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Synthesis and luminescent properties of branched oligophenylenefluorenes

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The spectrophotometric and luminescence studies on branched oligophenylenefluorenes have shown that the incorporation of *n*-octyl groups to the 9-position of the fluorene moiety does not interrupt the conjugation of internodal luminophore moieties, and there is also no aggregation or excimer emission both for functionalized and nonfunctionalized macromolecules in solution.

Currently, a search is under way for new polymers intensely emitting light and possessing properties that allow specific practical problems to be solved.¹ Poly-*p*-phenylenes are among the most efficient blue luminophores since they display good working characteristics in the production of plastic scintillators, solidphase lasers and various electroluminescent devices, and also have high quantum yields of fluorescence and molar absorption coefficients.² Fluorene and indenofluorene, as well as polymers based on them, are the most interesting and well studied phenylene luminophores.³ The main problems in the development of polymeric luminophores include fluorescence quenching due to π -stacking of conjugated chains and low solubility. A way to solve these problems is to functionalize oligomers by *n*-alkyl groups and synthesize branched systems that have higher solubilities than their linear analogues. However, *n*-alkyl groups can favour the interruption of the internodal moieties conjugation due to an increase in torsion angle between adjacent benzene rings leading to a decrease in fluorescence quantum yield.^{4,5} Thus, we performed a comparative study of branched oligomers, both containing and not containing functional *n*-octyl groups.

A few syntheses of branched phenylene oligomers in which 1,3,5-substituted benzenes are used as branching centres have been reported.^{6,7} However, the longest conjugated fragments in such oligomers either consist of eight or more benzene rings or have a variable length, which makes it more difficult to find out correlations between the macromolecular structure and lumine-scent properties. For this reason, we synthesised oligophenylene-fluorenes whose luminophore moieties have a fixed length and consist of seven conjugated benzene rings.

To synthesize branched oligomers, we first obtained trifunctional monomers **3a** and **3b** (Scheme 1). 2-Bromo-9,9-dioctylfluorene **1a** was obtained by dialkylation of bromofluorene with 1-bromooctane in the presence of NaOH and catalytic amounts of triethylbutylammonium chloride by a standard technique.⁸ Monoacetyl derivatives of fluorene and 9,9'-dioctylfluorene **2a,b** were obtained by the Friedel–Crafts reaction of the [MeCO·AlCl₄]



Scheme 1 Reagents and conditions: i, 1-bromooctane, NaOH, TEBA, DMSO, 25 °C, 12 h; ii, AcCl, AlCl₃, DCE, 0 °C, 1 h; iii, HC(OEt)₃, HCl (gas), benzene, 25 °C, 4 h.



Scheme 2 Reagents and conditions: i, Pd (dppf), 2 M K₂CO₃, toluene, 90 °C, 48 h.

complex with compounds **1a,b** in dichloroethane.⁹ Monomers **3a,b** were synthesized by trimerization cyclocondensation of compounds **2a,b** in the presence of ethyl orthoformate and dry gaseous HCl by the reported procedure.¹⁰ The products were characterised by ¹H NMR spectroscopy, mass spectrometry (EI), and elemental analysis.[†]

Branched oligophenylenefluorenes OPF-1 and OPF-2 were obtained from trifunctional monomers by the 'A₃+B₂' type Suzuki reaction, *i.e.*, the reaction of compounds **3a,b** with phenyl-bispinacoldiborate in the presence of the Pd ferrocenyl complex and 2 M aqueous K₂CO₃¹¹ (Scheme 2). The resulting oligophenylenefluorenes were characterised by ¹H NMR spectroscopy and elemental analysis.[†] The OPF-1 oligophenylenefluorene is only soluble in dichloromethane and chloroform, whereas OPF-2 is well soluble even in nonpolar solvents such as benzene and light petroleum.

The adjacent benzene rings in *p*-phenylene luminophores are somewhat tilted in the ground electronic S₀ state due to steric factors (repulsion of o-hydrogen atoms), but they are arranged in almost the same plane in the excited electronic S_1 state.¹² The adjacent rings of the fluorene moieties stay in the same plane in both states since they are additionally linked by a methylene bridge. In view of this, it was important to find out whether the branching 1,3,5-trisubstituted benzene ring is part of the *p*-phenylene luminophore moiety, since conjugation between the fluorene groups and 1,3,5-substituted benzene can be lacking due to planarity destruction. This is most likely to occur in oligomer OPF-2, in which the torsion angle between the specified moieties may be higher due to the bulky side groups. In order to clarify this issue, we synthesized (Scheme 1) model cyclotrimers without bromine atoms 3c,d that simulate the arrangement of substituted and non-substituted fluorene moieties with respect to the branching centre, i.e., the 1,3,5-trisubstituted benzene. For these model compounds and, for comparison, for 1,3,5-tri(p-diphenylyl)benzene 4,13 absorption and emission spectra in dichloromethane solution were obtained.[‡]



[†] For characteristics of compounds **1a,b**, **2a–d**, **3a–d**, OPF-1 and OPF-2, see Online Supplementary Materials.

The absorption spectrum of compound **4** is a wide structureless band with a maximum at 289 nm. At the same time, for **3c**, the main absorption maximum was observed at 315 nm and a shoulder peak at 296 nm [Figure 1(*a*)]. The **3d** absorption band batochromic shift in comparison with compound **4** can be explained by the fact that the structure of the phenylfluorene moiety in cyclotrimer **3d** in the ground S₀ state is more planar than that of the *p*-terphenyl moiety of compound **4**. The absorption spectra of compounds **3c** and **3d** virtually coincide. This suggests that the conjugated phenylfluorene moieties of both trimers have almost the same conformation in the ground S₀ state, *i.e.*, the *n*-octyl groups do not cause the rotation of fluorene moieties with respect to the branching centre. The small (by 3–4 nm) bathochromic shift of the **3c** absorption band in comparison with **3d** one may be due to the electrondonating nature of the *n*-octyl substituents.

The fluorescence spectra of compounds **4**, **3d** and **3c** obtained by excitation in absorption maxima are wide structureless bands with peaks at 362, 366 and 365 nm, respectively. This is in a good

Table 1 Spectral characteristics of model compounds 3c,d, 4 and oligomers OPF-1 and OPF-2 in dichloromethane solutions at 293 K (the main maximum is given in italic).

Compound	$\lambda_{ m max}^{ m abs}/ m nm$	$\lambda_{ m max}^{ m fl}/ m nm$	$arphi^{ m fl}$
3c	296, 315	365	0.31
3d	299, 319	366	0.41
4	289	362	0.32
OPF-1	325	369, 391	0.40
OPF-2	329	401, 422	0.58

^{*} Absorption spectra were recorded with a Cary 100-Scan spectrophotometer (Varian). Fluorescence spectra were measured using a Fluorolog 3-221 spectrofluorimeter (Horiba Jobin Yvon) in the reflection mode. The fluorescence spectra were obtained for the non-deaired dichloromethane solutions ($C \approx 10^{-6}$ M) and corrected for nonuniformity of detector spectral sensitivity. The fluorescence quantum yields were calculated with respect to a diphenylanthracene solution in dichloromethane ($\varphi^{\rm fl} = 0.9$)¹⁵ by the Vavilov equation

$$\varphi_i^{\rm fl} = \varphi_{\rm ref}^{\rm fl} \frac{A_{\rm ref} I_i}{A_i I_{\rm ref}}$$

where *i* is the test solution, 'ref' is the reference solution, φ is the quantum yield, *A* is absorbance, and *I* is the area under the curve of the fluorescence spectrum.



Figure 1 (1)–(5) Absorption spectra and (1')–(5') fluorescence spectra of (*a*) model compounds and (*b*) oligophenylenefluorenes in dichloromethane: (1) **4**, (2) **3d**, (3) **3c**, (4) OPF-1, and (5) OPF-2.

agreement with the statement that 1,3,5-trisubstituted benzene rings conjugate with biphenyl or fluorine moieties. The planarity of poly-*p*-phenylenes in the S₁ excited state was described previously.¹⁴ As a consequence, poly-*p*-phenylene luminophores demonstrate fluorescence quantum yields close to 1 in solutions. However, in our case, quantum yields for all models are lower than 1 (see Table 1). It might be due to the fact that one branch of cyclotrimers in S₁ excited state becomes planar and two others do not, *i.e.*, save a nonplanar conformation. Of course, for more detailed statement the quantum chemical calculations for models **4**, **3d** and **3c** in S₁ excited state are required.

Figure 1(b) shows the absorption and fluorescence spectra of oligophenylenefluorenes in dichloromethane. The absorption spectra of compounds OPF-1 and OPF-2 in comparison with models 3d and 3c are bathochromically shifted by 6 and 14 nm, while the shoulder at 300 nm is less pronounced (there is an inflection point in the same place). The absorption spectrum of oligomer OPF-2 contains another inflection point at 355 nm, owing to which the spectrum of the oligomer is somewhat broadened in comparison with the spectrum of model compound 3c. The bathochromic shift of the main maximum and the appearance of an another absorption band at long-wave edge are due to the formation of longer conjugated moieties in the oligomers in comparison with the models. The observed small increase in the Stokes shift may be due to a decrease in the hardness of *p*-phenylene moieties in oligomers; furthermore, the internodal moieties in the OPF-1 oligomer are harder than those in OPF-2.

The fluorescence spectra of oligomers OPF-1 and OPF-2 are bathochromically shifted with respect to the spectra of models **3d** and **3c** by 25 and 35 nm, respectively, and they do not depend on the excitation wavelength (300, 320 or 340 nm). Unlike the fluorescence spectra of the models, the spectra of oligomers contain vibrational structure elements. The fluorescence spectrum of the OPF-1 oligomer has a main maximum at 391 nm and a shoulder at 369 nm, as well as two inflection points in the region of the long-wave edge (at 415 and 447 nm). The spectrum of oligomer OPF-2 is shifted towards longer waves by about 8 nm in comparison with OPF-1 and its vibrational structure elements differ: there is an inflection point in place of the first maximum (at 377 nm) and a shoulder (at 422 nm) in place of the inflection point at 415 nm. The observed small bathochromic shift of OPF-2 absorption and fluorescence maxima in comparison with OPF-1 may be, as in cyclotrimers case, due to the electrondonating nature of the *n*-octyl substituents. The absence of a hypsochromic shift for OPF-2 absorption and fluorescence bands confirms the assumption that internodal moieties in both oligomers are in the same conformation forms, i.e. n-alkyl groups do not favour the interruption of the internodal moieties conjugation. It is also in a good agreement with fluorescence quantum yields for OPF-1 and OPF-2 (see Table 1). Like the fluorescence spectra of the models, the spectra of both oligomers show no fluorescence at 500-550 nm. This allows one to conclude that both functionalized and nonfunctionalized branched oligophenylenefluorenes do not form excimers or supramolecular structures in solution.

Thus, the results obtained show that the absence of luminophore moieties aggregation or excimer luminescence makes branched oligophenylenefluorenes advantageous over linear analogues. The model compounds and oligomers obtained in this study are promising materials for using them as blue luminophores in electroluminescent devices.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.01.004.

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