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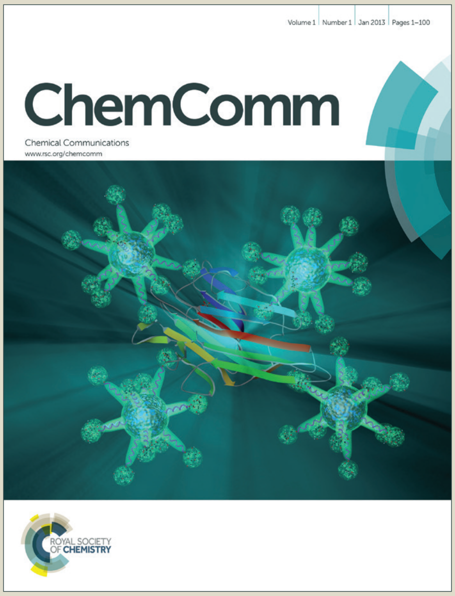

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π-Extended tetrathiafulvalene BODIPY (Ex-TTF-BODIPY): A redox switched "on-off-on" electrochromic system with two near-infrared fluorescent outputs

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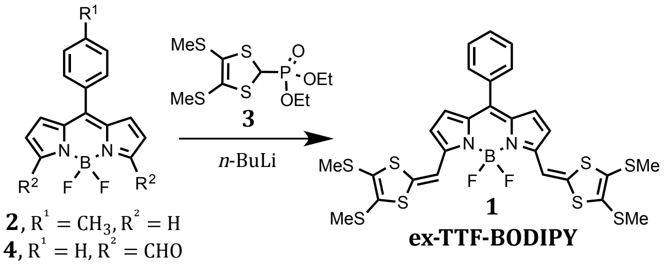
A π-extended tetrathiafulvalene-boradiazaindacene chimera, ex-TTF-BODIPY, has been prepared. The resulting system undergoes sequential one-electron oxidations, allowing access to both the mono-oxidized radical cationic and dicationic states. Additionally, ex-TTF-BODIPY displays electrochromic and electrofluorochromic behaviour in the near-IR portion of the electromagnetic spectrum and functions as a redox switched "on-off-on" emissive system.

The development of materials that absorb and/or emit light in the near-infrared (NIR) portion of the electro-magnetic spectrum is of current interest on account of their applicability in materials science, biochemistry and medical applications.[1] Of particular utility would be systems whose emission features could be controlled through application of an external stimulus. Such NIR active systems might see application as biological sensors or as sources of light at key communication wavelengths, among others.[1] One approach to achieving control over the fluorescence emission is through the use of redox active fluorophores.[2] These systems could, in principle, allow for the creation of reversible luminescence switches with multiple fluorescent "on" states coupled with a single "off" state. However, to date, only a small number of three-state electrofluorochromic organic systems have been reported.[3] Moreover, to the best of our knowledge, three-state organic systems that emit in the NIR[4] or which display redox-switchable "on-off-on" (as opposed to "on-on-off") features have yet to be described. Here we report an extended tetrathiafulvalene (TTF) boradiazaindacene (BODIPY) analogue, ex-TTF-BODIPY (**1**), that permits access to a strong "on," "off," and a second, weaker "on" NIR emissive state.

BODIPY (e.g., **2**) and its derivatives are a class of molecules that exhibit large absorption coefficients, high fluorescence quantum yields and excellent photostability and are thus frequently employed as dyes.[5] However, in unmodified form they absorb and emit at wavelengths shorter than 600 nm, precluding their use in NIR applications. Recent efforts to reduce the optical band gaps of BODIPYs, thereby pushing the emission to the red, include: i) re-placing the meso carbon with a nitrogen atom (forming aza-BODIPYs), ii) extending the π-conjugation pathway, via substitution or annulation, iii) substituting the central pyrrolic core with electron-donating groups and iv) rigidifying the BODIPY skeleton.[5,6] As yet, however, no redox switchable NIR-emitting systems have been reported as the result of these kinds of synthetic modifications.

Recently, several redox active fluorophore systems based on BODIPYs were published. These include ferrocene-,[7] flavin-[8] and TTF-appended[9] electrofluorochromic sensors whose optical response is "switched-on" upon oxidation of the molecules respective electron donor moieties. Unfortunately, the optical window of these systems lies outside (below) the NIR window. To address this latter deficiency, we have elected to "insert" a BODIPY subunit directly "into" the TTF skeleton. The resulting functionalized boradiazaindacene (ex-TTF-BODIPY, **1**) was expected to exhibit red-shifted absorption and emission properties, as a result of the appended electron donating dithiolidene rings and extended conjugation pathway. Further, the conjugated BODIPY core was expected to confer electronic communication between the dithiolidene rings, similar to other π-extended TTFs ("exTTFs").[10] The result, we anticipated would be a NIR-emitting system whose features could be tuned via redox modulation. As detailed below, these design expectations were met. Moreover, we have found that the ex-TTF-BODIPY approach allows controlled access to a set of strong "on," "off," and weaker "on" fluorescent states through stepwise oxidation of the dithiolidene subunits.



Scheme 1 Synthesis of Ex-TTF-BODIPY 1.

The synthesis of **1** (Scheme 1) entails a Horner-Wadsworth-Emmons type coupling of phosphonate ester **3**[11] with 1,9-diformyl-5-phenyl BODIPY **4**.[12] Deprotonation of **3** with *n*-BuLi,[13] followed by addition of **4**, resulted in the formation of **1** in 85% yield. The ultraviolet/visible/near infrared (UV/Vis/NIR) absorption spectrum of **1** was recorded in CH_2Cl_2 at 298 K and is shown in Fig. 1a. Ex-TTF-BODIPY **1** is characterized by an absorption maximum in the

NIR spectral region (λ_{max} = 754 nm) with less intense bands being observed throughout the visible region. The molar absorptivity at 754 nm is ε = 96,000 M^{-1} cm^{-1}, a value leading us to propose that **1** absorbs NIR radiation efficiently. The steady-state emission spectrum of **1** was measured (Fig. 2) by exciting the sample at the absorption maximum (754 nm) in CH_2Cl_2 at 298 K. A sharp fluorescence emission signal was observed under these conditions with a λ_{max} = 803 nm and an estimated fluorescence quantum yield of 0.43 (Table S1). This λ_{max} value is among the most red shifted (lowest energy) reported for BODIPY derivatives.[14]

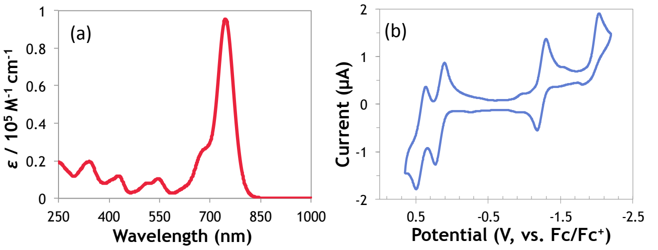


Fig. 1 (a) UV/vis/NIR absorption spectra of **1** recorded in CH_2Cl_2 at 298 K and (b) CV of a 1 mM CH_2Cl_2 solution of **1** at 298 K recorded in the presence of $TBAPF_6$ (100 mM) as the supporting electrolyte. Glassy carbon working electrode, Pt wire auxiliary electrode and Ag/AgCl reference electrode. Values reported are referenced to an internal Fc/Fc^+ standard.

The redox chemistry of **1** was studied (Fig. 1b) by cyclic voltammetry (CV) in CH_2Cl_2 at 298 K. Two, one-electron reversible oxidation waves are observed. The first (E^1_{ox}) is centred at ca. +0.17 V (vs. Fc/Fc^+), while the second (E^2_{ox}) is seen at ca. +0.44 V. The significant separation (> 0.25 V) between E^1_{ox} and E^2_{ox} is taken as an indication that the mono-oxidized radical cation state is accessible under these experimental conditions.

In previously reported π-extended TTFs with conjugated bridging moieties, the degree of Columbic repulsion between the positive charges localized on the oxidized dithiole rings was cited as the key factor leading to experimentally observed separation of the oxidation waves.[10] Although a large decrease in the E^2_{ox} - E^1_{ox} difference is seen for **1** (~0.27 V) as compared to pristine TTF (0.39 V),[15] the separation between the oxidation waves found in the case of **1** is larger than other π-extended TTFs separated by just a single double bond (0.16 V).[15,16] On this basis, we conclude that the separation in **1** is greater than what would be expected based on purely Columbic repulsion effects and most likely reflects the formation of a quinoidal structure (Scheme 2) in the case of $\mathbf{1}^{2+}$ and commensurate destruction of the aromaticity of one of the pyrrolic rings.

The reduction chemistry of **1** was also investigated by cyclic voltammetry and was found to be similar to that reported for unsubstituted BODIPY **2**.[12] For both **1** and **2**, the first reduction (E^1_{red}) processes are reversible and occur at nearly identical potentials (−1.24 and −1.25 V[17] vs. Fc/Fc^+ for **1** and **2**, respectively). Additionally, the second reduction potentials (E^2_{red}) of both **1** and BODIPY **2** are irreversible. However, that of **2** is considerably cathodically shifted (−2.29 V[17] vs. ca. −2.0 V).

Although the reduction chemistries of **1** and **2** are relatively similar, the oxidation chemistries of the two compounds are drastically different. Explicitly, the first oxidation wave for **2** appears at +1.23 V vs. Fc/Fc^+, a value 1.05 V higher than that for **1**. The net result is that **1** has a reduced band gap compared to **2**.

Oxidative titrations of **1** with tris(4-bromophenyl)aminium hexachloroantimonate ("magic blue") in CH_2Cl_2 at 298 K were followed (Fig. 3) by absorption spectroscopy. Upon treatment of **1** with increasing amounts of magic blue, the intensity of the band at λ_{max} = 754 nm was attenuated. Concurrently, increases in the intensities of a sharp, strong band at λ_{max} = 886 nm and a weaker, broad band at λ_{max} = 1572 nm were observed.[18] These changes in optical signature continued until one molar equivalent of magic blue had been added. At this point the original 754 nm band was no longer observed. Additionally, the newly formed peaks reached maximal intensity. Broad absorption bands at NIR wavelengths are diagnostic of TTF radical-cations.[19] Thus, the spectra obtained after addition of one equivalent of magic blue is assigned to the one-electron oxidized species $\mathbf{1}^{\bullet+}$.

The addition of further oxidant resulted in a decrease in the intensity of the peaks assigned to $\mathbf{1}^{\bullet+}$. However, the intensity of a broad band with λ_{max} = 1032 nm was seen to increase. This latter spectral feature is assigned to the two-electron oxidized dication $\mathbf{1}^{2+}$. After two molar equivalents of oxidant had been added, the peak attributed to $\mathbf{1}^{2+}$ reached maximal intensity. Further addition of oxidant resulted in no additional spectral changes associated with **1** or its oxidized daughter products. However, the intensity of the peak with λ_{max} = 700 nm, attributed to unreacted magic blue, increases as further equivalents of oxidant were added (data not shown).[20]

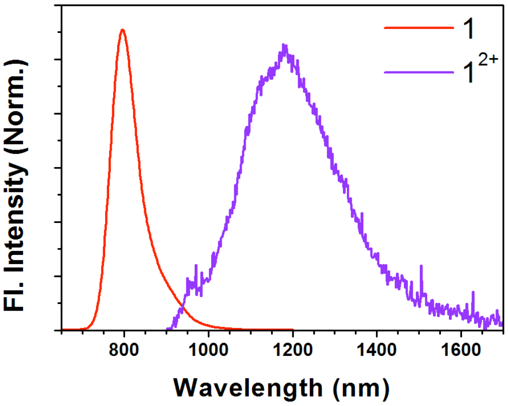
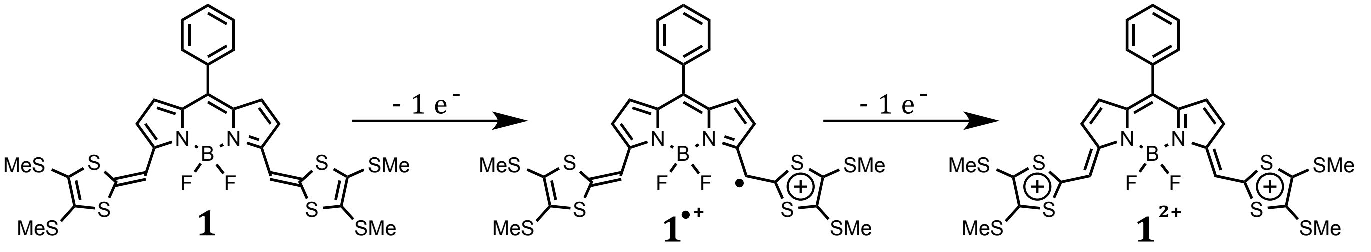


Fig. 2 Emission spectra of **1** (red) and $\mathbf{1}^{2+}$ (violet) as recorded in CH_2Cl_2 at 298 K. Excitation was carried out at 442 nm.

To correlate the changes in the absorption spectral features produced upon chemical oxidation with those seen under conditions of electrochemical analysis, spectroelectrochemical analyses were carried out (Fig. S1). Good correspondence between the methods was observed. Specifically, spectra closely resembling those assigned to **1**, $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$ from the spectral titration with magic blue were recorded after subjecting a sample of **1** to bulk-electrolysis at −0.05 V, + 0.35 V, and +0.75 V, respectively. 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. We thus propose that the response is reversible.

In agreement with the spectral changes seen during the oxidative titration and electrochemical analyses, molecular orbital (MO) calculations revealed reduced energy gaps between the HOMO and LUMO upon oxidization (Figs. S2 and S3; Table S2). The unprecedented low-lying absorption features of ex-TTF-BODIPY **1** are supported by the calculated MO structures. Specifically, these analyses reveal that an extension of the conjugation pathway, along with charge transfer (CT) interactions involving the electron donating dithiolidene rings, serve to lower the optical band gap. In the case of $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$, localization (and/or delocalization) of electron density onto the dithiolidene rings of the ex-TTF-BODIPY most likely results in the observed variations in the absorption spectra of the two oxidized forms of **1**. However, in all cases the calculated band gaps were substantially larger than the experimentally derived optical and/or electrical band gaps (see Table S2). This could reflect the fact that the calculations do not account for solvation or other effects associated with the actual experimental measurements. The calculations also revealed the presence of a reversed CT effect, involving charge transfer from the BODIPY moiety to the dithiolidene rings. This finding may account for the energetically stabilized dithiole rings generated upon oxidation.



Scheme 2 Stepwise oxidation of ex-TTF-BODIPY **1** to **1**$^{2+}$.

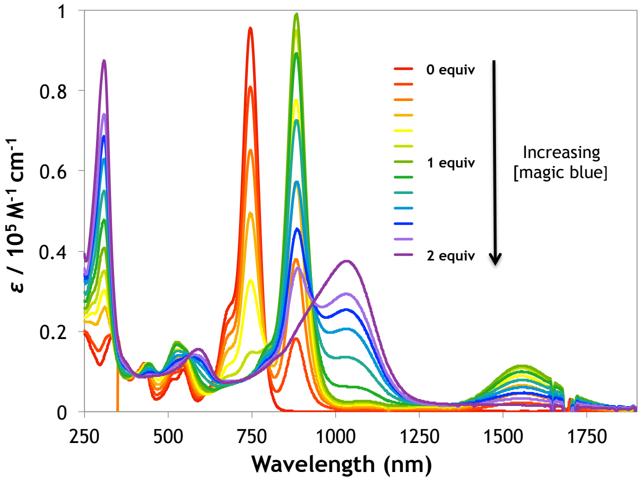


Fig. 3 Oxidative titrations of **1** with tris(4-bromophenyl)aminium hexachloroantimonate ("magic blue") in CH_2Cl_2 at 298 K. Of particular note are the spectra of pristine **1** (red), that recorded after one molar equivalent of magic blue has been added (yielding **1**$^{\bullet+}$, yellow-green), and the spectrum produced when two equivalent of magic blue have been added (giving **1**$^{2+}$, violet).

The change in the fluorescence intensity of **1** was also monitored under conditions of chemical oxidation. Addition of magic blue to a CH_2Cl_2 solution of **1** at 298 K, led to the attenuation of the signal at 803 nm. At the point when one molar equivalent of oxidant had been added (corresponding to the full conversion to **1**$^{\bullet+}$), the fluorescence signal at 803 nm was no longer detectable. Additionally, no new fluorescence signature was observed for **1**$^{\bullet+}$. It is thus considered to be a non-fluorescent "off" state of **1**.

Upon the addition of a second molar equivalent of oxidant, leading to the formation of **1**$^{2+}$ as inferred from the absorbance titration studies noted above, the appearance of a new, NIR fluorescence signal, albeit weak, was evident (Fig. 2). This emission peak extends from approximately 950 nm to 1450 nm with a $\lambda_{max} \approx 1185$ nm and an estimated fluorescence quantum yield of 4.8 x 10^{-4} (Table S1). To the best of our knowledge, this is the longest wavelength emission for a BODIPY derivative recorded to date.[14] The weak fluorescence is thought to result from a combination of factors, such as an increase in molecular rotation, a heavy atom effect attributed to the $SbCl_6^-$ counteranions, and the charges present on the dithiolium rings as revealed by the calculated MO structures (cf. Supporting Information).

In summary, ex-TTF-BODIPY **1** displays electrochromic and electrofluorochromic behavior that extends well into the NIR region of the electromagnetic spectrum. The neutral and dicationic states of **1** are fluorescent, whereas the one-electron oxidized state, **1**$^{\bullet+}$, is non-fluorescent. As a result, **1** acts as a redox switchable "on-off-on" fluorophore. The "on" states emit at dissimilar wavelengths, allowing for the states to be distinguished from one another. Optimization of the electronics and improvement of the fluorescence quantum yields could allow these types of molecules to find use in a variety of application areas, such as Bolean logic-gates, optical limiters, smart windows, and biochemical probes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: details of the methods, synthesis and characterization of all compounds, as well as spectroelectrochemical, and fluorescence quantum yield data. See DOI: 10.1039/c000000x/

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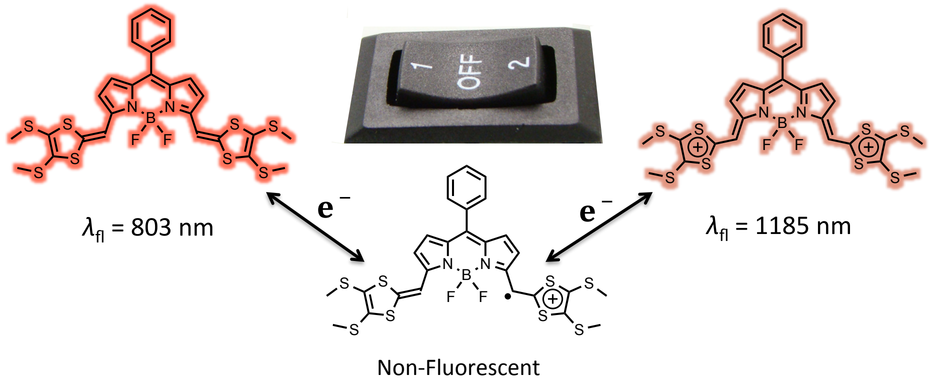

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