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ScienceDirect
Mendeleev Commun., 2014, **24**, 306–307

Mendeleev Communications

Organic field-effect transistors based on disubstituted perylene diimides: effect of alkyl chains on the device performance

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DOI: 10.1016/j.mencom.2014.09.020

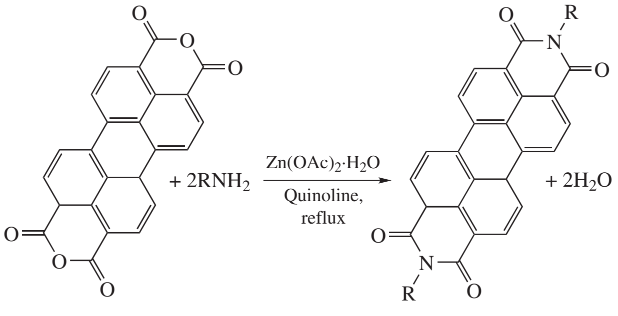
The preparation and systematic investigation of n-type semiconductor materials based on disubstituted perylene diimides (PDIs) possessing alkyl chains with variable length (from C_4 to C_{12}) are reported. It was shown that electrical characteristics of field-effect transistors can be tuned by changing the length of the alkyl chains in the PDIs used as semiconductor materials.

Perylene-3,4,9,10-tetracarboxydiimides, which are also known as perylene diimides (PDIs), were studied as industrial colorants and pigments.[1] These pigments have excellent chemical, thermal, photo and weather stability, and they can be applied as high-grade industrial paints.[2] In addition, perylene diimides exhibit high electron affinity and good charge transport properties. Thus, they can be used as n-type semiconductors in organic field-effect transistors (OFETs),[3,4] organic solar cells,[5] photoswitches,[6] laser dye applications[7] *etc*.

N,N'-Diphenyl-3,4,9,10-perylenetetracarboxylic diimide was among the first perylene diimides investigated in OFETs, which showed a field-effect electron mobility of 1.5×10^{-5} cm^2 V^{-1} s^{-1}.[8] The charge carrier mobility measured in similar devices based on unsubstituted perylene diimide was almost one order of magnitude lower (3.5×10^{-6} cm^2 V^{-1} s^{-1}).[9] Perylene diimides bearing alkyl substituents exhibited higher charge carrier mobility: 5.6×10^{-4}, 0.1, 5.0×10^{-2}, 0.6, 0.52, 2.1, 0.4 and 1.2 cm^2 V^{-1} s^{-1} for dimethyl-PDI,[10] dipentyl-PDI,[11] diheptyl-PDI,[12] dioctyl-PDI,[11] didodecyl-PDI,[11] ditridecyl-PDI,[13] dibutadecyl-PDI,[14] and dioctadecyl-PDI,[14] respectively. Unfortunately, these values were obtained in OFETs possessing different geometry, comprising different dielectric layers and fabricated using different film deposition techniques. Therefore, it is impossible to compare these data and reveal the most efficient PDI derivative with an optimum alkyl chain length suitable for the fabrication of high-performance OFETs.

Here, we report the preparation and characterization of disubstituted perylene diimides in order to reveal the effect of alkyl substituents on the performance of these semiconductor materials in OFETs.

The synthesis was carried out according to a known procedure based on the condensation of perylene-3,4,9,10-tetracarboxylic dianhydride with an appropriate aliphatic amine in a high-boiling solvent (quinoline) with the addition of a catalytic amount of zinc acetate (Scheme 1).[15] The PDIs obtained in 80–90% isolated yields were purified by multiple gradient vacuum sublimation. Commercial *N,N'*-dimethyl-3,4,9,10-perylenetetracarboxylic diimide **1** (Aldrich) was also purified by sublimation.



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2 R = C_4H_9
3 R = C_5H_{11}
4 R = C_6H_{13}
5 R = C_7H_{15}
6 R = C_8H_{17}
7 R = 2-ethylhexyl
8 R = $C_{10}H_{21}$
9 R = $C_{12}H_{25}$

Scheme 1

Organic field-effect transistors comprising PDIs as semiconductor materials were fabricated using the following procedure: The 40×60 mm glass slides were cleaned by sonication in a base piranha solution (a mixture of hydrogen peroxide and ammonia). Then, aluminum gate electrodes (~100 nm) were deposited on the glass slides by thermal vacuum evaporation. Thin and compact dielectric layers of aluminum oxide were formed on the surface of the gate electrodes by the electrochemical oxidation of aluminum in a potentiostatic regime at 10 V according to a procedure reported previously.[16] The passivation organic layer was deposited on the surface of the dielectric oxide by spin-coating a solution of benzocyclobutene-silicon resin (BCB) (concentration of ~4 mg ml^{-1}) and the subsequent annealing at 250 °C overnight in an argon atmosphere. Organic semiconductor material (PDI film, ~100 nm) was deposited by thermal evaporation in a vacuum of ~10^{-6} mbar at a rate of 2–3 Å s^{-1}. Finally, silver source and drain electrodes (80 nm) were deposited on the top of the organic semiconductor by thermal evaporation. Figure 1 shows the geometry of the fabricated device.

The current–voltage characteristics of the OFET devices were analyzed using a Keithley 2612A source measurement unit. Figure 2 shows the representative transfer and output characteristics of an OFET based on *N,N'*-didodecyl-3,4,9,10-perylenetetracarboxylic diimide **9**. Thus, the transistor works at a low voltage (6 V), and the current on/off ratio reaches 10^3–10^4.

The charge carrier mobilities of organic field-effect transistors were calculated from transfer characteristics in a saturation regime according to a standard method[17] (Table 1). The electrical characteristics of OFETs depend on the length of alkyl chains attached to the PDI core. An analysis of these data allowed us to

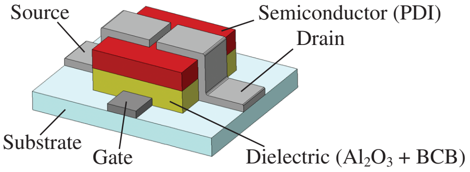

Figure 1 Top contact device structure of a field-effect transistor.

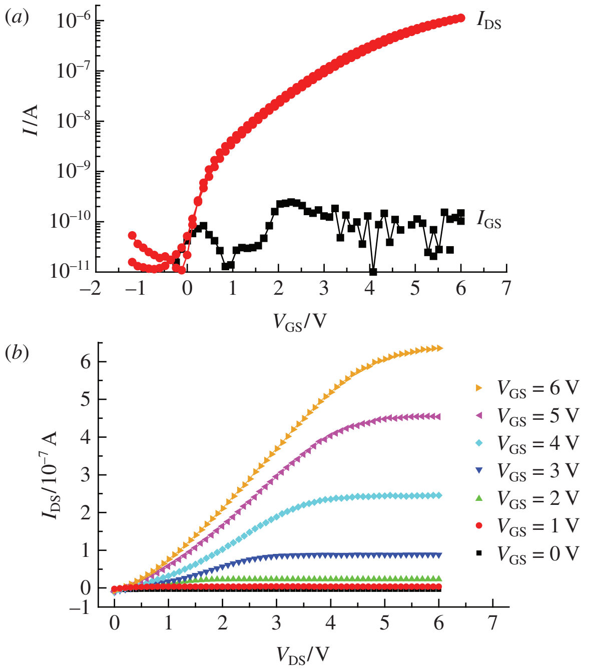

Figure 2 (*a*) Transfer and (*b*) output characteristics of an OFET based on *N*,*N'*-didodecyl-3,4,9,10-perylenetetracarboxylic diimide **9**.

find correlations between the molecular structure of the semiconductor materials and their performance in OFETs. Figure 3(*a*) shows that the charge carrier mobility increases on going from compounds with short chains (C_1–C_5) to PDIs bearing long alkyl substituents (C_{10}–C_{12}). It is also notable that PDI **7** bearing branched 2-ethylhexyl side chains showed inferior performance compared to the isomeric PDI **6** with linear *n*-octyl chains. It is most likely that the branched side chains induce a stronger disorder in the PDI films, which results in hindered charge transport and poor semiconductor performance.

The experimental data indicate that the length of the alkyl substituents has a strong effect on the electrical performance of PDI derivatives in OFETs. Charge transport in organic semiconductors strongly depends on the packing of molecules in thin films and on the strength of intermolecular electronic interactions. It is likely that alkyl chains affect both the ordering of PDIs in solid thin films *via* molecular π–π stacking and alkyl–alkyl chain interactions and electronic contacts between neighboring molecules. A strong difference in the organization of C_5-PDI (**3**) and C_{10}-PDI (**8**) thin films was found using scanning electron microscopy (SEM). Figure 4 shows that C_5-PDI forms rod-like aggregates with an average length of ~100 nm. On the contrary, C_{10}-PDI forms lamellas of approximately the same size. It is very likely that lamellar aggregates possess better charge transport properties compared to the rods due to unknown reasons (perhaps due to better interconnections), which result in their superior performance in OFETs. The observed different morphology of C_5-PDI and C_{10}-PDI is most probably related to their different crystal packing.

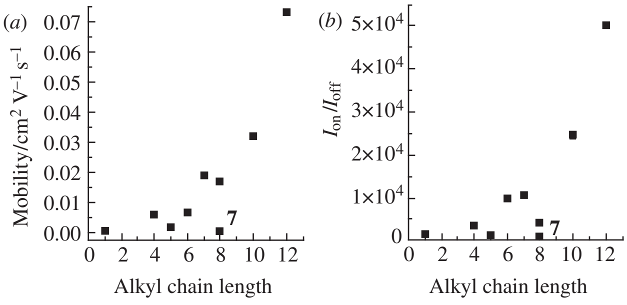

Figure 3 Dependence of (*a*) charge career mobility and (*b*) I_{on}/I_{off} ratio on the length of alkyl chains in the PDI molecules used as semiconductor materials in OFETs.

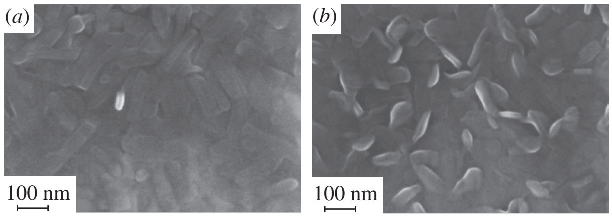

Figure 4 SEM images of the thin films of (*a*) C_5-PDI and (*b*) C_{10}-PDI.

Table 1 Electrical characteristics of OFETs (V_{DS} = 6 V).

PDI	V_{GS}/V	V_{Th}/V	I_{on}/I_{off}	$\mu_e/10^{-3}$ cm^2 V^{-1} s^{-1}
1	–1.0–6.0	–0.7	960	0.56
2	–1.5–6.0	–0.1	2700	6.0
3	–1.5–6.0	0.6	764	1.8
4	–1.5–6.0	1.8	10000	6.7
5	–1.2–6.0	1.2	11000	19.0
6	–1.0–6.0	1.5	4800	17.0
7	–1.2–6.0	1.8	466	0.47
8	–1.0–6.0	0.5	25700	32.0
9	–1.0–6.0	1.6	50000	73.2

In conclusion, we investigated eight different perylene diimides as semiconductor materials for OFETs. It was shown that increase in the length of the alkyl chains attached to the PDI core from C_1 to C_{12} improves both the charge carrier mobility and the on-off current ratio of the devices. The revealed correlation between the molecular structures of PDIs and their performances in OFETs might be useful in the design of advanced materials for organic electronics.

This work was supported by the Russian Ministry of Education and Science (contract no. 11.G34.31.0055) and the Russian Foundation for Basic Research (grant no. 12-03-31698).

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Received: 23rd December 2013; Com. 13/4275