

Partially Ladder-Type Molecule-Based Donor-Acceptor Conjugated Oligomer: Synthesis and Properties

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Received February 9, 2012, Accepted March 23, 2012

Key Words : Conjugated oligomer, Ladder-type acceptor, Donor-acceptor

The synthesis of organic semiconductors has been extensively developed in recent years due to the opportunity to fabricate low-cost and/or large-area electronic components.¹ Among them, ladder π -conjugated oligomers are regarded as promising materials due to their rigid coplanar structures and enhanced π -conjugation, which lead to a set of desirable properties, such as intense luminescence, high carrier mobility and environmental stability.²⁻⁵ We have recently developed new approaches to prepare the fully ladder-type conjugated oligomers utilizing the BBr_3 -promoted intramolecular cyclization.⁶ This method features with its fast and quantitative reaction to produce both electron-rich and electron-deficient conjugated systems with rigid planar structure.

Another important development in the synthesis of π -conjugated oligomers has been the utilization of donor-acceptor (D-A) type architectures within the backbone. The donor-acceptor systems cause partial intramolecular charge

transfer (ICT) that enables manipulation of the electronic structure, leading to low band gap semiconductors with relatively high charge carrier mobilities.^{7,8}

In a fusion of these two concepts, we present herein the synthesis of D-A alternating cooligomer **1** where the acceptor is based on the ladder-type planar molecule prepared by the BBr_3 -promoted lactonization and the alkylated thiophene is used as a donor (Figure 1). The photophysical, electro-

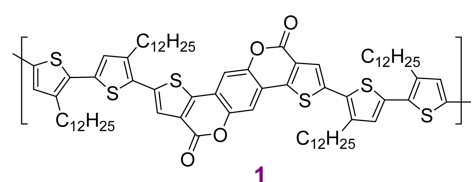
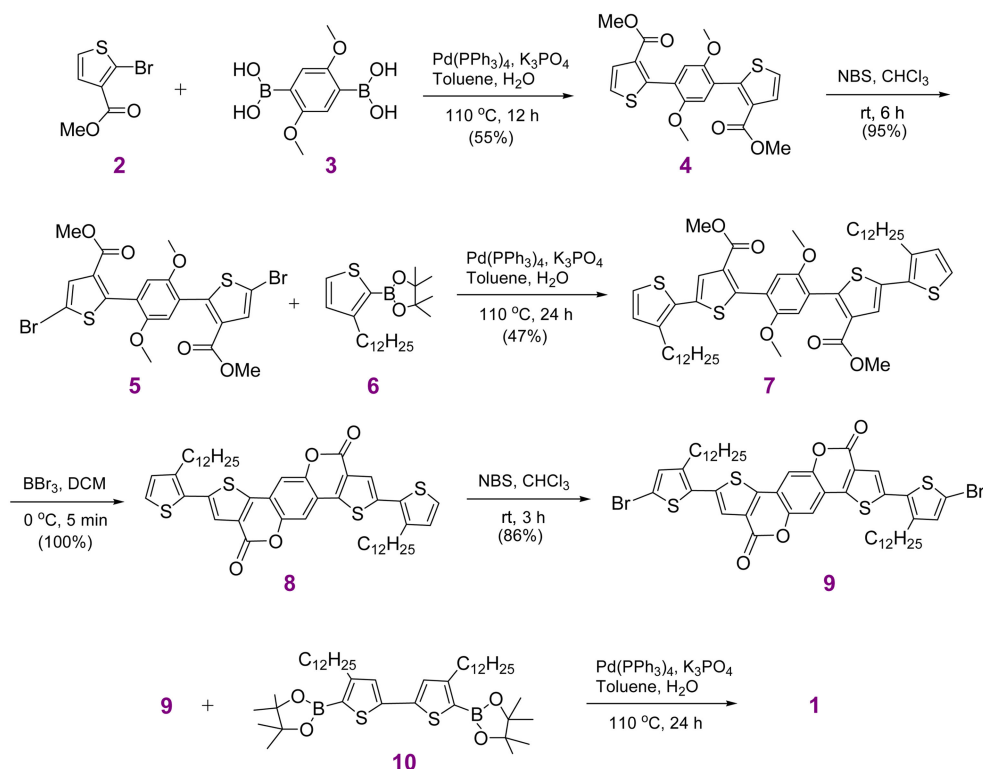


Figure 1. Partially ladder-type molecule-based donor-acceptor cooligomer **1**.



Scheme 1. Synthesis of the partially ladder-type molecule-based donor-acceptor cooligomer **1**.

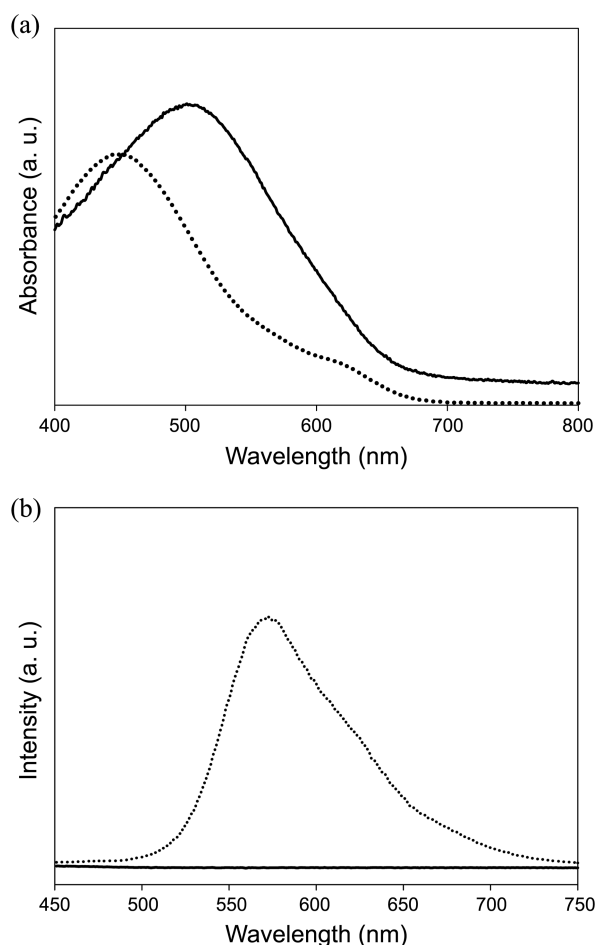
Table 1. Optical and electrochemical properties of oligomer **1**

Oligomer	UV-Vis absorption spectra			Emission spectra		CV	
	Solution ^a λ_{max} (nm)	Film λ_{max} (nm)	$E_{\text{g}}^{\text{opt}}$ ^b (eV)	Solution ^a λ_{max} (nm)	Film λ_{max} (nm)	HOMO (eV)	LUMO (eV)
1	484	540	1.90	573	-	-5.1	-3.2

^aSolution: in chloroform. ^b $E_{\text{g}}^{\text{opt}}$: optical bandgap estimated from the band edge (λ_{onset}) of the absorption spectra

chemical and crystalline properties of this partially ladder-type molecule-based donor acceptor cooligomer are further described.

Synthesis of the donor-acceptor cooligomer is depicted in Scheme 1.⁹ 2-Bromo thiophene methyl ester **2** was first cross-coupled with dimethoxy diboronic acid **3** under the Suzuki condition to give the precursor of the ladder-type acceptor **4**. In order to increase the solubility of the ladder-type acceptor, compound **4** was first brominated to **5** and cross-coupled with dodecyl thiophene boronic ester **6** to give the compound **7**. This was then cyclized by BBR_3 -promoted lactonization to afford compound **8**, which was then brominated to **9** for further polymerization. Finally, Pd-catalyzed Suzuki coupling reaction of **9** with bis(dodecyl thiophene) boronic ester **10** led to the desired partially ladder-type molecule-based D-A cooligomer **1**.

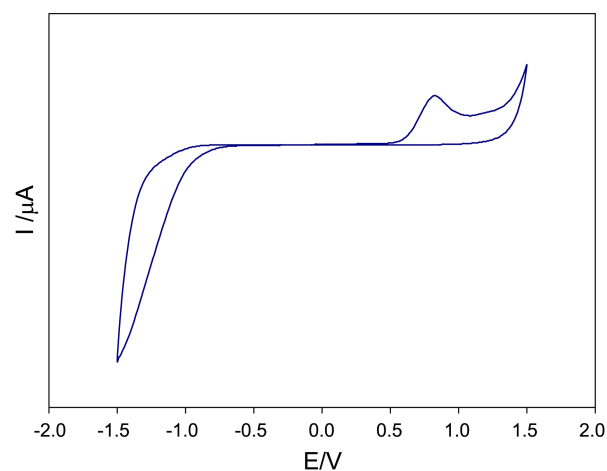
**Figure 2.** UV-Vis (a) and emission (b) spectra of the D-A oligomer **1** in CHCl_3 solution (dotted line) and on film (solid line).

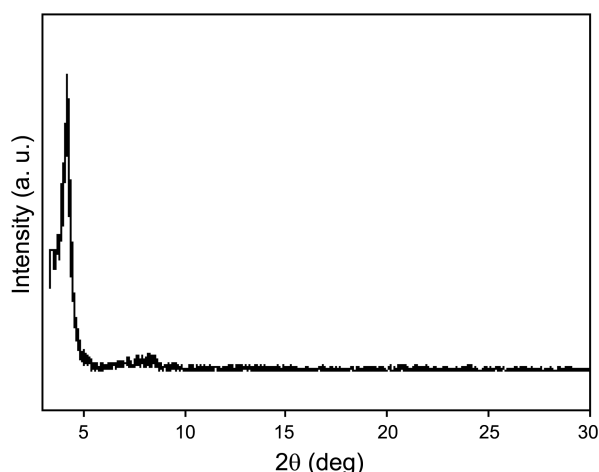
The D-A oligomer **1** was readily soluble in most organic solvents, and showed rather low molecular weight.¹⁰ TGA analysis of oligomer **1** revealed thermal stability up to 300 °C, after which temperature it started to degrade. No characteristic thermal transition was observed by DSC in the temperature range between 0 °C and 300 °C, indicating that structural ordering is not expected by thermal annealing.

The electronic properties of the D-A oligomer **1** were investigated by both UV-Vis absorption and emission spectroscopies both in solution and on film (Figure 2 and Table 1). Absorption maxima, λ_{max} , was observed at 490 nm in a chloroform solution and a significant red shift by 60 nm was observed on the film, indicating a well-ordered crystalline structure of the oligomer in its solid state. This was further evidenced by the emission spectra where the strong fluorescence of the oligomer **1** solution at 570 nm was quenched in its solid state by the strong intramolecular charge transfer within the molecule. An optical band gap of 1.9 eV was calculated from the onset absorption (660 nm) of the oligomer film. The narrow band gap is indicative of the efficient delocalization of π electrons, which is the result of the extended π -conjugation and intra- and intermolecular donor-acceptor interactions. The planar structure of the ladder-type acceptor is another reason for the narrow band gap.

The electrochemical redox behaviors of the D-A cooligomer **1** with its cast thin film were characterized by cyclic voltammetry (CV). The oxidation and reduction cyclic voltammograms of **1** is shown in Figure 3 and summarized in Table 1.

The HOMO level (ionization potential) was calculated

**Figure 3.** Cyclic voltammograms of the D-A oligomer film **1** coated on ITO electrodes measured in acetonitrile containing 0.1 M tetrabutylammonium phosphate solution at a scan rate of 50 mV/s at room temperature.



Scheme 4. X-ray diffraction pattern of the oligomer thin film (10 mg/mL in chloroform) drop coated on OTS modified silicon wafer. d -spacing was calculated by using Bragg's equation, $n\lambda = 2d\sin\theta$.

from the first oxidation onset via $E_{\text{HOMO}} = (E_{\text{ox-onset}}(\text{vs Ag/AgCl}) - E_{\text{ox}}(\text{Fc/Fc}^+ \text{ vs Ag/AgCl}))$.¹¹ The estimated HOMO energy level of oligomer **1** were -5.1 eV, indicating the stability of this material at ambient conditions. The LUMO level (electron affinity) was estimated by subtraction of the band gap energy E_g from the HOMO level following $E_{\text{LUMO}} = E_{\text{HOMO}} - E_g$, and was calculated as -3.2 eV. The small optical band gap (1.9 eV) and broad absorption band suggest that the oligomer **1** could be a useful material for photovoltaic and thin film transistor applications.

In addition, the crystalline nature of the oligomer **1** was estimated from the low angle X-ray diffraction (XRD) analysis. The XRD pattern of thin film of **1**, drop coated on OTS modified silicon wafer, shows a sharp first order (1,0,0) reflection peak at $2\theta = 4.19^\circ$, and the corresponding d spacing was calculated by Bragg's equation to be 21 \AA (Figure 4). Since the d spacing corresponds to the distance between polymer main chains in a lamellar packing structure, the result suggests a crystalline and well-ordered lamellar structure of the oligomer **1** in its solid state and thus efficient intermolecular charge transport through the polymer backbone is expected.

In conclusion, we have synthesized a thiophene-phenyl-thiophene-based lactone by BBr_3 -promoted cyclization and copolymerized with alkylated thiophene to produce partially ladder-type D-A oligomer. A small band gap with a broad

absorption band and crystallinity of this oligomer would make this new material attractive for various optoelectronic applications.

Acknowledgments. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (2009-0066062). Part of this work was also supported by the research fund of Incheon University in 2009.

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- See Supporting Information for details
- The GPC analysis of the oligomer **1** revealed molecular weights of $M_n = 4.9 \times 10^3$ and $M_w = 6.6 \times 10^3$, respectively.
- Ferrocenium/ferrocene (Fc^+/Fc) redox couple with a potential of 4.80 eV relative to vacuum as the reference potential was used.