

A new n-type low bandgap conjugated polymer P-co-CDT: synthesis and excellent reversible electrochemical and electrochromic properties†

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A n-type low bandgap conjugated polymer based on perylene diimide and cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, which exhibits excellent reversible electrochemical properties in both n-doping/dedoping and p-doping/dedoping processes, was designed, synthesized and characterized.

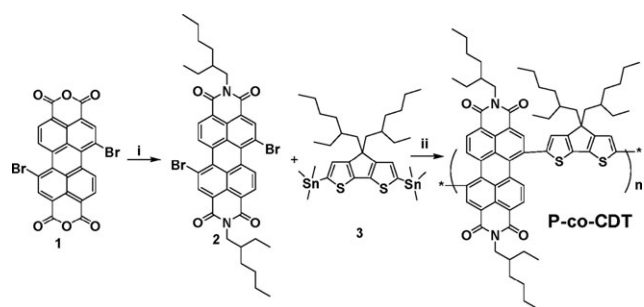
Conjugated polymers have recently attracted considerable attention because of their potential for use in electronic and electrochemical devices such as polymer light-emitting diodes (PLEDs),¹ polymer solar cells (PSCs),² sensors,³ electrochromics,⁴ and field effect transistors (FETs).⁵ For these applications, conjugated polymers with different energy levels, bandgaps and other electrochemical properties are required. Bandgap and molecular energy levels including the highest occupied molecular orbital level (HOMO) and lowest unoccupied molecular orbital level (LUMO) are important parameters for use in electronic devices such as PSCs and PLEDs, and hence many research works on conjugated polymers are focusing on bandgap and energy level control. At present, the majority of conjugated polymers in use are p-type materials, which can be used as electron donors or hole transport materials in electronic devices. The n-type conjugated polymers having low-lying LUMO level have attracted considerable attention recently due to their potential for use as electron acceptors,⁶ electron-transporting materials,⁷ and hole-blocking materials.⁸ Electrochemical reversibility of n-type conjugated polymers is also an important issue for use in electrochemical devices such as electrochromic devices and electrochemical capacitors or supercapacitors.^{9,10}

In this paper, we report a new n-type conjugated polymer based on *N,N'*-bis(2-ethylhexyl)-3,4,9,10-perylene diimide (compound **1**) and 4,4-bis(2-ethylhexyl)cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CDT, compound **2**) and named the polymer as P-co-CDT as shown in Scheme 1. Compound **3** was synthesized through the reported method,¹¹ and the detailed synthesis procedure for compound **2** and P-co-CDT are shown in the ESI.† The polymer exhibited excellent solubility in organic solvents including toluene, chlorobenzene, THF, and chloroform. The weight-average

molecular weight and polydispersity index were estimated as 18 K and 1.5, respectively, using GPC (polystyrene standards). TGA showed excellent thermal stability with an onset decomposition temperature under nitrogen of 380 °C.

The cyclic voltammetry (CV) curves of P-co-CDT are shown in Fig. 1. From the n-doping and the p-doping onset potential of the polymer, the LUMO and HOMO levels of the polymer were calculated to be -4.02 eV and -5.52 eV, respectively, corresponding to an electrochemical bandgap (E_g^{ec}) of 1.5 eV. Apparently, this polymer can serve as a n-type conjugated polymer because of its low-lying LUMO level. As reported,¹² an alternating copolymer of perylene diimide and dithienothiophene exhibits good electron transport properties. In particular it has been used as an electron acceptor material in polymer solar cells (PSC), and a power conversion efficiency of 1.5% was obtained with a broad incident photon-to-current conversion efficiency spectrum of up to 850 nm. The electron mobility of this material in an OFET device was found to be as high as $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹² As a result, we expect P-co-CDT to be a potential n-type material for electronic devices. In Fig. 2(a), it can be seen that there are well reversible p-doping/dedoping (oxidation/reduction) processes in the positive potential range and n-doping/dedoping (reduction/re-oxidation) processes in the negative potential range. Some p-type conjugated polymers such as polythiophenes also exhibit good reversibility, but there are few reports on n-type materials having good electrochemical reversibility for both the n- and p-doping processes.^{13d,14,15}

As reported, P-co-DT exhibited a reversible n-doping property, but its p-doping process was irreversible.¹² The comparison between P-co-CDT and P-co-DT indicates that the CDT units in P-co-CDT play an important role in its p-doping



Scheme 1 Synthetic route of P-co-CDT. Reagents and conditions: (i) 2-ethylhexylamine, DMF, 70 °C, overnight; (ii) Pd(PPh₃)₄, toluene, inert atmosphere, reflux, 48 h.

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† Electronic supplementary information (ESI) available: Experimental section; Scheme S1: Molecular structures of P-co-F and P-co-BDT. Fig. S1: CV plots of P-co-F, P-co-BDT and P-co-CDT. See DOI: 10.1039/b812489b

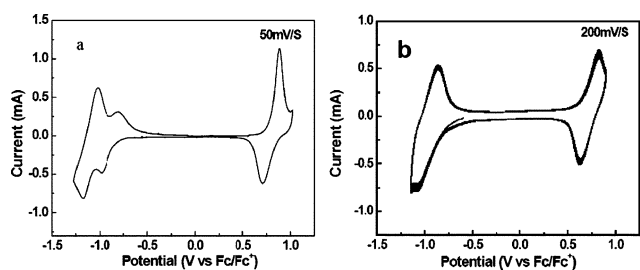


Fig. 1 Cyclic voltammograms of P-co-CDT in 0.1 mol L⁻¹ [Bu₄N]PF₆ acetonitrile solution: (a) one cycle with a scan rate of 50 mV s⁻¹; (b) 100 cycles with a scan rate of 200 mV s⁻¹.

property. In order to find a material with reversible n- and p-doping properties, the perylene-diimide unit was also copolymerized with two other conjugated units, 9,9-dioctylfluorene-2-7-diyl and 4,8-dioctylbenzo[1,2-*b*:4,5-*b'*]-dithiophene-2,6-diyl, where two new polymers, denoted as P-co-F and P-co-BDT, respectively, were synthesized. It was found that their p-doping processes are irreversible as seen in P-co-DT. As reported, the p-doping process of other two perylene-diimide contained polymers are also irreversible.¹⁵ The reason why only P-co-CDT exhibits a reversible p-doping property is currently being investigated and the results will be published soon. In order to make clear comparisons, the preliminary results from CV measurements and the molecular structures of P-co-F and P-co-BDT are provided in the ESI.†

In order to investigate electrochemical reversibility of P-co-CDT, we did 1000 scans on one sample using a Pt electrode in 0.1 mol L⁻¹ Bu₄NPF₆, CH₃CN solution under ambient atmosphere. In the CV measurements, silver wire was used as a quasi-reference electrode, and the system was calibrated by adding a very small amount of ferrocene. It should be noted that since the peak current in Fig. 1(b) is several times higher than that in Fig. 1(a) due to the higher scan speed, the voltage drop caused by the series resistance is increased, which increases the absolute value of the potential at the peak point in Fig. 1(b) as compared to that in Fig. 1(a).

In fact, in Fig. 1(b), only the first n-doping/dedoping process has taken place in the negative direction. During the first five scans, there is little change in the shape of the CV curves and the shape of the curves is stable. When increased up to 100 scans, the CV curves still repeated very well, as shown in Fig. 1(b). However, when extended up to 1000 scans, the shape of the CV curves changes gradually, and the current of the n- and p-doping/dedoping processes becomes slightly smaller, with the onset points of the curves showing little change. The sample also has good reversibility for both the n-doping and p-doping processes. We also observed that some small pieces of polymer film were detached from the Pt electrode, which should be the main reason for the current decrease of the n- and p-doping processes. Therefore, P-co-CDT should be a promising material for use in electrochemical capacitors or supercapacitors due to its excellent electrochemical reversibility.

In situ absorption spectra were measured to study the p-doping/dedoping process and electrochromic properties of conjugated polymers.^{4b,d,13} However, there are few reports on the absorption spectra change during the n-doping/dedoping processes of conjugated polymers.¹⁴ The *in situ* absorption spectra of P-co-CDT film in a 0.1 mol L⁻¹ [Bu₄N]PF₆ acetonitrile solution at different cathodic potentials with units of V vs. Fc/Fc⁺ were measured during the n-doping/dedoping and p-doping/dedoping processes as shown in Fig. 2(a)–(e). As shown in Fig. 1(a), the CV curve of P-co-CDT exhibited two reversible n-doping processes. Interestingly, *in situ* absorption spectra also exhibited two electrochromic steps during the n-doping/dedoping process. As shown in Fig. 2(a), the pristine film of P-co-CDT has three absorption peaks in the UV-visible range at 374, 500 and 708 nm. It can be seen that the absorption spectrum did not change until the potential was decreased to lower than -0.7 V. During the first n-doping process from -0.7 to -0.9 V, the peak at 500 nm decreased gradually and almost disappeared, and a new peak at about 753 nm appeared and increased gradually. During the second n-doping process from -0.9 to -1.04 V, the new peak at 753 nm decreased gradually and disappeared, but another

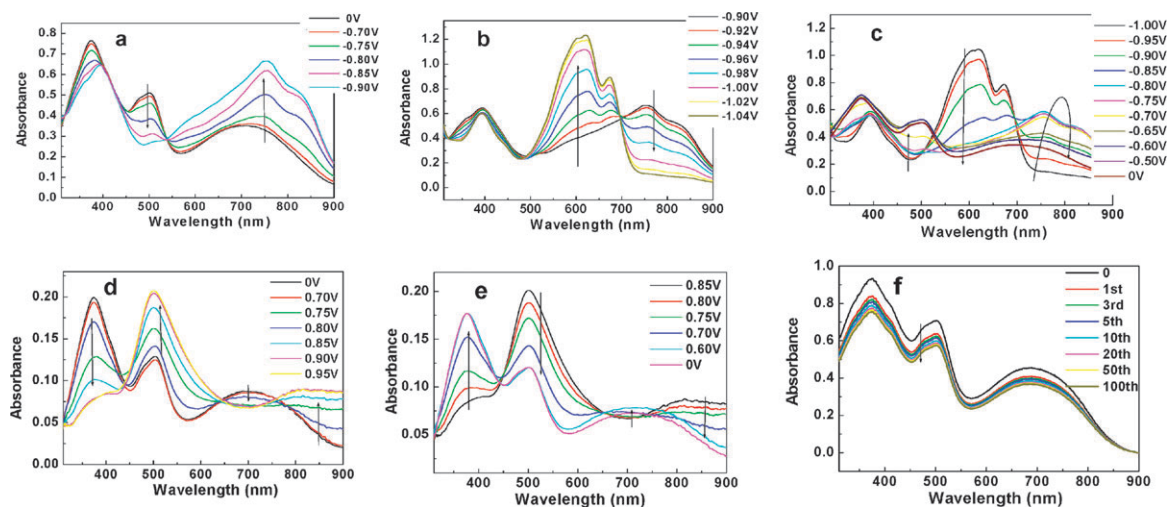


Fig. 2 *In situ* absorption spectra of P-co-CDT. (a) the first n-doping process from 0 to -0.9 V; (b) the second n-doping process from -0.9 to -1.04 V; (c) the n-dedoping process from -1.0 to 0 V; (d) the p-doping process from 0 to 0.95 V; (e) the p-dedoping process from 0.85 to 0 V; (f) absorption spectra in the neutral state after full CV scans, from 0 to -0.95 to 0.9 to 0 V.

new peak at about 620 nm appeared and increased very quickly. The absorption spectra of the n-dedoping process are shown in Fig. 2(c), and it can be seen that the absorption spectra exhibited good reversibility and gradually returned to its original shape.

P-co-CDT also exhibited an excellent reversible p-doping/dedoping property, and the *in situ* absorption spectra of the p-doping/dedoping process is provided in Fig. 2(d). As shown, the absorption spectrum began to change when the potential was increased beyond 0.7 V. During the p-doping process from 0.7 to 0.95 V, the absorption peaks at 374 and 708 nm were lowered step by step, but the peak at 504 nm and the absorption in near infrared region were elevated. As the potential returned to 0.6 V vs. Fc/Fc⁺, the absorption spectrum of P-co-CDT resumed to the original spectrum in its neutral state as shown in Fig. 2(e).

In Fig. 3, three photos of a P-co-CDT film on an ITO glass substrate in an electrochemical cell at 0, -0.8 and -1.0 V vs. Fc/Fc⁺ are shown, and the thickness of the film is about 40 nm. The P-co-CDT film had a pale yellow-green color in its neutral state; the film color shifted to a pale cyan in its first n-doping state, which then changed to pure blue in its second n-doping state. 100 scans were performed on one film. As shown in Fig. 2(f), we found that for the first three scans, the absorbance of the P-co-CDT film decreased slightly; however the absorption spectra showed little change in the remaining 97 scans. In order to investigate the stability of the electrochromism of P-co-CDT, we held the potential at -1.0 V for 24 h under ambient atmosphere. The absorption spectrum of the sample exhibited little change, which indicates that the electrochromism showed not only good reversibility but also good stability.

Additionally, since P-co-CDT can serve as an electron acceptor material in polymer solar cells (PSC)s, a PSC device was fabricated using P-co-CDT as the electron acceptor and poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl)] as the electron donor. A power conversion efficiency of 0.43%, with an open circuit voltage of 0.68 V and a J_{sc} of 1.4 mA cm⁻², was recorded in our preliminary test. Detailed information on the device fabrication and characterization is provided in the ESI.†

In summary, we have synthesized a novel n-type conjugated polymer, P-co-CDT, through Stille coupling reaction. P-co-CDT is a n-type small bandgap conjugated polymer, which exhibits good solubility in several kinds of solvents and good thermal stability below 380 °C. The electrochemical cyclic voltammogram of the polymer showed excellent reversible electrochemical properties in both the n-doping/dedoping and p-doping/dedoping processes. Therefore, P-co-CDT should be a promising material for use in electrochemical capacitors or supercapacitors. *In situ* absorption spectra of the polymer were investigated in detail, and the results demonstrate P-co-CDT as a promising electrochromic conjugated polymer, especially in the n-doping potential region. The preliminary testing results for PSC devices indicate that P-co-CDT can also be used as an n-type electron acceptor conjugated polymer material in polymer solar cells.



Fig. 3 Color of the P-co-CDT film in its neutral state, first n-doping state and second n-doping state (at 0, -0.8 and -1.0 V vs. Fc/Fc⁺) from left to right, respectively.

Additionally, P-co-CDT can also be used in other polymer optoelectronic devices such as n-channel OFET devices.

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