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Small isomeric push-pull chromophores based on thienothiophenes with tuneable optical (non)linearities

Jan Podlesný,^{a,b} Oldřich Pytela,^a Milan Klikar,^a Veronika Jelínková,^b Iwan V. Kityk,^c Katarzyna Ozga,^c Jaroslaw Jedryka,^c Myron Rudysh^{d,e} and Filip Bureš^{*a}

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Fourteen new D- π -A push-pull chromophores based on two isomeric thienothiophene donors and seven acceptors of various electronic nature have been designed and conveniently synthesized. In contrast to known thienothiophene push-pull molecules, the prepared small chromophores proved to be organic materials with easily tunable thermal, electrochemical and (non)linear optical properties. It has also been shown that small structural variation may bring significantly improved/varied fundamental properties. Very detailed structure-property relationships were elucidated within the systematically developed series of push-pull molecules, which may serve as useful guide in designing new D- π -A molecules based on fused thiofene scaffolds.

Introduction

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Thienothiophenes (TT) represent electron-rich bicyclic systems with two annulated thiophene rings that are frequently applied as inherent structural motif of π -conjugated materials for optoelectronics and photonics.¹ According to the sulphur atom mutual orientation, four regioisomers can be distinguished from which thieno[3,2-*b*]thiophene and thieno[2,3-b]thiophene are the most popular ones. These two heterocyclic scaffolds were firstly mentioned in 1935 and 1886 bv Challenger/Harrison² and Biedermann/Jacobson,³ respectively. In contrast to common single thiophene-derived molecules, TTs brings planar and rigidified π -system that allows enhanced intramolecular charge transfer (ICT) from/to the appended peripheral substituents. Since thiophene molecules are especially used as semiconductors, lightharvesting or photoluminescent substances, the molecular planarity of TT plays an important role. In D- π -A push-pull chromophores, both thieno[3,2-b]thiophene and thieno[2,3-b]thiophene may act as an auxiliary electron-releasing unit^{4–6} or a π -linker allowing the ICT between appended donors (D) and acceptors (A).7-9 Moreover,

TTs represent planar, extended and polarizable alternative to common π -linkers such as 1,4-phenylene or 2,5-thienylene.¹⁰ Due to the aforementioned features, TTs were successfully integrated into functional polymers forming emitting¹¹ or hole injection layer¹² of organic light-emitting diodes (OLED) as well as in various types of organic solar cells (OSC). Hence, TT-derived molecules are active electron-donating substances in bulk hetero-junction (BHJ) solar cells,^{13–15} functional dye in dye sensitized solar cells (DSSC)^{8,16} or hole transporting material in perovskite solar cells.^{17,18} They were also applied in organic *n*-type,^{19,20} *p*-type^{21,22} or ambipolar²³ semiconductors build in organic field-effect transistors (OFET).

Over the last two decades, several reports on TT push-pull molecules A - E with nonlinear optical (NLO) properties appeared in the literature (Figure 1). Thieno[3,2-b]thiophene has been utilized as a central π -conjugated linker **A** equipped with chalcogen electron donors and formyl, nitro and tricyanovinyl acceptors. Second order polarizabilities 15 to 43×10^{-30} esu were measured by electric field-induced second harmonic generation (EFISH).²⁴ Andreu et al. have thoroughly investigated thieno[3,2-b]thiophene either as aromatic (B) or molecules quinoid (C) π -linker in push-pull with 4H-pyranylidene donor and dicyanovinyl, thiobarbituric acid or tricyanofuran acceptors. Whereas quinoid TT derivatives showed NLO responses ranging from 2100 to 7900×10^{-48} esu, the aromatic arrangement induces slightly lower nonlinearities with $\mu\beta_0$ product between 650 and 5100 × 10⁻⁴⁸ esu.²⁵ However, push-pull chromophores with tricyanofuran (TCF] or thiobarbiturate acceptors showed μeta_0 values ranging from 2800 to 21900×10^{-48} esu.²⁶ Raposo et al. have focused on 5-arylthieno[3,2-b]thiophene scaffold D and its utilization in construction of push-pull chromophores.27 Variation of peripheral alkoxy/dialkylamino donors allowed tuning two-photon absorption (TPA) cross-section (σ_2) within the range of 82 to 836 GM.

^a Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice, 53210, Czech Republic

^{b.} Institute of Technology and Business in České Budějovice, Okružní 517/10, České Budějovice, 37001, Czech Republic

^{c.} Institute of Optoelectronics and Measuring Systems, Faculty of Electrical Engineering, Czestochowa University of Technology, Armii Krajowej 17, Czestochowa, 42-200, Poland

^{d.} Institute of Physics, Jan Długosz University, 13/15 Armii Krajowej Str., 42-201, Czestochowa, Poland

^{e.} Faculty of Physics, Ivan Franko National University of Lviv, 8 Kyrylo and Mefodiy Str., 79005 Lviv, Ukraine

Electronic Supplementary Information (ESI) available: [Synthesis of parent TT isomers **3** and **5**, ¹H and ¹³C NMR spectra, HR-MALDI-MS spectra, CV curves, UV-VIS absorption spectra, HOMO/LUMO localizations and nonlinear optical measurements]. See DOI: 10.1039/x0xx00000x

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Known TT-based NLOphores

X = O, S, Se, Te; A = CHO, NO₂, tricyanovinyl J. Chem. Soc. Perkin Trans. 2, 1996, 1377–1384.



A = thiobarbituric acid, tricyanofuran; n = 1-2*Tetrahedron*, 2013, **69**, 3919–3926.



Org. Biomol. Chem., 2013, 11, 6338-6349.



R = H, OMe, OEt, NEt₂, pyrrolidino. *Eur. J. Org. Chem.*, 2016, **2016**, 5263–5273.



Tetrahedron Lett., 2006, 47, 5599-5602.

Investigated TTs

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Figure 1 Structures of known and investigated TT-derived push-pull derivatives

In contrast to thieno[3,2-*b*]thiophene central $\sqrt{a_{\rm e}}$ linker onlits isomers are much less investigated. One⁰ example BGMOWS thieno[2,3-*b*]thiophene incorporated into dithiacyclophane **E** with enhanced hyperpolarizability to 21.6 × 10⁻³⁰ esu as measured by hyper-Rayleigh scattering (HRS).^{4,28}

From the aforementioned TT-derived NLOphores available in the literature, we can deduce:

- Thieno[3,2-*b*]thiophene is more investigated/popular than other TT regioisomers.
- TTs are mostly applied as a π -linker, not standalone donor.
- There is no systematic study distinguishing electronic behaviour of particular TT isomers.
- Also, there is no systematic study of the acceptor linked to TT.

Hence, we report herein a systematic study on two series of isomeric push-pull chromophores derived from thieno[3,2-b]thiophene and thieno[2,3-b]thiophene electron donors equipped with various electron-acceptor units at position 2 (Figure 1). Fundamental properties of TT based compounds 1a - g and 2a - g were investigated by electrochemistry, UV-VIS absorption spectra, differential scanning calorimetry (DSC)/thermogravimetry (TGA) and nonlinear optical SHG/THG measurements. The experimental data is further completed and supported by DFT calculations.

Results and discussion

Synthesis

Two series of push-pull chromophores 1a - g and 2a - g were synthesized as depicted on Scheme 1. The chromophores in series 1 were built on central thieno[3,2-b]thiophene 3, whereas thieno[2,3-b]thiophene 5 represents leitmotiv in series 2. The optimized synthesis of parent TT isomers 3 and 5 is shown in the ESI. Target molecules $\mathbf{a} - \mathbf{f}$ in both series were prepared via a two-step facile reaction sequence that utilizes Vilsmeier-Haack formylation and subsequent Knoevenagel condensation. Both aldehydes 4 and 6 were synthesised in high yields of 93 and 97 %, respectively. The Vilsmeier reagent had to be prepared separately by reacting phosphorus and *N*,*N*-dimethylformamide (DMF) oxvchloride with subsequent dropwise addition to a solution of **3** or **5** in DMF. The final Knoevenagel condensation utilized three commercially available precursors - indan-1,3-dione (a), *N*,*N*-diethylthiobarbituric acid (**b**) and malononitrile (**f**); *N*,*N*-dibutylbarbituric acid (c),29 ThDione (d)30 and *N*-butylrhodanine (e)³¹ were prepared according to literature. The final Knoevenagel reactions were carried out using aluminium oxide/DCM system at 25 °C²⁹ and provided the target chromophores in satisfactory yields 64 - 99 %, except for 2b (36%) and 2d (36%) that required repeated purification. The reaction with unsymmetrical N-butylrhodanine (e) afforded chromophores 1e and 2e as a mixture of E/Z isomers with the estimated ratio of 1:10 (based on ¹H NMR, see the ESI).

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Scheme 1 Overall synthetic route towards target TT chromophores $\mathbf{1a}-\mathbf{g}$ and $\mathbf{2a}$ -



Both series were completed by chromophores **1g** and **2g** bearing tricyanovinyl moiety that were introduced by reacting **3** or **5** with tetracyanoethylene (TCNE) in DMF.³² These electrophilic substitution reactions provided **1g** and **2g** in 36 and 45 %, respectively. All attempts to react lithiated **3** or **5** (*n*BuLi or LDA) with TCNE did not improve the yields.

Thermal behaviour

Thermal properties and stability of compounds 1a - g and 2a - g were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Melting points (T_m) and temperatures of thermal decomposition (T_d) were determined by DSC. Initial temperatures of thermal degradation (T_i) and temperatures of 5% weight loss (T_5) were determined by TGA. A representative thermogram of chromophore **2d** is shown on Figure 2 while T_m , T_d , T_i and T_5 values for all chromophores are listed in Table 1.

The parent unsubstituted TT isomers **3** ($T_m = 56 \text{ °C}$)³³ and **5** ($T_m = 6 \text{ °C}$)² differ significantly in their melting points by 50 °C.

However, the data gathered in Table 1 (T_m and T_d) show that thermal properties of compounds **1a** – **g** and **2a** – **g** are rather influenced by the appended electron acceptor. When considering the DSC measurements, the following structure-property relationships can be deduced:

- The highest melting points were recorded for 1d/2d and 1g/2g derivatives bearing ThDione or tricyanovinyl substituents (e.g. 1d/1g with T_m = 239/241 °C).
- An introduction of *N*-butyl chains lowers melting points by approximately 65 °C (e.g. 2b/2c with T_m = 216/150 °C).
- TTs bearing *N*-butylrhodanine or malononitrile moieties proved the highest thermal robustness in liquid phase (e.g. 2e/2f with $T_d = 340/345$ °C).
- *N*,*N*-Diethylthiobarbiturate-substituted compounds **1b** and **2b** showed the lowest *T*_d value of 250 °C.
- TTs **1e** and **2e** with *N*-butylrhodanine showed relatively early melting, postponed decomposition and thus resulting largest difference between T_m and T_d values (142 °C and 178 °C respectively).

According to DSC results, TGA did reveal impact of TT isomer used. An average difference in T_i values of the given pair of isomers is approximately 7 °C. The following general trends can be deduced from the measured TGA data:

- ThDione derivatives **1d** and **2d** possess the highest thermal stability (*T*_i = 229 °C and 236 °C, respectively).
- Cyano-substituted derivatives showed the lowest T_i values (180/168°C for 1f/2f and 196/184 °C 1g/2g).
- Compared to DSC (T_m), the influence of *N*-butyl chains is less evident from TGA data (T_i). However, compounds **c** and **e** showed T_i significantly higher than T_m , which indicates their thermally stable and non-volatile liquid phase (e.g. **1c** with $T_i = 226$ °C and $T_m = 160$ °C).

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On the contrary, cyano-substituted compounds f and g decomposed prior to melting (e.g. 1f with T_i = 180 °C and T_m = 226 °C). This holds true even for 1g and 2g with one of the highest melting points across both series.

Electrochemistry

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The electrochemical behaviour of target chromophores 1a - gand 2a – g was investigated by cyclic voltammetry (CV) in DMF. All target compounds showed irreversible reductions except for 1g and 2g whose reduction processes are reversible. The oxidation of 1a-e, 2b, 2d and 2e is represented by irreversible process. The half-wave potentials of the first oxidation $(E_{1/2(ox1)})$ for chromophores 1f, 1g, 2a, 2c, 2f and 2g were not determined due to localization of their oxidation process out of DMF potential window. Representative CV curves are listed in the ESI. The measured half-wave potentials of the first oxidation ($E_{1/2(ox1)}$ and reduction ($E_{1/2(red1)}$) as well as the corresponding HOMO (E_{HOMO}), LUMO (E_{LUMO}) energies³⁴ and their differences (ΔE) are listed in Table 1 and visualized in the energy level diagram shown in Figure 3 jointly with the DFT calculated values. The $E_{\rm HOMO}$ ranges from -5.58 to -5.86 eV, while E_{LUMO} from -3.26 to -3.96 eV. The ΔE values are within the range of 2.02 to 2.50 eV. Based on the measured electrochemical data, the following conclusions can be made.

- The particular chromophores in both series **1** and **2** obey the same trend (see Figure 3).
- With diminished alternation of E_{HOMO} values (as compared for available values for 1b/2b, 1d/2d and 1e/2e), the principal changes are seen on the LUMO level.
- The LUMO is slightly more negative/deepened for chromophores built on thieno[3,2-b]thiophene (except for 1a/2a).
- The average HOMO-LUMO differences between both series
 1 and 2 are below 0.1 V. Hence, the used TT isomer affects the electrochemical behaviour of the resulting chromophore negligibly.
- According to increasing ΔE (only limited electrochemical data available), the chromophores in series **1** can roughly be ordered as **b** > **a** \geq **d** > **e** > **c**. This order obey decreasing electron withdrawing efficiency of the appended acceptors.²⁹

Linear optical properties

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Fundamental optical properties of target chromophores were investigated by electronic absorption spectra measured in DMF at concentration of 1×10^{-5} M. Spectra of chromophores in series **1** are shown in Figure 4 (left) as a dependence of the molar extinction coefficient (ε) on the wavelength (λ). A full list of spectra can be found in the ESI. Table 2 summarizes the measured longest-wavelength absorption maxima (λ_{max}^{A}) and corresponding molar extinction coefficients (ε). The main feature of the spectra is presence of a single band located within the spectral range of 375 to 475 nm. The spectra shown in Figure 4 (right) compares chromophores **1d** and **2d** that differ in the used TT isomer (both ThDione acceptor). It is obvious that the spectrum of **1d** is slightly bathochromically shifted, which holds true for all pairs of chromophores. The average difference $\Delta \lambda_{\max}^{A}$ is 10 nm. This implies slightly higher electron releasing ability of thieno[3,2-b]thibphere (series **2**). This observation is consistent with the aforementioned electrochemical measurements.

Figure 4 (left) shows absorption spectra of all chromophores in series 1. Whereas the longest-wavelength absorption maxima were found within a spectral range of 389 - 446 nm, the corresponding extinction coefficients range from 12 to 46 M⁻ ¹cm⁻¹. Thus, the optical gap of TT push-pull molecules **1** and **2** can be tuned within a range of 3.19 - 2.78 eV by attaching various electron withdrawing moieties. The chromophores can be arranged in the following order according to their increasing optical gap: $\mathbf{b} > \mathbf{g} \ge \mathbf{d} > \mathbf{e} > \mathbf{a} > \mathbf{c} > \mathbf{f}$. This trend further extends the electrochemical outcomes and obeys the electron withdrawing efficiency of the appended acceptors (N,N-diethylthiobarbiturate > tricyanovinyl > ThDione > N-butylrhodanine > indan-1,3-dione > N,N-dibutylbarbiturate > dicyanovinyl).²⁹ As can be seen, simple $O \rightarrow S$ chalcogen replacement as in barbituric (c) and thiobarbituric acid (b) brings considerable bathochromic shift [compare also Thdione (d) and analogous indan-1,3-dione (a)]. Increasing number of cyano groups has similar effect, e.g. tricyanovinyl (g) and dicyanovinyl (f). Five-membered rhodanine (e) proved to be average electron acceptor among the investigated series.

Chromophores also considerably differ in their extinction coefficients. Chromophores featuring the acceptors with the most extended π -system (**d** and **a**) as well as rhodanine (**e**) showed the highest ε values. On the contrary, chromophores with the strongest acceptor, thiobarbituric acid (**b**) and tricyanovinyl (**g**), possess two- to three-times lower extinction coefficients.



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Table 1 Thermal, electrochemical and DFT calculated data for chromophores 1a – g and 2a – g DOI: 10.1039/C9OB00487													
Compound	<i>T</i> _m [°C]ª	<i>Т</i> _d [°С]ª	<i>Т</i> і [°С] ^ь	<i>Т</i> 5 [°С] ^ь	E _{1/2(ox1)} [V] ^c	E _{1/2(red1)}	Е _{номо} [eV] ^d	E _{LUMO} [eV] ^d	Δ <i>Ε</i> [eV]	E _{номо} Dft [eV] ^e	E _{LUMO} DFT [eV] ^e	∆E ^{DFT} [eV]	μ [D]e
1a	226	300	213	254	1.30	-1.02	-5.69	-3.37	2.32	-6.29	-3.12	3.17	2.9
1b	226	250	218	248	1.26	-0.79	-5.65	-3.60	2.05	-6.37	-3.20	3.17	7.9
1c	160	290	226	254	1.46	-0.98	-5.85	-3.41	2.44	-6.35	-3.02	3.33	5.8
1d	239	280	229	266	1.43	-0.89	-5.82	-3.50	2.32	-6.29	-3.19	3.10	3.1
1e	178	320	217	253	1.33	-1.09	-5.72	-3.30	2.42	-6.02	-2.99	3.03	6.7
1f	226	_ f	180	206	_g	-0.99	-	-3.40	-	-6.48	-3.16	3.32	11.1
1g	241	305	196	219	_g	-0.43	-	-3.96	-	-6.70	-3.81	2.89	12.7
2a	233	295	215	255	_g	-0.98	-	-3.41	-	-6.39	-3.02	3.37	2.1
2b	216	250	223	247	1.19	-0.83	-5.58	-3.56	2.02	-6.39	-3.15	3.24	7.7
2c	150	285	214	248	_g	-1.02	-	-3.37	-	-6.47	-2.96	3.51	5.6
2d	243	280	236	268	1.47	-0.93	-5.86	-3.46	2.40	-6.39	-3.10	3.29	2.3
2e	162	340	217	255	1.37	-1.13	-5.76	-3.26	2.50	-6.10	-2.94	3.16	7.1
2f	192	345	168	197	_g	-1.05	-	-3.34	-	-6.61	-3.04	3.57	11.6
20	220	270	19/	211	g	0.52		2 97		6 95	2 70	2.06	12.1

^aDetermined by DSC in open aluminous crucibles under N₂ inert atmosphere and with a scanning rate of 3 °C/min within the range of 25 – 400 °C. Melting point and temperature of decomposition were determined as intersection of the baseline and tangent of the peak (onset point). ^bDetermined by TGA in open alumina crucibles under N₂ inert atmosphere and with a heating rate of 3 °C/min within the range of 25 – 400 °C. The initial temperature of degradation was determined as the last common point of TGA curve and its first derivation (DTG curve). Temperature of 5% weight loss was determined by gradual horizontal step on TGA curve. ^cE_{1/2(ox1)} and $E_{1/2(red1)}$ are half-wave potentials of the first oxidation and reduction measured in DMF; all potentials are given vs SSCE. ^dRecalculated from the $E_{1/2(ox1/red1)}$ according to the equation - $E_{HOMO/LUMO} = E_{1/2(ox1/red1)} + 4.35 + 0.036$.³⁴ eCalculated at the DFT B3LYP/6-311++G(2df,p) level in DMF. ^fEvaporated at 350°C. ^eThe oxidation processes are localized out of the available potential window in DMF.

Nonlinear optical properties

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Due to their prospective application as high-speed communication modulators,³⁵ a significant effort is currently devoted to small organic molecules with NLO activity,36 especially those with donor/ π -linker doped with various heteroatoms.³⁷ Hence, beside linear optical properties, we have also investigated optical nonlinearities of TTs 1 and 2, second- and third-harmonic generations (SHG and THG) in particular. The SHG and THG measurements were carried out with 1064 nm Nd:YAG (SHG) and 1540 nm (THG) Er:glass fundamental laser beams. The application of the 1540 nm was caused by a necessity to avoid fundamental absorption at the third harmonic wavelength (about 513 nm). The frequency repetition of the beam pulses was varied within 10 to 30 Hz. The photothermal control has shown that the changes of temperature did not exceed 2 - 3 K. The set of filters at doubled (532 nm) and tripled frequency (513 nm) have been applied to spectrally separate the third order nonlinear optical signal from the first order. Samples with known parameter of the nonlinear optical susceptibilities have been used as reference specimens. The studied chromophores have been embedded into olygoetheracrylate photopolymer matrices and were additionally poled by dc-electric field similarly as we described in our earlier work.38

The principal results of the NLO measurements are given in Table 2. The experimental second-order polarizabilities (SHG) range from 0.62 to 2.45 pm·V⁻¹ and are clearly function of the appended acceptor. The measured SHG nonlinearities are very close to the recently obtained parameters of second order susceptibilities for substituted 1,3,5-triphenylpyrazolines measured by the same set-up (1.67 – 2.7 pm·V⁻¹).³⁹ The effect

of the used TT isomer is less pronounced. The highest SHG responses have been observed for chromophores 1d and 2d (2.45 and 2.38 pm·V⁻¹) with ThDione acceptor followed by their structural analogues **1a** and **2a** (1.71 and 2.03 $pm \cdot V^{-1}$) with indan-1,3-dione. Noticeable nonlinearities were also recorded for tricyanovinyl-terminated TTs 1g and 2g (1.80 and 1.70 pm·V⁻¹). 2b with Chromophores 1b and *N*,*N*-diethylthiobarbiturate residues afforded SHG nonlinearities of 1.31 and 1.35 pm·V⁻¹. Thus, the highest SHG responses were measured for chromophores with either strong electron acceptors (**d**, **g**, **b**) or with extended π -system (a). Chromophores bearing N,N-dibutylbarbiturate (c), N-butylrhodanine (e) and dicyanovinyl (f) proved less efficient SHG materials. Photoinduced SHG (PISHG) showed the same trends with the highest nonlinearities recorded for chromophores d, a and g. However, the PISHG was principally more stable than that measured for tetranuclear copper π -complexes with thiazolidinone ligands.⁴⁰ So, TTs **1** and **2** seem to be well-suited organic materials for tuning SHG as their responses are completely reversible after interrupting the process and no changes in the SHG were encountered.

Third-order NLO activity of TTs **1** and **2** has been examined by THG. Considering the data gathered in Table 2, it is obvious that chromophores **1c** and **2c** end-capped with *N*,*N*-dibutylbarbiturate acceptors possess very weak third nonlinearities (1.59 and 1.67 a.u.). This is in contrast to chromophores **1b** and **2b** with *N*,*N*-diethylthiobarbiturate that have shown the largest THG responses 8.22 and 7.30 a.u. This again implies that $O \rightarrow S$ chalcogen replacement plays very important role. Published on 20 March 2019. Downloaded on 3/21/2019 6:56:19 AM.

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Figure 4 UV-VIS absorption spectra of chromophores 1a – 1g (left) and comparison of absorption spectra between isomers 1d and 2d (right) All spectra were measured in DMF at c = 1 × 10-5 M.

Table 2 Optical properties of chromophores 1a – g and 2a – g											
Compound	λ_{\max}^{A} [nm (eV)] ^a	<i>€</i> [× 10 ³ M ^{−1} ·cm ^{−1}]ª	λ _{max} ^{TD-DFF} [nm (eV)] ^b	λ_{\max}^{ZINDO} [nm(eV)] ^b	SHG [pm·V ⁻¹] ^c	PISHG [pm·V⁻¹] ^d	THG [a.u.] ^e	eta [× 10 ⁻³⁰ esu] ^f	γ [× 10 ⁻²⁵ esu] ^g		
1a	433 (2.86)	40.5	405 (3.06)	453 (2.74)	1.71	2.01	7.97	76.8	2.06		
1b	446 (2.78)	12.2	405 (3.06)	468 (2.65)	1.31	1.82	8.22	17.7	16.13		
1c	414 (3.00)	37.5	368 (3.37)	459 (2.70)	0.71	1.02	1.59	33.1	17.51		
1d	441 (2.81)	43.9	415 (2.99)	459 (2.70)	2.45	2.61	4.09	10.4	1.52		
1e	434 (2.86)	46.0	413 (3.00)	431 (2.88)	0.78	1.12	7.40	58.0	0.98		
1f	389 (3.19)	36.8	353 (3.51)	446 (2.78)	0.80	1.32	7.40	25.1	0.11		
1g	445 (2.79)	20.5	398 (3.12)	467 (2.66)	1.80	2.28	7.45	57.4	0.09		
2a	413 (3.00)	40.1	382 (3.25)	415 (2.99)	2.03	2.31	2.44	66.1	2.27		
2b	444 (2.79)	16.4	390 (3.18)	436 (2.84)	1.35	1.83	7.30	21.4	11.33		
2c	406 (3.05)	29.2	365 (3.40)	426 (2.91)	0.62	0.92	1.67	31.3	12.91		
2d	430 (2.88)	37.6	392 (3.16)	422 (2.94)	2.38	2.55	3.40	88.1	1.35		
2e	423 (2.93)	57.0	402 (3.08)	396 (3.13)	0.80	1.31	5.60	55.6	0.90		
2f	383 (3.24)	28.6	350 (3.54)	408 (3.04)	0.76	1.35	5.60	22.2	0.03		
2g	430 (2.88)	23.9	394 (3.15)	435 (2.85)	1.70	2.22	5.60	48.1	0.03		

^aMeasured in *N*,*N*-dimethylformamide at concentration of 1 × 10⁻⁵ M. ^bCalculated at the DFT B3LYP/6-311++G(2df,p) level in vacuum ^cMeasured with a 1064 nm source fundamental laser beam. ^dPhotoinduced SHG. ^eMeasured with a 1540 nm source fundamental laser beam. ^fCalculated at the DFT B3LYP/6-311++G(2df,p) level in vacuum at 1064 nm. ^gCalculated by using the PM7 semi-empirical method implemented in MOPAC.

On the contrary, replacement of fused benzene ring as in indan-1,3-dione derivatives **1a** by thiophene in **1d** has detrimental effect on third order NLO activity. However, this is in contrast to opposite TT isomer **2a** vs. **2d**. Rhodanine, di- and tricyanovinyl-terminated chromophores **e**, **f** and **g** showed very similar THG values around 7.40 and 5.60 a.u. for TT isomers **1** and **2**, respectively. Compared to aforementioned 1,3,5-triphenylpyrazolines and copper π -complexes with thiazolidinone ligands, the measured THG responses of TTs **1** and **2** are slightly lower.

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appended double bond. The LUMO is mostly spread over the appended acceptor, partially also over the TT's π -conjugated system. Both HOMO and LUMO are partially separated which further confirms CT character of chromophores **1** and **2**. Derivatives **1b** and **2b** bearing thiobarbituric acid pendant possess the HOMO localized on the sulphur atom of the thiobarbiturate, the LUMO is spread over the whole π -system. This is in agreement to our recent observation²⁹ and also corresponds to localization of frontier orbitals reported by Khurana et al. for thiobarbiturates with none mezomeric donor.⁴³

The calculated ground-state dipole moments range from 2.1 to 12.7 D (Table 1) and are clearly function of the structure/symmetry. For instance, chromophores **f** and **g** bearing dicyanovinyl and tricyanovinyl groups possess the highest values of μ (11.1 – 12.7 D). On the contrary, the lowest dipole moments of 2.1 – 3.1 D were found for structural analogues **a** and **d** bearing indan-1,3-dione and ThDione.

Electronic absorption spectra of TTs 1 and 2 calculated by TD-DFT revealed one single band appearing within the range of 350 to 415 nm. Compared to experimental λ_{max}^{A} values are the calculated maxima λ_{max}^{TD-DFT} hypsochromically shifted. However, both quantities showed tight correlation. Chromophores in series 1 showed slightly red-shifted λ_{max}^{TD-DFT} values, which further confirms higher electron releasing ability of thieno[3,2-b]thiophene. TD-DFT calculation is also capable to identify chromophores with the weakest acceptors such as c and **f** but there is no clear trend in the remaining groups. ZINDO calculations confirmed However. the most bathochromically shifted maxima for chromophores **b**, **d** and **g**. The observed single band of the spectra is mostly generated by HOMO→LUMO and HOMO(-1)→LUMO transitions

The calculated NLO coefficients β and γ range from 10.4 to 76.8 × 10⁻³⁰ esu and from 0.03 to 17.51 × 10⁻²⁵ esu, respectively. The highest β coefficients were calculated for **a** and **d** chromophores, similarly to SHG (taking value for 1**d** as an outlier). For chromophores **g** and **e** with tricyanovinyl and rhodanine acceptors were also calculated noticeable nonlinearities. Semi-empirical PM7 calculation of γ identified chromophores **b** and **c** bearing (thio)barbiturate acceptors as the most active. This is in agreement with experiment that revealed thiobarbiturate derivatives 1b and 2b as most active THG materials. However, the results calculated for barbiturate derivatives 1c and 2c is in a complete contradiction.



Figure 5 HOMO and LUMO localizations in 1d

HOMO

DFT calculations

Spatial and electronic properties of all target chromophores 1a - g and 2a - g were investigated at the DFT level by using the Gaussian[®] 16 software package.⁴¹ The geometries of molecules 1a - g and 2a - g were optimized using DFT B3LYP/6-311G(2df,p) method. Energies of the HOMO and the LUMO, their differences and ground-state dipole moments μ were calculated on the DFT B3LYP/6-311++G(2df,p) level including DMF as a solvent (Table 1). First hyperpolarizabilities β were calculated on the DFT B3LYP/6-311++G(2df,p) level in vacuum at 1064 nm. Second hyperpolarizabilities γ were calculated by PM7 semiempirical method implemented in MOPAC⁴² using DFT-optimized geometries (Table 2). The electronic absorption spectra. longest-wavelength absorption maxima and corresponding electron transitions were calculated using TD-DFT and ZINDO (nstates = 8) B3LYP/6-311++G(2df,p) (Table 2). The calculated HOMO/LUMO energies of 1a - g and 2a - g are within the range of -6.85 to -6.02 eV and -3.81 to -2.94 eV, respectively (Table 1). As can be seen from the energy level diagram shown in Figure 3, the DFT-calculated $E_{\rm HOMO}/E_{\rm LUMO}$ are slightly under- an overestimated as compared to the electrochemical values. However, the used DFT method is clearly capable to describe trends within both series and, therefore, it can be considered as a reasonable tool for describing electronic and spatial properties of TTs ${\bf 1}$ and ${\bf 2}.$ A tight correlation has been found between complete experimental and DFT-calculated ELUMO values. By comparing corresponding pairs of chromophores, the LUMO energies of 1 with thieno[3,2-b]thiophene is slightly lower, similarly as found by electrochemistry.

The HOMO and LUMO localizations in representative chromophore **1d** are shown in Figure 5, for complete listing see the ESI. The HOMO is predominantly localized on the TT donor and partially also in alternating position of the



Conclusion

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In conclusion, we have designed small D- π -A chromophores utilizing thieno[3,2-b]thiophene and thieno[2,3-b]thiophene as electron donors. Fourteen new chromophores in two series were conveniently prepared via Vilsmeier-Haack formylation and Knoevenagel condensation or substitution. The fundamental optoelectronic properties were tuned by varying both donor and acceptor. The observed structure-property relationships within the investigated series of thienothiophenes 1 and 2 can be generalized as follows (Figure 6):

- Despite the parent TT isomers differ considerably in melting points, thermal properties of push-pull derivatives
 1 and 2 are mostly affected by the appended acceptor. Novel ThDione acceptor proved thermally very stable, whereas alkyl chains of (thio)barbiturate and rhodanine acceptors bring considerably lowered melting points but improved thermal robustness in liquid phase.
- Electrochemical measurements of TTs 1 and 2 revealed slightly improved electron donating ability of thieno[3,2-b]thiophene.
- Linear optical properties measured by electronic absorption spectra indicated bathochromically shifted longest-wavelength absorption maxima of TT **1** bearing thieno[3,2-*b*]thiophene.
- Molar extinction coefficients of chromophores 1 and 2 primarily depend on the π-system extension.
- The used acceptor also strongly affects the nonlinear optical properties.
- Based on the aforementioned observations, we can order electron withdrawing efficiency of the particular acceptors: N,N-diethylthiobarbiturate > tricyanovinyl > ThDione > N-butylrhodanine > indan-1,3-dione > N,N-dibutylbarbiturate > dicyanovinyl.

- As a general conclusion, appended acceptor seems to have larger influence on the 10.103 fundamental optoelectronic/thermal properties of 1 and 2 than parent TT isomer.
- Thieno[3,2-b]thiophene-derived push-pull molecules 1d and 1b bearing either polarizable ThDione or strong thiobarbiturate acceptors proved to be most efficient second- and third-order NLOphores.

In view of the current interest in functionalized organic conjugated molecules, we believe that the aforementioned structure-property relationships would serve as a guide in designing new molecules with tailored properties.

Experimental

Experimental procedures and characterization of compounds

Reagents and solvents were reagent-grade and were purchased from Penta, Aldrich, and Fluka and used as received. Dry THF was freshly distilled from Na/K alloy and diphenylmethanone under inert argon atmosphere. Solvents were evaporated on a Heidolph Laborota 4001 rotary evaporator. Column chromatography was carried out with silica gel 60 (particle size 0.040-0.063 mm, 230-400 mesh; Merck) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 obtained from Merck, with visualization by UV lamp (254 or 360 nm). Melting points (mp) were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected. ¹H and ¹³C NMR spectra were recorded in $CDCl_3$ or d_6 -DMSO at 400/100 MHz with a Bruker AVANCE III or 500/125 MHz with Bruker Ascend[™] at 25 °C. Chemical shifts are reported in ppm relative to the signal of Me₄Si. The residual solvent signal in the ¹H and ¹³C NMR spectra was used as an internal reference (CDCl₃ - 7.25 and 77.23 ppm, d₆-DMSO – 2.55 and 39.51 ppm). Coupling constants (J) are given in Hz. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were measured on a GC/EI-MS configuration comprised of an Agilent Technologies 7890B gas chromatograph (column HP5 30 m \times 0.25 mm \times 0.25 μ m) equipped with a 5977B MS detector (EI 70 eV, mass range 10 -1050 Da) and GC/EI-MS configuration comprised of an Agilent Technologies 6890N gas chromatograph (column HP-5MS 30 m \times 0.25 mm \times 0.25 μ m) equipped with a 5973 MS detector (EI 70 eV, mass range 33 – 550 Da). High-resolution MALDI mass spectra were measured using method "dried droplet" on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive ion mode over a normal mass range (m/z 50-2000) with the resolution 100.000 at m/z 400. The used matrix was 2,5dihydroxybenzoic acid (DHB). UV-vis spectra were recorded on a HP 8453 spectrophotometer in N,N-dimethylformamide (c 1 × 10⁻⁵ mol/L). Melting points and temperatures of decomposition were measured by differential scanning

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calorimetry (DSC) with a Mettler-Toledo STAR^e System DSC 2/700 equipped with FRS 6 ceramic sensor and cooling system HUBER TC100-MT RC 23. DSC curves were determined in open aluminous crucibles under N2 inert atmosphere and with a scanning rate of 3 °C/min within the range 25-400 °C. Thermogravimetric analysis (TGA) was carried out using a Mettler-Toledo STAR^e System TGA 2 equipped with horizontal furnace LF (400 W, 1100 °C), balance XP5 (resolution 1 µg) and cooling system HUBER minichiller 600. TGA curves were determined in open alumina 900 μ l crucibles under N₂ inert atmosphere and with a heating rate of 3 °C/min within the range 25 – 400 °C. The initial sample weight was approximately 7 mg. Electrochemical measurements were carried out in DMF containing 0.1 M Bu₄NBF₄ in a three electrode cell. The working electrode was glassy carbon disk (1 mm in diameter). As the reference and auxiliary electrodes were used leakless Ag/AgCl electrode (SSCE) containing filling electrolyte (3.4 M KCI) and titanium rod with a thick coating of platinum, respectively. All peak potentials are given vs. SSCE. Voltammetric measurements were performed by using an integrated potentiostat system ER466 (eDAQ Europe, Warszawa, Poland) operated with EChem Electrochemistry software. Elementary analyses were determined using EA 1108 Fisons instrument.

General procedure for Vilsmeier-Haack formylation

Appropriate thienothiophene **3** or **5** (1 g, 7.13 mmol) was dissolved in DMF (5 ml) and cooled to 0 °C. The mixture of phosphorus oxychloride (1.96 ml, 21.39 mmol) and DMF (5 ml) cooled to 0 °C was added dropwise. The reaction mixture was allowed to reach 25 °C and the reaction was subsequently stirred at 60 °C for 12 h. The resulting intermediate was poured over ice/water and pH was adjusted to 8 - 9 by adding sat. aq. Na₂CO₃. The product was extracted with DCM (3×100 ml), the organic extract was washed with water (3×200 ml), dried with sodium sulphate, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 1:1).

Thieno[3,2-b]thiophene-2-carbaldehyde 4

The title compound was synthesized from thieno[3,2-*b*]thiophene **3** following the general procedure. Pale brown solid. Yield 1.115 g (93 %). $R_f = 0.21$ (silica gel, DCM/hexane, 1:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): $\delta = 7.32$ (d, 1H, J = 5.6 Hz, Th), 7.69 (d, 1H, J = 5.6 Hz, Th), 7.93 (s, 1H, Th), 9.96 ppm (s, 1H, CHO). ¹³C-NMR (100 MHz, 25 °C, CDCl₃): $\delta = 120.27$; 129.25; 134.03; 139.30; 145.53; 145.84; 183.71 ppm. EI-MS (70 eV): m/z = 168 ([M⁺], 100 %), 139 (23), 95 (18), 69 (18).

Thieno[2,3-b]thiophene-2-carbaldehyde 6

The title compound was synthesized from thieno[2,3-*b*]thiophene **5** following the general procedure. Pale brown solid. Yield 1.164 g (97 %). $R_{\rm f}$ = 0.28 (silica gel, DCM/hexane, 1:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 7.30 (d, 1H, *J* = 5.4 Hz, Th), 7.44 (d, 1H, *J* = 5.4 Hz, Th), 7.92 (s, 1H, Th), 9.93 ppm (s, 1H, CHO). ¹³C-NMR (100 MHz, 25 °C, CDCl₃): δ

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= 121.51; 130.34; 131.11; 142.75; 146.92; 147.83; <u>183,51</u> ppm EI-MS (70 eV): *m/z* = 168 ([M⁺], 100 %), 95 (25), 45 (19). B00487D

General procedure for Knoevenagel condensation

Aldehyde **4** or **6** (70 mg, 0.42 mmol) and appropriate acceptor precursor (0.62 mmol) were dissolved in DCM (20 ml). Aluminium oxide (212 mg, 2.08 mmol, Brockmann II-III) was added and the reaction mixture was stirred at 25 °C for 12 h. Aluminium oxide was filtered off and the solvent was evaporated *in vacuo*.

Chromophore 1a

The title compound was synthesized from aldehyde **4** and indan-1,3-dione (91 mg) following the general procedure. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 2:1). Orange solid. Yield 122 mg (99 %). m.p. = 226 °C. R_f = 0.23 (silica gel, DCM/hexane, 2:1). ¹H-NMR (500 MHz, 25 °C, CDCl₃): δ = 7.35 (d, 1H, *J* = 5.0 Hz, Th), 7.70 (d, 1H, *J* = 5.0 Hz, Th), 7.76 – 7.81 (m, 2H, ArH), 7.96 – 8.00 (m, 3H, ArH + CH), 8.37 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 120.23; 123.17; 123.26; 124.98; 133.45; 134.62; 135.12; 135.31; 137.39; 139.80; 140.29; 140.53; 142.24; 150.05; 189.63; 190.41 ppm. HR-FT-MALDI-MS (DHB) *m/z*: calculated for C₁₆H₈O₂S₂ [M + H]⁺ 297.00385, found 297.00344. Elementary analysis: calculated for C₁₆H₈O₂S₂ (296.36): C 64.84, H 2.72, S 21.64; found C 65.09, H 2.71, S 21.70.

Chromophore 1b

The title compound was synthesized from aldehyde **4** and *N*,*N*-diethylthiobarbituric acid (124 mg) following the general procedure. The crude product was purified by column chromatography (silica gel, DCM/hexane, 2:1). Orange solid. Yield 138 mg (94 %). m.p. = 226 °C. $R_f = 0.34$ (silica gel, DCM/hexane, 2:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): $\delta = 1.30 - 1.36$ (m, 6H, 2 × CH₃), 4.55 – 4.63 (m, 4H, 2 × *N*-CH₂), 7.35 (d, 1H, *J* = 5.2 Hz, Th), 7.79 (d, 1H, *J* = 5.2 Hz, Th), 8.12 (s, 1H, CH), 8.76 ppm (s, 1H, Th). ¹³C-NMR (100 MHz, 25 °C, CDCl₃): $\delta = 12.60$; 12.69; 43.52; 44.26; 111.31; 120.45; 136.56; 137.50; 140.05; 140.15; 151.04; 153.97; 159.92; 161.14; 178.87 ppm. HR-FT-MALDI-MS (DHB) *m/z*: calculated for C₁₅H₁₄N₂O₂S₃ [M + H]⁺ 351.02902, found 351.02965. Elementary analysis: calculated for C₁₅H₁₄N₂O₂S₃ (350.48): C 51.40, H 4.03, N 7.99, S 27.45; found C 51.89, H 3.99, N 8.31, S 27.93.

Chromophore 1c

The title compound was synthesized from aldehyde **4** and *N*,*N*-dibutylbarbituric acid (149 mg) following the general procedure. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 1:1). Yellow solid. Yield 159 mg (97 %). m.p. = 160 °C. $R_f = 0.12$ (silica gel, DCM/hexane, 1:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): $\delta = 0.94 - 0.98$ (m, 6H, 2 × CH₃), 1.34 – 1.45 (m, 4H, 2 × CH₂), 1.60 – 1.70 (m, 4H, 2 × CH₂), 3.96 – 4.01 (m, 4H, 2 × N-CH₂), 7.33 (d, 1H, J = 5.2 Hz, Th), 7.74 (d, 1H, J = 5.2 Hz, Th), 8.08 (s, 1H, CH), 8.74 ppm (s, 1H, Th). ¹³C-NMR (100 MHz, 25 °C, CDCl₃): $\delta = 13.99$; 14.02; 20.39; 20.44; 30.38; 30.41; 41.76; 42.42; 110.90; 120.36; 135.78; 136.89; 139.67; 139.69; 149.79; 151.08; 153.12; 161.77; 162.66 ppm. HR-FT-MALDI-MS (DHB) *m/z*:

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ArH + CH), 8.17 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, $CDCl_3$): $\delta = 120.52$; 123.23; 123.30; 124.61; 130.28; 134.19; 135.16; 135.35; 137.23; 140.64; 140.86; 142.19; 147.09; 150.42; 189.73; 190.47 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for C₁₆H₈O₂S₂ [M + H]⁺ 296.99938, found 297.00403. Elementary analysis: calculated for C₁₆H₈O₂S₂ (296.36): C 64.84, H 2.72, S 21.64; found C 65.37, H 2.62, S 21.76.

(500 MHz, 25 °C, CDCl₃): δ = 7.31 (d, 1H, J = 5.0 Hz_{vi}Th), 3.43 (d,

1H, J = 5.5 Hz, Th), 7.76 – 7.80 (m, 2H, APP); 7.95³⁹8.00(PA,48P),

Chromophore 2b

The title compound was synthesized from aldehyde 6 and N,N-diethylthiobarbituric acid (124 mg) following the general procedure. The crude product was purified by crystallization from a mixture of DCM and hexane. Orange solid. Yield 53 mg (36 %). m.p. = 216 °C. R_f = 0.22 (silica gel, DCM/hexane, 1:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 1.29 – 1.36 (m, 6H, 2 × CH₃), 4.55 – 4.63 (m, 4H, 2 × N-CH₂), 7.32 (d, 1H, J = 5.2 Hz, Th), 7.45 (d, 1H, J = 5.2 Hz, Th), 8.03 (s, 1H, CH), 8.75 ppm (s,

1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 12.58; 12.66; 43.51; 44.23; 110.93; 120.56; 130.79; 137.96; 140.96; 146.80; 150.93; 154.94; 160.03; 161.13; 178.84 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for C₁₅H₁₄N₂O₂S₃ [M + H]⁺ 351.02902, found 351.02896. Elementary analysis: calculated for C₁₅H₁₄N₂O₂S₃ (350.48): C 51.40, H 4.03, N 7.99, S 27.45; found C 51.06, H 3.89, N 8.24, S 26.98.

Chromophore 2c

The title compound was synthesized from aldehyde 6 and N,N-dibutylbarbituric acid (149 mg) following the general procedure. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 1:1). Yellow solid. Yield 136 mg (83 %). m.p. = 150 °C. R_f = 0.2 (silica gel, DCM/hexane, 2:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 0.94 – 0.98 (m, 6H, 2 × CH₃), 1.34 – 1.45 (m, 4H, 2 × CH₂), 1.59 – 1.69 (m, 4H, 2 × CH₂), 3.96 – 4.01 (m, 4H, 2 × N-CH₂), 7.30 (d, 1H, J = 5.2 Hz, Th), 7.43 (d, 1H, J = 5.2 Hz, Th), 7.98 (s, 1H, CH), 8.72 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 14.00; 14.02; 20.39; 20.45; 30.37; 30.39; 41.76; 42.41; 110.53; 120.50; 130.49; 137.41; 140.50; 146.49; 149.71; 151.06; 153.85; 161.90; 162.68 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for $C_{19}H_{22}N_2O_3S_2$ [M + H]⁺ 391.11446, found 391.11395. Elementary analysis: calculated for C₁₉H₂₂N₂O₃S₂ (390.52): C 58.44, H 5.68, N 7.17, S 16.42; found C 58.83, H 5.62, N 7.19, S 16.14.

Chromophore 2d

The title compound was synthesized from aldehyde 6 and ThDione (94 mg) following the general procedure. The crude product was purified by flash chromatography (silica gel, DCM). Sandy brown solid. Yield 46 mg (36 %). m.p. = 243 °C. R_f = 0.22 (silica gel, DCM). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 7.31 (d, 1H, J = 5.2 Hz, Th), 7.43 (d, 1H, J = 5.2 Hz, Th), 7.96 (s, 2H, ThDi), 7.99 (s, 1H, CH), 8.12 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 120.53; 125.49; 125.55; 130.35; 132.19; 134.46; 138.86; 140.75; 146.15; 147.05; 147.11; 150.97; 182.89; 183.34 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for $C_{14}H_6O_2S_3 [M + H]^+ 302.96027$, found 302.96056.

calculated for $C_{19}H_{22}N_2O_3S_2$ [M - H]⁺ 389.09881, found 389.09916. Elementary analysis: calculated for C₁₉H₂₂N₂O₃S₂ (390.52): C 58.44, H 5.68, N 7.17, S 16.42; found C 59.11, H 5.66, N 7.83, S 16.28.

Chromophore 1d

The title compound was synthesized from aldehyde 4 and ThDione (94 mg) following the general procedure. The crude product was purified by flash chromatography (silica gel, DCM). Orange solid. Yield 85 mg (67 %). m.p. = 239 °C. R_f = 0.26 (silica gel, DCM). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 7.34 (d, 1H, J = 5.2 Hz, Th), 7.70 (d, 1H, J = 5.2 Hz, Th), 7.95 (s, 2H, ThDi), 7.97 (s, 1H, CH), 8.32 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 120.32; 125.43; 125.53; 132.60; 133.75; 134.87; 138.99; 139.76; 140.37; 146.08; 147.14; 150.53; 182.79; 183.28 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for $C_{14}H_6O_2S_3 [M + H]^+ 302.96027$, found 302.96005. Elementary analysis: calculated for C₁₄H₆O₂S₃ (302.39): C 55.61, H 2.00, S 31.81; found C 55.96, H 1.94, S 31.63.

Chromophore 1e

The title compound was synthesized from aldehyde 4 and *N*-butylrhodanine (117 mg) following the general procedure. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 1:1). Yellow solid. Yield 106 mg (74 %). m.p. = 178 °C. $R_{\rm f}$ = 0.37 (silica gel, DCM/hexane, 1:1). ¹H-NMR (500 MHz, 25 °C, CDCl₃): δ = 0.94 – 0.98 (m, 3H, CH₃), 1.35 – 1.43 (m, 2H, CH₂), 1.66 – 1.72 (m, 2H, CH₂), 4.10 – 4.14 (m, 2H, N-CH₂), 7.28 – 7.32 (m, 1H, Th), 7.57 – 7.60 (m, 2H, Th + CH), 7.90 – 7.92 ppm (m, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 13.92; 20.29; 29.27; 44.88; 120.04; 121.10; 126.18; 126.34; 131.89; 140.00; 140.54; 144.95; 167.79; 192.56 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for C₁₄H₁₃NOS₄ [M]⁺ 338.98745, found 338.98788. Elementary analysis: calculated for C₁₄H₁₃NOS₄ (339.52): C 49.53, H 3.86, N 4.13, S 37.78; found C 49.85, H 3.75, N 4.44, S 37.61.

Chromophore 1f

The title compound was synthesized from aldehyde 4 and malononitrile (41 mg) following the general procedure. The crude product was purified by column chromatography (silica gel, DCM/hexane, 1:1). Yellow solid. Yield 74 mg (81 %). m.p. = 226°C. $R_f = 0.17$ (silica gel, DCM/hexane, 1:1). ¹H-NMR (500 MHz, 25 °C, CDCl₃): δ = 7.35 (d, 1H, J = 5.0 Hz, Th), 7.77 (d, 1H, J = 5.0 Hz, Th), 7.85 (s, 1H, CH), 7.95 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 113.45; 114.24; 120.19; 130.54; 136.12; 137.15; 140.24; 147.88; 151.80 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for $C_{10}H_4N_2S_2$ [M + H + (DHB)]⁺ 371.01547, found 371.01541. Elementary analysis: calculated for $C_{10}H_4N_2S_2$ (216.28): C 55.53, H 1.86, N 12.95, S 29.65; found C 55.92, H 1.82, N 13.23, S 28.47.

Chromophore 2a

The title compound was synthesized from aldehyde 6 and indan-1,3-dione (91 mg) following the general procedure. The crude product was purified by column chromatography (silica gel, DCM/hexane, 2:1). Yellow solid. Yield 122 mg (99 %). m.p. = 233 °C. R_f = 0.35 (silica gel, DCM/hexane, 2:1). ¹H-NMR

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Elementary analysis: calculated for $C_{14}H_6O_2S_3$ (302.39): C 55.61, H 2.00, S 31.81; found C 56.04, H 1.95, S 33.20.

Chromophore 2e

The title compound was synthesized from aldehyde 6 and *N*-butylrhodanine (117 mg) following the general procedure. The crude product was purified by flash chromatography (silica gel, DCM/hexane, 1:1). Yellow solid. Yield 107 mg (75 %). m.p. = 162 °C. $R_{\rm f}$ = 0.36 (silica gel, DCM/hexane, 1:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 0.96 (t, 3H, J = 7.2 Hz, CH₃), 1.34 – 1.44 (m, 2H, CH₂), 1.65 – 1.73 (m, 2H, CH₂), 4.11 (t, 2H, J = 7.6 Hz, N-CH₂), 7.28 (d, 1H, J = 5.2 Hz, Th), 7.36 – 7.42 (m, 1H, Th), 7.52 (s, 1H, CH), 7.75 (s, 1H, 10 molar % of isomer 2, Th), 7.88 ppm (s, 1H, 90 molar % of isomer 1, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 13.92; 20.29; 29.27; 44.89; 120.55; 120.92; 126.20; 126.41; 129.98; 141.02; 144.24; 147.38; 167.79; 192.53 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for $C_{14}H_{13}NOS_4$ [M + H]⁺ 339.99527, found 339.99522. Elementary analysis: calculated for $C_{14}H_{13}NOS_4$ (339.52): C 49.53, H 3.86, N 4.13, S 37.78; found C 49.87, H 3.75, N 4.43, S 38.41.

Chromophore 2f

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The title compound was synthesized from aldehyde **6** and malononitrile (41 mg) following the general procedure. The crude product was purified by column chromatography (silica gel, DCM/hexane, 1:1). Lemon yellow solid. Yield 74 mg (82 %). m.p. = 192 °C. $R_{\rm f}$ = 0.17 (silica gel, DCM/hexane, 1:1). ¹H-NMR (500 MHz, 25 °C, CDCl₃): δ = 7.31 (d, 1H, *J* = 5.5 Hz, Th), 7.48 (d, 1H, *J* = 5.5 Hz, Th), 7.84 (s, 1H, CH), 7.89 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 113.45; 114.15; 120.73; 130.87; 131.39; 138.23; 146.84; 148.39; 151.66 ppm. HR-FT-MALDI-MS (DHB) *m/z*: calculated for C₁₀H₄N₂S₂ [M + H + (DHB)]⁺ 371.01547, found 371.01555. Elementary analysis: calculated for C₁₀H₄N₂S₂ (216.28): C 55.53, H 1.86, N 12.95, S 29.65; found C 55.35, H 1.79, N 13.09, S 29.50.

General procedure for synthesis of tricyanovinyl TT derivatives

Appropriate thienothiophene **3** or **5** (500 mg, 3.57 mmol) and tetracyanoethylene (548 mg, 4.28 mmol) were dissolved in DMF (5 ml). The reaction mixture was heated at 80 °C for 12 h. After cooling to 25 °C, DCM (100 ml) was added. The organic phase was washed with water (3×100 ml), dried with sodium sulphate, filtered and the solvents were evaporated *in vacuo*.

Chromophore 1g

The title compound synthesized from was thieno[3,2-*b*]thiophene **3** following the general procedure. The crude product was purified by column chromatography (silica gel, DCM/hexane, 2:1). Dark orange solid. Yield 310 mg (36 %). m.p. = 241 °C. R_f = 0.36 (silica gel, DCM/hexane, 2:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 7.38 (d, 1H, J = 5.2 Hz, Th), 7.92 (d, 1H, J = 5.6 Hz, Th), 8.29 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 83.60; 112.05; 112.30; 112.95; 120.31; 132.02; 133.87; 135.63; 139.26; 140.93; 149.56 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for $C_{11}H_3N_3S_2$ [M + H + (DHB)]⁺ 396.01072, found 396.01102. Elementary

analysis: calculated for C₁₁H₃N₃S₂ (241.29): C 54.75_{**} H₁₁H₂O₅ M₁₁H₂O₅ M₁₁H₂O₅ M₁₁H₂O₅ M₁₂H₁₂H₂O₅ M₁₂H₂O₅ M₁₂H₂ M₁₂H₂O₅ M₁₂H₂ M₁₂ M

Chromophore 2g

The title compound was synthesized from thieno[2,3-b]thiophene 5 following the general procedure. The crude product was purified by column chromatography (silica gel, DCM/hexane, 2:1). Orange solid. Yield 388 mg (45 %). m.p. = 230 °C. R_f = 0.34 (silica gel, DCM/hexane, 2:1). ¹H-NMR (400 MHz, 25 °C, CDCl₃): δ = 7.37 (d, 1H, J = 5.2 Hz, Th), 7.54 (d, 1H, J = 5.6 Hz, Th), 8.24 ppm (s, 1H, Th). ¹³C-NMR (125 MHz, 25 °C, CDCl₃): δ = 83.71; 111.86; 112.21; 112.84; 121.02; 132.20; 132.58; 133.70; 136.41; 147.15; 150.73 ppm. HR-FT-MALDI-MS (DHB) m/z: calculated for $C_{11}H_3N_3S_2$ [M + H + (DHB)]⁺ 396.01072, found 396.01121. Elementary analysis: calculated for C₁₁H₃N₃S₂ (241.29): C 54.75, H 1.25, N 17.41, S 26.58; found C 55.10, H 1.21, N 17.44, S 26.53.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 I. F. Perepichka and D. F. Perepichka, Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics, John Wiley and Sons, 2009.
- F. Challenger and Harrison, J. Inst. Pet. Technol., 1935, 21, 135–147.
 - A. Biedermann and P. Jacobson, *Chem. Ber.*, 1886, **19**, 2444–2447.
 - S. H. Mashraqui, S. Ghadigaonkar, M. Ashraf, A. Sri Ranjini, S. Ghosh and P. K. Das, *Tetrahedron*, 2007, **63**, 10011– 10017.
 - I. Meager, R. S. Ashraf, S. Rossbauer, H. Bronstein, J. E. Donaghey, J. Marshall, B. C. Schroeder, M. Heeney, T. D. Anthopoulos and I. McCulloch, *Macromolecules*, 2013, **46**, 5961–5967.
 - T. Inouchi, T. Nakashima and T. Kawai, Chem. Asian J., 2014, 9, 2542–2547.
 - A. Zhang, H. Xiao, S. Cong, M. Zhang, H. Zhang, S. Bo, Q. Wang, Z. Zhen and X. Liu, *J. Mater. Chem. C*, 2015, **3**, 370–381.
 - S. S. M. Fernandes, M. C. R. Castro, I. Mesquita, L. Andrade, A. Mendes and M. M. M. Raposo, *Dyes Pigm.*, 2017, **136**,

3

4

5

6

7

8

31

36

37

38

41

42

43

Journal Name

46–53.

- J. K. Lee, S. Lee and S. J. Yun, *Bull. Korean Chem. Soc.*, 2013,
 34, 2148–2154.
- J. Kulhánek, F. Bureš, J. Opršal, W. Kuznik, T. Mikysek and
 A. Růžička, Asian J. Org. Chem., 2013, 2, 422–431.
- 11 W. Tang, T. Lin, L. Ke and Z.-K. Chen, *J. Polym. Sci. Part A* 32 *Polym. Chem.*, 2008, **46**, 7725–7738.
- 12 E. N. Rodlovskaya, V. A. Vasnev, A. V Naumkin, A. A. Vashchenko and D. O. Goriachiy, *High Perform. Polym.*, 2017, **29**, 704–707.
- Q. Zhang, Y. Wang, B. Kan, X. Wan, F. Liu, W. Ni, H. Feng, T.
 P. Russell and Y. Chen, *Chem. Commun.*, 2015, **51**, 15268– 15271.
- V. Tamilavan, S. Kim, J. Sung, D. Y. Lee, S. Cho, Y. Jin, J. Jeong, S. H. Park and M. H. Hyun, Org. Electron. Phys., Mater. Appl., 2017, 42, 34–41.
- H. S. Lee, J. S. Lee, A. R. Jung, W. Cha, H. Kim, H. J. Son, J. H.
 Cho and B. S. Kim, *Polym*, 2016, **105**, 79–87.
- S. Zhu, Z. An, X. Chen, P. Chen and Q. Liu, *Dyes Pigm.*, 2015, 116, 146–154.
- X. Liu, F. Kong, F. Guo, T. Cheng, W. Chen, T. Yu, J. Chen, Z.
 Tan and S. Dai, *Dyes Pigm.*, 2017, **139**, 129–135.
- S.-H. Peng, T.-W. Huang, G. Gollavelli and C.-S. Hsu, J. 39 Mater. Chem. C, 2017, 5, 5193–5198.
- M. Durso, D. Gentili, C. Bettini, A. Zanelli, M. Cavallini, F. De Angelis, M. Grazia Lobello, V. Biondo, M. Muccini, R. Capelli and M. Melucci, *Chem. Commun.*, 2013, **49**, 4298–4300.
- Y. Shu, A. Mikosch, K. N. Winzenberg, P. Kemppinen, C. D.
 Easton, A. Bilic, C. M. Forsyth, C. J. Dunn, T. B. Singh and G.
 E. Collis, *J. Mater. Chem. C*, 2014, 2, 3895–3899.
- Z. Fei, P. Pattanasattayavong, Y. Han, B. C. Schroeder, F. Yan, R. J. Kline, T. D. Anthopoulos and M. Heeney, J. Am. Chem. Soc., 2014, 136, 15154–15157.
- J. Yue, S. Sun, J. Liang, W. Zhong, L. Lan, L. Ying, F. Huang,
 W. Yang and Y. Cao, J. Mater. Chem. C, 2016, 4, 2470– 2479.
- S. Mu, K. Oniwa, T. Jin, N. Asao, M. Yamashita and S. Takaishi, Org. Electron. Phys., Mater. Appl., 2016, 34, 23–27.
- 24 M. Blenkle, P. Boldt, C. Bräuchle, W. Grahn, I. Ledoux, H. Nerenz, S. Stadler, J. Wichern and J. Zyss, *J. Chem. Soc. Perkin Trans. 2*, 1996, 1377–1384.
- A. B. Marco, R. Andreu, S. Franco, J. Garín, J. Orduna, B. Villacampa, B. E. Diosdado, J. T. López Navarrete and J. Casado, Org. Biomol. Chem., 2013, 11, 6338–6349.
- A. B. Marco, R. Andreu, S. Franco, J. Garín, J. Orduna, B.
 Villacampa and R. Alicante, *Tetrahedron*, 2013, 69, 3919–3926.
- M. M. M. Raposo, C. Herbivo, V. Hugues, G. Clermont, M. C. R. Castro, A. Comel and M. Blanchard-Desce, *Eur. J. Org. Chem.*, 2016, 2016, 5263–5273.
- 28 S. H. Mashraqui, Y. S. Sangvikar and A. Meetsma, *Tetrahedron Lett.*, 2006, **47**, 5599–5602.
- M. Klikar, V. Jelínková, Z. Růžičková, T. Mikysek, O. Pytela,
 M. Ludwig and F. Bureš, *Eur. J. Org. Chem.*, 2017, 2017,
 2764–2779.
- 30 P. Solanke, S. Achelle, N. Cabon, O. Pytela, A. Barsella, B.

Caro, F. Robin-le Guen, J. Podlesný, M. Klikar, and Feileures. Dyes Pigm., 2016, 134, 129–138. DOI: 10.1039/C9OB00487D

- M. R. Busireddy, V. N. R. Mantena, N. R. Chereddy, B. Shanigaram, B. Kotamarthi, S. Biswas, G. D. Sharma and J. R. Vaidya, *Org. Electron.*, 2016, **37**, 312–325.
- K. Ogura, R. Zhao, T. Mizuoka, M. Akazome and S. Matsumoto, Org. Biomol. Chem., 2003, 1, 3845–3850.
- 33 K. B. Landenberger and A. J. Matzger, *Cryst. Growth Des.*, 2012, 12, 3603–3609.
- 34 A. A. Isse and A. Gennaro, J. Phys. Chem. B, 2010, 114, 7894–7899.
- C. Haffner, W. Heni, Y. Fedoryshyn, J. Niegemann, A. Melikyan, D. L. Elder, B. Baeuerle, Y. Salamin, A. Josten, U. Koch, C. Hoessbacher, F. Ducry, L. Juchli, A. Emboras, D. Hillerkuss, M. Kohl, L. R. Dalton, C. Hafner and J. Leuthold, *Nat. Photonics*, 2015, 9, 1–5.
 - L. R. Dalton, P. A. Sullivan and D. H. Bale, *Chem. Rev.*, 2010, **110**, 25–55.
 - H. Xu, D. Yang, F. Liu, M. Fu, S. Bo, X. Liu and Y. Cao, *Phys. Chem. Chem. Phys*, 2015, **17**, 29679–29688.
 - I. V. Kityk, R. I. Mervinskii, J. Kasperczyk and S. Jossi, Mater. Lett., 1996, 27, 233–237.
 - E. Gondek, J. Nizioł, A. Danel, M. Kucharek, J. Jędryka, P. Karasiński, N. Nosidlak and A. A. Fedorchuk, *Dyes Pigm.*, 2019, **162**, 741–745.
- A. A. Fedorchuk, Y. I. Slyvka, E. A. Goreshnik, I. V. Kityk, P.
 Czaja and M. G. Mys'kiv, *J. Molec. Struct.*, 2018, **1171**, 644–649.
 - Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
 - MOPAC2016, Version: 18.184W, James J. P. Stewart, Stewart Computational Chemistry, web: http://OpenMOPAC.net.
 - K. Aggarwal and J. M. Khurana, Spectrochim. Acta, Part A, 2015, **143**, 288–297.

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