Branched oligophenylenes containing octylphenotiazine and dioctylfluorene groups and phen-1,3,5-triyl branching center

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A series of branched oligophenylenes containing the dioctylfluorene and octylphenothiazine moieties was synthesized using the Suzuki reaction applied within the framework of the $A_2 + B_2 + B_3$ approach. 1,3,5-tris(7-Bromo-9,9-di-*n*-octylfluoren-2-yl)benzene and 1,3,5-tris-(4-bromophenyl)benzene were used as the branching co-monomers. It was shown that the fluorescence spectra of co-oligomers containing phenothiazine moieties are shifted to the long-wavelength region as compared to the spectra of that without such moieties.

Key words: branched oligophenylenes, Suzuki reaction, phenothiazine moieties, 1,3,5-triphenylbenzene, 1,3,5-tris(9,9-di-*n*-octylfluorene-2,7-ylene)benzene.

Electroluminescent polymers became applied as materials for the active layers of light-emitting diodes (PLED). A significant interest of researchers is attracted by the opportunity of employing these polymers in flat panel displays and illuminating devices.[1—4]

The introduction of molecular functional moieties, including chromophoric ones, into polymers allows one to modify their structure and create new materials that possess, *e.g.*, an adjustable fluorescence.[5]

Polyfluorene (PF)[6—10] and its derivatives are of particular interest among the photo- and electro-active conjugated polymers, since they can be successfully applied in PLED due to the high quantum efficiency of photoluminescence (PL), a good thermal stability, and the opportunity to introduce various functional groups at the position 9 of fluorene.

A series of polyfluorenes was previously synthesized *via* the introduction of units of various modifying comonomers into the polymer chain. Investigations of the opportunity to prepare highly-efficient red, green, and blue photoemitters based on them[11—13] confirmed the application perspectiveness of these polymers in PLED.

A covalent attachment of the chromophore to the polymer is the most widely used one among various methods for adjusting the color of LED, since this approach prevents the formation of aggregates. In the case of two chromophores mixed, the energy transfer occurs from the dye with a larger band-gap to the dye with the narrower band, and the emission from the latter is prevalent.[14,15] Chromophore fragments such as thiophene, bithiophene, benzothiazole, and benzodithiazole derivatives are currently applied for this purpose.[16—19] Phenothiazine is one among the available heterocyclic compounds containing electron-rich sulfur and nitrogen heteroatoms. Polymers and organic molecules[20,21] possessing moieties of phenothiazine or its derivatives have recently attracted an attention of researchers due to the unique optoelectronic properties that make these compounds being promising materials for applications in light-emitting diodes,[8] photovoltaic, and chemiluminescent devices.[17,18] It was assumed that the inclusion of phenothiazine or its derivatives in the PF chain should improve the hole conductivity and thus increase the electroluminescence efficiency.[12,22] Moreover, the nonplanar structure of the phenothiazine ring is capable of the aggregation inhibition.[12] The electron-rich phenothiazine ring is an excellent molecular building block to achieve the better emission and also hole conductivity in polymer electronic devices.

Taking into account the facts mentioned above, it was interesting to synthesize new fluorescent oligomers with a branched structure containing the fluorene, phenothiazine, and phenylene moieties. The Suzuki reaction was employed for the synthesis of soluble branched oligomers *via* a polycondensation of $A_2 + B_2 + B_3$ type.

Results and Discussion

In the present work, branched co-oligomers containing phenylene, fluorene, and also phenothiazine moieties were synthesized, and a primary analysis of their luminescent properties was carried out. At the first stage, the bifunctional monomer 3,7-dibromo-10-*n*-octylphenothiazine (**1**) was obtained. It was prepared *via* the two-step method[23] (Scheme 1).

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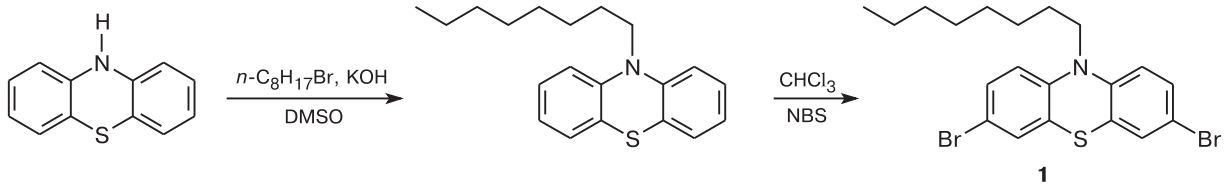
Scheme 1

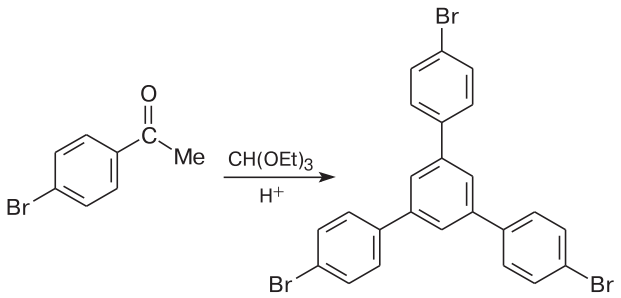


1

The octyl moiety was initially attached to phenothiazine. The bromination of 10-*n*-octylphenothiazine with *N*-bromosuccinimide (NBS) was carried out during the second step.

The branching monomer, 1,3,5-tris(4-bromophenyl) benzene,[24] was synthesized *via* the reaction of trimerization cyclocondensation of 4-bromoacetophenone in the presence of orthoformate ester[25] according to Scheme 2.

Scheme 2



The second branching monomer, 1,3,5-tris(7-bromo-9,9-di-*n*-octylfluoren-2-yl)benzene,[26–28] was obtained according to Scheme 3.

Synthesis of branched oligophenylenes was carried out by the Suzuki reaction *via* a polycondensation of $A_2 + B_2 + B_3$ type. The difference between obtained oligomers **O-1** and **O-2** is in the branching center, which is the 1,3,5-tris-(phen-1,4-ylene)benzene moiety in the first case (Scheme 4) and the 1,3,5-tris(9,9-di-*n*-octylfluorene-2,7-ylene)benzene moiety in the second one (Scheme 5).

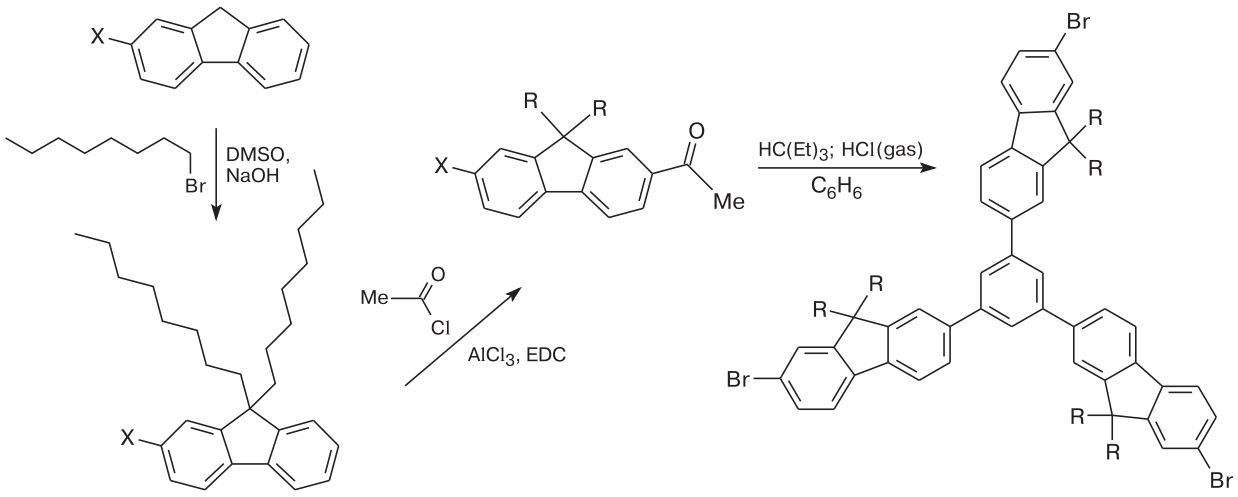
Oligomer O-3 did not contain any phenothiazine moieties and was synthesized for a comparison (Scheme 6).

The ratio between the tri- and di-halide compounds, which was used in these reactions, was 1 : 3.5. This ratio was selected since an increased proportion of the trifunctional monomer in the reaction leads to a partial jellification.

Usually, the molecular weights (M_W) of such branched oligomers are up to 8000 Da. Their values were determined by the sedimentation method,[29] since the data obtained by the GPC method according to the polystyrene standard were not reliable.

^{1}H NMR spectra of all the three oligomers are similar. The precise assignment of signals was not performed due to their complicated character. We followed the published data[30] for assigning the signals. In the aromatic region of ^{1}H NMR spectra of samples **O-1** (Fig. 1) and **O-3** (Fig. 2), the signals characteristic of protons of the fluorene and phenylene moieties can be identified in the range of

Scheme 3



R = *n*-C_8H_{17}

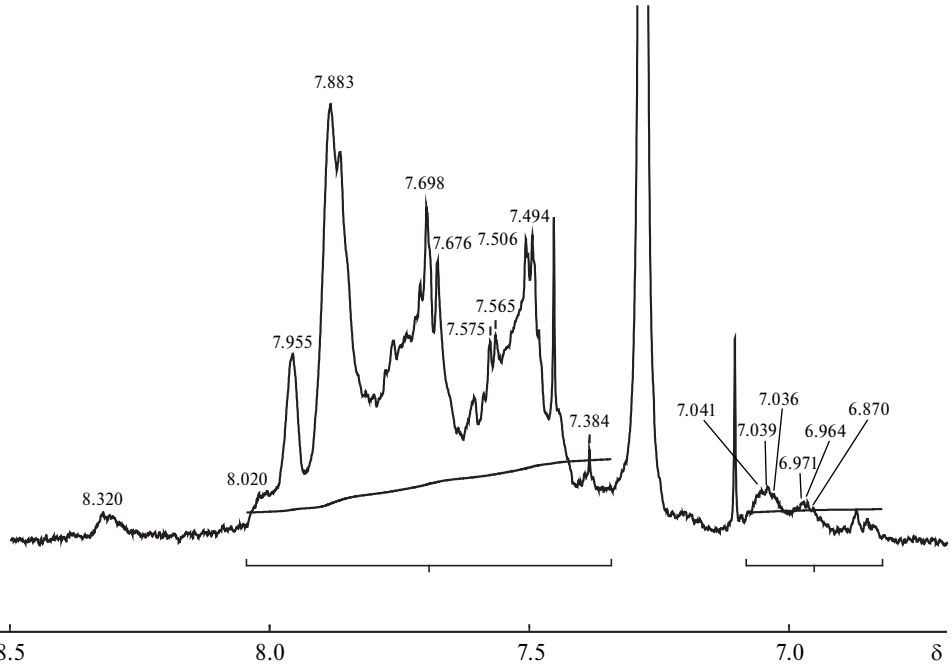
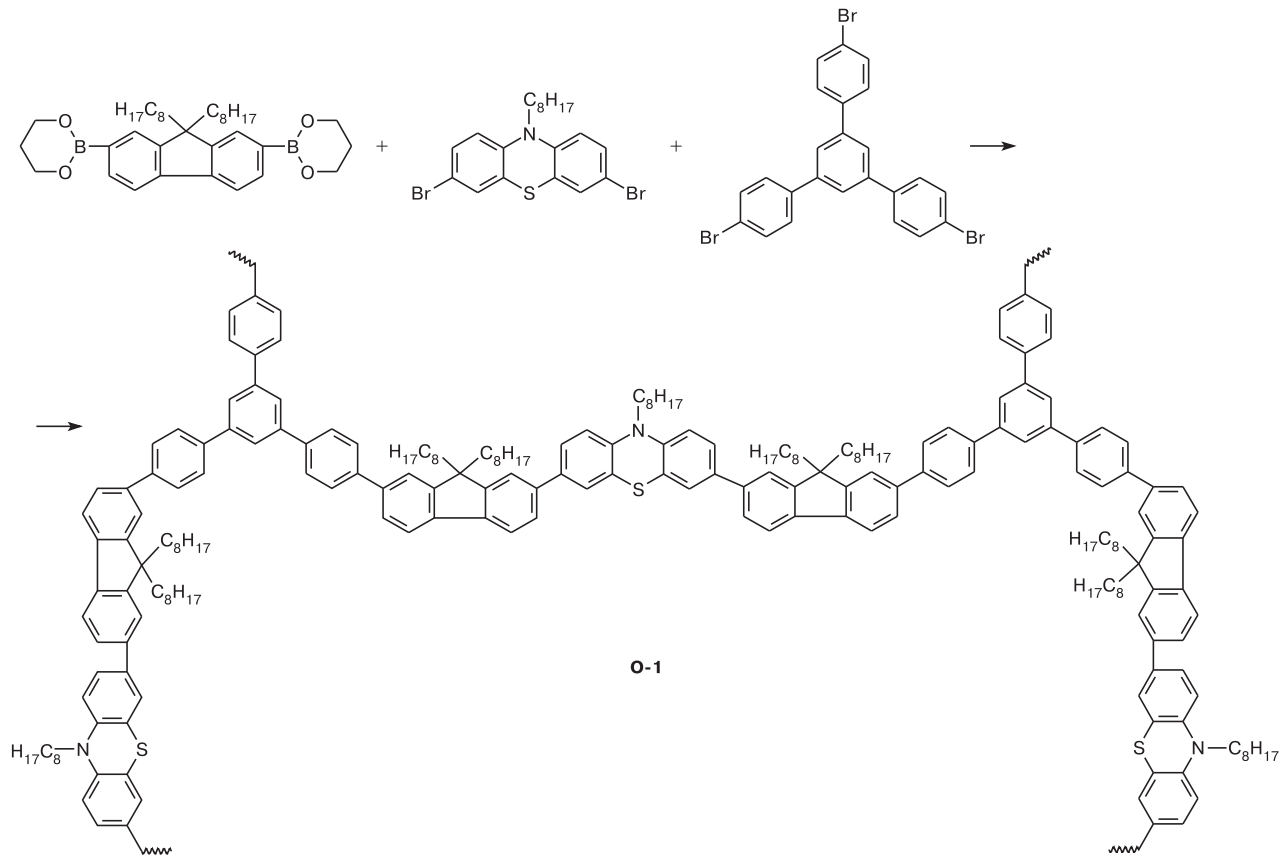
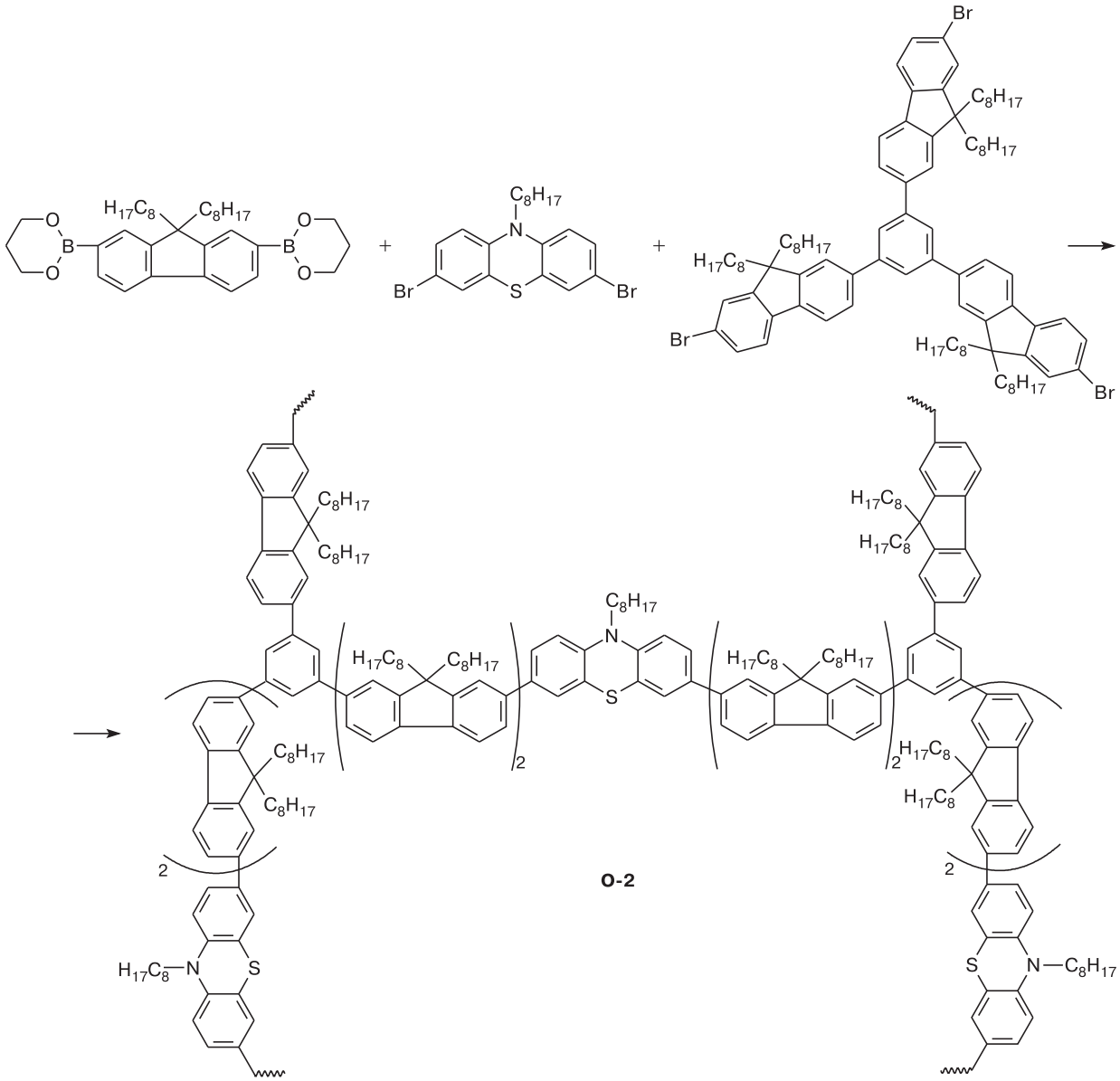


Fig. 1. ^{1}H NMR spectrum of the aromatic part of sample **O-1**.

Scheme 4



Scheme 5



O-2

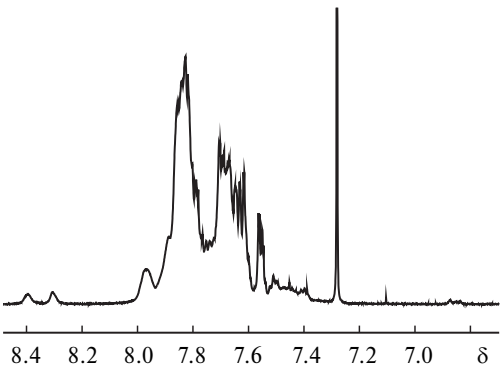
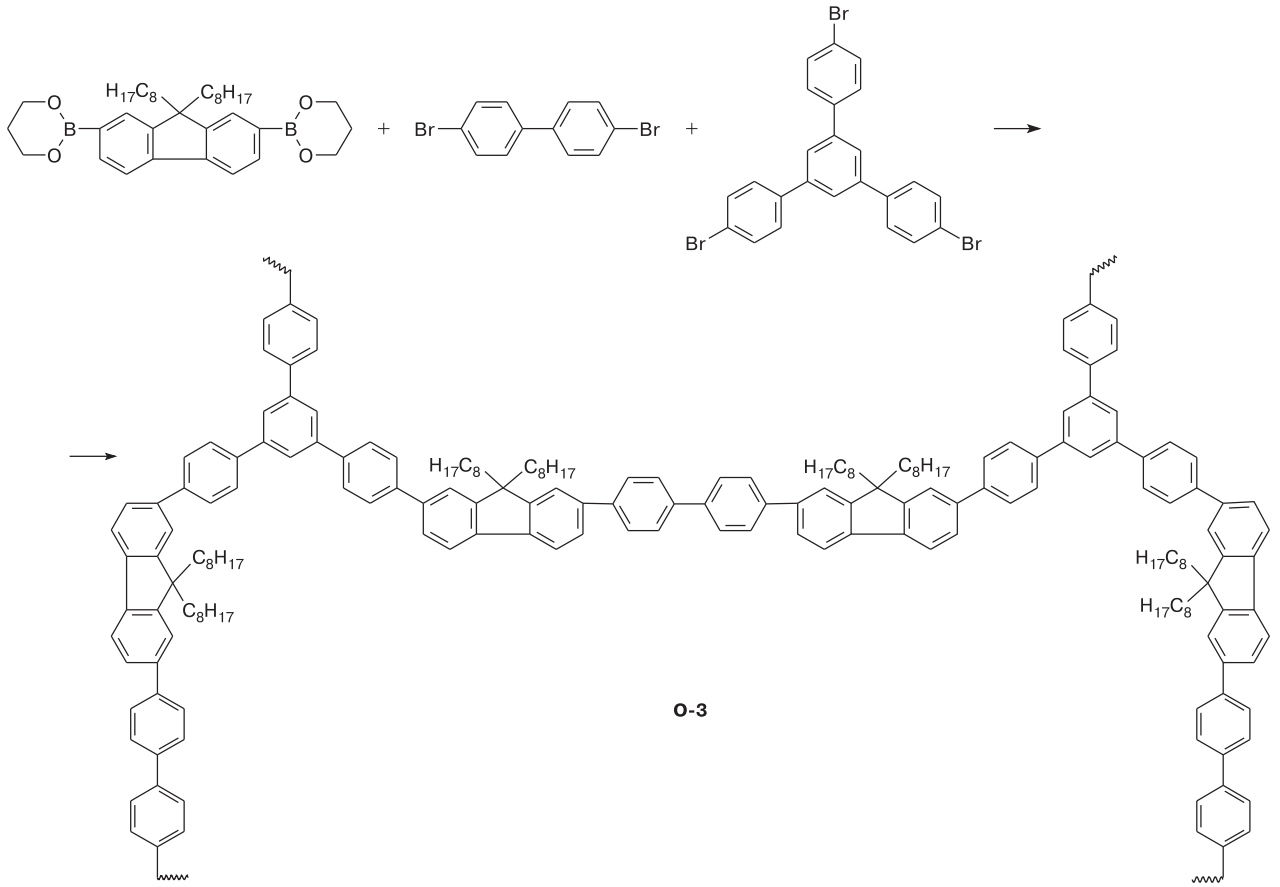


Fig. 2. ^{1}H NMR spectrum of the aromatic part of sample **O-3**.

7.4—8.4 ppm. At the same time, the spectrum of sample **O-1** contained signals related to the protons of phenothiazine moieties in the region of 6.8—7.1 ppm. The ^{1}H NMR spectrum of sample **O-2** is similar to that of **O-1**. The comparison of integral intensities of the proton signals in the aromatic and aliphatic regions of oligomers revealed that they are at the ratio of approximately 1 : 5.5 (**O-1**), 1 : 8.1 (**O-2**), and 1 : 2.2 (**O-3**), which confirmed a significantly smaller content of octyl groups in oligomer **O-3** due to the absence of substituted phenothiazine moieties and also the largest number of such groups in oligomer **O-2** due to the use of branching monomer with the substituted fluorene groups.

Scheme 6



The absorption spectra of solutions of the investigated oligomers are shown in Fig. 3. The spectrum of sample **O-3** appears as a broad structureless band with a major maximum at 345 nm (see Fig. 3, curve *3*). In the spectrum of sample **O-1**, the same band is marginally broadened (curve *1*), while its major maximum is located at a wavelength of 337 nm. The spectrum of sample **O-2** is an even broader band with the major maximum at 328 nm (see Fig. 3, curve *2*). The shape of this spectrum allowed us to suggest the presence of several chromophore fragments. In addition, the long-wavelength edges of absorption bands of samples **O-1** and **O-2** are approximately coincided and located in the region of 455—460 nm. It may be assumed that the phenothiazine moiety in the structure of these oligomers is responsible for the observed decrease of absorption bands.

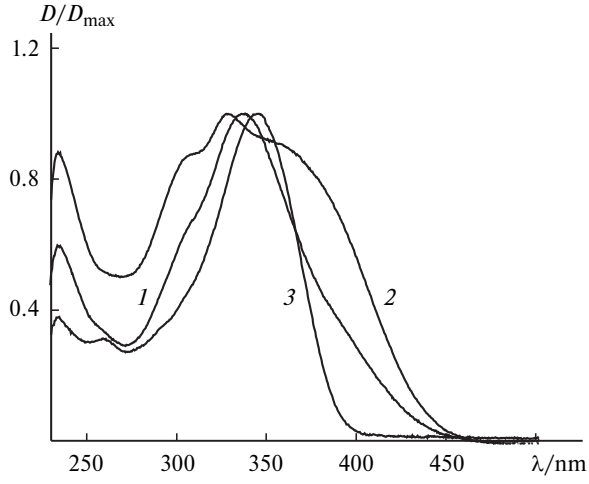


Fig. 3. Absorption spectra of the solutions of samples **O-1** (*1*), **O-2** (*2*), and **O-3** (*3*) in $CHCl_3$ (concentration of ~10^{-5} mol L^{-1}).

The fluorescence spectra of solutions of the investigated co-oligomers are significantly different from each other (Fig. 4). For instance, the fluorescence spectrum of sample **O-3** containing the chromophore moieties consisting of *p*-substituted benzene rings and fluorene is typical of phenylene oligomers and appears as a wide band with the major maximum at 403 nm (see Fig. 4, curve *3*). The spectra of samples **O-1** and **O-2** contain the two fluorescence bands with the major maxima at 393 and 493 nm (see Fig. 4, curves *1* and *2*, respectively), while the long-wave band is much more intense than the short-wave one.

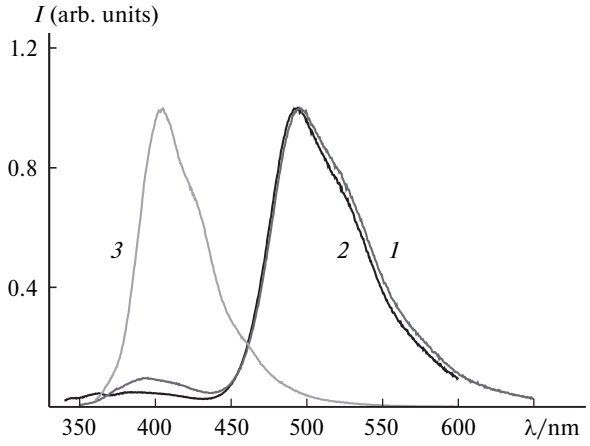


Fig. 4. Fluorescence spectra of the solutions of samples **O-1** (*1*), **O-2** (*2*), and **O-3** (*3*) in $CHCl_3$, recorded at the excitation wavelength corresponded to the maximum of absorption band (concentration of ~10^{-5} mol L^{-1}).

It appears due, most likely, to the inclusion of phenothiazine moiety into the chromophore fragments of oligomers. The fluorescence spectra of all the three compounds do not depend on the excitation wavelength. Moreover, the long-wavelength fluorescence bands of samples **O-1** and **O-2** are almost identical in their shape and position. This allows us to assume that the optical centers responsible for the long-wavelength fluorescence of these compounds possess a similar structure.

Therefore, the solutions of synthesized oligomers possess the fluorescence in the region of 350—650 nm, while the spectra of oligomers containing phenothiazine are shifted to the long-wave region. The obtained oligomers form thin transparent films that also exhibit the fluorescence, which allows them to be applied as the active layers in electroluminescent devices.

Experimental

1,3,5-tris(7-Bromo-9,9-di-*n*-octylfluoren-2-yl)benzene.[26—28] ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.90 (s, 3 H); 7.77 and 7.82 (both dd, 6 H, J = 7.7 Hz); 7.69 (s, 3 H); 7.63 (d, 3 H, J = 8.4 Hz); 7.50—7.53 (m, 6 H); 1.98—2.09 (m, 12 H); 1.06—1.25 (m, 60 H); 0.80—0.85 (m, 18 H); 0.67—0.74 (m, 12 H). Found (%): C, 75.1; H, 8.9; Br, 16.0. Calculated for $C_{93}H_{123}Br_3$ (%): C, 75.4; H, 8.4; Br, 16.2.

3,7-Dibromo-10-*n*-octylphenothiazine.[22] 10-*n*-Octylphenothiazine (11.1 g, 35 mmol) was dissolved in chloroform (200 mL) in a flask equipped with a magnetic stirrer, and the solution was cooled to 5 °C. *N*-Bromosuccinimide (14 g, 80 mmol) was then added in small portions to the reaction mixture. The reaction was carried out under stirring at 5 °C for 2 h. The reaction mixture was poured into water (400 mL), and the product was extracted with chloroform from the resulting mixture. The resulting extract was washed with water and dried over anhydrous magnesium sulfate. The solvents were evaporated, and the product was purified by column chromatography (silica gel, petroleum ether—benzene mixture of 1 : 1). The mass spectrum of compound **1** contains a molecular ion of 3,7-dibromo-10-*n*-octylphenothiazine ([M^+] 468). The ^{1}H NMR spectrum of synthesized product was completely corresponded to that of 3,7-dibromo-10-*n*-octylphenothiazine. ^{1}H NMR (300 MHz), δ: 7.34 (m, 4 H); 6.95 (d, 2 H); 3.81 (t, 2 H); 1.62 (m, 2 H); 1.31 (m, 2 H); 1.19 (m, 8 H); 0.81 (t, 3 H).

1,3,5-tris(4-Bromophenyl)benzene.[24] 4-Bromoacetophenone (7.962 g, 40 mmol) and orthoformate ester (8 mL, 48 mmol) were dissolved in benzene (24 mL) in a flask. Gaseous hydrogen chloride was bubbled through the solution at room temperature and under stirring for 3 h. The solution became brownish-red colored and the precipitate formation began during the first hour. The resulting precipitate was filtered off, washed with acetone and methanol, and dried. The yield of product recrystallized from chloroform was 43.6%. The ^{1}H NMR spectrum of synthesized product (see Fig. 1) was completely corresponded to that of 1,3,5-tris(4-bromophenyl)benzene.[24] ^{1}H NMR (500 MHz), δ: 7.68 (s, 3 H); 7.60 (d, 6 H, J = 8.5 Hz); 7.53 (d, 6 H, J = 8.5 Hz).

Bis(1,3-propanediol) ester of 9,9-dioctylfluorendiboronic acid (Aldrich, 97%) was used without purification.

Synthesis of co-oligomers (general procedure). Sample O-1. 1,3,5-tris(4-Bromophenyl)benzene (0.123 g, 0.226 mmol), bis-(1,3-propanediol) ester of 9,9-dioctylfluorendiboronic acid (0.631 g, 1.13 mmol), and 3,7-dibromo-10-*n*-octylphenothiazine (0.371 g, 0.791 mmol) were dissolved in toluene (5 mL) in the Schlenk tube equipped with a magnetic stirrer. Aqueous K_2CO_3 solution (2 M, 2 mL) was added to the reaction mixture, and the gaseous products were repeatedly evacuated from the reaction mixture under stirring *in vacuo*. Tetrakis(triphenylphosphino) palladium (0.156 g, 0.135 mmol) was then added to the reaction, and the reaction system was again evacuated and filled with argon. The mixture was heated to 70 °C and held at this temperature under stirring for 3 days. After cooling the reaction solution, the product was precipitated with an organic mixture (methanol : water, 9 : 1). The precipitate was filtered off, washed with methanol, and extracted with chloroform in the Soxhlet apparatus for 5 h; the product solution in chloroform was evaporated, and the product was precipitated with ethanol. The precipitate was filtered off, washed with ethanol, and dried *in vacuo*. The product was isolated as a yellow powder in the yield of 49.3%.

Samples O-2 and **O-3** were synthesized according to the similar procedure.

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