ANALYSIS OF BRANCHED OLIGOPHENYLENE BY ABSORPTION AND FLUORESCENCE SPECTRA

R. N. Nurmukhametov,[a] A. V. Shapovalov,[b*] A. M. Sergeev,[a]
N. S. Kushakova,[b] and I. A. Khotina[b]

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A branched oligophenylene has been synthesized based on 1,3,5-tri(4´-bromophenyl)benzene. Absorption and fluorescence spectra were studied and fluorescence quantum yields and lifetimes were measured for the compound in solution. It is demonstrated that the absorption spectrum is a superposition of p-quaterphenyl, p-terphenyl, and biphenyl chromophore absorption bands in a 1:2:1 ratio. The oligomer fluorescence spectrum is found to depend on the excitation wavelength. It is shown that the oligomer fluorescence is determined by two fluorochromic groups, namely fragments with branched p-terphenyl and p-quaterphenyl units. The main fluorescence maxima for these fluorochromic groups coincide with each other and lie in the vicinity of λ = 360 nm. A very weak fluorescence band found in the region 380–440 nm is excited by light with a wavelength lying beyond the oligomer self-absorption region. The reasons for a decrease in fluorescence quantum yields of branched models and the studied oligophenylene as compared with those of linear p-polyphenylene chromophores are discussed.

Keywords: branched oligophenylenes, p-phenyls, UV absorption, fluorescence, quantum yield, fluorescence lifetime.

Introduction. Branched oligomers have become very interesting in the last decade in connection with the search for novel materials with combinations of practically useful properties [1–3]. A promising area for application of branched oligomers containing luminophores is the development of new active additives to plastic scintillators [4], dye lasers [5, 6], and light-emitting diodes in semiconducting photodiodes [7–9]. The preparation of branched oligomers and polymers with luminophores is a relatively new area. Comparatively few systems of this type have been prepared. Furthermore, their photophysical properties and their property–structure relationships are almost uninvestigated. One of the reasons for this situation is the difficulty of determining their molecular structures because the process for forming branched oligomers is random in nature [10, 11].

Herein a synthesized branched polymer (the Experimental section describes the synthetic method) is analyzed using spectrophotometry and fluorescence. According to the putative reaction, the produced macromolecule should have *p*-quaterphenyl (PQP) units at the branches and diphenyl (DP) and *p*-terphenyl (PTP) chromophores as the terminal groups. Issues with the determination of the ratio of these three chromophores in the produced macromolecule are examined. The units responsible for the fluorescence of the oligomer and the interactions between them are identified. These problems are resolved using a comparison of spectral data for the oligophenylene and the model low-molecular-weight compounds PTP, PQP, and their branched analogs containing three PTP and PQP moieties.

Experimental. The monomer 1,3,5-tri(4′-bromophenyl)benzene was prepared via the trimerization of 4-bromoacetophenone in benzene in the presence of triethylorthoformate and dry gaseous HCl by the standard method [12]. The oligophenylene was produced by Ni-catalyzed polycondensation of 1,3,5-tri(4′-bromophenyl)benzene by the literature method [13] in DMF using $NiCl_2$/PPh$_3$/Zn as a catalyst (oligomer **I**). The second step consisted of adding a

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*To whom correspondence should be addressed.

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[a]L. Ya. Karpov Institute of Physical Chemistry, Moscow, Russia; e-mail: nurm@cc.nifhi.ac.ru; [b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 119991, Russia; e-mail: shapovalov-alex@yandex.ru. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 78, No. 1, pp. 35–42, January–February, 2011. Original article submitted October 21, 2010.

1.5 molar excess of bromobenzene in order to reduce the number of unreacted functional groups in the macromolecule (oligomer **II**):
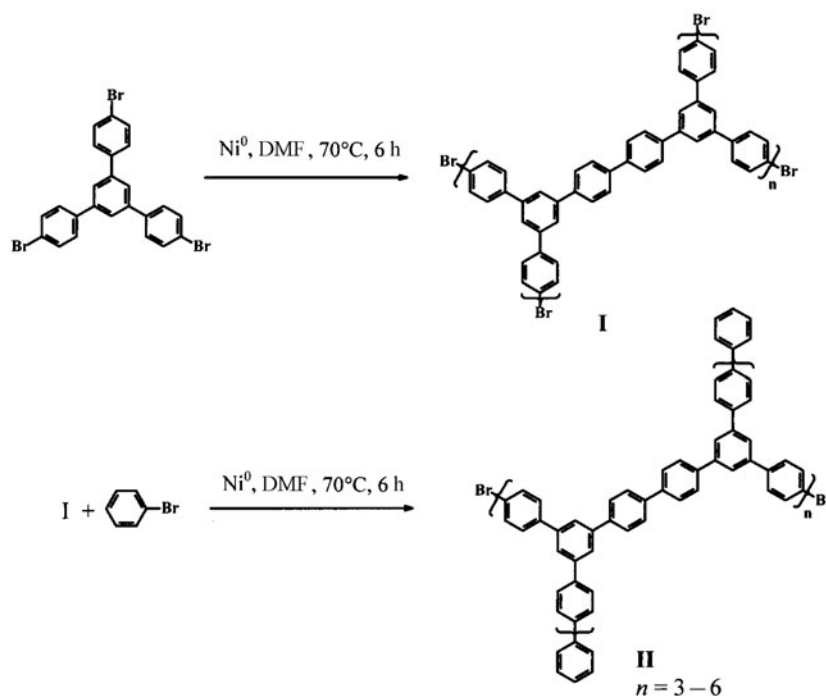
1,3,5-Tridiphenylbenzene (TDB) was prepared by cyclotrimerization of 4-acetylbiphenyl [12], which was synthesized by Friedel–Crafts acylation of biphenyl in dichloroethane [14]. Analogously, trimerization of 4′-bromobiphenylacetyl produced 1,3,5-tri(4″-bromodiphenyl)benzene, the Suzuki reaction of which with phenylboronic acid [15] synthesized 1,3,5-tri-*p*-terphenylbenzene (TTB):

TDB

TTB
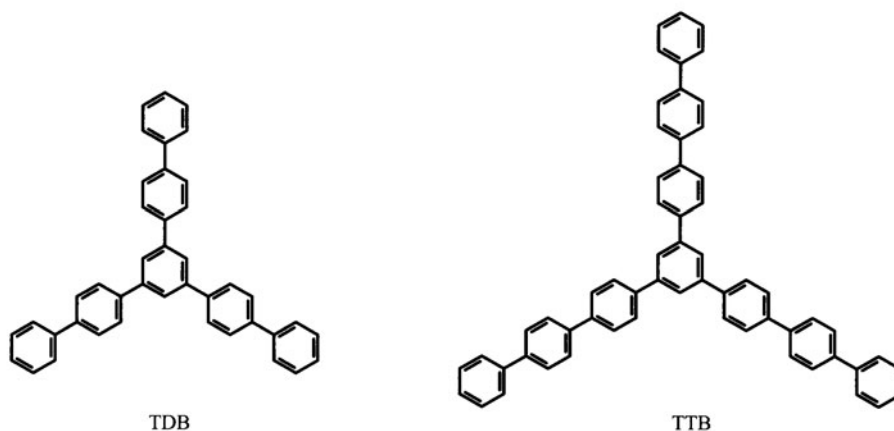
The compositions and chemical structures of the model TDB and TTB were confirmed by elemental analysis, ^{1}H PMR spectroscopy, and mass spectrometry. The studied oligophenylene **II** dissolved completely at room temperature in polar organic ($CHCl_3$, CH_2Cl_2, THF, toluene) and amide (DMF, N-methyl-2-pyrrolidone) solvents to form transparent solutions. Spectrophotometry and luminescence analysis (see below) were used to determine the chemical structure of the produced oligomer. Absorption spectra were measured on a Varian Cary 100 Scan spectrophotometer ($L = 0.1$ cm for $C \sim 10^{-4}$ M solutions in CH_2Cl_2). The molar mass of a unit, $M_{eq} = 764$ g/mol, was used to calculate the oligomer concentration. Fluorescence spectra were measured at room temperature on a Horiba Jobin Yvon Fluorolog 3-221 spectrofluorimeter. Fluorescence spectra of solutions were recorded in 1×1-cm cuvettes at an angle
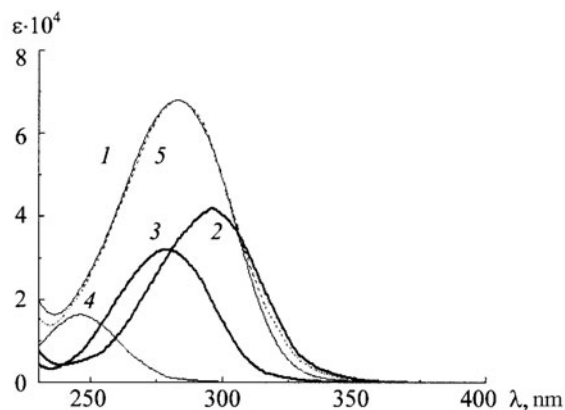
Fig. 1. Absorption spectra of solutions of oligomer (1), PQP (2), PTP (3), DP (4); solvent for PQP, cyclohexane:benzene [5]; for all others, CH_2Cl_2; superposition of PQP, PTP, and DP bands for a 1:2:1 concentration ratio (5).

TABLE 1. Spectral and Luminescence Properties of Model Compounds and Oligomer in Methylenechloride for Undeaerated Solutions and Samples

Compound	λ_{max}^{abs}, nm	ε, L/mol·cm	λ_{max}^{fl}, nm	$\Delta\nu$, cm^{-1}	φ_{fl}, %		τ, ns	
					this work	[5]	this work	[5]
DP	249	16,160	305, 317, 325	9620	9	17	4.4	16.0
PTP	280	31,740	325, 339, 354	6216	76	84	0.8	1.0
PQP[a]	293	42,110	346, 264, 385	6657	–	82	–	0.8
TPB	254	65,160	349	10,717	16	26	15.4	42.5
TDB	288	93,000	359	6867	32	18	8.5	20.0
TTB	306	121,000	356, 373	4590	60	–	1.2	–
Oligomer	283, 303	68,000	360	7559	26	–	8.5	–
Oligomer[b]	284	–	360	7441	–	–	–	–
Oligomer[c]	286	–	370, 388, 416	9192	–	–	–	–

[a]Data obtained in cyclohexane:benzene for de-oxygenated solutions [5].

[b]Data obtained in polystyrene film.

[c]Data obtained in the solid state.

of 90°. Fluorescence spectra of films were recorded by reflection at an angle of 45°. The relative fluorescence quantum yields (φ_{fl}) of all compounds were measured in dilute solutions ($C \sim 10^{-6}$ M). The standard was a solution of diphenylanthracene in CH_2Cl_2 (for undeaerated solutions, $\varphi = 0.9$ [16]). The excitation sources for measurement of fluorescence lifetimes (τ) were laser diodes with pulse length $d < 100$ ps. Fluorescence quantum yields (φ_{fl}) and lifetimes (τ) were measured for undeaerated solutions of the samples in CH_2Cl_2.

Results and Discussion. The UV absorption and luminescence spectra of the produced oligomer are presented below. The absorption and fluorescence spectra of several model low-molecular-weight compounds had to be studied in order to complete the analysis. A comparison of the spectra of these compounds and the oligomer suggested an explanation for the spectral and luminescence properties of the latter.

Figure 1 shows the solution absorption spectrum of the branched macromolecule. It contains a broad band at 240–340 nm with a maximum at 283 nm. It was necessary to define the chromophores incorporated into the oligomer in order to explain the origin of the observed broad absorption band. As already noted, the macromolecule was syn-
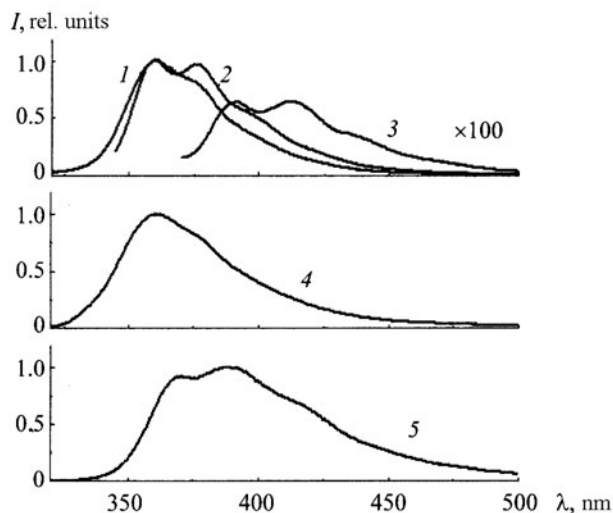
Fig. 2. Fluorescence spectra of oligomer solutions in CH_2Cl_2 for excitation by light with $\lambda_{ex} = 280$ (1), 340 (2), and 360 nm (3); in polystyrene (4) and the solid state (5).

thesized by forming a new C–C bond during the reaction of 1,3,5-tri(4′-bromophenyl)benzenes. The absorption spectrum of 1,3,5-triphenylbenzene is known to exhibit a long-wavelength band that practically coincides with the position of the DP band whereas the extinction coefficient at the band maximum is more than three times greater than that of DP (Table 1) [17, 18]. This feature was explained in the cited studies by the fact that adding phenyl rings to the m-positions does not increase the conjugation chain. Therefore, the position of the absorption band of the *m*-polyphenyls coincides with that of the DP band whereas its intensity increases in proportion to the number of biphenyl chromophores in the molecule.

The benzene rings in the macromolecule are bonded not only through the *m*-positions but also the *p*-positions. Therefore, the macromolecule comprises both biphenyl and PTP and PQP chromophores. Figure 1 shows the absorption bands of these groups. A curve representing a superposition of the DP bands, a PTP band of doubled intensity, and a PQP band was constructed. The resulting curve coincided with the absorption spectrum of the oligomer. Thus, the spectrophotometric data led to the conclusion that the macromolecule contained three types of chromophores. The number of PTP groups was twice that of PQP whereas the number of DP and PQP groups was about the same. An oligomer with degree of oligomerization 3–4 agreed well with this ratio of chromophores. We note that this result should be considered approximate because there is some interaction between these groups that produces a slight bathochromic shift in their bands. Table 1 shows that the absorption band maximum of the oligomer is shifted relative to that of PTP by 3 nm. The shoulder at 303 nm is shifted relative to PQP by 10 nm. Therefore, the positions of these bands in the oligomer do not coincide exactly with those of the linear model compounds. It is interesting to compare the maxima of linear and branched models. Branched polyphenyls that were prepared by addition of biphenyls and PTP groups to 1,3,5-benzene (branching center) were used as models. PTP (in TDB) and PQP (in TTB) units were used as the branches in these branched molecules. The band maximum of TDB was shifted bathochromically relative to that of PTP by 8 nm; the maximum of TTB relative to PQP, 13 nm, i.e., the same agreement was not found for the longer *p*-phenyl fragments as for DP and 1,3,5-triphenylbenzene.

Let us examine the structural features of the *p*-polyphenyls. The benzene ring in DP in the ground electronic state is known to be twisted relative to the central bond by 24° [17]. The rotation angle between the terminal phenyl rings in PTP reaches 40° [19]. An analogous rotation occurs in PQP [19]. This non-planar structure of the p-polyphenyls results in a decrease of the absorption band bathochromic shift when the number of benzene rings in the examined molecules is increased. This angle is even greater in the long *p*-polyphenyls so that the π-conjugation is disrupted between distant phenyl rings in the chain and a limit to the absorption-band shift appears as the length of the *p*-phenyl chain in increased ($\lambda_{lim} = 339$ nm) [18].
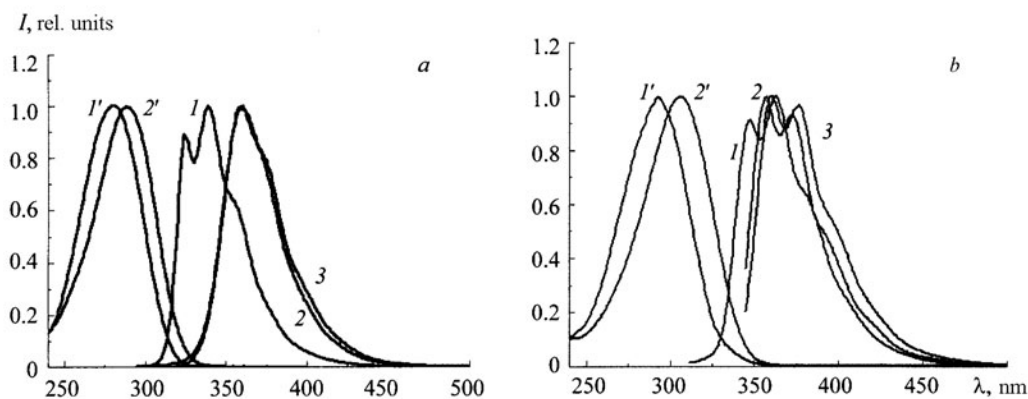
Fig. 3. Fluorescence and absorption spectra of solutions of PTP (1, 1′), TDB (2, 2′), and oligomer (3) for λ_{ex} = 280 nm (a); PQP (1, 1′), TTB (2, 2′), and oligomer (3) for λ_{ex} = 340 nm (b); fluorescence (1–3); absorption (1′ and 2′); PQP solutions in cyclohexane:benzene [5]; others, in CH_2Cl_2.

The oligomer exhibits in UV light a bright blue fluorescence in both the liquid and solid states. Figure 2 shows fluorescence spectra of the oligomer that were obtained under various conditions. The solution fluorescence spectrum lies in the range 330–450 nm. The shape of the solution fluorescence spectrum changes slightly depending on the wavelength of the exciting light (Fig. 2, curves 1 and 2). The fluorescence band excited by light with λ_{ex} = 260–300 nm has a maximum at 360 nm and a shoulder at 376 nm. Excitation by light with λ_{ex} = 340 nm produces a spectrum with the same principal maximum but a new peak (376 nm) instead of the shoulder. The emission band (Fig. 2, curve 2) undergoes a slight bathochromic shift (by ~3–5 nm). Luminescence studies revealed another unexpected result. A weak structured band coinciding with the spectrum of *p*-hexaphenyl could be detected upon excitation of the solution outside of the oligomer absorption band (λ_{ex} = 360 nm) [20]. The intensity of this fluorescence band (Fig. 2, curve 3) increased by two orders of magnitude. This indicated that the synthesized oligomer had formed anomalous units (a term first introduced by V. V. Korshak [11]) with the *p*-hexaphenyl structure. The fluorescence band of a solid solution in polystyrene practically coincided with that of the solution (Fig. 2, curve 4). The fluorescence band maximum of the oligomer in polystyrene was located at λ = 358–360 nm. The shoulder at 375 nm was less pronounced in its fluorescence spectrum. The band shape turned out to be independent of the wavelength of the exciting light (250, 260, 300, 320 nm). The fluorescence spectrum of the oligomer film was shifted by ~10 nm toward longer wavelengths than that of the solution spectrum (Fig. 2, curve 5). It featured two maxima of about equal strength (at 369 and 385 nm). The shape of the spectrum did not depend on the excitation wavelength. The fluorescence spectrum of the oligomer film will be analyzed in more detail in a separate publication.

A comparison of the solution spectra of the oligomer and the low-molecular-weight compounds enabled the chromophore units of the macromolecule that were responsible for its fluorescence to be identified (Table 1, Fig. 3). The bathochromic shift of the solution TTB absorption band relative to the corresponding TDB band turned out to be even slightly greater than the shift of the PQP band relative to PTP (Table 1). Moreover, the coincident positions of the fluorescence band maxima of the first pair of molecules with a branched structure seemed surprising whereas the bathochromic shift of the fluorescence band was ≈15–20 nm with elongation of the *p*-polyphenyl chain on one ring (PTP–PQP). The reason for this discrepancy was explained by studying synchronous scanning spectra at the excitation/fluorescence wavelengths with $\Delta\lambda$ = 5 nm. The resulting spectra were constructed on the excitation wavelength scale (Fig. 4). The synchronous spectrum of TTB was a relatively narrow band with a maximum at 348 nm. However, the synchronous spectrum of TDB was broader, from 320 to 370 nm. The long-wavelength edges of both bands were about the same. The broadening of the synchronous scanning band of TDB (its slow migration to longer wavelengths) indicates that other absorption centers that are responsible for this slow migration of the synchronous spectrum band were present in addition to the molecular centers. It can be assumed that these centers are weakly bound associates of
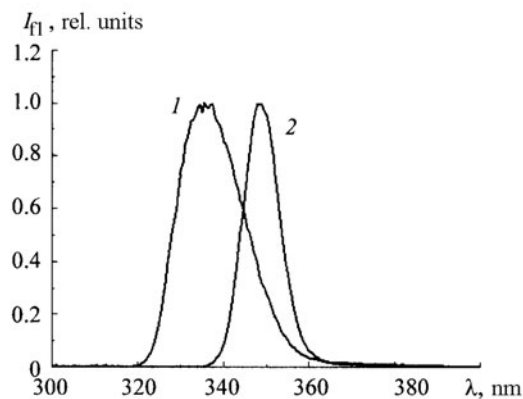
Fig. 4. Synchronous scanning spectra with difference between excitation and fluorescence wavelengths $\Delta\lambda = 5$ nm for TDB (1) and TTB (2) in CH_2Cl_2.

chromophoric groups. Excitation of them produces a new emission at longer wavelength [21]. Then it was found that the solution fluorescence spectrum of the oligomer excited by light with $\lambda = 260–300$ nm was similar to that of TDB (Fig. 3a); with wavelength $\lambda = 340$ nm, to that of TTB (Fig. 3b). Thus, it seemed that the oligomer fluorescence was determined not by one but by two emission centers with TDB- and TTB-like structures.

The fluorescence quantum yields of PTP and PQP are known to be close to unity [5, 19, 20]. However, they are much less than unity for the branched model compounds and the oligomer (Table 1). The reason for the high quantum yield of the linear p-polyphenyls is curious. As noted above, PTP and PQP are non-planar in the ground electronic state. The planes of the phenyl rings of these molecules are rotated relative to each other. This disrupts the conjugation between rings in the chain that are far from each other. Non-planar aromatic molecules are known to have increased intersystem crossing constants and enhanced radiationless deactivation processes of their fluorescent S_1^*-state [22]. A remarkable feature of electronically excited PTP and PQP is that they become planar in the fluorescent S_1^*-state. This was reported earlier [19]. The same conclusion was made based on spectral features of PTP and PQP luminescence [18]. Flattening of PTP and PQP in the electronically excited S_1^*-state is the factor that gives it a high fluorescence quantum yield. The marked decrease of the quantum yield in the branched molecules ($\varphi_{TDB} = 32\%$; $\varphi_{TTB} = 60\%$) is due to the fact that this factor is apparently not significant for them. Only one of the electronically excited branches of the molecule adopts a planar structure whereas the other branches remain non-planar. Furthermore, the electronically excited S_1^*-state in the examined molecules is triply degenerate. Therefore, its energy level is split into three components. The fluorescence transition in them occurs from the lowest of these sublevels. The probability of a radiative transition is apparently less than for the linear p-polyphenyls. The fluorescence lifetimes of the branched models argue in favor of this (Table 1). However, this question can only be answered using quantum-chemical calculations of the branched molecules. Obviously these same factors have an influence on the quantum yield and lifetime of the studied oligomer.

Conclusion. The spectral and luminescence properties of the studied oligophenylene differ insignificantly from those of linear p-polyphenyls (PTP and PQP) and practically coincide with those of branched models (TDB and TTB). The produced oligomer has two emission centers that have the same properties as the branched phenylene models. It was concluded that the luminescence properties of the branched oligophenylene are almost completely determined by p-terphenyl chromophores bonded to a central 1,3,5-substituted benzene ring. An anomalous unit with the p-hexaphenyl structure was formed (in small quantities) during the synthesis of the oligomer. The expected advantages of the produced oligomer over low-molecular-weight compounds are, first, that chromophores in the oligomer form compact groups. Therefore the concentration-effect barrier will be lowered without distorting the absorption properties. Thanks to this, the extinction coefficient will be much higher than for linear p-polyphenyls. Second, a solid film of the oligomer is a transparent homogeneous medium and fluoresces. This enables the generation to be studied not only in solution but also in the solid state.

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