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D- π -A chromophores with a quinoxaline core in the π -bridge and bulky aryl groups in the acceptor: Synthesis, properties, and femtosecond nonlinear optical activity of the chromophore/PMMA guest-host materials



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ABSTRACT

Novel D- π -A chromophores with quinoxaline/quinoxalinone core in the π -conjugated bridge and various bulky groups in the acceptor moiety have been synthesized and systematically investigated at molecular level by UV–Vis spectroscopy, DFT calculations, electrochemical and TGA-DSC methods as well as at materials level by the example of PMMA-based composite polymer materials doped with different chromophore contents using molecular modeling and SHG technique. Chromophores exhibit positive dioxane/chloroform solvatochromic shift of ca. 50 nm, high values of first hyperpolarizability and dipole moment, small energy gap and good thermal stability. Tolyl and cyclohexylphenyl substituents unlike phenyl can be treated as most effective isolating groups, preventing chromophore pronounced aggregation even at 30 wt% content. Femtosecond nonlinear optical (NLO) activity was studied for poled thin guest-host polymer films with various chromophore acceptor shows maximal NLO coefficient, d_{3_a} values among the studied materials (37 pm/V) as well as good long-term stability of NLO response together with excellent chromophore thermal stability (T_d = 256 °C). Composite materials doped with quinoxaline chromophores are photostable with respect to laser pulses with peak intensities up to 11 GW/cm².

1. Introduction

Nonlinear optical (NLO) materials are presented as acentric inorganic crystals, for example, lithium niobate [1], and promising for the generation of intense coherent deep- UV light fluorooxoborates [2,3], useful for THz generation organic crystals [4] and various poled thin film chromohore-containig organic materials: composite polymer materials, molecular glasses, molecular composite glasses [5]. Organic materials with quadratic NLO properties attract considerable research interest due to their potential use in optoelectronic devices to promote development of such areas as telecommunications and information technology [6–8]. The key constructing blocks for such materials are the second-order NLO chromophores. To achieve large optical nonlinearities (large molecular first hyperpolarizability) various "push-pull" molecules have been designed and systematically investigated [9–11]. Molecular engineering of organic chromophores has evolved in various directions. There was an increase in the length of the chromophore π -bridge due to the introduction of additional vinyl units [12,13], including conformationally locked-in cyclopentene [14], cyclohexene [14–18], pyrane [19] or tetrahydronaphtalene [20] ring frameworks. The incorporation of heterocyclic moiety, mainly thiophene ring [18, 21–23], in the π -bridge was widely used in the design of NLO

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chromophores. Other heterocyclic, as a rule π -excessive, moieties, such as pyrrole [24], furan [25], which serve as auxiliary donor, were also used. Variation of donor [14,15,17,25-32] and acceptor [13,15,18, 33-36] terminal fragments including the selection of the optimal ratio of donor-acceptor strength was another important structural factor in the design of NLO chromophores. NLO activity of more complex chromophore systems has also been investigated; among them were Y-type chromophores with two donor fragments [23,37–39], bichromophores [40-42], macrocyclic chromophores [43], etc. Heteroaromatics played an important role in the design of NLO chromophores, but mostly π -excessive heterocycles were incorporated into the π -bridge of chromophores, thiazole being the only exception [44,45]. Two decades ago it was shown theoretically that the introduction of a π -deficient heterocycle in the π -bridge can lead to the enhancement of the first hyperpolarizability values [46]. Some azine functionalized π -conjugated dyes with NLO and photoluminescence properties have been recently developed [47-49]. According to our theoretical studies, the chromophores with the quinoxaline core in the π -bridge exhibit significant NLO activity [50,51], and for some chromophores it was confirmed experimentally [52,53]. Our present investigations focus on the novel type of NLO chromophores with incorporated π -deficient quinoxaline/quinoxalinone core in the π -bridge, bulky aromatic substituent in acceptor and its effect on optical, electrochemical and thermal properties of chromophores as well as on femtosecond NLO activity of guest-host chromophore-containing polymer materials. Composite materials doped with D-π-A chromophores with bulky (isolating) group in donor moiety show enhancement of macroscopic NLO activity due to a decrease in the dipole-dipole interaction and the establishment of non-centrosymmetric organization of chromophores in the materials [54–57].

2. Materials and techniques

2.1. Chromophores characterization

The NMR, UV-Vis, IR and MALDI spectra were registered on the equipment of Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS. NMR experiments were performed with Bruker AVANCE-600 and AVANCE-400 (600 and 400 MHz for ¹H NMR, 150 and 100 MHz for 13 C NMR) spectrometers. Chemical shifts (δ in ppm) are referenced to the solvents. The mass spectra were obtained on Bruker UltraFlex III MALDI TOF/TOF instrument with p-nitroaniline as a matrix. UV-Vis spectra were recorded at room temperature on a PerkinElmer Lambda 35 spectrometer 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 3.5 \times 10⁻⁵ mol/L. The thermal stabilities of chromophores were investigated by simultaneous thermal analysis (thermogravimetry/differential scanning calorimetry - TG/DSC) using NETZSCH (Selb, Germany) STA449 F3 instrument. Approximately 2.6-3.7 mg samples were placed in an Al crucible with a pre-hole on the lid and heated from 30 to 600 °C. The same empty crucible was used as the reference sample. High-purity argon was used with a gas flow rate of 50 mL/min. TG/DSC measurements were performed at the heating rates of 10K/min. The reaction progress and the purity of the obtained compounds were controlled by TLC on Sorbfil UV-254 plates with visualization under UV light. Voltammograms were recorded with a BASi Epsilon potentiostat/ galvanostat (USA) at 25 °C in dichloromethane solutions under dry nitrogen atmosphere. All measurements were carried out with 0.2 M Bu₄NBF₄ as the supporting electrolyte, platinum working electrode (0.02 cm²), platinum auxiliary electrode, and Ag/AgNO₃ reference electrode. All potentials were referred against the ferrocenium/ferrocene redox couple.

2.2. Chromophores synthesis

Aldehydes **6**, **7** and Me-TCF_{Ar} acceptors **8b**,**c** were synthesized according to the literature [52,53,58-60].

2.2.1. 2-(3-Cyano-4,5-dimethyl-5-phenylfuran-2(5H)-ylidene) malononitrile (8a)

To stirred solution of 3-(4-cyclophenyl)-3-hydroxybutan-2-one (1.0 g, 61 mmol) in dry pyridine (5 mL) malononitrile (0.81 g, 12.3 mmol) was added at 0 °C. The temperature of the reaction mixture was slowly raised to rt and the reaction mixture was stirred for another 5 h. Then the reaction mixture was poured into water and the precipitate was filtered and washed with water. When a few drops of acetic acid were added to the solution, a precipitate again was formed, which was filtered and washed with water. Yield 0.75 g (54%). White-gray powder, mp 177 °C (EtOH).¹H NMR (400 MHz, CDCl₃): 7.50–7.46 (m, 3H, *m*,*p*-Ph), 7.23–7.19 (m, 2H, *o*-Ph), 2.24 (s, 3H, CH₃), 2.02 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 182.2, 175.7, 133.9, 130.5, 129.6, 125.0, 110.8, 110.3, 109.0, 104.8, 101.5, 58.9, 22.3, 14.5. IR (ν_{max} , cm⁻¹, KBr): 3067 (CH), 2997 (CH), 2230 (C=N), 2219 (C=N), 1620 (C=C), 1597 (C=C).

2.2.2. Synthesis of chromophores with phenylquinoxaline moiety

A solution of aldehyde **6** (115 mg, 0.25 mmol), **Me-TCF**_{Ar} (**8a-c**) (0.22 mmol) and anhydrous ethanol (2 mL) was stirred for 7–14 h (7h in case of **8a**, 14 h in case of **8b**, 10 h in case of **8c**) at 70 °C, then cooled to rt. After removal of the solvent by rotary evaporation, the residue was purified by silica-gel column chromatography (eluent: petroleum ether/ethyl acetate = $7:1 \rightarrow$ petroleum ether/ethyl acetate = 3:1) to give a product as black powder.

2.2.2.1. 2-(3-Cyano-4-((E)-2-(6-((E)-4-(dibutylamino)styryl)-3-phenyl-

quinoxalin-2-yl)vinyl)-5-methyl-5-phenylfuran-2(5H)-ylidene)malononi*trile* (*DBA-VQ_{Ph}V-TCF_{Ph}*). Yield 87 mg (56%). $R_f = 0.47$ (hexane/ethyl acetate 2:1). ¹H NMR (600 MHz, CDCl₃): δ 8.06–8.00 (m, 3H, H-7,8 quinoxaline, 1H of -CH=CH-TCF), 7.94 (s, 1H, H-5 quinoxaline), 7.54 (dd, J = 7.4, 7.4 Hz, 1H, p-Ph), 7.49–7.31 (m, 10H, Ph, m-Ph, 3,5-H aniline, 1H of -CH=CH-DBA), 7.29 (d, J = 15.7, 1H, -CH=CH-TCF), 7.10 (d, J = 8.0 Hz, 2H, o-Ph), 7.03 (d, J = 16.3 Hz, 1H, -CH=CH-DBA), 6.66 (d, J = 8.6 Hz, 2H, 2,6-H aniline), 3.33 (t, J = 7.6 Hz, 4H, NCH₂), 2.06 (s, 3H, Me), 1.65-1.57 (m, 4H, NCH₂CH₂), 1.43–1.35 (m, 4H, N(CH₂)₂CH₂), 0.98 (t, *J* = 7.3 Hz, 6H, CH₃). ¹³C NMR (150 MHz, CDCl₃): 175.0, 172.5, 155.8, 148.9, 143.2, 143.1, 143.0, 142.80, 141.5, 137.2, 135.0, 133.9, 130.5, 129.8, 129.6, 129.4, 128.9, 128.8, 125.7, 124.7, 123.4, 121.7, 120.0, 111.7, 111.2, 110.6, 109.7, 103.3, 99.1, 59.2, 50.8, 29.5, 24.1, 20.3, 14.0. IR (ν_{max} , cm⁻¹, KBr): 3446 (CH), 2928 (CH), 2228 (CN), 1579 (C=C, C=N), 1511 (C=C). MALDI-TOF: 707 [M+H]+.

2.2.2.2. 2-(3-Cyano-4-((E)-2-(6-((E)-4-(dibutylamino)styryl)-3-phenyl-

quinoxalin-2-yl)vinyl)-5-methyl-5-(p-tolyl)furan-2(5H)-ylidene)malononitrile (DBA-VQ_{Ph}V-TCF_{Tol}). Yield 97 mg (61%). R_f = 0.22 (hexane/ethyl acetate 3:1). ¹H NMR (600 MHz, CDCl₃): δ 8.06–8.00 (m, 3H, H-7,8 quinoxaline, 1H of -CH=CH-TCF), 7.96 (s, 1H, H-5 quinoxaline), 7.54 (dd, *J* = 7.4, 7.4 Hz, 1H, *p*-Ph), 7.47–7.30 (m, 7H, *o*,*m*-Ph, 3,5-H aniline, 1H of -CH=CH-DBA), 7.30 (d, *J* = 15.7, 1H, -CH=CH-TCF), 7.12 (d, *J* = 8.3 Hz, 2H, 3,5-H *p*-Tol), 7.04 (d, *J* = 16.3 Hz, 1H, –CH=CH–DBA), 6.98 (d, J = 8.3 Hz, 2H, 2,6-H p-Tol), 6.66 (d, J = 8.8 Hz, 2H, 2,6-H aniline), 3.32 (t, J = 7.6 Hz, 4H, NCH₂), 2.38 (s, 3H, MeC₆H₄), 2.03 (s, 3H, MeTCF), 1.65-1.55 (m, 4H, NCH₂CH₂), 1.43-1.34 (M, 4H, N $(CH_2)_2CH_2$, 0.97 (t, J = 7.3 Hz, 6H, CH₃). ¹³C NMR (150 MHz, CDCl₃): 175.0, 172.8, 155.8, 148.9, 143.2, 143.0, 142.9, 141.9, 140.8, 137.2, 133.9, 131.9, 130.3, 129.8, 129.4, 129.3, 128.8, 128.7, 125.7, 124.8, 123.4, 121.7, 120.2, 111.7, 111.3, 110.7, 109.7, 103.3, 99.3, 59.0, 50.8, 29.5, 24.1, 21.3, 20.3, 14.0. IR ($\nu_{\rm max}, {\rm cm}^{-1}, {\rm KBr}$): 3443 (CH), 2929 (CH), 2230 (CN), 1583 (C=C, C=N), 1514 (C=C). MALDI-TOF: 721 [M+H]⁺. 2.2.2.3. 2-(3-Cyano-5-(4-cyclohexylphenyl)-4-((E)-2-(6-((E)-4-(dibutylamino)styryl)-3-phenylquinoxalin-2-yl)vinyl)-5-methylfuran-2(5H)-ylidene)malononitrile (**DBA-VQ**_{Ph}**V-TCF**_{PhCy}). Yield 85 mg (49%). $R_f =$ 0.37 (hexane/ethyl acetate 3:1). ¹H NMR (400 MHz, CDCl₃): δ 8.07–7.97 (m, 3H, H-7.8 quinoxaline, 1H of -CH=CH-TCF), 7.93 (s, 1H, H-5 quinoxaline), 7.57 (dd, J = 7.3, 7.3 Hz, 1H, p-Ph), 7.50–7.27 (m, 8H, o, m-Ph, 3,5-H aniline, 1H of -CH=CH-DBA, 1H of -CH=CH-TCF), 7.14 (d, J = 8.5 Hz, 2H, 3,5-H p-CyPh), 7.03 (d, J = 16.5 Hz, 1H, -CH=CH-DBA), 6.99 (d, J = 8.5 Hz, 2H, 2,6-H p-CyPh), 6.66 (d, J = 8.7 Hz, 2H, 2,6-H aniline), 3.33 (t, J = 7.6 Hz, 4H, NCH₂), 3.40 (t, J = 7.6 Hz, 4H, NCH₂), 2.55-2.46 (m, 1H, Cy), 2.03 (s, 3H, Me), 1.92-1.81 (m, 4H, Cy), 1.80-1.73 (m, 1H, Cy), 1.67-1.56 (m, 4H, NCH₂CH₂), 1.48-1.35 (m, 8H, N(CH₂)₂CH₂, 4H of Cy), 1.32-1.20 (m, 1H, Cy), 0.98 (t, J = 7.3 Hz, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 175.1, 172.7, 155.8, 150.7, 148.9, 143.2, 143.0, 142.9, 142.8, 141.5, 137.2, 133.8, 132.2, 129.8, 129.4, 129.3, 128.8, 128.7, 128.0, 125.7, 124.8, 123.4, 121.7, 120.1, 111.7, 111.3, 110.7, 109.7, 103.2, 99.3, 58.9, 50.8, 44.2, 34.2, 34.1, 29.4, 26.7, 26.0, 24.1, 20.3, 14.0. IR (ν_{max} , cm⁻¹, KBr): 3462 (CH), 2927 (CH), 2229 (CN), 1582 (C=C, C=N), 1512 (C=C). MALDI-TOF: 789 [M+H]⁺.

2.2.3. 2-(3-Cyano-5-(4-cyclohexylphenyl)-4-((E)-2-(6-((E)-4-(dibutylamino)styryl)-3-oxo-4-propyl-3,4-dihydroquinoxalin-2-yl)vinyl)-5methylfuran-2(5H)-ylidene)malononitrile (**DBA-VQ**_{on}**V-TCF**_{PhCv})

A mixture of aldehyde 7 (60 mg, 0.13 mmol), Me-TCF_{PhCy} (8c) (46 mg, 0.13 mmol) and anhydrous ethanol (1 mL, A and B) or anhydrous ethanol (2.2 mL) and methylene chloride (0.8 mL, C) was stirred for 6 h (A), 40 h (B) and 144 h (C) at 70 °C (A), 50 °C (B) and rt (C), respectively, then cooled to rt (A and B). After removal of the solvent by rotary evaporation, the residue was purified by silica-gel column chromatography (eluent: methylene chloride/ethyl acetate = 250:1) to give a product as black powder. Yield 34 mg (33%, A), 58 mg (56%, B), 36 mg (35%, *C*). $R_f = 0.32$ (hexane/ethyl acetate 2.5:1). ¹H NMR (600 MHz, CDCl₃): *δ* 7.99 (d, *J* = 16.2 Hz, 1H, −CH=CH-TCF), 7.78 (d, *J* = 8.6 Hz, 1H, H-8 quinoxaline), 7.67 (d, J = 16.2 Hz, 1H, -CH=CH-TCF), 7.56 (d, J = 8.6 Hz, 1H, H-7 quinoxaline), 7.43 (d, J = 8.5 Hz, 2H, 3,5-H aniline), 7.29 (d, J = 8.4 Hz, 2H, C₆H₄Cy), 7.26 (d, J = 8.4 Hz, 2H, C₆H₄Cy), 7.24 (d, J = 16.0 Hz, 1H, -CH=CH-An), 7.15 (s, 1H, H-5 quinoxaline), 6.94 (d, J = 16.0 Hz, 1H, -CH=CH-An), 6.65 (d, J = 8.5 Hz, 2H, 2,6-H aniline), 4.26-4.19 (m, 1H, N-CH₂), 4.19-4.12 (m, 1H, N-CH₂), 3.33 (t, J = 7.4 Hz, 4H, N-CH₂), 2.60-2.49 (m, 1H, Cy), 2.21 (s, 3H, CH₃), 1.90-1.79 (m, 6H, 4H of Cy, N(CO)CH₂CH₂), 1.78-1.72 (m, 1H, Cy), 1.67-1.64 (m, 4H, N-CH2CH2), 1.44-1.34 (m, 8H, N-(CH2)2CH2, 4H of Cy), 1.32–1.23 (m, 1H, Cy), 1.09 (t, J = 7.4 Hz, 3H, CH₃), 0.98 (t, J = 7.4 Hz, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): 175.1, 172.7, 154.7, 150.7, 149.1, 146.36, 143.7, 140.6, 134.0, 133.9, 133.0, 132.6, 131.6, 128.9, 128.0, 125.9, 122.9, 122.0, 121.5, 121.1, 111.8, 111.4, 110.9, 110.7, 110.0, 103.2, 99.8, 58.6, 50.8, 44.2, 44.1, 34.2, 34.1, 29.5, 26.7, 26.0, 24.4, 20.6, 20.3, 14.0, 11.4. IR (ν_{max} , cm⁻¹, KBr): 3068 (C–H), 3030 (C-H), 2957 (C-H), 2928 (C-H), 2855 (C-H), 2229 (C=N), 1657 (C=O), 1582 (C=N, C=C). MALDI-TOF: 771 [M+H]⁺.

2.3. DFT calculations

Structure and NLO characteristics of chromophores under study were calculated in the framework of Density Functional Theory (DFT). Chromophores geometrical parameters were optimized in gas phase at B3LYP/6-31G(d) level and electric characteristics (dipole moments, μ , components of linear polarizability tensor, α_{ij} , and first hyperpolarizability tensor, β_{ijk}) were calculated at the M06-2X/aug-cc-pVDZ level; the use of M06-2X density functional [61,62] and Dunning basis sets [63,64] are recognized as an adequate choice for this purpose [65–67]; further on the computational level for electric characteristics calculations is denoted as B3LYP/6-31G(d)//M06-2X/aug-cc-pVDZ. These chromophores are systems with intramolecular charge transfer, the dominating component of first hyperpolarizability tensor is β_{zzz} ,

where z-axis coincides with the charge transfer direction along the molecule. Average linear polarizability α_{av} is calculated as

$$\alpha(av) = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right),$$

and β_{tot} as

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

The calculations were performed by Jaguar program package [68, 69].

2.4. Atomistic modeling

To estimate the isolating ability of substituents in acceptor fragment of the chromophores, molecular modeling of composite materials with PMMA as polymer matrix and chromophores-guests was carried out. The chromophore content in considered composite polymer materials was 20, 25 and 30 wt%. Composite polymer materials were packed in the amorphous cell under compressive protocol (NPT ensemble) (Fig. S1) in the course of multistage simulation to get density close to that of real polymer. Polymer matrix was modeled by 10 chains each containing 60 monomer units. Such oligomer size provides sufficient flexibility of chains, it contains 10 Kuhn segments [70] Polymer chains and chromophores in such a cell experience steric hindrances due to environment. Chromophore number in a cell was tuned according the chromophore molecular weight and the desired weight content in composite material; weight content is indicated in round parentheses after composite system notation. Molecular modeling was performed with Desmond program [71] using OPLS3e force field [72].

2.5. Film fabrication, poling and NLO measurements

The guest-host polymer materials were prepared with PMMA as polymer matrix ($T_g = 103$ °C) and chromophores under study as guests. Thin polymer films were cast onto glass substrates (cover glasses 100 µm thick) from a 5-7% solution of the polymer in cyclohexanone via spincoating at 5000 rpm for 90 s. After casting, the samples were kept in a vacuum drying oven at room temperature for 10-16 h to remove the solvent residue. Films were poled at the corona-triode setup in the corona discharge field, voltage 6.5 kV, poling time \sim 20 min, the distance from the tungsten needle electrode to the surface of the film being 1 cm; the field was applied to the films heated to 108-118 °C. Second harmonic generation (SHG) was performed by the femtosecond amplified laser system which allowed measuring the SHG intensity emitted by the sample without any micro-objective or another focusing system. The principal scheme of the experimental setup is presented in the Supplementary information and in [73]. The laser system produced pulses with the following parameters: the wavelength is 1028 nm, the pulse repetition rate is 3 kHz, pulse duration is 200 fs, a pulse energy is 164 µJ, and mean power of the laser beam is 492 mW. The beam diameter of 3 mm resulted in the peak pulse intensity of about 11.6 GW/cm². SHG intensity was measured by using a z-cut α-quartz crystal as a source of a reference signal. We followed [74] to obtain the NLO coefficient of the sample d_{33.s}:

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{I_s/I_q} \, \frac{l_{c,q}}{l_s} F,$$

where $d_{11,q}$ is known quartz nonlinear coefficient (0.45 pm/V), I_s and I_q are SHG intensities produced by the sample and the quartz, respectively, and measured in the same configuration, $l_{c,q}$ is quartz coherence length related to 1028 nm (assumed as 13 µm), l_s is sample thickness (of 0.3 µm mean value), F is correction factor (1.2 when $l_{c,q} \gg l_s$). It was assumed in analyzing experimental data that $d_{33}/d_{13} \approx 3$.

3. Results and discussion

3.1. Synthesis

The synthetic routes for chromophores with quinoxaline/quinoxalinone core in the π -bridge are shown in Scheme 1. Starting from *amph*imethylbromoquinoxalines 1 and 2, chromophore precursors 6 and 7 have been synthesized in the two step reactions: palladium-catalyzed Heck reaction of compounds 1/2 and 3 and followed by Riley oxidation of ethenes 4 and 5 with selenium dioxide. Finally, condensations of al-dehydes 6 and 7 with the various Me-TCF_{Ar} acceptor **8a-c** gave chromophores DBA-VQ_{ph}V-TCF_{Ph}, DBA-VQ_{ph}V-TCF_{Tol}, DBA-VQ_{ph}V-TCF_{PhCy} and DBA-VQ_{on}V-TCF_{PhCy} (Scheme 1, Fig. 1).

3.2. Photophysical properties

The chromophores photophysical properties were studied in seven solvents of different polarity: dioxane ($\varepsilon = 2.2$), chloroform ($\varepsilon = 4.8$), 1,2-dichloromethane ($\varepsilon = 8.9$), dimethylformamide ($\varepsilon = 36.7$), acetonitrile ($\varepsilon = 37.5$), dimethylsulfoxide (45.0) and ethylene carbonate (EC, $\varepsilon = 89.8$). UV–Vis absorption spectra of all chromophores exhibit a similar broad π - π^* intramolecular charge-transfer (CT) absorption band in the visible region in the range 597–662 nm (Fig. 2, Table 1).

Chromophores showed a positive solvatochromic shift from dioxane to chloroform solution and then solvatochromism inversion was observed giving negative solvatochromic shift from chloroform to polar solvent (CH₃CN, DMF, DMSO or EC). The values of positive solvatochromic shift for all chromophores are close ($\Delta \lambda = 51-53$ nm), while negative solvatochromic shift for chromophores with quinoxaline core in the π -bridge when passing from chloroform to acetonitrile ($\Delta \lambda =$

52-56 nm) is one and a half times greater than that for quinoxalinonebased chromophore **DBA-VQ**_{on}**V-TCF**_{PhCy} ($\Delta\lambda = 33$ nm). Solvatochromic inversion is a characteristic phenomenon for D-π-A chromophores with a heterocyclic core in the π -bridge [55,75–77]. However it should be noted that the solvatochromic behavior of the chromophore **DBA-VQ**_{on}**V-TCF**_{PhCv} with the quinoxalinone core in the π -bridge, which shows the predominance of the positive solvatochromic shift over the negative one, makes it similar to FTC-type chromophores [55] with thiophene moiety for which this phenomenon is the same, unlike the closely related chromophore $DBA-VQ_{Ph}V-TCF_{PhCy}$ with a quinoxaline core in the π -bridge, for which this phenomenon is opposite. The value of the solvatochromic effect often directly correlates with the value of the first hyperpolarizability for related systems [45,54,78]. Chromophores with dialkyl aniline donor and tricyanofuranyl acceptor bonded by vinylene-Z-vinylene (-CH=CH-Z-CH=CH-) π -bridge, where Z are vinylene (-CH=CH-) [78], thiophene [45,54,55], thiazole [45], quinoxaline/quinoxalinone (Table 1) moieties, exhibit close dioxane/chloroform solvatochromic shift (53 nm, 46-61 nm, 47 nm, 51-53 nm, respectively).

3.3. DFT calculations of chromophores first hyperpolarizability

The values of chromophores electric characteristics are presented in Table 2 together with the data for pristine **7-DBA-VQV-TCF** chromophore [53] which does not contain any bulky group in the acceptor fragment.

The comparison of β_{tot} values for all five chromophores are also given in Fig. S2. To study the mutual effect of the acceptor substituent and the nature of the π -electron bridge we have compared the electric characteristics of two chromophores with TCF_{PhCy} acceptor and quinoxaline/



Scheme 1. Synthesis of TCF-based chromophores with divinylquinoxaline π -bridge.



Fig. 1. Chemical structure of the synthesized chromophores.

qinoxalinone bridges: DBA-VQPhV-TCFPhCy and DBA-VQonV-TCFPhCy. The data of Table 2 and Fig. S2 demonstrate the effect of bulky substituents in the acceptor fragment on the value of first hyperpolarizability. The introduction of phenyl and tolyl groups (chromophores DBA-VQPhV-TCFPh and DBA-VQPhV-TCFTol gives most promising examples: the value of β_{tot} differs insignificantly from the value for 7-DBA-VQV-TCF, besides the presence of substituents results in the flattening of the structure (Fig. S3) which promotes the increase of the first hyperpolarizability. According to the visualization of the dihedral angle between the plane of the quinoxaline bridge and the plane of TCF fragment, the value of this angle does not exceed 20° for 7-DBA-VQV-TCF, it becomes significantly smaller for DBA-VQPhV-TCFPh and DBA-VQPhV-TCFTol (6° and 13°, respectively) and is equal to 46° and 77° for DBA-VQPhV-TCFPhCy and DBA-VQonV-TCFPhCy, respectively. The increase of the angle correlates with the decrease of the first hyperpolarizability value. We have also analyzed the frontier orbitals of the chromophores under study (Fig. 3); the corresponding energies together with the value of the energy gap are given in Table 3. The visualization of frontier orbitals (Fig. 3) confirms that all chromophores are CT ones, in all of them HOMO occupies mainly donor fragment and adjacent region of the bridge, while LUMO is concentrated at the other part of the bridge and the acceptor fragment. Orbital energies have very close values as well as ΔE_g values for all chromophores (Table 3).

3.4. Electrochemical study

For structures with several redox-active centers linked by unsaturated bridges it is especially interesting to clarify the relationship between redox properties and peculiarities of intramolecular electron transfer as well as mutual influence of the centers on these properties. Redox processes are the basis of numerous functions in biology, chemistry, including materials chemistry and particularly NLO activity. Combination of redox-active moieties in a sole molecule of a D- π -A chromophore typically leads to significant changes in its redox properties in comparison with those of individual fragments. The chromophore molecules proposed in this study include dialkylarylamine donor, which is oxidized reversibly, quinoxaline core, which is easily and reversibly reduced and oxidized [79–81], as well as TCF_{Ph} terminal electron acceptor, also capable to reversible oxidation [82] and reduction [83]. The electrochemical study of chromophores assembled from these redox-active units capable to reversible electron transfers (oxidations and reductions) is of great interest as assessing and predicting the energy gap values (optical and electrochemical) of chromophores, these estimations providing an important tool for selection of structures with the highest NLO activity.

The redox properties of the NLO chromophores were studied by cyclic and differential pulse voltammetries (CV and DPV) in dichloromethane containing tetrabutylammonium tetrafluoroborate (0.2 M) as the supporting electrolyte. These results are presented in Table 4 and in Fig. 4.

To estimate the HOMO-LUMO energy gaps according to electrochemistry data we used recently proposed approach [84], based on close relation of the oxidation and reduction potentials with the energies of the HOMO and LUMO levels of organic NLO chromophore. Due to irreversibility or low reversibility of redox processes we used DPV potentials values (as the ones closest usually to the formal oxidation and reduction potentials) to calculate the frontier orbitals energy [27,35,76, 77,84,85].

The electrochemistry picture is very similar for all chromophores under study: quasi-reversible oxidation and irreversible reduction are observed; energy gaps for chromophores vary insignificantly what is in accordance with the DFT estimations (Table 4). These rather close values for the studied chromophores seem to be quite expected: in conformity with the HOMO and LUMO visualization (Fig. 3) the A.A. Kalinin et al.



Fig. 2. UV-Vis experimental spectra of studied chromophores in different solvents.

Table 1		
Photophysical properties	of the studied	chromophores.

$\lambda_{\rm max}$, nm (ε , 10 ³ ·M ⁻¹ cm ⁻¹)							$\Delta\lambda_{max}^{a}$, nm	$\Delta \lambda_{max}^{b}$, nm	
	1,4-dioxane	CHCl ₃	CH_2Cl_2	CH ₃ CN	DMF	DMSO	EC		
DBA-VQ _{Ph} V-TCF _{Ph}	599 (34.2)	652 (28.3)	636 (26.9)	596 (30.4)	604 (20.3)	614 (22.0)	608 (24.9)	53	56
DBA-VQ _{Ph} V-TCF _{Tol}	596 (34.0)	646 (25.4)	632 (28.4)	592 (34.4)	604 (24.0)	612 (28.5)	607 (27.4)	50	54
DBA-VQ _{Ph} V-TCF _{PhCy}	597 (35.9)	648 (30.8)	633 (28.6)	596 (30.6)	608 (22.2)	617 (26.8)	611 (21.2)	51	52
$DBA\text{-}VQ_{on}V\text{-}TCF_{PhCy}$	609 (39.2)	662 (30.9)	657 (38.3)	629 (34.3)	639 (20.0)	647 (21.7)	643 (27.9)	53	33

^a -dioxane/CHCl₃.

^b –CHCl₃/CH₃CN.

Table 2

Electrical characteristics of the studied chromophores calculated at the B3LYP/ 6-31G(d)//M062X/aug-cc-pVDZ level.

Chromophores	μ (D)	$\alpha_{\rm av}$ (10 ⁻²⁴ esu)	β_{zzz} (10 ⁻³⁰ esu)	β_{tot} (10 ⁻³⁰ esu)
7-DBA-VQV-TCF [53]	19.5	118.8	789	875
DBA-VQ _{Ph} V-TCF _{Ph}	20.2	126.6	815	890
DBA-VQ _{Ph} V-TCF _{Tol}	20.1	130.0	775	841
DBA-VQ _{Ph} V-TCF _{PhCy}	16.8	129.4	622	619
DBA-VQonV-TCFPhCy	21.5	123.6	472	517

introduction of the substituents to the chromophores acceptor fragment almost does not affect the frontier orbitals. However, quantitatively the electrochemical estimations give notably smaller values than DFT and optical ones. The smallest gap $\Delta E_{\rm el}$ corresponds to **DBA-VQonV-TCF**_{PhCy}, which coincides with the estimated optical gap $\Delta E_{\rm opt}^{\rm opt}_{\rm max}$ ($\Delta E^{\rm opt}_{\rm max}$) 1240/ λ_{max} , λ_{max} taken from Table 1), because chromophore DBA-VQonV-TCF_{PhCy} has the largest λ_{max} amongst the studied here compounds. The largest electrochemical gap is characteristic of chromophore 7-DBA-VQV-TCF, the basic structure from which all other derivatives with substituents were obtained. This observation also coincides with the results of the optical gap estimation, namely, the large ΔE^{opt}_{max} value for 7-DBA-VQV-TCF ($\lambda_{max} = 619$ nm [53]. E_{HOMO} almost coincide for all chromophores, E_{LUMO} change insignificantly, being slightly lower only for DBA-VQonV-TCF_{PhCy}. Relatively, the results of the energy trends estimation by electrochemical calculation and optical data ($\Delta E_{opt}^{\lambda max}$) are in good agreement (Table 5), although the absolute values of the optical gaps calculated on the basis of λ_{max} are overestimated traditionally.

3.5. Thermal properties

The thermal stabilities of chromophores were investigated by



Fig. 3. Frontier orbitals of 7-DBA-VQV-TCF (a), DBA-VQ_{Ph}V-TCF_{Ph} (b), DBA-VQ_{Ph}V-TCF_{Tol} (c), DBA-VQ_{Ph}V-TCF_{PhCy} (d) and DBA-VQ_{on}V-TCF_{PhCy} (e).

Table 3	
Frontier orbital energies and ΔE_g^{DFT} values for the studied chromophores.	

Chromophores	E(HOMO), eV	E(LUMO), eV	$\Delta E_g^{DFT,}eV$
7-DBA-VQV-TCF	-5.18	-3.28	1.90
DBA-VQ _{Ph} V-TCF _{Ph}	-5.17	-3.24	1.93
DBA-VQ _{Ph} V-TCF _{Tol}	-5.16	-3.22	1.94
DBA-VQ _{Ph} V-TCF _{PhCy}	-5.18	-3.29	1.89
DBA-VQonV-TCFPhCy	-5.20	-3.05	2.15

simultaneous TG/DSC analysis. Fig. 5 shows the thermogravimetric curves of studied chromophores. The investigated quinoxaline-based chromophores exhibit the similar character of weight loss and have high thermal stability: the decomposition temperatures at which 5% mass loss occurs at heating are above 267 °C. However, only for chromophores **DBA-VQ**_{Ph}**V-TCF**_{PhCy} TGA and DSC decomposition temperature agrees well (values T_d^a and T_d^b in Table 6). For chromophores **DBA-VQ**_{Ph}**V-TCF**_{Tol} TGA and DSC decomposition temperatures are markedly different; similar behavior was found for the

Table 4

Electrochemical data (CV peak potentials, DPV potentials) for oxidation-reduction of chromophores and calculated frontier orbitals energy values (eV). $E_{HOMO} = -(E_{HOMO})$	E
$[DPV_{JOX VS. FC+/FC}] + 4.8)(eV), E_{LUMO} = -(E[DPV, red vs. Fc+/Fc] + 4.8)(eV).$	

Chromophores	Cyclic votammetry (E, V)		DPV potentials (\	/)	$E_{\rm HOMO}$, eV	$E_{\rm LUMO}$, eV	$\Delta E^{\rm el}$, eV
	Oxidation	Reduction	Oxidation	Reduction			
7-DBA-VQV-TCF	$E_{p}^{f}=0.25; E_{p}^{r}=0.13;$ $\Delta E=$ quasi-rev.	$E_p^f = -0.92$; irrev.	0.21	-0.83	-5.01	-3.97	1.04
$DBA\text{-}VQ_{Ph}V\text{-}TCF_{Ph}$	$E_{p}^{f} = 0.24; E_{p}^{r} = 0.14;$ $\Delta E = quasi-rev.$	$E_p^{\rm f}=-0.90; irrev.$	0.21	-0.80	-5.01	-4.00	1.01
$DBA\text{-}VQ_{Ph}V\text{-}TCF_{Tol}$	$E_p^f = 0.23; E_p^r = 0.14;$ $\Delta E = quasi-rev.$	$E_p^{\rm f}=-0.91;irrev.$	0.20	-0.82	-5.00	-3.98	1.02
$DBA\text{-}VQ_{Ph}V\text{-}TCF_{PhCy}$	$E_p^f = 0.25; E_p^r = 0.14;$ $\Delta E = quasi-rev.$	$E_p^{\rm f}=-0.91;irrev.$	0.20	-0.81	-5.00	-3.99	1.01
$DBA\text{-}VQ_{on}V\text{-}TCF_{PhCy}$	$E_{p}^{f}=0.24; E_{p}^{r}=0.12;$ $\Delta E=$ quasi-rev.	$E_p^{\rm f}=-0.83; irrev.$	0.20	-0.75	-5.00	-4.05	0.95

Conditions: CH₂Cl₂/0.2 M Bu₄NBF₄, Pt working electrode; AgNO₃ reference electrode, recalculated to Fc⁺/Fc; substrate concentration 1–2 mM.



Fig. 4. Cyclic voltammograms of investigated chromophores in $\rm CH_2Cl_2-0.2~M~Bu_4NBF_4,~scan$ rate 100 mV/s.

Table 5	
Energy gaps of the studied chromophores	, evaluated by different methods.

Chromophore	$\lambda_{\rm max}$, nm ^a	$\Delta E^{\text{opt,}}_{\text{max}} \text{ eV}^{\text{a}}$	$\Delta E_{\rm g}^{ m DFT}$	$\Delta E^{\rm el}, {\rm eV}^{\rm a}$
7-DBA-VQV-TCF	619 [<mark>53</mark>]	2.00	1.90	1.04
DBA-VQ _{Ph} V-TCF _{Ph}	636	1.95	1.93	1.01
DBA-VQ _{Ph} V-TCF _{Tol}	632	1.96	1.94	1.02
DBA-VQ _{Ph} V-TCF _{PhCy}	633	1.96	1.89	1.01
DBA-VQonV-TCFPhCy	657	1.89	2.15	0.95

^a In CH₂Cl₂.

chromophore **7-DBA-VQV-TCF** [53]. The studied compounds appeared as highly crystalline ones with melting points (T_m) at 189 °C, 195 °C and 248 °C for chromophores with Ph, Tol and CyPh substituents in acceptor, respectively (Fig. 6, Table 6). The presence of an endothermic peak at 148 °C for **DBA-VQ**_{Ph}**V-TCF**_{Tol} attracts attention, which is apparently indicates at the recrystallization, since no mass loss is observed at this temperature.

3.6. Atomistic modeling of PMMA-based composite materials

All the considered polymer composite systems were packed in amorphous cell with density, close to that of real polymer, ranging from 1.051 to 1.065 g/cm³; the results of simulations are summarized in Table 7. In all the composite systems studied here some proportion of



Fig. 5. TGA curves of $DBA-VQ_{Ph}V-TCF_{Ph}$ (a), $DBA-VQ_{Ph}V-TCF_{Tol}$ (b) and $DBA-VQ_{on}V-TCF_{PhCy}$ (c).

Table 6	
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Thermal properties of the studied chromophores.

Chromophore	$DBA\text{-}VQ_{Ph}V\text{-}TCF_{Ph}$	$DBA\text{-}VQ_{Ph}V\text{-}TCF_{Tol}$	DBA-VQonV-TCFPhCy
T _d ^a , °C	287	275	267
T _d ^b , °C	232	236	256
T _m , °C	189	195	248
3		1 1	

 $^{\rm a}\,$ TGA, temperature at which 5% mass loss occurs at heating. $^{\rm b}\,$ DSC.

chromophores-guests are noncovalently bound with each other by π - π interactions of different structural moieties, the number of bound chromophores depends on the chromophore concentration in the material. Among stacked structures both parallel and antiparallel arrangement of chromophore dipole moments is revealed for all the chromophores. In composite material **DBA-VQ**_{Ph}**V-TCF**_{Ph}(20)/**PMMA** (Fig. 7(a)) 12 chromophores out of 21 are noncovalently bound by π - π interactions, all pairwise except one trimer (Fig. 7(b), (c)). In two chromophores intramolecular bonds between their rings are formed. Phenyl substituent in acceptor (Ph(A)) also participates in the noncovalent bonds formation, such bonds are formed between phenyl substituents in the bridge (Ph(B)) and in acceptor (Ph(B)-Ph(A), between bridge (B) and Ph(A) (B-Ph(A)).

In the case of DBA-VQ_{Ph}V-TCF_{Ph}(25)/PMMA 17 chromophores out of 28 are bound noncovalently, all the moieties are involved in bonding including Ph(A) in four cases.

At further increase of the chromophore DBA-VQPhV-TCFPh load up



Fig. 6. DSC curves of DBA-VQ_{Ph}V-TCF_{Ph} (a), DBA-VQ_{Ph}V-TCF_{Tol} (b) and DBA-VQ_{on}V-TCF_{PhCy} (c).

Table 7

Composite systems with considered chromophores-guests: number of chromophores in a cell (N), number of noncovalently bound chromophores (Nb), portion of noncovalently bound chromophores (%), maximum number of chromophores in aggregate (M), material density $\rho(g/cm^3)$.

Composite system	Ν	Nb	%	М	ρ
DBA-VQ _{Ph} V-TCF _{Ph} (20)/PMMA	21	12	57	3	1.065
DBA-VQ _{Ph} V-TCF _{Ph} (25)/PMMA	28	17	61	2	1.053
DBA-VQ _{Ph} V-TCF _{Ph} (30)/PMMA	36	23	64	5	1.065
DBA-VQ _{Ph} V-TCF _{Tol} (20)/PMMA	20	4	20	3	1.056
DBA-VQ _{Ph} V-TCF _{Tol} (25)/PMMA	28	7	25	4	1.052
DBA-VQ _{Ph} V-TCF _{Tol} (30)/PMMA	36	15	42	3	1.060
DBA-VQ _{Ph} V-TCF _{PhCy} (20)/PMMA	19	4	21	2	1.065
DBA-VQ _{Ph} V-TCF _{PhCy} (25)/PMMA	25	10	40	4	1.051
DBA-VQ _{Ph} V-TCF _{PhCy} (30)/PMMA	33	16	48	3	1.053
DBA-VQonV-TCFPhCy(20)/PMMA	20	6	33	2	1.062
DBA-VQonV-TCFPhCy(25)/PMMA	26	7	27	3	1.053

to 30 wt% 23 chromophores out of 36 are involved in noncovalent bonding with each other, chromophores are bound most antiparallely, Ph(A) forms noncovalent bonds with donor (D), B and Ph(B). In some chromophores intramolecular π - π -stacking is realized (Ph(B)-Ph(A)). At 30 wt% content the chromophores begin to aggregate with the formation of clusters up to 5 molecules (Table 7), i.e. aggregation becomes pronounced. Chromophore distribution in material is rather nonuniform – chromophores are concentrated in one place in a cell (Fig. S4). The proportion of chromophores involved in noncovalent bonding with each other is increased from 57 to 64% with the chromophore content growth from 20 to 30%, but pronounced chromophore aggregation is revealed only at 30 wt% content.

Only 4 chromophores out of 20 are noncovalently bound by π - π interactions in composite material DBA-VQ_{Ph}V-TCF_{Tol}(20)/PMMA, all pairwise except one trimer. Tolyl substituent in acceptor also participates in the intermolecular noncovalent bonds formation with Ph(B) (Ph (A)-Ph(B)), with bridge (Ph(A)-B). Intramolecular π - π -stacking is also revealed in three chromophores, such chromophores do not interact with any other ones. The number of non-covalently bound chromophores increases to 7 in DBA-VQ_{Ph}V-TCF_{Tol}(25)/PMMA, i.e. 25% (7 of 28) of chromophores are involved in intermolecular π - π interactions, phenyl ring of acceptor substituent participates in noncovalent bonding with acceptor and bridge rings of other chromophores. It should be mentioned, that at 25 wt% content no pronounced aggregation of chromophores was revealed – maximum size of one aggregate is only 4 chromophores, although chromophores are not very uniformly

distributed over the cell (Fig. S5(a)). At 30 wt% content (Fig. S5(b)) 15 chromophores of 36 are noncovalently bound in **DBA-VQ**_{Ph}V-**TCF**_{Tol}(30)/**PMMA** system, tolyl substituent participating in noncovalent binding. In some chromophores intramolecular bonds are also realized with participation of tolyl substituent. In the case of tolylsubstituted acceptor maximum number of chromophores in aggregate is only 3 independently on the chromophore content in material.

In DBA-VQ_{Ph}V-TCF_{PhCy}(20)/PMMA material the chromophores are rather uniformly distributed (Fig. S6(a)), 4 out of 19 chromophores are involved in π - π -interactions with each other, all pairwise. Phenyl fragment of acceptor substituent does not participate in noncovalent bonding. Dimers are bound via donor-donor and donor-bridge interactions.

In **DBA-VQ**_{Ph}**V-TCF**_{PhCy}(25)/**PMMA** the chromophores are still rather uniformly spread over the material, 10 chromophores out of 25 are noncovalently bound with each other, maximum number of chromophores in aggregate reaches 4 units, all parallel to each other. Only one antiparallel pair of stacked chromophores was detected. In **DBA-VQ**_{Ph}**V-TCF**_{PhCy}(30)/**PMMA** (Fig. S6(b)) 16 chromophores of 33 are noncovalently bound with each other by π - π interactions of various moieties. In some chromophores intramolecular bonds between Phe(B) and phenyl ring of PhCy substituent in acceptor are revealed. PhCy(A) participates in noncovalent binding with various moieties of other chromophores (D, Ph(B), B), but in all the revealed cases furanyl ring itself is not involved in noncovalent bonding of chromophores; similar observation was made when considering composite materials with chromophores-guests, containing furanyl acceptor [52].

Composite polymer materials with a NLO chromophore which is representative of another class – quinoxalinone ones - were also considered, chromophore-guest is **DBA-VQ**_{on}**V-TCF**_{PhCy} with quinoxalinone fragment in π -electron bridge. In **DBA-VQ**_{on}**V-TCF**_{PhCy}(20)/ **PMMA** composite system (Fig. S7(a)) 6 chromophores out of 20 are noncovalently bound (Table 7), all pairwise, and one stacking dimer is formed due to interaction of phenyl moiety of PhCy substituent with one of bridge rings. In all dimers chromophores are antiparallelly arranged. In **DBA-VQ**_{on}**V-TCF**_{PhCy}(25)/**PMMA** (Fig. S7(b)) composite system 7 out of 26 chromophores are π - π bound, maximum size of an aggregate is three, in one dimer Ph of PhCy substituent participates in bonding with bridge of the neighbouring chromophore, this substituent does not prevent chromophore parallel arrangement.

Summarizing consideration of composite materials with chromophores-guests, one can see, that the proportion of noncovalently bound chromophores increases with the chromophore content growth in all composite materials, the size of the aggregate is maximal for DBA-VQ_{Ph}V-TCF_{Ph}(30)/PMMA, reaching 5 units. As for other quinoxaline-based substituted chromophores DBA-VQ_{Ph}V-TCF_{Tol} and DBA-VQ_{Ph}V-TCF_{PhCy}, the size of the chromophore aggregate does not exceed 4 units (Table 7) for all three considered concentrations. In composite materials DBA-VQ_{on}V-TCF_{PhCy} the chromophore content increase does not result in growth of the chromophore aggregate size, and proportion of chromophores involved in noncovalent binding is very close for two considered concentrations.

Tolyl and cyclohexylphenyl substituents can be treated as most effective ones, preventing chromophore pronounced aggregation even at 30 wt% content. As for phenyl substituent, it can't completely isolate the chromophores-guests, the size of an aggregate reaches 5 units.

3.7. NLO performance

The thin films of guest-host polymer materials were prepared with PMMA as polymer matrix and studied chromophores as guests to study macroscopic NLO activity. Polymer films were poled in a corona discharge field. The quality of orientation was controlled by the absorption change in UV–Vis spectra detected before and after poling (Fig. 8), and characterized by order parameter, η (Table 8), calculated by the following formula: $\eta = 1$ - A/A_0 , where A and A₀ are the absorptions



Fig. 7. Amorphous cell with DBA-VQ_{Ph}V-TCF_{Ph}(20)/PMMA (a); examples of intramolecular (b) and intermolecular (c) noncovalent bonding.



Fig. 8. UV–Vis electron absorption spectra registered before and after poling for DBA-VQ_{Ph}V-TCF_{PhCy}/PMMA (a) and DBA-VQ_{on}V-TCF_{PhCy}/PMMA (b) films with chromophore load 25 wt%.

of the polymer films after and before poling [5,37,86-88].

NLO coefficients were obtained by the SHG technique using amplified femtosecond pulses at a wavelength of 1028 nm. For each case the effective generation of the second harmonic is observed in a wide range of pump beam incidence angles $(20^{\circ}-80^{\circ})$ with a maximum in the vicinity of 60° (Fig. 9).

NLO activity for chromophore **DBA-VQ**_{Ph}**V-TCF**_{Ph} with large value of first hyperpolarizability (Table 2) was studied more thoroughly and thin polymer films doped with this chromophore in various concentrations (15 wt%, 20 wt%, 25 wt% and 30 wt%) were fabricated. The composite materials **DBA-VQ**_{Ph}**V-TCF**_{Ph}(20)/**PMMA** and **DBA-VQ**_{Ph}**V-TCF**_{Ph}(25)/**PMMA**) show close d_{33} values 29 pm/V, which are maximum amongst considered here **DBA-VQ**_{Ph}**V-TCF**_{Ph}/**PMMA** composite materials (Table 8, Fig. 10). The increase of the chromophore load up to 30 wt% leads to decrease of NLO activity of polymer material **DBA-VQ**_{Ph}**V-TCF**_{Ph}(30)/**PMMA**. This observation is in line with the results for **DBA-VQ**_{Ph}**V-TCF**_{Ph}/**PMMA** composite materials simulation – 30 wt % chromophores load results in most pronounced chromophores aggregation.

Composite materials DBA-VQ_{Ph}V-TCF_{Tol}/PMMA exhibit similar behavior to that for DBA-VQ_{Ph}V-TCF_{Ph}/PMMA: NLO activity is maximum at 20–25 wt% chromophore load, but *d*₃₃ values are 10% higher than in the case of DBA-VQ_{Ph}V-TCF_{Ph}/PMMA at the same chromophore content. NLO activity of DBA-VQ_{Ph}V-TCF_{PhCy}/PMMA unlike DBA-VQ_{Ph}V-TCF_{Ph}/ PMMA and DBA-VQ_{Ph}V-TCF_{Tol}/PMMA demonstrates a more pronounced weight concentration dependence: starting from 23 pm/V at 20 wt% load, *d*₃₃ value arises to 37 pm/V at 25 wt% chromophore content. Increase in the chromophore load up to 30 wt% leads to decrease of NLO coefficient to 27 pm/V for DBA-VQ_{Ph}V-TCF_{PhCy}(30)/PMMA. This value is by 17% larger than *d*₃₃ of DBA-VQ_{Ph}V-TCF_{PhCy}(20)/PMMA, while the *d*₃₃ values for DBA-VQ_{Ph}V-TCF_{Ph}(30)/PMMA and DBA-VQ_{Ph}V-TCF_{Tol}(30)/PMMA, on the contrary, are by 38% and 35% less than the values of DBA-VQ_{Ph}V-TCF_{Ph}(20)/PMMA and DBA-VQ_{Ph}V-TCF_{Tol}(20)/PMMA, correspondingly. The presence of a bulky substituent in the *p*-position of phenyl ring in TCF

Table 8

NLO coefficients (d_{33}), order parameters (η), λ_{max} of polymer film and film thickness (h).

Sample, chromophore(load, wt %)/polymer	h, nm	λ, nm	η	<i>d</i> ₃₃ , pm/V
DBA-VQ _{Ph} V-TCF _{Ph} (15)/PMMA	350	619	0.28	22
DBA-VQ _{Ph} V-TCF _{Ph} (20)/PMMA	450	618	0.27	29
DBA-VQ _{Ph} V-TCF _{Ph} (25)/PMMA	400	621	0.20	29
DBA-VQ _{Ph} V-TCF _{Ph} (30)/PMMA	330	624	0.21	16
DBA-VQ _{Ph} V-TCF _{Tol} (20)/PMMA	260	619	0.27	31
DBA-VQ _{Ph} V-TCF _{Tol} (25)/PMMA	410	621	0.26	35
DBA-VQ _{Ph} V-TCF _{Tol} (30)/PMMA	140	625	0.33	23
DBA-VQ _{Ph} V-TCF _{PhCy} (20)/PMMA	330	627	0.27	23
DBA-VQ _{Ph} V-TCF _{PhCy} (25)/PMMA	530	626	0.25	37
DBA-VQ _{Ph} V-TCF _{PhCy} (30)/PMMA	260	630	0.30	27
DBA-VQonV-TCFPhCy(10)/PMMA	342	647	0.37	21
DBA-VQonV-TCFPhCy(15)/PMMA	220	646	0.35	32
DBA-VQonV-TCFPhCy(20)/PMMA	405	648	0.30	28
DBA-VQonV-TCFPhCy(25)/PMMA	400	649	0.25	27



Fig. 9. The experimental SHG intensity on the incidence angle of femtosecond laser radiation dependence for DBA-VQ_{Ph}V-TCF_{PhCy}/PMMA with chromophore load 25 wt%.



Fig. 10. The d_{33} values chromophore/PMMA materials.

acceptor leads to an increase in macroscopic NLO activity, even at higher chromophore content in polymer film, despite a decrease in first hyperpolarizability of chromophore **DBA-VQ**_{Ph}**V-TCF**_{PhCy} compared to that for **DBA-VQ**_{Ph}**V-TCF**_{Ph} according to DFT; thus, cyclohexylphenyl group exhibits good isolating ability, what is supported by molecular modeling results. In order to clarify the NLO effect in more detail, chromophore **DBA-VQ**_{on}**V-TCF**_{PhCy} with quinoxalinone core instead of quinoxaline one in the π -bridge and TCF_{PhCy} acceptor was synthesized (Scheme 1, Fig. 1). Due to a

decrease in NLO activity of DBA-VQonV-TCFPhCv/PMMA with an increase in the chromophore content from 20 wt% to 25 wt% polymer films doped with 10 wt% and 15 wt% of chromophore DBA-VQonV-TCFPhCv were also fabricated. Maximum of d₃₃ values (32 pm/V) arises at 15 wt% chromophore load, wherein NLO activities of poled films DBA-VQonV-TCF_{PhCv}(20)/PMMA and DBA-VQonV-TCF_{PhCv}(25)/PMMA are close to each other and differ insignificantly form that for DBA-VQonV-TCFPhCv/ PMMA(15). The molecular modeling of polymer composites DBA-VQonV-TCF_{PhCv}/PMMA did not reveal pronounced chromophore aggregation at 20 and 25 wt% chromophore load, thus demonstrating good isolating ability of CyPh substituent. According to DFT calculations, chromophore DBA-VQonV-TCFphCv possesses a large dipole moment in comparison with chromophore DBA-VQ_{Ph}V-TCF_{PhCy} (22 D and 17 D, correspondingly, Table 2), and this fact may be the reason for the shift of the NLO activity maximum towards the low chromophore content in the polymer matrix. The decrease in d_{33} value of DBA-VQ_{on}V-TCF_{PhCy}/PMMA (Table 8, Fig. 10) in comparison with that for $DBA-VQ_{Ph}V-TCF_{PhCy}/PMMA$ correlates with the first hyperpolarizability of chromophores DBA-VQonV-TCFPhCy and DBA-VQ_{Ph}V-TCF_{PhCy} (Table 2).

3.8. Temporal and photochemical and stability

Three materials with chromophores containing Ph, Tol, CyPh substituents in the acceptor fragment preserve more than 90% of d_{33} after annealing at 50 °C for 100 h (92%, 93 and 91% for materials with Ph, Tol and CyPh substituents, respectively). In contrast, only 52% of the initial d_{33} value of the poled film of **DBA-V-TCF(20)/PMMA**, without quinoxaline core in the π -bridge, was kept after 100 h.

Composite materials doped with quinoxaline chromophores are photostable with respect to laser pulses with intensities up to 11.6 GW/ $\rm cm^2$ and up to at least 700 J exposure dose.

4. Conclusion

Four chromophores - representatives of a novel class of NLO D-π-A chromophores with π -deficient heterocyclic moiety in the conjugated bridge were synthesized. Quinoxaline or quinoxalinone cores have been incorporated into chromophore π -bridge together with bulky group introduced in acceptor moiety to study the effect of these factors on electrochemical, linear and nonlinear optical, and thermal properties of these compounds as well as on chromophore aggregation in polymer materials doped with title chromophores and on NLO activity of thin poled polymer film of guest-host materials. Chromophores exhibit a similar broad π - π * intramolecular charge-transfer (CT) absorption band in the visible region in the range 597-662 nm in UV-Vis absorption spectra, positive solvatochromic shift at changing solvent from dioxane to chloroform; solvatochromism inversion was observed to give negative solvatochromic shift at changing solvent from chloroform to polar solvent. The introduction of a bulky cyclohexylphenyl substituent leads to non-planar geometry of the chromophores, decreasing the value of the first hyperpolarizability. The value of the energy gap decreases when passing from quinoxaline-based to quinoxalinone-based chromophores. The thermal stability of chromophores grows with increasing the size of the substituent in acceptor. Tolyl and cyclohexylphenyl substituents in acceptor moiety promote the decrease of pronounced aggregation even at 30 wt% content. Femtosecond nonlinear optical activity of poled thin PMMA films, doped with chromophores with various weight content, have been investigated by SHG technique ($\lambda = 1028$ nm). The films are photostable with respect to laser pulses with peak intensities up to 11 GW/cm². DBA-VQ_{Ph}V-TCF_{PhCy}/PMMA, doped with 25 wt% of chromophore with quinoxaline core in the π -bridge and bulky cyclohexylphenyl group in acceptor, exhibits d_{33} values maximal among those for the studied materials; it demonstrates a good temporal stability of NLO response and excellent chromophore thermal stability.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108801.

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