Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 567–569

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

Sergey D. Tokarev, Yulia A. Sotnikova, Alexander V. Anisimov, Yurii V. Fedorov, Gediminas Jonusauskas, Dmitriy A. Lypenko, Vladimir V. Malov, Alexey R. Tameev, Eugene I. Mal'tsev and Olga A. Fedorova

Table of contents

Experimental Section

All reagents and solvents were purchased from Acros, Aldrich, Merck and used without additional purification. Solvents were purified by standard procedures. Spectroscopic grade MeCN, was used for spectroscopic and fluorimetric measurements.

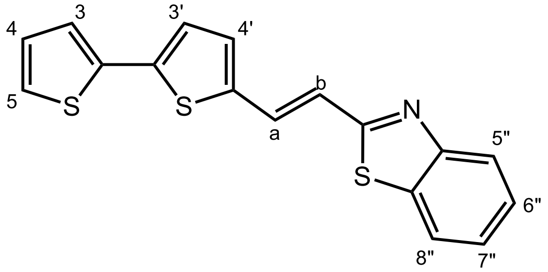
^{1}H and ^{13}C (APT method) NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. The chemical shifts and spin-spin coupling constants were determined with accuracy of 0.01 ppm and 0.1 Hz, respectively.

The electron impact mass spectra of were recorded on a Finnigan Polaris Q instrument. The energy of ionizing electrons was 70 eV. 1 mass. % solutions of compounds in CH_2Cl_2 or $CHCl_3$ (0.2 μl) were loaded into quartz micro-ampoules, which were inserted into the heated tip of the direct input rod. Thermomass spectrograms were filmed in the process of stepped (after 50 ºC) heating of ampoules from 50 to 150 ºC. Before heating the samples in the same temperature range, the thermomass spectrogram of the empty ampoule was usually taken to confirm an absence of any impurities in the ampoule and rod.

Elemental analysis was performed at the A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences.

Fluorescence spectra were measured at 20±1 °C with a FluroLog-3-221 spectrofluorometer (Horiba Scientific). UV-vis spectra were measured using a two channel spectrophotometer Varian-Cary 300 and an Avantes AvaSpec-2048 spectrophotometer.

Synthesis of (*E*)-2-[2-(2,2'-bithiophen-5-yl)vinyl]benzo[*d*]thiazole (1)



A solution of 2,2'-bithiophene-5-carbaldehyde [S1] (1.55 mmol, 300 mg) and 2-methylbenzo[*d*]thiazole (1.55 mmol, 196 µl) in DMSO (7 ml) was stirred for 10 minutes, then KOH 50% water solution (18.75 ml) was added, and the mixture was left without stirring for 2 days in the dark. After completion the reaction, the precipitate was filtered off, washed with water and methanol and dried on a filter. The orange powder on a filter was a pure product (0.91 mmol, 297 mg, yield 62%).

^{1}H NMR (CDCl$_3$; δ; ppm, J/Hz): 7.04 (dd, 1H, ^{3}J=3.8, ^{3}J=4.9) H(4); 7.12-7.18 (m, 3H) H(a,b), H(3,3',4'); 7.25 (d, 1H, ^{3}J=3.4) H(3,3',4'); 7.27 (d, 1H, ^{3}J=4.9) H(5); 7.37 (dd, 1H, ^{3}J=7.8, ^{3}J=7.6), 7.48 (dd, 1H, ^{3}J=7.6, ^{3}J=7.8) H(6",7"); 7.61-7.65 (d, 1h, ^{3}J=15.9) H(a,b); 7.85 (d, 1H, ^{3}J=7.8), 8.00 (d, 1H, ^{3}J=7.8) H(5",8")

^{13}C NMR (CDCl$_3$; δ; ppm): 120.62; 121.47; 122.76; 124.39; 124.53; 125.26; 125.33; 126.40; 128.04; 130.06; 130.44 (CH); 119.28; 134.20; 136.85; 139.34; 141.96 ;166.35 (C).

Calculated for $C_{17}H_{11}NS_3$ (%): C, 62.73; H, 3.41; N, 4.30; found (%): C, 62.51 H, 3.67; N, 4.09.

MS, m/z (%): calcd. 325.5; found 324.592 [M-H$^-$]$^+$ (100).

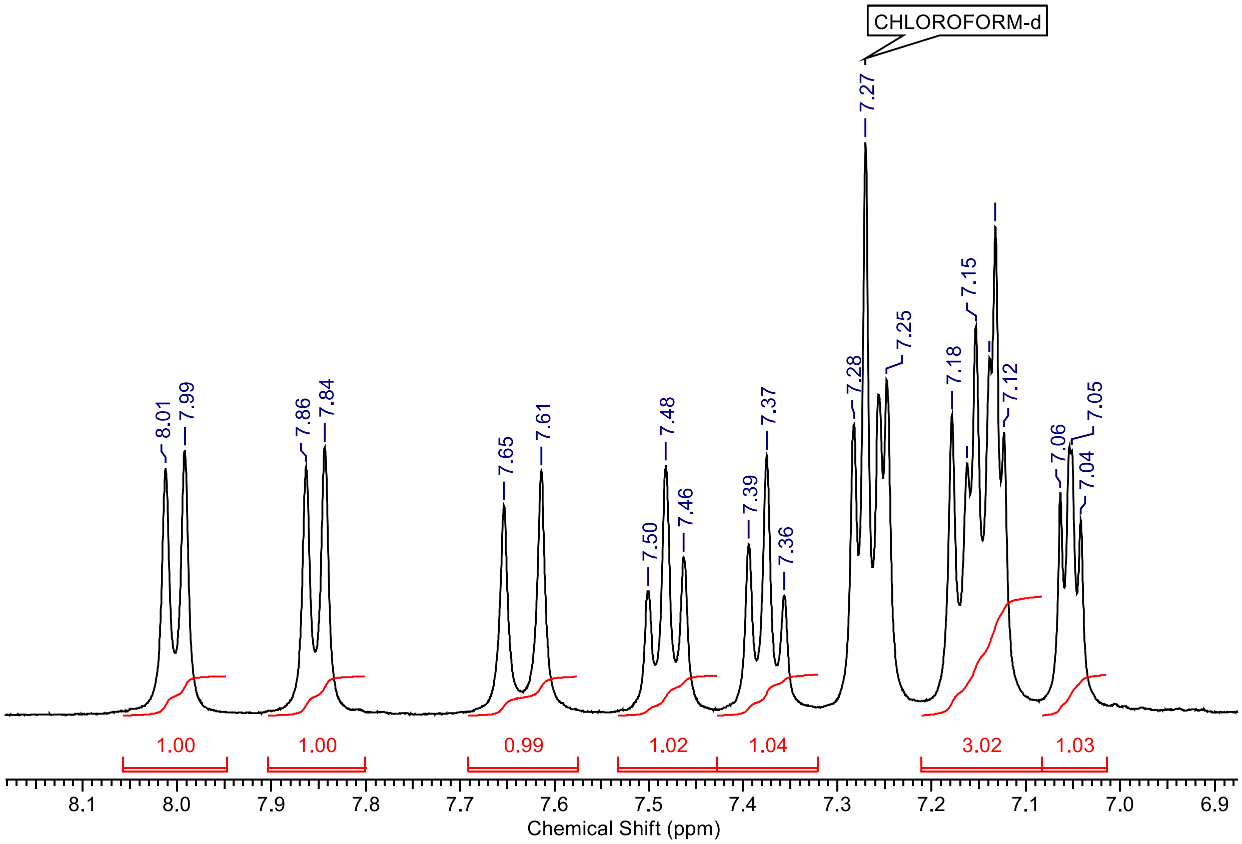


Figure S1. ^{1}H NMR-spectra of dye **1** in CDCl$_3$, Bruker 400 MHz.

Photophysical properties

Absorption and emission spectra

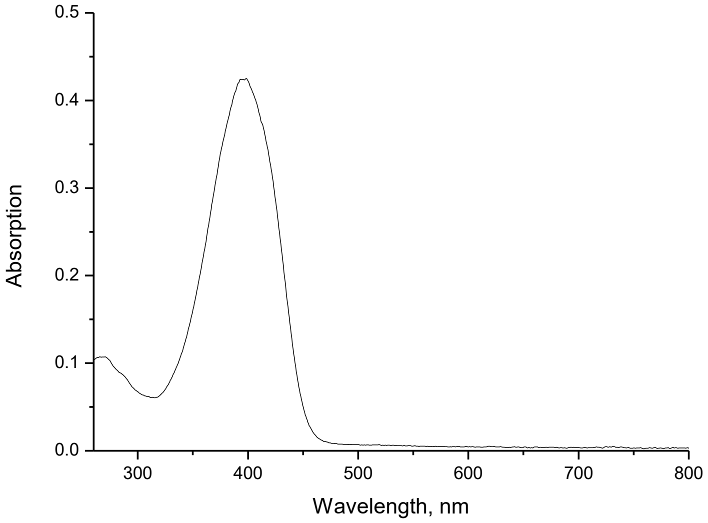


Figure S2. Electronic absorption spectrum of **1** in acetonitrile, C=10^{-5} M.

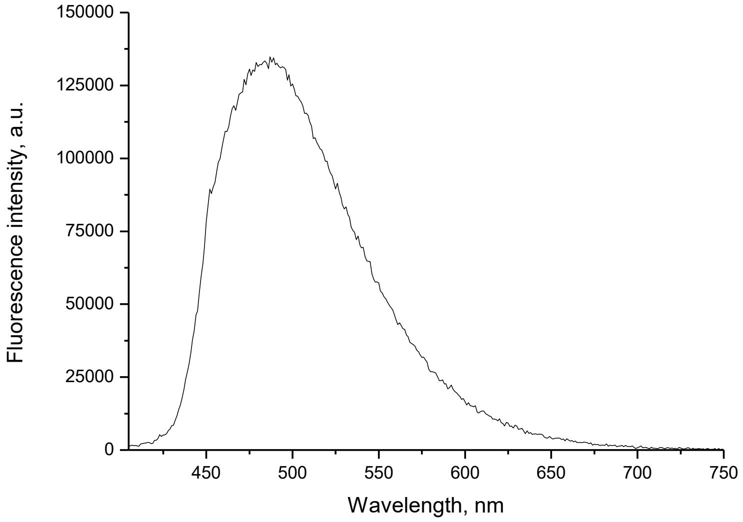


Figure S3. Normalized fluorescence emission spectrum of **1** in acetonitrile, λ_{ex} = 400 nm.

Fluorescence quantum yield All measured fluorescence spectra were corrected for nonuniformity of detector spectral sensitivity. Anthracene (φ_{fl} = 0.27) in ethanol was used as a reference for the fluorescence quantum yield measurements. The fluorescence quantum yields were calculated using equation:

$$\varphi_i = \varphi_0 \frac{(1 - 10^{-A_0}) * S_i * n_i^2}{(1 - 10^{-A_i}) * S_0 * n_0^2},$$

where φ_i and φ_0 are the fluorescence quantum yields of the studied solution and the standard compound, respectively; A_i and A_0 are the absorptions of the studied solution and the standard, respectively; S_i and S_0 are the areas underneath the curves of the fluorescence spectra of the studied solution and the standard, respectively; and n_i and n_0 are the refractive indices of the solvents for the substance under study and the standard compound (n_i = 1.3404, acetonitrile; n_0 = 1.361, ethanol).

Quantum yields of *trans-cis*-isomerization 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 [S2] from the absorption spectra of the *E*-isomer and the spectra of two photostationary states obtained by photoirradiation at two different wavelengths.

To obtain the photostationary states of **1**, we used photoirradiation at λ = 365 and 436 nm. Assuming that the ratio of quantum yields of the backward and forward reactions of $E \rightleftarrows Z$-photoisomerization ($\varphi_{Z\rightarrow E}/\varphi_{E\rightarrow Z}$) is independent of the irradiation wavelength, we calculated the fraction of the *Z*-isomer in the photostationary state, the absorption spectrum of the corresponding *Z*-isomer, and the ratio of quantum yields of the forward and backward reactions of photoisomerization.

The quantum yields of the forward and backward reactions of $E \rightleftarrows Z$-photoisomerization were calculated as follows [S3].

For the reversible photochemical reaction

$$\mathrm{A} \overset{h\nu}{\rightleftharpoons} \mathrm{B}$$

the equations for the rate of formation of substances A and B are written in the form

$$\frac{d[A]}{dt} = -\varphi_{A\rightarrow B} \cdot I_{abs}^{A} + \varphi_{B\rightarrow A} \cdot I_{abs}^{B},$$

$$\frac{d[B]}{dt} = +\varphi_{A\rightarrow B} \cdot I_{abs}^{A} - \varphi_{B\rightarrow A} \cdot I_{abs}^{B},$$

where I_{abs}^{A} and I_{abs}^{B} are the amounts of radiation quanta absorbed by substances A and B within time *dt*; $\varphi_{A\rightarrow B}$ and $\varphi_{B\rightarrow A}$ are the quantum yields of the forward and backward reactions, respectively; *d[A]* and *d[B]* are the changes in the number of molecules of the corresponding substances A and B within time *dt*.

The amount of quanta absorbed by substances A and B is determined as follows:

$$I_{abs}^{A} = I_{abs}^{\Sigma} \cdot \left(\frac{D_A}{D_\Sigma}\right),$$

$$I_{abs}^{B} = I_{abs}^{\Sigma} \cdot \left(\frac{D_B}{D_\Sigma}\right),$$

in this case

$$I_{abs}^{\Sigma} = I_0(1 - 10^{-D_\Sigma}),$$

where D_Σ is the total absorption of all components, D_A and D_B are the absorption by the corresponding substance, I_{abs}^{Σ} is the total amount of absorbed radiation quanta within time *dt*, and I_0 is the incident radiation intensity.

The quantum yields $\varphi_{A\rightarrow B}$ and $\varphi_{B\rightarrow A}$ were determined by the numerical solution of the corresponding differential equations using the primarily specified value and the ratio of quantum yields of the forward and backward reactions preliminarily measured using the Fisher method. The quantum yield values were optimized by the iteration method using the program Sa3.3 developed by Dominique Lavabre and others (http://pagesperso-orange.fr/cinet.chim/index.html). The absolute light intensity I_0 was measured using the ferrioxalate actinometer [S4]. The measurement accuracy does not exceed 20%.

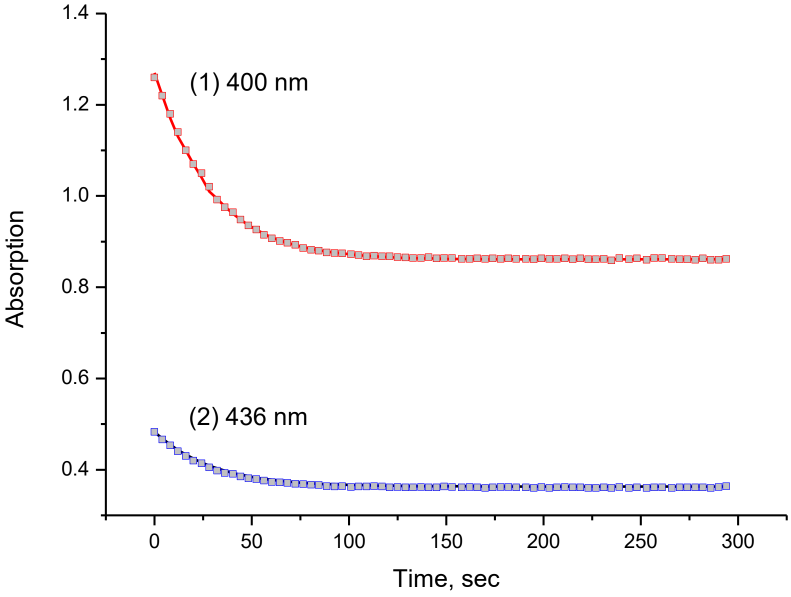


Figure S4. The time dependence of the **1** (C = 3×10^{-5} M, acetonitrile) absorption (squares) at λ=400 nm (1) and λ=436 nm (2) upon irradiation at λ=436 nm and fitted curves for quantum yields $\varphi_{E\rightarrow Z}$ = 0.55; $\varphi_{Z\rightarrow E}$ = 0.13; and light intensity at λ=436 nm I = 2.26×10^{-6} Einstein L^{-1} s^{-1}.

Voltammetry studies

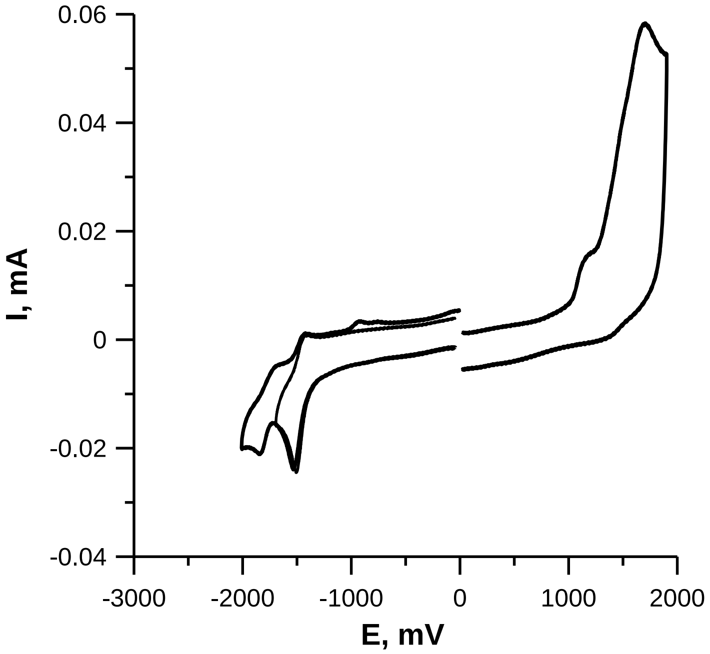


Figure S5. Cyclic voltamogramm of dye **1**.

Charge mobility measurements

In thin layers of the composites, charge carrier mobility (μ) was measured by using the technique of charge extraction by linearly increasing voltage (CELIV) with metal-insulator-semiconductor (MIS) diode structures. A thin layer of the **PF-EP/1** (5 wt.%) composite of the thickness d_s ranged between 100 nm and 130 nm was deposited onto the SiO_2/ITO/glass substrate by spin coating of the 5 mg/ml solution in the ethanol/acetonitrile (95:5 v/v) mixture at rate of 1000 rpm and dried at 60℃ for 3 h. Then a 80 nm thick Al top electrode was deposited onto the composite layer by thermal evaporation of the material under 10^{-6} mbar vacuum at rate of 1 Å s^{-1}. A charge carrier blocking SiO_2 layer of the thickness d_i = 70 nm was preliminary deposited onto ITO-coated glass by magnetron scattering at 10^{-3} mbar.

The CELIV set-up included a digital USB-oscilloscope (DL-Analog Discovery, Digilent Co.), which played roles of master pulse generator and transient current pulse monitor. *RC* constants were at least a factor of 20 smaller than the time scales of interest. The bias was swept in the range between 10 and 100 kHz.

A small charge extraction regime of the MIS-CELIV experiment was used. The condition $\Delta j \leq j(0)$ where Δj is a maximum current of the unipolar charge carriers and $j(0)$ is a capacitance current [S5]. The corresponding small-charge transit time t_{max} for the sheet of carriers to reach the extracting contact defines the mobility as following [S5]:

$$\mu = \frac{2d_s^2}{At_{max}^2}(1+f)$$

where the ratio between the geometric capacitances of the organic semiconductor and the SiO_2 insulator layers $f \equiv (\varepsilon_s\ d_i)/(\varepsilon_i\ d_s)$ is ranged between ~0.34 and ~0.45 for dielectric constant is ε_i =3.9 and ε_s=~2.5 for SiO_2 and PF-EP/dye (5 wt.%) composite, respectively.

References

S1. Y.-S. Kim and Y.-A. Son, *Mol. Cryst Liq. Cryst.*, 2011, **551**,163.

S2. E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704.

S3. N. E. Shepel, O. A. Fedorova, E. N. Gulakova, A. S. Peregudov, V. V. Novikov and Y. V. Fedorov, *Dalton Trans.*, 2014, **43**, 769.

S4. C. A. Parker, *Photoluminescence of Solutions*, Amsterdam, Elsevier, 1968.

S5. O. J. Sandberg, M. Nyman, S. Dahlström, S. Sandén, B. Torngren, J.-H. Smått and R. Österbacka, *Appl. Phys. Lett.*, 2017, **110**, 153504.