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Novel small oligothiophene molecules with phenylene and naphthalene cores as promising absorber materials for organic solar cells

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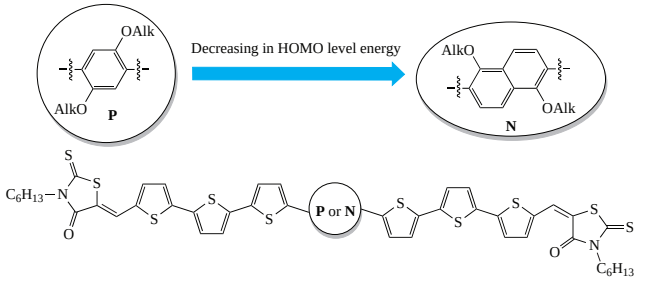
New small molecules bearing either phenylene or naphthalene core in combination with thiophene and rhodanine periphery moieties were synthesized by the Stille cross-coupling reaction. Their evaluation for prototypes of organic solar cells showed that replacing phenylene moiety by the naphthalene one caused decrease in the HOMO energy, while the open-circuit voltage and fill factors of solar cells based on these materials were significantly improved to manifest maximum power conversion efficiencies to 5.3%.



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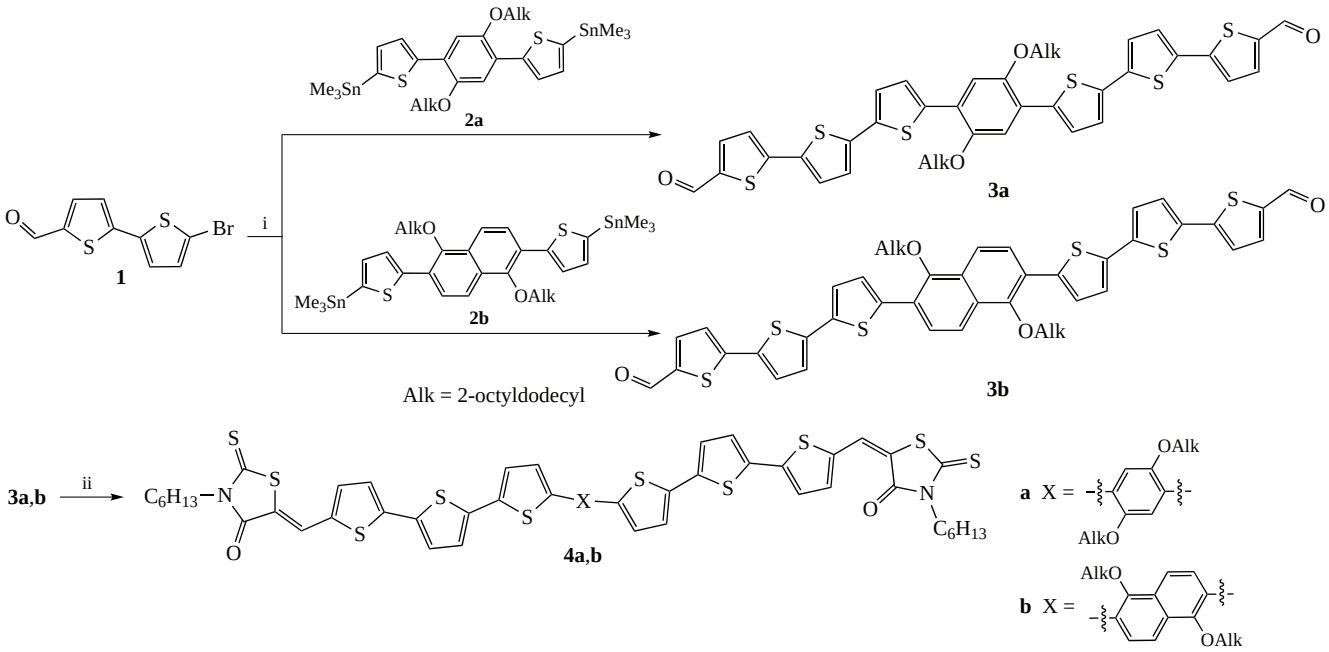
Currently, organic solar cells (OSCs) utilizing not only polymeric materials but also based on small molecules are demonstrating impressive power conversion efficiencies (PCEs) reaching 18%.[1,2] Small molecules were introduced as donor materials in bulk-heterojunction cells in 2006.[3] The photoactive small molecules draw a significant attention[4–6] due to their constant composition, well-defined structure and physicochemical properties.[7–11] At the same time, low molecular weight semiconductor materials are generally more crystalline than polymers that results in enhanced charge mobilities and overall improved photovoltaic performance of solar cells based on them.[12–14] In contrast to conjugated polymers, small molecules can be prepared and isolated with a high degree of purity using chromatographic methods and vacuum sublimation. The so-called 'push-pull' strategy (alternation of donor and acceptor units) is most commonly employed in the design of conjugated small molecules for OSCs. This approach became preferable due to the possibility of tuning optoelectronic properties of small molecules.[15]

Rhodanine,[16] dicyanovinyl[17] and indanedione derivatives are most often selected as the terminal acceptor units.[18] The electron-donating core usually comprised thiophene, benzodithiophene, dithienosilole, cyclopentadithiophene, carbazole and fluorine cores.[19–21] Benzodithiophene (BDT) moiety possessing rigid fused structure is of special interest since BDT-based molecules are currently among the best 'state-of-art' materials in various fields of organic electronics.[22,23] Positions 4 and 8 in BDT molecule can be diversely modified, which can be used for tailoring properties of this family of compounds.[24] However, the synthesis of BDT is a complicated multi-step process, therefore, search for alternative available structures seems topical. For example, a simpler small molecule was synthesized *via* replacing BDT with a dialkoxybenzene moiety combined with two thiophene residues.[25] In this case, a planar π-conjugated structure is formed due to intramolecular non-covalent bonding between the sulfur atoms of thiophene units and oxygen atoms of dialkoxybenzene.

A similar approach is employed in the present work. Herein, we have selected not only phenylene as the central core unit, but also its extended analogue, naphthalene, in order to evaluate possible effects of such structural modification. Taking into account previous results,[26,27] we expected that the introduction of naphthalene could decrease HOMO energy, which would consequently allow us to achieve high open-circuit voltages in solar cells designed with the considered small molecules.[28] We used unsubstituted terthiophene moieties for design of small molecules. DFT calculations reveal that the arrangement of alkyl on a thiophene fragment results in increase of the dihedral angle between adjacent fragments.[25,29] Therefore, we did not use alkyl substituents on thiophene units, but introduced more bulky alkyl groups into the central benzene or naphthalene cores. This modification allowed us to improve the efficiencies of OSCs from 3.4 to 4.7% without additional treatment.[25]

Scheme 1 shows the structures and synthesis of the reported small molecules. Compounds **2a** and **2b** were prepared according to the known procedures.[27,30] The target compounds **4a** and **4b** were obtained from **2a** and **2b**, respectively, *via* their Stille cross-coupling with 5′-bromo-2,2′-bithiophene-5-carbaldehyde and the subsequent Knoevenagel condensation of the corresponding products with alkyl-substituted derivative of rhodanine (see Scheme 1). The structures of products **4a**,**b** were confirmed by NMR spectra, MS data, elemental analysis and HPLC.

The optical properties of compounds **4a**,**b** were studied both in solutions and thin films. Their absorption edges for solutions in 1,2-dichlorobenzene were close to each other being in the range of 545–560 nm. In the case of thin films, compound **4a** demonstrated a greater bathochromic shift of the absorption band as compared to **4b**, namely, 160 nm (**4a**) *vs.* 115 nm (**4b**). The observed red shifts indicate a good self-assembling of the materials in thin films enabling efficient supramolecular electronic interactions. Optical band gaps for the each material were calculated from the edge of the absorption band (Table 1). The replacement of phenylene with naphthalene leads to an



Scheme 1 *Reagents and* conditions: i, toluene, $Pd(PPh_3)_4$, reflux; ii, *N*-hexylrhodanine, $CHCl_3$, NEt_3, 60 °C.

Table 1 Electrochemical and optical properties of compounds **4a** and **4b**.

Compound	E^{ox}_{onset}/V[a]	HOMO[b]/LUMO[c]/eV	λ_{max}[d]/nm	λ_{edge}[d]/nm	λ_{max}[e]/nm	λ_{edge}[e]/nm	E_g/eV
4a	0.41	–5.51/–3.79	486	561	588	721	1.72
4b	0.63	–5.73/–3.85	472	545	542	660	1.88

[a] *vs.* Fc^+/Fc. [b] $E_{HOMO} = -e(E^{ox}_{onset} + 5.1)$. [c] $E_{LUMO} = E_{HOMO} + E^{opt}_g$. [d] In 1,2-dichlorobenzene solution. [e] In thin film.

increase in the energy gap of the small molecule from 1.72 to 1.88 eV, which is expected to affect the number of harvested photons.

The electrochemical properties of **4a**,**b** were investigated using cyclic voltammetry (CV). The acquired CV data [Figure 1(*b*)] allowed us to determine oxidation potentials of the designed materials and calculate HOMO energy levels (see Table 1). The replacement of phenylene with naphthalene leads to decrease in the HOMO energy of the material. Therefore, it can be expected that **4b**-based OSCs should demonstrate higher open-circuit voltages as compared to ones based on **4a**.

Each of the designed small molecules was evaluated in composites with the fullerene derivative [70]PCBM in laboratory prototypes of OSCs with standard configuration: ITO/PEDOT:PSS (60 nm)/active layer (100–180 nm)/Mg (60nm)/Al (50 nm). Figure 2 and Table 2 demonstrate the current voltage characteristics and external quantum efficiency (EQE) spectra of the OSCs comprising **4a**,**b**.The solar cells comprising **4b** deliver solar light power conversion efficiency (PCE) of 5.3%. Due to the decreased HOMO energy of **4b**, it delivers high open circuit

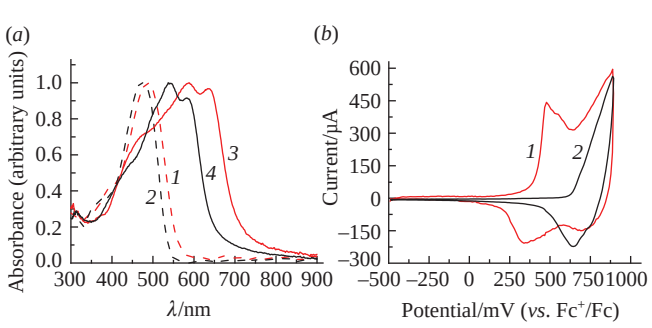


Figure 1 (*a*) Absorption spectra of (*1*) **4a** in 1,2-dichlorobenzene, (*2*) **4b** in 1,2-dichlorobenzene, (*3*) **4a** film, (*2*) **4b** film and (*b*) cyclic voltammograms for (*1*) **4a** and (*2*) **4b**.

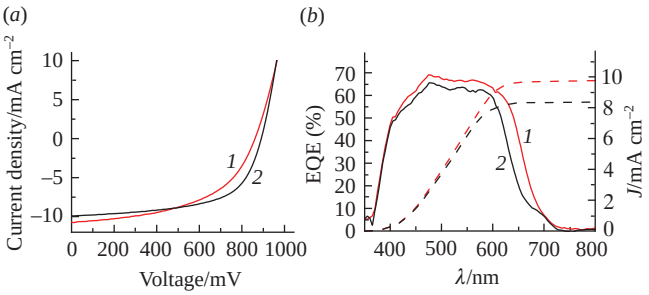


Figure 2 (*a*) *J*–*V* characteristics of solar cells comprising blends of (*1*) **4a**/[70]PCBM and (*2*) **4b**/[70]PCBM and (*b*) their EQE spectra.

voltage in solar cells of ~900 mV, which is exceeding the value obtained for devices based on **4a**.

The solar cells incorporating **4a** as electron donor photoactive material also delivered a decent PCE of 4.7%. Higher photocurrents of 10.7 mA cm^{-2} obtained using **4a** (*vs.* 9.9 mA cm^{-2} using **4b**) correlate with the electronic properties of these materials, *i.e.* the difference in their band gaps (see Table 1). These results are also supported by the EQE spectra [see Figure 2(*b*)].

In conclusion, we have synthesized two new compounds based on thiophene, benzene, naphthalene, and rhodanine and

Table 2 Processing conditions and parameters of organic solar cells based on **4a** and **4b**.

Composite	Processing conditions	V_{OC}/mV	J_{SC}/mA cm^{-2}	FF (%)	η (%)
4a/[70]PCBM	1:1,[a] 5000 rpm[b]	862	10.7	51	4.7
4b/[70]PCBM	1:1, 4000 rpm	891	9.9	60	5.3

[a] Small molecule:[70]PCBM ratio (by weight). [b] Spin-coating frequency for the deposition of active layer.

featured them as promising electron donor materials for organic solar cells. The replacement of phenylene core with the extended naphthalene moiety leads to a decrease in the material HOMO energy and an associated increase in the open circuit voltage of solar cells. The naphthalene-based small molecule in combination with [70]PCBM delivered power conversion efficiency of >5% in organic solar cells. The obtained results clearly demonstrate a good potential of naphthalene derivatives to be applied in design of new materials for organic electronics. Further investigations of these materials, *e.g.* their testing in combination with non-fullerene acceptors, may allow us to achieve even higher power conversion efficiencies in organic solar cells.

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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.2020.09.044.

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