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CHEMICAL TECHNOLOGY ====

New Quinoxaline-Containing Monomers for Narrow-Bandgap Polymers

M. L. Keshtov^a, S. A. Kuklin^{a,*}, I. O. Konstantinov^a, D. Yu. Godovskii^a, Y. Zou^c, I. E. Ostapov^b, E. E. Makhaeva^b, and Academician A. R. Khokhlov^a

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Abstract—Two new fused quinoxaline-containing monomers—2,3-bis(9-(2-decyltetradecyl)-9*H*-carbazol-3-yl)dithieno[3,2-*f*:2'3'-*h*]quinoxaline (**M1**) and 2,5-di(nonadecan-3-yl)bis[1,3]thiazolo[4,5-*a*:5',4'-*c*]bis-thieno[3,2-*h*:2',3'-*j*]phenazine (**M2**)—have been synthesized in high yields of 88 and 83% as promising building blocks of D-A polymers for photovoltaic applications. The optical bandgaps, found from the absorption edge, are 2.79 and 2.88 eV, respectively. The HOMO/LUMO energies of **M1** and **M2** are -5.83/-2.96 and -5.83/-2.98 eV, respectively. Both monomers have low-lying HOMO levels, which is favorable for a high

open-circuit voltage and a high stability in air in the development of PSCs. The E_g^{ec} values of monomers **M1** and **M2** are 2.87 and 2.85 eV and are consistent well with the optical bandgap (2.79 and 2.88 eV, respectively).

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In the last decade, bulk heterojunction polymer solar cells (PSCs) have attracted considerable attention of researchers owing to their advantages (over inorganic photovoltaics), such as low cost, small mass, processability, good mechanical flexibility, and the possibility of fabricating large-area devices [1].In recent few years, PSCs have significantly advanced in efficiency, overcoming 13% [2, 3]. This success has been mainly achieved through the synthesis of new conjugated polymers. However, it is believed that the efficiency exceeding 15% is necessary for commercialization. To further enhance the efficiency, new approaches and new ideal high-performance conjugated polymers are required.

To design an ideal conjugated polymeric donor material, the following conditions should be met:

(a) broad and strong absorption in the visible and near-IR ranges;

(b) the HOMO and LUMO energies appropriate for providing the highest open-circuit voltages and the difference between the LUMO energies of the donor and acceptor sufficient for exciton dissociation;

(c) high and balanced charge mobility for increasing the fill factor (FF) and short-circuit current (J_{sc}) ; (d) a high molecular weight and good solubility in common organic solvents.

With taking into account these requirements, it has been demonstrated that an efficient way for creating ideal high-performance copolymers is to use the donor-acceptor (D-A) approach. Various classes of conjugated polymers have been suggested for PSCs. Narrow-bandgap conjugated D-A polymers based on benzodithiophene and/or thieno[3,4-b]thiophene and 5,6-difluoro-2,1,3-benzothiadiazole structures are frequently used and recommend themselves as high-performance semiconductor materials for PSCs [4, 5]. To further improve the characteristics of devices, some efficient approaches have been used, such as introducing fused heterocycles and conjugated side chains into the polymer chain and addition of functional groups. However, most of the highly efficient donor polymers are synthesized through complicated multistep routes, which increases the production cost [6]. In this respect, quinoxaline (Qx) derivatives are unique building blocks for the development of various optoelectronic polymers because of their straightforward synthesis, planar and rigid conjugated structure, and the ease of modification by introducing flexible alkyl chains (to improve solubility and crystallinity) and conjugated side groups (to additionally affect the energy levels, absorption, charge mobility, morphology, and microstructure of active layers) and by creating multi-fused structures (to reduce the bandgap by increasing the effective conjugation length), which results in a considerable increase in the short-circuit current density and fill factor in PSCs. Qx derivatives are also of significant interest and are

^aNesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia

^bMoscow State University, Moscow, 119991 Russia

^cCentral South University, Changsha, China

^{*}e-mail: ineos-50@mail.ru



Scheme 1.

widely used in many fields, such as light-emitting diodes [7], nonlinear optical devices [8], electroluminescent materials [9], and pharmacology [10]. Recently, the efficiency of PSCs based on Qx polymers exceeded 11%, which is one of the best among

PSCs. Thus, it can be stated that Qx-based polymers have a large potential for high-performance PSCs [11]. Although the efficiency of Qx-based PSCs has achieved high values in a last few years, they are still below the desired level [12]. It is believed that further

Table 1. Optical and electrochemical properties of monomers M1 and M2

Monomer	λ_{max} , nm		E^{OX} (A)	E ^{red} (1)	FHOMO(eV)	FLUMO(eV)	$F^{ec}(\mathbf{A})$	$F^{\text{opt}}(\mathbf{A})$
	solution	film	$L_{\text{onset}}(\mathbf{v})$	$L_{\text{onset}}(\mathbf{v})$		L (CV)	L_{g} (ev)	L_{g} (CV)
M1	294; 408	294; 412	1.44	-1.43	-5.83	-2.96	2.87	2.79
M2	263; 305; 405	264; 305; 405	1.42	-1.43	-5.83	-2.98	-2.85	2.88

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Fig. 1. ¹H NMR spectrum of monomer M1 in CDCl₃.

development of Qx-based monomers will lead soon to PSC efficiencies not inferior to the world standards. In this paper we report new fused quinoxaline-containmonomers-2,3-bis(9-(2-decyltetradecyl)-9Hing carbazol-3-vl)dithieno[3,2-f:2'3'-h]quinoxaline (M1) 2,5-di(nonadecan-3-yl)bis[1,3]thiazolo[4,5and a:5',4'-c]bisthieno[3,2-h:2',3'-j]phenazine (M2)—as promising building blocks of D-A polymers for applications and consider the effect of the molecular structure on optoelectronic and electrochemical properties. Compound M1 was synthesized in seven stages according to Scheme 1 through successive transformations beginning from 2,7-ditrimethylsilylthieno[3,2-g] [1]benzothiophene-4,5-dione (1) introduced into the reaction with tetrabutylammonium fluoride to give thieno[3,2-g][1]benzothiophene-4,5-dione (2),which was treated with hydroxylamine hydrochloride in the presence of pyridine to give N, N-dihydroxythieno[3,2-g] [1]benzothiophene-4,5-diimine (3) in 85% yield. The latter was reduced with anhydrous thieno[3,2-g][1]benzothiophene-4,5-SnCl₂ to diamine (4) in 59% yield. Then, carbazole was reacted with 1-bromo-2-octyldodecane in the presence of sodium hydride to yield 9-(2-decyltetradecyl)-9Hcarbazole (7), which was then acylated with oxalyl

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chloride in the presence of pyridine to give an α -dike-1,2-bis(9'-(2"-decyltetradecyl)carbazol-3'tone. yl)ethan-1,2-dione (8). The condensation of diamine 4 [13] with α -diketone 8 led to the target monomer (M1) in a high yield of 88%. Monomer M2 was synthesized according to Scheme 1: in this case, α -diketone 16 was synthesized in seven stages through successive transformations involving (i) the synthesis of α -ethylstearic acid 10 by treating compound 9 with LDA in the presence of tetramethylethylenediamine and, then, with ethyl iodide; (ii) the reaction of α -ethvlstearic acid with carbonyldiimidazole (CDI) and aqueous ammonia to give α -ethylstearamide 11; (iii) the treatment of **11** with Lawesson's reagent (LR) to produce ethylstearic acid thioamide 12. 2-(1-Ethylheptadecyl)-1,3-thiazole 13 was synthesized by cyclization of compound 12 in the presence of bromoacetaldehyde diethylacetal and a catalytic amount of hydrochloric acid. The lithiation of compound 13 with the subsequent treatment with CBr_4 gave bromide 14. The latter was treated with LDA and CuCl₂ to give aromatic dibromide 15 in 91% yield. The lithiation of 4,4'-dibromo-2,2'-bis(1-ethylheptadecyl)-5,5'-bi-1,3-thiazole (15) followed by the treatment with diethyl oxalate gave α -diketone **16** in 37% yield. The



Fig. 2. ¹H NMR spectrum of monomer M2 in CDCl₃.

condensation of diamine **4** [13] with α -diketone **16** resulted in the target monomer, 2,5-di(nonadecan-3-yl)bis[1,3]thiazolo[4,5-*a*:5',4'-*c*]bisthieno[3,2-*h*:2',3'-*j*]phenazine (**M2**) in 83% yield.

The composition and structure of intermediate compounds 2-16 as well as of the target products— 2,3-bis(9-(2-decyltetradecyl)-9*H*-carbazol-3-

yl)dithieno[3,2-f:2'3'-h]quinoxaline (M1) and 2,5di(nonadecan-3-yl)bis [1, 3]thiazolo[4,5-a:5',4'*c*]bisthieno[3,2-*h*:2',3'-*j*]phenazine (M2)—were confirmed by elemental analysis data and ¹H and ¹³C NMR. The ¹H NMR spectrum of **M1** (Fig. 1) shows multiplets at δ (ppm) 8.73–8.68 (m, 2H), 8.52–8.42 (m, 2H), 8.10 (d, J = 7.6 Hz, 2H), 7.74-7.56 (m, 4H),7.52-7.40 (m, 4H), and 7.32-7.13 (m, 4H) from 18 aromatic protons; the signal at δ 4.15 (d, J = 7.3 Hz, 4H) corresponds to the four protons of the methylene groups adjacent to the nitrogen atom of the carbazole groups. The singlet at 2.12 ppm (br s, 2H) is assigned to two ternary aliphatic protons of alkyl groups. The multiplets in the range of δ 1.31–0.85 ppm (80H) arise from the other alkyl protons. Although the ¹H NMR spectrum of M1 is complicated, the aromatic-to-aliphatic integrated intensity ratio corresponds to the suggested structure. The ¹H NMR spectrum of M2 (Fig. 2) shows two signals at δ 8.86 and 7.66 ppm from two aromatic protons of the thiophene moiety. The high-field range at δ 3.60, 2.15–1.75, 1.10, and 0.89 ppm shows the signals characteristic of the protons of the CH₂ groups adjacent to the thiazole rings and terminal CH₃ groups. The signals of the other 30 aliphatic protons of the alkyl chain are observed in the range of δ 1.20–1.50 ppm. In the spectrum of **M2**, the integrated intensity ratio of all the signals corresponds to the suggested structure.

The optical properties of **M1** and **M2** were studied by UV spectroscopy: the results are summarized in Table 1, and the absorption spectra of **M1** and **M2** films are shown in Fig. 3. The absorption maxima for **M1** and **M2** in solution and films are observed at 233, 293, and 407 and 264, 305, and 407; 233, 294, and 412; and 266, 311, and 413 nm, respectively. The absorption spectra of the monomers in films are slightly redshifted as compared to the spectrum of solutions; most likely, this is related to a more ordered structure in the solid state (Table 1). The optical bandgaps (E_g^{opt}) of **M1** and **M2**, found from the absorption edges (λ_{edge}) by the equation $E_g^{opt} = 1240/\lambda_{edge}$, are 2.79 and 2.88 eV.



Fig. 3. Normalized absorption spectra of monomers M1 and M2 in films.



Fig. 4. CVA curves of monomers M1 and M2 in thin films at a sweep rate of 50 mV/s.

The electrochemical properties of M1 and M2 were studied by cyclic voltammetry (CVA); the results are presented in Table 1, and the corresponding CVA curves are shown in Fig. 4. CVA of the films was carried out in a 0.1 M Bu₄NPF₆ solution in acetonitrile at a sweep rate of 50 mV/s. A platinum electrode was used as a counter electrode, and the external reference was Fc/Fc⁺. The CVA curve (Fig. 4) 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. From the oxidation and reduction onset potentials

 $(E_{\text{onset}}^{\text{ox}} \text{ and } E_{\text{onset}}^{\text{red}}$, respectively) of the CVA curves of the monomers, the HOMO and LUMO energies and

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the bandgap width (E_g^{ec}) of the monomers were calculated by the following equations:

HOMO =
$$-(E_{onset}^{ox} + 4.4)$$
 (eV),
LUMO = $-(E_{onset}^{red} + 4.4)$ (eV),
 $E_{g}^{ec} = (E_{onset}^{ox} - E_{onset}^{red})$ (eV).

The HOMO/LUMO energies of monomers M1 and M2 are -5.83/-2.96 and -5.83/-2.98 eV, respectively. Both monomers have low HOMO energies, which is favorable for a high open-circuit voltage (V_{oc}) and a high stability in air of polymers based on them

and PSCs. The electrochemical band gaps (E_g^{ec}) of monomers **M1** and **M2**, found from the CVA curves,

are 2.87 and 2.85 eV and are consistent well with the optical band gap (2.79 and 2.88 eV, respectively) within the experimental error.

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