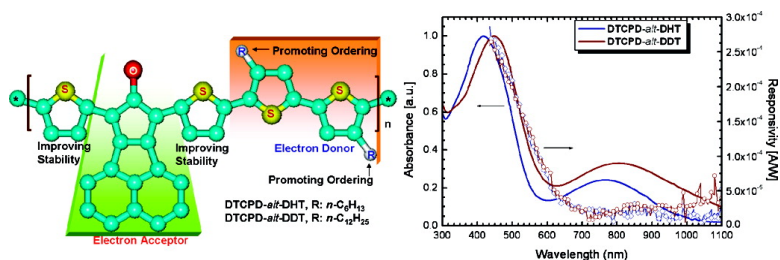## Communication

Visible#Near Infrared Absorbing Dithienylcyclopentadienone#Thiophene Copolymers for Organic Thin-Film Transistors

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Visible−Near Infrared Absorbing Dithienylcyclopentadienone−Thiophene Copolymers for Organic Thin-Film Transistors

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Solution-processable organic semiconductors with relatively high-mobility are required for printing low-cost organic thin-film transistor (OTFT) circuits for flexible electronics.[1−6] Thiophene-based conjugated polymers have been extensively studied as materials for such applications.[7−10] In particular, as a result of the structural regularity of the polymer backbone, regioregular poly(3-hexylthiophene) (rr-P3HT) exhibits a relatively high charge-carrier (hole) mobility.[11,12]

Another important development in the synthesis of π-conjugated polymers has been the utilization of donor−acceptor architectures within the backbone. The donor−acceptor systems cause partial intramolecular charge transfer (ICT) that enables manipulation of the electronic structure (HOMO/LUMO levels), leading to low band gap semiconducting polymers[13−18] with relatively high charge carrier mobilities.[19−26]

To create a push−pull system, we have recently prepared a series of polymers based on diaryl-dithienylcyclopentadienone (2,5-dithienyl-3,4-(1,8-naphthylene)cyclopentadienone, **DTCPD**), revealing a broad absorption band covering practically the whole visible region.[27,28]

Given the attractive properties of **DTCPD** and those of the regioregular thiophene-based materials, we have combined the two units into a new polymer repeat unit. Following the ICT strategy, 4,4′-dialkyl-[2,2′]bithiophene (**DAT**) moieties are selected as an electron-rich comonomer for **DTCPD** since tail-to-tail regio-positioning of the alkyl chains on the thiophene monomer helps promote self-organization, while minimizing any steric interactions between neighboring alkyl groups, thus preserving backbone planarity.[29] Besides, it is expected that the unsubstituted thiophene units in **DTCPD** can increase the ionization potential (IP) via improving rotational freedom,[30,31] possibly resulting in enhanced oxidative stability when compared to that of the poly(alkylthiophene)s.

Herein, we present the synthesis of a series of alternating **DTCPD**−**DAT** copolymers (**DTCPD-***alt***-DHT** and **DTCPD-***alt***-DDT**) and the initial characterization of these copolymers. We report the first examples of the performance of organic field-effect transistors (OFETs) fabricated from **DTCPD**-based copolymers (Figure 1).

The synthesis of the donor−acceptor copolymers is depicted in Scheme 1. First, 2,5-dithienyl-3,4-(1,8-naphthylene)cyclopentadi-
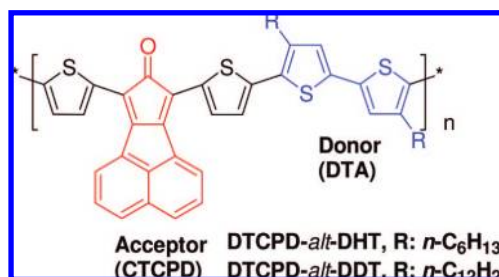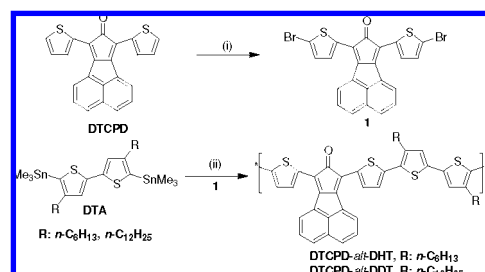

Figure 1. Chemical structures of **DTCPD**, **DTCPD-***alt***-DHT**, and **DTCPD-***alt***-DDT**.

Scheme 1[a]

[a] Reagent and conditions: (i) Br₂ in AcOH/CH₂Cl₂, 95% (ii) Pd(PPh₃)₂Cl₂ with conventional heating or Pd₂(dba)₃/(o-tolyl)₃P with microwave heating in chlorobenzene.

enone (**DTCPD**) was prepared by procedures described earlier (DCC-mediated and double Knoevenagel condensation).[27,28] The desired 2,5-di(5-bromothienyl)-3,4-(1,8-naphthylene)cyclopentadi-enone (**1**) was obtained after treatment with bromine in acetic acid/dichloromethane (95%). 4,4′-Dialkyl[2,2′]bithiophenes (**DAT;** 4,4′-dihexyl[2,2′]bithiophene (**DHT**) and 4,4′-didodecyl[2,2′]bithiophenes (**DDT**))[32] were converted to the corresponding distannyl comonomers via dilithiation and subsequent reaction with trimethylstannyl chloride.[33] The **DTCPD** units were incorporated with the **DAT** comonomer into the polymer backbone via palladium(0)-mediated Stille-type polycondensation, affording a series of **DTCPD-***alt***-DAT** copolymers (**DTCPD-***alt***-DHT** and **DTCPD-***alt***-DDT**). This synthetic protocol utilizes two symmetrical monomers, thus avoiding the regio-irregularities that can occur during the polymerization of asymmetric monomers.[7] Gel-permeation chromatography (GPC) analysis against a PS standard yields a number-averaged molecular mass (M_n) of 4700 and 6200 gmol⁻¹ for **DTCPD-***alt***-DHT** and **DTCPD-***alt***-DDT** respectively with a polydispersity (PDI) of 1.39 and 1.71.

There are many examples of the application of microwave irradiation as a heat source to reduce reaction times and increase

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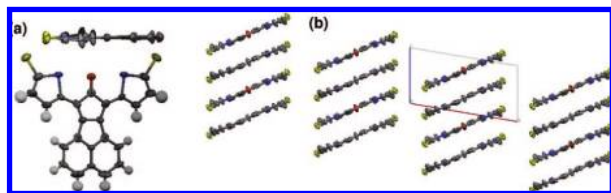
Figure 2. (a) Single crystal (the top view displays the planarity) and (b) molecular packing (view along the *b*-axis) of **1**. Carbon, sulfur, oxygen, hydrogen, and bromine atoms are colorized in gray, blue, red, white, and yellow, respectively. The solvent (EtOH) is omitted for clarity.

Figure 3. UV−vis absorption spectra of **DTCPD-*alt*-DHT** (blue line) and **DTCPD-*alt*-DDT** (red line) in chloroform and corresponding photoconductivity (scatter).

Figure 4. Cyclic voltammetry and in situ conductivity (red) showing p-doping but not n-doping.

the yield and the molecular weight of metal-mediated cross-coupling reactions.[29,34−38] We therefore investigated a microwave-facilitated synthesis of the **DTCPD-DAT**-based copolymers with improved molecular weights. Although both **DTCPD-*alt*-DHT** and **DTCPD-*alt*-DDT** were successfully synthesized by using a microwave-assisted heating protocol, the polymerization fails to yield high molecular weight copolymers (M_n = 4500−6000 gmol^{-1}). The reason for the low molecular weights is likely the poor solubility of the monomer **1** and/or reduced stability of the intermediate palladium complexes involving **DTCPD** units.

Monomer **1**'s unique structure was determined by single crystal X-ray structure analysis (Figure 2).[39] A close face-to-face $\pi-\pi$ stacking motif is observed, where the interplanar distance is ∼3.57 Å and the shortest intermolecular C−C contact is 3.27 Å, allowing a sheet-like columnar network. Interestingly, two thiophene units face the same direction (syn conformation) as the oxygen atom of the cyclopentadienone, very likely due to the intramolecular interaction between S and O, leading to the coplanarity between thiophene groups and the cyclopentadienone core.

The molecular packing of the copolymer series in thin films cast from solution (onto a Si wafer as substrate) was studied by X-ray diffraction (XRD) analysis. No scattering patterns are observed, suggesting a macroscopically disordered, amorphous solid.

The thermal properties of the copolymers were investigated by differential scanning calorimetry (DSC) in a nitrogen atmosphere at a heating rate of 10 °C/min. We observed neither a glass transition (T_g) nor any other thermal process (such as the existence of a liquid crystalline phase) between 25 and 300 °C (see Supporting Information).

Cyclic voltammograms of the copolymers show two clearly reversible reduction peaks at E_{red} = −0.731 and −1.175 V vs Ag/AgCl for **DTCPD-*alt*-DHT** and −0.689 and −1.132 V for **DTCPD-*alt*-DDT** in the n-doping process respectively (see Supporting Information, SI). These can be assigned to the reduction of the cyclopentadienone moieties to anion radicals. In the oxidative region, irreversible oxidation waves for **DTCPD-*alt*-DHT** and **DTCPD-*alt*-DDT** are observed at 0.899 and 0.885 V respectively, arising from p-doping of the thiophene units. The ionization potential (IP) values estimated from the onset[40] are 5.02 eV for **DTCPD-*alt*-DHT** and 5.04 eV for **DTCPD-*alt*-DDT**, somewhat greater than that of poly(alkylthiophene)s,[19] implying the relatively enhanced oxidation stability due to the increase in flexibility through the unsubstituted thiophene units in the backbone.[31]

The UV−vis absorption spectra of both copolymers in chloroform solution are similar in shape, exhibiting a strong and broadband covering the visible (vis) to near-infrared (NIR) range (Figure 3). To elucidate the photogeneration of charge carriers and their subsequent migration by diffusion or drift in an electric field, the steady-state photoconductivity spectra of the copolymers in thin films were investigated. Surprisingly and quite disappointingly, the low-energy bands centered at 767 and 806 nm for **DTCPD-*alt*-**
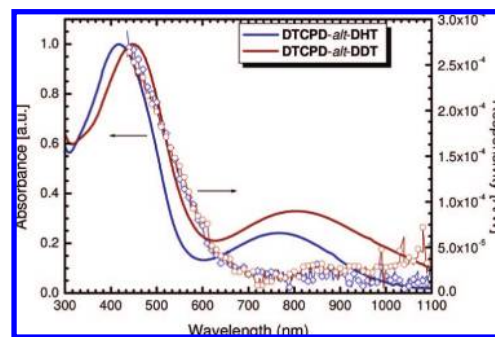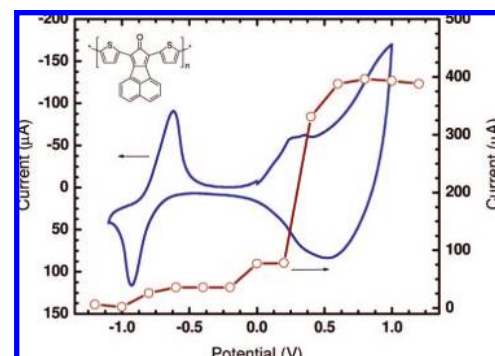
DHT** and **DTCPD-*alt*-DDT**, respectively, revealed no photoresponse (Figure 3), essentially negating the proposition, supported by electrochemistry, that cyclopentadienone-containing conjugated backbones should lead a low-band gap material.[41] This unexpected result is difficult to explain. One possibility is that the NIR absorption band of the polymer is simply due to *independent, localized cyclopentadienone moieties*. In support of this rationalization, **DTCPD** as well as tetraphenyl cyclopentadienone monomers exhibit very similar NIR bands to **DTCPD-*alt*-DHT** and **DTCPD-*alt*-DDT**, except that the monomers' spectra are slightly blue-shifted. We also cannot rule out that the cyclopentadienone moieties are possible electron trap sites. This conclusion is supported by the fact that in situ conductivity measurements show increased conductivity upon p-doping of poly(**DTCPD**) but *no change in conductivity upon n-doping* (see Figure 4 and SI). Although measurements have been performed on very rough films,[42] we were not comfortable with the results and thus reported the data as raw current; however, using an average thickness of 400 nm, a maximum p-doped conductivity of ca. 10^{-2} S cm^{-1} was obtained. To precisely confirm various hypotheses, we are currently studying the unusual optoelectronic properties within various donor−acceptor molecular architectures.

All field-effect transistors (FETs) were fabricated in the top contact geometry as described in the Experimental Section (Figure 5a). Figure 5b shows the transfer characteristics, $|I_{ds}|$ vs V_{gs} and $|I_{ds}|^{1/2}$ vs V_{gs} (both at V_{ds} = −60 V), of FETs fabricated using **DTCPD-*alt*-DHT** and **DTCPD-*alt*-DDT**, respectively, as the active layer. These I_{ds} vs V_{gs} curves obtained from both **DTCPD-*alt*-DHT** and **DTCPD-*alt*-DDT** are typical of p-type semiconductors, as might be expected from the thiophene building blocks in the main backbone. The hole mobilities deduced from the slopes of $I_{ds}^{1/2}$ vs V_{gs} are estimated to be μ_{DHT} = 7.80 × 10^{-3} cm^2 V^{-1} s^{-1} (on/off
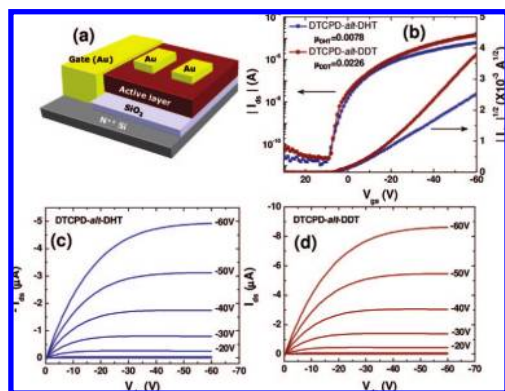
Figure 5. (a) Schematic diagram of p-type OFET structure ($L = 50$ μm, $W = 1.5$ mm) with **DTCPD**-*alt*-**DHT** (blue line) and **DTCPD**-*alt*-**DDT** (red line), respectively: (b) transfer curves in saturated regime; (c and d) the output curves at different gate voltages.

ratio $\sim 10^5$) for the **DTCPD**-*alt*-**DHT** and $\mu_{DDT} = 2.26 \times 10^{-2}$ cm^2 V^{-1} s^{-1} (on/off ratio $\sim 10^6$) for the **DTCPD**-*alt*-**DDT**. The slightly higher value obtained from the **DTCPD**-*alt*-**DDT** implies that the longer alkyl groups can induce better structural order in the solid state. Both **DTCPD**-*alt*-**DHT** and **DTCPD**-*alt*-**DDT** provide excellent FET output characteristics with clear saturation (Figure 5c and d). The highest current of **DTCPD**-*alt*-**DDT** at $V_{gs} = -60$ V and $V_{ds} = -60$ V is higher than that of **DTCPD**-*alt*-**DHT**. This is consistent with the higher mobility inferred from the transfer characteristic curves. Further investigations toward a detailed understanding of the transport mechanisms within the donor−acceptor systems and their influence on the optoelectronic properties are in progress.

In summary, the push−pull strategy was applied to two alternating copolymers (**DTCPD**-*alt*-**DHT** and **DTCPD**-*alt*-**DDT**), comprising electron donor (thiophene) and acceptor (cyclopentadienone) units in the backbone. The macromolecules (oligomers) were synthesized by Stille-type polycondensation. Our results illustrate despite low molecular weights the first example of a **DTCPD**-based copolymer with a substantial field-effect mobility for use in displays. Furthermore, these materials reveal an atypical correlation between absorption and photoresponse, which is in contrast to most conjugated polymers, where the spectral dependence of the photoconductivity coincides with the spectral dependence of the absorption. Currently further studies are underway to optimize and clarify these donor−acceptor architectures, in particular the materials based on **DTCPD** that can lead to a favorable strategy toward rational design of materials with higher mobility.

Supporting Information Available: Text giving full experimental details for the synthesis of all new materials as well as the measurements, differential scanning calorimetry (DSC), cyclic voltammograms, XRD patterns, UV−vis absorption spectra, the in situ conductivity measurement, and crystal data tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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