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Azadipyrromethene-Based Conjugated Oligomers with Near-IR Absorption and High Electron Affinity

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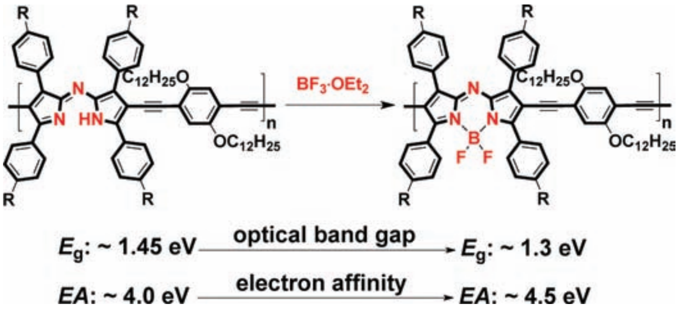
ABSTRACT



Solution-processable conjugated oligomers incorporating red-light absorbing azadipyrromethenes (aza-DIPY) within the main chain were synthesized via palladium-catalyzed Sonogashira coupling reactions. Thin films of these compounds absorbed light up to ∼1000 nm and displayed reversible reductions as ascertained by cyclic voltammetry experiments. Reactions with trifluoroboron etherate yielded materials displaying a unique combination of good solubility in organic solvents, low optical band gaps (∼1.3 eV), and high electron affinity (∼4.5 eV).

Conjugated molecules and polymers continue to attract the attention of scientists due to their semiconducting properties that make them suitable for a range of electronic applications, including photovoltaics, field-effect transistors, light emitting diodes, electrochromics, light detectors, and sensors.[1] Their main advantage over their inorganic counterparts is that they can be solution-processed to give flexible, lightweight functional films, allowing for low-cost and large scale production.[2] In several organic electronic applications, both electron-donating (*p*-type) and electron-accepting (*n*-type) materials are critical, yet most high-performance conjugated compounds are *p*-type.[3] Stable *n*-type conjugated compounds with high electron affinity ($EA > 4$) are still relatively rare.[4] Most electron-accepting materials are either fullerene-based or with fluorocarbon, cyano, or imide electron-withdrawing groups.[3,5] Examples incorporating electron-deficient boron in the main chain are also emerging.[6] Of the limited number of *n*-type conjugated compounds available to date, very few combine solution processability and low band gaps < 1.5 eV.[7] Compounds with this unique combination of properties would be especially desirable for organic photovoltaics (OPV), where current best OPVs do not significantly harvest sunlight at longer wavelengths, i.e. > 750 nm, or

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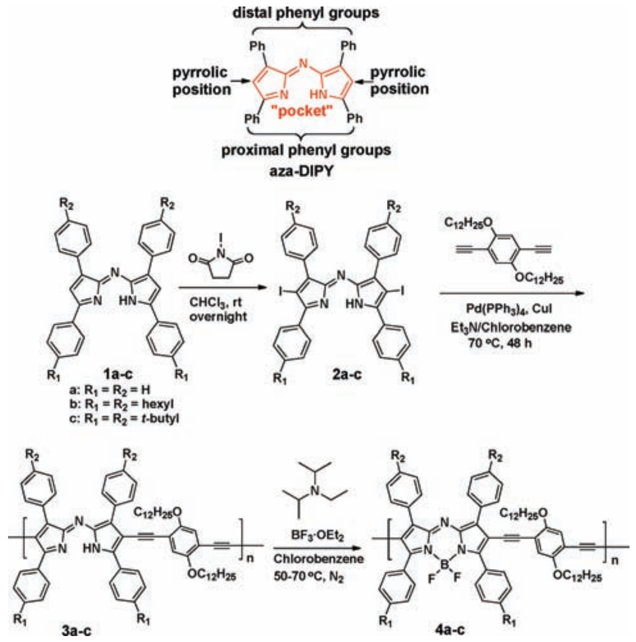
< 1.6 eV,[8] and where the dominant electron acceptors are fullerene derivatives that do not absorb light at these longer wavelengths.[9]

Here, we explore using red-light absorbing tetraphenylazadipyrromethene (aza-DIPY, Scheme 1) dyes[10] as building blocks for the synthesis of *n*-type conjugated materials with low band gaps and high electron affinity. Aza-DIPYs are particularly interesting because they are easy to reduce.[11] In addition, the strong coordinating properties of the "pocket" nitrogens in azadipyrromethene molecules allow their electronic properties to be readily tuned.[12] Aza-DIPY dyes are often chelated with BF_2 (aza-BODIPY) to red-shift light absorption by reducing rotational freedom at the core.[13] Complexation with BF_2 also shifts the reduction potential positive, thus increasing electron affinity.[11] We are aware of only one study that has incorporated aza-BODIPY dyes into conjugated polymers by polymerization of 1,4-diethynyl-2,5-dialkyloxybenzene with aza-BODIPY molecules where the reactive halogen is on either the distal or proximal phenyl rings of aza-BODIPY.[14] Due to extension of the conjugation length, these conjugated polymers showed near-IR photoluminescence in solution. To our knowledge, linear conjugated polymers with aza-DIPY and aza-BODIPY dyes incorporated into the polymer backbone through the active pyrrolic positions have not yet been studied. We synthesized alternating oligomers of aza-DIPY and phenylene acetylene. The alkyl substituents on the phenyl groups were varied to tune their solubility in organic solvents. These compounds had strong absorption throughout the visible and extending into the near-IR region and could be readily reduced. The aza-DIPY moieties were further chelated with BF_2, which further increased solubility, lowered the band gaps, and stabilized the HOMO and LUMO energy levels, resulting in materials with a unique combination of low band gaps and high electron affinity.

Scheme 1. Structure of Aza-DIPY and Synthetic Route for Conjugated Oligomers



Azadipyrromethenes **1a**–**c** (Scheme 1) were synthesized following the method developed by O'Shea and coworkers.[15] Iodination of aza-DIPYs at the pyrrolic positions was obtained in good yields by reacting the aza-DIPYs with *N*-idodosuccinimide (NIS). The synthesis of the oligomers was effected using the Sonogashira–Hagihara coupling reactions of **2a**–**c** with 1,4-bis(dodecyloxy)-2,5-diethynylbenzene in the presence of $Pd(PPh_3)_4$ (10 mol %) and CuI (10 mol %) in a mixed solvent of chlorobenzene/Et_3N (v/v = 3:1) at 70 °C for 48 h. Conjugated oligomers **3a**–**c** were obtained as metallic dark solids. ^1H NMR and MALDI TOF MS confirmed the expected structure (see Supporting Information). Chelation of aza-DIPY moieties with BF_2 were performed by reacting **3a**–**c** with excess trifluoroboron etherate in chlorobenzene at 50–70 °C under N_2 for 24 h. **4a**–**c** were isolated as black solids. The reaction did not occur at room temperature whereas, at higher temperatures, unwanted side reactions and insoluble materials resulted. Successful complexation of aza-DIPY moieties with BF_2 was confirmed by ^{19}F NMR, ^{11}B NMR, and MALDI-TOF MS. The chemical shifts in ^{19}F NMR (~ -131 ppm) and ^{11}B NMR (0.9–2.0 ppm) confirmed the tetracoordination state of the boron atom. Attempts of using **2a**–**c** chelated with BF_2 as the reacting monomers led to the loss of BF_2[16] and isolation of only a small amount of *p*-phenylene ethynylene homopolymer.

The physical properties of these materials are summarized in Table 1. **3a**–**c** were cleaned by performing a series of Soxhlet extractions with methanol, acetone, hexanes, and

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Table 1. Physical Properties of the Oligomers

	GPC[a]				
	M_n (kDa)	M_w (kDa)	PDI (M_w/M_n)	solubility[b] (mg/mL)	T_d[c] (°C)
3a	1.6	2.7	1.7	2	266
3b	3.4	6.2	1.8	9	334
3c	10	27	2.7	14.5	281
4a	2.2	4.1	1.8	2.5	260
4b	3.5	6.0	1.7	22	311
4c	11	24	2.1	25	287

[a] Determined by GPC in chloroform using polystyrene standards. [b] Measured in chlorobenzene at room temperature. [c] 5% weight loss determined by TGA under N_2.

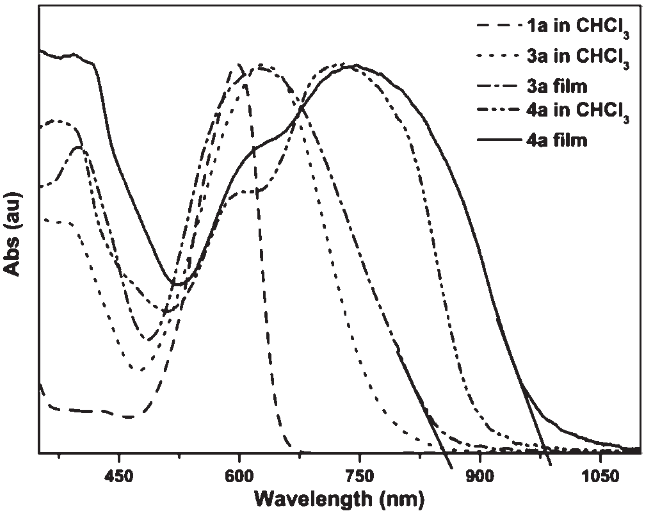

Figure 1. Absorption spectra of **1a**, **3a**, and **4a** in chloroform and **3a**/**4a** in drop-casted films. The straight lines shown were used to estimate the optical band gaps.

chloroform. Desired products were recovered from the chloroform fractions. Molecular weights estimated by gel permeation chromatography (GPC) were modest and increased with the aza-DIPY phenyl substituent in the order of H < hexyl < *tert*-butyl. Polydispersity indices (1.7–2.1) were as expected for this type of step polymerization. We hypothesize that molecular weights were limited by solubility. Conducting the reactions in THF or lowering the temperature to 50 °C yielded products with lower molecular weights. The chloroform fractions of **3a**–**c** were soluble in chlorinated organic solvents, such as chloroform and chlorobenzene, and their solubility increased as expected in the order of **3a** < **3b** < **3c**. In addition, although **3c** was thoroughly extracted with chloroform, there was still a fair amount of **3a** or **3b** left after their chloroform extraction. The leftover solids were further extracted with chlorobenzene, but the products recovered from the chlorobenzene fraction could not be fully characterized due to their limited solubility. Compared to their precursors, compounds **4a**–**c** had slightly higher molecular weights and higher solubility. All oligomers were thermally stable with 5% weight loss onsets occurring in the range of 260 to 334 °C based on thermogravimetry analysis (TGA). Differential scanning calorimetry (DSC) analysis between −90 °C and 250–300 °C showed no phase transitions, suggesting that these oligomers have very rigid chains.

The UV–vis absorption spectra for the series with unsubstituted aza-DIPY moieties (**1a**, **3a**, **4a**) are shown in Figure 1. Aza-DIPY ligands in chloroform generally had a strong narrow absorption at ~600 nm corresponding to a $\pi \rightarrow \pi^*$ transition (**1a**: λ_{max} = 596 nm, **1b**: 614 nm, **1c**: 607 nm). Incorporating aza-DIPY ligands into oligomers red-shifted the absorption maxima from 596 nm for **1a** to 624 nm for **3a** and significantly broadened the absorption spectra. This is attributed to the increased conjugation length with the phenylene ethynylene moieties. Chelation with BF_2 further red-shifted the absorption spectra to 729 nm for **4a**. All optical properties are summarized in Table 2. A deep blue thin film with a metallic tint was easily formed by drop-casting a 1 mg/mL chlorobenzene solution of **3a** onto a piece of glass. An optical band gap of 1.45 eV was calculated based on the absorption onset. The absorption spectrum of **4a** further red-shifted to the near-IR region, with an optical band gap estimated at 1.26 eV (982 nm) and absorption tailing up to 1100 nm (1.13 eV). In films, the compounds with *tert*-butyl substituents (**3c** and **4c**) showed the most red-shifted maximum absorption peaks, perhaps due to their longer conjugation length. The substituents on the phenyl rings, on the other hand, had little effect on optical band gaps. DFT calculations of model compounds (shown in Supporting Information) show that hexyl and *tert*-butyl substituents have little effect on HOMO–LUMO energy gaps. In addition, the presence of these substituents did not affect the planarity of the aza-DIPY-phenylene acetylene conjugated units.

Solutions of **3a**–**c** had negligible emission around 800 nm under ambient conditions, and complexation with BF_2 did not enhance emission intensity. This is in contrast to the report by Chujo and co-workers, where the conjugation was extended through the phenyl groups of aza-BODIPY instead of the pyrrolic positions.[14] We hypothesize that our materials, being linear, can better π-stack and form aggregates, which would quench luminescence. Consistent with this hypothesis, no emission could be detected from films of these compounds.

The electrochemical properties of the conjugated oligomers are summarized in Table 2, and cyclic voltammograms of **3a** and **4a** are shown in Figure 2. All oligomers showed two consecutive reversible reduction peaks and an irreversible oxidation peak. Chelation with electron-withdrawing BF_2 shifted the reduction and oxidation peaks positively, with a larger shift for the reduction waves. The first reduction of **4a** had an $E_{1/2}$ of −0.64 V vs Ag/Ag^+, corresponding to ~−0.34 V vs SCE. This value is more positive than $E_{1/2}$ for the first reduction of both aza-BODIPY and the aza-BODIPY dimer,[11b] consistent with

Table 2. Optical and Electrochemical Properties

	λ_{abs}[a] (nm)	λ_{abs}[b] (nm)	E_g, opt[c] (eV) (nm)	$E_{1/2}$,red (V) vs Ag/Ag$^+$	E_{pa} (V) vs Ag/Ag$^+$	HOMO[d] (eV)	LUMO[d] ($-EA$) (eV)	E_g, elec. (eV)
3a	624	625	1.45 (856)	−1.08, −1.60	0.76	−5.28	−4.06	1.22
3b	686	686	1.43 (869)	−1.15, −1.62	0.79	−5.30	−3.97	1.33
3c	678	712	1.46 (852)	−1.04, −1.67	0.97	−5.39	−4.08	1.31
4a	729	746	1.26 (982)	−0.64, −1.42	0.96	−5.47	−4.51	0.96
4b	716	738	1.25 (990)	−0.77, −1.55	1.11	−5.45	−4.40	1.05
4c	813	828	1.33 (935)	−0.63, −1.44	1.26	−5.67	−4.50	1.17

[a] Maxima in chloroform. [b] Maxima in films. [c] Estimated optical band gaps from the spectra in films. [d] HOMO and LUMO energy levels were estimated from the onset of the oxidation and reduction waves, respectively, using the value of 5.1 for Fc/Fc$^+$ vs vacuum.[17] The $E_{1/2}$ of Fc/Fc$^+$ was observed at +0.081 V vs Ag/Ag$^+$. Electron affinity (EA) was estimated as the absolute value of the LUMO energy level.

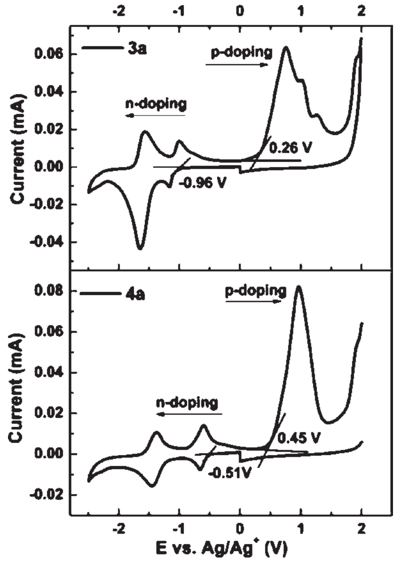

Figure 2. Cyclic voltammetry (CV) plots of **3a** and **4a** film drop-casted on a glassy carbon working electrode and measured in 0.1 M Bu_4NPF_6 acetonitrile solution using a $Ag/AgNO_3$ nonaqueous reference electrode. Straight lines illustrate how the onsets were estimated.

stabilization of radical anions through either increased conjugation length or $\pi-\pi$ stacking. HOMO and LUMO energy levels were estimated from the onsets of the oxidation and reduction waves, respectively. The electrochemical band gaps estimated were low, e.g. 1.2 eV for **3a**, and even lower for the **4a**−**c** series. The values were lower than the estimated optical band gaps, perhaps due to the estimation method (see Figure 1 and 2). All compounds had a HOMO energy level deeper than the air stability threshold of about −5.2 eV,[18] indicating that these compounds should be oxidatively stable in air. LUMO energy levels for the **3a**−**c** series were −4.0 to −4.1 eV. Chelation with BF_2 stabilized the LUMO energy levels by about 0.4 eV to give compounds with high electron affinity. For comparison, the LUMO energy level of electron acceptor [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) is −4.2 eV.[18] These oligomers therefore have great potential as electron acceptors in organic electronics.

In conclusion, we have demonstrated the first example of incorporating aza-DIPY into the backbone of conjugated oligomers/polymers through the active pyrrolic positions. The synthesized compounds have broad absorption in the red and near-IR region. Furthermore, they can be readily and reversibly reduced, pointing to their potential as *n*-type conjugated materials for organic field-effect transistors and organic solar cells. Complexation of azadipyrromethene moieties with BF_2 further stabilized both HOMO and LUMO energy levels, lowered the band gaps, and increased solubility, giving a class of materials with a unique combination of low band gaps and high electron affinity. Varying substituents on the phenyl rings influenced solubility and the chain length but had little effect on the band gaps. This is consistent with the DFT calculations of model compounds. The readily tunable properties of the aza-DIPY moieties by substitution on the phenyl rings and complexation with different metals in the nitrogen "pocket" offer the versatility of synthesizing variable aza-DIPY-based oligomers and polymers with interesting electronic properties. Charge-transport properties and evaluation of these compounds in organic solar cells are underway.

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Supporting Information Available. Detailed experimental procedures of synthesis, characterization, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.