

Conference Paper

Organic Chromophores with Nonlinear Optical Properties for Electro-optical Modulators

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The appearance of multiple data sources, the ever-increasing demand for speed in a single transmission channel lead to explosive, exponential growth of traffic in subscriber access networks, which inevitably leads to the creation of fifth-generation networks (5G). In such networks, modulation/demodulation systems and multiplexing/demultiplexing of streams with data rates above 10 Gb/s (up to 100 GHz) play an enormous role.

Electrooptical modulators are used in civil, military and space segments in devices of radio-photonics, in optical communications (telecom, 1.3, 1.5 μm) and optical signal processing; in optical interconnections for data processing centers (Datacom, 0.84 μm) and interchip/intra-chip data transmission (computercom), communication systems of the generation 5G. The development of new functional electro-optic materials with improved characteristics will allow modulation at frequencies of tens or even hundreds of gigahertz with minimal contribution of the modulator to the noise parameters of the system, which is especially important for low-signal radio frequency applications. Considering the high demand for such materials in advanced developments, incl. military, and the absence of domestic producers, the development of this direction is critical in terms of ensuring the sovereignty of the country.

Currently, most of the existing modulators operate on the basis of lithium niobate, which allows modulating the signal with a frequency of up to 20 GHz, which is inadequate. The required values in modern conditions are 80-100 GHz.

As an alternative to inorganic crystals underlying such modulators, organic polymeric nonlinear optical materials with a quadratic response to an applied high intensity electric field can be used. Already now, such materials are used in photonics and optoelectronics, in particular, in broadband and high-speed digital information fiber-optic communication systems production with electro-optical signal modulation by means of Mach-Zehnder modulators (Figure 1). [1-9]

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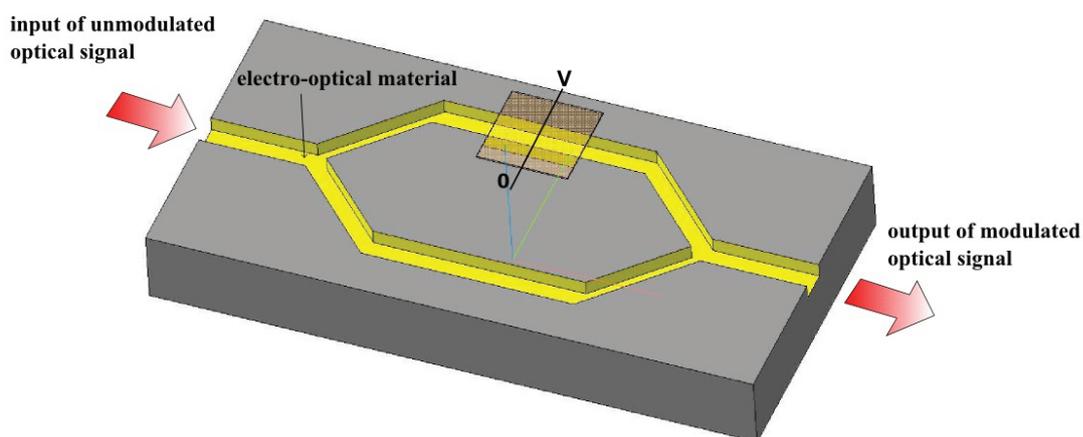


Figure 1: Schematic representation of the electro-optical Mach-Zehnder modulator.

Among the advantages of polymeric materials, it is worth noting the high values of nonlinear electrical susceptibility, rapid response, exceptional chemical diversity—the ability to introduce different functional groups into the material and thus vary the physicochemical properties, as well as the comparative ease of production and processing. On the basis of organic polymers, materials with quadratic nonlinear optical characteristics are currently being created, which significantly exceed the corresponding parameters of inorganic materials. For example, the electro-optical coefficient r_{33} for LiNbO_3 is 30 pm/V, while the same index for a number of organic materials reaches 300 pm/V and above. Such devices are being actively developed in the world. The leading countries in this area are the United States, Japan, China, and Korea [1-9]. The urgency of this direction development is determined by the absence of domestic manufactures of modulators based on organic electro-optical polymer materials. There is no industrial production of electro-optical polymer materials in Russia, which leads to a backlog in the technology of high-speed digital information fiber-optic systems.

The functionality of organic electro-optic polymer materials is a result of the presence of active chromophores in them, which are the so-called push-pull systems. Chromophores consist of electron-withdrawing and electron-donating fragments, separated by a conjugated bridge. (Figure 2)

As acceptor fragments, the derivatives of 2-(3-cyano-5,5-disubstituted furan-2 (5H)-ylidene) malononitrile [1-5], ethylene-1,1,2-tricarbonitrile [6], 2,2'-(1H-ylidene-1,3 (2H)-diylylene)dimalononitrile, nitrobenzene [7,2], etc. (Figure 2).

Synthesis of the starting 2-methyl-3-cyanochromone (1) and 4-methyl-3-cyanocoumarin (4) was carried out according to the previously developed methods [8] and [9]. Trans 2-[2-(5-bromothiophen-2-yl)vinyl]-4-oxo-4H-chromone-3-carbonitrile (2a), trans 2-[2-(4-bromophenyl)vinyl]-4-oxo-4H-chromone-3-carbonitrile (2b), trans 2-[2-(4-diethylaminophenyl)vinyl]-4-oxo-4H-chromone-3-carbonitrile (2c) and trans 4-[2-(5-bromothiophen-2-yl)-vinyl]-3-cyanocoumarin (5) were prepared by Knoevenagel reaction of 2-methyl-3-cyanochromone (1) or 4-methyl-3-cyanocoumarin (4) with the corresponding aldehyde in the presence of catalytic amounts of piperidine. The reaction proceeds with slight heating in an ethanol medium for 30-40 min, while the products were isolated with yields of 20 to 80%. (E)-2-(2-(5-(4-(dimethylamino)phenyl)thiophen-2-yl)vinyl)-4-oxo-4H-chromene-3-carbonitrile (LS-686) and (E)-2-(2-(4-(4-(dimethylamino)phenyl)phenyl)vinyl)-4-oxo-4H-chromene-3-carbonitrile (LS-701) were prepared by cross-coupling the compound (2) and (E)-2-(2-(5-(4-(dimethylamino)phenyl)thiophen-2-yl)vinyl)-2-oxo-2H-chromene-3-carbonitrile (LS-684) with 4-dimethylaminophenylboronic acid in the presence of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and catalytic amounts of $[\text{Pd}(\text{PPh}_3)_2]\text{Cl}_2$. A study of the spectral characteristics of the compounds obtained showed (Fig. 1, A) that the compounds have intense absorption bands with two maxima. In the transition from 3-cyanochromones to 3-cyanocoumarins, a significant bathochromic shift of the absorption bands from 17 to 77 nm is observed. In this case, 3-cyanochromones have fluorescence in the 550-640 nm range, in contrast to 3-cyanocoumarins. The LS-684 connection is virtually identical to the known and widely used TCVDPA connection.

A study of the spectral characteristics (Table 1) of the compounds obtained showed (Fig. 1, A) that the compounds have intense absorption bands with two maxima. Moving from 3-cyanochromones to 3-cyanocoumarins, a significant bathochromic shift of the absorption bands from 17 to 77 nm is observed. In this respect, 3-cyanochromones have fluorescence in the 550-640 nm range, in contrast to 3-cyanocoumarins. Compound LS-684 have almost identical properties to the known and widely used compound TCVDPA.

Thus, representatives of new classes of chromophores based on the derivatives of 3-cyanochromones and 3-cyanocoumarins containing the donor fragment at position 4 and 2, respectively, were obtained, their spectral characteristics were studied. Comparison of the properties of the compounds obtained with the properties of known chromophores, for example, TCVDPA allows us to conclude that the future study of these classes of compounds and their possible use in electro-optical modulators is promising.

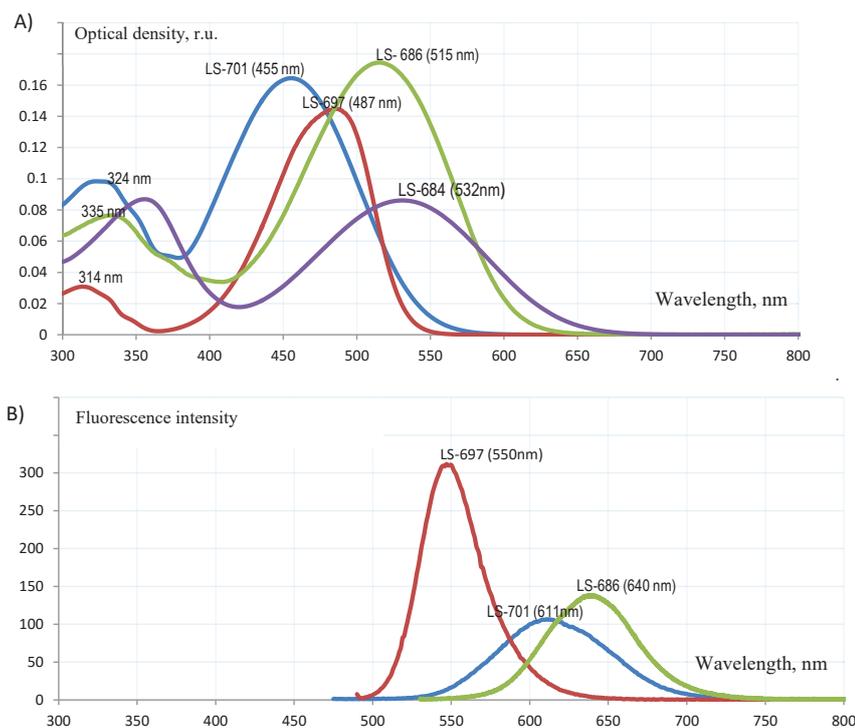


Figure 3: A) Absorption spectrum of LS-686, LS-697, LS-701 in chlorobenzene at a concentration of 0.01 mg/ml; B) Fluorescence spectra of LS-686, LS-697, LS-701 in chlorobenzene at a concentration of 0.01 mg/ml; 0.003 mg/ml; and 0.03 mg/ml, respectively.

TABLE 1: Physicochemical properties of obtained compounds.

#	Structure	λ_{abs} , nm (D)*	λ_{flu} *	I, a.u.	mp	Yield, %
1	2a	392 nm (0,9) (0.05mg/ml in CB)	-	-	252-254°C.	75%.
2	2b	350 nm (0,5) (0.05mg/ml in CB)	-	-	235-237°C	40.6%.
3	2c (LS-697)	314(0,578), 487(2.85) (0.2mg/ml in CB)	547 nm	330,136 (CB, 0,003mg/ml)	214°C.	67%
4	LS-686	335 nm (0,076) 516 nm(0,17) (0.01mg/ml in CB)	640 nm	104	289-290°C.	28%
6	5	-	-	-	198°C	40%
5	LS701	324 (0,49) nm 455 (0,82) nm (0.05mg/ml in CB)	611 nm	106(CB, 0,003mg/ml)	272-275°C.	44 %
6	LS-684	356 nm (0,52) 531nm (0,51) (0.06mg/ml in CB)	-	-	227°C	30%.

* Optical properties were investigated in solutions of chlorobenzene. λ_{abs} , nm is the absorption wavelength of the compounds, D is the optical density, λ_{flu} is the fluorescence wavelength, I, fluorescence intensity

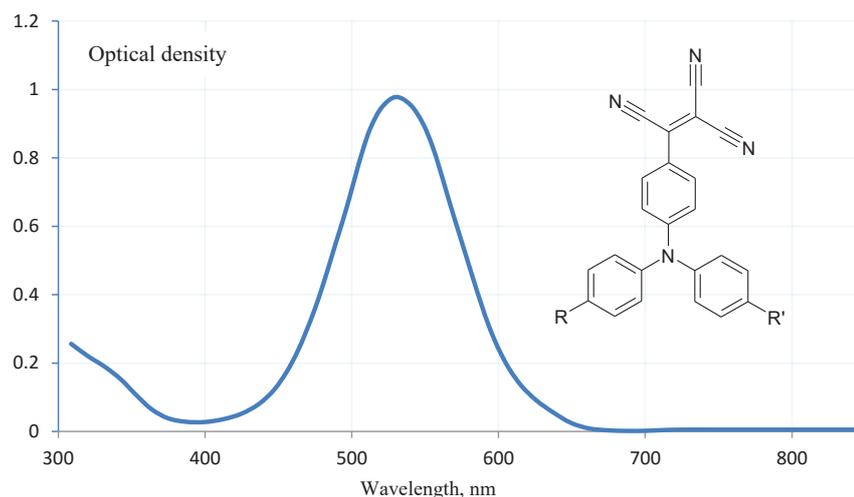


Figure 4: General formula and absorption spectra of TCVDPA in methylene chloride.

1. Experimental

NMR spectra were recorded on a Bruker AM-300 (300 MHz) instrument in DMSO- d_6 or $CDCl_3$. EI mass spectra were measured on a Finnigan MAT INCOS 50 instrument using a direct inlet system; the ionization energy was 70 eV. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000; internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile (flow rate 3 μ L/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. Melting points were measured on a Boetius hot-stage apparatus (uncorrected). The reaction mixtures were analyzed, and the purity of all products was checked by TLC on Silica gel 60 F254 plates (Merck).

1.1. Knoevenagel reaction (general method)

To 185 mg (1 mmol) of 2-methyl-3-cyanochromone or 4-methyl-3-cyanocoumarin in 6 ml of ethanol 1.1 mmol of the corresponding aldehyde is added and a drop of piperidine. The mixture is stirred with heating for 1-28 hours. The mixture is cooled, the precipitate formed is filtered off, washed with ethanol. The product was purified by column chromatography (hexane/methylene chloride 2: 1).

1.2. (E)-2-[2-(5-bromothiophen-2-yl)vinyl]-4-oxo-4H-chromone-3-carbonitrile (2a)

The product was obtained at refluxing for 1.5 hours. Yield 75% %. ^1H NMR (300 MHz, CDCl_3) δ 8.24 (d, $J = 7.8\text{Hz}$, 1H), 7.89 (d, $J = 15.3\text{Hz}$, 1H), 7.78 (s, 1H), 7.63-7.40 (m, 2H), 7.14 (s, 2H), 6.97 (d, $J = 15.6\text{ Hz}$, 1H). HRMS: found m/z 357.9530; calculated for $\text{C}_{16}\text{H}_8\text{BrNO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 357.9532.

1.3. (E)-2-[2-(4-bromophenyl) vinyl]-4-oxo-4H-chromone-3-carbonitrile (2b)

The product was obtained at refluxing for 28 hours. The yield was 40.6%. ^1H NMR (300 MHz, CDCl_3) δ 8.24 (d, $J = 7.9\text{Hz}$, 1H), 7.86 (d, $J = 15.9\text{Hz}$, 1H), 7.79 (d, $J = 8.5\text{Hz}$, 1H), 7.69-7.38 (m, 6H), 7.27 (d, $J = 3.5\text{ Hz}$, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 173.72, 167.25, 154.93, 141.61, 135.19, 132.76, 132.57, 129.92, 126.57, 126.20, 122.37, 117.94, 117.31, 113.21, 98.64. ^{13}C NMR (75 MHz, CDCl_3) δ 173.72, 167.25, 154.93, 141.61, 135.19, 132.76, 132.57, 129.92, 126.57, 126.20, 126.09, 122.37, 117.94, 117.31, 113.21, 98.64.

1.4. (E)-2-[2-(4-diethylaminophenyl)-vinyl]-4-oxo-4H-chromone-3-carbonitrile (2c)

The product was obtained at refluxing for 2 hours in a yield of 67%. ^1H NMR (300 MHz, CDCl_3) δ 8.19 (d, $J = 7.7\text{Hz}$, 1H), 7.81 (d, $J = 15.4\text{Hz}$, 1H), 7.72 (t, $J = 7.3\text{Hz}$, 1H), 7.54 (d, $J = 8.5\text{ Hz}$, 3H), 7.42 (t, $J = 7.5\text{Hz}$, 1H), 6.96 (d, $J = 15.4\text{Hz}$, 1H), 6.67 (d, $J = 8.8\text{Hz}$, 2H), 3.45 (q, $J = 7.0\text{ Hz}$, 4H), 1.24 (t, $J = 7.1\text{Hz}$, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.18, 168.81, 154.96, 150.55, 143.92, 134.51, 131.42, 125.92, 125.83, 122.36, 121.05, 117.70, 114.40, 111.47, 109.54, 95.07, 44.66, 12.61. HRMS: found m/z 345.1606; calculated for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 345.1598.

1.5. (E)-4-[2-(5-bromothiophen-2-yl)-vinyl]-3-cyanocoumarin (5)

The product was obtained at refluxing for 2 hours with a yield of 40%. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.21 - 7.98 (m, 1H), 7.94-7.67 (m, 2H), 7.67 - 6.21 (m, 5H). HRMS: found m/z 357.9530; calculated for $\text{C}_{16}\text{H}_8\text{BrNO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 357.9532.

1.6. Cross-coupling reaction (general procedure)

247 mg (1.5 mmol) of 4-dimethylaminophenyl boronic acid, 550 mg of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, 40 mg of $[\text{Pd}(\text{PPh}_3)_2]\text{Cl}_2$ and 25 ml of CH_3CN are added to 1 mmol of bromo derivative 2 or 5. The mixture is refluxed for 1.5 hours. After completion of the reaction (TLC control), the mixture was evaporated and the product was isolated by column chromatography (hexane/methylene chloride 2: 1).

1.7. (E)-4-[2-(2-(5-(4-(dimethylamino)phenyl)thiophen-2-yl)vinyl)-4-oxo-4H-chromene-3-carbonitrile (LS-686)

The yield is 28%. Yield: 44%. ^1H NMR (300 MHz, CDCl_3) δ 8.24 (d, $J = 7.8\text{Hz}$, 1H), 7.94 (d, $J = 15.8\text{Hz}$, 1H), 7.86-7.58 (m, 9H), 7.50 (t, $J = 7.5\text{Hz}$, 2H), 7.33 (s, $J = 10.1\text{Hz}$, 1H), 3.12 (s, 6H). HRMS: found m/z 399.1171; calculated for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 399.1162; found m/z 421.0990; calculated for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 421.0981; found m/z 437.0737; calculated for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{K}]^+$ 437.0721.

1.8. (E)-2-(2-(4-(4-(dimethylamino)phenyl)phenyl)vinyl)-4-oxo-4H-chromene-3-carbonitrile (LS-701)

Yield 44%. ^1H NMR (300 MHz, CDCl_3) δ 8.24 (d, $J = 7.8$ Hz, 1H), 7.94 (d, $J = 15.8$ Hz, 1H), 7.86 – 7.58 (m, 9H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.33 (s, $J = 10.1$ Hz, 1H), 3.12 (s, 6H). HRMS: found m/z 393.1604; calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 393.1598; found m/z 415.1430; calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$ 415.1417; found m/z 431.1167; calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{M}+\text{K}]^+$ 431.1156.

1.9. (E)-2-(2-(5-(4-(dimethylamino)phenyl)thiophen-2-yl)vinyl)-2-oxo-2H-chromene-3-carbonitrile (LS-684)

The yield is 30%. ^1H NMR (300 MHz, CDCl_3) δ 8.03 (d, $J = 15.8\text{Hz}$, 1H), 7.95 (d, $J = 8.1\text{Hz}$, 1H), 7.70 (t, $J = 7.5\text{Hz}$, 1H), 7.56 (d, $J = 7.9\text{Hz}$, 2H), 7.49-7.38 (m, 3H), 7.34 (d, $J = 2.9\text{Hz}$, 1H), 7.20 (d, $J = 2.6\text{Hz}$, 1H), 7.08 (d, $J = 15.8\text{Hz}$, 1H), 6.80 (d, $J = 2.7\text{Hz}$, 1H), 3.06 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 158.00, 156.84, 153.52, 150.83, 150.37, 137.99, 137.42, 134.58, 127.81, 127.21, 127.03, 126.17, 125.09, 122.23, 117.97, 117.34, 115.09, 114.66, 112.76, 95.14, 40.60. HRMS: found m/z 399.1171; calculated for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 399.1162; found m/z 421.0990; calculated for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 421.0981; found m/z 437.0737; calculated for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{K}]^+$ 437.0721.

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