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Synthesis of 2,6-diiodo-4,4-ethylenedioxy-4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene and conjugated copolymers on its basis

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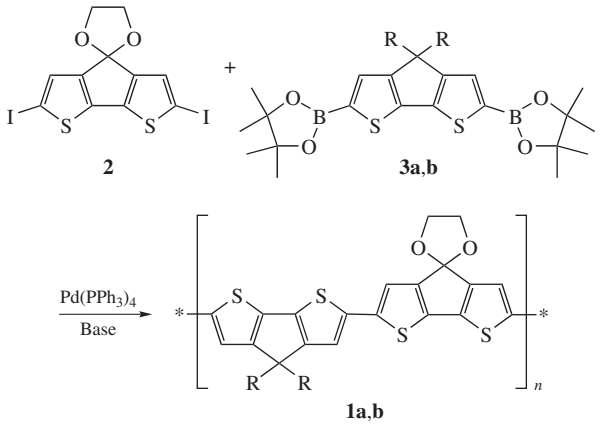
New synthesised conjugated copolymers based on 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene exhibit the absorption of light in the red spectral region with the maximum at 580–590 nm and optical bandgaps of 1.85–1.88 eV. Organic photovoltaic cells prepared from composites of these copolymers with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) showed the efficiency up to 0.5%.

Over the last decade attention of the scientific community to organic semiconducting polymeric materials has been increasing due to the possibility of their usage in the new generations of optoelectronic devices.[1] Conjugated copolymers based on 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene derivatives are among promising materials to be employed in photovoltaic cells,[2] light-emitting diodes,[3] and thin-film transistors.[4] Depending on the chemical nature of the used monomer precursors, the obtained copolymers can have high solubility, good transport properties, and a narrow band gap, which predetermine the fields of their possible applications.[5,6] The aim of the present study was the synthesis of new alternating conjugated copolymers **1a**,**b** based on 4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene derivatives and investigation of their optical and photovoltaic properties (Scheme 1).



Scheme 1

Copolymers **1a** and **1b** were synthesised by the Suzuki cross-coupling, using 2,2-diiodo-4,4-ethylenedioxy-4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene **2** as the dihalo co-monomer and 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-dioctyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]thiophene **3a** or 2,6-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene **3b** as the diorganoboron counterparts.

The choice of the monomer precursors was made according to the fact that the dioxolane group not only promotes the planarization of the polymer system as a whole and, consequently, increases the effective conjugation length, but also leads to a significant red shift of the absorption spectra of the copolymers.[7] The presence of the solubilizing octyl or ethylhexyl substituents in building blocks **3a** and **3b**, respectively, provides sufficient solubility of the final polymer products in usual organic solvents such as THF, toluene, xylene, chloroform, chlorobenzene, *etc*.

The dioxolane monomer **2** was prepared as shown in Scheme 2. Lithium dithienylmethoxide **4** was synthesized by the reaction of 3-thienyllithium (obtained by the lithiation of 3-bromothiophene with *n*-butyllithium) with ethyl formate. The lithiation of intermediate **4** with two equivalents of Bu^nLi followed by treatment with 1,2-diiodoethane led to bis(2-iodo-3-thienyl)methanol **5**† in 91% yield. The oxidation of the latter with pyridinium chlorochromate (PCC) afforded bis(2-iodo-3-thienyl)methanone **6** in 94% yield.[8] 2,2-Bis(2-iodo-3-thienyl)-1,3-dioxolane **7** was synthesized by the ketalization of ketone **6** with ethylene glycol in refluxing benzene for 30 h in the presence of *p*-toluenesulfonic acid with azeotropic removal of water. The yield of this reaction was improved from 72%[9] to 95% by the use of the Dean–Stark

† *Bis(2-iodo-3-thienyl)methanol* **5**. A solution of 3-bromothiophene (5 g, 30.7 mmol) in hexane (10 ml) was added dropwise to a solution of Bu^nLi (19.5 ml, 1.6 M solution in hexane, 30.6 mmol) in THF (24 ml) cooled to –70 °C for 20 min, keeping the temperature below –65 °C. The reaction mixture was stirred at –50 °C for 1 h. The mixture was then cooled to –70 °C, and ethyl formate (1.14 g, 15.3 mmol) was added. The reaction mixture was stirred at –50 °C for 0.5 h. After that the temperature was raised to 20 °C, then cooled down to –35 °C and a second portion of Bu^nLi (20.5 ml of 1.6 M solution in hexane, 32.1 mmol) was added. After lithiation, a solution of 1,2-diiodoethane (9.05 g, 33.7 mmol) in THF (12 ml) was added. The reaction was stirred at 20 °C for additional 1 h. Then, a 10% aqueous solution of Na_2SO_3 (50 ml) and Et_2O (200 ml) were added to the reaction mixture, followed by the addition of a water solution of HCl (1 N, 50 ml). The ether layer was rinsed with water to reach pH 7 and dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator. The product was purified by column chromatography on silica gel [eluent, hexane–ethyl acetate (95:5)] to furnish a white powder (12.23 g, yield 89%), mp 114–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44 (d, 2H), 6.93 (d, 2H), 5.76 (d, 1H), 2.35 (d, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 146.5, 131.4, 126.8, 75.3, 71.6. MS (EI) *m*/*z*: 448 (M^+). Found (%): C, 24.20; H, 1.36; S, 14.41. Calc. for $C_9H_6I_2OS_2$ (%): C, 24.12; H, 1.35; S, 14.31.

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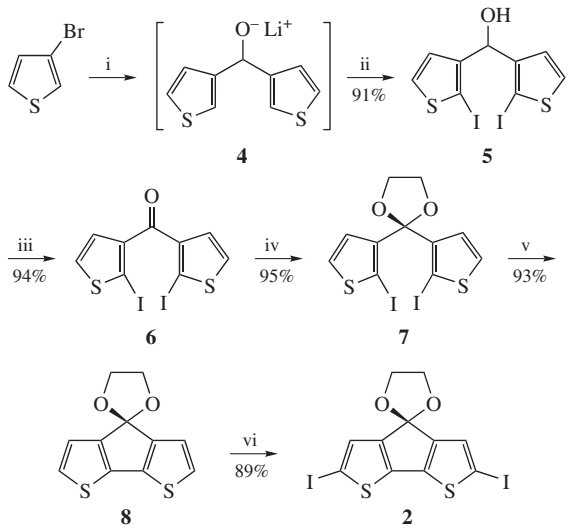
Table 1 The molecular weight and optical characteristics of copolymers **1a**,**b**.

Copolymer	M_n^a	M_w^a	M_w/M_n	λ_{abs}^b/nm (ε/dm^3 mol^{-1} cm^{-1})	ΔE_{opt}^b/eV	λ_{lum}^b/nm [Q (%)]
1a	7500	12500	1.67	590 (65392)	1.85	670 [1.8±0.4]
1b	6700	10000	1.49	580 (31667)	1.88	659 [1.7±0.4]

[a] M_n is the number-average molecular weight, M_w is the weight-average molecular weight. The M_n, M_w and M_w/M_n values were determined by GPC with calibration based on polystyrene standards and THF as the solvent. [b] Optical characteristics of dilute solutions of the compounds in THF; λ_{abs} is the absorption maximum, λ_{lum} is the luminescence maximum, ΔE_{opt} is the optical band gap calculated from the absorption band edges, ε is the molar absorption coefficient, Q is the luminescence quantum yield.



Scheme 2 *Reagents and conditions*: i, THF–hexane, Bu^{n}Li (1 equiv.), –70 °C → –50 °C, then HC(O)OEt (0.5 equiv.); ii, Bu^{n}Li (2.1 equiv.), hexane, –35 °C → 20 °C, then 1,2-diiodoethane (3.1 equiv.), –35 °C → 20 °C, aqueous HI; iii, PCC, CH_2Cl_2, 0 °C → 20 °C, 6 h; iv, $HOCH_2CH_2OH$, TsOH (cat.), C_6H_6, reflux, 30 h; v, Cu, DMF, 15 h; vi, THF, Bu^{n}Li (2.1 equiv.), –78 °C → 20 °C, then 1,2-diiodoethane (2.1 equiv.), –35 °C → 20 °C.

trap containing a dehydrating agent. The intramolecular Ullmann reaction[10] of **7** catalyzed by copper powder gave 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b′*]dithiophene **8** in 93% yield. The target compound **2** was obtained by the double lithiation of **8** upon treatment with 1,2-diiodoethane.‡ Diorganoboron derivatives **3a** and **3b** were prepared according to the known procedures.[11–13] The purity and chemical structures of all the intermediates as well as final compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.§

The synthesis of copolymers **1a**,**b** by the Suzuki cross-coupling (Scheme 1) of monomeric precursors **2** and **3a**,**b**, respectively, was carried out in THF in the presence of a 2 M aqueous solution of Na_2CO_3 as a base and a catalytic amount of $Pd(PPh_3)_4$ for 16 h in argon under the microwave heating at atmospheric pressure.¶ The molecular weight characteristics of the copolymers synthesized were determined by GPC using polystyrene standards (Table 1).††

The absorption and luminescence spectra of the copolymer **1b** are presented in Figure 1 (the spectra exhibited by **1a** are almost identical). The spectra were measured in the range 200–800 nm in dilute THF solutions with a concentration of 10^{-5}–10^{-6} mol dm^{-3} to avoid self-absorption (Table 1).‡‡ The data obtained demonstrate that the absorption maxima for both copolymers, located at 580 and 590 nm for **1a** and **1b**, respectively, are significantly shifted into the red region as compared to both the poly(3-octylthiophene) standard (λ_{abs} = 446 nm)[15] and poly(4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b′*]dithiophene) (λ_{abs} = 560 nm).[16] The maxima of the luminescence spectra, located at 670 and 659 nm for **1a** and **1b**, respectively, exhibit a significant long-wavelength shift as well. The spectral shifts could be attributed to the spiro-connection of the 4,4-ethylenedioxy group with the conjugated polymer backbone, so that the lone pairs of the oxygen atoms might have certain orbital interactions with the π-electrons of the polymer backbone. Such a kind of orbital interactions enables the oxygen atoms serving as electron-donating groups to effectively lower the HOMO and thus reduce the band gap.[16]

‡ *2,6-Diiodo-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b′*]dithiophene* **2**: Bu^{n}Li (10.5 ml, 1.57 M solution in hexane, 16.5 mmol) was added to a solution of compound **8** (1.3 g, 5.5 mmol) in THF (45 ml) cooled to –78 °C. Stirring was continued for 0.5 h, then the temperature was allowed to reach 20 °C. After another cooling to –78 °C, a solution of 1,2-diiodoethane (4.88 g, 17.3 mmol) in THF (10 ml) was added dropwise. The reaction mixture was allowed to warm up to room temperature, and a 10 wt% aqueous solution of Na_2SO_3 (25 ml) and Et_2O (150 ml) were added with vigorous stirring. The organic layer was separated, rinsed with water until pH 7 and dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator. The product was purified by recrystallization from toluene to furnish 2.5 g (93%) of the pure light-brown solid; mp 183–185 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.1 (s, 2H), 4.22 (s, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 150.16, 143.28, 130.72, 106.48, 73.30, 65,20. MS (EI) *m/z*: 488 (M^+). Found (%): C, 27.18; H, 1.19; S, 12.88. Calc. for $C_{11}H_6I_2O_2S_2$ (%): C, 27.07; H, 1.24; S, 13.14.

§ The ^{1}H, ^{13}C NMR spectra were recorded on a Bruker Avance II 300 spectrometer at 300 and 75.5 MHz, respectively. All spectra were obtained using $CDCl_3$ as the solvent and TMS as the internal standard.

¶ *Synthesis of copolymers* **1a**,**b** *(general procedure)*. To a mixture of comonomers (in the 1:1 molar ratio) in THF (15 ml), tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (5 mol%) and 2 M aqueous solution of Na_2CO_3 (3 ml) were added. The mixture was heated at 70 °C in a microwave apparatus (the SEM Discovery System, USA) under argon for 16 h. After cooling, butyl acetate and water (5:1) were added. The organic layer was separated and rinsed with water to reach pH 7. After that an aqueous solution of sodium diethyldithiocarbamate (7.5%, 10 ml) was added and the mixture was boiled for 2 h. Then the aqueous layer was separated and the organic layer was rinsed with water to reach pH 7 and dried over anhydrous Na_2SO_4. The product was purified by column chromatography on silica gel (eluent toluene, 70 °C) followed by recrystallization from toluene. The copolymers isolated were solid dark-purple substances with metallic luster. The yield was 65–70% of the theoretical amount.

For **1a**: ^{1}H NMR ($CDCl_3$) δ: 7.03 (s, 2H), 6.97 (s, 2H), 4.36 (s, 4H), 1.95–1.72 (m, 4H), 1.30–1.10 (overlapping peaks, 20H), 1.07–0.90 (m, 4H), 0.84 (t, 6H, *J* 6.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 158.76, 150.43, 140.12, 137.65, 136.81, 135.32, 117.81, 117.44, 116.97, 107.49, 65.40, 54.10, 37.70, 31.81, 30.02, 29.29, 24.56, 22.62, 14.10. Found (%): C, 68.16; H, 6.72; S, 20.12. Calc. for $C_{36}H_{42}O_2S_4$ (%): C, 68.09; H, 6.67; S, 20.20.

For **1b**: ^{1}H NMR ($CDCl_3$) δ: 7.02 (s, 2H), 6.98 (s, 2H), 4.36 (s, 4H), 2.02–1.77 (m, 4H), 1.12–0.83 (overlapping peaks, 18H), 0.76 (t, 6H, *J* 7.1 Hz), 0.64 (t, 6H, *J* 7.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 158.30, 150.36, 140.23, 137.24, 135.79, 129.02, 128.21, 118.32, 116.96, 107.60, 65.44, 54.04, 43.11, 35.15, 34.16, 28.57, 27.40, 22.80, 14.15, 10.71. Found (%): C, 68.19; H, 6.64; S, 20.11. Calc. for $C_{36}H_{42}O_2S_4$ (%): C, 68.09; H, 6.67; S, 20.20.

†† GPC analysis was performed on a Shimadzu GPC chromatograph (Japan), detectors – refractometer RID-10A and diode array SPD-M10AVP, columns – Phenomenex (USA) 7.8×300 mm filled with a Phenogel sorbent (pore sizes of 10^3 and 10^4 Å), eluent – THF.

‡‡ The absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer (Japan). The fluorescence spectra were measured on the scanning spectrofluorimeter developed and constructed at ISPM RAS equipped with a 150 W arc xenon lamp as the pumping source, two Seya–Namioka-type monochromators and two photoelectronic multipliers.[14]

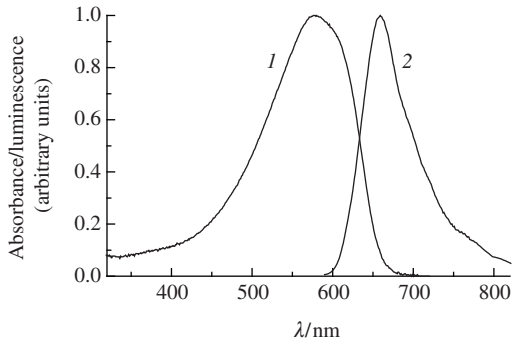


Figure 1 (*1*) Absorption and (*2*) luminescence spectra of copolymer **1b**.

Copolymers **1a**,**b** were blended with the [60]fullerene derivative of [6,6]-phenyl-C_{61}-butyric acid methyl ester ([60]PCBM)[§§] and the resulting composites were evaluated as the active-layer materials to be utilized in organic photovoltaic cells. A schematic layout of the investigated solar cells is shown in Figure 2. As can be seen from the current–voltage curves measured in the dark, the prepared devices subjected to AM1.5 solar radiation provided by a KHS Steuernagel solar simulator with a light intensity of 100 mW cm^{-2} exhibited a pronounced photovoltaic effect. The short-circuit current (I_{SC}), the open circuit voltage (V_{OC}), the fill factor (FF) and the power conversion efficiency (η) were determined from the current–voltage curves (Table 2). As shown in Table 2, the composites of copolymers **1a**,**b** with [60]PCBM had relatively low power conversion efficiencies of 0.14% and 0.5%, respectively. Nevertheless, these values could potentially be improved significantly by varying the ratio between the donor and acceptor materials in the blend, by optimizing the nanomorphology of the active layer of the device, and by the fine tuning of the molecular structures and physical properties of the materials. Increase in molecular weight of the polymers might also improve their performance in the organic solar cells.

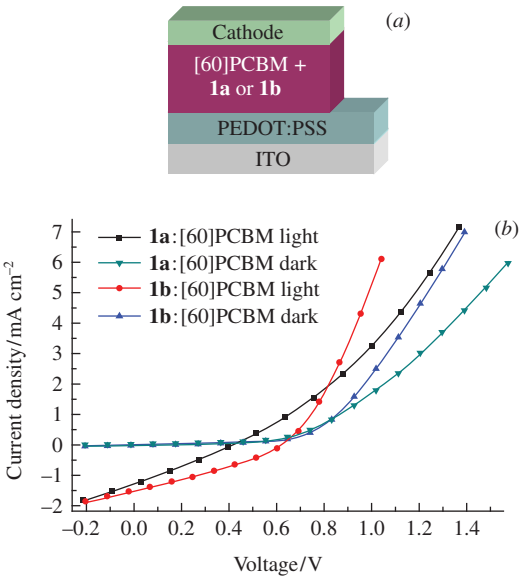


Figure 2 (*a*) The schematic architecture of the organic solar cells and (*b*) the current–voltage characteristics of the devices based on the composites of polymers **1a**,**b** and [60]PCBM.

[§§] The molecular formula of PCBM, description of the manufacturing method of the photovoltaic cells and composition of the individual functional layers, and other experimental details are given in ref. 17.

Table 2 Parameters of the organic photovoltaic cells based on the composites of polymers **1a**,**b** and fullerene derivative [60]PCBM.

Composite	I_{SC}/mA cm^{-2}	V_{OC}/mV	FF (%)	η (%)
1a + [60]PCBM, 1:2	0.73	297	26	0.06
1a + [60]PCBM, 1:2[a]	1.45	365	27	0.14
1b + [60]PCBM, 1:2	2.94	561	32	0.50

[a]The cell was subjected to heat treatment at 155 °C for 3 min.

In summary, an effective method for the synthesis of 2,6-diiodo-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene was developed, and copolymers **1a**,**b** containing alternating units of cyclopenta[2,1-*b*:3,4-*b*′]dithiophene with dioxolane and dialkyl groups were prepared. The copolymers obtained possess good solubility, the absorption spectrum shifted towards the longer wavelengths, and narrow band gaps. The preliminary results suggest that the synthesized copolymers derived from monomer **2** might be considered as promising electron-donor materials for organic photovoltaic devices.

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