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5,6-Bis(octyloxy)-2,1,3-benzoxadiazole-based (X–DADAD)$_n$ polymers incorporating electron-donor building blocks used as photoactive materials in organic solar cells

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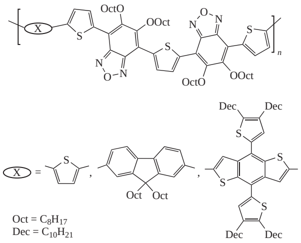
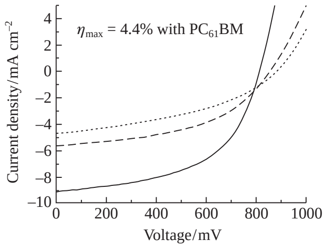
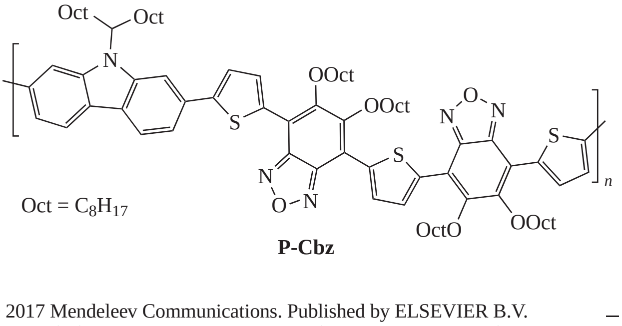
Three alternating (X–DADAD)$_n$-type copolymers bearing different building blocks (X) in combination with benzoxadiazole (A) and thiophene (D) units were synthesized and studied as photoactive materials in organic solar cells. Superior short circuit currents and power conversion efficiencies (up to 4.4%) were reached when thiophene rather than fluorene or benzodithiophene was used as an X unit.





Recently, organic photovoltaics demonstrated significant progress mainly due to the development of promising electron donor push-pull type copolymers.[1–5] However, the commercialization of these technologies is still challenging because of limited device operation lifetimes and power conversion efficiencies.[6] We have designed novel benzothiadiazole-based (X–DADAD)$_n$-type conjugated polymers, which demonstrated optimal optoelectronic characteristics, excellent photostability and respectable photovoltaic efficiency (> 6%) in both spin-coated and roll-to-roll processed devices.[7–10] More recently, we used bis(octyloxy)benzoxadiazole instead of benzothiadiazole for designing (X–DADAD)$_n$-type conjugated polymers.[11] However, the application of *N*-alkylcarbazole as an X unit did not allow us to reach the desired optoelectronic characteristics of materials. In particular, large optical band gaps (E_g) of the carbazole-based polymer **P-Cbz** limited the short circuit currents of solar cells, causing quite modest power conversion efficiencies. Replacing carbazole with stronger electron-donating blocks, such as thiophene and benzodithiophene, is a commonly used way of decreasing the band gap of conjugated polymers. Therefore, we pursued the design of bis(octyloxy)benzoxadiazole-based polymers **P1** and **P2** in order to improve the optoelectronic and photovoltaic properties of the materials. Additionally, we designed polymer **P3** incorporating fluorene as an X unit. The replacement of carbazole by fluorene results in increased open circuit voltages in polymer solar cells.[12,13] Therefore, we expected that **P3** would deliver enhanced open circuit voltage and, consequently, power conversion efficiency in solar cells.



P-Cbz

Polymers **P1** and **P2** were synthesized using the Stille polycondensation of monomer **M1** with bis(trimethylstannyl)thiophene **M2** or benzodithiophene-based monomer **M3** (Scheme 1). Polymer **P3** was obtained *via* the Suzuki–Miyaura polycondensation reaction involving monomer **M1** and commercially available **M4** (Scheme 1).

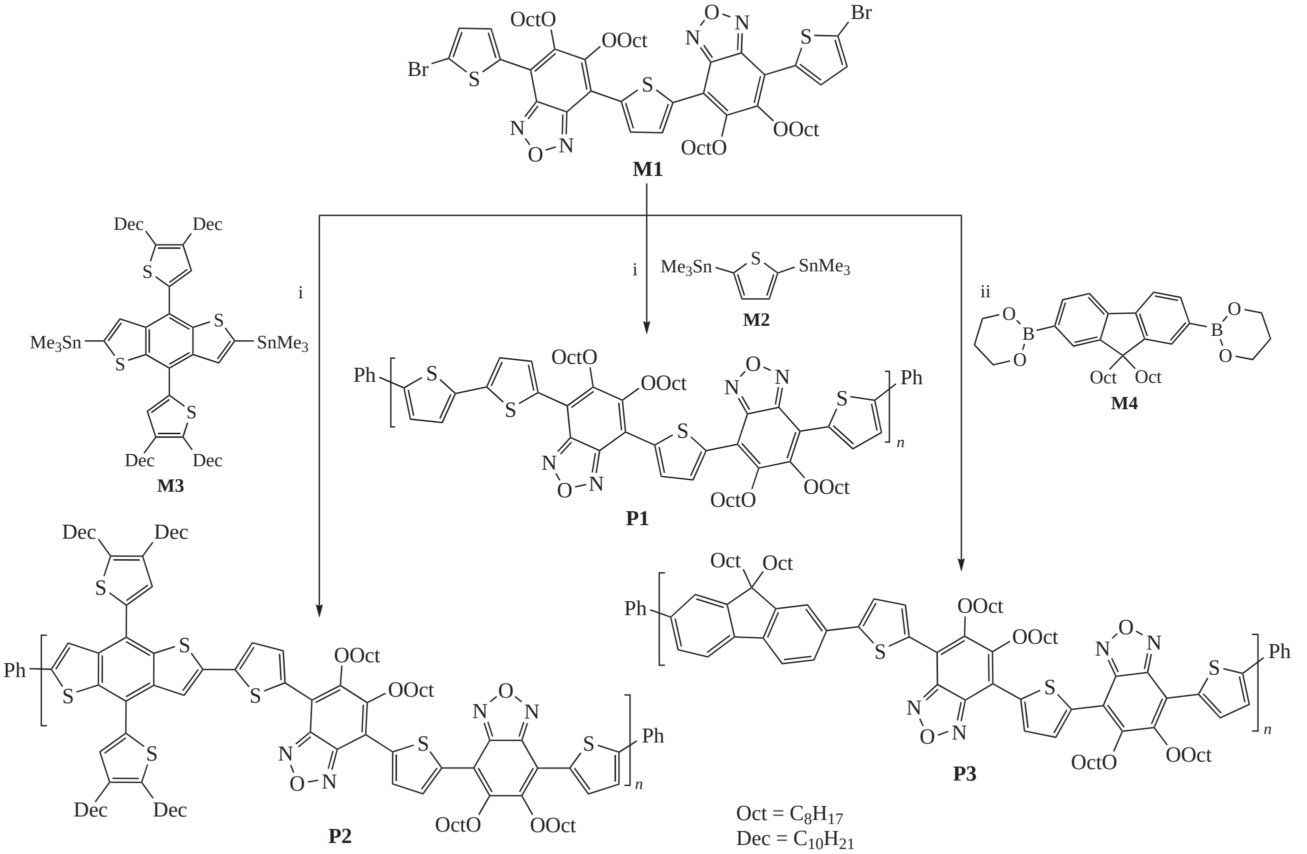
Gel permeation chromatography was used to determine the average molecular weights (M_w) and polydispersity indices (PDI) of **P1**–**P3** against a series of polystyrene standards (Table 1). Note that polymer **P3** has a much higher molecular weight than those of **P1** and **P2** obtained using the Stille polycondensation. The M_w of **P1** was limited by its low solubility in toluene resulting in the precipitation of the low molecular weight material from the reaction mixture in the course of synthesis.

The absorption spectra of **P1**–**P3** in thin films are shown in Figure 1(*a*). The replacement of carbazole (**P-Cbz**) with fluorene (**P3**) did not result in significant changes in the optical properties of the conjugated polymers. On the contrary, the introduction of

Table 1 Characteristics of the polymers **P1**–**P3**.

Polymer	M_w/g mol^{-1}	PDI	$E_{\text{ox onset}}$/ V *vs.* Fc$^+$/Fc	HOMO[a]/ eV	LUMO[b]/ eV	E_g/eV
P-Cbz	88 000	1.5	0.59	–5.69	–3.84	1.85
P1	16 800	1.2	0.40	–5.50	–3.78	1.72
P2	56 000	3.4	0.61	–5.71	–3.97	1.76
P3	110 400	2.9	0.69	–5.79	–3.90	1.89

[a] HOMO energies were estimated from the onsets of oxidation waves in cyclic voltammograms [Figure 2(*b*)] following the reported procedure.[14]
[b] LUMO energies were calculated as E(HOMO) + E_g.



Scheme 1 *Reagents and conditions*: i, Pd(PPh_3)$_4$, toluene, reflux, 3–6 h, for termination: 0.1 mmol of **M2**, reflux, 0.5 h, then 2 mmol of bromobenzene, reflux, 0.5 h; ii, Pd(PPh_3)$_4$, toluene, 2 M K_2CO_3/H_2O, aliquat 336, reflux, 3–6 h, for termination: 0.1 mmol of phenylboronic acid, reflux, 0.5 h, then 2 mmol of bromobenzene, reflux, 0.5 h.

stronger electron-donating thiophene (**P1**) and benzodithiophene (**P2**) building blocks lowered considerably the band gap of materials. Polymer **P1** demonstrated the smallest E_g, which can be explained by the electronic action of a thiophene ring in combination with supramolecular organization effects. Indeed, the absence of solubilizing side chains from the thiophene units can enhance the intermolecular packing of polymer **P1** chains in thin films in comparison with two other materials.

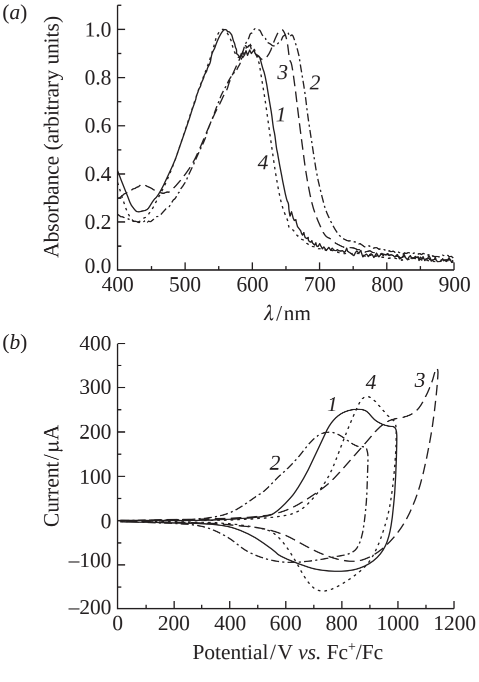


Figure 1 (*a*) Absorption spectra of thin film of (*1*) **P-Cbz**, (*2*) **P1**, (*3*) **P2** and (*4*) **P3** and (*b*) their cyclic voltammograms.

Electrochemical properties were investigated for thin films of conjugated polymers deposited on glassy carbon disc electrodes. Cyclic voltammograms of **P-Cbz** and **P1**–**P3** are shown in Figure 1(*b*). Replacing carbazole building block in **P-Cbz** with fluorene in **P3** results in an increased oxidation potential (lower HOMO energy level). This allows one to expect improved open circuit voltages in solar cells based on this material. Surprisingly, the replacement of carbazole with benzodithiophene building block with stronger electron donating properties did not cause a considerable reduction of the oxidation potential of **P2** in comparison with **P-Cbz**. Thus, **P2** shows similar HOMO energy as **P-Cbz** and significantly reduced E_g, which is a good combination of properties with respect to photovoltaic applications. On the contrary, polymer **P1** incorporating a thiophene unit as X block showed a 200 mV lower oxidation potential, as compared to that of **P-Cbz**.

Copolymers **P1**–**P3** were studied as electron-donor materials in organic solar cells in combination with [60]PCBM used as an electron-acceptor component. The *J*–*V* characteristics and EQE spectra of devices are shown in Figure 2, and the parameters of solar cells are given in Table 2. The best performance was achieved for solar cells based on **P1** bearing alternating thiophene and bis(octyloxy)benzoxadiazole units. This result was unexpected taking into account low molecular weights of **P1** and poor solubility of this material in organic solvents, which are important for the formation of a proper morphology of composite thin films.[15,16] Even more surprising was the fact that devices based on the **P1**/[60]PCBM blends demonstrated high open circuit voltages of >800 mV, which are very comparable with the V_{OC} values delivered by polymers **P2**–**P3** and **P-Cbz** in the

Table 2 Photovoltaic properties of **P1**–**P3** and **P-Cbz**.

System	Weight ratio	V_{OC}/mV	J_{SC}/mA cm^{-2}	FF (%)	η (%)
P-Cbz/[60]PCBM[a]	1:1.5	845	7.2	42	2.5
P1/[60]PCBM	1:2	822	9.9 (8.3)[b]	54	4.4
P2/[60]PCBM	1:2	856	5.6 (5.3)	48	2.3
P3/[60]PCBM	1:2	890	6.1 (4.6)	43	2.3

[a] Data for **P-Cbz** from ref. 11. [b] Calculated from EQE spectra.

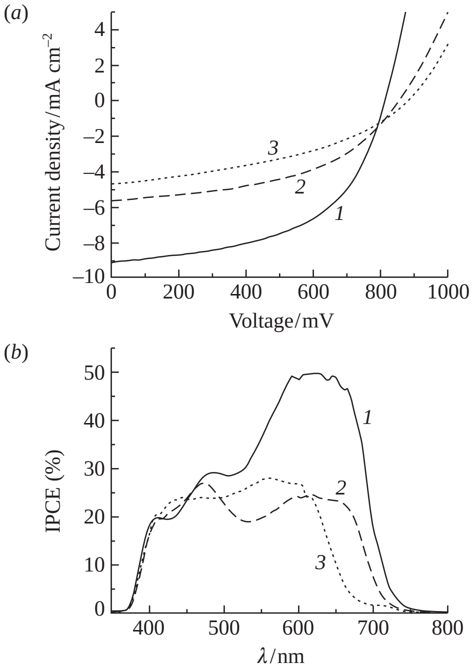


Figure 2 (*a*) *J–V* characteristics and (*b*) EQE spectra of solar cells comprising **P1**–**P3**: (*1*) **P1**/[60]PCBM, (*2*) **P2**/[60]PCBM and (*3*) **P3**/[60]PCBM.

respective solar cells. This experimental finding contradicts the electrochemistry data showing that **P1** undergoes oxidation at 100–200 mV lower potentials compared to **P2**, **P3** and **P-Cbz**. Considering the ultimate value of V_{OC} for the **P1**/[60]PCBM system estimated as energy offset between HOMO of **P1** and LUMO of PCBM, we can conclude that the energy loss for this system is ~0.50 V, which is considerably smaller than that for the vast majority of other polymers.[17] This finding suggests that a more detailed study of polymer **P1** and similar structures can reveal a promising pathway for overcoming severe V_{OC} losses in organic photovoltaics.

The performance of solar cells based on **P1**–**P3** is strongly limited by low J_{SC} and FF values, which suggest that charge transport can be hindered in the blends due to their non-optimal morphology (the AFM images of polymer/[60]PCBM composites are shown in Figure S1, Online Supplementary Materials). No signs of phase separation were observed for the thin films of **P2**/[60]PCBM blends thus suggesting that the fullerene and polymer components form a homogeneous solid solution, where the transport of charge carriers is strongly suppressed. On the contrary, the composites of **P1** and **P3** with [60]PCBM demonstrated large-scale phase separation. The formation of large (> 50 nm in size) clusters leads to significant recombination losses, which limit the short circuit current of the devices and reduce dramatically their power conversion efficiencies.

In conclusion, we synthesized and characterized three new bis(octyloxy)benzoxadiazole-based (X–DADAD)$_n$ polymers and applied them as electron-donor materials in bulk-heterojunction organic solar cells. Tailoring the chemical structure of polymers by implementation of different building blocks resulted in an improvement of the optoelectronic characteristics of conjugated polymers while going from fluorene to benzodithiophene and then to thiophene. Thiophene-based polymer **P1** demonstrated the lowest E_g of 1.72 eV and delivered appreciably high open circuit voltage and decent photovoltaic efficiency of 4.4% using [60]PCBM as an electron acceptor component. The photovoltaic performance of **P1** and related polymers can be further improved by increasing their molecular weights, optimizing the solubility in organic solvents and tuning the morphology of their blends with electron acceptor counterparts.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.03.034.

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