EXCIMER FORMATION IN OLIGO[2,5-BIS(HEXADECYLOXY)-1,4-PHENYLENE]S FOLLOWED BY FLUORESCENCE SPECTROSCOPY

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Using the steady-state and time-resolved fluorescence spectroscopy, the behavior of "hairy-rod" oligo- and poly[2,5-bis(hexadecyloxy)-1,4-phenylene]s in tetrahydrofuran solutions was investigated. The materials were prepared by the Yamamoto coupling reaction using zinc as a reducing metal, the nickel(II)/triphenylphosphine complex as a catalyst, and 2,2′-bipyridine as a coligand. The appropriate oligomer fractions were separated by fractional precipitation and characterized by GPC and end group analysis. The fluorescence quantum yield of oligomers and polymers increased with their increasing conjugation length. The fluorescence emission spectra of polymers and longer oligomers exhibited one emission maximum at 390 nm with a single-exponential decay and fluorescence lifetimes (τ) around 1 ns. The substitution in positions 2 and 5 forces the adjacent backbone benzene units out of the plane, which results in twist angles 60–80°, and the bulky substituents exclude the cofacial sandwich-type configuration necessary for excimer formation. However, with shorter oligomers, another emission band at 460 nm appeared. Fluorescence decays at 460 nm were found to be double-exponential with longer excited-state lifetimes [*e.g.* τ_1 = 6.9 ns (76%), τ_2 = 2.4 ns (24%)]. With shorter oligomers (dimer, trimer), we assume a sandwich-type configuration with sufficiently close interchain distance and hence the excimer can form. Hydrophobic interactions of long aliphatic side chains in a polar medium play an important role in the excimer formation.

Keywords: Time-resolved fluorescence spectroscopy; Fluorescence lifetime; Excimer; Fluorescence quantum yield; Conjugated polymers; Poly(1,4-phenylene)s; Polyphenylenes; Yamamoto coupling; Suzuki coupling.

The excimer formation has been found quite common for small organic molecules; the studies[1–3] have shown that their basic supramolecular structures are cofacial sandwich-type configurations with interplanar distances of ≈0.3–0.4 nm. In conjugated polymers, a pair of chains may form an excimer when one of them is excited by light. Just as in the case of an excimer formed by a pair of molecules, the stability of the excimer arises

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from overlapping π orbitals on the two chains[4]. It is therefore a requirement for excimer formation that the two chains must be parallel over a length of at least several monomer units[5], with an interchain distance of ≈0.3–0.4 nm. The distance must be small enough for their π orbitals to overlap but not so strongly that the ground states can form a new stable molecule. Symmetry requires that the wavefunction must be a quantum-mechanical superposition of the state with excitation on one chain and the state with excitation on the other chain. Emission from an excimer has a lower frequency than that from one of the molecules excited when isolated because of the lower energy in the excimer state and because in the final state, where both chains are in their ground states, they repel each other. The excimer emission characteristically has a longer lifetime because, as follows from the symmetry of the electronic wavefunction in the excimer state, the radiative transition to the ground state is forbidden[6]. Electroluminescence of conjugated polymers has attracted a great deal of attention since the first light-emitting devices (LEDs) were fabricated[7] on the basis of poly(1,4-phenylenevinylene) (PPV). The interest in the emission from PPV for LED reasons led to extensive studies aimed to determine what excitations are generated by light in PPV and a number of its derivatives. An important contribution to the problem of the existence of excimers or polaron pairs in PPV was found in the cyano derivative, poly{[2,5-bis(hexyloxy)-1,4-phenylene]cyanovinylene} (CN-PPV)[8]. Comparing the emission from films with that from dilute solutions, it was found that the former is red-shifted, with a much longer lifetime (20 times), broad and featureless. These properties and the lack of additional low-frequency absorption indicate the formation of excimers in the film. In the studies of photoinduced absorption on poly{[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene]-vinylene} (MEH-PPV), it was found that the long-lived excitations are excimers even though they do not emit[9]. Detailed calculations based on their ground-state geometry showed that excimers probably decayed nonradiatively.

Recently[10,11] we have studied the electroluminescence (EL), photoluminescence (PL), and film morphology characteristics of LEDs based on poly[2,5-bis(isopentyloxy)-1,4-phenylene] (IP-PPP) and its blends with poly[methyl(phenyl)silanediyl] (PMPSi). Compared with the PL spectrum of IP-PPP, the EL spectrum was red-shifted and, as the time of LED operation increased, the contribution of yellow emission increased. LEDs prepared by the Langmuir–Blodgett technique, where well-organized films with parallel-ordered polymer chains were used, proved the aggregate formation responsible for yellow emission.

In this paper we have synthesized poly[2,5-bis(hexadecyloxy)-1,4-phenylene] (HD-PPP) and its oligomers as an example of so-called "hairy-rod" macromolecules with a linear rigid backbone and flexible hairy alkyl side chains. Transition electron microscopy of such polymers revealed a sandwich-type structure with layers of aliphatic side chains perpendicular and layers of the backbone parallel to the substrate surface[12,13]. We believe that long alkyl side chains could be an efficient hindrance to possible aggregate or excimer formation in films for LEDs. Here, the steady-state and time-resolved fluorescence behavior and excimer formation in tetrahydrofuran (THF) solutions of HD-PPP and its oligomers was studied.

EXPERIMENTAL

Materials

2,5-Dibromohydroquinone. To a suspension of hydroquinone (82.6 g, 0.75 mol) in acetic acid (750 ml), a solution of bromine (239.7 g, 1.5 mol Br_2) in acetic acid (75 ml) was added dropwise (2 h) keeping the temperature below 40 °C. The reaction mixture was stirred for 10 h and the precipitate formed was filtered off. The volume of the reaction mixture was reduced to one half thus obtaining another part of the product. Yield: 112 g (56%). Recrystallization from water–ethanol gave nearly white crystalline product. M.p. 190–191 °C (ref.[14] 190–191 °C, ref.[15] 186 °C). For $C_6H_4Br_2O_2$ (267.9) calculated: 26.90% C, 1.50% H, 59.65% Br; found: 26.91% C, 1.52% H, 59.41% Br.

2-Bromohydroquinone was prepared by a similar procedure to that for 2,5-dibromohydroquinone using 27.5 g (0.25 mol) of hydroquinone and 40 g (0.25 mol) of bromine in the reaction. The crude material was recrystallized from chloroform. Yield: 21.3 g (45%). M.p. 110 °C (ref.[16] 110.5 °C). For $C_6H_5BrO_2$ (189.0) calculated: 38.13% C, 2.67% H, 42.28% Br; found: 37.95% C, 2.61% H, 42.35% Br.

1,4-Dibromo-2,5-bis(hexadecyloxy)benzene. 2,5-Dibromohydroquinone (13.4 g, 0.05 mol) was dissolved in ethanolic potassium hydroxide (7.0 g KOH in 150 ml of ethanol) and refluxed. 1-Bromohexadecane (76.3 g, 0.25 mol) was added slowly and the reaction mixture was refluxed for 10 h. After cooling to room temperature, the resulting precipitate was filtered off, washed with water and dried. The organic material was dissolved in hot toluene, filtered and the solvent was evaporated. The product was crystallized from acetone–toluene (charcoal). Yield: 28.9 g (82%). M.p. 86–87 °C. For $C_{38}H_{68}Br_2O_2$ (716.8) calculated: 63.68% C, 9.56% H, 22.30% Br; found: 63.93% C, 9.60% H, 22.31% Br. ^1H NMR ($CDCl_3$): 0.87 (t, 6 H, J = 6.6, 2 × CH_3); 1.26 (s, 52 H, 26 × CH_2); 1.78 (m, 4 H, J = 6.7, 2 × O-C-CH_2); 3.93 (t, 4 H, J = 6.6, 2 × OCH_2); 7.07 (s, 2 H, H-arom.). FT IR (film on KBr): 2 917, 2 846 (C–H, stretching); 1 675 (C=C, stretching); 1 460 (CH_2, scissoring); 1 359 (CH_3, bending); 1 264 (C–O, stretching); 1 211 (CH_2, twisting); 1 061 (C–C, stretching); 804, 721 (CH_2, rocking); 522 (C–Br).

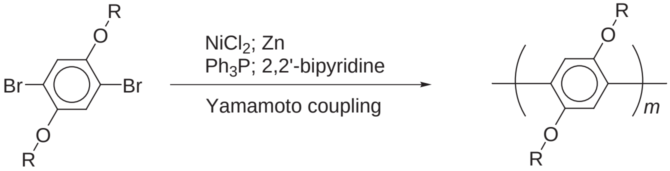
1,4-Dibromo-2,5-bis(decyloxy)benzene was prepared by a similar procedure to that for the hexadecyl derivative above, using 1-bromodecane (0.25 mol) as alkylation agent. Yield: 18.10 g (66%). M.p. 67–69 °C. For $C_{26}H_{44}Br_2O_2$ (548.5) calculated: 56.94% C, 8.09% H, 29.14% Br; found: 57.13% C, 8.14% H, 28.92% Br. ^1H NMR ($CDCl_3$): 0.87 (t, 6 H, J = 6.6, 2 × CH_3); 1.27 (s, 28 H, 14 × CH_2); 1.78 (m, 4 H, J = 6.6, 2 × O-C-CH_2); 3.93 (t, 4 H, J = 6.6, 2 ×

OCH_2); 7.07 (s, 2 H, H-arom.). FT IR (film on KBr): 2 917, 2 848 (C–H, stretching); 1 680 (C=C, stretching); 1 463 (CH_2, scissoring); 1 360 (CH_3, bending); 1 268 (C–O, stretching); 1 210 (CH_2, twisting); 1 061 (C–C, stretching); 804, 726 (CH_2, rocking); 521 (C–Br).

2-Bromo-1,4-bis(hexadecyloxy)benzene. Alkylation of 2-bromohydroquinone (6.25 g, 0.033 mol) with 1-bromohexadecane (61.0 g, 0.20 mol) in ethanolic potassium hydroxide (5.0 g KOH in 100 ml EtOH) was performed similarly to that for the dibromo derivative above. Yield: 18.3 g (86%). M.p. 64–65 °C. For $C_{38}H_{69}BrO_2$ (637.9) calculated: 71.56% C, 10.90% H, 12.53% Br; found: 71.48% C, 10.64% H, 12.68% Br. ^{1}H NMR ($CDCl_3$): 0.87 (t, 6 H, *J* = 6.6, 2 × CH_3); 1.26 (s, 52 H, 26 × CH_2); 1.74 (m, 4 H, *J* = 6.7, 2 × O-C-CH_2); 3.87 and 3.93 (2 × t, 4 H, *J* = 6.6, 2 × OCH_2); 7.08 (m, 3 H, *J* = 3.9, H-arom.). FT IR (film on KBr): 2 917, 2 846 (C–H, stretching); 1 673 (C=C, stretching); 1 462 (CH_2, scissoring); 1 359 (CH_3, bending); 1 267 (C–O, stretching); 1 217 (CH_2, twisting); 1 044 (C–C, stretching); 790, 722 (CH_2, rocking); 522 (C–Br).

2,2′,5,5′-Tetrakis(hexadecyloxy)biphenyl was prepared by the method developed for coupling of aryl chlorides[17]. 2-Bromo-1,4-bis(hexadecyloxy)benzene (6.37 g, 10 mmol), zinc powder (2.20 g, 33.6 mmol), nickel(II) chloride (0.13 g, 1 mmol), triphenylphosphine (1.04 g, 4 mmol), 2,2′-bipyridine (0.16 g, 1.01 mmol) and *N*,*N*-dimethylacetamide (50 ml) were degassed under argon in a special glass reactor equipped with a magnetic stirrer and three-way valve. The reactor was heated (80 °C) with vigorous stirring for 18 h. After cooling, the reaction mixture was poured into methanol–water (800 ml, 1 : 1 by volume) and 5 ml concentrated HCl was added. The organic precipitate (upper layer) was filtered off, dried, extracted with hot toluene (250 ml) and treated with charcoal. The toluene solution was reduced (100 ml); after addition of ethanol, a white product crystallized. Yield: 3.55 g (63%). M.p. 82–83 °C. For $C_{76}H_{138}O_4$ (1 115.9) calculated: 81.80% C, 12.47% H; found: 81.87% C, 12.44% H. ^{1}H NMR ($CDCl_3$): 0.87 (t, 12 H, *J* = 6.6, 4 × CH_3); 1.26 (s, 104 H, 52 × CH_2); 1.72 (m, 8 H, *J* = 6.9, 4 × O-C-CH_2); 3.88 (t, 8 H, *J* = 6.6, 4 × OCH_2); 6.78 (m, 6 H, H-arom.). FT IR (film on KBr): 2 917, 2 850 (C–H, stretching); 1 680 (C=C, stretching); 1 466 (CH_2, scissoring); 1 359 (CH_3, bending); 1 268 (C–O, stretching); 1 216 (CH_2, twisting); 1 034 (C–C, stretching); 826, 724 (CH_2, rocking).

Oligo[2,5-bis(hexadecyloxy)-1,4-phenylene]s (**1**, **2**, and **3**, Scheme 1). A special glass reactor equipped with a magnetic stirrer and three-way valve was charged with 1,4-dibromo-2,5-bis(hexadecyloxy)benzene (7.16 g, 10 mmol), zinc powder (2.20 g, 33.6 mmol), nickel(II) chloride (0.13 g, 1 mmol), triphenylphosphine (1.04 g, 4 mmol) and 2,2′-bipyridine (0.16 g,



1-6

	m	R
1	≈ 4-6	*n*-$C_{16}H_{33}$
2	≈ 2-4	*n*-$C_{16}H_{33}$
3	≈ 2-3	*n*-$C_{16}H_{33}$
4	≈ 10	*n*-$C_{16}H_{33}$
5	≈ 15	*n*-$C_{16}H_{33}$
6	≈ 15	*n*-$C_{10}H_{21}$

SCHEME 1

1.01 mmol). The reactor was evacuated several times, flushed with argon and 90 ml of *N*,*N*-dimethylformamide (DMF; bubbled with argon for 30 min) was added. The vacuum–argon cycles were repeated several times, then the reactor was closed and heated (75 °C) for 72 h with vigorous stirring. After cooling to room temperature, the solid was filtered off and extracted with THF. The extract was precipitated into methanol. Yield: 0.68 g of the oligomer fraction **1** (M_w = 2 280, M_n = 1 870). The DMF solution was precipitated into methanol. Yield: 2.85 g of the oligomer fraction **2** (M_w = 1 410, M_n = 1 160). Oligomer fraction **2** (1.0 g) was dissolved in 60 ml THF and 40 ml of methanol was added. The precipitated material was filtered off and the solution was evaporated yielding the oligomer fraction **3** (0.76 g, M_w = 1 210, M_n = 1 080). All the three fractions were characterized by GPC (Fig. 1) and elemental analysis. Found: 78.73% C, 11.87% H, 3.92% Br for **1**; 76.82% C, 11.54% H, 6.63% Br for **2**; 75.92% C, 11.25% H, 7.60% Br for **3**. ^{1}H NMR (deuterated THF) and FT IR spectroscopy confirmed the structure of monomer units in oligomers. FT IR of **3** (film on KBr): 2 920, 2 852 (C–H, stretching); 1 679 (C=C, stretching); 1 466 (CH_2, scissoring); 1 390 (CH_3, bending); 1 272 (C–O, stretching); 1 216 (CH_2, twisting); 1 043 (C–C, stretching); 827, 724 (CH_2, rocking); 520 (C–Br). The vibration band at 520 cm^{-1} for oligomers **2** and **1** decreases as a consequence of increasing molecular weight. UV (THF): λ_{max} 304 nm, ε_{304} 3 900 l mol^{-1} cm^{-1} for **1**; λ_{max} 297 nm, ε_{297} 3 020 l mol^{-1} cm^{-1} for **2**; λ_{max} 296 nm, ε_{296} 2 760 l mol^{-1} cm^{-1} for **3**.

Poly[2,5-bis(hexadecyloxy)-1,4-phenylene]s (**4** and **5**, Scheme 1). A glass reactor was charged in the same way as above for oligomers. The reaction mixture was heated (105 °C) for 12 days with vigorous stirring. After cooling to room temperature, the reaction mixture was poured into methanol (700 ml) and acidified with concentrated HCl (10 ml). The crude material was filtered off, dried and dissolved in THF (200 ml at 50 °C). The solution was filtered, evaporated to a volume of *ca* 30 ml and precipitated into methanol (300 ml). Yield: 4.25 g (76%) of polymer **4** (M_w = 3 890, M_n = 1 980). Polymer **4** (1.0 g) was dissolved in 60 ml of

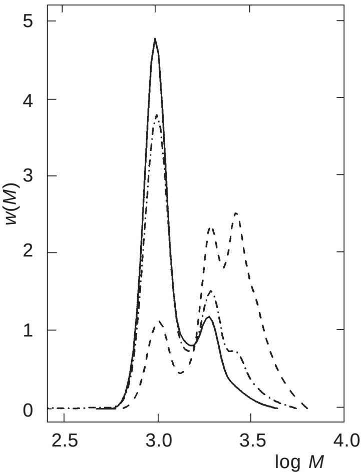
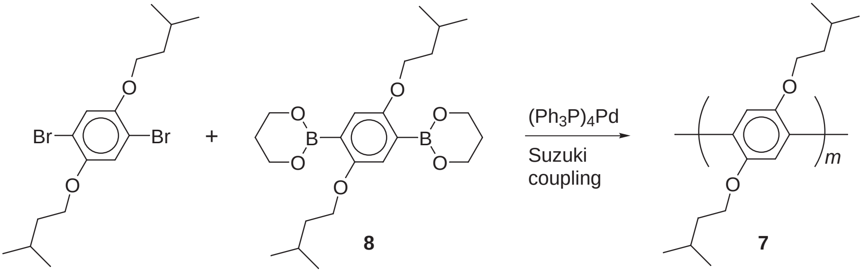


FIG. 1
Normalized weight distribution functions, *w*(*M*), determined by GPC analyses in tetrahydrofuran for oligomers **1** (dashed line), **2** (dashed and dottted line), and **3** (solid line)

THF (50 °C) and left to precipitate in a fridge (5 °C). The solid was filtered off and dried. Yield: 0.54 g of polymer **5** (M_w = 5 940, M_n = 3 970). Both polymers were characterized by GPC, ^{1}H NMR, FT IR, and elemental analysis. Found: 80.15% C, 11.81% H, 1.92% Br for **4** and 81.26% C, 12.13% H, 1.42% Br for **5**. UV (THF): λ_{max} 315 nm, ε_{315} 4 900 l mol^{-1} cm^{-1} for **4**; λ_{max} 325 nm, ε_{325} 5 800 l mol^{-1} cm^{-1} for **5**. ^{1}H NMR of **5** ($CDCl_3$): 0.86 (t, 6 H, 2 × CH_3); 1.24 (s, 52 H, 26 × CH_2); 1.72 (m, 4 H, 2 × O-C-CH_2); 3.87 (m, 4 H, 2 × OCH_2); 6.80 (m, 2 H, H-arom.). FT IR of **5** (film on KBr): 2 920, 2 852 (C–H, stretching); 1 677 (C=C, stretching); 1 469 (CH_2, scissoring); 1 390 (CH_3, bending); 1 273 (C–O, stretching); 1 220 (CH_2, twisting); 1 040 (C–C, stretching); 825, 721 (CH_2, rocking).

Poly[2,5-bis(decyloxy)-1,4-phenylene] (**6**, Scheme 1). A glass reactor was charged under argon (see above) with 1,4-dibromo-2,5-bis(decyloxy)benzene (8.23 g, 15 mmol), zinc powder (3.30 g, 50 mmol), nickel(II) chloride (0.20 g, 1.5 mmol), triphenylphosphine (1.56 g, 6 mmol) and 2,2′-bipyridine (0.24 g, 1.52 mmol). The reaction mixture was heated (80 °C) for 10 days with vigorous stirring. After cooling to room temperature, the reaction mixture was poured into methanol (600 ml) and acidified with concentrated HCl (10 ml) to remove excess of zinc. The polymer was filtered off and dried (4.13 g). The crude material was dissolved in THF, filtered, and precipitated into methanol. Yield: 3.14 g (54%) of polymer **6**. The polymer was characterized by ^{1}H NMR, FT IR, GPC (M_w = 3 750, M_n = 2 580), and elemental analysis. Found: 80.10% C, 11.02% H, 0.30% Br. ^{1}H NMR (deuterated THF): 0.87 (t, 6 H, 2 × CH_3); 1.26 (s, 28 H, 14 × CH_2); 1.70 (m, 4 H, 2 × O-C-CH_2); 3.86 (m, 4 H, 2 × OCH_2); 6.74 (m, 2 H, H-arom.). FT IR (film on KBr): 2 922, 2 855 (C–H, stretching); 1 678 (C=C, stretching); 1 470 (CH_2, scissoring); 1 382 (CH_3, bending); 1 270 (C–O, stretching); 1221 (CH_2, twisting); 1 062 (C–C, stretching); 822, 790, 722 (CH_2, rocking); very weak 524 (C–Br). UV (THF): λ_{max} 315 nm, ε_{315} 4 500 l mol^{-1} cm^{-1}.

Poly[2,5-bis(isopentyloxy)-1,4-phenylene] (**7**, Scheme 2). This polymer was prepared by the aryl–aryl coupling reaction of bis(cyclic ester) of 2,5-bis(isopentyloxy)benzene-1,4-diboronic acid with propane-1,3-diol (**8**) and 1,4-dibromo-2,5-bis(isopentyloxy)benzene in the presence of tetrakis(triphenylphosphine)palladium according to the described procedure[18]. The prepared material was characterized by ^{1}H and ^{13}C NMR, FT IR, GPC (M_w = 35 000, M_n = 21 000) and elemental analysis. The spectral methods confirmed the structure of **7**. The degree of polymerization (P_n) was estimated from ^{1}H NMR to be 37, which corresponds with GPC results. ^{1}H NMR ($CDCl_3$): 0.77–0.92 (m, 12 H, 4 × CH_3); 1.49 (t, 4 H, 2 × O-C-CH_2); 1.65 (m, 2 H, 2 × CH); 3.88 (m, 4 H, 2 × OCH_2); 6.90–7.03 (m, 2 H, H-arom.). ^{13}C NMR ($CDCl_3$): 20.77 (4 C, CH_3); 23.41 (2 C, alif. C-3); 36.64 (2 C, alif. C-2); 66.70 (2 C, alif. C-1); 116.49 (2 C, arom. 3,6-C); 126.14 (2 C, arom. 1,4-C); 148.71 (2 C, arom. 2,5-C). UV-VIS and fluorescence data are summarized in Tables I and II.



SCHEME 2

TABLE I
Relative fluorescence quantum yield (Q) and maximum wavelength (λ_{max}) of absorption, excitation, and emission spectra for oligomers **1**–**3** and polymers **4**–**7** in tetrahydrofuran

Oligomer or polymer	λ_{max}, nm			Q
	absorption spectrum	excitation spectrum	emission spectrum	
1	304	330	390	0.08
2	297	330	390	0.04
2	297	340	460	0.03
3	296	345	465	0.02
4	315	335	390	0.38
5	325	340	395	0.46
6	315	335	390	0.25
7	335	340	400	0.59[a]

[a] The value was taken from ref.[27] and verified with a carbazole standard.

TABLE II
Fluorescence lifetimes analyzed by single-exponential (τ) or double-exponential (τ_1, τ_2) fit for oligomers **1**–**3** and polymers **4**–**7** in tetrahydrofuran (λ_{ex}, excitation wavelength; λ_{em}, emission wavelength)

Oligomer or polymer	λ_{ex}, nm	λ_{em}, nm	τ, ns	τ_1, τ_2, ns (rel B_1, B_2, %)
1	335	390	1.02	[a]
2	335	390	1.00	[a]
2	335	460	(4.63)	6.03 (66), 2.11 (34)
3	338	465	(5.69)	6.88 (76), 2.35 (24)
4	335	390	1.02	1.01 (99.5), 35.7 (0.5)
5	338	400	0.82	[a]
6	338	400	1.03	[a]
7	338	400	0.77	[a]

[a] The decay was virtually single-exponential.

Methods and Procedures

Steady-state fluorescence spectra were measured with a Hitachi Perkin–Elmer MPF-2A spectrometer in L-format and corrected[19] for the calculation of the fluorescence quantum yields. The spectral sensitivity coefficient was determined using a tungsten lamp having a known spectral distribution and standard fluorescence spectra[20] of 2-naphthol and *N*,*N*-dimethyl-3-nitroaniline.

The relative fluorescence quantum yield (*Q*) of oligomers **1**–**3** and polymers **4**–**6** was calculated[21] from

$$Q = Q_S \frac{A_S}{A} \frac{n^2}{n_S^2} \frac{\int_\lambda I(\lambda)\,\mathrm{d}\lambda}{\int_\lambda I_S(\lambda)\,\mathrm{d}\lambda}, \tag{1}$$

where subscript S denotes a standard compound, A is the absorbance of a solution at the excitation wavelength, n the refractive index of the solvent and $I(\lambda)$ the intensity of fluorescence at wavelength λ. The "inner filter effect" was eliminated using solutions of the same absorbance (A = 0.4). Polymer **7** in dichloromethane[22] (Q_S = 0.59) and carbazole in cyclohexane[23] (Q_S = 0.38) were used as standard compounds. The area under the corrected emission spectrum was evaluated by numerical integration. The relative fluorescence quantum yields are given in Table I.

The fluorescence lifetime (τ) was obtained with a time-resolved fluorimeter FL 900 CDT (Edinburgh Analytical Instruments, U.K.) using the time-correlated single-photon counting (TCSPC) method[19,24]. TCSPC is a digital technique, counting photons, which are time-correlated in relation to the excitation pulse. Summing over many pulses, a probability histogram of counts *versus* time channels was built up. Experiments were continued until 10 000 counts in the peak channel were collected (Figs 5 and 6). Excitation of the samples was carried out by a thyratron-controlled pulse lamp nF 900 having the repetition frequency rate 40 kHz. The lamp was filled with nitrogen (>99.995%) at 150 kPa. The intensity of the emission beam was adjusted so that 800 fluorescence photons or less were observed per second (*ca* 2% of repetition frequency). The time-resolved and lamp profile measurements were performed in L-format of a centrally illuminated cuvette (1 × 1 × 4 cm). The lamp pulse (profile) was measured using a scattering solution of LUDOX (DuPont) closely spaced in time to a particular fluorescence decay. The theoretical fluorescence decay, $F(t)$, analyzed by deconvolution of the lamp pulse with the impulse response of the sample, is given by

$$F(t) = \mathrm{C} + \sum_{\mathrm{i}} B_i \exp(-t/\tau_i), \tag{2}$$

where B_i is a preexponential factor representing the fractional contribution to the time-resolved decay of the component with a lifetime τ_i [rel $B_i = (B_i\,\tau_i/\Sigma B_i\tau_i) \times 100\%$], C is background and t is time. Least-square analysis of the observed time-resolved decay, $R(t)$, was used for estimation of the impulse response function $F(t)$. The goodness-of-fit parameter, χ^2, was calculated from

$$\chi^2 = \sum_t \frac{[R(t) - R_\mathrm{C}(t)]^2}{R(t)} = \sum_t \left[\frac{R(t) - R_\mathrm{C}(t)}{\sigma(t)}\right]^2 = \sum_t u^2(t), \tag{3}$$

where $R_C(t)$ is the calculated decay of fluorescence, $\sigma(t)$ the standard deviation of each data point and $u(t)$ the weighted residuals. From Poisson statistics the standard deviation is known to be the square root of the number of photon counts, $\sigma(t) = [R(t)]^{1/2}$. In TCSPC it is straightforward relationship between χ^2 and residuals. The value of χ^2 is the sum of the squared deviations between the measured values $R(t)$ and the expected values $R_C(t)$, each divided by squared deviations expected for the number of detected photons. The values $\chi^2 < 1.7$ are typical of a good fit. The residuals are the difference between the measured values $R(t)$ and the expected values $R_C(t)$, weighted by the standard deviation of each data point. A good fit should give a residual curve that only contains random noise distributed around zero (Fig. 5). The excitation and emission wavelengths and the measured fluorescence lifetimes are summarized in Table II.

Molecular weights of the polymers and oligomers were determined using a GPC chromatograph (Laboratory Instruments, Czech Republic) equipped with RI and UV 254 nm detectors, a column 8 × 600 mm (PSS 10 000, PSS, Germany), and data collection and treatment (Data Monitor, Watrex, Czech Republic). Polystyrene standards (PL Laboratories, U.K.) were used for calibration. The synthesized 2,2′,5,5′-tetrakis(hexadecyloxy)biphenyl (dimer model) was used as an external standard to verify the polystyrene calibration at low molecular weights. The samples were measured in THF, which was dried over molecular sieve 4A and distilled.

UV-VIS spectra were taken on a Perkin–Elmer Lambda 20 spectrometer. Molar absorption coefficients (ε) of oligomers and polymers are expressed per monomer unit. ^{1}H and ^{13}C NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz in $CDCl_3$ or deuterated THF using hexamethyldisiloxane as an internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants (J) in Hz. FT IR spectra (ν in cm^{-1}) were measured using a Perkin–Elmer Paragon 1000 PC Fourier transform infrared spectrometer in KBr pellets or as a film on KBr.

RESULTS AND DISCUSSION

Procedures for the preparation of structurally defined oligo- and poly(1,4-phenylene)s were developed on the basis of numerous synthetic principles of organic and organometallic chemistry. The availability of more effective methods for the aryl–aryl coupling of small molecules is an important driving force in the development of new synthetic strategies for substituted poly(1,4-phenylene)s and other poly(arylene)s. In particular, the Pd(0)-catalyzed aryl–aryl coupling according to Suzuki[25] (arylboronic acid plus aryl halide or tosylate) and the nickel(0)- or nickel(II)-mediated coupling according to Yamamoto[26] (aryl halide or tosylate plus aryl halide or tosylate) have been most successfully employed. Both synthetic methods have been used very frequently in the last decade.

The Suzuki method is used mainly in the cases, where high-molecular-weight materials are to be prepared. Typical degrees of polymerization (P_n) range from 30 to 100. We used this method for the preparation of polymer **7** (Scheme 2), which served as the standard material for the fluorescence quantum yield (Q) determination (Eq. (1)). Using an oligomer approach, MALDI-TOF mass spectrometry and HPLC, the "effective conjugation length" of IP-PPP was determined[27] as 11. The synthesized polymer **7** ($P_n \approx 37$, $M_w = 35\ 000$, $M_n = 21\ 000$) had average molecular-weight parameters substantially higher and its use as fluorescence standard was thus confirmed. The published value[22] for IP-PPP ($Q_S = 0.59$) was verified for polymer **7** using another fluorescence standard (carbazole in cyclohexane)[23]. The measured values of Q for oligomers and polymers **1**–**6** are shown in Table I. The fluorescence quantum yield increases with the average molecular weight of the fractions or, more specifically, with increasing conjugation length of the samples.

On the other hand, we have used the Yamamoto method for the preparation of oligomers **1**–**3** and polymers **4**–**6** (Scheme 1). For nickel-mediated coupling of 1,4-dibromobenzene derivatives, we used the nickel(II)/triphenylphosphine complex as a catalyst, zinc as the reducing metal, and 2,2′-bipyridine as a coligand. This method is convenient for the syntheses of materials with lower molecular weights; the average values of P_n usually range from 10 to 15. The determined molecular-weight parameters of polymers **4**–**6** (see Experimental) were in agreement with the expected values. Reducing the reaction time and temperature, oligomer fractions **1**–**3** were prepared. Their GPC characteristics (normalized distribution functions) are shown in Fig. 1. In fraction **1**, hexamers and tetramers prevail, some dimers being also present. The ratio of hexamer : tetramer : dimer can be roughly estimated from the peak heights as 2.5 : 2.5 : 1. Similarly for fraction **2**, the hexamer : tetramer : dimer ratio can be estimated as 1 : 2 : 5 and finally for fraction **3**, the tetramer : dimer ratio was approximately 1 : 5 if the presence of hexamers was found to be negligible (shoulder). In spite of the fact that the GPC chromatograph used was calibrated using polystyrene standards, the molecular weights of the oligomer peaks fit well keeping in mind the molecular weight of the monomer unit being 557. The synthesized biphenyl derivative (dimer model) was used as an external standard, which confirmed the assumed dimer positions in Fig. 1 (*i.e.*, the peaks with molecular weight around 1 000). The results of elemental analysis supported the average composition of fractions **1**–**3**. The content of bromine (end group) decreases (**3** > **2** > **1**) with increasing average P_n. Also for polymers **4**–**6** is the bromine content (and, consequently, calculated average P_n) in good agreement with GPC analyses.

Fluorescence emission spectra of oligomers **1** and **2** in THF are shown in Fig. 2. Oligomer fraction **1** has one emission maximum at 390 nm and similar maxima were observed for polymers **4**–**6** (Table I). Unsubstituted poly(1,4-phenylene) possesses a 23° twist between the adjacent benzene units due to *ortho*-hydrogen interaction. The substitution in positions 2 and 5 forces the adjacent benzene units even further out of the plane, resulting[28] in twist angles 60–80°. Such twist angles and long hexadecyloxy substituents exclude the cofacial sandwich-type arrangement with interplanar chain distances of ≈0.3–0.4 nm necessary for excimer formation. That is why we did not observe an excimer emission from polymers **4**–**6**. Even tetramers and hexamers of **1** are too long to form an excimer structure. On the other hand, oligomers **2** show two emission maxima at 390 and 460 nm (Fig. 2). The maximum at 460 nm increases with increasing concentration of **2** in solution. Fraction **2** contains mainly dimers and we assume that the excimer formation is responsible for the emission at a longer wavelength. The maximum of the excitation spectrum for emission at 460 nm is red-shifted in comparison with the excitation spectrum maximum for emission at 390 nm (Table I). If the excimer is excited in oligomers **2** at 360 nm, its emission at 460 nm prevails and the shoulder only is observed at 390 nm (Fig. 3). Another increase in the excimer formation was observed with oligomer fraction **3**, where the content of long oligomer chains was further decreased by fractional precipitation. The emission of the excimer at 465 nm was observed as a main peak and the emission at 390 nm was found to be negligible. The excitation and emission spectra of the excimer in oligomers **3** were compared with those of polymers **4**, where the excimer was not

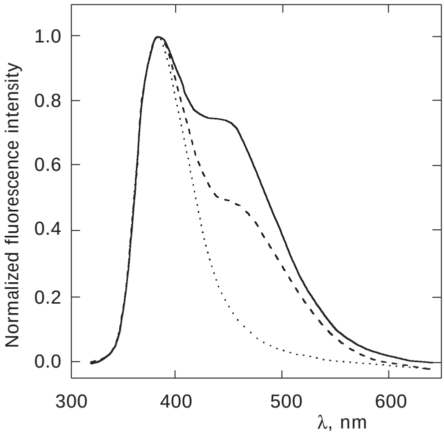


FIG. 2
Fluorescence emission spectra (λ_{ex} = 330 nm) of oligomers **1**, c = 0.20 g l^{-1} (dotted line); **2**, c = 0.20 g l^{-1} (dashed line) and c = 0.84 g l^{-1} (solid line) in tetrahydrofuran

formed (Fig. 4). The excimer formation causes a red shift both in emission (from 390 to 460 nm) and excitation (from 335 to 345 nm) spectra. On the contrary, the absorption spectra are red-shifted with increasing degree of conjugation, *i.e.* with increasing P_n (Table I). Oligomers **2** and **3** did not

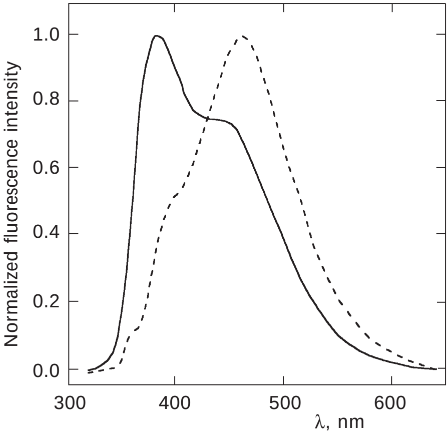


FIG. 3

Fluorescence emission spectra of oligomer fraction **2** (c = 0.84 g l^{-1}) at excitation wavelength 330 nm (solid line) or 360 nm (dashed line) in tetrahydrofuran

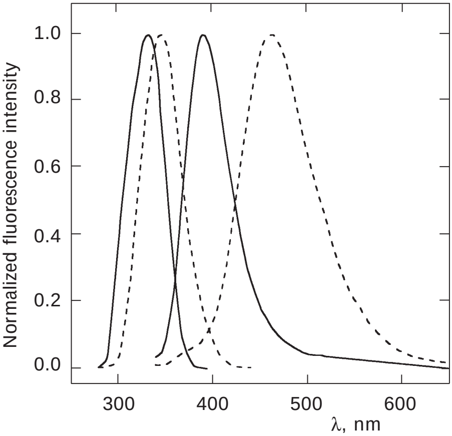


FIG. 4

Fluorescence excitation ($\lambda_{em} = \lambda_{max}$) and emission ($\lambda_{ex} = \lambda_{max}$) spectra of polymer **4** (solid line) and oligomer fraction **3** (dashed line) in tetrahydrofuran, c = 0.04 g l^{-1}

show additional absorption at longer wavelengths, which could indicate the ground state interaction. Consequently, the emission at 460–465 nm was assigned rather to excimers than to aggregates (polaron pairs).

The excimer emission should exhibit a longer fluorescence lifetime because the radiative transition to the ground state is forbidden. Oligomers and polymers **1**–**7** were studied in THF by time-resolved fluorescence spectroscopy (Table II). The emission decay curves at 390–400 nm were found to be practically single-exponential (Eq. (*2*)) with fluorescence lifetimes around 1 ns (Fig. 5 shows typical data). The values of χ^2 (Eq. (*3*)) were less than 1.3 for single-exponential fit and were not improved by double-exponential fit. When such fit was tested, the content of the longer component was 0.5% or less (Table II, polymer **4**). Fluorescence decays at 460–465 nm were double-exponential, exhibiting longer lifetimes than those at 390–400 nm. A comparison of the emission decay curves at 460 and 390 nm is shown in Fig. 6. In decays at 460 nm, the longer component ($\tau_1 \approx 6.0$–6.9 ns) prevails [Eq. (*2*); rel $B_1 \approx 70\%$] over the short component ($\tau_2 \approx 2.1$–2.4 ns; rel $B_2 \approx 30\%$). The single-exponential values shown in Table II (in brackets)

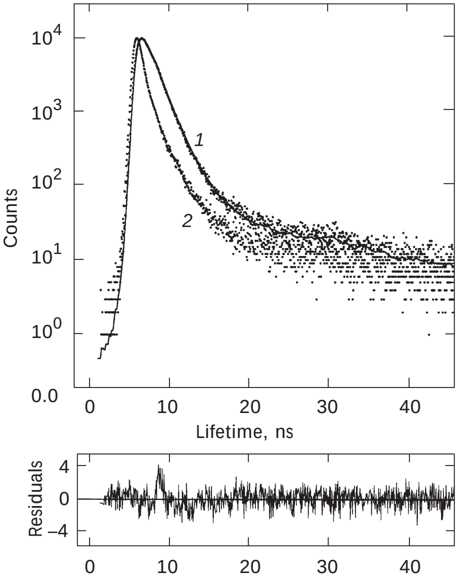


FIG. 5
Time-resolved fluorescence decay of polymer **4** (τ = 1.02 ns, λ_{ex} = 335 nm, λ_{em} = 390 nm, χ^2 = 1.23) in tetrahydrofuran (*1*), the measured lamp pulse (*2*) and the weighted residuals

for decays at 460–465 nm are average values (≈5 ns) just for an approximate comparison with those for decays at 390 nm. Otherwise their χ^2 values are too high (>1.7), the double-exponential fit being necessary to use to calculate the fluorescence lifetimes.

From fluorescence behavior of oligomers **2** in solvents of different polarity, we believe that hydrophobic interactions of hexadecyloxy side chains play an important role in the excimer formation. The fluorescence emission spectrum of **2** in THF (medium-polarity solvent) was compared (Fig. 7) with those in ethanol (polar solvent) or hexane (nonpolar solvent). In polar ethanol, hydrophobic interactions support the excimer formation, the excimer emission at 460 nm being observed as the main peak. The insolubility of higher oligomers in this solvent explains nearly total absence of the emission at 390 nm. In nonpolar hexane are oligomers **2** completely soluble but the main emission at 390 nm indicates that excimers were not formed. Hydrophobic interactions of side chains are not effective in this solvent and the molecules are too separated by side chains to form the sandwich structure. The maxima of excitation spectra in ethanol and hexane were found to be at 340 and 330 nm, respectively, which is in agreement with the discussion above. The measured fluorescence lifetimes in hexane for emission at 390 nm (τ = 0.85 ns) or in ethanol for emission at 460 nm [τ_1 = 6.45 ns (76%), τ_2 = 1.68 ns (24%)] supported the steady-state results. Hydrophobic

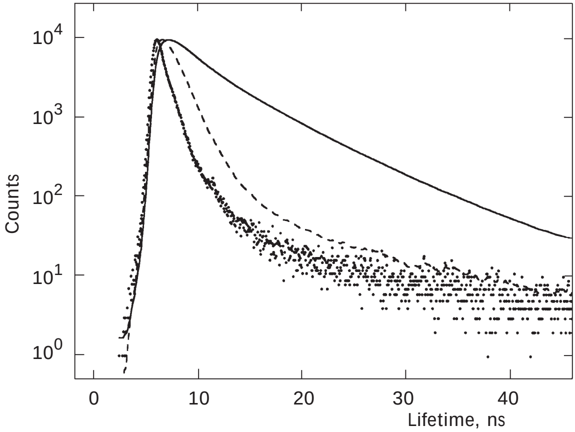


FIG. 6

Time-resolved fluorescence decay of oligomer fraction **2** (λ_{ex} = 335 nm) in tetrahydrofuran for emission at 460 nm (τ_1 = 6.03 ns (66%), τ_2 = 2.11 ns (34%), χ^2 = 1.19) (solid line) or at 390 nm (τ = 1.00 ns, χ^2 = 1.05) (dashed line) and the measured lamp profile (dots) interactions of aliphatic side chains of polymers or low-molecular-weight alkane models in polar medium were described[29,30].

In conclusion, we have synthesized and characterized "hairy-rod" polymers, poly[2,5-bis(hexadecyloxy)-1,4-phenylene] and poly[2,5-bis(decyloxy)-1,4-phenylene], by the Yamamoto coupling reaction. In solution, the long side substituents created structural hindrance resulting in an out-of-plane twist angle between the adjacent benzene rings. For steric reasons, polymer chains are not able to give rise to sandwich configurations with distances suitable for excimer formation. Consequently, we have found out a single fluorescence emission band at 390 nm with the single-exponential lifetime close to 1 ns. However, in the case of short oligomers, we observed another emission band at 460 nm with longer double-exponential lifetime [6.9 ns (76%), 2.4 ns (24%)]. Such behavior was observed in the oligomer fractions, where dimers prevail. We assume that in the case of dimer or, possibly, trimer, the sandwich-type arrangement with sufficiently close interchain distances can arise and an excimer can be formed. Hydrophobic interactions of aliphatic side chains in polar media were found to be favorable for the excimer formation. The investigation of polymers will continue in the solid state (films) for utilization in the organic LED construction. Because the excimer formation is an unfavorable process, the polymers will be fractionally precipitated before use to remove short oligomers.

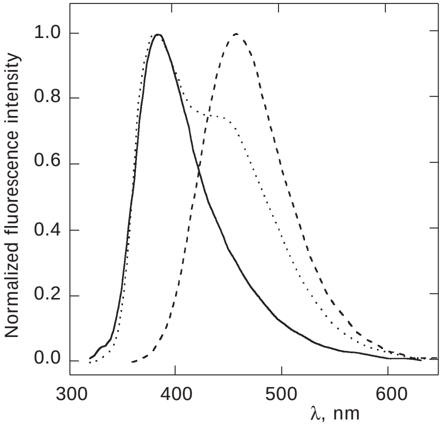


FIG. 7
Fluorescence emission spectra ($\lambda_{ex} = \lambda_{max}$) of oligomer fraction **2** in solvents of different polarity: hexane (solid line), tetrahydrofuran (dotted line), ethanol (dashed line)

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SYMBOLS

A	absorbance
B	preexponential factor
C	background constant
c	concentration, g l^{-1}
F	theoretical time-resolved fluorescence intensity, a.u.
I	steady-state fluorescence intensity, a.u.
J	NMR coupling constant, Hz
M	molecular weight
M_n	number-average molecular weight
M_w	weight-average molecular weight
n	refractive index
P_n	degree of polymerization
Q	fluorescence quantum yield
R	observed time-resolved fluorescence intensity, a.u.
t	time, s
u	weighted residuals
w	weight distribution function
χ^2	goodness-of-fit parameter
ε	molar absorption coefficient, l mol^{-1} cm^{-1}
λ	wavelength, nm
λ_{em}	emission wavelength, nm
λ_{ex}	excitation wavelength, nm
λ_{max}	wavelength of the maximum of a spectrum, nm
σ	standard deviation
τ	fluorescence lifetime, ns

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