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Synthesis and Optical Properties of Soluble Near-Infrared Arylene Bisthienoimidazole Dyes

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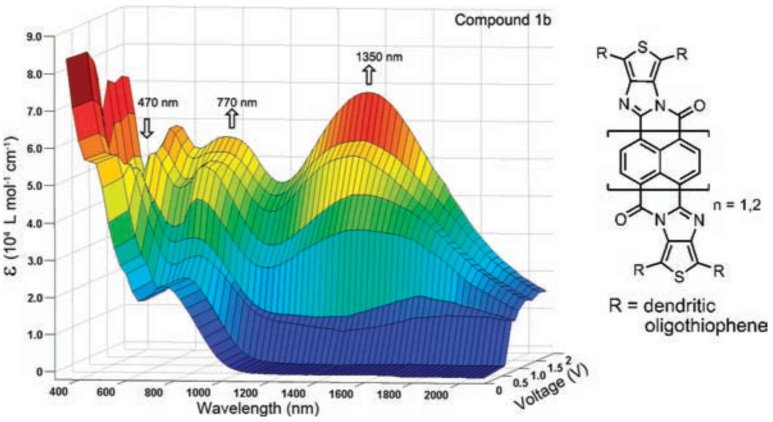
ABSTRACT



Soluble, film-forming near-infrared arylene bisthienoimidazole dyes with a band gap of 1.2−1.3 eV are electrochromic and absorb strongly at the telecommunication wavelengths (1310 and 1550 nm) in the oxidized state.

Perylene pigments are dimides and bisimidazoles of perylene-3,4,9,10-tetracarboxylic acid, and perinone pigments are made from naphthalene-l,4,5,8-tetracarboxylic acid or its monoanhydride. As pigments, they are used in automotive, architectural, and industrial paints, printing inks, and stains and have excellent light and speed fastness. Perylene and perinone pigments have also been explored as electrophotographic photoreceptors[1] and for use in optical disks.[2] Recently, perylene and perinone pigments, despite their relatively poor solubility, have been explored as semiconductor materials for use in optoelectronic devices such as organic solar cells and transistors.[3]

The growing interest in this class of organic materials is also attributed to advances in structural modification, morphological control, and band gap tuning. Perylene dianhydrides and derivatives are now readily manipulated structurally at the "bay" region (the 1,6,7 and 12 positions) and end position.[4] It is known that the "bay" substituents can affect electronic and optical properties, while the imide substituents can effectively alter aggregation and solubility.

Typical examples are *N*,*N*′-dioctyl-3,4,9,10-perylenetetercarboxylic diimide (PDI-8, Figure 1),[5] perylene-3,4,9,10-tetracarboxylic bisbenzimidazole (PTCBI, Figure 1),[6]

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and poly(benzobisimidazobenzophenanthroline) (PBBL).[7] However, because of poor solubility, much less effort has been made toward the synthesis of structurally more complicated and possibly lower band gap naphthalene and perylene bisimidazoles.

It has been shown in one case (PDI-3T, Figure 1) that introduction of thienoimidazole into the perylene pigment structure results in a significant bathochromic shift in absorption spectra and a decrease in the band gap.[8] PDI-3T contains the mixed perylene imide and thienoimidazole and shows the maximum absorption peak at 610 or 90 nm red shift relative to perylene diimide (PDI-8).[5,9] Among perylene pigments containing the imide, benzimidazole, and thienoimidazole units, in reference to the imide, the benzimidazole unit lowers the band gap mainly due to the change of the LUMO level and the thienoimidazole unit is able to raise the HOMO level, leading to the band gap reduction (Figure 1).

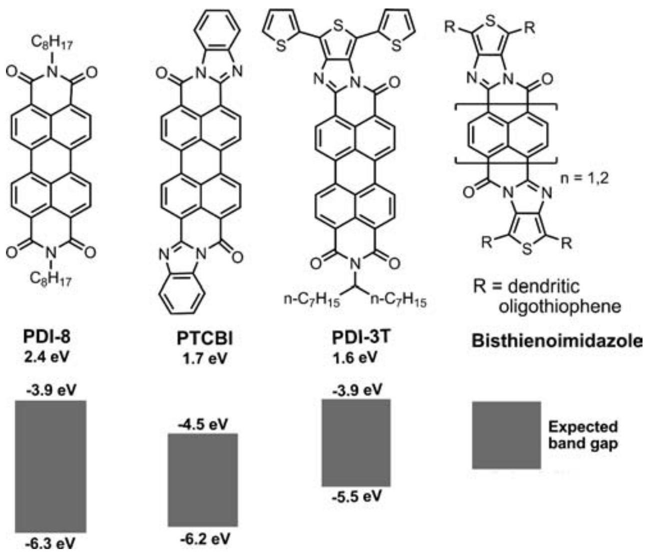
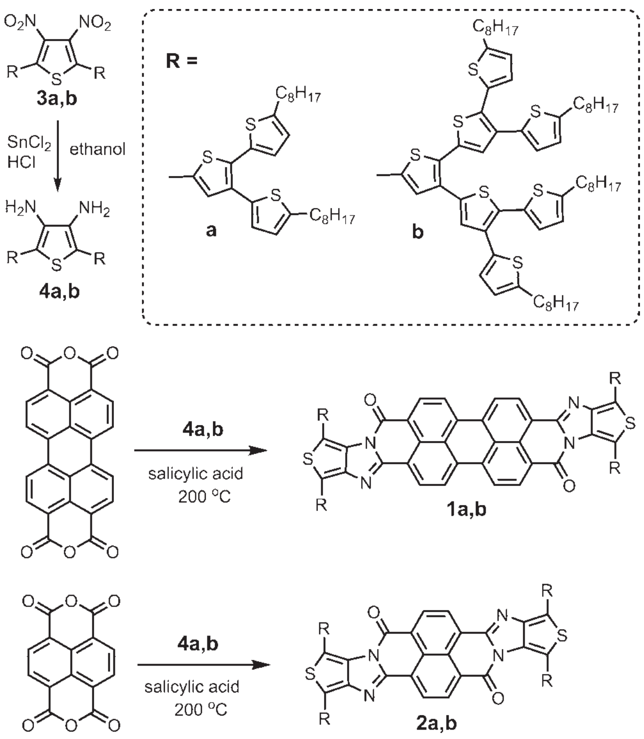


Figure 1. Chemical structures and energy levels of some perylene pigments and designed bisthienoimidazole dyes.

Guided by this preliminary finding of the structure-band gap correlation for the perylene pigments, we propose a new family of low-bandgap bisthienoimidazole dyes (Figure 1), in which various substituent (R) groups could be selected for different purposes. Herein we report soluble near-infrared (NIR) bisthienoimidazole dyes bearing three and seven-thiophene dendron substituents (**1a**,**b** and **2a**,**b**, Scheme 1), which are derived from readily available perylene dianhydride and naphthalene dianhydride and dendritic oligothiophenes. The introduction of the two thienoimidazole units in the naphthalene and perylene systems ensures the low band gap or absorption into the NIR region (i.e., > 750 nm) by further raising the HOMO level. The dendritic oligothiophenes are designed to bring the unique optoelectronic property and also impart the solubility to the target bisthienoimidazole dyes.

Scheme 1. Synthetic Routes to Bisthienoimidazoles **1a**,**b** and **2a**, **b**



Scheme 1 outlines the synthetic routes to the target compounds **1a**,**b** and **2a**,**b**. 2,5-Dibromo-3,4-dinitrothiophene[10] and dendritic oligothiophene intermediates[11] were prepared according to the literature methods. Compounds **3a** and **3b** were synthesized by the Stille reaction and reduced to diamines **4a** and **4b** in high yields (90%). The cyclization of diamines with the corresponding dianhydrides in melt salicylic acid gave the final compounds in 40−60% yields. It should be noted that each of final products may contain two structural isomers that exhibit the same optical property but are extremely difficult to be separated.

Unlike most perylene and perinone pigments, these bisthienoimidazole dyes are readily soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, chlorobenzene, and toluene, owing to the long alkyl groups and the twisted and branched oligothiophene moieties. Compound **2b** has the highest solubility among all; the solubility of **1b** in chlorobenzene is as high as 100 mg/mL at room temperature. The smooth thin films could be cast or spin coated. These dyes show good thermal stability with the onset temperatures for 2%

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Table 1. Optical and Band Gap Data of Compounds **1a**,**b** and **2a**,**b**

compd	$\lambda_{\max}^{\mathrm{abs}}$ (nm)[a]	$\lambda_{\max}^{\mathrm{abs}}$ (nm)[b]	log ε[a]	HOMO (eV)	LUMO (eV)	band gap (eV) E^c	band gap (eV) $E_{\mathrm{op}}{}^d$
1a	752	781	4.38	−5.03	−3.83	1.20	1.22
1b	758	840	4.37	−5.18	−3.99	1.19	1.21
2a	713	737	4.27	−5.13	−3.89	1.24	1.30
2b	715	745	4.26	−5.06	−3.81	1.25	1.28

[a] Measured in dichloromethane with a concentration of 1×10^{-5} M. [b] Measured as film. [c] From electrochemical data, $E_{(\mathrm{HOMO})} = -(E_{\mathrm{ox}}{}^{\mathrm{onset}} + 4.46)$ (eV), $E_{(\mathrm{LUMO})} = -(E_{\mathrm{red}}{}^{\mathrm{onset}} + 4.46)$ (eV). [d] Optical band gap $= 1240/\lambda^{\mathrm{abs}}{}_{\mathrm{onset}}$ (eV).

weight loss in nitrogen, assessed by thermogravimetry, at 285 and 357 °C for **1a** and **1b**, and 285 and 335 °C for **2a** and **2b**, respectively (Figure S1, Supporting Information).

The absorption spectra of the four compounds in dichloromethane are shown in Figure 2 (top). All of them absorb above 750 nm with tailing near 1000 nm. The absorption bands in the UV−vis region below 550 nm are attributed to the $\pi-\pi^*$ transitions of the conjugated oligothiophene units, and those at the longer wavelength are due to the extended conjugation of arylene bisthienoimidazole moiety. The maximal peaks of compounds **1a** and **1b** are red-shifted about 60 nm in comparison with **2a** and **2b**, owing to a longer conjugation length of the perylene unit. The optical properties of these dyes were further characterized as thin films (Figure 2, bottom). Relatively small bathochromic shifts (typically 20−30 nm) in absorption spectra were observed when compared with those in solution (Table 1), indicating that the site-isolation effect brought by the dendritic oligothiophene units could significantly diminish the strong intermolecular interaction of naphthalene and perylene bisthienoimidazoles.

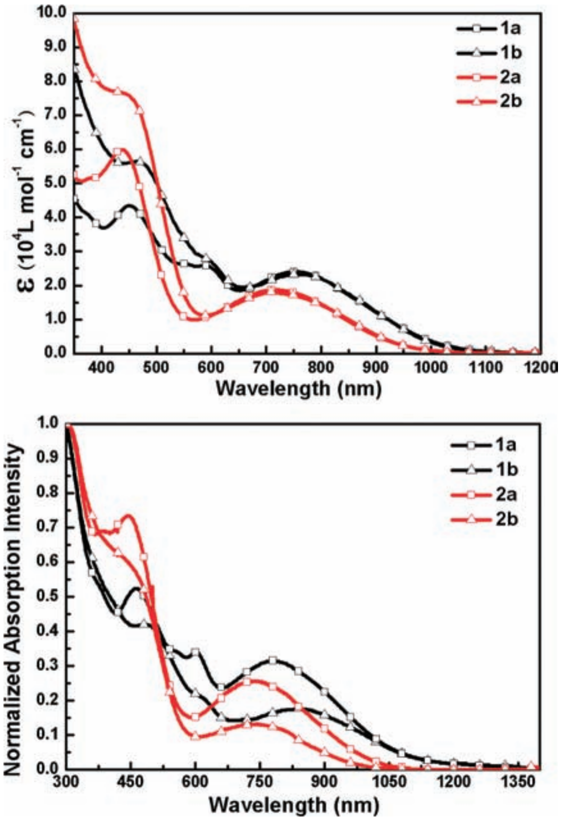

Figure 2. Absorption spectra of compounds **1a**,**b** and **2a**,**b** in dichloromethane (top) and as films (bottom).

The electrochemical properties of these bisthienoimidazole dyes were investigated by cyclic voltammetry (CV) (Figure S2, Supporting Information). They are all electrochemically active and have almost the same first anodic peak (at about 0.6 V), attributed to the oxidation of thiophene groups. Unlike **1a** and **2a** showing clear redox couples, the cathodic scans of **1b** and **2b** showed very weak, ill-defined reduction potentials, presumably because of the shielding effect of large thiophene dendrons.

The band gap values were calculated for **1a**,**b** and **2a**,**b** from the electrochemical data, which are consistent with those calculated from the absorption spectra (Table 1). Compounds **1a** and **1b** have almost the same band gap although they have different thiophene dendrons, while **2a** and **2b** have a larger band gap, due to shorter conjugation length of the naphthalene moiety.

A spectroelectrochemical study was done in order to investigate their NIR electrochromic properties. The spectroelectrochemical spectra of **1b** and **2b** are shown in Figure 3 (those of **1a** and **2a** in Figure S3, Supporting Information). The absorption spectra changed quite significantly when partially and fully oxidated from the neutral state. An intense peak at the telecommunication wavelengths of 1300−1500 nm appeared upon oxidation, which has not been seen for most naphthalene and perylene diimides as they are typically cathodically electrochromic.

In the neutral form, the solution of compound **1a** absorbs strongly at 450 nm, which is characteristic of oligothiophene. The peak at 450 nm gradually decreased by applying a voltage from 0 to 1.2 V, and kept unchanged at a higher voltage (1.8 V), due to the complete conversion to the radical cations (polarons) of oligothiophene. The same phenomenon was also observed for **1b** at 470 nm, **2a** at 437 nm and **2b** at 442 nm, respectively.

Compounds **1a** and **2a** having the same branched oligothiophene unit have different absorption spectra above 500 nm at the same oxidation potential, indicating the

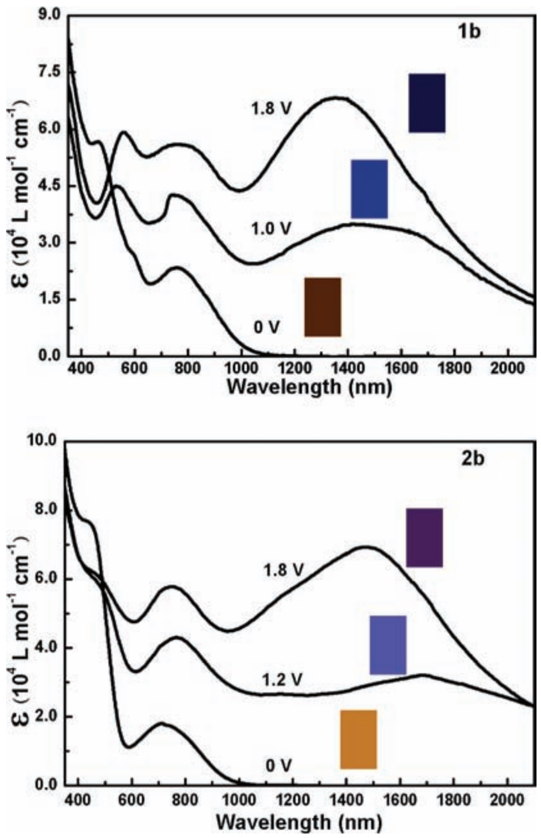

Figure 3. Absorption spectra of **1b** and **2b** in 0.1 M Bu_4NPF_6/CH_2Cl_2 and the corresponding colors at applied potentials.

influence of the arylene cores. In addition, compounds **1a** and **1b** having the different dendritic oligothiophenes also displayed quite different NIR absorption spectra upon oxidation. Therefore, the electrochromic properties of these bisthienoimidazole dyes are influenced by both arylene core and thiophene dendrons.

It is worth noting that **1b** and **2b** have attractive visible and NIR electrochromic characteristics (Figure 3), as evident by high color contrast, on–off NIR absorption, and low switching voltages (1.0 and 1.2 V for **1b** and **2b**, respectively). Both of them have an intense peak ($\varepsilon > 6 \times 10^4$ L mol^{-1} cm^{-1}) at the telecommunication wavelengths of 1310 and 1550 nm upon oxidation. This NIR absorption feature is quite different from many conjugated polythiophenes, which usually show rather broad plateau in the NIR region.[12] This is a result of the polarons being isolated on the dendritic oligothiophene, which can not recombine into bipolaron due to the lack of an effective resonance conjugation by the oligothiophene unit itself or connected via the arylene bisbenzimidazole core.[13] The formation of discrete conjugated segments with effective conjugation length are determined by the mode of connection and twist angles between monomeric units. In comparison, oligothiophene **3a** is not electrochromic at a potential up to 1.8 V. Higher oligomer **3b** is weakly electrochromic with a minor spectral change only at 700 nm at the potential of 1.4–1.8 V (Figure S3, Supporting Information) because its average effective conjugation length is still too short to accommodate a bipolaron state.[13]

No significant changes in absorption were observed for these compounds, except for **1a**, during the electrochemical reduction (Figure S3, Supporting Information). The absorbance of **1a** at 750 nm increased and a new peak at 1250 nm appeared when a negative potential was applied at 0.7 V. The observed NIR absorption is likely attributed to the dimer formation of the radical anion.[14]

In conclusion, four bisthienoimidazoles have been successfully synthesized as a representative for a new family of arylene bisthienoimidazole dyes. These bisthienoimidazole dyes are readily soluble in common organic solvents, absorb above 750 nm with tailing near 1000 nm and are electrochromic with an intense absorption at the telecommunication wavelengths upon oxidation. Good processability, film-forming and NIR-absorbing properties, as well visible–NIR dual electrochromism make arylene bisthienoimidazole dyes potentially useful for device applications such as variable optical attenuator[15] and NIR photovoltaic devices.[16]

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Supporting Information Available. Experimental details, TG traces, CV, and electrospectrochemistry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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