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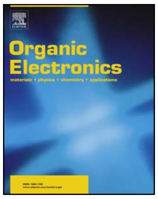

Effects of bridging atom in donor units and nature of acceptor groups on physical and photovoltaic properties of A-π-D-π-A oligomers

Jie Min[a,b,*,1], Yuriy N. Luponosov[c,**,1], Dmitry A. Khanin[d], Petr V. Dmitryakov[d], Evgeniya A. Svidchenko[d], Svetlana M. Peregudova[e], Linda Grodd[f], Souren Grigorian[f,g], Sergei N. Chvalun[d], Sergei A. Ponomarenko[c,h], Christoph J. Brabec[b,i]

[a] Institute for Advanced Studies (IAS) of Wuhan University, Wuhan, Hubei 430072, PR China
[b] Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstraße 7, 91058, Erlangen, Germany
[c] Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Profsoyuznaya St. 70, Moscow, 117393, Russia
[d] National Research Centre "Kurchatov Institute", 1, Akademika Kurchatova pl., Moscow, 123182, Russia
[e] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, Moscow, 119991, Russia
[f] Department of Physics, University of Siegen, Walter-Flex-Strasse 3, 57068, Siegen, Germany
[g] Aix-Marseille Univ, Univ Toulon, CNRS, IM2NP, Avenue Escadrille Normandie Niemen - Case 142, F-13397, Marseille, France
[h] Chemistry Department, Moscow State University, Leninskie Gory 1-3, Moscow, 119991, Russia
[i] Bavarian Center for Applied Energy Research (ZAE Bayern), Immerwahrstraße 2, 91058, Erlangen, Germany

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ABSTRACT

The synthesis of a series of novel A-π-D-π-A oligomers bearing either electron-donating dithieno[3,2-*b*:2′,3′-*d*]silole (DTS) or dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) units linked through a bithiophene π-bridge with the electron-withdrawing methyldicyanovinyl (DCV) or N-ethylrhodanine (Rh) groups is described. In order to evaluate the effects of different donor-acceptor combinations on various physical properties of the oligomers they are comprehensively studied by UV–Vis spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and cyclic voltammetry (CV). Replacing the DTS by DTP as well as the DCV by Rh leads to increasing of HOMO energy levels and slight decreasing of LUMO energy levels, respectively. The DTP-based oligomers have a red shift in absorption spectra and an increased solubility as compared to the DTS-based analogs. Replacing the acceptor DCV unit by Rh also results in significantly higher solubility, but the Rh-based oligomers exhibit weaker intermolecular interactions, poorer optical absorption of sun light as well as lower charge carrier mobility in blends. Altogether, the structural improvement of the DTS-DCV and DTP-DCV blends upon annealing correlates well with the observed photovoltaic performances in organic solar cells. These results give more insight how to fine-tune and predict physical properties and photovoltaic performance of small A-π-D-π-A molecules having different donor-acceptor combinations in their chemical structures and thus providing a molecular design guideline for the next generation of high-performance photovoltaic materials.

1. Introduction

Organic photovoltaic (OPV) materials are under intense study because they offer the possibility of producing flexible and/or semi-transparent devices via solution processed methods [1]. In recent decades, many π-conjugated small molecules of donor-acceptor (D-A) structure have been applied in bulk heterojunction (BHJ) organic solar cells (OSCs) [2]. Compared with their polymeric counterparts, small molecules have definite molecular weights, easily controlled high purity, more reproducible device performances, and also offer unique device fabrication techniques such as vacuum deposition [3]. Besides, the crystalline nature of conjugated small molecules can lead to better semiconducting properties [4]. Recently, OSCs made with solution-processed small molecule materials have shown rapid progress. Many small molecules have reached power conversion efficiencies (PCEs) of over 10% [5,6], i.e. comparable to those of polymer solar cells (PSCs) in the most promising BHJ configuration [7].

A highly functional design of D-A oligomers for OPV requires the parallel optimization of multiple properties, like achieving sufficient molecular solubility in non-halogenated solvents, guaranteeing high

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[*] Corresponding author. Institute for Advanced Studies (IAS) of Wuhan University, Wuhan, Hubei 430072, PR China.
[**] Corresponding author. Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences, Profsoyuznaya St. 70, Moscow, 117393, Russia
E-mail addresses: Min.Jie@whu.edu.cn (J. Min), luponosov@ispm.ru (Y.N. Luponosov).
[1] J. Min and Y. N. Luponosov contributed equally to this work.

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absorptivity in thin films, engineering of the suitable molecular energy levels, enhancing charge transport as well as photochemical and thermal stability, etc. [8] Thus, in order to meet simultaneously all these specific requirements, the structural components in photovoltaic donor materials, including donor/acceptor units, conjugated π-bridges, alkyl side chains and/or pendant chains, heteroatom substitutions, should be modified and designed very carefully [2,9,10]. Reviewing the promising small molecules [2,6], one can be found that most of them exhibited a A-π-D-π-A molecular backbone (e.g. BDTT-S-TR [4], BTID-1F [6], DR3TBDTT [11], BTR [12], *etc.*), and some basic parameters of the D-A molecules, such as electrochemical stability, hole mobility, optical absorption range, energy levels of frontier molecular orbitals etc. are specified mainly by the nature of donor and acceptor units combination. Furthermore, selecting various donor and acceptor units can also dramatically influence intermolecular packing and the BHJ morphology, which has already been shown to be an essential design criterion for improving photovoltaic performance [2,13–15]. Thus, there is an urgent need for investigating the effect of D-A combinations in various types of small molecules, which can not only provide a more detailed insight into their correlation between the blend microstructure and physical and photovoltaic performance as a function of either donor or acceptor units, but also introduce subtle design strategies.

Nowadays, the most attractive linear oligomers for BHJ OSCs are based on benzo[1,2-*b*:4,5-*b′*]dithiophene (BDT) as the central donor unit and 3-alkylrhodanine (alkyl-Rh) groups as acceptor unit due to their excellent physical and chemical properties [2,4,16]. In addition, we have systematically investigated various properties of the star-shaped molecules depending on the various donor (triphenylamine (TPA) or *tris*(2-methoxyphenylmine) (*m*-TPA)) and acceptor (dicyanovinyl (DCV) or alkyl-Rh) combinations [17]. Our works have demonstrated that usage of alkyl-Rh unit instead of DCV groups in star-shaped molecules leads to wider optical/electrochemical bandgaps but higher solubility and better photovoltaic performance. However, the main drawback for the star-shaped molecules is their poor optical absorption spectra [17–19]. In addition, we also reported on the linear dithieno[3,2-*b*:2′,3′-*d*]silole (DTS)-based oligomer with DCV groups, which demonstrated more red-shifted absorption spectra and higher photovoltaic properties in solution processed OSCs as compared to the star-shaped molecules [20,21]. Moreover, Bäuerle and coworkers reported on the series of D-A oligomers of the similar linear architecture based on donor dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP) and acceptor DCV blocks, which demonstrated an impressive optical absorption in the long-wave region and photovoltaic performance [22]. Thus, systematic analysis of the influence of various structural components of the molecules with A-π-D-π-A motif on fine-tuning of their properties is important and necessary to achieve highly efficient OSCs.

In this paper, three novel linear oligomers, namely DTS-Rh, DTP-DCV and DTP-Rh, with methyldicyanovinyl (DCV-Me) or N-ethylrhodanine (Rh) as the acceptor groups and either DTS or DTP as the donor core were designed and synthesized (Fig. 1). Comprehensive study of thermal, structural, optical and electrochemical properties, blend morphology and charge transport, as well as photovoltaic performance of these oligomers in comparison to each other and previously published DTS-DCV [20,21], allows us to evaluate drawbacks and benefits for each of the D-A combination.

2. Results and discussion

2.1. Synthesis

The general synthetic strategy developed recently for these linear molecules [20] was extended successfully for the oligomers in this work (Fig. 1). It includes several consecutive reaction stages as outlined in Fig. 2. First, the organoboron bithiophene precursors (1a-b) with 5,5-dimethyl-1,3-dioxane protective groups and bromine-containing derivatives of DTS or DTP (2c or 2d) were prepared [20,21]. Second, the obtained precursors with bromine and organoboron functions were subject to further Suzuki cross-coupling, which gave a series of oligomers (3) with protected carbonyl function. Removing the protective groups was successfully achieved by treatment of the corresponding solution of either acetal or ketal in THF with 1M HCl to give a poorly soluble aldehyde (4bd) and batch of ketones (4). Finally, Knoevenagel condensation between the oligomers with carbonyl functions and malononitrile in pyridine and under microwave heating gave the target compounds in isolated yields of 83–88%.

^{1}H and ^{13}C NMR spectroscopy, mass-spectroscopy and elemental analysis were used to characterize the chemical structure and purity of these molecules (see Supporting). The solubility of the oligomers was measured in chloroform at room temperature (see Table 1). Comparison of the solubility values of these four oligomers showed that the usage of Rh acceptor unit significantly increases solubility (14/17 gL^{-1} for DTS-Rh and DTP-Rh vs. 5/8 gL^{-1} for DTS-DCV and DTP-DCV, respectively) due to presence of the solubilizing ethyl groups. In addition, it should be noted that DTP-based oligomers were found to be a bit more soluble as compared to the analogs having DTS as donor unit (8/17 gL^{-1} for DTP-DCV and DTP-Rh vs. 5/14 gL^{-1} for DTS-DCV/DTS-Rh, respectively).

2.2. Thermal properties of the oligomers

Thermal properties of these four oligomers were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are shown in Fig. 3 and summarized in Table 1. All oligomers exhibit single, sharp and strong endothermic peaks at the first heating (Fig. 3a), as well as relatively high values of melting temperature (T_m) and melting enthalpy (ΔH_m), which indicates their crystalline nature [23]. One can see, that among this series of oligomers, DTS-DCV has the smallest melting entropy (ΔS_m) underlining its highly ordered crystalline phase, which is in a good agreement with the lowest solubility value of DTS-DCV. Replacement of DCV acceptor groups by Rh ones leads to an increase of ΔS_m especially for DTS-DCV/DTS-Rh pair. Effect of the donor core on phase behavior is not so unambiguous, since in the case of DTS-DCV/DTP-DCV pair it leads to the increase in ΔS_m value for the DTP-based oligomer, whereas for DTS-Rh/DTP-Rh it leads to an inverse effect.

The oligomers possess very high thermal as well as thermo-oxidative stability (Fig. 3b and c). The decomposition temperature (T_d), corresponding to 5% weight losses, was found to be above 350° C in air and above 390 °C under an inert atmosphere (see Table 1). Oligomers with the Rh acceptor groups have slightly lower T_d in air as compared to those of DCV-based molecules. This fact can be explained by presence of the aliphatic group in Rh unit, which probably decomposes first at high temperatures in the presence of oxygen.

2.3. Optical and electrochemical properties

Optical absorption spectra of the oligomers in chloroform solution and thin films are shown in Fig. 4, and the relative optical data are summarized in Table 2. In chloroform solution, the shape of the absorption spectra of the oligomers are quite similar and exhibit two bands, whereas the band at high-energy region is usually ascribed to a π-π* transition of the conjugated backbone and the intensive band in low-energy region is ascribed to the intramolecular charge transfer (ICT) transition. Note that, in solution, the DTP-based oligomers have 25–30 nm more red-shifted maximums of the absorption spectra (λ_{abs}) as compared to the DTS-based oligomers, which can be attributed to a stronger electron-donating character of the DTP unit as compared to the DTS one leading to a reduced optical bandgap. However, effect of the electron-withdrawing group on the absorption spectrum in solution is not so pronounced and λ_{abs} at long-wave region is almost the same for the Rh- and DCV-containing analogs. Comparison of the molar extinction coefficients (K_{ext}) among this series of the molecules allows