SPECTRAL, ELECTROCHEMICAL AND CALCULATED PROPERTIES OF QUADRUPOLAR CHROMOPHORES BASED ON TETRAFLUOROBENZENE

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Absorption/emission and electrochemical properties of four new quadrupolar push-pull-push molecules with central tetrafluorobenzene acceptor and two peripheral N,N-dihexylamino and O-hexyloxy donor groups were investigated. Experimental data were completed with quantum-chemical calculations. The extent of the intramolecular charge-transfer and nonlinear optical properties were elucidated in terms of structure-property relationships. The electronic nature of the appended donor group, length, planarity and composition of the π-linker (combination of 1,4-phenylene, 2,5-thienylene and acetylenic subunits) are the most important factors affecting the linear as well as nonlinear optical properties.

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Introduction

Fluorinated organic molecules are undoubtedly an important class of organic molecules that found large applications across many branches of modern sciences [1-3]. Beside well-known and widely used trifluromethyl group (CF_3), tetrafluorobenzene moiety (C_6F_4) has recently also been recognized as useful acceptor unit and, subsequently, has been utilized in various push-pull molecules featuring optical nonlinearities [4-8]. Hence, in our two previous communications [9-10] we have reported on the synthesis of new quadrupolar D-π-A-π-D molecules based on a central tetrafluorobenzene (TFB) acceptor and two peripheral alkoxy and dialkylamino donors.
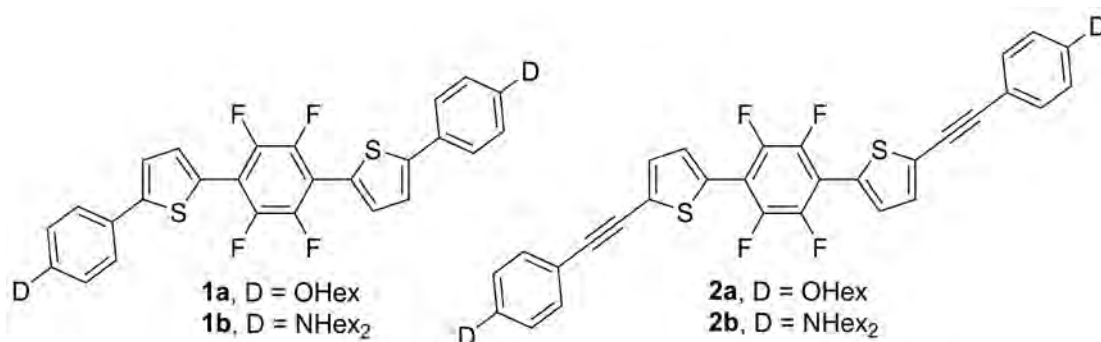

Fig. 1   General structure of investigated compounds **1a-b** and **2a-b**

In this article, we report the investigation of absorption/emission properties, electrochemical behavior and quantum-chemical calculations of compounds **1a-b** and **2a-b** (Fig. 1) Whereas the central TFB unit polarizes the π-system *via* its overall electron withdrawing character, the peripheral hexyloxy and *N,N*-dihexylamino groups behave as electron donors. In such quadrupolar arrangement, intramolecular charge-transfer (ICT) from the peripheral donors to the central acceptor occurs and the molecule becomes polarized. Derivatives **1a-b** and **2a-b** bearing long hexyl chains were chosen in order to enhance their solubility in common organic solvents.

Experimental

General

Compounds **1a-b** and **2a-b** were synthesized according to procedure described in the literature [10]. Electrochemical measurements were carried out in *N,N*-di-methylformamide (DMF) containing 0.1 M Bu_4NPF_6 in a three electrode cell by

cyclic voltammetry (CV) and rotating disk voltammetry (RDV). The working electrode was a platinum disc (2 mm in diameter) for CV and RDV experiments. As the reference and auxiliary electrodes were used saturated calomel electrode (SCE) separated by a bridge filled with a supporting electrolyte and Pt wire, respectively. All potentials are given *vs*. SCE. Voltammetric measurements were performed using a potentiostat PGSTAT 128N (AUTOLAB, Metrohm Autolab B.V., Utrecht, the Netherlands) operated *via* NOVA 1.10 software. The absorption spectra were measured on a UV/Vis Perkin-Elmer Lambda 35 spectrophotometer at room temperature. The steady-state fluorescence spectra were measured on a Perkin-Elmer LS 55 spectrophotometer. The instrument provides corrected excitation spectra directly; the fluorescence spectra were corrected for the characteristics of the emission monochromator and for the photomultiplier response. For fluorescence measurements, very weakly absorbing solutions (optical density ~ 0.05 at the exciting wavelength in 1-cm cell) were used. The fluorescence spectra were recorded by excitation at absorption maxima. The fluorescence quantum yields (q_F) were measured using a quinine sulfate (q_F ¼ 0.54 in 0.5 mol l^{-1} H$_2$SO$_4$) standard [11].

Results and Discussion

Electrochemistry

Electrochemical measurements were carried out in DMF by cyclic voltammetry (CV) and rotating disk voltammetry (RDV). The measured half-wave potentials $E_{1/2}$ are summarized in Table I. The first oxidation was likely localized on the hexyloxy and *N,N*-dihexylamino donor groups and for hexyloxy-substituted chromophores **1a** and **2a** represents irreversible one-electron process. For dihexyalmino-substituted compounds **1b** and **2b**, the first oxidations are reversible processes involving more electrons. The first oxidation potentials range from +0.73 to +1.25 V. On the contrary, the first reduction involves central tetrafluorobenzene acceptor unit as reversible one-electron process. The measured half-wave potentials $E_{1/2(red1)}$ range from −1.76 to −1.48 V. As can be clearly seen, both potentials depend primarily on the donor group attached. A replacement of weak hexyloxy donor with strong *N,N*-dihexylamino group resulted in lowered $E_{1/2(ox1)}$ (e.g., **1a** vs. **1b** — +1.25 vs. +0.73 V). Within the particular series of compounds **1a/b** and **2a/b**, the first reduction potentials are very similar (−1.68/−1.76 and −1.48/−1.53 V), which reflects the presence of the same TFB electron acceptor. However, the observed differences in $E_{1/2(red1)}$ between compounds **1a/2a** and **1b/2b** (0.20 and 0.23 V) must be elucidated as a result of the π-system extension by additional acetylenic unit. This structural change significantly flattened the π-system and allowed more efficient ICT, which

resulted in lowered first reduction potentials and, subsequently, also in lowered electrochemical gaps. Hence, replacement of the hexyloxy with N,N-dihexylamino donor group and planarization of the π-system led to chromophore **2b** with the lowest HOMO-LUMO difference of 2.32 V.

Table I Electrochemical data for chromophores **1a-b** and **2a-b**

Comp.	D	$E_{1/2(ox1)}$ V	$E_{1/2(red1)}$ V	$E_{1/2(ox1)} - E_{1/2(red1)}, \Delta E$ V	E_{HOMO} eV	E_{LUMO} eV
1a	OHex	1.25	−1.68	2.93	−5.08	−2.59
1b	NHex$_2$	0.73	−1.76	2.49	−5.6	−2.67
2a	OHex	1.15	−1.48	2.63	−5.5	−2.87
2b	NHex$_2$	0.79	−1.53	2.32	−5.14	−2.82

Absorption and Emission Spectra

Optical properties of target chromophores were investigated by absorption and emission spectra as shown for representative chromophores **1b** and **2a** in Fig. 2. The absorption/emission maxima, $\lambda^A_{max}/\lambda^A_{max}$, molar absorption coefficient, ε, Stokes shift, and fluorescence quantum yields, q_F, are presented in Table II. The absorption spectra are dominated by intensive CT-bands appearing between 383 and 434 nm. The position of these longest-wavelength absorption bands is mainly affected by the appended donor group. Whereas hexyloxy-substituted compounds **1a/2a** possess CT-bands appearing at $\lambda^A_{max} = 383/389$ nm, N,N-dihexylamino analogues **1b/2b** showed significantly red-shifted bands at 434/424 nm ($\Delta\lambda^A_{max} = 51/35$ nm). In contrast to electrochemical measurements, the π-system planarization by adding acetylenic spacer between the 1,4-phenylene and 2,5-thienylene units (**1a** vs **2a** or **1b** vs **2b**) has diminished effect on the absorption spectra. The positions of the longest-wavelength emission maxima λ^E_{max} range from 443 to 539 nm and showed similar trends seen for the absorption peaks. Namely, the λ^E_{max} position is mainly influenced by the strength of the appended donor and less by the π-system. N,N-Dihexylamino-substituted derivatives **1b/2b** showed generally larger Stokes shift than hexyloxy-substituted analogues **1a/2a** (98/115 vs. 60/59 nm). The calculated fluorescent quantum yields range from 0.14 to 0.64. In comparison with hexyloxy derivatives **1a** and **2a**, the fluorescence spectra of N,N-dihexylamino derivatives are significantly bathochromicaly shifted; consequently the diminished q_F of **1b** and **2b** may be explained by increasing efficiency of non-radiative internal conversion (S1-S0).
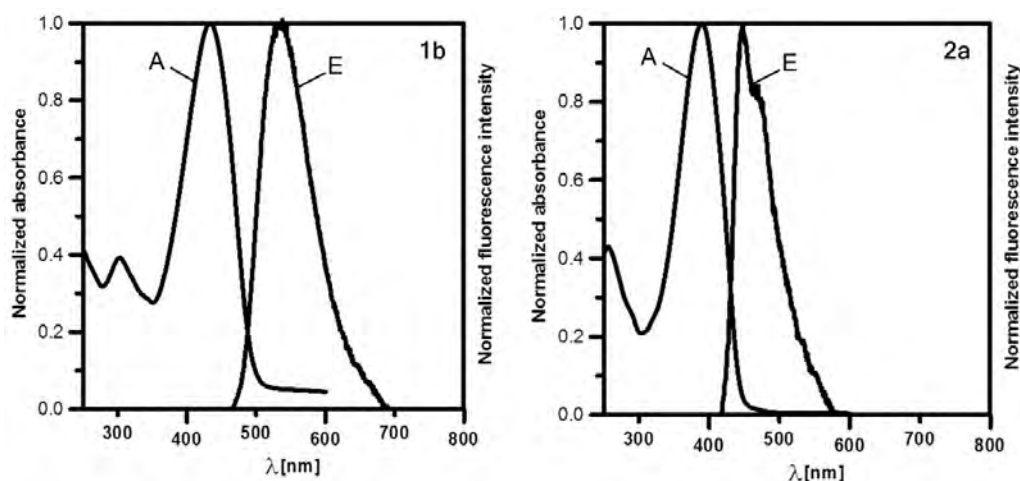
Fig. 2 Representative normalized absorption (A) and emission (E) spectra of compounds **1b** and **2a** measured in CH_2Cl_2

Table II Optical properties of target chromophores **1a-b** and **2a-b**

Comp.	D	λ^{A}_{max}, nm (eV)/ ε, 10^3 mol^{-1} dm^3 cm^{-1}	λ^{E}_{max} nm (eV)	Stokes shift nm	q_F
1a	OHex	383 (3.24)/65.6	443 (2.80)	60	0.64
1b	NHex$_2$	434 (2.86)/73.8	532 (2.33)	98	0.3
2a	OHex	389 (3.19)/81.7	448 (2.77)	59	0.55
2b	NHex$_2$	424 (2.92)/76.2	539 (2.30)	115	0.14

Calculations

The geometry optimizations and energies of the HOMO and the LUMO were calculated using Gaussian 09W [12] package at the DFT level with B3LYP/6-31G(d) basis set. Ground-state dipole moment μ and the first and second hyperpolarizabilities β and γ were calculated for the optimized geometries using program MOPAC2012 [13] (Table III). Although the absolute values of calculated energies HOMO and LUMO differ from those obtained by electrochemistry, they showed tight linear correlation (R^2 = 0.8952, Fig. 3) and, therefore, the used computational method can be considered as a reliable tool describing electronic parameters of compounds **1-2**. The HOMO and LUMO levels in **1b** and **2a** were further visualized in program OPChem [14] as shown in Fig. 4. These pictures clearly illustrate charge separation in both types of structures. Whereas the HOMO is spread over the peripheral donors and the adjacent π-linker, the LUMO is mostly localized on the central TFB acceptor.

Table III   Calculated electronic parameters of **1a-b** and **2a-b**

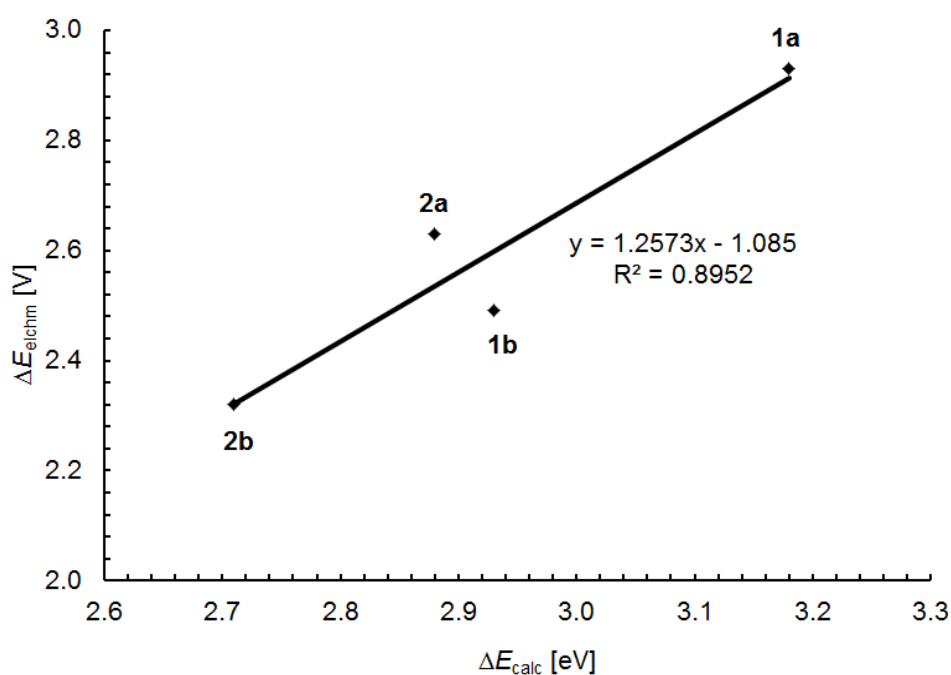| Comp.	D	E_{HOMO} eV	E_{LUMO} eV	ΔE eV	μ D	β 10^{-27} esu	γ 10^{-24} esu
1a	OHex	−5.05	−1.87	3.18	3.10	2.09	2.94
1b	NHex$_2$	−4.57	−1.64	2.93	0.19	0.05	1.00
2a	OHex	−5.01	−2.13	2.88	0.41	0.23	2.08
2b	NHex$_2$	−4.67	−1.96	2.71	1.51	0.94	1.97

Fig. 3   Correlations of the electrochemically measured and calculated HOMO-LUMO gaps
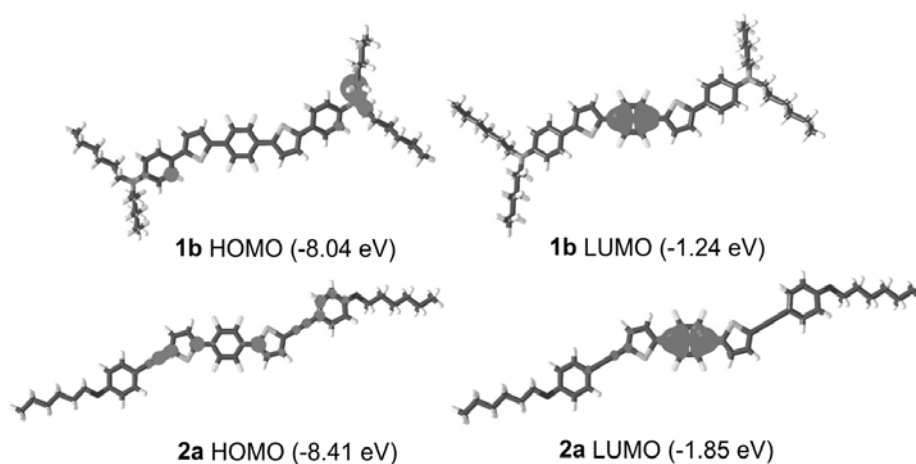

Fig. 4   HOMO and LUMO visualization in molecules **1b** and **2a**

Considering both types of derivatives centrosymmetric, expected ground state dipole moments μ should be zero. The calculated values range between 3.10-0.19 D. The nonzero values can be attributed to the peripheral flexible alkyl chains of the hexyloxy and *N,N*-dihexylamino substituents. The calculated nonzero ground state dipole moments affect primarily the first hyperpolarizability β. Hence, the highest calculated β value of 2.09×10^{-27} esu was calculated for derivative **1a** with the highest dipole moment (3.10 D). Anyway, in centrosymmetric molecules is the first hyperpolarizability β generally vanished. Excluding overestimated value for **1a**, the second hyperpolarizabilities γ mimic partially the trends seen by electrochemistry and absorption/emission spectroscopy. Stronger donors and extension/planarization of the π-system led to increased second-order hyperpolarizability.

Conclusion

Four new quadrupolar D-π-A-π-D chromophores with central tetrafluorobenzene acceptor unit and two peripheral hexyloxy and *N,N*-dihexylamino donor groups were investigated. The π-conjugated system comprises combination of 1,4-phenylene and 2,5-thienylene units (chromophores **1a/b**) as well as an additional triple bond spacer (chromophores **2a/b**). The extent of the ICT was further studied by electrochemistry and absorption/emission spectra and supported by quantum-chemical calculations. As demonstrated, electronic nature of the appended electron donors (OHex vs. $NHex_2$) affects the measured and calculated properties most significantly. In addition, incorporation of an additional acetylenic spacer between 1,4-phenylene and 2,5-thienylene subunits caused planarization of the π-linker and modestly affects the optoelectronic properties. Considering all aforementioned properties, chromophores **2b** and **1b** showed the lowest electrochemical HOMO-LUMO gap, the most bathochromically shifted absorption/emission bands and generally best trade-off between the measured and calculated properties, which make them the chromophores with the most efficient ICT within the studies series of compounds.

Acknowledgement

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References

[1]   Special issue on "Fluorine chemistry" Smart B.E., ed.: Chem. Rev. **96**, 1555 (1996).

[2]   Special issue on "Organo-fluorine chemistry", O'Hagan D., ed.: Beilstein J. Org. Chem. **4**, 11 (2008).

[3]   Special issue on "Organo-fluorine chemistry II", O'Hagan D., ed.: Beilstein J. Org. Chem. **6**, 36 (2010).

[4]   Matsui M.: J. Fluor. Chem. **96**, 65 (1999).

[5]   Romaniello P., Lelj F.: J. Fluor. Chem. **125**, 145 (2004).

[6]   Zhang Y., Wang L., Wada T., Sasabe H., Wen J.: J. Fluor. Chem. **77**, 97 (1996).

[7]   Woo H.Y., Liu B., Kohler B., Korystov D., Mikhailovsky A., Bazan G.C.: J. Am. Chem. Soc. **127**, 14721 (2005).

[8]   Charlot M., Porrès L., Entwistle C.D., Beeby A., Marder T.B., Blanchard-Desce M.: Phys. Chem. Chem. Phys. **7**, 600 (2005).

[9]   Kulhánek J., Bureš F., Pytela O., Pippig F., Danko M., Mikysek T., Padělková Z., Ludwig M. J. Fluor. Chem. **161**, 15 (2014).

[10] Ramaiyan M., Kulhánek J., Bureš F.: Sci. Pap. Univ. Pardubice, Ser. A **20**, 249 (2014).

[11] Birks J.B., Dyson D.J.: Proc. R. Soc. A **275**, 135 (1963).

[12] Gaussian 09, Revision D.01, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G. A., Nakatsuji H., Caricato M., Li, X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A. Jr., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Keith T., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas O., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J.: Gaussian, Inc., Wallingford CT, 2013.

[13] MOPAC2012, Stewart J.J.P., Stewart Computational Chemistry, version 13.286W, webpage: http://OpenMOPAC.net.

[14] Pytela O., OPchem, version 6.2, 2014, http://pytela.upce.cz/OPgm.