

Synthesis of indole-based chromophores with TCF acceptor and the study of the quinoxalinone core effect on the linear and nonlinear optical properties

Liliya N. Islamova,^a Alexey A. Kalinin,^{*a} Polina V. Lebedeva,^a Guzel M. Fazleeva,^a Olga D. Fominykh,^a and Marina Yu. Balakina^{a,b}

^a Arbuzov Institute of Organic and Physical Chemistry FRC Kazan Scientific Center of Russian Academy of Sciences, Arbuzov Str. 8, 420088 Kazan, Russia

^b Kazan Federal University, Alexander Butlerov Institute of Chemistry, 420111, Kremlin Str. 29, Building 1, Kazan, Russia

Email: kalesha007@mail.ru

Dedicated to Prof. Budnikova in recognition of her scientific contributions to the fields of organic chemistry, electrochemistry, and catalysis

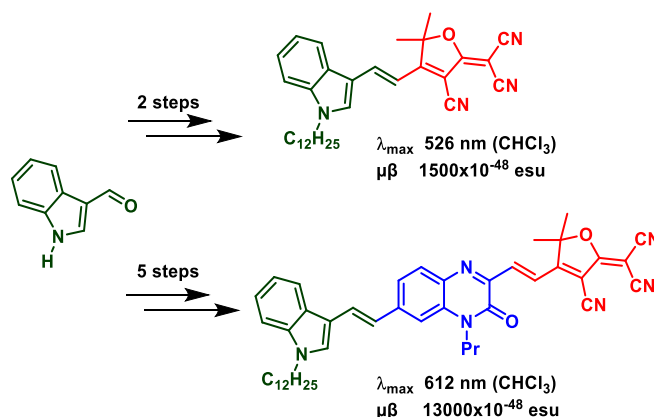
Received 09-08-2022

Accepted Manuscript 10-25-2022

Published on line 11-10-2022

Abstract

D— π —A chromophores with indole donor and tricyanofuranyl acceptor moieties connected by vinylenes and divinyl quinoxalinone π -conjugated bridges have been synthesized and their linear and nonlinear optical properties were studied. Chromophores exhibit intramolecular charge-transfer (ICT) absorption band in the visible region, positive solvatochromism, and are transparent at 850 nm. The indole-based chromophore with divinylquinoxalinone π -conjugation bridge shows large $\mu\beta$ value ($\sim 13000 \cdot 10^{-48}$ esu); the incorporation of the vinyl quinoxalinone unit leads to a significant increase in the values of the first hyperpolarizability.



Keywords: NLO chromophore, indole, quinoxaline-2-one, tricyanofuran, first hyperpolarizability

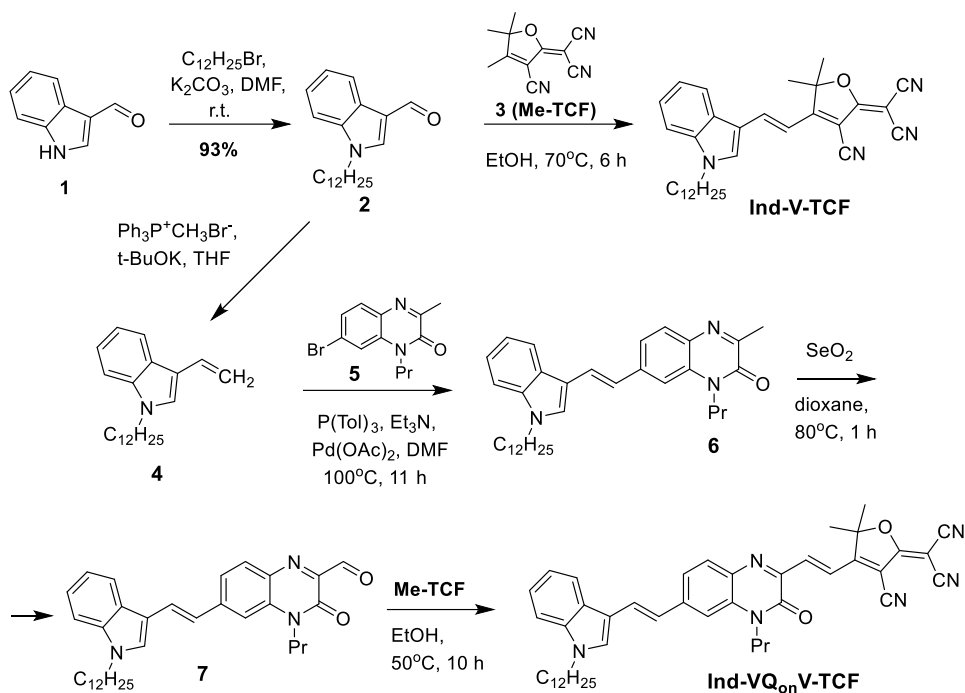
Introduction

Quinoxaline dyes due to their optical properties have found technical applications as electroluminescent materials, organic semiconductors and as suitable ligands in coordination chemistry.¹⁻³ The combination of the quinoxaline core with other aromatic, heteroaromatic, ethylene, and acetylene moieties results in the tuning of the photophysical properties of such polyconjugated quinoxaline-based chromophores. Aminostyrylquinoxaline compounds exhibit luminescent properties,⁴⁻¹³ manifest halochromism,^{4,8} mechanofluorochromism,⁹⁻¹¹ the ability of gelation¹³ providing the development of pH and metal ions sensors and dye-sensitized solar cells (DSSC) devices^{14,15} on their basis. Compounds both with quinoxaline and various other heterocyclic cores (pyrrole,^{16,17} indolizine,¹⁸⁻²¹ quinoline,²² thiophene,²³ carbazole²⁴) in one molecule can be used as sensors for some cations^{16,18,22} and anions,¹⁷ and as pH sensors²³ as well. At the same time they are interesting for application in the redox-switched binding,¹⁸ and creation of organic light-emitting diodes (OLEDs).²⁴ Chromophores with quinoxaline core as a π -bridge component in D- π -A dyes exhibit rather high nonlinear optical (NLO) activity both at the molecular level (theoretical prediction²⁵⁻²⁸) and macroscopic level in composite materials.²⁶⁻²⁸

π -Excessive indole heterocyclic system attracts the attention of researchers as a new type of non-aniline donor in NLO chromophores.²⁹⁻³¹ At the same time, up to now indole-based chromophores with a short bridge were mainly studied.^{29,30} In this article, we have synthesized two chromophores with an indole donor, vinylene or divinylquinoxalinone π -bridge, and a tricyanofuran (TCF) acceptor, studied their optical (linear and nonlinear) properties, and examined the effect of vinylquinoxalinone unit on these properties by comparing the characteristics of the obtained chromophores.

Results and Discussion

Indole-based chromophore with short vinylene π -bridge **Ind-V-TCF** has been synthesized via a two-step procedure starting from indole-3-carboxaldehyde: alkylation by dodecylbromide with the formation of *N*-dodecyl derivative **2**³² and following Knoevenagel condensation with 3-cyano-2-dicyanomethylene-4,4,5-trimethyl-2,5-dihydrofuran (**Me-TCF**)³³ (Scheme 1). The long-chain dodecyl substituent was used to increase the chromophore solubility in organic solvents. Nowadays Me-TCF is widely used as a strong electron acceptor moiety in the structure of chromophores exerting NLO properties.³⁴⁻³⁶ Introduction of vinylquinoxalinonyl moiety in the π -bridge with an aim to prepare an "extended" chromophore **Ind-VQ_{on}V-TCF** brings about three additional steps. Olefin **4** obtained from aldehyde **2** via Wittig reaction reacts with 7-bromo-3-methyl-1-propylquinoxalin-2-one³⁷ to give 1,2-disubstituted olefin product **6** (Heck reaction). Oxidation of compound **6** by selenium dioxide results in formation of quinoxalinone-based aldehyde **7**, which reacts with **Me-TCF** in ethanol under base-free conditions to form the desired chromophore **Ind-VQ_{on}V-TCF** in a moderate yield. All 1,2-disubstituted olefin derivatives were obtained as *E*-isomers: $J_{H-C=CH}$ 16 Hz in ¹H NMR spectra.



Scheme 1. Synthesis of chromophores **Ind-V-TCF** and **Ind-VQ_{on}V-TCF**.

Photophysical properties of dyes were studied in solvents of different polarity ($\epsilon = 2\div 39$, Figure 1, Table 1). ICT absorption band of both dyes is manifested in the visible region. Elongation of π -bridge by quinoxalinone-vinyl unit leads to bathochromic shift of absorption maximum of **Ind-VQ_{on}V-TCF** in all solvents by 61-86 nm. This is slightly less than the bathochromic shift caused by the introduction of an additional vinyl thiophene moiety in the π -bridge (up to 94 nm in chloroform solution).³⁸ Chromophore **Ind-VQ_{on}V-TCF** exhibits blue shift (12 nm and 54 nm in CHCl_3) in UV-Vis spectra in comparison with chromophores **DMA-VQ_{on}V-TCF**³⁹ and **DBA-VQ_{on}V-TCF**²⁷ with dimethyl/dibutylaniline donors, correspondingly, and the same π -bridge and acceptor moiety. Comparing the chromophores of the dialkylaniline-vinylthiophenyl-tricyanofuran composition⁴⁰ and **Ind-VQ_{on}V-TCF**, one can note that the replacement of the divinylthiophene bridge by divinylquinoxalinone one and the replacement of the dialkylaniline donor by indole one leads to a noticeable hypsochromic shift (up to 73 nm in chloroform solution) of the absorption maximum of the chromophore **Ind-VQ_{on}V-TCF**, making it transparent in the short-wavelength infrared region (at 850 nm). Both chromophores are characterized by solvatochromism: positive solvatochromic shifts of 31 and 39 nm are observed when passing from 1,4-dioxane to chloroform. Due to its low polarity, dioxane stabilizes mainly the ground state, which is less polar than the excited one. As a result, greater amount of energy is required to transfer the electron density from a donor to an acceptor causing the blue shift of absorption maximum compared to the case of more polar solvents. An increase in the polarity of the solvent upon passing from dioxane to chloroform (dichloromethane) leads to a greater stabilization of the excited state, resulting in the decrease of the energy gap and the red shift of the absorption band in chloroform. Chromophore **Ind-VQ_{on}V-TCF** exhibits significantly greater negative solvatochromic shift in comparison with that for **Ind-VQ_{on}V-TCF** (Table 1).

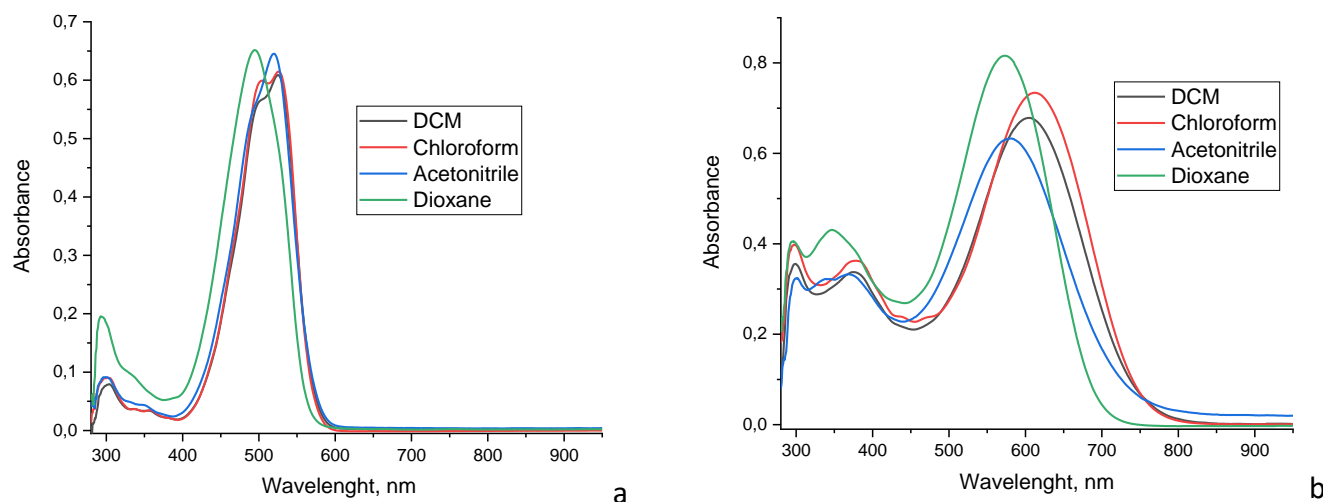


Figure 1. Experimental electronic absorption spectra of **Ind-V-TCF** (a) and **Ind-VQ_{on}V-TCF** (b).

Table 1. Photophysical properties of **Ind-V-TCF** and **Ind-VQ_{on}V-TCF**

Compound	λ_{\max} , nm/eV (ϵ , $10^3 \cdot \text{M}^{-1} \cdot \text{cm}^{-1}$)				$\Delta\lambda_{\max}^a$, nm/eV	$\Delta\lambda_{\max}^b$, nm/eV
	1,4-dioxane	CHCl ₃	CH ₂ Cl ₂	CH ₃ CN		
Ind-V-TCF	495/2.50 (46.5)	526/2.36 (43.9)	525/2.36 (43.5)	520/2.38 (49.6)	31/0.14	6/0.02
Ind-VQ_{on}V-TCF	573/2.16 (32.6)	612/2.02 (29.4)	605/2.05 (27.1)	581/2.13 (25.3)	39/0.14	31/0.10

^a – dioxane/CHCl₃.

^b – CHCl₃/CH₃CN.

The structure of both chromophores was optimized at the B3LYP//6-31G* level, as a result of which conformers **Ind-V-TCF-I** and **Ind-VQ_{on}V-TCF-I** were obtained (Figure 2). The conformational search in the OPLS4 force field resulted in a number of conformers, and subsequent refinement of the geometry of the minimum energy conformer by optimization, provided conformers **Ind-V-TCF-II** and **Ind-VQ_{on}V-TCF-II** (Figure 3).

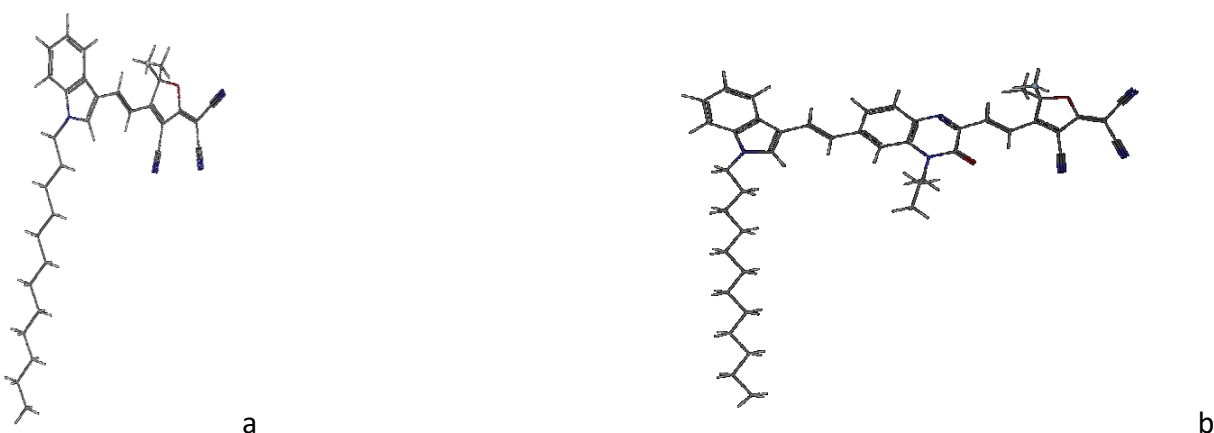


Figure 2. Optimized structures of chromophores **Ind-V-TCF-I** (a), **Ind-VQ_{on}V-TCF-I** (b).

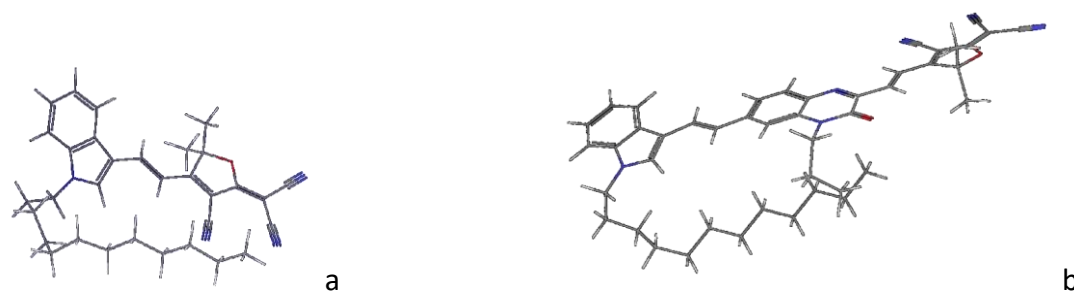


Figure 3. Optimized structures of conformers **Ind-V-TCF-II** (a) and **Ind-VQ_{on}V-TCF-II** (b).

The dihedral angles between the structural units of the chromophores are given in Table 2, for conformers **I** the dodecyl substituents are elongated and arranged almost perpendicular to the chromophore skeleton (Figure 2), and for conformers **II**, the dodecyl substituent is extended along the backbone of the molecules (Figure 3).

Table 2. The dihedral angles between the units of the chromophores **Ind-V-TCF-I,II** and **Ind-VQ_{on}V-TCF-I,II**, determined from the conformational search and as a result of optimization at the B3LYP/6-31G(d) level (D – donor, B – bridge, A – acceptor moieties; Ind denotes the angles between cycles in indole moiety, B denotes the angles between cycles in quinoxalinone moiety)

Angle, °	Ind-V-TCF-I	Ind-V-TCF-II	Ind-VQ_{on}V-TCF-I	Ind-VQ_{on}V-TCF-II
	opt	Conf Search/opt	opt	Conf Search/opt
D-B			45.5	17.9/15.6
B-A			5.7	2.7/4.3
Ind	0.0	1.1/1.6	0.5	0.7/0.1
D-A	0.4	25.2/22.8	51.8	20.7/20.8
B			1.7	0.4/1.0

As can be seen from Table 2, the **Ind-V-TCF-I** conformer is quite flat, while in the **Ind-V-TCF-II** conformer the angle between the donor and acceptor is about 20°, i.e. the dodecyl substituent, being located along the chromophore backbone, somewhat distorts the chromophore (Figure 3a). In the case of the **Ind-VQ_{on}V-TCF-I** chromophore, the dodecyl substituent distorts the chromophore, leading to a noticeable twisting of the donor fragment relative to the bridge (the angle between the donor and the bridge and the donor and acceptor is 45.5° and 51.8°, respectively). The rest of the chromophore remains flat, the deviation does not exceed 6°. The conformer **Ind-VQ_{on}V-TCF-II** is characterized by a flatter structure than that of **Ind-VQ_{on}V-TCF-I**: the angle between the donor and the bridge is 17.9°. In the optimized structure, this angle is 15.6° (Table 2). The **Ind-V-TCF-II** and **Ind-VQ_{on}V-TCF-II** conformers have fairly flat backbone structures.

The electric molecular characteristics of chromophores, calculated at M06-2X//aug-cc-pVDZ level for optimized structures of **Ind-V-TCF-I,II** and **Ind-VQ_{on}V-TCF-I,II** conformers, are summarized in Table 3. The dipole moments and polarizabilities of one chromophore differ little depending on the conformer; as for β_{tot} , its value is somewhat larger (by ~10%) for **Ind-V-TCF-I** compared to **Ind-V-TCF-II**, which is consistent with the structure of conformers: **Ind-V-TCF-I** is flatter than **Ind-V-TCF-II**; for the **Ind-VQ_{on}V-TCF-II** conformer, β_{tot} is

slightly higher (by ~8%) than for **Ind-VQ_{on}V-TCF-I**, what is also in agreement with the flatter structure of **Ind-VQ_{on}V-TCF-II**. Comparison of the properties of the **Ind-V-TCF-I,II** and **Ind-VQ_{on}V-TCF-I,II** chromophores shows that chromophores with a divinylquinoxalinone bridge have larger dipole moment values (by ~25%), approximately doubled polarizability values, and strongly different β_{tot} values - in the case of conformers **Ind-V-TCF-I** and **Ind-VQ_{on}V-TCF-I** the difference is ~ 6 times, and for **Ind-V-TCF-II** and **Ind-VQ_{on}V-TCF-II** it reaches 8 times, demonstrating the efficiency of divinylquinoxalinone bridge compared to vinylene one. Even greater differences were found in the values of chromophore figure-of-merit $\mu\beta$ – in the case of the **Ind-VQ_{on}V-TCF-I** chromophore, it reaches $\sim 13000 \cdot 10^{-48}$ esu, that, in combination with optical transparency at a wavelength of 850 nm, makes it possible to consider such a chromophore as a promising candidate to be used in EO modulators with operating wavelength 850 nm.⁴¹ For previously explored chromophores, which were transparent at 850 nm, the $\mu\beta$ value was up to $7300 \cdot 10^{-48}$ esu. Changing indole donor for dibutylaniline one in **DBA-VQ_{on}V-TCF** leads to the growth of β value by ~45%, however, this is accompanied by a noticeable bathochromic absorption maximum shift in electronic spectrum.^{27,28}

Table 3. Dipole moment, μ , D, linear polarizability, α , $\cdot 10^{-24}$ esu, and first hyperpolarizability, β_{tot} , $\cdot 10^{-30}$ esu, of the **Ind-V-TCF** and **Ind-VQ_{on}V-TCF** chromophores (M06-2X/aug-cc-pVDZ//B3LYP/6-31G(d) level)

Property	Ind-V-TCF-I	Ind-V-TCF-II	Ind-VQ_{on}V-TCF-I	Ind-VQ_{on}V-TCF-II
μ_{tot}	16.5	17.3	22.3	21.0
$\alpha(\text{av})$	71.8	67.7	122.1	119.5
β_{tot}	95	80	591	641
$\mu\beta$	1533	1194	13068	11690

Conclusions

Two new indole-based D— π —A chromophores with tricyanofuranyl acceptor and short vinylene (**Ind-V-TCF**) and divinylquinoxalinone (**Ind-VQ_{on}V-TCF**) π -conjugated bridges have been synthesized by a multistep procedure. Both chromophores exhibit intramolecular charge-transfer (ICT) absorption band in the visible region and positive solvatochromism. The lengthening of π -bridge by vinylquinoxalinone unit leads to a significant increase in the values of the first hyperpolarizability (by 6–8 times) and an even greater increase in the $\mu\beta$ value (by 8-10 times). The large $\mu\beta$ value ($\sim 13068 \cdot 10^{-48}$ esu) in combination with optical transparency at a wavelength of 850 nm makes the **Ind-VQ_{on}V-TCF** chromophore a promising candidate for further research aimed at creating electro-optic devices operating in the shortwave infrared window.

Experimental Section

General. The IR, NMR, UV-vis spectra and elemental analysis were registered on the equipment of Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS. Infrared (IR) spectra were recorded on the Bruker Vector-22 FT-IR spectrometer. NMR experiments were performed with AVANCE-400 (400 MHz for ¹H

NMR, 100 MHz for ^{13}C NMR) spectrometer. Chemical shifts (δ in ppm) are referenced to the solvents. UV–vis spectra were recorded at room temperature on a UV-6100 Ultraviolet/Visible Spectrophotometer using 10 mm quartz cells. Spectra were registered with a scan speed of 480 nm/min, using a spectral width of 1 nm. All samples were prepared in solution with the concentrations of ca $\sim 1.4\text{--}2.5 \cdot 10^{-5}$ mol/L. The melting points, mp, of chromophores were determined by Melting Point Meter MF-MP-4. Organic solvents used were purified and dried according to standard methods. The reaction progress and the purity of the obtained compounds were controlled by TLC on Sorbfil UV-254 plates with visualization under UV light. The elemental analysis was carried out on a CHNS analyzer Vario Macro cube (Elementar Analysensysteme GmbH, Germany). The samples were weighed on Sartorius Cubis II (Germany) microbalance in tin capsules. VarioMacro Software V4.0.11 was used to evaluate the data received.

DFT calculations. Structure of the studied chromophores and their electric characteristics (dipole moments, μ , molecular polarizability, α , components of first hyperpolarizability tensor, β_{ijk}) were calculated in the framework of Density Functional Theory (DFT). Chromophores geometrical parameters were optimized in gas phase at B3LYP//6-31G(d) level. To reveal the variety of chromophore conformers, conformational search was performed with OLPS4 force field,⁴² the structure of the most stable conformer was then refined by DFT. Electric characteristics of two pairs of the conformers, differing by mutual arrangement of dodecyl substituent in donor and the chromophore skeleton, were calculated at the M06-2X//aug-cc-pVDZ level; the use of M06-2X density functional^[43,44] and Dunning basis sets^[45,46] are recognized as an adequate choice for this purpose.^[47,48] The value of β_{tot} is calculated as

$$\beta_{\text{tot}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}; \beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq k} (\beta_{ikk} + \beta_{kik} + \beta_{kki}), \quad i = x, y, z.$$

The conformational search is performed with Macromodel program,⁴⁹ calculations of geometrical parameters and chromophore electric properties are performed by Jaguar program package.^{50,51}

(E)-2-(3-Cyano-4-(2-(1-dodecyl-1H-indol-3-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (Ind-V-TCF). A mixture of aldehyde **2** (100 mg, 0.319 mmol), **Me-TCF** (64 mg, 0.321 mmol) and anhydrous ethanol (0.2 mL) was stirred for 6 h at 70 °C, then cooled to room temperature. The reaction mixture was filtered through a Schott funnel, the precipitate was washed with ethanol (1 mL x 3), dried. Yield 115 mg (73%). Purple powder; mp 168–169 °C; R_f 0.287 (CH_2Cl_2). IR (ν_{max} , cm^{-1} , KBr): 2923 (C-H), 2852 (C-H), 2225, 1544 (C=N, C=C), 1496, 1480, 1398, 1375, 1340, 1289, 1245, 1231, 1205, 1152, 1129, 1109, 800, 746. ^1H NMR (400 MHz, CDCl_3) δ : 8.05 (d, J 15.9 Hz, 1H, H-ethene), 7.90 (m, 1H), 7.74 (s, 1H), 7.50 – 7.34 (m, 3H), 6.88 (d, J 15.9 Hz, 1H, H-ethene), 4.21 (t, J 7.2 Hz, 2H, NCH_2), 1.96–1.88 (m, 2H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.78 (s, 6H, CH_3), 1.40–1.31 (m, 4H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 1.30–1.24 (m, 14H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 0.87 (t, J 6.8 Hz, 3H, $\text{N}(\text{CH}_2)_{11}\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3) δ : 176.5 (C), 175.0 (C), 142.2 (CH), 138.3 (C), 137.3 (CH), 125.8 (C), 124.6 (CH), 123.5 (CH), 121.0 (CH), 114.5 (C), 112.7 (C), 112.0 (C), 111.7 (C), 111.3 (CH), 109.2 (CH), 96.8 (C), 93.0 (C), 54.3 (C), 47.6 (CH), 31.9 (CH), 29.7 (CH), 29.6 (2CH), 29.5 (CH), 29.4 (CH), 29.3 (CH), 29.1 (CH), 26.84 (CH), 26.76 (CH), 22.6 (CH), 14.1 (CH). Anal. calcd. (%) for $\text{C}_{32}\text{H}_{38}\text{N}_4\text{O}$ (494.30): C, 77.70; H, 7.74; N, 11.33; found C, 77.51; H, 7.80; N, 11.30.

1-Dodecyl-3-vinyl-1H-indole (4). To the stirred under argon mixture of methyl triphenylphosphonium bromide (411 mg, 1.2 mmol), THF (2 mL) potassium *tert*-butylate (215 mg, 2 mmol) was added. The mixture was stirred for 1 h while cooling to 0 °C and 1-dodecyl-1H-indole-3-carbaldehyde (300 mg, 1 mmol) solution in THF (1 mL) was added. The mixture was stirred for 4 h at room temperature. Solvent was evaporated under vacuum. The residue was solved in hexane and kept at 5 °C for 24 h. The next day, the precipitate was filtered, the filtrate was evaporated to give the yellow oil. Yield 148 mg (50%). R_f 0.42 (hexane). IR (ν_{max} , cm^{-1} , KBr): 2926 (C-H),

2854 (C-H), 1627, 1532, 1469, 1394, 1186, 1121, 878, 750. ^1H NMR (400 MHz, CDCl_3) δ : 7.39–7.22 (m, 4H), 7.16 (s, 1H), 7.00–6.93 (m, 1H), 5.78 (dd, J 17.8, 1.6 Hz, 1H, H-ethene), 5.23 (dd, J 11.3, 1.6 Hz, 1H, H-ethene), 4.03 (t, J 7.2 Hz, 2H, NCH_2), 1.86–1.78 (m, 2H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.46–1.25 (m, 18H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_9\text{CH}_3$), 1.02 (t, J 6.8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ : 136.7 (C), 129.3 (CH), 128.3 (CH), 128.1 (C), 126.9 (CH), 121.6 (CH), 120.0 (CH), 119.6 (CH), 113.9 (C), 109.4 (CH), 46.0 (CH), 31.7 (CH), 29.9 (CH), 29.41 (CH), 29.35 (CH), 29.3 (CH), 29.1 (CH), 29.0 (CH), 26.7 (CH), 22.5 (CH), 13.9 (CH). Anal. calcd. (%) for $\text{C}_{22}\text{H}_{33}\text{N}$ (311.26): C, 82.83; H, 10.68; N, 4.50; found C, 82.77; H, 10.80; N, 4.51.

(E)-7-(2-(1-Dodecyl-1H-indol-3-yl)vinyl)-3-methyl-1-propylquinoxalin-2(1H)-one (6). A mixture of olefin **4** (148 mg, 0.48 mmol), quinoxalinone **5** (134 mg, 0.48 mmol), tri(*o*-tolyl)phosphine (14 mg, 0.048 mmol), $\text{Pd}(\text{OAc})_2$ (5 mg, 0.022 mmol), Et_3N (120 mg, 1.19 mmol), and anhydrous DMF (1 mL) was stirred for 11 h at 100 °C. The reaction mixture was cooled, poured into water, and extracted with CH_2Cl_2 . The organic layer was separated, washed with water, dried over anhydrous MgSO_4 , filtered. The solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent petroleum ether – EtOAc, 5:1) to give product **6**. Yield 106 mg (44%). Yellow oil; R_f 0.375 (hexane/EtOAc, 1:0.3). IR (ν_{max} , cm^{-1} , KBr): 2953 (C-H), 2926 (C-H), 2854 (C-H), 1653 (C=O), 1605 (C=N, C=C), 1532, 1468, 1396, 1373, 1162, 1115, 951, 739. ^1H NMR (400 MHz, CDCl_3) δ : 8.03 (dd, J 7.2, 1.5 Hz, 1H), 7.76 (d, J 8.4 Hz, 1H), 7.54 (dd, J 8.4, 1.7 Hz, 1H), 7.43 (d, J 16.3 Hz, 1H, H-ethene), 7.39 (dd, J 7.6, 1.5 Hz, 1H), 7.35 (s, 1H), 7.34 – 7.22 (m, 3H), 7.18 (d, J 16.3 Hz, 1H, H-ethene), 4.28–4.24 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 4.12 (t, J 7.2 Hz, 2H, $\text{NCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 2.61 (s, 1H, CH_3), 1.92–1.82 (m, 4H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.38–1.32 (m, 4H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 1.31–1.22 (m, 14H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 1.12 (t, J 7.4 Hz, 3H, $\text{N}(\text{CH}_2)_2\text{CH}_3$), 0.90 (t, J 6.8 Hz, 3H, $\text{N}(\text{CH}_2)_{11}\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3) δ : 156.6 (C), 155.2 (C), 140.3 (C), 137.1 (C), 132.9 (C), 131.8 (C), 129.7 (CH), 128.5 (CH), 126.1 (C), 124.3 (CH), 123.3 (CH), 122.4 (CH), 120.4 (CH), 120.3 (CH), 120.2 (CH), 113.6 (C), 110.6 (CH), 109.9 (CH), 46.5 (CH), 43.6 (CH), 31.9 (CH), 30.1 (CH), 29.6 (2CH), 29.5 (CH), 29.4 (CH), 29.3 (CH), 29.2 (CH), 26.9 (CH), 22.6 (CH), 21.4 (CH), 20.6 (CH), 14.1 (CH), 11.4 (CH). Anal. calcd. (%) for $\text{C}_{34}\text{H}_{45}\text{N}_3\text{O}$ (511.36): C, 79.80; H, 8.86; N, 8.21; found C, 79.75; H, 8.95; N, 8.20.

(E)-6-(2-(1-Dodecyl-1H-indol-3-yl)vinyl)-3-oxo-4-propyl-3,4-dihydroquinoxaline-2-carbaldehyde (7). A mixture of compound **6** (56 mg, 0.110 mmol), selenium dioxide (15 mg, 0.135 mmol) and dioxane (0.5 mL) was stirred at 80 °C for 1 h under argon and then cooled to room temperature. The solvent was removed at reduced pressure, and the residue was purified by silica-gel column chromatography (eluent: hexane / ethyl acetate 5:2). Yield 25 mg (43%). Burgundy powder; mp 103–105 °C, R_f 0.275 (hexane: ethyl acetate 1:0.5). IR (ν_{max} , cm^{-1} , KBr): 2955 (C-H), 2924 (C-H), 2852 (C-H), 1722 (C=O), 1645 (C=O), 1592 (C=N, C=C), 1506, 1468, 1438, 1395, 1384, 1170, 1136, 948, 736. ^1H NMR (400 MHz, CDCl_3) δ : 10.45 (s, 1H, CHO), 8.01 (dd, J 7.1, 1.6 Hz, 1H), 7.98 (d, J 8.6 Hz, 1H), 7.63 (dd, J 8.6, 1.6 Hz, 1H), 7.55 (d, J 16.2 Hz, 1H, H-ethene), 7.41 (s, 1H), 7.40–7.25 (m, 4H) 7.17 (d, J 16.2 Hz, 1H, H-ethene), 4.31–4.27 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 4.14 (t, J 7.2 Hz, 2H, $\text{NCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 1.93–1.83 (m, 4H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.37–1.31 (m, 4H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 1.30–1.21 (m, 14H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 1.13 (t, J 7.4 Hz, 3H, $\text{N}(\text{CH}_2)_2\text{CH}_3$), 0.87 (t, J 6.8 Hz, 3H, $\text{N}(\text{CH}_2)_{11}\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3) δ : 189.6 (CH), 154.9 (C), 145.4 (C), 144.3 (C), 137.4 (C), 135.1 (C), 133.0 (CH), 132.1 (C), 129.9 (CH), 127.5 (CH), 126.0 (C), 122.8 (CH), 122.4 (CH), 121.4 (CH), 120.8 (CH), 120.3 (CH), 113.5 (C), 110.5 (CH), 110.2 (CH), 46.8 (CH), 43.5 (CH), 31.9 (CH), 30.0 (CH), 29.6 (2CH), 29.53 (CH), 29.45 (CH), 29.3 (CH), 29.2 (CH), 27.0 (CH), 22.7 (CH), 20.7 (CH), 14.1 (CH), 11.5 (CH). Anal. calcd. (%) for $\text{C}_{34}\text{H}_{43}\text{N}_3\text{O}_2$ (525.34): C, 77.68; H, 8.24; N, 7.99; found C, 77.48; H, 8.19; N, 7.85.

2-(3-Cyano-4-((E)-2-(6-((E)-2-(1-dodecyl-1H-indol-3-yl)vinyl)-3-oxo-4-propyl-3,4-dihydroquinoxalin-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (Ind-VQ_{on}V-TCF). A mixture of aldehyde **7** (20 mg, 0.038 mmol), Me-TCF (7 mg, 0.035 mmol) and anhydrous ethanol (0.1 mL) was stirred for 10 h at 50 °C, then

cooled to room temperature. The solvent was removed at reduced pressure, and the residue was purified by silica-gel column chromatography (eluent: hexane / ethyl acetate 50:10). Yield 8 mg (30%). Black powder; mp 183-184 °C, R_f 0.46 (hexane: ethyl acetate 1:0.5). IR (ν_{\max} , cm^{-1} , KBr): 2924 (C-H), 2853 (C-H), 2228, 1655 (C=O), 1581 (C=N, C=C), 1528, 1485, 1436, 1374, 1285, 1161, 1135, 962, 748. ^1H NMR (400 MHz, CDCl_3) δ : 8.02 (d, J 8.0 Hz, 1H), 7.99 (s, 2H, H-ethene), 7.84 (d, J 8.5 Hz, 1H), 7.64 (dd, J 8.7, 1.6 Hz, 1H), 7.57 (d, J 16.2 Hz, 1H, H-ethene), 7.43 (s, 1H), 7.41 (d, J 8.4 Hz, 1H), 7.36–7.27 (m, 1H), 7.25 (s, 1H), 7.18 (d, J 16.2 Hz, 1H, H-ethene), 4.33–4.26 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 4.17 (t, J 7.2 Hz, 2H, $\text{NCH}_2(\text{CH}_2)_{10}\text{CH}_3$), 1.95–1.84 (m, 4H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 1.83 (s, 6H), 1.38–1.33 (m, 4H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 1.30 – 1.21 (m, 14H, $\text{N}(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_7\text{CH}_3$), 1.14 (t, J 7.4 Hz, 3H, $\text{N}(\text{CH}_2)_2\text{CH}_3$), 0.88 (t, J 6.8 Hz, 3H, $\text{N}(\text{CH}_2)_{11}\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3) δ : 174.8 (C), 173.3 (C), 155.0 (C), 146.3 (C), 144.4 (C), 139.3 (CH), 137.4 (C), 134.1 (C), 133.1 (C), 131.9 (CH), 130.3 (CH), 127.3 (CH), 125.9 (C), 122.9 (CH), 122.5 (CH), 121.7 (CH), 121.0 (CH), 120.8 (CH), 120.4 (CH), 113.6 (C), 111.4 (C), 110.8 (C), 110.6 (CH), 110.4 (CH), 109.8 (C), 103.1 (C), 98.0 (C), 58.6 (C), 46.8 (CH), 44.2 (CH), 31.9 (CH), 30.0 (CH), 29.6 (2CH), 29.54 (CH), 29.46 (CH), 29.3 (CH), 29.2 (CH), 27.0 (CH), 26.6 (CH), 22.7 (CH), 20.7 (CH), 14.1 (CH), 11.5 (CH). Anal. calcd. (%) for $\text{C}_{45}\text{H}_{50}\text{N}_6\text{O}_2$ (706.40): C, 76.46; H, 7.13; N, 11.89; found C, 76.35; H, 7.19; N, 11.85.

Acknowledgements

L.N. Islamova and P.V. Lebedeva gratefully acknowledge the financial support of the Russian Science Foundation (grant no. N $^{\circ}$ 21-73-00060) for the chromophore synthesis and study of their linear and nonlinear optical properties.

Supplementary Material

Copies of ^1H and ^{13}C NMR spectra associated with this manuscript are presented in the Supplementary Material file in the online version.

References

1. Achelle, S.; Baudequin, C.; Plé, N. *Dyes Pigm.* **2013**, *98*, 575-600.
<https://doi.org/10.1016/j.dyepig.2013.03.030>
2. Nosova, E. V.; Achelle, S.; Lipunova, G. N.; Charushin, V. N.; Chupakhin, O. N. *Rus. Chem. Rev.* **2019**, *88*, 1128- 1178.
<https://doi.org/10.1070/RCR4887>
3. Gedefaw, D.; Prosa, M.; Bolognesi, M.; Seri, M.; Andersson, M. R. *Adv. Energy Mater.* **2017**, 1700575.
<https://doi.org/10.1002/aenm.201700575>
4. Jaung, J.-Y. *Dyes Pigm.* **2006**, *71*, 245-250.
<https://doi.org/10.1016/j.dyepig.2005.07.008>
5. Achelle, S.; Barsella, A.; Baudequin, C.; Caro, B.; Robin-le Guen, F. *J. Org. Chem.* **2012**, *77*, 4087–4096.
<https://doi.org/10.1021/jo3004919>

6. Burganov, T. I.; Katsyuba, S. A.; Sharipova, S. M.; Kalinin, A. A.; Monari, A.; Assfeld, X. *Phys. Chem. Chem. Phys.* **2018**, *20*, 21515-21527.
<https://doi.org/10.1039/C8CP03780A>
7. Burganov, T. I.; Katsyuba, S. A.; Islamova, L. N.; Fazleeva, G. M.; Sharipova, S. M.; Kalinin, A. A.; Monari, A.; Assfeld, X. *Dyes Pigm.* **2019**, *170*, 107580.
<https://doi.org/10.1016/j.dyepig.2019.107580>
8. Gerasimova, T. P.; Burganov, T. I.; Katsyuba, S. A.; Kalinin, A. A.; Islamova, L. N.; Fazleeva, G. M.; Ahmadeev, B. S.; Mustafina, A. R.; Monari, A.; Assfeld, X.; Sinyashin, O. G. *Dyes Pigm.* **2021**, *186*, 108958.
<https://doi.org/10.1016/j.dyepig.2020.108958>
9. Zhan, Y.; Hu, H. *Dyes Pigm.* **2019**, *167*, 127-134.
<https://doi.org/10.1016/j.dyepig.2019.04.016>
10. Zhao, J.; Sun, J.; Simalou, O.; Wang, H.; Peng, J.; Zhai, L.; Xue, P.; Lu, R. *Dyes Pigm.* **2018**, *151*, 296-302.
<https://doi.org/10.1016/j.dyepig.2018.01.005>
11. Zhan, Y.; Hu, H. *Dyes Pigm.* **2019**, *167*, 127-134.
<https://doi.org/10.1016/j.dyepig.2019.04.016>
12. Zhan, Y.; Wang, Y. *Dyes Pigm.* **2020**, *173*, 107971.
<https://doi.org/10.1016/j.dyepig.2019.107971>
13. Li, K.; Xue, P.; Shen, Y.; Liu, J. *Dyes Pigm.* **2018**, *151*, 279-286.
<https://doi.org/10.1016/j.dyepig.2018.01.010>
14. Jung, C. Y.; Song, C. J.; Yao, W.; Park, J. M.; Hyun, I. H.; Seong, D. H.; Jaung, J. Y. *Dyes Pigm.* **2015**, *121*, 204-210.
<https://doi.org/10.1016/j.dyepig.2015.05.019>
15. Park, J. M.; Jung, C. Y.; Wang, Y.; Choi, H. D.; Park, S. J.; Ou, P.; Jang, W.-D.; Jaung, J. Y. *Electrochim. Acta* **2019**, *298*, 650-662.
<https://doi.org/10.1016/j.electacta.2018.12.133>
16. Wang, L.; Wong, W.-K.; Wu, L.; Li, Z.-Y. *Chem. Lett.* **2005**, *34*, 934-935.
<https://doi.org/10.1246/cl.2005.934>
17. Sessler, J. L.; Maeda, H.; Mizuno, T.; Lynch, V. M.; Furuta, H. *J. Am. Chem. Soc.* **2002**, *124*, 13474-13479.
<https://doi.org/10.1021/ja0273750>
18. Yanilkin, V. V.; Nastapova, N. V.; Stepanov, A. S.; Kalinin, A. A.; Mamedov V. A. *Russ. Chem. Bull.* **2009**, *58*, 89-94.
<https://doi.org/10.1007/s11172-009-0013-7>
19. Mamedov, V. A.; Kalinin, A. A.; Samigullina, A. I.; Mironova, E. V.; Krivolapov, D. B.; Gubaidullin, A. T.; Rizvanov, I. Kh. *Tetrahedron Lett.* **2013**, *54*, 3348-3352.
<https://doi.org/10.1016/j.tetlet.2013.04.052>
20. Mamedov, V. A.; Kalinin, A. A.; Gubaidullin, A. T.; Katsuba, S. A.; Syakaev, V. V.; Rizvanov, I. K.; Latypov, Sh. K. *Tetrahedron* **2013**, *69*, 10675-10687.
<https://doi.org/10.1016/j.tet.2013.09.014>
21. Mamedov, V. A.; Kalinin, A. A.; Yanilkin, V. V.; Gubaidullin, A. T.; Latypov, Sh. K.; Balandina, A. A.; Isaikina, O. G.; Toropchina, A. V.; Nastapova, N. V.; Iglamova, N. A.; Litvinov, I. A. *Russ. Chem. Bull.* **2005**, *54*, 2616-2625.
<https://doi.org/10.1007/s11172-006-0165-7>
22. Han, H.; Liu, Y. R.; Dong, C.; Han, X. *J. Lumin.* **2017**, *183*, 513-518.
<https://doi.org/10.1016/j.jlumin.2016.11.065>

23. Moshkina, T. N.; Nosova, E. V.; Lipunova, G. N.; Valova, M. S.; Charushin, V. N. *Asian J. Org. Chem.* **2018**, *7*, 1080-1084.
<https://doi.org/10.1002/ajoc.201800217>
24. Reddy, M. R.; Han, S. H.; Lee, J. Y.; Seo, S. Y. *Dyes Pigm.* **2018**, *153*, 132-136.
<https://doi.org/10.1016/j.dyepig.2018.02.020>
25. Fominykh, O. D.; Kalinin, A. A.; Sharipova, A. V.; Levitskaya, A. I.; Balakina, M.Yu. *Comput. Mat. Science* **2020**, *183*, 109900.
<https://doi.org/10.1016/j.commatsci.2020.109900>
26. Kalinin, A. A.; Sharipova, S. M.; Burganov, T. I.; Levitskaya, A. I.; Fominykh, O. D.; Vakhonina, T. A.; Ivanova, N. V.; Khamatgalimov, A. R.; Katsyuba, S. A.; Balakina, M.Yu. *J. Photochem. Photobiology A.* **2019**, *370*, 58-66.
<https://doi.org/10.1016/j.jphotochem.2018.10.034>
27. Fominykh, O. D.; Kalinin, A. A.; Sharipova, S. M.; Sharipova, A. V.; Burganov, T. I.; Smirnov, M. A.; Vakhonina, T. A.; Levitskaya, A. I.; Kadyrova, A. A.; Ivanova, N. V.; Khamatgalimov, A. R.; Nizameev, I. R.; Katsyuba, S. A.; Balakina, M.Yu. *Dyes Pigm.* **2018**, *158*, 131-141.
<https://doi.org/10.1016/j.dyepig.2018.05.033>
28. Kalinin, A. A.; Islamova, L. N.; Shmelev, A. G.; Fazleeva, G. M.; Fominykh, O. D.; Dudkina, Y. B.; Vakhonina, T. A.; Levitskaya, A. I.; Sharipova, A. V.; Mukhtarov, A. S.; Khamatgalimov, A. R.; Nizameev, I. R.; Budnikova, Y. H.; Balakina, M. Y. *Dyes Pigm.* **2021**, *184*, 108801.
<https://doi.org/10.1016/j.dyepig.2020.108801>
29. Song, L.; Zhang, H.; Shi, X.; Zhang, J.; Wang, K.; Zhang, J.; Lia, M.; Ao, Y. *Mater. Lett.* **2022**, *307*, 130959.
<https://doi.org/10.1016/j.matlet.2021.130959>
30. Keles, E.; Yahya, M.; Aktan, E.; Aydinler, B.; Seferoglu, N.; Barsella, A.; Seferoglu, Z. *J. Photochem. Photobiol. A* **2020**, *402*, 112818.
<https://doi.org/10.1016/j.jphotochem.2020.112818>
31. Gong, W.; Li, Q.; Li, Z.; Lu, Ch.; Zhu, J.; Li, S.; Yang, J.; Cui, Y.; Qin, J. *J. Phys. Chem. B*, **2006**, *110*, 10241-10247.
<https://doi.org/10.1021/jp055449z>
32. Qian, L.; Zhou, Y.; Liu, M.; Huang, X.; Wu, G.; Gao, W.; Ding, J.; Wu, H. *RSC Adv.* **2017**, *7*, 42180-42191.
<https://doi.org/10.1039/C7RA06951K>
33. Moerner, W. E.; Twieg, R. J.; Kline, D. W.; He, M. Fluorophore compounds and their used in biological systems. Patent US 2007/0134737 A1, 2007, June, 14.
34. Liu, J.; Ouyang, C.; Huo, F.; He, W.; Cao, A. *Dyes Pigm.* **2020**, *181*, 108509.
<https://doi.org/10.1016/j.dyepig.2020.108509>
35. Sharipova, S. M.; Kalinin, A. A. *Chem. Heterocycl. Compd.* **2017**, *53*, 36–38.
<https://doi.org/10.1007/s10593-017-2017-9>
36. Seferoglu, Z. *Org. Prep. Proced. Int.* **2017**, *49*, 293–337.
<https://doi.org/10.1080/00304948.2017.1336052>
37. Sharipova, S. M.; Gilmutdinova, A. A.; Krivolapov, D. B.; Khisametdinova, Z. R.; Kataeva, O. N.; Kalinin, A. A. *Chem. Heterocycl. Compd.* **2017**, *53*, 504-510.
<https://doi.org/10.1007/s10593-017-2084-y>
38. Yamada, T.; Aoki, I.; Miki, H.; Yamada, Ch.; Otomo A. *Mater. Chem. Phys.* **2013**, *139*, 699-705.
<https://doi.org/10.1016/j.matchemphys.2013.02.020>

39. Kalinin, A. A.; Sharipova, S. M.; Burganov, T. I.; Dudkina, Yu. B.; Khamatgalimov, A. R.; Katsyuba, S. A.; Budnikova, Yu. H.; Balakina M. Yu. *Dyes Pigm.* **2017**, *146*, 82-91.
<http://dx.doi.org/10.1016/j.dyepig.2017.06.062>
40. Zhang, X.; Aoki, I.; Piao, X.; Inoue, Sh.; Tazawa, H.; Yokoyama, Sh.; Otomo, A. *Tetrahedron Lett.* **2010**, *51*, 5873-5876.
<https://doi.org/10.1016/j.tetlet.2010.08.060>
41. Wu, J.; Wang, W.; Chen, K.; Luo, J. *J. Mater. Chem. C*, **2020**, *8*, 5494-5500.
<https://doi.org/10.1039/D0TC000332H>
42. Harder, E.; Damm, W.; Maple, J.; Wu,; Reboul, M.; Xiang, J.Y. et al. *J. Chem. Theor. Comput.* **2016**, *12*, 281–96.
<https://doi.org/10.1021/acs.jctc.5b00864>
43. Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theor. Comput.* **2006**, *2*, 364–382.
<https://doi.org/10.1021/ct0502763>
44. Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
<https://doi.org/10.1007/s00214-007-0310-x>
45. Kendall, R. A.; Dunning, T. H.; Harrison, R. H. *J. Chem. Phys.* **1992**, *96*, 6796–806.
<https://doi.org/10.1063/1.462569>.
46. Woon, D. E.; Dunning T. H. Jr. *J. Chem. Phys.* **1994**, *100*, 2975–2988.
<https://doi.org/10.1063/1.466439>
47. Johnson, L. E.; Dalton, L. R.; Robinson, B. H. *Acc. Chem. Res.* **2014**, *47*, 3258–3265.
<https://doi.org/10.1021/ar5000727>.
48. Levitskaya, A. I.; Kalinin, A. A.; Fominykh, O.D.; Vasilyev, I. V.; Balakina, M. Yu. *Comp. Theor. Chem.* **2016**, *1094*, 17–22.
<https://doi.org/10.1016/j.comptc.2016.08.021>
49. Schrödinger Release 2022-1: MacroModel, Schrödinger, LLC, New York, NY, 2022.
50. Schrodinger release 2021-3: Jaguar, Schrodinger. New York, NY: LLC; 2021.
51. Bochevarov, A. D.; Harder, E.; Hughes, T.F.; Greenwood, J.R.; Braden, D. A.; Philipp, D. M. *Int. J. Quant. Chem.* **2013**, *113*, 2110–42.
<https://doi.org/10.1002/qua.24481>

This paper is an open access article distributed under the terms of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>)