

Synthesis of indole-based chromophores with a tricyanofuranyl acceptor and the study of the effect of the quinoxalinone core in the π -electron bridge 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

Received mm-dd-yyyy

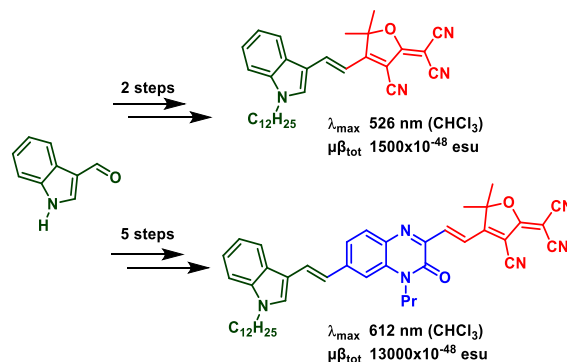
Accepted Manuscript mm-dd-yyyy

Published on line mm-dd-yyyy

Dates to be inserted by editorial office

Abstract

D— π —A chromophores with indole donor and tricyanofuranyl acceptor moieties connected by vinylene 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 elongation of the bridge by 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

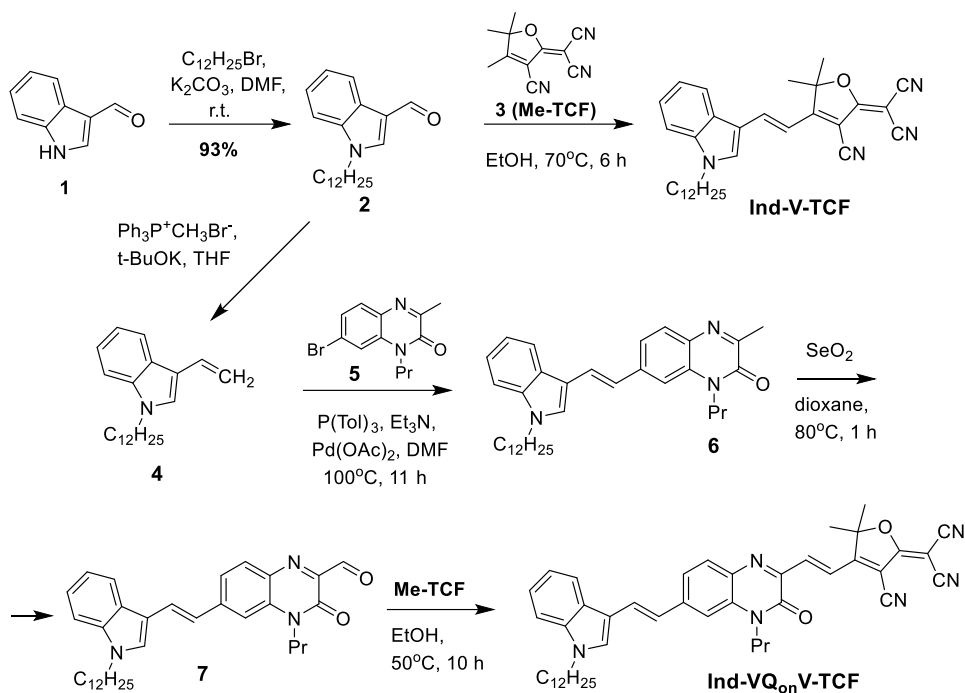
Introduction

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 including redox-switched binding,¹⁸ pH sensors²³; they are also promising in the 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.⁶⁻²⁸

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 established 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 in two step procedure starting from 3-indolecarbaldehyde: alkylation by dodecylbromide with the formation of *N*-dodecyl derivative **2**²⁹ and following Knoevenagel condensation with 3-cyano-2-dicyanomethylene-4,4,5-trimethyl-2,5-dihydrofuran (**Me-TCF**)³⁰ (Scheme 1). Elongated dodecyl substituent was used to increase the chromophore solubility both in organic solvents. Me-TCF is widely used as the strong acceptor in the synthesis and study of NLO chromophores.³¹⁻³³ Introduction of additional vinylquinoxalinonyl moiety in the π -bridge in the case of obtaining the chromophore **Ind-VQ_{on}V-TCF** led to increasing the number of synthetic steps to five. Olefin **4** obtained from aldehyde **2** (Wittig reaction) reacts with 7-bromo-3-methyl-1-propylquinoxalin-2-one³⁴ to give 1,2-disubstituted olefin product **6** (Heck reaction). Oxidation of compound **6** by selenium dioxide leads to quinoxalinone-based aldehyde **7**, which reacts with **Me-TCF** without base in ethanol to form the desired chromophore **Ind-VQ_{on}V-TCF** in moderate yield. All 1,2-disubstituted olefin derivatives were obtained as *E*-isomers: $J_{\text{H-C=CH}}$ 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 ($\epsilon = 2\div 39$, Fig. 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).³⁵ Comparing the chromophores of the dialkylaniline-vinylthiophenvinyl-tricyanofuran composition 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**,³⁶ making it transparent in the short-wavelength infrared region (at 850 nm). Both chromophores are characterized by solvatochromism; they demonstrate close positive solvatochromic shifts of 31 and 39 nm, while chromophore **Ind-VQ_{on}V-TCF** exhibits significantly greater negative solvatochromic shift (Table 1).

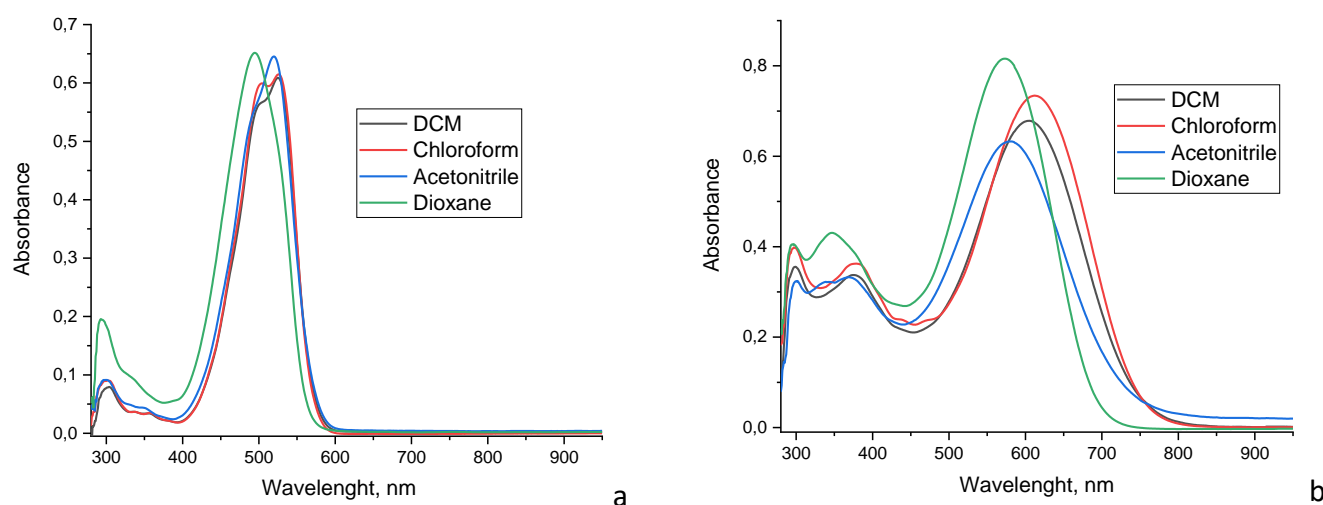


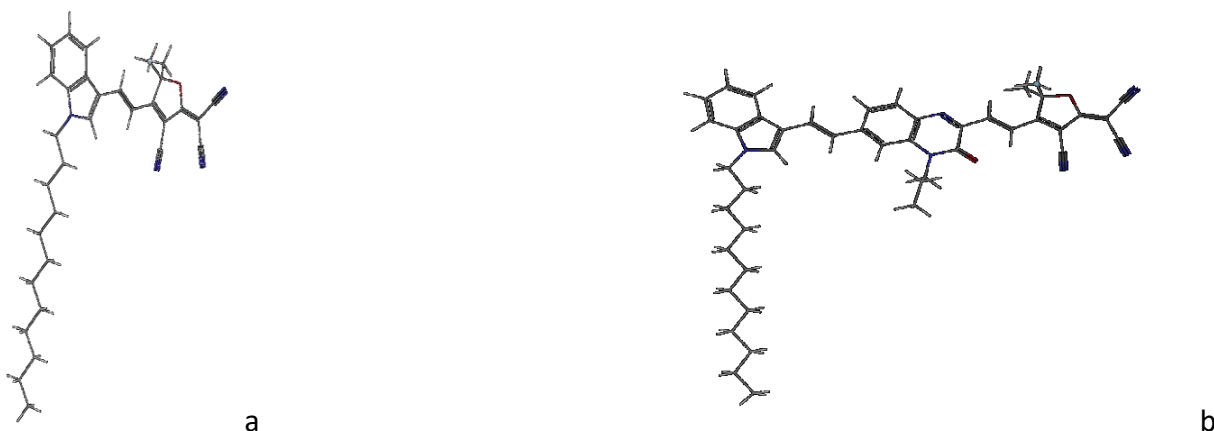
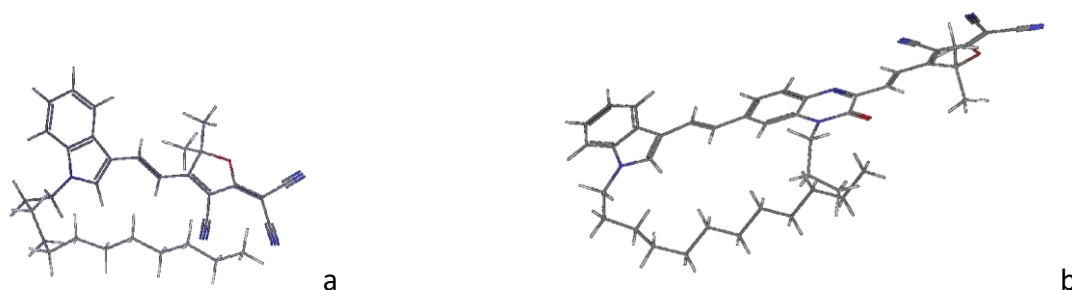
Figure 1. Experimental electronic absorption spectra of **Ind-V-TCF** (a) and **Ind-VQ_{on}V-TCF** (b).

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 (Fig. 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** (Fig. 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 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 (Fig. 2), and for conformers **II**, the dodecyl substituent is extended along the backbone of the molecules (Fig. 3).

Table 2. The 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 (Fig. 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.³⁷ For previously explored chromophores, which were transparent at 850 nm, the $\mu\beta$ value was up to $7300 \cdot 10^{-48}$ esu.

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.

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,³⁸ 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^[39,40] and Dunning basis sets^[41,42] are recognized as an adequate choice for this purpose.^[43,44] The value of β_{tot} is calculated as

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

The conformational search is performed with Macromodel program,⁴⁵ calculations of geometrical parameters and chromophore electric properties are performed by Jaguar program package.^{46,47}

(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 (CH₂Cl₂). 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, CDCl₃) 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, NCH₂), 1.96-1.88 (m, 2H, NCH₂CH₂(CH₂)₉CH₃), 1.78 (s, 6H, CH₃), 1.40–1.31 (m, 4H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 1.30–1.24 (m, 14H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 0.87 (t, J 6.8 Hz, 3H, N(CH₂)₁₁CH₃). ¹³C NMR (100 MHz, CDCl₃) 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 C₃₂H₃₈N₄O (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, CDCl₃) 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, NCH₂), 1.86–1.78 (m, 2H, NCH₂CH₂(CH₂)₉CH₃), 1.46–1.25 (m, 18H, N(CH₂)₂(CH₂)₉CH₃), 1.02 (t, J 6.8 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) 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 C₂₂H₃₃N (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), Pd(OAc)₂ (5 mg, 0.022 mmol), Et₃N (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 CH₂Cl₂. The organic layer was separated, washed with water, dried over anhydrous MgSO₄, 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, CDCl₃) 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, NCH₂CH₂CH₃), 4.12 (t, *J* 7.2 Hz, 2H, NCH₂(CH₂)₁₀CH₃), 2.61 (s, 1H, CH₃), 1.92–1.82 (m, 4H, NCH₂CH₂(CH₂)₉CH₃, NCH₂CH₂CH₃), 1.38–1.32 (m, 4H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 1.31–1.22 (m, 14H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 1.12 (t, *J* 7.4 Hz, 3H, N(CH₂)₂CH₃), 0.90 (t, *J* 6.8 Hz, 3H, N(CH₂)₁₁CH₃). ¹³C NMR (100 MHz, CDCl₃) 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 C₃₄H₄₅N₃O (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, CDCl₃) 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, NCH₂CH₂CH₃), 4.14 (t, *J* 7.2 Hz, 2H, NCH₂(CH₂)₁₀CH₃), 1.93–1.83 (m, 4H, NCH₂CH₂(CH₂)₉CH₃, NCH₂CH₂CH₃), 1.37–1.31 (m, 4H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 1.30–1.21 (m, 14H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 1.13 (t, *J* 7.4 Hz, 3H, N(CH₂)₂CH₃), 0.87 (t, *J* 6.8 Hz, 3H, N(CH₂)₁₁CH₃). ¹³C NMR (100 MHz, CDCl₃) 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 C₃₄H₄₃N₃O₂ (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, CDCl₃) 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, NCH₂CH₂CH₃), 4.17 (t, *J* 7.2 Hz, 2H, NCH₂(CH₂)₁₀CH₃), 1.95–1.84 (m, 4H, NCH₂CH₂(CH₂)₉CH₃, NCH₂CH₂CH₃), 1.83 (s, 6H), 1.38–1.33 (m, 4H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 1.30 – 1.21 (m, 14H, N(CH₂)₂(CH₂)₂(CH₂)₇CH₃), 1.14 (t, *J* 7.4 Hz, 3H, N(CH₂)₂CH₃), 0.88 (t, *J* 6.8 Hz, 3H, N(CH₂)₁₁CH₃). ¹³C NMR (100 MHz, CDCl₃) 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 C₄₅H₅₀N₆O₂ (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^o21-73-00060) for the chromophore synthesis and study of their linear and nonlinear optical properties.

Supplementary Material

Copies of ¹H and ¹³C 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. 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>
30. 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.
31. Liu, J.; Ouyang, C.; Huo, F.; He, W.; Cao, A. *Dyes Pigm.* **2020**, *181*, 108509.
<https://doi.org/10.1016/j.dyepig.2020.108509>
32. Sharipova, S. M.; Kalinin, A. A. *Chem. Heterocycl. Compd.* **2017**, *53*, 36–38.
<https://doi.org/10.1007/s10593-017-2017-9>
33. Seferoglu, Z. *Org. Prep. Proced. Int.* **2017**, *49*, 293–337.
<https://doi.org/10.1080/00304948.2017.1336052>
34. 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>
34. 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>
35. 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>
36. 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>
37. Wu, J.; Wang, W.; Chen, K.; Luo, J. *J. Mater. Chem. C*, **2020**, *8*, 5494-5500.
<https://doi.org/10.1039/D0TC00332H>
38. 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>
39. Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theor. Comput.* **2006**, *2*, 364–382.
<https://doi.org/10.1021/ct0502763>
40. Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
<https://doi.org/10.1007/s00214-007-0310-x>
41. Kendall, R. A.; Dunning, T. H.; Harrison, R. H. *J. Chem. Phys.* **1992**, *96*, 6796–806.
<https://doi.org/10.1063/1.462569>
42. Woon, D. E.; Dunning T. H. Jr. *J. Chem. Phys.* **1994**, *100*, 2975–2988.
<https://doi.org/10.1063/1.466439>
43. Johnson, L. E.; Dalton, L. R.; Robinson, B. H. *Acc. Chem. Res.* **2014**, *47*, 3258–3265.
<https://doi.org/10.1021/ar5000727>
44. 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>
45. Schrödinger Release 2022-1: MacroModel, Schrödinger, LLC, New York, NY, 2022.

46. Schrodinger release 2021-3: Jaguar, Schrodinger. New York, NY: LLC; 2021.
47. 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/>)