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Mendeleev Commun., 2019, **29**, 567–569

Mendeleev Communications

Donor–acceptor (*E*)-2-[2-(2,2′-bithiophen-5-yl)vinyl]benzo[*d*]thiazole: synthesis, optical, electrochemical studies and charge transport characteristics

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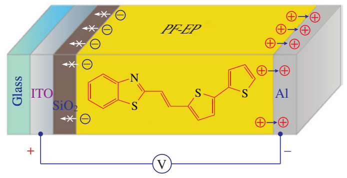
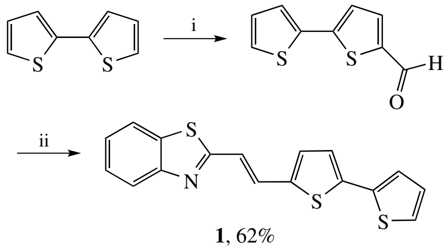
DOI: 10.1016/j.mencom.2019.09.030

Condensation of 2-methylbenzothiazole with 2,2′-bithiophene-5-carbaldehyde affords the title compound, a new chromophore. This compound was used for the doping of poly[9,9-bis(6-diethoxylphosphorylhexyl)fluorene], and the obtained composites demonstrated high electron mobility (1.50×10^{-4} cm^2 V^{-1} s^{-1}) in contrast to dopant-free matrixes.



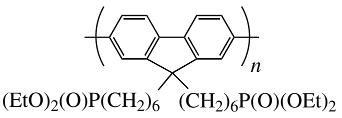
Small molecular chromophores have attracted much attention as active components in organic photonic devices due to their reproducible preparation, easy functionalization, facile purification and high monodispersity.[1–6] Donor–acceptor (D–A) typed π-conjugated organic compounds are widely explored as active materials for organic solar cells[7–10] with the aim to reduce the band gap for broadening the range of absorption.[1,2,11] Moreover, they were shown to have a great potential to get high power conversion efficiency (PCE) and demonstrated good ease of device fabrication.[12] Another important field of application is the use of molecular organic semiconductors (MOSs) as active charge transporting layers in various devices of flexible electronics.[13–15] The relationship between the structure and properties of p-type, n-type and ambipolar semiconductors is still intensively studied. The latter have been developed to a much lesser extent although they are key components for realizing complementary metal-oxide semiconductor (CMOS) digital integrated circuits[16–19] and organic light-emitting transistor (OLET) devices.[20–22]

We synthesized and studied bithiophene derivative **1** containing vinylbenzo[*d*]thiazole moiety (Scheme 1) for the doping of poly[9,9-bis(6-diethoxylphosphorylhexyl)fluorene] (PF-EP). Compound **1** contains a π-electron donor thiophene moieties connected through a double bond as a linker with a π-electron heterocyclic acceptor. The synthesis of compound **1** involved the Vilsmeier–Haack formylation of 2,2′-bithiophene.[23] Obtained 2,2′-bithiophene-5-carbaldehyde was subjected to condensation with 2-methylbenzothiazole in the presence of KOH (see Online Supplementary Materials).



1, 62%

Scheme 1 *Reagents and conditions*: i, Me_2NCHO, $POCl_3$, CH_2Cl_2; ii, 2-methylbenzothiazole, KOH, DMSO.



PF-EP

The absorption and emission maxima of compound **1** in different solvents are outlined in Table 1 and Figure 1. The positions of absorption and fluorescence bands are not dependent on the solvent nature, whereas the quantum yield and life time of excited state increase remarkably in DMSO as compared with acetonitrile and ethyl acetate. The effect could be connected with the higher viscosity of DMSO. The low value of the fluorescence quantum yield is known for styrylthiophene derivatives and is due to the occurrence of competitive fast ISC (intersystem crossing) process or non-radiative relaxation.[24] It is noteworthy that large Stokes shift (>120 nm) was observed for compound **1**. The redox potentials of compound **1** are summarized in Table 1. The cyclic voltammogram in MeCN is shown in Figure S6 (see Online Supplementary Materials).[†]

In contrast to fluorescence, irradiation of compound **1** with light at λ = 436 nm brings about *E*,*Z*-photoisomerization with

Table 1 Optical and electrochemical characteristics of dye **1**.[a]

Solvent	λ^{abs}/nm	λ^{fl}/nm	Φ_{fl}	$\Phi_{E\text{–}Z}/\Phi_{Z\text{–}E}$	*t*/ps	$t_{radiative}$/ns	*E*/eV HOMO	*E*/eV LUMO
EtOAc	474	596	0.005		55	11		
MeCN	472	597	0.0045	0.55/0.13	30	6.7	–5.87	–3.23
DMSO	474	605	0.014		105	7.5		

[a] λ^{abs} – maximum absorption position, λ^{fl} – maximum fluorescence position, Φ_{fl} – quantum yield of fluorescence, $\Phi_{E\text{–}Z}/\Phi_{Z\text{–}E}$ – quantum yields of forward and backward *E–Z*-photoisomerization, *t* – excited state lifetime, $t_{radiative}$ – radiative excited state lifetime, *E* HOMO – energy level of the highest occupied electronic level, *E* LUMO – energy level of the lowest unoccupied electronic level.

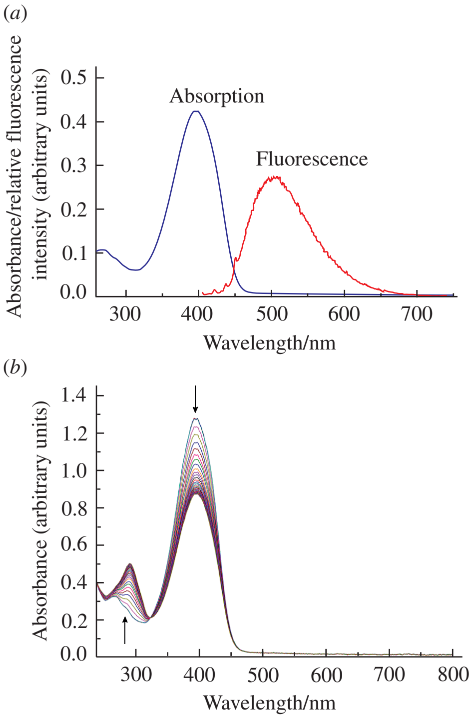


Figure 1 (*a*) Absorption and fluorescence spectra of dye **1**, λ_{ex} = 400 nm; (*b*) change of absorption spectra upon irradiation with light 436 nm, $C_1 = 3\times10^{-5}$ mol dm^{-3}, MeCN, *T* = 294 K.

sufficiently high quantum yield (0.55), while the back *Z,E*-isomerization is less effective (see Table 1).

For clarifying the charge transport mechanism, polymer and dye composite films were prepared from the solutions. In this study, PF-EP served as a wide band-gap host polymer with HOMO and LUMO levels of 5.7 and 2.2 eV, respectively.[26] A thin (100–130 nm) PF-EP/**1** (5 wt%) composite layer was deposited onto the SiO_2(70 nm)/ITO/glass substrate by spin coating of the 5 mg ml^{-1} solution in the ethanol/acetonitrile (95 : 5 v/v) mixture at the rate of 1000 rpm and dried at 60 °C for 3 h. Then an 80 nm thick Al top electrode was deposited onto the composite layer by thermal evaporation under 10^{-6} mbar vacuum at the rate of 1 E s^{-1} (Figure 2). Charge carriers mobility in films of neat PF-EP and dye **1** composite was measured using the MIS-CELIV technique.[27,28] The dye composite possesses ambipolar charge transport ability due to the presence of both electron donor and acceptor groups in the molecules (Table 2). HOMO and LUMO levels are responsible for the hopping transport of hole and electrons, respectively. Molecules of **1** can participate in the charge transport since the mean distance between them in the polymer matrix is about 2 nm, provided they are distributed uniformly.[‡]

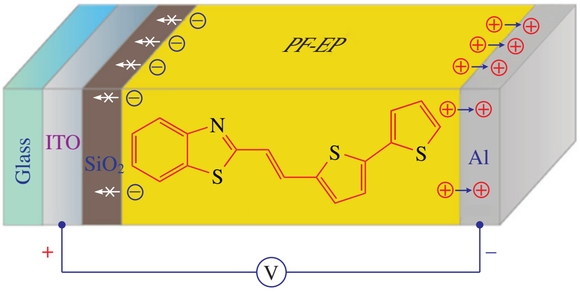


Figure 2 Schematic diagram of MIS-CELIV measurement device.

Table 2 LUMO–HOMO levels (eV) and charge carrier mobility (cm^2 V^{-1} s^{-1}) in polymer matrix doped with 5 wt% of compound **1**.

Material	LUMO	Electron mobility	HOMO	Hole mobility
PF-EP	–2.2	2.50×10^{-5}	–5.7	1.94×10^{-4}
PF-EP + **1**	–3.23	1.50×10^{-4}	–5.87	3.27×10^{-5}

The electron mobility value in the PF-EP/**1** composite turned out to be six times larger than that in the neat PF-EP. This is a considerable evidence for the electron transport over the dye molecules. As the LUMO level of the dye is located 1 eV lower than that of the polymer, electron trapping by the polymer is impossible. Moreover, owing to this an additional manifold of the electron transporting sites within bandgap of the polymer forms.

On the contrary, the hole mobility value in the composite is found to be less than that in the neat PF-EP. In this case, we suggest that the HOMO levels of the polymer positioned only 0.17 eV higher than that of dyes serve as traps for the holes hopping over dye molecules. In turn, the dye molecules can serve as steric hindrance for the holes hopping over the polymer HOMO levels.

To conclude, novel D–π-A chromophore **1** in solution demonstrates the effective photoisomerization to *Z*-isomer, low quantum yield of fluorescence and quite large Stokes shift. The combination of benzothiazole residue with thiophene fragments provides the chemical compound that exhibits efficient ambipolar charge transport ability in composition with PF-EP polymer. The photoisomerization of compound **1** in polymeric matrix has not been observed. The fact indicates that the irradiation does not affect charge transport, which was found early for some photochromes.[29] The future synthesis and analysis of benzothiazole–thiophene structures may be promising in the search for new compounds with better optoelectronic characteristics.

[†] UV-VIS spectra were measured using a two-channel spectrophotometer Varian-Cary 300 and an Avantes AvaSpec-2048 spectrophotometer. To determine the quantum yields of the forward and backward reactions of $E \rightleftarrows Z$-photoisomerization of **1**, we preliminarily calculated the absorption spectra of the corresponding *Z*-isomer and the ratios of quantum yields for the forward and backward reactions of $E \rightleftarrows Z$-photoisomerization using the Fisher method[25] from the absorption spectra of the *E*-isomer and the spectra of two photostationary states obtained by photoirradiation at two different wavelengths. Fluorescence spectra were measured at 20 ± 1 °C with a FluroLog-3-221 spectrofluorometer (Horiba Scientific). Anthracene (φ_{fl} = 0.27) in ethanol was used as a reference for the fluorescence quantum yield measurements.

[‡] See detail description in Online Supplementary Materials.

This work was supported by the Russian Science Foundation (grant no. 18-73-00047). The use of equipment from Center of collective facilities of A. N. Nesmeyanov Institute of Organoelement Compounds is gratefully acknowledged.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.030.

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Received: 10th April 2019; Com. 19/5878