Supporting Information:

Synthesis and Characterisation of BODIPY Radical Anions

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Experimental

All reagents and solvents were purchased from Aldrich Chemicals, Alfa Aesar or Fisher Scientific UK, and used without further purification unless otherwise stated. Toluene was pre-dried over Na wire prior to passing through a column of 4 Å molecular sieves, degassed and stored over a potassium mirror. Triethylamine was dried/stored over 4 Å molecular sieves and degassed. All reactions were carried out using Schlenk conditions, under an atmosphere of dinitrogen or argon where noted. Column chromatography was performed on either silica gel (Merck silica gel 60, 0.2-0.5 mm, 50-130 mesh) or activated, basic, alumina (Brockmann I, 50-200μm) as appropriate. ^1H, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra were measured using a Bruker DPX 400 MHz spectrometer. Residual signals of solvent were used for reference for ^1H and $^{13}C\{^1H\}$ NMR spectroscopy while $BF_3{\cdot}OEt_2$ was used as an external reference for $^{11}B\{^1H\}$ NMR measurements. Microanalyses were performed by Stephen Boyer, London Metropolitan University. MS spectra (ESI) were determined using a Bruker Daltonics microTOF mass spectrometer.

Synthetic Procedures

1 was prepared using the literature method,[S1] but using Schlenk conditions to ensure the absence of atmospheric oxygen and moisture giving the product in 45% yield. Spectroscopic data was consistent with that reported in the literature.[S1]

2 was prepared by two distinct routes (Scheme 1). First, following the literature procedure[S2] and second by a new synthetic pathway as described below.

Novel synthetic route to ***2****.* A solution of 2,3-dicyano-5,6-dichlorobenzoquinone (255 mg, 1.125 mmol, 1 eq.) in toluene (10 mL) was added to a solution of 5-phenyldipyrromethane (500 mg, 1.125 mmol, 1 eq.) also in toluene (10 mL) and stirred at room temperature for 1 hour. Triethylamine (1.1 mL, 7.8 mmol, 6.93 eq.) was added to the reaction mixture followed immediately by B-bromocatecholborane (1.57 g, 7.8 mmol, 6.93 eq.). After stirring for a further 45 minutes, the mixture was washed with water (2 x 20 mL) and dried over Na_2SO_4. Filtration, followed by the removal of solvent under reduced pressure, gave a red/brown oil. Purification was achieved by column chromatography (basic alumina, hexane/dichloromethane 3:2) to afford **2** as a red powder (248 mg, 65.3 %). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ_H / ppm 6.52 (m, 2H, Pyrr-H), 6.83 (m, 2H, Ar-H), 6.90 (m, 2H, Ar-H), 7.01 (d, 2H, J = 4 Hz, Pyrr-H), 7.57 – 7.63 (m, 5H, Ar-H), 7.74 (s, 2H, Pyrr-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ_C / ppm 118.84 (Ar-C), 119.45 (Ar-C), 128.50 (Pyrr-C), 130.49 (Ar-C), 130.82 (Ar-C), 130.90 (Ar-C), 132.16 (CR_3), 145.08 (Pyrr-C), 150.98 (Ar-C).^{11}B{^{1}H} NMR (128MHz, $CDCl_3$, 300K): δ_B / ppm 6.60. IR (ATR) : ν / cm^{-1} 2963 w, 1552m, 1473w, 1410m, 1387w, 1258s, 1240m, 1218m, 1153m, 1073s, 1043m, 1026m, 967w, 907w, 798s, 738w, 722m. EI-MS (MeOH, +ve mode) : *m/z* calculated 338.17; observed 361.11 [M + Na]. Anal. Calc. for $C_{21}H_{15}N_2O_2B$: C, 74.59 ; H, 4.47 ; N, 8.28. Found: C, 74.67; H, 4.34 ; N, 8.14 %.

Single crystal X-ray diffraction structural studies. Single crystal diffraction data for **2** were collected on an Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector. Data were collected at 90(2) K using mirror-monochromated Cu *Kα* radiation (*λ* = 1.5418 Å).

Electrochemical and Optical Spectroscopy Investigations. Dichloromethane (Fisher) was freshly distilled from calcium hydride under an atmosphere of dinitrogen. Ferrocene (Aldrich) was used as received. [^{n}Bu$_4$N][BF$_4$] was prepared by literature methods.[S3] Cyclic voltammetric and coulometric studies were carried out using an Autolab PGSTAT20 potentiostat. Standard cyclic voltammetry was carried out under an atmosphere of argon using a three-electrode arrangement in a single-compartment cell. A glassy carbon working electrode, a Pt wire secondary electrode and a saturated calomel reference electrode, chemically isolated from the test solution *via* a bridge tube containing electrolyte solution and fitted with a porous vycor frit, were used in the cell. The solutions were 10^{-3} M in test compound and 0.4 M in [^{n}Bu$_4$N][BF$_4$] as supporting electrolyte. Redox potentials are quoted *versus* the ferrocenium-ferrocene couple used as an internal reference.[S4] Compensation for internal resistance was not applied.

Bulk electrolysis experiments, at a controlled potential, were carried out using a two-compartment cell. The Pt/Rh gauze basket working electrode was separated from the wound Pt/Rh gauze secondary electrode by a glass frit. A saturated calomel reference electrode was bridged to the test solution through a vycor frit orientated at the centre of the working electrode. The working electrode compartment was fitted with a magnetic stirrer bar and the test solution was stirred rapidly during electrolysis. Solutions were 0.4 M in [^{n}Bu$_4$N][BF$_4$] as supporting electrolyte and 10^{-3} M in test compound and were prepared using Schlenk line techniques. Electrolysed solutions were transferred to quartz tubes, *via* a Teflon canula, for analysis by EPR spectroscopy. EPR spectra were recorded on a Bruker EMX spectrometer and simulated using WINEPR SimFonia (Shareware version 1.25, Brüker Analytische Messtechnik GmbH).

UV/vis spectroelectrochemical experiments were carried out with an optically transparent electrochemical (OTE) cell (modified quartz cuvette, optical pathlength 0.5 mm).[S5] A three-electrode configuration, consisting a Pt/Rh gauze working electrode, a Pt wire secondary electrode (in a fritted PTFE sleeve) and a saturated calomel electrode, chemically isolated from the test solution *via* bridge tube containing electrolyte solution and terminated in a porous frit, was used in the cell. The potential at the working electrode was controlled by a Sycopel Scientific Ltd. DD10M potentiostat. The UV/vis spectra were recorded on a Perkin Elmer Lambda 16 spectrophotometer. The cavity was purged with dinitrogen and temperature control at the sample was achieved by flowing cooled dinitrogen gas across the surface of the cell.

Fluorescence spectroelectrochemistry was carried out in a standard 1 cm pathlength quartz cuvette using a reticulated vitreous carbon working electrode, a coiled platinum/rhodium gauze secondary electrode and a silver/silver chloride reference electrode. The working electrode configuration was based on the design of Kirchhoff [S6] and the secondary electrode was isolated from the test solution using a bridge tube filled with electrolyte solution and terminated with a glass frit. The cell was purged with argon throughout the experiment. Spectra were recorded at ambient temperature on a Jobin Yvon Horiba FluoroMax-3 spectrometer and the potential at the working electrode was controlled using an Autolab PGSTAT20 potentiostat. Under these conditions fluorescence quenching upon reduction was irreversible. Experiments to evaluate the effect of adding a CH_2Cl_2 solution of $[NEt_4]_2[Fe_4S_4(SPh)_4]$ to a CH_2Cl_2 solution of **1** were carried out under a dinitrogen atmosphere.

DFT Calculations. DFT calculations were performed on models of **1** and **2** as neutral and singly reduced molecules in order to complement observations made in the EPR. The geometry optimizations of the models of **1** and **2** were performed without any restraints. The calculations employed a basis set suitable for EPR simulations, EPR-II,[S7] for C, N, O and H atoms. The calculations were performed with Gaussian 03 Revision D. 01.[S8]

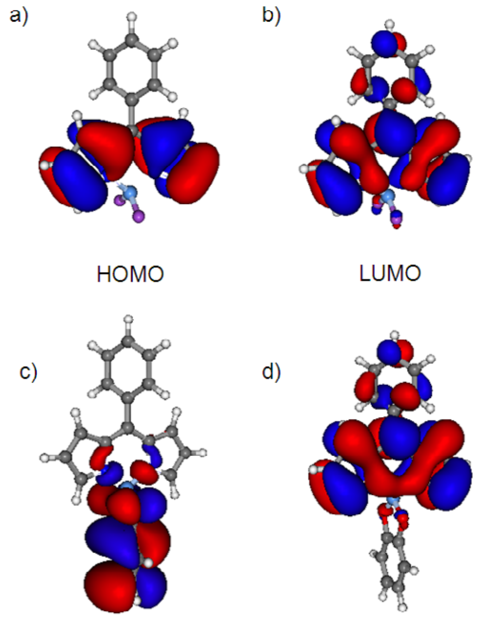


Figure S1. Isosurfaces at 0.025 e Å^{-3} and energies (eV) for the HOMOs a) -6.25 eV **1**; c) -5.30 eV **2**, difference in energy is 3.08 eV; and LUMOs b) -3.17 eV **1**; d) -3.22 eV **2**, difference in energy is 2.08 eV.

Table S1. Comparison of selected bond lengths (Å) and angles (^{o}) for **1** and **2**.

	B-N / Å X-ray	*B-N / Å Calc*	*B-F(O) / Å X-ray*	*B-F(O) / Å Calc*
1	1.5473(9)[i]	1.567	1.3815(10)[i]	1.383
		1.569		1.381
2[ii]	1.562(2)	1.562	1.483(2)	1.469
	1.551(2)	1.562	1.462(2)	1.469
	1.536(2)		1.498(2)	
	1.536(2)		1.474(2)	

	N-B-N / ^{o} X-ray	*N-B-N / ^{o} Calc*	*N-B-F(O) / ^{o} X-ray*	*N-B-F(O)/ ^{o} Calc*	*F(O)-B-F(O) / ^{o} X-ray*	*F(O)-B-F(O) / ^{o} Calc*
1	106.38(7)[i]	104.832	109.75(4)[i]	110.134	110.28(9)[i]	111.626
			110.30(4)[i]	110.010		
			109.75(4)[i]	109.604		
			110.30(4)[i]	110.421		
2[ii]	104.43(11)	104.599	113.11(12)	111.517	106.11(11)	105.687
	105.44(11)		111.51(12)	111.835	105.22(12)	
			110.11(12)	111.837		
			111.67(12)	111.517		
			112.09(12)			
			110.62(12)			
			111.78(12)			
			111.82(12)			

[i] reference S9. [ii] Two molecules in the asymmetric unit.

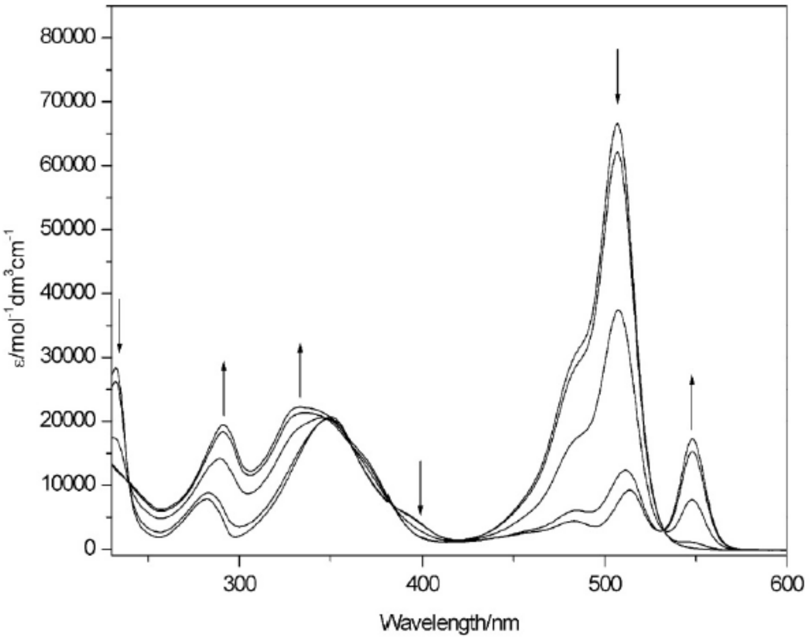
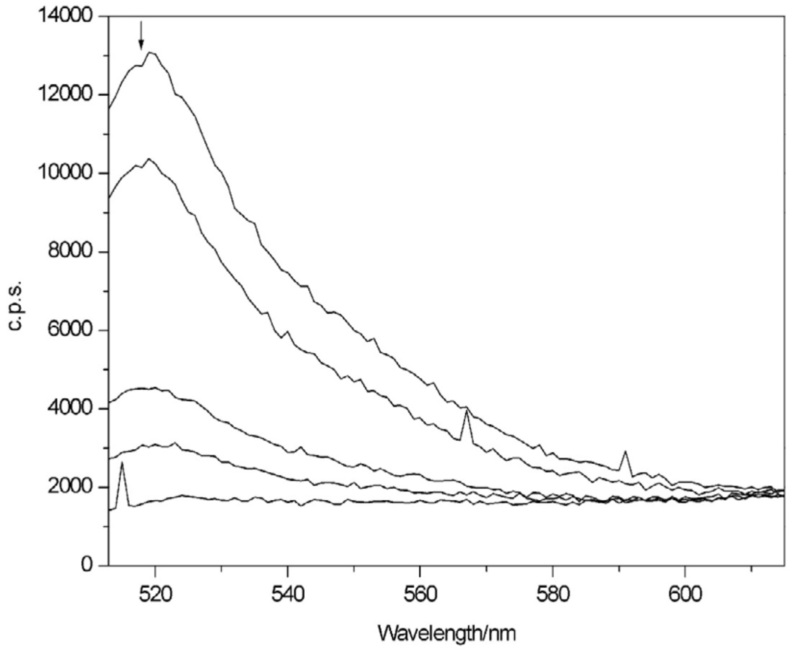
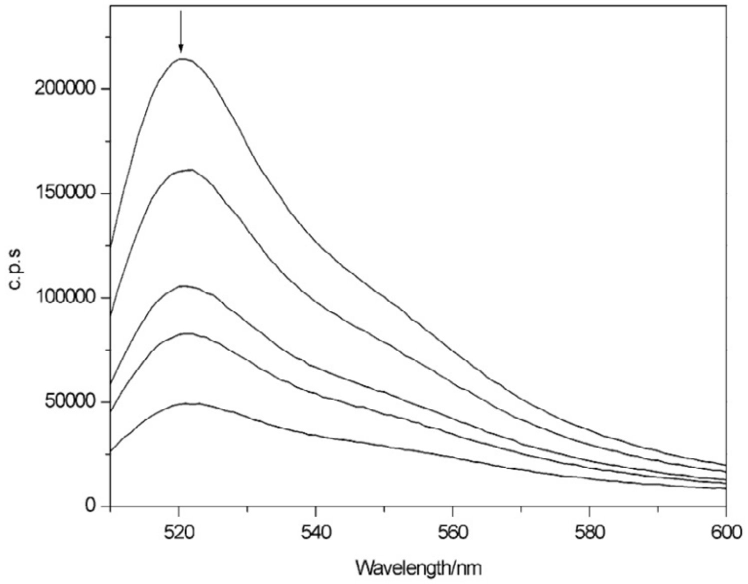


Figure S2. UV-visible spectra for **2**; arrows indicate the inter-conversion of **2** to **2^{-}**. Spectra recorded in CH_2Cl_2 containing [$^{n}Bu_4N$][BF_4] (0.4 M) using spectroelectrochemical methods**.**



a)



b)

Figure S3. a) Uncorrected emission spectra of **1** (l_{ex} = 503 nm) in CH_2Cl_2 containing 0.4 M [^{n}Bu$_4$N][BF$_4$] as the supporting electrolyte recorded *in situ* during electrochemical reduction. Arrow indicates the effect of reduction; b) Uncorrected emission spectra of **1** (l_{ex} = 503 nm) in CH_2Cl_2 upon addition of a solution of $[NEt_4]_2[Fe_4S_4(SPh)_4]$ leading to quenching of the fluorescence.

Table S2. Cyclic voltammetric[a] and UV/vis spectroscopic[b] data for **1, 2,** [**1**]$^-$ and [**2**]$^-$.

	RED^{I} E$_{1/2}$/V	**RED^{II} E$_p$^{c}/V**	**OX^{I} E$_p$^{a}/V**	**ΔE Fc$^+$/Fc**
1	-1.19 (0.08)	-2.17	+1.19	(0.08)
2	-1.15 (0.07)	-2.13	+0.80	(0.07)
	Neutral λ$_{max}$/nm (ε x 10^4/mol^{-1}dm^{3}cm^{-1})	**Anion λ$_{max}$/nm (ε x 10^4/mol^{-1}dm^{3}cm^{-1})**		
1	231 (2.4), 273 (0.2), 348 (1.9), 501 (7.8)	291 (1.4), 339 (2.2), 479 (0.4), 508 (1.0), 542 (1.9)		
2	233 (2.9), 283 (0.8), 349 (2.1), 507 (6.7)	291 (2.0), 332 (2.2), 482 (0.4), 514 (0.9), 548 (1.8)		

[a] Potentials ($E_{1/2} = (E_p^a + E_p^c)/2$) in V *vs.* Fc$^+$/ Fc quoted to the nearest 0.01 V. Data reported at 0.1 Vs^{-1} for ca. 2 mM (**1**) and 1 mM (**2**) test solutions in CH_2Cl_2 containing 0.4 M [^{n}Bu$_4$N][BF$_4$] as the supporting electrolyte. The anodic/cathodic peak separation ($\Delta E = E_p^a - E_p^c$) is given in brackets where applicable. [b] Spectra recorded at 273 K in CH_2Cl_2 containing [^{n}Bu$_4$N][BF$_4$] (0.2 M) recorded using an optically transparent electrode

Table S2. Isotropic Fermi Contact Couplings calculated for **1** and **2** using basis sets suitable for EPR simulations.

Atom	a.u.	MHz	Gauss	10^{-4} cm^{-1}
1 using EPR-II[S7]				
1 C(13)	0.00049	0.54637	0.19496	0.18225
2 C(13)	0.00000	0.00005	0.00002	0.00002
3 C(13)	0.00049	0.54662	0.19505	0.18233
4 N(14)	0.00026	0.08481	0.03026	0.02829
5 C(13)	0.00000	0.00493	0.00176	0.00165
6 C(13)	0.00001	0.01415	0.00505	0.00472
7 C(13)	0.00005	0.06168	0.02201	0.02057
8 C(13)	0.00005	0.05993	0.02139	0.01999
9 C(13)	0.00001	0.01382	0.00493	0.00461
10 C(13)	0.00000	0.00446	0.00159	0.00149
11 N(14)	0.00027	0.08837	0.03153	0.02948
12 B(11)	0.00000	0.00000	0.00000	0.00000
13 F(19)	0.00101	4.24553	1.51491	1.41616
14 F(19)	0.00101	4.23459	1.51101	1.41251
15 C(13)	0.00000	0.00000	0.00000	0.00000
16 C(13)	0.00579	6.51084	2.32323	2.17178
17 C(13)	0.00091	1.01869	0.36349	0.33980
18 C(13)	0.00000	0.00000	0.00000	0.00000
19 C(13)	0.00091	1.02111	0.36436	0.34061
20 C(13)	0.00578	6.49837	2.31878	2.16762
21 H(1)	0.00000	0.00017	0.00006	0.00006
22 H(1)	0.00000	0.01554	0.00555	0.00518
23 H(1)	0.00000	0.00301	0.00108	0.00101
24 H(1)	0.00000	0.00296	0.00106	0.00099
25 H(1)	0.00000	0.01581	0.00564	0.00527
26 H(1)	0.00000	0.00031	0.00011	0.00010
27 H(1)	0.00000	0.01498	0.00535	0.00500

28	H(1)	0.00016	0.71573	0.25539	0.23874
29	H(1)	0.00000	0.00000	0.00000	0.00000
30	H(1)	0.00016	0.71759	0.25605	0.23936
31	H(1)	0.00000	0.01513	0.00540	0.00505

2 using EPR-II[S7]

1	C(13)	0.00049	0.54637	0.19496	0.18225
2	C(13)	0.00000	0.00005	0.00002	0.00002
3	C(13)	0.00049	0.54662	0.19505	0.18233
4	N(14)	0.00026	0.08481	0.03026	0.02829
5	C(13)	0.00000	0.00493	0.00176	0.00165
6	C(13)	0.00001	0.01415	0.00505	0.00472
7	C(13)	0.00005	0.06168	0.02201	0.02057
8	C(13)	0.00005	0.05993	0.02139	0.01999
9	C(13)	0.00001	0.01382	0.00493	0.00461
10	C(13)	0.00000	0.00446	0.00159	0.00149
11	N(14)	0.00027	0.08837	0.03153	0.02948
12	B(11)	0.00000	0.00000	0.00000	0.00000
13	F(19)	0.00101	4.24553	1.51491	1.41616
14	F(19)	0.00101	4.23459	1.51101	1.41251
15	C(13)	0.00000	0.00000	0.00000	0.00000
16	C(13)	0.00579	6.51084	2.32323	2.17178
17	C(13)	0.00091	1.01869	0.36349	0.33980
18	C(13)	0.00000	0.00000	0.00000	0.00000
19	C(13)	0.00091	1.02111	0.36436	0.34061
20	C(13)	0.00578	6.49837	2.31878	2.16762
21	H(1)	0.00000	0.00017	0.00006	0.00006
22	H(1)	0.00000	0.01554	0.00555	0.00518
23	H(1)	0.00000	0.00301	0.00108	0.00101
24	H(1)	0.00000	0.00296	0.00106	0.00099
25	H(1)	0.00000	0.01581	0.00564	0.00527
26	H(1)	0.00000	0.00031	0.00011	0.00010
27	H(1)	0.00000	0.01498	0.00535	0.00500
28	H(1)	0.00016	0.71573	0.25539	0.23874
29	H(1)	0.00000	0.00000	0.00000	0.00000
30	H(1)	0.00016	0.71759	0.25605	0.23936
31	H(1)	0.00000	0.01513	0.00540	0.00505

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