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5,6-Bis(9-(2-decyltetradecyl)-6-fluoro-9*H*-carbazol-3-yl)naphtho[2,1-*b*:3,4-*b*']dithiophene as a Promising Donor Structure for D–A Conjugated Copolymers with a Narrow Bandgap

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Abstract—A new carbazole-containing naphthodithiophene derivative—heteroaromatic compound 5,6bis[9-(2-decyltetradecyl)-9*H*-carbazol-3-yl]naphtho[2,1-*b*:3,4-*b*']dithiophene (**M1**)—has been synthesized. The compound will be used by us as a weak donor structural block for fabricating narrow-bandgap D–A conjugated polymers. The composition and structure of **M1** have been confirmed by elemental analysis data, IR spectroscopy, and ¹H and ¹³C NMR. The synthesized compound has a low HOMO energy (-5.4 eV), which is favorable for a high open-circuit voltage. Monomer **M1** can be used as a promising weak donor moiety in D–A conjugated polymers for solar photovoltaics.

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Polymer solar cells (PSCs) have attracted considerable attention of researchers as a promising energy source owing to their advantages, such as low cost, processability, and the possibility of fabricating lightweight and flexible large-area devices [1, 2]. To date, PSCs have significantly advanced in efficiency, overcoming 13% [3, 4]. However, it is believed that the PSC efficiency on the order of 15% is necessary for commercialization [5]. Rational design of "ideal" polymers is the most efficient way of producing highperformance PSCs.

Polymers with "ideal" photovoltaic properties should have (i) a narrow bandgap ($E_{\rm g} \sim 1.4 \, {\rm eV}$) and broad absorption spectrum for obtaining high short-circuit current, (ii) a low HOMO energy (~ -5.4 eV) for providing high open-circuit voltages, (iii) a low LUMO energy (~ -3.9 eV) for efficient exciton dissociation, (iv) a coplanar structure and good crystallinity in the solid state to enhance charge carrier mobility, and (v) suitable solubility.

As is known, the efficiency of PSCs is directly proportional to the short-circuit current density (J_{sc}) , the open-circuit voltage (V_{oc}), and the fill factor (FF), which are three key parameters determining the performance of PSCs. To achieve the highest efficiency of PSCs, these three quantities should be simultaneously balanced by tailoring the properties of conjugated polymers. Conjugated polymers with perfectly alternating donor (D) and acceptor (A) blocks in the polymer chain represent an efficient approach to achieve required optical properties and frontier MO energies of polymers.

To design ideal polymers with low HOMO energies $(\sim -5.4 \text{ eV})$ and a narrow bandgap (1.4-1.6 eV), the "weak donor-strong acceptor" approach is suggested. When developing the structures of donor moieties, first of all, its electron-donating ability, which strongly affects the HOMO energy and the bandgap width of a conjugate polymer, should be controlled. For this purpose, fused conjugated fragments are mainly used owing to the possibility of tuning their electronic properties, as well as the effect of appropriate conjugated polymers on the charge carrier mobility.

Fluorene is among the most popular weak donor structure used in D–A polymers. Fluorene-based conjugated polymers have a low HOMO energy (about -5.5 eV) and, hence, large V_{op} (about 1 V). However, these polymers have relatively large bandgap width, which prevents the efficient light absorption.

To overcome this problem, a thiophene analogue of fluorene, cyclopentadithiophene (CPT) has been developed. CPT is a stronger donor than fluorene, which leads to a considerable decrease in the bandgap width of the corresponding conjugated polymers

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Scheme 1.

(about 1.4 eV). However, the HOMO energy of CPTbased polymers is as large as -5.2 eV, which leads to low V_{oc} values (0.5–0.6 V). Thus, a weak donor fragment with the donor ability intermediate between fluorene, on the one hand, and CPT and benzodithiophene (BDT) fragment, on the other hand, is required. Among such promising classes of heteroaromatic cyclic compounds are naphthodithiophene (NDT) derivatives containing two thiophene rings fused with a naphthalene moiety, which are planar structures with a π -conjugated system favorable for strong intramolecular π -conjugation and intermolecular π -stacking; the NDT moiety exhibits the electron-donating ability intermediate between those of fluorene and CPT [6]. NDT derivatives with pronounced weak donor properties in D-A copolymers are favorable for a decrease in the HOMO energy, which leads to an increase in the open-circuit voltage and, as a result, to an increase in the efficiency of PSCs [7].

In this paper, we report the development and synthesis of a new monomer—5,6-bis[9-(2-decyltetradecyl)-9H-carbazol-3-yl]naphtho[2,1-b:3,4-b']dithiophene (**M1**) based on NDT containing carbazole moieties in the 5- and 6-positions (Scheme 1). It has been noted above that compounds of this type form π stacking structures, which is favorable for the enhancement of the hole conductivity. The naphthodithiophene monomer is a weak donor, which, being incorporated in D–A polymers, favors the decrease in the HOMO energy and the increase in the open-circuit voltage and, as a result, the improvement of the PSC efficiency.

It should be noted that all reported NDTs contained alkyl or alkoxy groups in the 5- and 6-positions. The use of carbazole moieties has not been previously described. The introduction of the carbazole fragment gives a great advantage for several reasons: first, since the fluorene moiety is rather electronegative, the addition of the electron-donating nitrogen atom somewhat increases the electron density in the carbazole moiety so that the HOMO energy of polymers based on carbazole-containing monomer M1 increases and approach the HOMO energy of the ideal polymer. The presence of the N-H group in carbazole makes it possible to introduce alkyl substituents that promote good solubility in organic solvents. In addition, the substitution of the benzene nucleus in benzodithiophene (BDT) by a more electron-withdrawing naphthalene nucleus in compound M1 leads to a decrease in the bandgap width and to a lowering of the HOMO energy. The introduction of fluorine atoms into the main or side chains also contributes to a decrease in the HOMO energy without a significant change in the LUMO energy, as well as to the formation of an ordered structure due to intra- and intermolecular C-H...F...S interactions [8, 9].

RESULTS AND DISCUSSION

Monomer M1 was synthesized according to Scheme 1 through the reaction of *p*-fluorophenylhydrazine hydrochloride (1) with cyclohexanone to give 6-fluoro-2,3,4,9-tetrahydro-1H-carbazole (2) in 84% yield. Then, compound 2 was treated with a iodine solution in dimethyl sulfoxide at 115°C. The resulting mixture was placed into an autoclave, where triethylamine and a catalyst (10% Pd on carbon) were added, and hydrogenated at a pressure of 20 atm and 60°C for 5 h; this treatment led to 3-fluoro-9*H*-carbazole (3) in 80% yield as a light beige powder.

Then, carbazole derivative **3** was alkylated with 1bromo(2-decyltetradecane) to give 9-(2-decyltetradecyl)-3-fluoro-9*H*-carbazole (**4**); further reaction of **4** with *N*-bromosuccinimide and bis(pinacolato)diboron catalyzed by $PdCl_2(dppf)$ led to oily 9-(2-decyltetradecyl)-3-fluoro-6-(4,4,5,5-tetramethyl-1,3,2dioxoborolan-2-yl)-9*H*-carbazole (**6**) in 58% yield.

Then, the bromination of *o*-dimethoxybenzene with *N*-bromosuccinimide led to 1,2-dibromo-4,5-dimethoxybenzene (**8**) as large white crystals in 92% yield, and its reaction with thiophene-3-boronic acid under Suzuki conditions gave 1,2-bis(thiophen-3-yl)-4,5-dimethoxybenzene (**9**) in 85% yield. Treatment of compound **9** with anhydrous iron chloride in nitromethane and then with BBr₃ led to oxidative cyclization to form 5,6-dimethoxynaphtho[2,1-*b*:3,4-*b*]dithiophene (**10**) (yield 49%) and compound **11** (yield 99%), respectively.

The reaction of compound **11** with $[CF_3(SO_2)]_2O$ in the presence of triethylamine gave intermediate bis(triflate) compound **12** in 72% yield. At the last stage, the reaction of twofold molar excess of compounds **6** and **12** in the presence of sodium carbonate

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and $PdCl_2(dppf)$ as catalysts gave target compound— 5,6-bis(9-(2-decyltetradecyl)-6-fluoro-9*H*-carbazol-3-yl)naphtho[2,1-*b*:3,4-*b*']dithiophene (**M1**)—as a light oily product in 61% yield.

The composition and structure of intermediate compounds and target product **M1** have been proved by elemental analysis data and ¹H, ¹³C, and ¹⁹F NMR. The aromatic region of the ¹H NMR spectrum of **M1** (Fig. 1a) shows one singlet, four doublets, three doublets of doublets, and one triplet of doublets. The singlet at $\delta = 8.52$ ppm corresponds to the protons of the benzene ring of the naphthalene moiety. Two doublets at $\delta 8.03$ (d, J = 5.4 Hz) and 7.51 ppm (d, J = 5.4 Hz) arise from the H(b) and H(a) protons of the fused thiophene rings, respectively.

The doublet at $\delta = 7.14$ ppm has the spin coupling constant (SCC) J = 8.6 Hz; the same SCC is observed for a more complicated signal at 7.30 ppm (dd, $J_1 = 8.6$ Hz, $J_2 = 1.5$ Hz). It is clear from the figure that these two signals are from the aromatic protons H(f) and H(e) in the *ortho* position to each other, and the latter is coupled to the H(d) proton in the *meta* position (the corresponding SCC is 1.5 Hz). The doublet at $\delta = 8.21$ ppm shows a similar splitting (1.4 Hz); hence, it corresponds to the H(d) proton.

The triplet of doublets at δ 7.21 ppm (td, $J_1 = 8.9$ Hz, $J_2 = 2.5$ Hz) arises from the H(h) proton in the *ortho* position to the F and H(g) atoms; the doublet splitting (J = 2.5 Hz) is due to the coupling to H(i). The signal of the H(g) proton is observed at 7.27 ppm (dd, $J_1 = 4.1$ Hz, $J_2 = 8.0$ Hz) and is partially overlapped by the solvent signal. The signals in the aliphatic region at $\delta = 4.03$ (d, J = 7.3 Hz, 2H), 2.08 (m, 1H), and 0.94 ppm (t, 7.3 Hz) correspond to the protons of the CH₂ group directly bonded to the nitrogen atom, to the H atom of the tertiary CH group, and to the terminal CH₃ groups, respectively. The other broadened signals in the alkyl region arise from the methylene protons of the alkyl substituents. The integrated intensities of all the signals correspond to the suggested structure.

The aromatic region of the ¹³C NMR spectrum shows 20 signals; in particular, the doublet at δ 156– 158 ppm (d, ¹ J_{C-F} = 238.0 Hz) is due to the carbon atom bonded to the fluorine atom. The assignment of the other signals was performed using heteronuclear 2D NMR. Analysis of the spectrum of (¹H, ¹³C) single bond correlations (Scheme 2) demonstrates that the signals at δ 129.15, 126.66, 123.74, 123.03, 121.69, 113.23 (d, ² J_{C-F} = 25.4 Hz), 109.45 (d, ³ J_{C-F} = 8.9 Hz), 108.54, and 106.00 (d, ² J_{C-F} = 23.5 Hz) arise from nine aromatic carbon atoms C19, C6, C1, C2, C9, C14, C15, C18, and C12, respectively.

This signals has been assigned owing to the existence of direct C–H coupling. The signals of quaternary aromatic C atoms have been assigned using the $(^{13}C, ^{1}H)$ multiple bond correlation spectrum



Fig. 1. (a) 1 H and (b) 13 C NMR spectra of compound M1 in CDCl₃.



(Scheme 3). For example, the spectrum shows crosspeaks corresponding to multiple bond coupling of CH and CH₂ groups with aromatic carbon atoms with δ = 129.15, 137.57 and 137.57, 140.65 ppm. It has been shows above that the signal at δ = 129.15 ppm is due to the C19 atom. Taking into account the literature ¹³C NMR chemical shifts of carbazole moiety the presence of the fluorine atom, we assigned the signals at δ = 137.57 and 140.65 ppm to the C16 and C17 atoms, respectively.

Analogously, the signals at $\delta = 139.52$, 134.38, 132.74, 132.14, 126.76, 123.30, and 122.35 ppm were assigned to the C7, C3, C8, C4, C5, C11, and C10 atoms, respectively (Fig. 1b).

The optical properties of **M1** were studied by UV spectroscopy. The absorption maxima for **M1** in chloroform and in films are observed at 302, 362 and 302, 387 nm, respectively (Fig. 2). It should be noted that the absorption spectrum of the **M1** film is red-shifted from the absorption spectrum of the solution (Fig. 2). This is presumably associated with a more ordered structure of **M1** in the solid state. The optical bandgap

width E_{g}^{opt} of compound **M1** calculated from the absorption edge of the film (383 nm) is 3.24 eV.

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The electrochemical properties of **M1** were studied by cyclic voltammetry (CVA). The CVA curve (Fig. 3) shows one reduction peak at negative voltages and one oxidation peak at positive voltages. The cathodic peak of reduction is presumably related to the formation of radical anions of the thiophene derivative and the anodic peak of oxidation, to the radical cations of the thiophene moiety. The oxidation and reduction onset potentials ($E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{red}}$, respectively) of **M1** are +1.24 and -1.41 V. The HOMO and LUMO energies and the electrochemical bandgap width E_{g}^{ec} of compound **M1** calculated by the equations HOMO = $-e(E_{\text{onset}}^{\text{ox}} + 4.4)$ (eV), LUMO = $-e(E_{\text{onset}}^{\text{red}} + 4.4)$ (eV), and E_{g}^{ec} = HOMO – LUMO (eV) are -5.64, -2.65, and 2.65 eV, respectively.

It should be noted that the introduction of two donor carbazole substituents into compound **M1** led to a lowering of the HOMO energy as compared with the known structural analogues containing methyl and phenyl groups (-5.28, -5.39, and -5.41 eV, respectively) [10, 11]. The introduction of a fluorine atom into the carbazole moiety led to a lowering of the HOMO energy (-5.64 eV) as compared with the non-fluorinated analogue (-5.57 eV) [12].



Compound M1 synthesized by us is a structural moiety with rather low energies of frontier MOs: their values are close to those for the low-molecular-weight

Optical absorption, rel. units

Solution

Film

1.0

0.8

0.6

0.4

0.2





Fig. 3. CVA curve of M1 in a 0.1 M Bu₄NPF₆ solution in acetonitrile at a scan rate of 50 mV/s.

0 300 400 500 600 Wavelength, nm

Fig. 2. Normalized absorption spectra of M1 in the film and chloroform ($c = 10^{-5} \text{ mol/L}$).

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zole moieties since, as mentioned above, fluorine atoms tend to form additional S...F contacts, which improves the morphology of the films and contributes to the increase in the fill factor and, hence, the efficiency of solar photovoltaics. The introduction of fluorine atoms also contributes to a decrease in the HOMO energy, which favors an increase in the opencircuit voltage and imparts good stability in air to **M1**. New monomer **M1** is a promising donor "building block" in synthesis of D–A polymers for organic photovoltaics.

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REFERENCES

- Chen, C.C., Dou, L., Zhu, R., Chung, C.H., Song, T.B., and Zheng, Y.B., ACS Nano, 2012, vol. 6, pp. 7185– 7190.
- Colsmann, A., Puetz, A., Bauer, A., Hanisch, J., Ahlswede, E., and Lemmer, U., *Adv. Energ. Mater.*, 2011, vol. 1, pp. 599–603.

- Yang, Sh.-Sh., Hsieh Z-Chun, Keshtov, M. L., Sharma. G.D., and Chen, F.-Ch., *Sol. RRL*, 2017, vol. 1, p. 1700174. doi 10.1002/solr.201700174
- Zhao, W., Li, S., Yao, H., Zhang, S., Zhang, Y., Yang, B., and Hou, J., J. Am. Chem. Soc., 2017, vol. 139, pp. 7148–7151.
- Janssen, R.A.J. and Nelson, J., Adv. Mater., 2013, vol. 25, pp. 1847–1858.
- Muhlbacher, D., Scharber, M., Morana, M., Zhu, Z., Waller, D., Gaudiana, R., and Brabec, C., *Adv. Mater.*, 2006, vol. 18, pp. 2884–2889.
- Zhou, H., Yang, L., Stuart, A.C., Price, S.C., Liu, S., and You, W., *Angew. Chem.*, *Int. Ed.*, 2011, vol. 50, pp. 2995–2998.
- Reichenbacher, K., Suss, H.I., and Hulliger, J., J. Chem. Soc. Rev., 2005, vol. 34, pp. 22–30.
- Pagliaro, M. and Ciriminna, R., J. Mater. Chem., 2005, vol. 15, pp. 4981–4991.
- Yang, L., Zhou, H., and You, W., J. Phys. Chem. C, 2010, vol. 114, no. 39, pp. 16793–16800.
- 11. Zhou, H., Yang, L., Xiao, S., Liu, S., and You, W., *Macromolecules*, 2010, vol. 43, pp. 811–820.
- Keshtov, M.L., Kuklin, S.A., Godovskii, D.Yu., Konstantinov, I.O., Krayushkin, M.M., Peregudov, A.S., and Khokhlov, A.R., *Dokl. Chem.*, 2016, vol. 467, part 1, pp. 94–99.

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