### Synthesis and photovoltaic properties of thieno[3,2-b]thiophenyl substituted benzo[1,2-b:4,5-b’]dithiophene copolymers

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Synthesis and photovoltaic properties of thieno[3,2-b]thiophenyl substituted benzo[1,2-b:4,5-b']dithiophene copolymers

Zeyun Xiao, Jegadesan Subbiah, Kuan Sun, David J. Jones, Andrew B. Holmes and Wallace W. H. Wong*

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A new benzo[1,2-b:4,5-b']dithiophene (BDT) building block with 4,8-disubstitution using 2-(2-ethylhexyl)-3-hexylthieno[3,2-b]thiophene as the substituent has been designed and synthesized. The new building block has been copolymerized with benzothiadiazole (BT) and 5,6-difluorobenzothiadiazole (fBT) by Suzuki and Stille coupling polymerization to synthesize donor-acceptor conjugated polymers. The optical and electrochemical properties of the synthesized copolymers were studied. Bulk heterojunction solar cells were fabricated using the donor-acceptor copolymers in conjunction with PC_{71}BM and exhibited up to 4.20% power conversion efficiency.

Introduction

Bulk heterojunction (BHJ) polymer solar cells consisting of a blend of conjugated polymer donor and a fullerene acceptor as the photoactive layer have attracted considerable attention during the last decade. Materials innovation, especially the development of the conjugated polymer donor, is one of the major forces that has driven the improvements in device performance reaching power conversion efficiency (PCE) of over 9%. Among various conjugated polymers developed for BHJ solar cells, the two-dimensional conjugated (“2D conjugated”) polymers, in which conjugated side chains are orthogonally attached to the polymer backbone, are particularly interesting due to their superior optical and electrical properties. One of the most successful examples of this concept has been demonstrated on polymers containing benzo[1,2-b:4,5-b']dithiophene (BDT) building block on their backbone. The “2D conjugated” polymers exhibited red-shifted absorption spectra, significantly higher hole mobility, and greatly improved photovoltaic properties, in comparison with the two alkoxy substituted polymer analogues. Meanwhile, extending the fused-rings systems along the polymer backbone can also lead to enhancement in the optical absorption profile, charge carrier mobility, and BHJ solar cell performance. In a polymer system containing the dithieno[2,3-d:2′,3′-d’]benzo[1,2-b:4,5-b’]dithiophene (BDT) building block on their backbone, it was hypothesised that the device performance improvement was a result of lower positive charge density and exciton binding energy. Dithienogermole has also been extended by incorporating thieno[3,2-b]thiophene with the aim of enforcing coplanarity, reducing rotational disorder, lowering reorganization energy and increasing charge carrier mobility.

In BHJ polymer solar cells, BDT based copolymers are among the most frequently used donor materials. A number of dithienyl-BDT containing polymers have been used in high performance solar cell devices (Fig. 1). In this study, the orthogonal thiophene units on the BDT core was replaced by thieno[3,2-b]thiophene units (Fig. 1). It was envisaged that the introduction of two alkyl chains on the thieno[3,2-b]thiophene units would provide the solution processability required for material characterisation and device fabrication. Extending of the fused ring system in the 2D direction is expected to broaden the light absorption of the material with enhanced high energy absorption bands. In addition, the 2D conjugation would allow the delocalization of holes over the side chain, thus lowering...
the local charge density and the Coulombic interactions between
the hole and the electron in the donor-acceptor interface.\textsuperscript{21-23}

Compared with extending the fused-ring systems along the
polymer backbone, the extending of a fused ring in the side
chains could also maintain the solubility and processability of the
conjugated polymers. To achieve low highest occupied molecular
orbital (HOMO) energy level and thus the high open circuit
voltage ($V_{oc}$), benzothiadiazole (BT) and 5,6-difluoro-2,1,3-
benzothiadiazole (fBT) were used as the acceptor un-
its for the synthesis of the donor-acceptor conjugated polymers.\textsuperscript{13, 19, 24-27}

**Synthesis and characterization**

**Monomer and polymer synthesis**

The synthetic route for preparing the 4,8-bis(2-(2-ethylhexyl)-3-
hexylthieno[3,2-b]thiophene) BDT monomers is shown in
Scheme 1. 2-(2-Ethylhexyl)-3-hexylthieno[3,2-b]thiophene 7 was
obtained by Kumada coupling of 2-bromo-3-hexylthieno[3,2-
b]thiophene 6 and 2-ethylhexyl bromide with the catalyst of
Pd(dppf)Cl\(_2\) after deprotonation with butyl lithium, compound 7
was treated with 4,8-dihydrobenzeno[1,2-b:4,5-b']dithiophen-4,
8-dione and then reduced with tin(II) chloride to give BDT 8 in
72% yield. Compound 8 was converted into the diodo monomer
10 or bistrimethylstannyl monomer 9 with n-butyl lithium and
then iodine or trimethyltin chloride. The copolymerization of the diodo monomer 10 and the BT
monomer 11 by Suzuki coupling polymerization was very
efficient (Scheme 2).\textsuperscript{29} Polymerization time of 0.5 hour was
enough for high MW polymer and further increase of the
polymerization time lead to large quantity of insoluble polymer.
The resulting polymer was purified by precipitation from methanol
and subsequent Soxhlet extraction with methanol,
acetone, hexane, dichloromethane, and chloroform. The fBT
monomer 12 is not stable in the hot basic condition employed in
the Suzuki coupling polymerization, so the fBT monomer 12 was
copolymerized with the bistrimethylstannyl monomer 9 by Stille
coupling polymerization (Scheme 2).\textsuperscript{29} In comparison with the
Suzuki coupling polymerization, the Stille coupling
polymerization was much slower and took 2 days. The resulting
polymer P2 was purified in a similar way to that of the polymer
P1. The yields of P1 and P2 were 43% and 39%, respectively. Polymers P1 and P2 were soluble in chlorinated solvent such as
chlorobenzene and o-dichlorobenzene, but not soluble in acetone,
toluene, hexane or acetonitrile. The molecular weight and
polydispersity (PDI) of the polymers were determined using high
temperature gel-permeation chromatography (GPC) in
trichlorobenzene at 120 °C (Figures S1 and S2). The number-
average molecular weight ($M_n$) of P1 and P2 were 28,900 and
10,500 g/mol, respectively. Thermal properties of the polymers
were investigated using differential scanning calorimetry (DSC).
No significant thermal transitions were observed in DSC analysis
in the range of 40 to 300 °C for both polymers (Fig. S3).
Optical properties and energy levels

The UV-vis absorption spectra of the polymers in chloroform are shown in Fig. 2a. Both polymers exhibited broad absorption from 300 nm to 700 nm. The absorption maximum ($\lambda_{\text{max}}$) of P1 was located at 648 nm and the onset absorption ($\lambda_{\text{onset}}$) was at 731 nm (Table 1). Polymer P2 showed slightly red shifted $\lambda_{\text{onset}}$ due to the more electron withdrawing properties of the fBT unit (the $\lambda_{\text{max}}$ and $\lambda_{\text{onset}}$ of P2 were at 644 and 740 nm, respectively). The longest wavelength absorption band could be assigned to the intramolecular charge transfer (ICT) between the acceptor units of the film absorption, the $\lambda_{\text{onset}}$ of the P1 and P2 films was determined to be 740 nm and 747 nm respectively. This corresponds to an optical energy gaps of 1.68 eV for P1 and 1.66 eV for P2 (Table 1). P1 and P2 showed solution fluorescence emission maximum at 720 and 707 nm respectively when photo-excited at 650 nm. Very weak solid film fluorescence emission was recorded at 725 and 716 nm for P1 and P2 film, respectively (Table 1). Electrochemical properties of the polymers were investigated via cyclic voltammetry (CV) using a three-electrode cell with a glass carbon working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ pseudo reference electrode (Fig. 3). Ferrocene was used as the internal reference. The measurements were performed in an acetonitrile solution containing 0.1 M Bu$_4$NPF$_6$ at a scan rate of 50 mV s$^{-1}$. Film samples prepared by drop-casting of dichlorobenzene solutions of the polymers onto the glass carbon electrode. Polymer P1 showed irreversible oxidation peak around at 0.98 V, while P2 displayed a slight higher irreversible oxidation peak of 1.02 V (Fig. 3). The onset potentials of the oxidation were used to calculate the HOMO energy levels of the polymers. Using the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple as reference (4.8 eV below vacuum), the HOMO energy levels of the P1 and P2 were determined at -5.46 and -5.50 eV, respectively. The onset reduction potentials were used to calculate the LUMO energy levels which were at -3.61 and -3.68 eV for P1 and P2, respectively (Table 1). The HOMO-LUMO energy gap measured from these electrochemical experiments were slightly larger than the optical energy gap (Table 1). From the CV measurement results, both polymers showed low lying HOMO energy levels which is good for achieving high $V_{oc}$ solar cells. The introduction of the fluorine atom only caused a small perturbation in the HOMO energy level of the resulting polymer.

Table 1 The optical properties and electronic energy levels of the polymers P1 and P2.

<table>
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<tr>
<th>Polymer</th>
<th>Molecular weight (g/mol)$^a$</th>
<th>UV-vis $\lambda_{\text{max}}$ (nm)$^b$</th>
<th>Absorption coefficient at $\lambda_{\text{max}}$ (L cm$^{-1}$ g$^{-1}$)$^c$</th>
<th>UV-vis $\lambda_{\text{onset}}$ (nm)$^d$</th>
<th>Optical energy gap (eV)$^e$</th>
<th>PL $\lambda_{\text{max}}$ (nm)$^f$</th>
<th>$E_{\text{HOMO}}$ (eV)$^g$</th>
<th>$E_{\text{LUMO}}$ (eV)$^h$</th>
<th>HOMO-LUMO gap by CV (eV)$^i$</th>
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<tr>
<td>P1</td>
<td>28,900 (1.9)</td>
<td>648 (652)</td>
<td>16.7</td>
<td>731 (740)</td>
<td>1.68</td>
<td>720 (725)</td>
<td>-5.46</td>
<td>-3.61</td>
<td>1.85</td>
</tr>
<tr>
<td>P2</td>
<td>10,500 (3.3)</td>
<td>644 (657)</td>
<td>16.9</td>
<td>740 (747)</td>
<td>1.66</td>
<td>707 (716)</td>
<td>-5.50</td>
<td>-3.68</td>
<td>1.82</td>
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$^a$ Molecular weight data obtained by GPC calibrated against polystyrene standards with polydispersity index in brackets. $^b$ UV-vis absorption maxima in chloroform solution and as thin films in bracket. $^c$ Calculated at the absorption maximum in chloroform solution (0.04 g/L). $^d$ UV-vis onset absorption in chloroform solution and as thin films in bracket. $^e$ Calculated from thin film absorption onset. $^f$ Fluorescence emission maxima in chloroform solution and as thin films in bracket. $^g$ Measured using cyclic voltammetry.

![Normalized UV-vis absorption spectrum of polymers P1 and P2](a) in chloroform solution and (b) in the solid films.

![Cyclic voltammetry curves showing oxidation and reduction processes of polymer films](b)
Device fabrication and characterization

The photovoltaic device performance of polymers P1 and P2 were investigated. A schematic diagram of the solar cells with inverted device architecture [ITO/ZnO/active layer/MoO3/Ag] is shown in Fig. 4a. o-Dichlorobenzene (oDCB) was chosen as the processing solvent due to its good solvent properties and low vaporization rates. Optimized blend ratio of polymer/PC71BM 1:2 was used for spin coating of the active layer. The blend film absorption is shown in Fig. S5. The devices were studied under the illumination of AM 1.5 G, 100 mW cm$^{-2}$. The current density to voltage ($J$-$V$) curves of the polymer/PC71BM devices are displayed in Fig. 4b and the photovoltaic performance is listed in Table 2. The P1:PC71BM (1:2) devices showed an average PCE of 2.6% with a $V_{oc}$ of 0.90 V, a fill factor (FF) of 42%, and a short circuit current density ($J_{sc}$) of 6.8 mA cm$^{-2}$. The use of solvent additive, 1,8-diodooctane (DIO), was found to be very effective in improving the device performance. With 2.5% (volume ratio) of DIO in the processing solvent oDCB, the BHJ solar cell performance increased by 40% with a greatly improved $J_{sc}$ of 10.2 mA cm$^{-2}$ leading to PCE of 3.90% (Table S1). The increasing of the $J_{sc}$ and FF could be due to the improved morphology as evidenced by morphology studies (vide infra). Thermal annealing of the DIO processed solar cells at 120 °C for 3 minutes further increased the PCE to 4.20% (Table 2).

The photovoltaic device performance of polymers P1:PC71BM blend films is shown in Fig. 4c. The EQE curves of the P1:PC71BM devices derived from $J$-$V$ measurements. Clearly, the EQE values for P1 are higher than those of P2 based solar cells, which agree with the higher $J_{sc}$ values of the devices derived from P1.

Space-charge-limited current (SCLC) measurement was conducted to study the hole and electron mobility of the polymer/PC71BM blend films (Fig. S7 and S8). Hole only and electron only devices were fabricated (see ESI for details). According to Mott-Gurney law, SCLC theory can be described as $J = 9e_{0}\varepsilon_{r}\mu(V_{a}V_{oc}V_{bi})^{2/3}d^{2}$, where $J$ is current density, $\varepsilon_{0}$ is permittivity of vacuum, $\varepsilon_{r}$ is relative permittivity of the material, $\mu$ is mobility, $V_{a}$ is applied voltage, $V_{oc}$ is built-in voltage, and $d$ is the thickness of the active film. By this method, the hole mobility of P1:PC71BM (1:2) blend film was determined to be 1.3 $\times$ 10$^{-5}$ cm$^{2}$ V$^{-1}$ s$^{-1}$ which was higher than that of the P2:PC71BM (1:2) blend film (6.9 $\times$ 10$^{-6}$ cm$^{2}$ V$^{-1}$ s$^{-1}$) (Fig. S7). The electron mobility of the blends films were similar in the 10$^{-4}$ cm$^{2}$ V$^{-1}$ s$^{-1}$ range (Fig. S8). This means that the charge transport in the P1:PC71BM film was more balanced than that of the P2:PC71BM film. The result correlated to the higher $J_{sc}$ obtained from the P1 based solar cell devices.

The surface morphology of the polymer:PC71BM blend films were investigated using tapping mode AFM and the images are shown in Fig. 5. Compared to the blend film of P2:PC71BM which gave lower $FF$ and $J_{sc}$, P1:PC71BM blend film displayed a clear, phase-separated morphology in the nanometre scale. Nanometre phase separation is thought to be good for charge separation and transport as evidenced in many high performance polymers. The blend film of P1:PC71BM with DIO as solvent additive was also studied which gave even more evident phase separation. The percolated biphasic structure showed domain sizes in several tens of nanometres. Such phase separated film morphology should contain large donor/acceptor interface for exciton dissociation, small-enough domains that ensure all the photogenerated excitons have chances to move to donor/acceptor interface, and effective transportation pathways for both hole and electron carriers. The changes induced by addition of DIO could be due to the preferential interaction of DIO with the alkyl

![Fig. 4](image-url)
substituents of the benzodithiophene repeat unit which affects the morphology of the blends.\textsuperscript{16, 49}

**Conclusions**

A new BDT unit, 4,8-bis((2-(2-ethylhexyl)-3-hexylthieno[3,2-b]thiophene) BDT, was designed, synthesized, and applied for the construction of donor-acceptor conjugated copolymers. Compared with the polymers with extended fused-ring systems along the polymer backbone,\textsuperscript{12-14, 50} the newly synthesized polymers featured extending fused-ring systems in a 2D manner by substituting thiophene with thieno[3,2-b]thiophene. Copolymerization of the new BDT unit with BT or fBT provided polymers with abrupt absorption in the visible light region and low-lying HOMO energy levels. Application of these polymers in BHJ solar cells provided high \( V_{oc} \) of 0.90 V and optimization of the solar cells by solvent additives gave PCE of 4.20%. This is close to the performance of the diethenyl-BDT analogue of similar molecular weight.\textsuperscript{53} Compared with the fused dithienobenzodithiophene system,\textsuperscript{12} polymer P1 showed reasonable performance indicating that using fused ring units orthogonal to the polymer backbone is a promising strategy for future polymer design.

**Experimental**

Unless noted, all materials were reagent grade and used as received without further purification. Compound 6 was synthesized following literature procedures.\textsuperscript{51, 52} All the other starting compounds and reagents are commercially available.\textsuperscript{10} Experimental methods and instruments can be found in the Supplementary Information.

2-(2-Ethylhexyl)-3-hexylthieno[3,2-b]thiophene (7). To a stirred mixture of Mg (0.84 g, 35 mmol) and catalytic amount of iodine in dry Et\(_2\)O (30 mL) was added ethylhexyl bromide (5.79 g, 30 mmol) dropwise. After addition, the mixture was stirred at reflux for another 2 h. The resulting Grignard reagent was transferred dropwise to another flask containing Pd(dppf)Cl\(_2\) (200 mg) and compound 6 (6.06 g, 20 mmol) in dry Et\(_2\)O (30 mL) at 0 \( ^\circ \)C. After addition of the Grignard reagent, the reaction mixture was reacted at 0 \( ^\circ \)C for 2 h, room temperature for 2 h and reflux 2 h. After cooling to room temperature, the reaction mixture was quenched with ice slowly. The organic phase was washed with \( \text{H}_2\text{O} \), evaporated solvent under vacuum and the residue was passed a short column (silica gel, petroleum ether) to remove the catalyst. Pure compound 7 was obtained as colorless oil after high vacuum distillation (3.3 g, 49%).\textsuperscript{55} IR (petroleum ether) \( \nu \) 2956, 2924, 2856, 1458, 1378, 910, 707 cm\(^{-1}\); \(^1\)H NMR (\( \delta \), CDCl\(_3\)) 7.25 (d, \( J = 6.0 \) Hz, 1 H), 7.17 (d, \( J = 5.6 \) Hz, 1 H), 2.72 (d, \( J = 6.8 \) Hz, 2 H), 2.65 (t, \( J = 7.6 \) Hz, 2 H), 1.68 (m, 3 H), 1.25-1.40 (m, 14 H), 0.89 (m, 9 H); \(^13\)C NMR (CDCl\(_3\)) 140.6, 140.3, 135.1, 130.4, 124.7, 119.8, 41.8, 33.2, 32.5, 31.6, 29.3, 28.9, 28.8, 28.1, 25.6, 23.0, 22.6, 14.1, 14.0, 10.9; MS (ESI\textsuperscript{+}) \( m/z \) 336 [M]+; HRMS (ESI\textsuperscript{+}) \( m/z \) calcd. for C\(_{28}\)H\(_{32}\)S\(_2\) 336.1940 found. 336.1950.

4,8-Bis((2-(2-ethylhexyl)-3-hexylthieno[3,2-b]thiophene) BDT (8). A solution of compound 7 (1.01 g, 3.0 mmol) in THF (10 mL) was cooled to -78 \( ^\circ \)C. \( n \)-BuLi (2.4 M, 1.5 mL) was added slowly and the mixture was stirred for 3 h at room temperature. A suspension of 4,8-dihydrobenzen[e1,2-b:4,5-b']dithiophen-4,8-dione (220 mg, 1.0 mmol) in THF (10 mL) was then added and the mixture was stirred and slowly warmed to room temperature. A solution of SnCl\(_2\) (758 g, 5 mmol) in 10% HCl (10 mL) was added and the mixture was stirred at 60 \( ^\circ \)C overnight. After cool to room temperature, most solvent was removed and the residue was dissolved in Et\(_2\)O, washed with 1 M HCl and \( \text{H}_2\text{O} \). After removal of the solvent, the product was purified by column chromatography (SiO\(_2\), petroleum ether) as a yellow solid (620 mg, 72%).\textsuperscript{56} IR 0.40 (petroleum ether); mp 63-65 \( ^\circ \)C; \(^1\)H NMR (CDCl\(_3\)) \( \delta \) (ppm): 7.73 (d, \( J = 6.0 \) Hz, 2 H), 7.58 (s, 2 H), 7.49 (d, \( J = 6.0 \) Hz, 2 H), 2.79 (d, \( J = 6.4 \) Hz, 4 H), 2.72 (t, \( J = 7.6 \) Hz, 4 H), 1.75 (m, 4 H), 1.68 (m, 2 H), 1.28-1.50 (m, 28 H), 0.90 (m, 18 H); \(^13\)C NMR (CDCl\(_3\)) \( \delta \) (ppm): 141.1, 141.0, 139.4, 138.8, 136.8, 135.2, 130.8, 127.8, 124.3, 123.4, 120.7, 41.8, 33.3, 32.6, 31.6, 29.4, 28.9, 28.2, 25.6, 23.1, 22.6, 14.2, 14.1, 10.9; MS (ESI\textsuperscript{+}): 858

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**Fig. 5** AFM images of films spin coated from P1/PC\(_71\)BM 1:2 (a and d), P1/PC\(_71\)BM 1:2 with 2.5% DIO (b and e) and P2/PC\(_71\)BM 1:2 (c and f). (a), (b) and (c) are height images; (d), (e) (f) are phase images. All images are 2 \( \times \) 2 \( \mu \)m.
Polymer P1. The diodo compound 10 (0.1 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]-thiadiazole (BT) (compound 11, 0.1 mmol), 4 mol% of Pd(dba)$_3$ and 32 mol% of P(o-tolyl)$_2$ was added to a vial. A drop of the Aliquat 336 was added as phase transfer catalyst. Under nitrogen, dry toluene (1 mL) was added as solvent and the mixture was stirred for 2 days. Phenyl trimethyltin was added and the polymer was end capped for 1 hour followed by end capping with bromobenzene for another 1 hour. Then the reaction mixture was cooled to room temperature, and the polymer was precipitated by addition of 50 mL methanol, filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexanes, dichloromethane and chloroform. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid polymer was dried under vacuum. Yield: 43%. M$_n$ = 10,500 g/mol, PDI = 3.3; IR (neat) ν 2924, 2853, 1435, 1376, 1011, 800, 722 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ (ppm): 7.85 (s, 2 H), 7.49 (s, 2 H), 2.79 (d, J = 6.8 Hz, 4 H), 2.74 (t, J = 7.6 Hz, 4 H), 1.74 (m, 4 H), 1.67 (m, 2 H), 1.30-1.50 (m, 28 H), 0.90 (m, 18 H). Elemental analysis calcd (%): C 65.46, H 6.28, N, 2.56; found: C 65.67, H 6.17, N, 2.56.

Fabrication and characterization of the BHJ polymer solar cells. Polymer solar cells were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. First a thin layer of ZnO nanoparticle (30 nm) was deposited on the ultrasonically cleaned ITO substrates by spin coating (25 mg/mL in ethanol, 3000 rpm). ZnO nanoparticles were synthesized by a sol-gel method using zinc acetate dihydrate and tetramethylammonium hydroxide. The active layer of the devices was deposited by spin coating ODCB solution containing 10 mg of polymer and 20 mg of PC$_7$BM. The films were then transferred to a metal evaporation chamber and MoO$_3$ (10 nm) and Ag (100 nm) were deposited through a shadow mask (active area was 0.1 cm$^2$) at approximately 1 x 10$^{-6}$ torr. Film thickness was determined by Veeco Dektak 150+Surface Profiler. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m$^2$ AM 1.5G illumination conditions. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PV measurements Inc.) certified by the National Renewable Energy Laboratory.

Acknowledgements

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Notes and references


53. The study on the dithienyl-BDT analogue of P1 will be published elsewhere.