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Tunable Photophysical Properties of Thiophene Based Chromophores: Conjoined Experimental and Theoretical Investigation

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*Corresponding authors: <u>anna.popczyk@pwr.edu.pl</u>, <u>abdelkrim.elghayoury@univ-angers.fr</u> ABSTRACT

In this paper we report synthesis and photophysical properties of six novel thiophene derivatives (ThD) with D- π -A structure. The subject of this work are three nitrophenyls (1) BT-Th-NO₂ and three benzonitriles (2) BT-Th-CN, substituted at different positions of aromatic ring ((a) *ortho*-, (b) *meta*- or (c) *para*-). Dyes were obtained using simple three-step synthesis and their chemical structures were confirmed by ¹H and ¹³C NMR, IR as well as high resolution mass spectrometry. The influence of positional isomerism on optical properties has been explored experimentally and theoretically. The photophysical properties were investigated using steady-state as well as time-resolved spectroscopy and the obtained results were supported by quantum-chemical calculations. TD-DFT calculations indicated that charge-transfer strength can be correlated with the observed optical properties. In addition, the influence of the acceptor position on photoluminescence spectra, fluorescence quantum yields and emission lifetimes was specified. We show that ThD optical properties can be tuned in wide spectral range by the change made in only single step of synthesis reaction.

Keywords: Thiophene derivatives, charge transfer, push-pull chromophores, quantum yield, TD-DFT

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1. Introduction

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There is a constant need for developing materials for optoelectronic and photonic applications. Organic molecules stand out among other materials, mostly because of their low-cost synthesis, non-complicated methods of production and easy way of recycling.¹⁻⁷ Chromophores multifunctionality is beneficial trait in wide range of applications spanning from nonlinear optics or light amplification to energy storage and solar cells technology.⁸⁻²⁰ Those desired features are frequently shown by low-molecular *push-pull* chromophores containing an electron-donating (D) and electron-accepting (A) groups covalently bonded with a π -conjugated bridge (D- π -A). Such molecular design supports intramolecular charge transfer (CT) which occurs upon excitation of the molecule with external light source and can be beneficial for certain nonlinear optical properties or solar cells manufacture. In present work we show that broadband tuning of the optical properties is possible by a simple change of the substitution position ((a) ortho-, (**b**) *meta*- or (**c**) *para*-) at the final stage of the ThD synthesis. $^{21-25}$ It is known that photophysical properties strongly depend on the nature of the excited-states. The extension of conjugation influences the separation of excitons that causes fast electron transfer between donor and acceptor.²⁶ Hence, the modification of donor and acceptor moieties, as well as π -conjugated spacer has a critical impact on CT phenomenon.²⁷⁻³⁰ Mentioned type of molecules are classified as diarylethene - where the conversion between two isomers occurs around carbon-carbon double bond and it can be controlled by external factors i.e. temperature or light. Control over the isomers conversion can be used in designing molecules for modern technologies such as all-optical switching or holography.^{31–37}

The influence of electron withdrawing or accepting groups on physicochemical properties of D- π -A molecules has been widely discussed in scientific literature. Many groups have already investigated the origin of the heterocyclic ring's role in photophysical properties by substituting one of the phenyl ring with different types of cyclic structure such as pyrazoline, pyrole, furan and dimethoxybenzene.^{38–45} In this manuscript the main focus is on the impact of structural isomerism and influence of the excitation-induced CT on the optical properties of D- π -A molecular systems. We show that simple one step modification in synthesis can lead to significant change in the optical properties of thiophene derivatives. It should be noted that all examined compounds contain thiophene (benzothiophene to the lesser extent) as an electron-donating group and nitrophenyl or benzonitrile as an acceptor groups that exhibit strong electron-accepting properties ($\sigma_p = 0.66$ and 0.78 for CN and NO₂, respectively).⁴⁶ We emphasize that benzothiophene shows efficient luminescence.⁴⁷ Moreover, the recent

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investigation of cyano and nitro groups' influence on the solvatochromism of emission^{Vie}particle Online these compounds as potential candidates for sensors. ⁴⁸

2. Methods

2.1. Experimental section

In order to confirm the chemical structures of the synthesized products, typical spectroscopic measurements have been carried out. Nuclear magnetic resonance (NMR) spectra were obtained on Bruker 300 MHz spectrometer with chemical shifts expressed in ppm (parts per million), whereas infrared (IR) spectra were measured on Bruker Vertex 70 spectrometer in range of 400–4000 cm⁻¹. High resolution mass spectrometry was recorded on Jeol JMS 700 with isobutane as a matrix, using chemical ionisation (CI) method.

2.2. Photophysical measurements

Absorption spectra were measured at room temperature in quartz cuvettes by Shimadzu UV 1800 Spectrometer for solutions of $c = 2.40 \times 10^{-5}$ M concentration of the dye in chloroform (CHCl₃) solution. Emission spectra were measured for the same solutions using Shimadzu RF-6000 Spectrofluorometer. For the fluorescence quantum yield (QY) a relative method was used, with solution of fluorescein in ethanol as a reference. By comparing the area under measured fluorescence spectra of investigated compounds and reference, estimation of QY comes straightforward from equation (1),

$$\Phi_s = \Phi_{ref} * \frac{I_s A_{ref}}{I_{ref} A_s} * \frac{n_s^2}{n_{ref}^2}$$
(1)

where Φ_{ref} is fluorescence quantum yield of fluorescein solution, I_s and I_{ref} are the integrated areas under the emission spectrum for sample and reference respectively, A_s and A_{ref} are the fraction of exciting light which is absorbed at the excitation wavelength in case of sample and reference and n denotes refractive index of used solvent.

Fluorescence lifetimes were measured using a home-built setup based on PicoQuant HydraHarp 400 Multichannel Picosecond Event Timer and two lasers: a picosecond diode laser PicoQuant LDH-P-C-405B working at 405 nm with repetition frequency set to 5 MHz or a tunable Ti:Sapphire femtosecond oscillator SpectraPhysics MaiTai with repetition frequency 80 MHz. In the latter case the laser was tuned to 810 nm and its output was frequency-doubled in a BBO (*beta*-barium borate) crystal to provide excitation at 405 nm. Excitation power at the sample position was in the range of 0.5 to 25 μ W. The sample solution was placed in a 10x10 mm

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quartz cuvette. Experiments were carried out in the L-geometry, with the fluorescence Mighted Online collected at the right angle to the direction of the excitation beam. The collected light passed through a long-pass cut-off filter in order to remove scattered excitation light and through a polarizer with its transmission axis oriented at the magic angle (54.7°) with respect to the polarization of the excitation beam in order to eliminate the influence of rotational diffusion. The fluorescence light was focused on the entrance slit of a Czerny-Turner monochromator (Acton Research SpectraPro 150) used to select a given wavelength from the fluorescence spectrum. After the monochromator the light was detected with a Hamamatsu R3809U-50 photomultiplier sensitive in the 160-850 nm range. The output signal from the photomultiplier was amplified with an Ortec Model 9327 amplifier prior to routing to the HydraHarp module. The overall instrumental response function, measured by scattering the excitation light in a suspension of titanium dioxide, was narrower than 80 ps full width at half of maximum (FWHM). The data were analyzed using the DecayFit 1.4 free software [DecayFit -Fluorescence Decay Analysis Software 1.4, FluorTools, www.fluortools.com]. Fluorescence lifetimes were estimated through fitting the decay curves with multiexponential decay functions:

$$I(t) = \sum_{i} I_{i} e^{-t/\tau_{i}}$$
⁽²⁾

where *t* is time, I_i are amplitudes of the decay components, and τ are the decay times of the respective components. The fluorescence quantum yield and the fluorescence lifetimes (the dominant components) were used to calculate the radiative (k_r) and non-radiative (k_{nr}) rate constants, with the following system of equations:

$$\tau = \frac{1}{k_r + k_{nr}} \tag{3}$$

$$\Phi_{fl} = \frac{k_r}{k_r + k_{nr}} \tag{4}$$

2.3. Computational details

Within present work we took advantage on Kohn-Sham formulation of Density Functional Theory (DFT) in order to get insight into electronic structure of examined compounds. All DFT and TD-DFT calculations were preformed using so-called *ultrafine* pruned grid. In order to include solvent effects (chloroform) into computations we used different variants of Polarizable Continuum Model (PCM).^{49,50} The linear-response (LR-PCM) variant was used for optimization and respective frequency calculations, whereas transition energies were

determined using corrected linear-response (cLR-PCM) scheme.⁵¹ The ground-state (GS), determined geometries were optimized using improved thresholds such as, optimization threshold tightened to 10⁻⁵ au and self-consistent field set to 10⁻¹⁰ au. Vibrational frequency calculations confirmed that obtained GS geometries correspond to minima on respective potential energy surfaces. Examined compounds were expected to exhibit intramolecular charge transfer, thus we choose computational protocol proven to be efficient for difluoroborates derivatives displaying CT.^{27,52} In particular, the optimization and subsequent frequency calculations were carried out with M06-2X/6-31G(d) theory level whereas computations of transition energies were performed with larger 6-311+G(2d,p) atomic basis set. Finally the charge-transfer parameters (distance d_{CT}, charge q and dipole moment difference in Franck-Condon region μ_{CT}) were determined using Le Bahers approach.^{53,54} Presented density difference plots have been simulated at LR-PCM-TD- M06-2X/6-311+G(2d,p) using 0.002 au as a contour value. In these plots red (blue) orbs indicates increase (decrease) of electron density upon electronic transitions. All described calculations were performed using Gaussian16 Rev. A.03. ⁵⁵

3. Synthesis

Commercially available reagents purchased from Sigma Aldrich were used without additional purification along with the required solvents. Investigated compounds were prepared according to Horner-Wittig method and all reactions were carried under argon conditions. The synthesis of intermediate 5-(benzo[b]thiophen-2-yl)thiophene-2-carbaldehyde, as well as the synthesis of necessary phosphonates was thoroughly described in ESI and supported by NMR characterization (see ESI S3–S6). Synthesis of presented compounds required only three-step path to achieve desired thiophene derivatives (Scheme 1). The change of reagents in the last step allowed to obtain six different compounds characterized by different properties.

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Scheme 1. (a) Synthesis route and (b) chemical structures of investigated compounds.

3.1. Synthesis of (E)-2-(5-(2-nitrostyryl)thiophen-2-yl)benzo[b]thiophene: BT-Th-oNO₂ (1a)

Under argon, in a Schlenk flask, diethyl 2-nitrobenzylphosphonate (0.09 mL, 0.41 mmol) was dissolved in 5 mL of extra dry DMF, afterwards the mixture was stirred in an icebath. Then potassium tert-butoxide (0.62 mmol, 1M in EtOH) was added dropwise and the resulting solution was stirred for 15 minutes. In the second flask a 5-(benzo[b]thiophen-2-yl)thiophene-2-carbaldehyde (100 mg, 0.41 mmol) was dissolved in 10 mL of extra dry DMF. Afterwards the potassium (4-cyanophenyl) (diethoxyphosphoryl) methanide from the first flask was added dropwise and stirred in an icebath for 2 hours. The mixture was then warmed up to room temperature and stirred overnight. Afterwards the mixture was precipitated with water (50 mL) and filtered off. After being dried overnight, BT-Th-oNO₂ was obtained as an orange powder with 79% yield (118 mg). ¹H NMR (CDCl₃, 300 MHz) δ /ppm: 8.00 (d, J = 8.2 Hz, 1H), 7.77 (m, 3H), 7.60 (t, J = 7.5 Hz, 1H), 7.48 (s, 1H), 7.46 (d, J = 16.00 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.34 (m, 2H), 7.24 (d, J = 3.9 Hz, 1H), 7.21 (d, J = 16.5 Hz, 1H), 7.12 (d, J = 3.8 Hz, 1H). ¹³C{1H} NMR (125 MHz, CDCl₃) δ/ppm: 148.0, 142.1, 140.5, 139.4, 138.0, 137.0, 133.3, 132.6, 128.9, 128.2, 128.0, 126.7, 125.8, 125.2, 125.03, 125.00, 123.8, 123.3, 122.4, 120.5. HRMS(CI) m/z: [M]⁺ calcd. for C₂₀H₁₃NO₂S₂: 363.0388; found: 363.0389. Selected IR bands (cm^{-1}) : v = 1600, 1519, 1335, 949, 888, 850, 818.

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3.2. Synthesis of (E)-2-(5-(3-nitrostyryl)thiophen-2-yl)benzo[b]thiophene: BT-Th-mNO₂ (1b)

BT-Th-mNO₂ was obtained in the same way as BT-Th-oNO₂ compound, using diethyl 3nitrobenzylphosphonate instead of diethyl 2-nitrobenzylphosphonate in the first step of reaction. The final product was a yellow powder and the yield of the reaction was 65% (97 mg). ¹H NMR (DMSO-d6, 300 MHz) δ /ppm: 8.45 (s, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 16.3 Hz, 1H), 7.69 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 3.8 Hz, 1H), 7.36 (m, 2H), 7.32 (d, *J* = 3.9 Hz, 1H), 7.19 (d, *J* = 16.3 Hz, 1H). ¹³C {1H} NMR (125 MHz, CDCl₃) δ /ppm: 149.0, 141.9, 140.5, 139.4, 138.9, 137.6, 137.1, 132.3, 129.9, 128.9, 126.2, 125.9, 125.1, 125.0, 124.7, 123.8, 122.4, 122.3, 120.9, 120.4. HRMS(CI) m/z:[M]⁺ calcd. for C₂₀H₁₃NO₂S₂: 363.0388 Da; found: 363.0384 Da. Selected IR bands (cm⁻¹): v = 1619, 1521, 1426, 1350, 957, 887, 866, 845, 826.

3.3. Synthesis of (E)-2-(5-(4-nitrostyryl)thiophen-2-yl)benzo[b]thiophene: BT-Th-pNO₂ (1c)

This compound was synthesized by following the procedure of synthesis for BT-Th-oNO₂, although using diethyl 4-nitrobenzylphosphonate as a starting compound. The final product was an orange powder. The yield of the synthesis was 68% (101 mg). ¹H NMR (CDCl₃, 300 MHz) δ /ppm: 8.20 (d, *J* = 8.8 Hz, 2H), 7.73 (m, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.44 (s, 1H), 7.33 (d, *J* = 15.5 Hz, 1H), 7.32 (m, 2H), 7.23 (d, *J* = 3.8 Hz, 1H), 7.11 (d, *J* = 3.8 Hz, 1H), 6.92 (d, *J* = 16.00 Hz, 1H). ¹³C {1H} NMR (125 MHz, CDCl₃) δ /ppm: 146.9, 143.6, 141.8, 140.5, 139.5, 138.2, 136.9, 130.0, 129.5, 126.9, 126.3, 126.1, 125.9, 125.1, 124.5, 123.8, 122.4, 120.6. HRMS (CI) m/z:[M]⁺ calcd. for C₂₀H₁₃NO₂S₂: 363.0388 Da; found: 363.0395 Da. Selected IR bands (cm⁻¹): v = 1585, 1504, 1423, 1337, 965, 947, 888, 868, 845, 824.

3.4. Synthesis of (E)-2-(2-(5-(benzo[b]thiophen-2-yl)thiophen-2-yl)vinyl)benzonitrile: BT-Th-oCN (2a)

Under argon, in a Schlenk flask, diethyl 2-cyanobenzylphosphonate (0.07 mL, 0.41 mmol) was dissolved in 5 mL of extra dry DMF and the mixture was stirred in icebath. Then potassium *tert*-butoxide (0.62 mmol, 1M in ethanol) was added dropwise to the solution and stirred for 15 minutes. In the second flask 5-(benzo[b]thiophen-2-yl)thiophene-2-carbaldehyde (100 mg, 0.41 mmol) was dissolved in 10 mL of extra dry DMF. Afterwards the potassium (4-cyanophenyl)

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 (diethoxyphosphoryl) methanide from the first flask was added dropwise and the whole mixturfiele online was stirred in an icebath for 2 hours. The final mixture was warmed to room temperature and stirred overnight. Yield of the reaction was equal to 84% (118 mg). ¹H NMR (DMSO-d6, 300 MHz) δ /ppm: 8.00 (d, *J* = 8.1 Hz, 1H), 7.94 (m, 1H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.76 (s, 1H), 7.74 (d, *J* = 16.0 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 3.9 Hz, 1H), 7.43 (m, 1H), 7.35 (m, 2H), 7.34 (d, *J* = 3.9 Hz, 1H), 7.13 (d, *J* = 16.0 Hz, 1H). ¹³C {1H} NMR (125 MHz, DMSO-d6) δ /ppm: 141.4, 140.1, 139.2, 138.4, 136.7, 135.8, 133.5, 133.3, 130.4, 128.3, 126.54, 126.52, 125.47, 125.17, 125.15, 123.9, 123.0, 122.5, 121.0, 117.8, 109.8. HRMS (CI) m/z: [M]⁺ calcd. for C₂₁H₁₃NS₂: 343.0489 Da; found: 343.0487 Da. Selected IR bands (cm⁻¹): v = 2220, 1617, 1590, 1453, 1425, 983, 938, 888, 826.

3.5. Synthesis of (E)-3-(2-(5-(benzo[b]thiophen-2-yl)thiophen-2-yl)vinyl)benzonitrile: BT-Th-mCN (**2b**)

BT-Th-mCN was obtained as a yellow powder with 77% yield (109 mg) by using the same procedure as for BT-Th-oCN compound, only with employing diethyl (3-cyanobenzyl)phosphonate as the starting reactant. ¹H NMR (DMSO-d6, 300 MHz) δ /ppm: 8.11 (s, 1H), 7.92 (m, 2H), 7.83 (m, 1H), 7.7 (m, 2H), 7.70 (m, 1H), 7.58 (d, *J* = 17.8 Hz, 1H), 7.45 (d, *J* = 3.8 Hz, 1H), 7.33 (m, 2H), 7.27 (d, *J* = 3.8 Hz, 1H), 7.03 (d, *J* = 16.3 Hz, 1H). ¹³C {1H} NMR (125 MHz, DMSO-d6) δ /ppm: 142.1, 140.1, 138.3, 137.9, 136.1, 135.9, 131.0, 130.9, 130.0, 129.8, 129.1, 126.4, 126.3, 125.1, 125.1, 124.0, 123.8, 122.5, 120.4, 118.8, 112.0. HRMS (CI) m/z:[M]⁺ calcd. for C₂₁H₁₃NS₂: 343.0489 Da; found: 343.0489 Da. Selected IR bands (cm⁻¹): v = 2226, 1590, 1426, 941, 888, 825.

3.6. Synthesis of (E)-4-(2-(5-(benzo[b]thiophen-2-yl)thiophen-2-yl)vinyl)benzonitrile: BT-TPh-pCN (2c)

This compound was synthesized following the synthesis procedure of BT-Th-oCN, although to substitute nitryl group in *para* position, the diethyl (4-cyanobenzyl)phosphonate was used. The final product was obtained as an yellow powder with 69 % yield (97 mg). ¹H NMR (CDCl₃, 300 MHz) δ /ppm: 7.73 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.29 (m, 2H), 7.27(d, *J* = 16.6 Hz, 1H), 7.21 (d, *J* = 3.8 Hz, 1H), 7.08 (d, *J* = 3.9 Hz, 1H), 6.86 (d, *J* = 16.1 Hz, 1H). ¹³C{1H} NMR (125 MHz, DMSO-d6) δ /ppm: 142.0, 141.3, 140.1, 138.4, 136.3, 136.1, 132.7, 129.7, 127.1, 126.8, 126.5, 125.20, 125.15, 125.1, 123.8, 122.5, 120.5,

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119.0, 109.5. HRMS(CI) m/z:[M]⁺ calcd. for $C_{21}H_{13}NS_2$: 343.0489 Da; found: 343.0484 [eDaticle Online Datic Online Datic 10.1039/C9NJ00575G] Selected IR bands (cm⁻¹): v = 2224, 1596, 1425, 961, 945, 887, 861, 816.

4. Results and discussion

Normalized absorption spectra of all examined derivatives are presented in Figure 1. As can be seen, absorption band maxima of CN derivatives are localized in a very narrow spectral range (393–404 nm), whereas respective maxima positions of NO₂ analogues are spanned across fivetimes wider area (378-424 nm). Although examined compounds differ only in the substitution position at the acceptor moiety, the (a) ortho- and (c) para-substituted derivatives are characterized by much broader and rather structureless absorption bands, in comparison with narrow and well-structured bands of molecules containing the acceptor in (b) meta- position. As expected, the absorption maxima of (c) para-substituted derivatives (Table 1) are redshifted with respect to their (b) meta-counterparts. It's worth mentioning that 1a absorption maximum is located at a shorter wavelength than that of 1b. Clearly, the absorption bands related to 1 derivatives are the subject of more prominent spectral shifts. In order to explain differences between spectral features of 1 and 2 quantum-chemical calculations were performed. Firstly, we checked whether chosen structures (see Scheme 1) are the most stable conformers. Hence we appointed the other potentially stable conformers to be ones obtained by rotation of the benzothiophene and/or nitrile or nitro-substituted phenyl ring by 180°. Consequently, full set of examined structures included 4 conformers for all ortho- and meta-substituted compounds and 2 conformers for all para- derivatives (see ESI, examined conformers section). Performed analysis of calculated Gibbs free energies revealed that structures depicted in Scheme~1 are indeed the most stable conformers of examined compounds. Thus, henceforth we will present only the data computed for those structures.

Secondly, we calculated vertical excitation energies and compared them with measured absorption maxima (Table 1). It should be noted that these are not the same physical quantities, and thus cannot be straightforwardly compared, since one cannot measure vertical transition energy. However, the vertical approximation is proven to be sufficient in predicting the trends among the homologous compounds' series. This in fact is confirmed by discrepancies between E_{vert} and λ_{abs} not exceeding 0.2 eV⁵⁶, which prove that this approximation is adequate for our needs. As can be seen, calculated E_{vert} values reproduce nicely trends observed from experiment absorption spectra, namely the *meta*- derivatives are the most blue-shifted, whereas *para*-substituted compounds exhibit largest batochromic shifts among both series. Performed calculations indicate that except of **1a**, all absorption maxima correspond to $S_0 \rightarrow S_1$ electronic

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transition associated with CT process (see discussion below). Nevertheless, a little moracle online puzzling situation is observed in case of **1a** (*ortho*-)compound, where one can see strongly broadened spectra with somewhat two visible peaks, one around 376 nm and the second at 404 nm. Indeed, the former peak is more intense which is quite surprising, since it is not consistent with expected trends (*ortho*-substituted more blue-shifted than *meta*- derivative), nor calculated trends. Conducted computation revealed that in case of **1a** the latter, slightly less intense peak is associated with $S_0 \rightarrow S_1$ transition characterized with strong CT, whereas maximum observed at 376 nm is associated with energetically higher-lying $S_0 \rightarrow S_2$ transition. Nevertheless, according to calculations, $S_0 \rightarrow S_2$ transition should be connected with significantly lower peak intensity.

Table 1. Computed vertical excitation energies and absorption maxima measured in chloroform solution.

	Simu	Exp. data		
Compound	E _{vert} [nm]	f	$\lambda_{abs} [nm]$	
1 a	385	1.289	(376) 404	
1b	378	1.428	393	
1c	404	1.674	424	
2a	378	1.552	397	
2b	372	1.590	394	
2c	383	1.744	404	

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Figure 1. Normalized absorption and emission spectra for 1 (a,b) and 2 (c,d).

Compound	Density difference plot	d _{CT} [Å]	q _{СТ} [е]	Δμ _{CT} [D]
1a		3.49	0.58	9.70
1b		3.04	0.49	7.14

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1c	 4.34	DOI 0.56	View Article Onlir 10.1039/C9NJ00575 11.60
2a	2.41	0.48	5.27
2b	 2.18	0.46	4.64
2c	 2.89	0.47	6.51

In Table 2 we summarized the outcome of theoretical calculations covering CT-related parameters and corresponding density difference plots. Obtained results were calculated for the lowest-lying $\pi \rightarrow \pi^*$ transition, which is associated with high oscillator strength (Table 1). As can be seen, the charge is being transferred mainly from central thiophene ring, acting as electron donor, to NO₂/CN acceptor group which confirms the CT nature of the examined transitions. Notably, benzothiophene unit is acting as secondary donor which is most visible in case of 1c derivative. As expected, the CT strength rises with increase of the distance between donor and acceptor d_{CT}. Consequently, (b) *meta*-substituted derivatives (d_{CT}=2.18 Å for 2b and d_{CT}=3.04 Å for 1b) exhibits weakest CT, while for the (c) *para*- analogues (d_{CT}=2.89 Å for 2c and d_{CT}=4.34 Å for 1c) CT is the strongest. This statement is confirmed by increase in dipole moment change values $\Delta\mu_{CT}$, which also follow *meta*<*ortho*<*para* order in both series.

However it should be stressed out, that $\Delta\mu_{CT}$ are much larger for nitro-substituted compounds (in range of 7.14-11.60 D) than for their nitrile analogues (4.64-6.51 D. Noteworthy, the presented simulation results reproduce the trends observed for absorption spectra (Figure 1), since band maxima of 1 (nitrophenyl) derivatives are spanned across much wider range (48 nm)

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than their 2 (benzonitrile) counterparts (7 nm). On other hand, the transferred charge values of a trice online are quite similar for all compounds, i.e. for 2 derivatives they oscillate around 0.47 e, while in case of 1 they vary from 0.49 e to 0.58 e. Notably, the difference between CT strength of 1 (nitrophenyl) and 2 (benzonitrile) derivatives is also reflected by a change in the size of lobes depicting electron density difference among acceptor moieties (Table 2). Summarizing all results presented above, NO₂ derivatives are characterized by much stronger CT character than their CN counterparts. Moreover, the abovementioned results are consistent with the Hammett substituent constants, according to which NO₂ group is also stronger acceptor than the CN. Worth to mention are strong Stokes shifts visible for every compound, which values vary from 3000 cm⁻¹ to over 6000 cm⁻¹, depending on substituent and pattern. For both groups the lowest value was obtained for the compounds with acceptor moiety attached in b (meta-) position. Surprisingly, the highest Stokes shift values among molecules with cyano substituent was observed for 2a (ortho- position), whereas for the NO₂ series it was, as predicted, 1c (paraposition). The theoretical findings, explaining the quantum-chemical background of investigated molecules photophysics are in good accordance with the experimental data (c.f. Table 3).

Comp	λ _{abs} [nm]	ε[M ⁻¹ cm ⁻¹]	λ _{fl} [nm]	Δν [cm ⁻¹]	$\pmb{\varPhi}_{fl}$	τ _i [ns]	<i>k_r</i> ×10 ⁸ [s ⁻¹]	<i>k_{nr}×</i> 10 ⁹ [s ⁻¹]
1a	376	31800	466	5136	<10-2	0.55 (0.905) 2.1 (0.095)	-	-
1b	393	48000	447	3074	<10-3	0.033 ^b (0.979) 0.44 (0.019) 4.4 (0.002)	-	-
1c	424	38500	572	6102	0.15	0.20° (-0.180) 1.14 (0.820)	1.3	0.75
2a	397	41600	480	4356	0.15	0.19 (0.905) 0.44 (0.094) 6.0 (0.001)	7.1ª	4.0ª
2b	394	67700	465	3857	0.22	0.47 (1.000) 14 (<0.001)	4.7	1.7
2c	404	60800	485	4134	0.18	0.29 (0.992) 1.7 (0.006) 6.1 (0.002)	6.1	2.8

Table 3. Main photophysical parameters for synthesized compounds measured in chloroform

 λ_{abs} - absorption maxima λ_{fl} – fluorescence maxima, Δv – Stokes shift , Φ_{fl} – fluorescence quantum yield calculated in reference to fluorescein (2.0 × 10⁻⁵ M, EtOH), τ_i – fluorescence decay components (dominant component printed in bold) with their respective contribution, k_r – radiative rate constant (calculated from the dominant component, except 2a), k_{nr} – non-radiative rate constant.

^a calculated from the weighted average of two dominant components ($\tau_{avg} = 0.213$ ns), ^b shorter then IRF, ^c raise of the fluorescence intensity

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In case of fluorescence measurements, **1** compounds exhibit emission maxima at $\lambda_{\text{em}} = 466$ fmm finite column $\lambda_{\text{em}} = 447$ nm and $\lambda_{\text{em}} = 572$ nm for **1a**, **1b**, **1c** derivatives respectively. On the other hand, **2** fluorescence maxima are localized at $\lambda_{\text{em}} = 480$ nm, $\lambda_{\text{em}} = 465$ nm and $\lambda_{\text{em}} = 485$ nm for **2a**, **2b**, **2c** respectively. In both groups fluorescence maxima are located at the shortest wavelengths for acceptors at the *meta*- position, whereas the largest redshifts are visible for acceptors at the *para*- position (**c**). Surprisingly, the fluorescence quantum yield is the highest for **2b**, whereas for both **2a** and **2c** fluorescence quantum yields have similar values (~16%). Nitro-substituted molecules (group **1**), exhibit lower fluorescence intensity than their cyano counterparts (group **2**). As presented in Table 3, molecules substituted at *ortho*- (**1a**) and *meta*- (**1b**) positions show negligible fluorescence intensity, whereas for **1c** (*para*- position) it is over hundred times higher.

Fluorescence decay curves recorded in chloroform (Figure 2) revealed complicated behavior of fluorescence in both groups of molecules. For all compounds two or three decay components were necessary to reproduce the experimental kinetics. It should be noted that for molecules **1b** and all **2** the longest component (in the nanosecond range) has the relative amplitude of the order of 10⁻³ which is attributed rather with the impurities or products of photodecomposition than to the synthesized molecules intrinsic properties.

Fluorescence decays for 2b and 2c (Figure 2b) can be considered to be mono-exponential with the fluorescence lifetimes equal to 0.47 and 0.29 ns respectively. For these molecules timeresolved fluorescence measurements do not suggest any excited-state processes nor presence of various isomers in the solutions. In contrast, the pair of molecules substituted at the *-ortho* position (**1a**, **2a**) exhibits two non-negligible decay components, with the slower one contributing approximately 10% of the overall fluorescence decay. In this case a presence of two emitting species could be suspected, however it is not supported by steady-state absorption and fluorescence spectra.



Figure 2. Fluorescence decay curves for (a) **1a-c** (recorded with excitation by the picose condicte Online diode laser) and (b) **2a-c** (recorded with the femtosecond laser used for excitation) families of compounds recorded in CHCl₃, at room temperature, for excitation wavelength $\lambda = 405$ nm.

The most complicated behaviors are observed for **1b** and **1c**. The fluorescence decay recorded for **1b** contains a very fast component, whose decay time is significantly shorter than the width of the instrumental response function of the apparatus used and thus it could not be reliably determined. The second component has the decay time similar to fluorescence lifetimes of other molecules (0.44 ns) and contributes approximately 2% of the fluorescence decay. Such behavior indicates that the fluorescence of the primarily excited form is very efficiently quenched, as confirmed by its very low quantum yield. The longer decay component can be attributed to a fluorescent photoisomer formed in the excited state with a low yield in an isomerization process competing with the radiationless deactivation.

The last molecule - 1c, is the only one where a fast (0.2 ns) raise of the fluorescence intensity is followed by a relatively slow (1.14 ns) decay. It indicates a process in the excited state of 1c, which leads to formation of longer-lived fluorescent species. However, in contrast to 1b, the primarily excited form is not deactivated efficiently, and the product is produced with a high yield. The structure of the molecules and the results of quantum chemical calculations suggest that charge transfer and isomerization by rotation around the double carbon bond can be involved in the excited-state processes. Nevertheless, the exact identification of these processes requires further photophysical studies of the synthesized compounds.

For molecules whose fluorescence originates mainly from a single species radiative and nonradiative transition rate constant were calculated using relationships between fluorescence quantum yields and fluorescence lifetimes (See eq. (3) and eq. (4)). In every case the nonradiative rate constant is several times higher than the radiative rate constant. Both values are visibly lower for **1c** than for molecules of the **2** group. This might be due to the stronger intramolecular charge transfer occurring in the molecule with the nitro group.

5. Conclusions

In this work we present synthesis of six novel thiophene derivatives combined with their photophysical properties characterization. The compounds were characterized with steady-state and time-resolved spectroscopic techniques and the experimental results were supported by quantum chemical calculations. We showed that molecules with the acceptor substituted in different positions exhibit diverse photophysical features. Quantum chemical calculations

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confirmed that observed differences in spectral properties of absorption are directly connected de Online with changes in the strength of the transitions CT character. Therefore (b) meta-substituted derivatives manifesting moderate CT are characterized with well-structured, narrow absorption spectra, while bands of (a) ortho- and (c) para- analogues, displaying much stronger CT character, are red-shifted, broad and rather structureless. Quite similar features are observed in emission spectra. Nevertheless, interpretation of fluorescence-related parameters tends to be more puzzling. Although we observe significant enhancement of QY (especially for ortho- and meta- derivatives) when replacing NO₂ acceptor with CN group, there is no systematic relationship between QY values and the acceptor substitution position. However, in 1 series, change of acceptor substitution position from para- to ortho- and/or meta- resulted in almost complete fluorescence quenching. We proved that by simple modification in the molecular structure, made in the last synthesis step, the photophysical properties can be significantly tuned. Such behavior is beneficial and makes the prepared compounds as valuable candidates for applications in organic electronics and photonics. To summarize, we synthesized and characterized thiophene derivatives. Dyes can be obtained using simple synthesis protocol with high reaction yields and their optical properties can be tailored in broad spectral range through the constitutional isomerism in one reaction step.

Corresponding authors

Notes

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The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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Synthesis and theoretical investigation of six donor-acceptor thiophene based derivatives with tunable photophysical properties.

