocean Optics USB2000+ CCD spectrometer using a CH instrument electrochemical analyser, CHi660e.

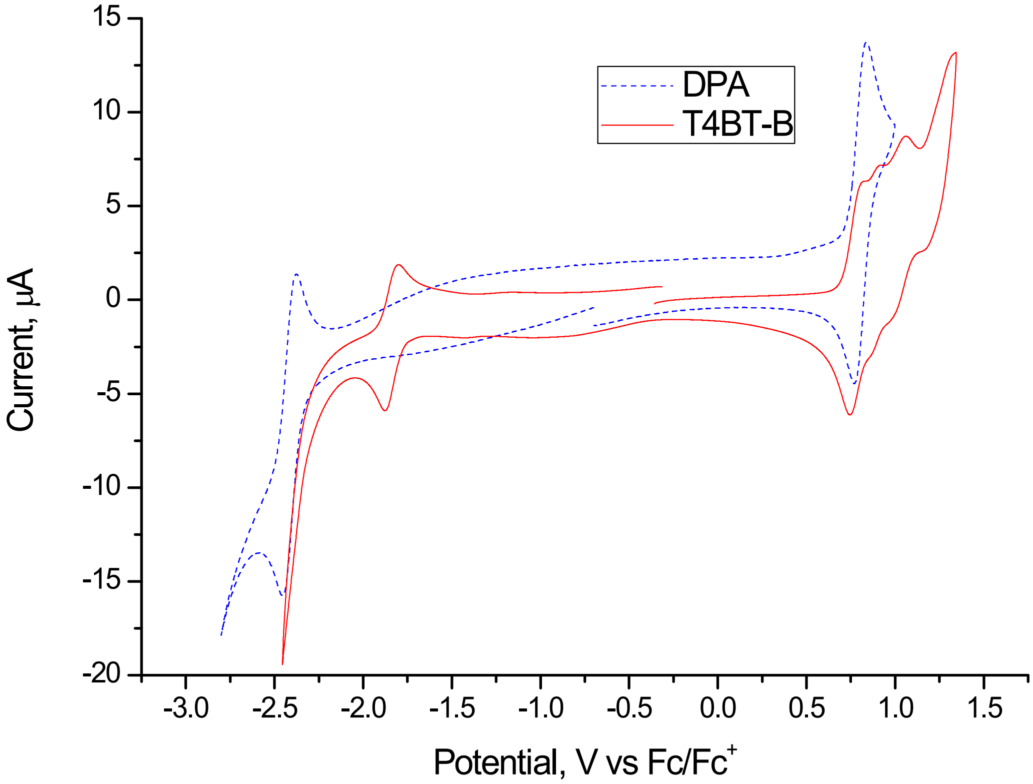
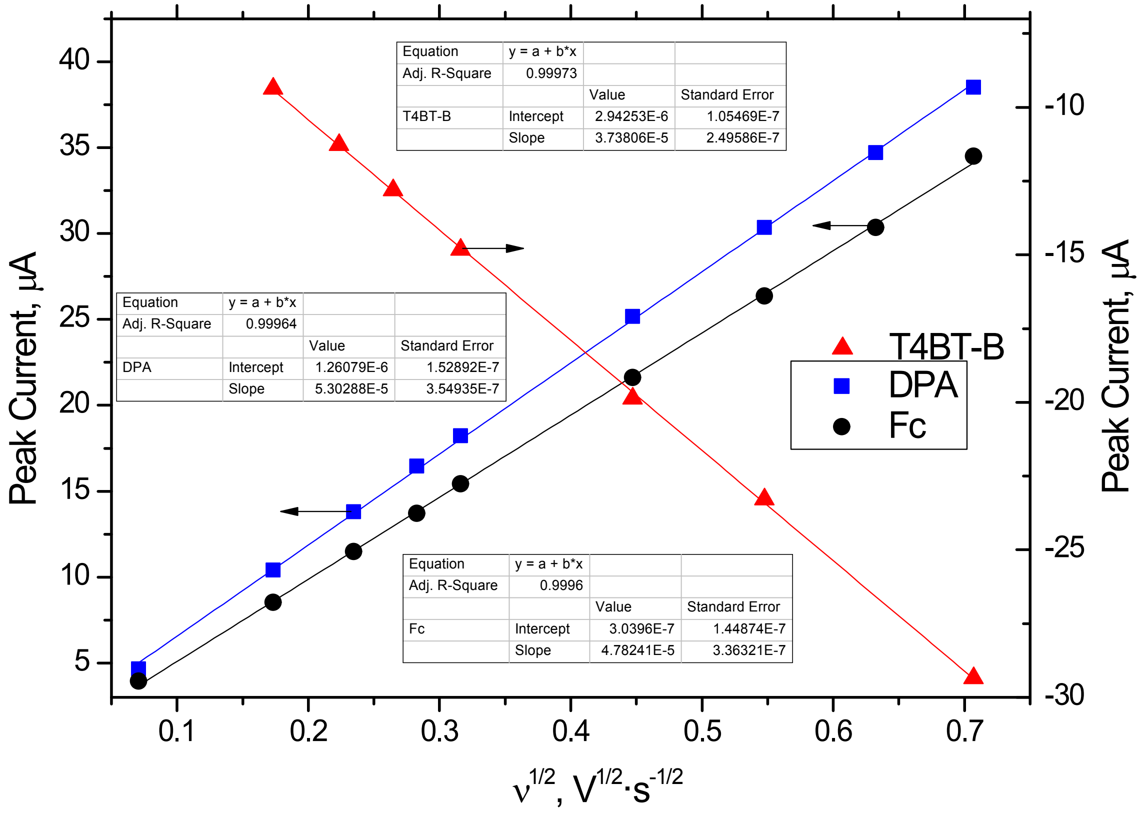


Figure S1. Solution-state cyclic voltammograms of DPA (blue-dashed line) and **T4BT-B** (red-solid line). Experimental conditions: scan rate 0.1 V s^{-1}, solvent CH_2Cl_2, supporting electrolyte 0.1 M tetrabutylammonium hexafluorophosphate ((TBA)PF_6), platinum disc electrode diameter of 2 mm. The voltammograms were referenced using an internal ferrocene standard.



Equation	y = a + b*x		
Adj. R-Square	0.99973		
		Value	Standard Error
T4BT-B	Intercept	2.94253E-6	1.05469E-7
	Slope	3.73806E-5	2.49586E-7

Equation	y = a + b*x		
Adj. R-Square	0.99964		
		Value	Standard Error
DPA	Intercept	1.26079E-6	1.52892E-7
	Slope	5.30288E-5	3.54935E-7

Equation	y = a + b*x		
Adj. R-Square	0.9996		
		Value	Standard Error
Fc	Intercept	3.0396E-7	1.44874E-7
	Slope	4.78241E-5	3.36321E-7

Figure S2. The scan rate experiment for **T4BT-B** (4.31×10^{-4} M), DPA (9.68×10^{-4} M) and Fc (1.00×10^{-3} M): red triangles – cathodic peak current values of **T4BT-B** reduction wave; blue squares and black circles – anodic peak current values of DPA and Fc oxidation waves, respectively. The peak current is plotted against the square root of the scan rate and the solvent conditions were acetonitrile for Fc and a mixture of acetonitrile (50%): benzene (33%): toluene (17%) for **T4BT-B** and DPA. The experiments were performed using 0.1 M supporting electrolyte $(TBA)PF_6$ with a 2 mm diameter Pt disc (the area of the electrode A = 0.0372 cm^2 was estimated by calibration on Fc and assuming 2.28×10^{-5} $cm^2\cdot s^{-1}$ for its D value).

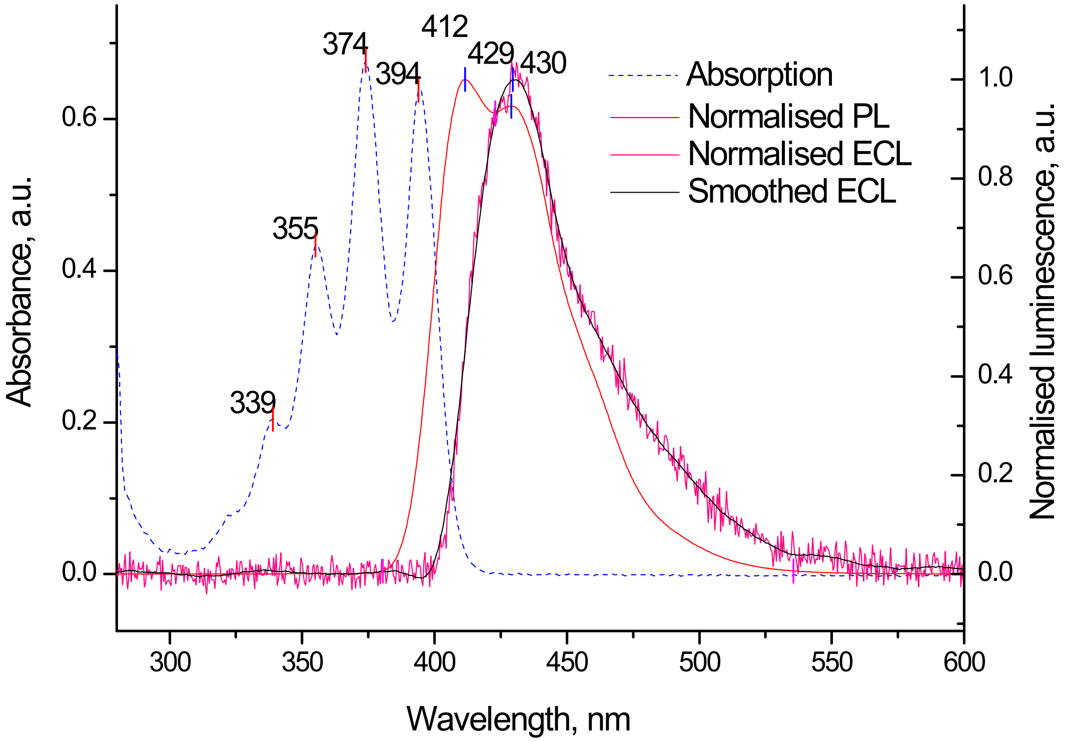


Figure S3. Absorption (blue-dashed), normalised PL (red) and ECL (magenta and black for smoothed spectrum) spectra of DPA in a mixture of acetonitrile (50%): benzene (33%): toluene (17%).

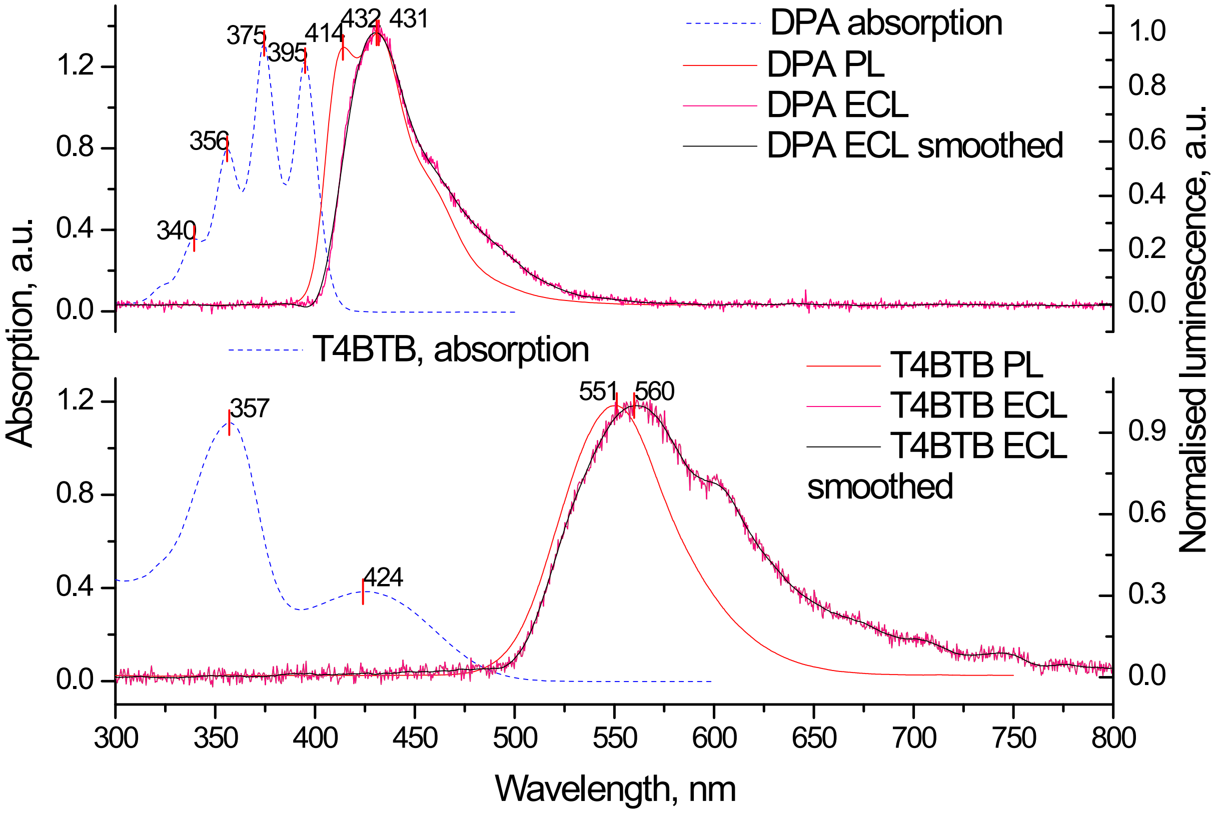


Figure S4. Absorption (blue-dashed), normalised PL (red) and ECL (magenta and black for smoothed spectrum) spectra in CH_2Cl_2 for DPA (top panel) and **T4BT-B** (bottom panel)

Figure S5. A view from the bottom of the cell containing a solution of **T4BT-B** under ambient light (left) and in the dark before (middle) and during (right) the ion annihilation ECL experiment.

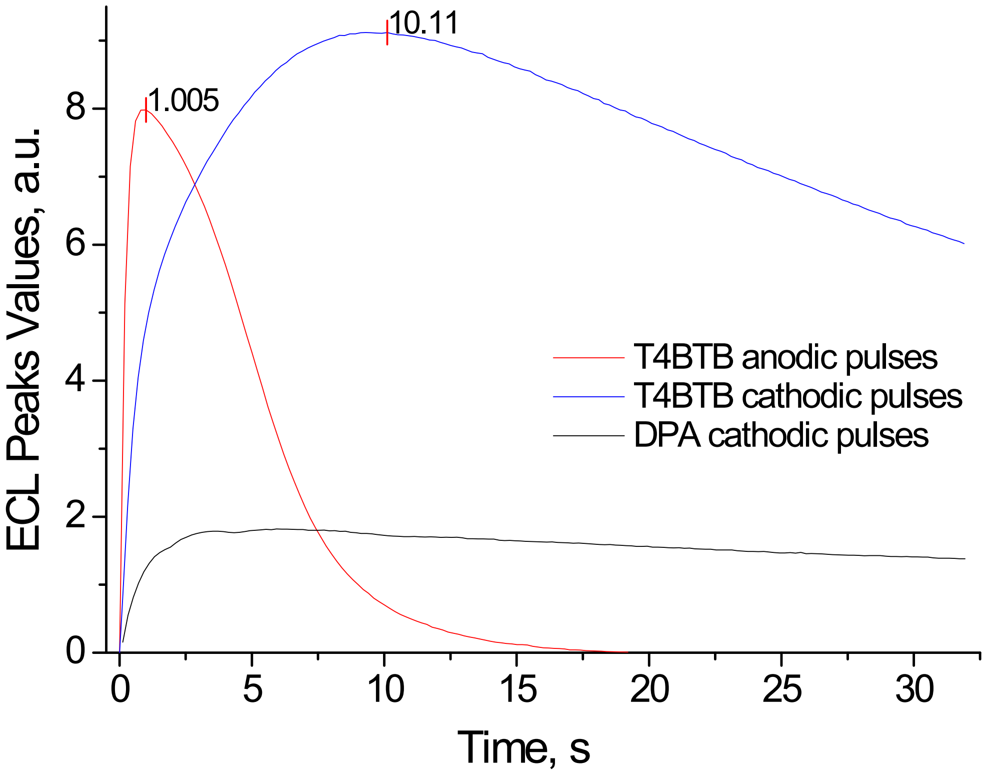


Figure S6. Ions annihilation ECL peaks values on cathodic pulses for DPA (black line), **T4BT-B** (blue line) and on anodic pulses for **T4BT-B** (red line).

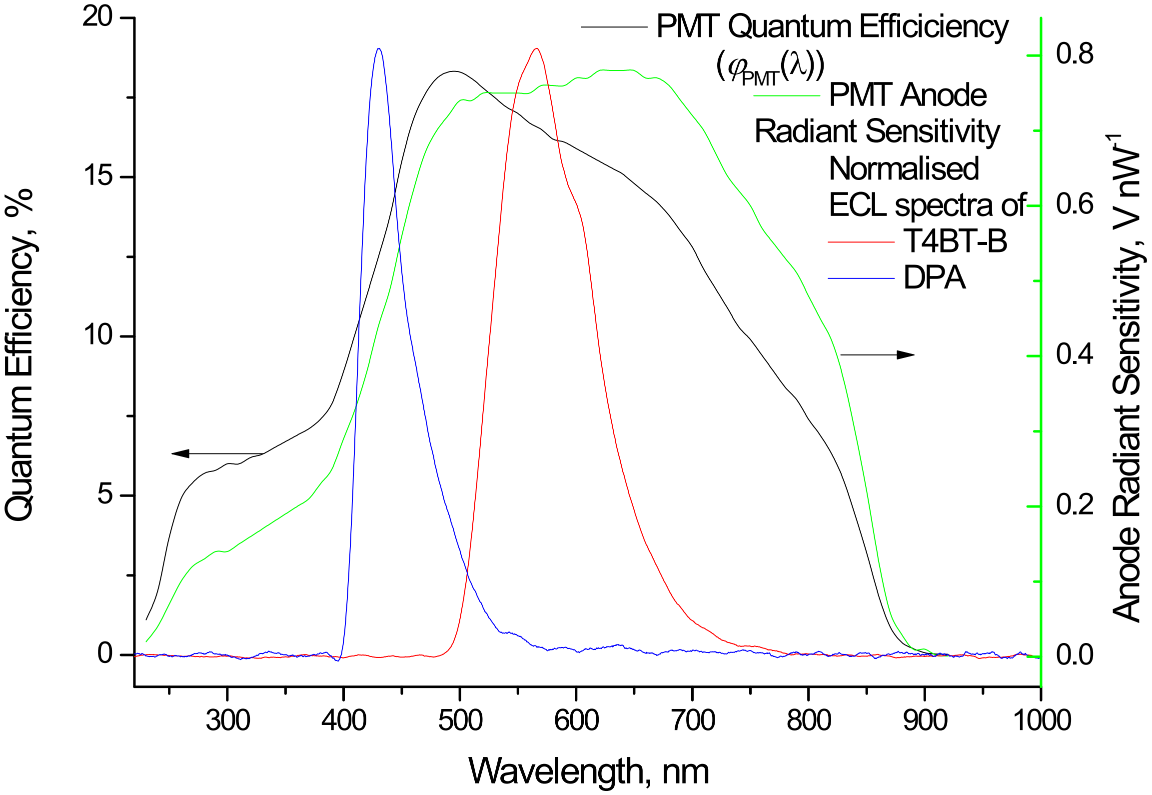


Figure S7. Quantum efficiency ($\varphi_{PMT}(\lambda)$, black line) and anode radiant (green line) spectral sensitivity functions along with normalised smoothed ECL spectra (scale not shown) in a mixture of acetonitrile (50%): benzene (33%): toluene (17%) of DPA (blue line) and **T4BT-B** (red line).