New Redox Stable Low Band Gap Conjugated Polymer Based on an EDOT−BODIPY−EDOT Repeat Unit

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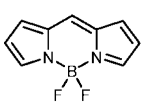
The compound 4,4-difluoro-4-borata-3*a*-azonia-4*a*-aza-*s*-indacene, more commonly known as BODIPY, has enjoyed a high and rapidly escalating level of interest over the past decade.[1] This dye-type material, which can be likened to a porphyrin subunit, has been studied mainly in applications related to its strong absorption and fluorescence properties.[2,3] Recent examples of the applications of BODIPY include biological tags with visible/near IR emission,[4,5] mechanical rotors,[6] lasing,[7−9] dye sensitized solar cells,[10] electroluminescence (EL),[11] and electrogenerated chemiluminescence (ECL).[12]



BODIPY

The incorporation of the BODIPY unit into conjugated polymers (CPs) is a fascinating prospect. In particular, the strong absorption/emission and tunable color characteristics[13] of BODIPY derivatives mark them as ideal components in copolymers for electrochromic, optoelectronic, and organic solar cell devices. To the best of our knowledge, BODIPY has not been studied as a main chain component in conjugated macromolecular structures, although an organoboron polymer[14] and a BODIPY−quaterthiophene−BODIPY triad have been reported[15] and a series of BODIPY dyes have been used in blends with CPs for organic solar cell devices.[16] In addition to their electronic properties, BODIPY derivatives also exhibit variable redox chemistry, and they have been used as electron donors[17] and acceptors.[18] In the latter case, BODIPY comonomers have the potential of lowering the band gap of CPs (and stabilizing their reduced states), since donor and acceptor units within conjugated structures are able to bring the HOMO/LUMO energy levels closer together. For organic solar cell applications low band gap CPs are highly desirable, but the stability of doped states is often poor in such materials. A recent and appropriate example is given by poly(acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine),[19] which has a remarkably low band gap of approximately 0.5 eV but demonstrates very poor reversibility upon p-doping.

In this work, we report the synthesis of a conjugated polymer containing the BODIPY structure as a main chain component. The material has a low band gap of approximately 0.8 eV, and the reversibility of both n- and p-doping processes in this polymer is outstanding. The synthesis of the monomer unit (**3**) is summarized in Scheme 1. Functionalization of the BODIPY unit with 3,4-ethylenedioxythiophene (EDOT) was chosen because of the well-known facile electropolymerizability of the EDOT unit and its derivatives.[20] A mixture of 3,5-dichloro-8-(4-nitrophenyl)-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene **1**,[21] 2-(trimethyltin)-3,4-ethylenedioxythiophene **2**,[22] and tetrakis(triphenylphosphine)palladium(0) was reacted in anhydrous DMF over 2 h at 160 °C via microwave assisted heating. The product was purified by column chromatography and recrys-

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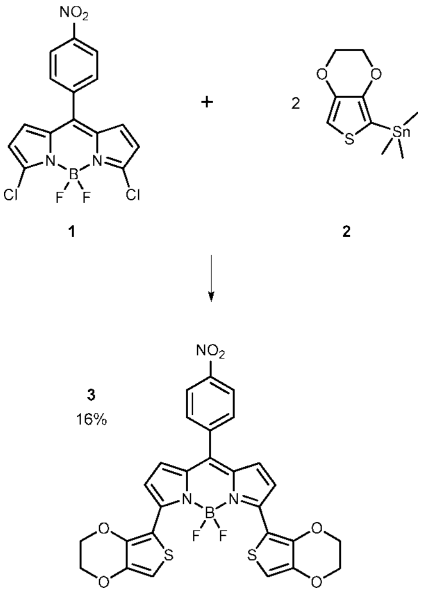
Scheme 1[a]



[a] Reagents and conditions: Pd(PPh$_3$)$_4$, DMF, microwave, 2 h, 160 °C.

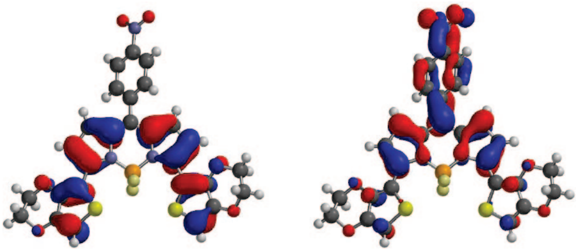


Figure 1. HOMO (left) and LUMO (right) frontier orbitals of compound **3**.

tallized from ethyl acetate/hexane to give a deep red crystalline solid (**3**, 16% yield).[23]

The redox properties of monomer **3** were assessed using cyclic voltammetry. The compound undergoes two irreversible oxidations at +0.40 and +1.07 V, one reversible reduction at $E^{1/2} = -1.20$ V, and a second irreversible reduction at −2.42 V (values quoted vs ferrocene in dichloromethane solution, using glassy carbon as the working electrode and TBAPF$_6$ as the electrolyte). DFT calculations performed at the B3LYP/6-31G* level (SPARTAN 08) indicate that the oxidation site is localized on the EDOT−pyrrole units, while electrons are injected into the BODIPY core (Figure 1). The HOMO and LUMO plots clearly indicate an intramolecular charge transfer (ICT) pathway between the two conjugated segments of the molecule, a process which has been observed previously in a donor−acceptor BODIPY derivative.[10] Noticeably, there is a significant contribution from the nitrophenylene group in the LUMO, despite the large twist angle between the nitrophenylene group and the BODIPY core (ca. 129°), due to steric repulsion between aromatic protons. The EDOT units are also twisted out of the plane of the aromatic BODIPY segment (ca. 28−35°). Here, the thiophene rings are arranged with the sulfur atoms interacting with the BF$_2$ functionality through noncovalent S···F short contacts (2.84 Å, sum of the van der Waals radii for S and F = 3.45 Å[24]). Since the fluorine atoms point away from the plane of the aromatic pyrroles, such an intramolecular interaction could well be responsible for the nonplanar arrangement between EDOT and pyrrole rings.

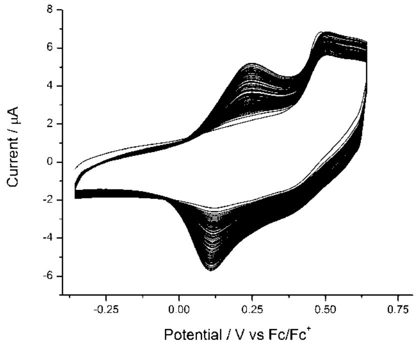


Figure 2. Electropolymerization of compound **3** (ca. 10^{-4} M) on a glassy carbon working electrode in dichloromethane solution, using a Pt wire counter electrode, Ag wire pseudoreference electrode, and *n*-tetrabutylammonium hexafluorophosphate as the electrolyte (0.1 M).

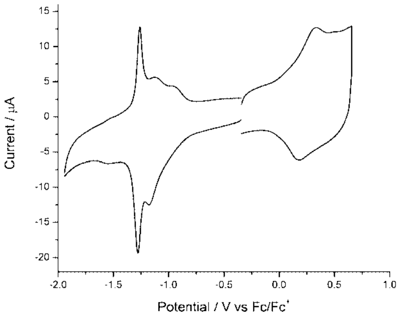


Figure 3. Cyclic voltammogram of poly(**3**) deposited on a glassy carbon electrode in acetonitrile solution, using a Pt wire counter electrode, Ag wire pseudoreference electrode, and *n*-tetrabutylammonium hexafluorophosphate as the electrolyte (0.1 M).

Compound **3** was polymerized via electrochemical oxidation by repetitive cycling over the first oxidation wave. The growth of the polymer over 50 cycles is presented in Figure 2, which shows an increase of current with each cycle and the development of a new peak at a lower oxidation potential, due to the lower oxidation potential of the emerging polymer. Under these conditions, the film thicknesses were in the range 100−300 nm, whereas 150 cycles gave films with 400−500 nm thickness.

The redox properties of the polymer were investigated by cyclic voltammetry in monomer-free acetonitrile solution (Figure 3). The repeat unit within the polymer chain is represented by a bis-EDOT unit bonded to the BODIPY system. On the basis of the well-known electron donating properties of EDOT oligomers and the HOMO plot of compound **3**, the broad oxidation wave (E_{pa} +0.34 V, E_{pc} +0.18 V) is attributed to the removal of electrons from bis-EDOT components. The onset of this redox wave (−0.12 V) gives a HOMO value of −4.68 eV for poly(**3**) (given

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(23) Experimental data for compound **3**: mp 311−312 °C. Found: C, 54.79; H, 3.18; N, 7.45. $C_{27}H_{18}BF_2N_3O_6S_2$ requires: C, 54.65; H, 3.06; N, 7.08%. MS LDI-TOF [M]$^+$ 593.03. ^{1}H NMR (CDCl$_3$): 8.37 (2H, d, J = 8.75 Hz), 7.71 (2H, d, J = 8.7 Hz), 7.25 (2H, d, J = 4.5 Hz), 6.72 (2H, s), 6.65 (2H, d, J = 4.5 Hz), 4.35 (4H, m), 4.27 (4H, m).

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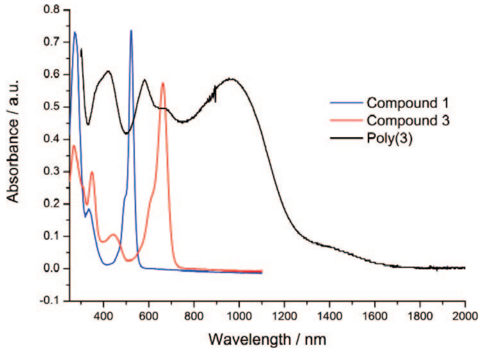

Figure 4. Absorption spectra for compounds **1**and **3** in dichloromethane solution and poly(**3**) as a thin film.

that the HOMO of ferrocene is −4.8 eV). Reduction of the polymer is more complex, and the voltammogram shows at least three coalesced processes with the two most prominent waves giving half-wave potentials of −1.27 (ΔE_{pc-pa} 60 mV) and −1.42 V (ΔE_{pc-pa} 20 mV). The onset of the first reduction process (−0.92 V) represents a LUMO of −3.88 eV, giving an electrochemical band gap of 0.8 eV for poly(**3**). Remarkably, both oxidation and reduction processes for the polymer are highly reversible.

The absorption spectra of compounds **1** and **3** (dichloromethane solution) and poly(**3**) (thin film) are shown in Figure 4. Compound **1** displays absorption maxima at 274, 335, 493 (sh), and 522 nm (62 700 M^{-1} cm^{-1}). In **3** the shape of the spectrum is very similar, with all but the shortest wavelength peak red-shifted. The longest wavelength band has a maximum at 662 nm (55 500 M^{-1} cm^{-1}), with a shoulder at 611 nm. The longest wavelength peak is attributed to an intramolecular charge transfer process between the EDOT units and the central dipyrrolo structure. An additional peak is also identified at 443 nm, due to the introduction of the EDOT units. The solution state emission spectra (in dichloromethane) for the two compounds gave peak maxima at 543 nm for **1** and 676 nm for **3** (see Supporting Information). The quantum yields were determined to be 0.56 for **1** and 0.05 for **3**, showing that the emission is significantly quenched by the EDOT units. The absorption spectrum of poly(**3**) was recorded at −0.2 V (vs Ag) in a spectroelectrochemical cell, since the polymer is easily air-oxidized and this potential corresponds to the neutral state. The spectrum extends well into the near IR and gives broad bands centered at 417, 580, and 966 nm. There is evidence of slight oxidation of the polymer from a shallow band that extends over the region of 1295−1589 nm. This complicates the determination of the onset wavelength of the main band at 966 nm, but the range covers 0.78−0.96 eV which is close to the band gap determined by cyclic voltammetry.

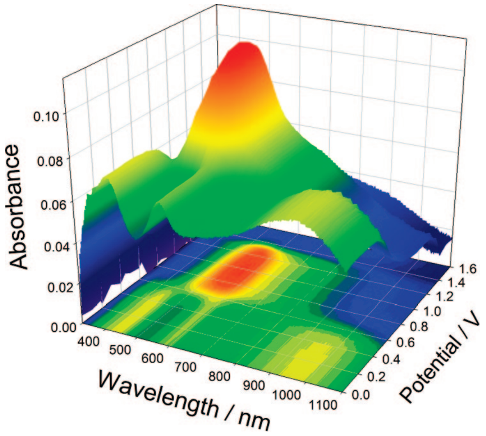

Figure 5. UV−vis spectroelectrochemical plot of poly(**3**) over the oxidation wave of the polymer. The potentials are referenced vs Ag wire pseudoreference electrode; the solvent was acetonitrile.

To investigate the p-doping process more thoroughly, poly(**3**) was grown on indium doped tin oxide (ITO) glass, and UV−vis spectroelectrochemical experiments were carried out from 0 to +1.6 V (Figure 5). It is clear from this experiment that the oxidation of the polymer changes the electronic properties of the conjugated system dramatically. A fresh peak (cf. Figure 4) is observed immediately at 590 nm, representing the initial removal of electrons from the bis-EDOT units and the generation of polarons. At higher potentials (>+0.6 V), the peaks at 417, 580, and 966 nm diminish with the concomitant growth of a new strong peak at 562 nm. The latter is the signature of a localized bipolaron state, located within the pyrrole--(EDOT)$_2$−pyrrole repeat unit. Visually, the polymer changes from a green color to a pink−violet state through the course of this experiment. Above +1.4 V, the polymer dissolves into the bulk solution, presumably due to the highly charged state attained at this potential. Stability studies at lower potentials show that there is a loss of 29% in electrochemical activity between −0.35 V and +0.65 V (oxidation) and 35% between −1.55 V and −0.35 V (reduction), over 250 repetitive cycles (see Supporting Information).

In conclusion, we have presented the synthesis of a conjugated polymer incorporating the BODIPY unit. The highly efficient absorption characteristics of the dye molecule make such polymers highly attractive for organic photovoltaic devices. Moreover, as a comonomer unit with EDOT, this fascinating molecule provides a low band gap polymer in which both reduction and oxidation processes are reversible.

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Supporting Information Available: Polymer redox stability studies and PL spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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