Visible and Near-Infrared Absorbing, Low Band Gap Conjugated Oligomers Based on Cyclopentadieneones

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Introduction. The ability to manipulate the structure and energy levels of π-conjugated organic polymers allows them to be tailored to meet the electronic and physical demands of various applications. Of particular interest in this field are low band gap organic polymers, specifically those with band gaps below 1.5 eV. In such materials a greater number of charge carriers can be thermally promoted to conducting states providing the potential for intrinsic conductivity, as opposed to extrinsic conductivity in which chemical doping generates charge carriers.[1−3] Low band gap materials can find applications in photovoltaics and data transfer, and are of interest for their ability to absorb light in the visible and near-infrared regions of the spectrum.[4−10] One way to design low band gap polymers is to alternate well-matched donor and acceptor moieties in the conjugated backbone of the molecule.[11−14] Another approach is to polymerize a monomer with a small $\pi-\pi^*$ gap such that the resulting polymer has a further reduced band gap. In this paper we provide details of the synthesis and optical as well as electrochemical properties of new materials based on conjugated cyclopentadieneone units alternating with bithiophene or biphenyl.[15] Each material displays a low band gap in optical and electrochemical studies. Conceptually, the polymers described here were expected to have a low band gap because they consisted of alternating electron donor (bithiophene) and acceptor (tetraarylcyclopentadienone) units.[16] However, tetraphenylcyclopentadienone absorbs throughout the visible spectrum, with a HOMO–LUMO gap near 1.6 eV. In principle, and if it were not a synthetic impossibility, a polymer based strictly on a repeating cyclopentadienone ought to have a gap smaller than 1.5 eV. In the case of the polymers presented in this paper, the small gap is probably a result of both a weak electron transfer between bithiophene and cyclopentadienone as well as the small $\pi-\pi^*$ gap of the latter.

Results and Discussion. *Synthesis.* The synthesis of poly(dithienylcyclopentadieneone) [poly(DTCPD)], **5a** (Scheme 1), began with the self-condensation[17] of thiopheneacetic acid using DCC and DMAP to yield 1,3-dithienyl-2-propanone, **2a,b**. The DTCPD derivative, **4a**, was then prepared via a double Knoevenagel condensation[18] with acenenaphthenequinone and **2a** to form a dark green, almost black solid. Chemical oxidative polymerization with ferric chloride was carried out to yield **5a** as an intractable black powder. To improve solubility, a 4-heptylphenyl group was substituted at the most remote position of the fluoranthene moiety (Scheme 1). The synthesis of the soluble CPD derivative, **4b**, was accomplished via a double Knoevenagel condensation between **3b,c** (see Supporting Information) and **2a,b**. The polymerization of **4b** to **5b** was accomplished using ferric chloride.

The diphenyl derivative, **5c**, was synthesized in order to create a polymer that would retain the ability to absorb a large portion of the visible spectrum, while increasing the band gap. The synthesis of the biphenyl derivative began with a self-condensation of a 2-(4-bromophenyl)acetic acid mediated by DCC and DMAP to yield 1,3-bis(4-bromophenyl)propan-2-one, **2c**. The formation of monomer **4c** was accomplished by a double Knoevenagel condensation between **2c** and **3b,c**. Chemical polymerization of monomer **4c** to the corresponding polymer **5c** was accomplished via a Yamamoto polymerization to yield a soluble dark green-to-black material.

Proton NMR spectroscopy of the polymers revealed very broad aromatic peaks that were likely the result of aggregation; however, ESR measurements were performed to rule out a swift T_2 relaxation by open shell species (radical anions or cations) in the polymer backbone. Solid state ESR revealed one narrow peak with a *g*-value of 2.0024 and one broad peak with a *g*-value of 2.0353. When the ESR measurements were repeated in 1,2-dichlorobenzene, the narrow peak remained while the broad peak was barely observable, suggesting that the broad peak was associated with impurity states typical of organic polymers in the solid state. Furthermore, the measurements indicated an extremely low spin concentration, commonly observed in "pure", non-open-shell organic solids.

Visible and Near-Infrared Absorption Spectroscopy. All spectroscopic samples were solutions of the analyte in 1,2-dichlorobenzene. Each compound, exhibited a strong absorption between 200 and 500−600 nm, followed by a second band between 500−650 and 800−1400 nm (Figure 1). Because of the insolubility of polymer **5a**, optical studies were not performed. As **4a** and **4b** only differ by a heptylphenyl side group, the band gap of **4b** is very similar to that of **4a** (Table 1). However, a slight red shift of **4b** with respect to **4a** is observed. This suggests that, while it is rotated out of the plane of the naphthalene moiety, the phenyl group interacts weakly with the rest of the molecule. In the backbone phenyl-substituted species, the monomer (**4c**) and its polymer (**5c**) exhibit essentially identical electronic spectra, implying that polymerization does not increase the conjugation length. Because a *p*-phenylene is more sterically demanding and not nearly as electron-donating as 2,5-thienylene, the interaction between the donor and acceptor unit is reduced in the former.[19] In effect, polymer **5c** behaves electronically more like a series of noninteracting monomers than a conjugated polymer.

Electrochemical Studies. For each compound, the electrochemical band gap was determined by measuring the difference between the onsets of oxidation and reduction (Figure 2). All six species show two quasi-reversible reduction processes; the first can be attributed to the formation of the radical anion and the second to the formation of the dianion.[20] Both thiophene-containing polymers displayed quasi-reversible oxidation waves.

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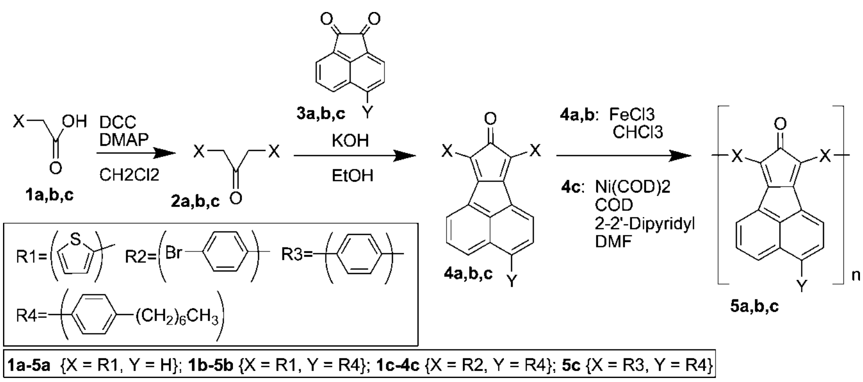
Scheme 1. Synthesis of 4a,b,c and 5a,b,c



However, the full oxidation processes of monomers **4a** and **4b** were not observed because the oxidative scans were kept intentionally brief to prevent electropolymerization. To measure the insoluble polymer, **5a**, monomer **4a** was electrochemically polymerized onto the working Pt electrode by performing 10 oxidative cycles to 1.5 V in dichloromethane. The resulting film was rinsed and placed in a fresh electrolyte solution. The scans of the phenylene derivatives reveal a reversible oxidative process for monomer **4c** but an irreversible oxidation for polymer **5c**. All electrochemical band gaps were found to be within 0.08 eV of those measured optically (Table 1).

Table 1. Optical, Electrochemical, and Calculation Data for Compounds 4a,b,c and 5a,b,c

	λ_{max} (nm)[a]	onset (nm)[b]	$E_{g,opt}$ (eV)[c]	$E_{g,cv}$ (eV)[d]	$E_{g,calc}$ (eV)[e]
4a	671	845	1.47	1.5	
5a				1.1	1.15
4b	684	850	1.46	1.5	2.11
5b	908	1450	0.86	0.9	
4c	605	760	1.62	1.7	2.37
5c	608	780	1.59	1.6	

[a] Maximum absorption of the long wavelength feature. [b] The intercept of the slope of the absorption tail with the minimum absorption. [c] Calculated from the onset. [d] Difference between the onsets of the first reduction and the oxidation. [e] Band gaps obtained at PBC/B3LYP/6-31G(d) level of theory. Heptyl group was omitted in calculations.

Band Gap Calculations. Reliable estimations of the band gaps of conjugated polymers can be obtained computationally using periodic boundary conditions (PBC) extrapolation, combined with hybrid density functional theory (DFT). DFT calculations with PBC were performed on the species found in Table S2 (see Supporting Information) to test the feasibility of the bithiophene−tetraarylcyclopentadienone polymer as a low band gap material and to reconcile experimental findings with calculation. Though there is good agreement between the calculated and experimental results for polymer **5a** (Table 1), larger HOMO–LUMO gaps were calculated for **4b** and **4c**.

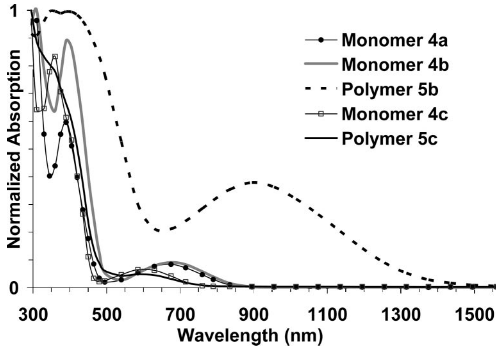


Figure 1. Visible and near-infrared absorption spectra. The spectrum of each compound was normalized to its main absorption maximum (typically ∼310 nm).

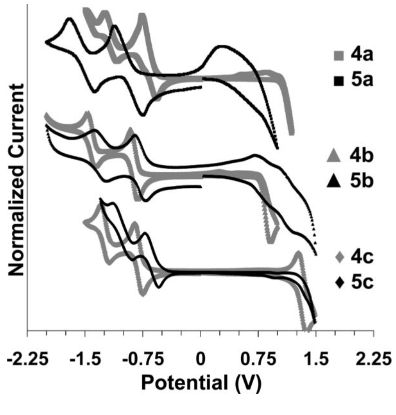


Figure 2. Cyclic voltammetry. Potentials are plotted vs a silver quasi-reference electrode, and the half-wave potential for the ferrocene couple occurred at 0.28 eV. The magnitude of the current was normalized to unity.

Conclusions. Three polymers based on tetraarylcyclopentadienone were synthesized and found to have band gaps between 1.5 and 0.9 eV by cyclic voltammetry and absorption spectroscopy. The disagreement between the calculated and observed band gap values for **5c** is possibly due to the adoption of different torsion angles than those calculated for the energy optimized structure. Because of the small rotational barrier, the actual structure could be more planar, which would appreciably lower the band gap.[21] Indeed, if in polymer **5c** all torsional angles of the polymer backbone are constrained to 20°, while all other geometrical parameters are optimized, the predicted band gap narrows to 1.88 eV. Further work to improve solubility and preliminary device studies are currently underway.

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Supporting Information Available: Experimental details; synthesis of compounds **4a,b,c** and **5a,b,c**; Scheme S2 synthesis of **3b,c**; calculation details; Table S2 calculation results.[22−26] This material is available free of charge via the Internet at http://pubs.acs.org.

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