



Synthesis of a near-infrared light-absorbing polymer based on thiophene-substituted Aza-BODIPY

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Abstract

An alternating conjugated polymer with thiophene-substituted aza-boron dipyrromethene (BODIPY) was synthesized in which the carbon atom at the *meso*-position in the ligand moiety was replaced by nitrogen. Initially, it was found that the synthesized polymer had a significant near-infrared (NIR) light-absorbing ability. In the absorption spectrum, a large absorption band (molar extinct coefficient $\epsilon_{\max} = 48,000 \text{ M}^{-1} \text{ cm}^{-1}$) with a peak at 864 nm was detected in the deep NIR region, even above 1300 nm. From cyclic voltammetry (CV) data, the energy levels of the frontier orbitals were determined. Accordingly, the polymer had a deep lowest unoccupied molecular orbital (LUMO) level (-4.01 eV), and this value was similar to that of the monomer. This result indicates that extension of π -conjugation throughout the polymer main-chain influenced only the highest occupied molecular orbital (HOMO) level while preserving the LUMO.

Introduction

Construction of conjugated systems based on main-chain-type polymers containing heteroatoms is a valid strategy not only for obtaining desirable electronic properties according to preprogrammed designs but also for achieving superior functions distinct from each element. From this viewpoint, light-absorption ability and narrow-band gap electronic structures have been often enhanced by introducing boron into the conjugated system throughout the polymer main-chains [1, 2]. For instance, by employing boron dipyrromethenes (BODIPYs), efficient light-harvesting antennae [3–5] and multi-luminescent materials [6–9] can be readily fabricated with conjugated polymers. Therefore, the development of main-chain-type conjugated polymers containing organoboron units is an area of particular interest with high

relevance, especially for producing advanced organic optoelectronic materials [1, 2, 10, 11].

We have recently proposed a new concept for material design based on “element-blocks,” which are defined as a minimal functional unit composed of heteroatoms [12, 13]. Simultaneously, by combination and assembly of element-blocks, “element-block polymers” can be obtained, and the realization of new characteristics exceeding the monomer properties is expected. We have focused on boron-containing “element-block polymers” as a platform for constructing functional luminescent materials because of their versatile optical properties [14–20]. Near-infrared (NIR) light-absorbing polymers are useful for a wide variety of applications, such as photovoltaics and biological systems, and by employing BODIPY derivatives with narrow-band gaps as a monomer, the desired functions were obtained [21–29]. BODIPYs are also recognized as a promising candidate for realizing highly efficient NIR-absorbing polymers because of their intrinsic large molar extinct coefficient ϵ values and sharp absorption bands observed via spectroscopy [30]. Aza-BODIPYs with a nitrogen atom instead of carbon at the *meso*-position in the dipyrromethene ligand are a promising candidate for NIR dyes because of their intrinsic narrow band gaps [31–34]. According to investigations on electronic structures, it was suggested that π -conjugation can be expanded more effectively by introducing co-monomers at the bottom aryl groups [35]. Indeed, it was shown that the conjugated

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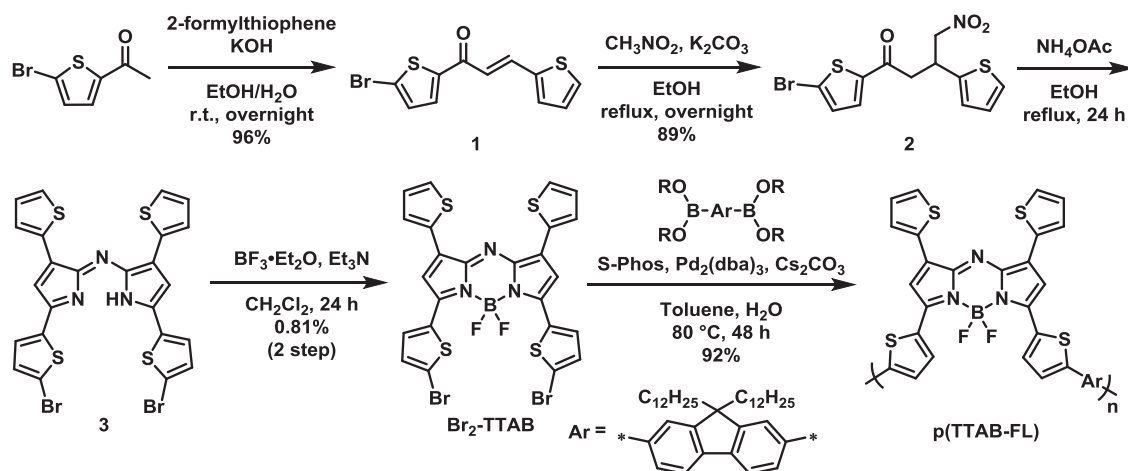
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polymers containing aza-BODIPYs in their main-chains provided deeply redshifted absorption and emission bands compared to their monomers [36, 37]. Recently, thiophene-substituted aza-BODIPYs were reported, and their superior NIR absorption and emission properties were revealed [38–43]. To achieve deep NIR absorption by aza-BODIPYs, we have also designed and synthesized aza-BODIPYs substituted with furan instead of thiophene for improving molecular planarity [44]. From optical measurements, it was demonstrated that the absorption and emission bands were shifted to the longer wavelength region. In these studies, it was also proposed that the extension of π -conjugation should be responsible for narrowing band gaps. Based on these data, we presumed that further extension can be expected by employing conjugated polymers with aza-BODIPYs. Hence, we designed a conjugated polymer with thiophene-substituted aza-BODIPY.

Herein, the synthesis and photophysical properties of an alternating conjugated polymer comprising thiophene-substituted aza-BODIPY in the main-chain are reported for the first time. An aza-BODIPY monomer with four thiophenes in the dipyrromethene ligand and two bromines at the bottom thiophenes was prepared and polymerized via the Pd-catalyzed Suzuki–Miyaura coupling reaction. The polymer showed a considerably redshifted absorption band compared to that of the monomer in the NIR region. Evaluation of the energy levels of the polymer revealed that the narrower band gap of the polymer compared to that of the monomer unit originated from increasing only the HOMO level by polymerization.

Results and discussion

The synthetic route for the thiophene-substituted aza-BODIPY monomer (Br_2 -TTAB) is outlined in Scheme 1.



Scheme 1 Synthetic route for the aza-BODIPY-containing polymer

Hetero-aldol condensation followed by conjugate addition proceeded quantitatively, and the brominated precursors **1** and **2** were obtained in good yields, while elimination of bromine atoms occurred during the reaction to afford **3**. Additionally, it was difficult to isolate **3** from the mono- and non-substituted ligands. Thus, purification was performed after complexation with boron difluoride. Although the reaction yield was very low due to the generation of byproducts and the intrinsically low coupling yield, the dibromide monomer Br_2 -TTAB was successfully obtained. The product showed good stability toward air and moisture, and significant degradation was hardly observed under visible light irradiation. Moreover, owing to the good solubility of the monomer in common organic solvents such as chloroform, tetrahydrofuran (THF), and toluene, characterization and then polymerization were feasible.

The polymerization of the monomer (Br_2 -TTAB) with the fluorene co-monomer was achieved via the Pd-catalyzed Suzuki–Miyaura coupling reaction (Scheme 1). The polymer properties were effectively determined using size-exclusion chromatography calibrated with polystyrene standards in THF ($M_n = 1500$, $M_w/M_n = 3.4$). According to the molecular weights of the repeated units (aza-BODIPY: 518, fluorene: 499), it was observed that the products should be oligomers containing several repeating units. Although it was proposed that the effective conjugation length should be much longer than that of the synthesized polymer, we assumed that the lengths obtained were long enough for evaluating the influence of extending π -conjugation throughout the polymer main-chains on electronic properties. The polymeric products showed good stability and moderate solubility in organic solvents, allowing ^1H and ^{11}B NMR spectra to be obtained (Charts S1–S4). From the chemical shifts of the signal peaks in both NMR spectra, we concluded that the products after polymerization have the desired structure.

Table 1 Optical and electrochemical properties of the products

	$\lambda_{\text{abs,max}}$ (nm) ^a	ϵ_{max} (M ⁻¹ cm ⁻¹) ^b	$\lambda_{\text{abs,onset}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) ^c	E_{red} (V) ^{d,e}	HOMO (eV) ^f	LUMO (eV) ^g
TTAB	741	100,000	772	1.61	-0.76	-5.65	-4.04
Br ₂ -TTAB	756	120,000	785	1.58	-0.69	-5.69	-4.11
p(TTAB-FL)	864	48,000	980	1.27	-0.79	-5.28	-4.01

^a Measured in THF solution (1.0×10^{-5} mol L⁻¹)

^b Determined at the absorption maxima

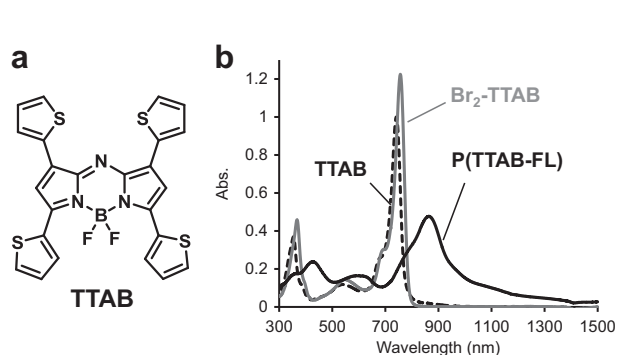
^c Estimated from the onset wavelength in the absorption spectra in THF

^d Carried out in dichloromethane with 0.1 M Bu₄NPF₆ as a supporting electrolyte

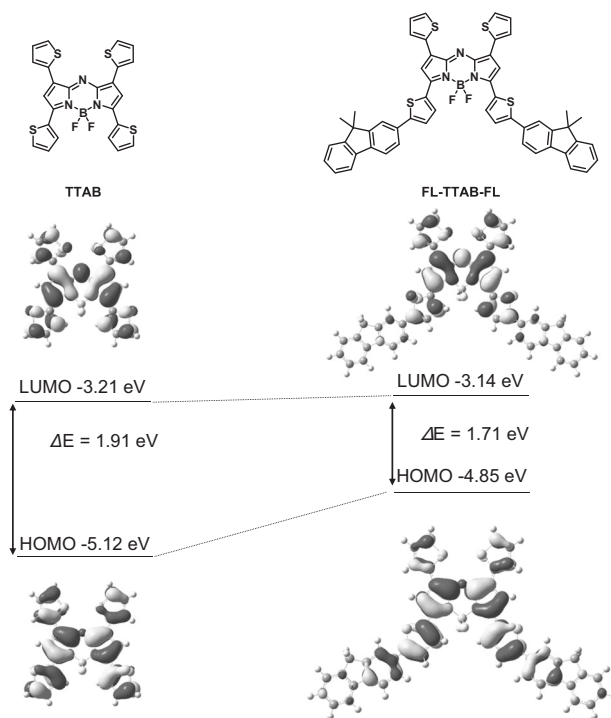
^e Determined from the onset potential in the first reduction waves

^f Calculated from the LUMO and optical band gap ($E_{\text{g}}^{\text{opt}}$) of the synthesized compounds, HOMO = LUMO - $E_{\text{g}}^{\text{opt}}$ (eV)

^g Calculated from the empirical formula, LUMO = - E_{red} - 4.80 (eV) [45]

**Fig. 1** a Structure of TTAB. b UV-Vis-NIR absorption spectra of the compounds in THF (1×10^{-5} M)

The optical properties of the synthesized polymers were investigated (Table 1). Tetrathienyl aza-BODIPY (TTAB, Fig. 1a) and the monomer (Br₂-TTAB) were also analyzed for comparison. TTAB was prepared according to previous reports [38, 39]. Figure 1b shows the ultraviolet (UV)-visible (Vis) absorption spectra in THF (1.0×10^{-5} mol L⁻¹). Both TTAB and Br₂-TTAB showed strong and sharp absorption bands at approximately 750 nm derived from the $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition. The absorption band of the polymer p(TTAB-FL) was observed in a longer wavelength region than those of TTAB and Br₂-TTAB. A strong $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transition was observed in the NIR region with a peak at 864 nm. The peak wavelength was shifted by over 100 nm compared to those of the small molecules. Furthermore, significant absorption was detected even above 1300 nm. This result clearly indicates that conjugation should be efficiently extended throughout the fluorene copolymers. We also investigated the emissive properties of the polymer, and the emission intensity was under a detectable level, suggesting that the polymer has weak emission properties, possibly because of the heavy-atom effect as well as structural distortion of the polymer main-chains [44].

**Fig. 2** Structures and molecular orbital diagrams for the LUMO and HOMO of TTAB and FL-TTAB-FL calculated with DFT (B3LYP/6-31G(d)//B3LYP/6-31G(d)). (Color figure online)

To investigate the electronic states, CV measurements were performed (Table 1, Fig. S1). All three compounds showed two reduction peaks. These results indicate that these BODIPY compounds can easily accept electrons. The LUMO energy levels were estimated from the onsets of the first reduction waves by an empirical formula [45]. The HOMO energy levels were calculated with the LUMO energy levels and optical energy band gaps ($E_{\text{g}}^{\text{opt}}$) of the corresponding compounds (Table 1). Accordingly, it was found that the LUMO energy level of the polymer was very similar to those

of the monomer and TTAB. In contrast, the E_g^{opt} of the polymer was significantly smaller. These data indicate that the HOMO energy level was elevated by the extension of conjugation after polymerization and the resulting narrower band gap of the polymer. Finally, the absorption band could be detected in the longer wavelength region.

To gather detailed information on the electronic structures of the compounds, computer calculations were performed using density functional theory (DFT). FL-TTAB-FL, which is the alternative model of p(TTAB-FL) and TTAB, was evaluated by calculation (Fig. 2). It was clearly shown that all the HOMOs and LUMOs delocalized throughout the TTAB moieties. It should be noted that the HOMO of FL-TTAB-FL spread even to the fluorene units, whereas the LUMO seemed to be delocalized within the TTAB moieties. It was proposed that the electron-donating character of the fluorene units could be responsible for only the HOMO being extended. These results correspond to the CV data. It was suggested that the HOMO energy level of the polymer model became higher than that of TTAB by extending π -conjugation throughout the polymer main-chains. On the other hand, the LUMO energy level was slightly influenced by the co-monomer units.

Conclusion

A deep NIR-absorbing polymer with thiophene-substituted aza-BODIPY was synthesized via a conventional Pd-catalyzed cross-coupling reaction based on the strategy for expanding conjugated systems by employing polymer structures. The synthetic polymer showed a strong absorption band even in the region above 1300 nm. Furthermore, the LUMO energy level of the polymer was revealed from CV measurements, which showed that the low-lying LUMO of the thiophene-substituted aza-BODIPY was maintained after polymerization. If the polymer is used as an electron-carrier material in organic optoelectronic devices, modulation of each energy level should be essential for optimizing device efficiencies. In this study, it was demonstrated that only the HOMO level can be altered by polymerization. Thus, our findings and materials could be particularly applicable for fabricating efficient polymer-based electric devices.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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