Electronic Supplementary Information (ESI)

π-Extended tetrathiafulvalene BODIPY (Ex-TTF-BODIPY): A redox switched "on-off-on" electrochromic system with two near-infrared fluorescent outputs

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Materials and General Methods

All chemicals were obtained from Acros chemicals or TCI America in reagent grade purity and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was dried by passage through two columns of activated alumina. Column chromatography was performed using Silicycle Silia Flash[®] P60 grade silica gel (40-63 μ M). Thin layer chromatography (TLC) analyses were performed on silica gel (glass backed, 250 μ M) or neutral alumina TLC plates (polyester backed, 200 μ M) both obtained from Sorbent Technologies.

Proton (400 MHz) and ¹³C (100 MHz) NMR spectra were measured using a Varian 400/54/ASW instrument. Chemical shifts (δ -scale) are reported in ppm relative to standard solvent shifts for CDCl₃ (7.26 ppm ¹H, and 77.2 ppm for ¹³C). UV-Vis-NIR spectra were recorded on a Cary 5000 spectrometer in a 1 cm quartz cuvette. HR-mass spectra were recorded on an Agilent 6530 Accurate Mass QTOF/LC-MS (ESI) and an Ionospec 9.4 FT-ICR (MALDI).

NIR Fluorescence Measurements

For the observation of steady-state fluorescence spectra in NIR region, photomultiplier tubes (Hamamatsu, H9170-75 and R5108), a lock-in amplifier (EG&G, 5210) combined with a mechanical chopper and a CW He-Cd laser (Melles Griot, Omnichrome 74) for photo-excitation at 442 nm were used. To estimate the fluorescence quantum yield, IR-140 (Sigma Aldrich, $\Phi_{fl} = 16.7\%$) and *meso*-hexakis(pentafluorophenyl) substituted [26]hexaphyrin ($\Phi_{fl} = 0.019\%$) were used as reference dyes for the neutral and dication forms of ex-TTF-BODIPY **1**, respectively.^{1, 2} We controlled the experimental conditions, such as the response time and the signal threshold of the lock-in amplifier, the slit widths, and the applied current for the photomultiplier tube, as well as the absorbance at the excitation wavelength (442 nm). Under identical experimental conditions, the fluorescence quantum yields were estimated to be 4.3×10^{-1} and 4.8×10^{-4} for 1 and its dication form, respectively (Table S1).

Table S1. Experimental details associated with the fluorescence quantum yield measurements for the neutral (1) and dication forms (1^{2+}) of ex-TTF-BODIPY. Absorbance data were acquired at 442 nm, which was the excitation wavelength provided by a CW He-Cd laser.

	Absorbance (O.D.)	Integrated Fluorescence Intensity	Slope	Quantum Yield
neutral 1	0.00626	0.00678		
	0.01912	0.03645	1.267	4.3x10 ⁻¹
	0.03470	0.04367		
dication 1 ²⁺	0.03370	0.01167		
	0.05570	0.03016	0.323	4.8x10 ⁻⁴
	0.10675	0.03793		

Electrochemical Measurements

All CV electrochemical measurements were carried out using a CV-50 electrochemical analyzer in CH_2Cl_2 at 298 K using 0.1 M TBAPF₆ as the supporting electrolyte and a 50 mV/s scan rate. A glassy carbon working electrode was used, as well as a platinum wire counter electrode and an Ag/AgCl reference electrode. The working electrode was routinely polished using standard polishing procedures. All potentials were referenced to Fc/Fc^+ by direct in situ measurements. Spectroelectrochemical measurements were performed using a specialized 1 mm path length

cuvette/electrochemical cell. A semitransparent Pt mesh was used as the working electrode, a Pt wire was used as the counter electrode and Ag/AgCl was used as the reference electrode.

Spectroelectrochemical Measurements

To correlate the changes in the absorption spectral features produced upon chemical oxidation conditions of with those seen under electrochemical analysis, spectroelectrochemical analyses were carried out (Fig. S1). For spectroelectrochemical studies, a CV-50 electrochemical analyzer was used as the potentiostat. The working electrode was platinum mess, the reference was Ag/AgCl and the counter electrode was a Pt wire. For the studies, a solution of 1 was subjected to bulk electrolysis for two minutes (starting at -50 mV (vs. Fc/Fc⁺)) in a specialized 1 mm path length cuvette with a semi-transparent platinum-mesh working electrode. Following electrolysis, an UV/vis/NIR absorption spectrum was taken. Subsequent to the absorption reading, the potential was increased anodically by 100 mV and the solution re-subjected to bulk electrolysis. This was continued until the point where the potential reached 750 mv. Above this potential, no additional changes in the absorption spectra were recorded. Following the reading at 750 mv, the potential was reversed and set again at -50 mV. After several minutes at this potential, the original spectrum was restored.

The spectra obtained under electrochemical conditions are not as well defined as those obtained when **1** is subjected to chemical oxidation. However, a good correspondence between the methods was observed. For instance, when the potential was -0.05 V, the absorption spectrum resembles that of unreacted **1** with an intense peak with $\lambda_{max} \approx 750$

nm clearly visible. As inferred from CV analysis, at this potential only the neutral form of 1 is present in solution. Upon increasing the voltage to potentials more positive than the first oxidation of **1**, an increase in the intensity of the peaks with $\lambda_{max} \approx 890$ and 1570 nm is seen. These changes closely mimic those observed after the addition of one equivalent of chemical oxidant. At +0.35 V (between the first and second oxidation waves of 1 as gauged from CV analysis), both transient peaks reach a maximum. Moreover, the peak centred at $\lambda_{\text{max}} \approx 750$ nm, corresponding to 1, is no longer visible. Thus, in analogy to what is seen under conditions of chemical oxidation, this spectrum is thought to reflect the presence of the radical cation 1^{+} . Increasing the potential to higher voltages results in an attenuation of the peaks assigned to 1^{+} and an increase in those assigned to 1^{2+} . Specifically, a broad peak at $\lambda_{max} \approx 1030$ nm is seen. At +0.75 V this peak reaches its maximum intensity. Further increases in the voltage produced no further spectral changes, as would be expected based on both the CV and chemical oxidation data. When the potential was brought back to -0.05 V and the sample was subject to bulk electrolysis for several minutes, the original spectral features were restored. This is taken as evidence that the response is reversible.



Figure S1. Spectroelectrochemical oxidation of **1** from -50 mV (red) to 750 mV (violet) in CH₂Cl₂ at 298 K. The sample was subject to bulk electrolysis for two minutes before commencing the spectroscopic reading. The sample was then subjected to further electrochemical oxidation by increasing the potentials anodically in 100 mV intervals. The values reported are referenced to Fc/Fc⁺.

Quantum Mechanical Calculations

Quantum mechanical calculations were performed with the Gaussian 09 program suite.³

All optimization calculations were carried out by the density functional theory (DFT)

method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-

Parr correlation functional (B3LYP),^{4,5} employing the 6-31G(d,p) basis set. In the cases

of oxidized forms $(1^{+} \text{ and } 1^{2^{+}})$, the possible spin states and multiplicities were estimated.

Calculated and Energetic Band Gap Values

Energetic band gap values from calculations carried out in the absence of solvation and other experimental effects, along with those obtained from the optical and electrochemical analyses are given in Table S2. A schematic representation of the calculated band gaps is given in Figure S2.



Figure S2. DFT calculation of a) **1**, b) $\mathbf{1}^+$, and c) $\mathbf{1}^{2+}$ using the B3LYP functional with the 6-31G(d,p) basis set. The energy gaps (ΔE) are the calculated energetic differences between the HOMO and LUMO in the absence of solvation or other experimental affects.

Туре	Calculated	Optical	Electrical
1	2.34 V	1.64 V	1.41 V
1· ⁺	2.26 V (α spin)	0.79 V	0.27 V
	0.54 V (β spin)		
1^{2+}	0.45 V (singlet)	1.20 V	NA
	2.06 V (triplet, α		
	spin)		
	0.90 V (triplet, β		
	spin)		

Table S2. Calculated and experimental band gaps for $1, 1^{+}$, and 1^{2+}



Figure S3. Frontier molecular orbital (MO) structures of 1 and its oxidized forms.

Synthetic Procedures

1,9-Diformyl-5-phenyldipyrromethane (4)

Compound 4 was prepared following synthetic protocols similar to those previously reported.⁶ Briefly, 500 mg (1.80 mmol) of 5-phenyldipyrromethane was dissolved in 30 mL of toluene and the mixture was heated to 90 °C until the compound was completely dissolved. While maintaining the temperature at 90 °C, 600 mg (2.64 mmol) of 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added and the solution was stirred for 1 h. At this point, TLC analyses (1:3 ethyl acetate:hexanes, eluent) revealed that nearly all of the starting material had been consumed. The reaction flask was removed from the heat source and allowed to cool for 10 minutes. Then, 2.20 mL (15.8 mmol) of triethylamine, followed in rapid succession by 2.0 mL (16.2 mmol) of BF₃•Et₂O, were added to the solution. Immediately, a fluorescent product was observed. The solution was stirred for a further 30 min and then evaporated to dryness. The residue was purified by column chromatography over silica gel using 1:3 ethyl acetate:hexanes ($R_{\rm f} = 0.4$) as the eluent. The product, compound 4, was isolated as a bright yellow-orange solid. ¹H NMR $(CDCl_3, 400 \text{ MHz}, 298 \text{ K})$: δ 7.14 (d, $J = 4.3 \text{ Hz}, 2\text{H}, \beta$ -H), 7.23 (d, $J = 4.3 \text{ Hz}, 2\text{H}, \beta$ -H), 7.40–7.55 (m, 5H, Ph-H), 10.51 (br s, 2H, CHO). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 120.4, 129.7, 130.5, 131.5, 132.8, 138.0, 144.1, 149.9, 153.8, 184.3. HRMS-Positive-ESI: m/z 278.1042. Calcd.: 278.1055.

Ex-TTF-BODIPY (1)

In anhydrous THF, under a nitrogen atmosphere, 215 mg (0.65 mmol) of phosphonate ester 3^7 , was dissolved. The solution was then cooled to -78 °C in a dry ice/acetone bath. At this time, 0.3 mL (0.75 mmol) of a 2.5 M solution of *n*-butyllithium in hexanes was

slowly added to the reaction *via* a syringe. After this, the solution was stirred for 30 min. Then, 100 mg of **4** (0.31 mmol) was added, the cooling bath was removed, and the reaction was allowed to warm to room temperature. After stirring at room temperature for 30 min, the solvent was evaporated using a rotary evaporator. The resulting residue was dissolved in dichloromethane and extracted twice with water and then an additional time with a saturated aqueous NaCl solution. The solvent was removed under reduced pressure and the residue was purified via flash column chromatography (30% hexanes in ethyl acetate, eluent) over silica gel. The second spot, light maroon in color, was collected and was found to be the desired product.⁸ ¹H NMR (CDCl₃, 400 MHz, 298 K): δ 2.45 (s, 6H, S-Me), 2.48 (s, 6H, S-Me), 6.68 (d, *J* = 4.2 Hz, 2H, β -H), 6.77 (d, *J* = 4.2 Hz, 2H, β -H), 7.20 (s, 2H, vinyl-H), 7.45–7.55 (m, 5H, Ph-H). ¹⁹F NMR (CDCl₃, 400 MHz, 298 K): δ –141.9 (q, ¹*J*(F-B), 2F) ¹³C NMR δ 19.5, 19.6, 96.1, 105.9, 117.6, 126.3, 127.9, 129.0, 129.4, 130.7, 134.9, 135.7, 136.0, 143.6, 150.4. HR-MS-Positive-MALDI-Found: 679.9711. Calcd. 679.9688. MP > 200 °C.



Figure S4. ¹H NMR spectrum (400 MHz) of ex-TTF-BODIPY **1** recorded in CDCl₃ at 298 K.



CDCl₃ at 298 K.

Notes and References

- 1. K. Rurack, M. Spieles, Anal. Chem. 2011, 83, 1232.
- T. K. Ahn, J. H. Kwon, D. Y. Kim, D. W. Cho, D. H. Jeong, S. K. Kim, M. Suzuki, S. Shimizu, A. Osuka, D. Kim, *J. Am. Chem. Soc.*, 2005, **127**, 12856.
- Gaussian 09, Revision A.02. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J.

Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K.
Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N.
Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J.
Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C.
Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A.
Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B.
Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

- 4. A. D. Becke, J. Chem. Phys. 1993, 98, 1372.
- 5. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, 37, 785.
- N. Pereira, A. C. Serra, M. Pineiro, A. M. d'A. Rocha Gonsalves, M. Abrantes, M. Laranjo, and F. Botelho, *Porphyrins Phthalocyanines* 2010, 14, 438.
- 7. A. J. Moore, and M. R. Bryce, J. Org. Chem. 1994, 59, 6847.
- 8. Compound 1 must be columned quickly on silica gel. Leaving compound 1 on the column for prolonged periods of time led to degradation and the formation of an uncharacterised blue-green decomposition product, which was intensely colored and had a slower retention time. Additionally, dichloromethane and chloroform solutions of 1 left on the bench and exposed to light at room temperature led to the formation of a similar blue-green product over several hours. However, thoroughly drying 1 after isolation gave a bench stable crystalline compound. Additionally, dichloromethane and chloroform solutions of 1 that were carefully protected from light or stored at low temperature (277 K) proved stable for weeks.