Synthesis and Characterization of Monodisperse Oligofluorenes

Jungho Jo,+[b] Chunyan Chi,+[a] Sigurd Höger,[c] Gerhard Wegner,*[a] and Do Y. Yoon*[b]

Abstract: An efficient synthesis of 9,9-bis(2-ethylhexyl)fluorene oligomers up to the heptamer is reported, with repetitive Suzuki and Yamamoto coupling reactions employed in the synthesis. The key steps for preparation of the essential intermediates include Pd-catalyzed transformation of aryl bromides to aryl boronic esters (Miyaura reaction) and the application of the much higher reactivity of aryl boronic esters over aryl bromides in the Pd-catalyzed cross-coupling reaction with aryl diazonium salts. Variation of the UV/Vis absorption and photoluminescence characteristics with chain length is reported. Moreover, glass transition and liquid-crystal characteristics of the oligomers are described and compared with those of the polymer.

Keywords: fluorene · glasses · liquid crystals · oligomerization · photoluminescence

Introduction

9,9-Disubstituted polyfluorenes find extensive scientific and technological application as efficient organic blue-light-emitting diode materials.[1,2] Polyfluorenes show extremely high photoluminescence quantum yields, high thermal and oxidative stability, and good solubility in common organic solvents for easy processing by spin- or dip-coating methods.[3] They also exhibit interesting thermotropic liquid-crystal characteristics,[4] and consequently, upon annealing in the nematic melts, the polymer chains were shown to be easily aligned on a rubbed polyimide surface.[5] Such an alignment of the polymer results in the polarization of the emitted light and improves the charge carrier mobility, a prerequisite for the fabrication of an organic thin-film transistor.[6] Thus, the ability of the polyfluorenes to align excellently paves the way to make thin films with highly anisotropic electrooptical and electrical properties.[7]

Polyfluorenes are readily prepared by Ni^0-mediated coupling of the corresponding dibromo monomers. Polymers obtained by this method have weight-averaged molecular weights (M_w) of the order of several hundred thousand with polydispersities of around three (according to GPC analysis against polystyrene standards). The long chain lengths and the polydispersity in chain lengths lead to complex structural characteristics of the thin films and make it very difficult to establish a proper structure–property relationship. Moreover, the normal synthetic procedure leads to incorporation of a small amount of chemical defects, which may be responsible for undesirable green-band emission characteristics.[8]

Therefore, for better understanding of the structure–property relationships of polyfluorenes, it would be very helpful to study the properties of a series of pure oligomers with well-defined length and no chemical defects. The absorption spectra of a series of oligomers will allow the estimation of the effective conjugation length of the polymer.[9] In addition, a detailed study of the photoluminescence spectra of pure oligomers may help to solve questions concerning the origin of the green-emission band observed in the photoluminescence and electroluminescence spectra of polyfluorene films.[10] Moreover, well-defined, defect-free oligofluorenes may also be welcome as active materials in organic light-emitting diodes and organic thin-film transistors.

Monodispersed dialkyl fluorene oligomers were first reported by Klaerner and Miller.[11] They showed that the Ni^0-mediated oligomerization of 2,7-dibromo-9,9-bis(*n*-hexyl)fluorene in the presence of 2-bromofluorene as an end-capping agent gives a mixture of oligomers and low-molecular-weight polymers that could be fractionated by HPLC. From the spectroscopic properties of the samples, the effective

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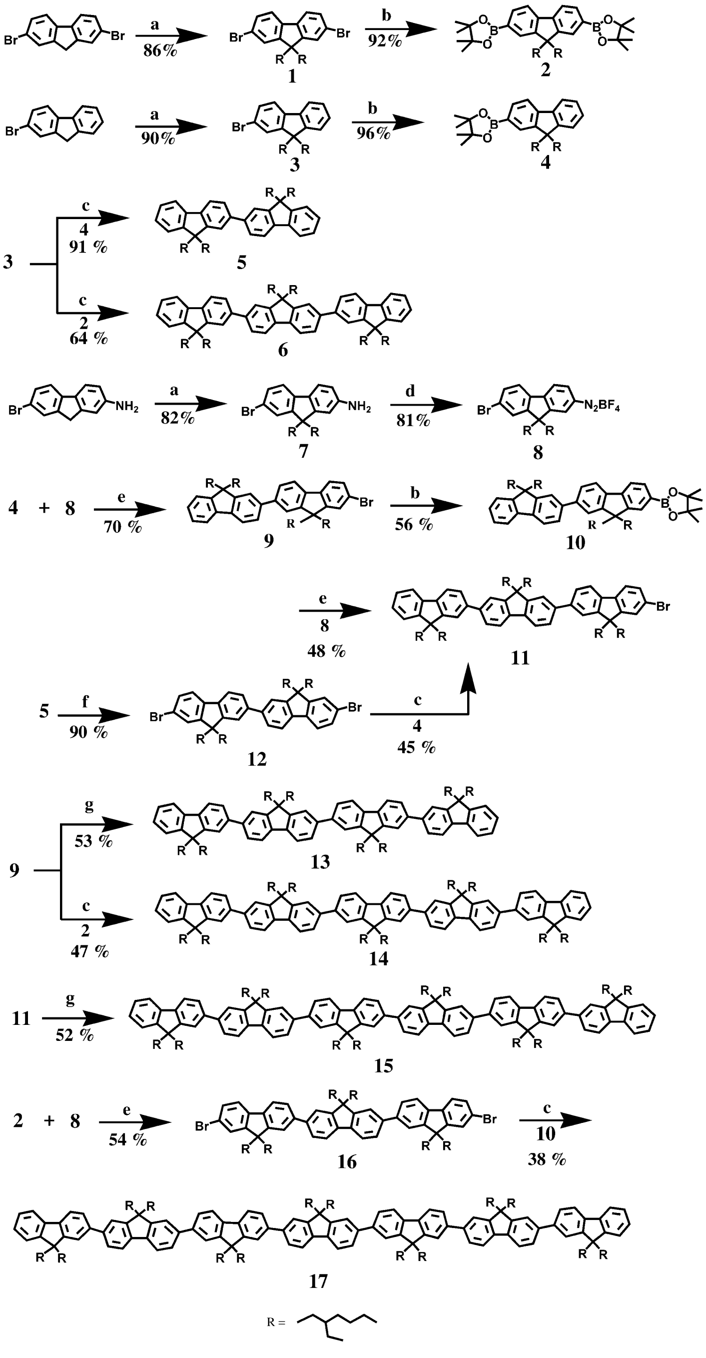
conjugation length was estimated to be approximately 12 fluorene units. Lee and Tsutsui prepared a series of oligofluorenes up to the tetramer by a repetitive 2*n* divergent approach from 2,7-dibromo-9,9-bis(*n*-hexyl)fluorene, with coupling with bis(*n*-hexyl)fluorene-2-borate and subsequent bromination of the coupling product.[12] Anemian et al. synthesized monodisperse dihexylfluorene oligomers up to the hexamer by a combination of Suzuki and Yamamoto coupling reactions.[13] Oligomers with *n* repeating units containing only one bromine atom at positions 2 or 7 on the end fluorenes were prepared by coupling the corresponding monoboronate ($n-1$) with 2-bromo-7-iodo-9,9-bis(*n*-hexyl)-fluorene at the iodo site, which is significantly more reactive than the bromo site. The resulting monobromo oligomers were then coupled by a Yamamoto reaction. Most recently, a detailed description of the synthesis, optical properties, and solid-state properties of defined oligofluorenes, up to the hexadecamer, containing chiral substituents at position 9 was presented by Geng et al.[14] Here again, the iodo/bromo selectivity in the Suzuki coupling reaction and the use of trimethylsilyl groups as dormant iodides were used as key factors in the oligomer synthesis.

The enormous success of the Suzuki reaction[15] in the preparation of these oligomers arises from the high yield of the coupling reaction together with the easy availability of the boronic acids and the boronates.[16] They are prepared in good to excellent yields by halogen–metal exchange and subsequent trapping of the aryl lithium compound with trialkylborates. Recently, the scope of this reaction has been dramatically expanded by the discovery that aryl boronates are also available directly from the aryl halides by a Pd^0-catalyzed reaction with the pinacol ester of diboron (the Miyaura reaction).[17] This transformation avoids the use of strongly basic organometallic reagents and thus allows the preparation of a wide variety of functionalized aryl boronic esters.

Here, we present the synthesis of oligofluorenes from the dimer up to the heptamer by Suzuki and Yamamoto reactions,[18] with the Miyaura reaction employed for the first time for the preparation of the aryl boronates. Also, we have taken advantage of a large difference in the reactivity between aryl diazonium salts and aryl bromides in the Suzuki coupling reaction[19] in the preparation of the key intermediates. The oligomers have been characterized with regards to their optical (absorption and photoluminescence) properties and their phase behavior, including glass transition and liquid-crystal characteristics. Finally, the properties of the oligomers are compared with those of the polymer in order to gain new insights into the polymer properties.



Scheme 1. Synthesis of the oligofluorenes: a) 2-Ethylhexyl bromide, 50% aqueous NaOH/DMSO, room temperature; b) bis(pinacolato)diboron, AcOK/DMF, $[Pd(dppf)Cl_2]$, 60 °C; c) $[Pd(PPh_3)_4]$, toluene/aqueous Na_2CO_3, reflux; d) $BF_3 \cdot OEt_2$, butylnitrite/dichloromethane, −10 °C; e) $Pd(OAc)_2$/EtOH, reflux; f) Br_2, dichloromethane, reflux; g) $[Ni(cod)_2]$, COD, Bipy, toluene/DMF, 80 °C. DMSO = dimethylsulfoxide, DMF = *N,N*-dimethylformamide, dppf = 1,1′-bis(diphenylphosphanyl)ferrocene, COD = cycloocta-1,5-diene, Bipy = 2,2′-bipyridine.

Results and Discussion

Synthesis of oligofluorenes: The synthetic route towards the oligofluorenes is shown in Scheme 1. First, 2,7-dibromofluorene and 2-bromofluorene were alkylated with 2-ethylhexyl bromide to give the di- and monobromides of fluorene, **1** and **3**, respectively. Both of these compounds, as well as the corresponding boronic acids, have already been reported in the literature.[11–14] However, in our synthesis, we transformed the aryl bromides into the corresponding aryl boronic esters with the Miyaura reaction. In these reactions the corresponding boronic esters, **2** and **4**, are formed in high yields (>90%) and can easily be purified by column chromatography. Compounds **4** and **2** were then coupled with **3** to give the fluorenyl dimer **5** and trimer **6**, respectively.

To synthesize the longer fluorene oligomers, the unsymmetrical monobrominated intermediates, such as **9** and **11**, are essential. However, these intermediates cannot be obtained directly by bromination of **5** or **6** with bromine, since statistical product mixtures are obtained which are very difficult to separate on a large scale. One possibility to obtain the monobrominated intermediates is to use compounds with one potential reaction site in a protected form (for example, trimethylsilyl groups instead of bromo or iodo functionalities[20]) as described by Geng et al.[14] Another way is to use fluorene derivatives with two reaction sites of significantly different reactivity. In the latter case, the use of bromoiodofluorene derivatives is quite obvious since the reactivity of aryl iodides towards the Suzuki coupling is substantially higher than the reactivity of aryl bromides; this concept has already been used by Anemian et al.[13]

A good alternative approach is to use the large reactivity difference between aryl diazonium salts and aryl bromides in the cross-coupling reaction with aryl boronates. Since the reaction with aryl diazonium salts does not need a base such as Na_2CO_3, which is essential in the Suzuki coupling reaction with aryl bromides, the coupling reaction takes place only at the site of the diazonium salt. Hence, we employed this reaction in our synthetic procedure as follows.

2-Amino-7-bromofluorene was alkylated with 2-ethylhexyl bromide to give **7** in 82 % yield; **7** was subsequently transformed into the corresponding diazonium salt **8** (81 %). Cross-coupling reaction of **4** and **8** with $Pd(OAc)_2$ gave **9** in 70 % yield within an hour. This result shows that the reactivity difference between aryl diazonium salts and aryl halides is larger than that between aryl iodides and aryl bromides. **9** was transformed into the corresponding boronic ester **10** in 56 % yield with the Miyaura reaction. Subsequently, the cross-coupling reaction of **10** and **8** gave **11** in 48 % yield.

Another method we have used to obtain the monobromides is to treat the monoboronate with an excess of the dibromofluorene. Indeed, the coupling of **4** with an excess of **1** was successfully performed by using only 1.5 equivalents of **1** to give the monobrominated dimer **9** in 50 % yield (not shown in Scheme 1). Similarly, the monobrominated trimer **11** was obtained in 45 % yield by the reaction of **4** with 1.5-fold excess of the dibrominated product **12**, which was prepared from **5** in 90 % yield.[21] Both methods led to identical compounds, thereby demonstrating the validity of our synthetic methodology.

Yamamoto homocoupling reactions of **9** and **11** gave the fluorenyl tetramer **13** and hexamer **15**, respectively, both in ≈50 % yield. The fluorenyl pentamer **14** was obtained with a cross-coupling reaction of **9** and **2** in 47 % yield. The high reactivity of the diazonium salts was also used to prepare the dibromofluorenyl trimer **16**, which was obtained in 54 % yield by coupling of **2** and **8**. Although **16** can, in principle, also be prepared by the bromination of **6**, a detailed mass spectral analysis of the crude reaction products showed that varying amounts of tribromide contaminate the dibromide. Since even small amounts of an impurity affect the liquid-crystalline behavior of the oligomers, we avoided the bromination of the fluorenyl trimer and higher oligomers in our oligomer synthesis. The fluorenyl heptamer **17** was obtained in 38 % yield by cross-coupling reaction of **10** and **16**.

Optical properties of oligofluorenes: Electronic absorption spectra of monodisperse oligo(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) compounds **5**, **6**, **13**, **14**, **15**, and **17** in diluted chloroform solution with the same fluorene unit concentration (1.0×10^{-5} M) are shown in Figure 1 and the data are collected in Table 1.

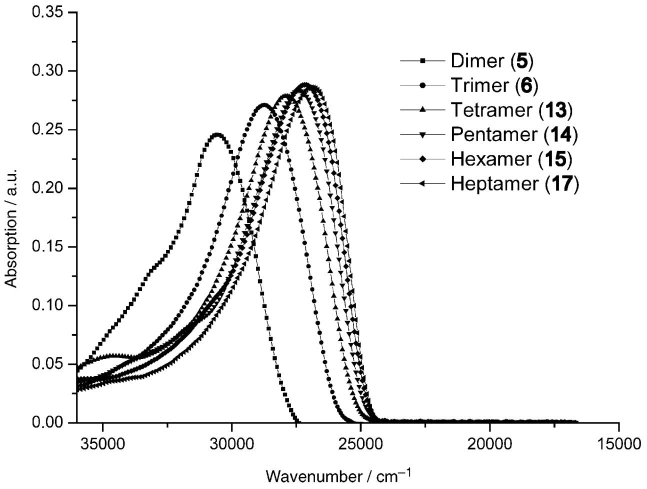


Figure 1. UV/Vis absorption of oligofluorenes (dimer to heptamer) in chloroform solution at room temperature at a fixed concentration of fluorene repeat units of 1.0×10^{-5} mole L^{-1}.

The oligofluorenes exhibit unstructured absorption bands, as is also seen for polyfluorenes.[3] The absorption maximum is red-shifted with increasing number (n) of fluorene units. The molar extinction coefficients (ε) of the oligofluorenes show a good approximation of a linear increase with n from dimer to heptamer, as seen in Table 1. The increment is 30.3×10^3 L mol^{-1} cm^{-1} for each repeat unit. The plot of the wave number of the maximum absorption versus $1/n$ follows

Table 1. Summary of UV/Vis absorption ($\nu_{max(abs)}$) and photoluminescence ($\nu_{max(PL)}$) spectra for the fluorene oligomers and polymer, from chloroform solutions and solid films.[a]

Sample	Solution				Film		
	$\nu_{max(abs)}$ [cm^{-1}]	ε_{max} [L mol^{-1} cm^{-1}]	$\nu_{max(PL)}$ [cm^{-1}]		$\nu_{max(abs)}$ [cm^{-1}]	$\nu_{max(PL)}$ [cm^{-1}]	
dimer **5**	30580	49170	27400	25970	30400	27100	25770
trimer **6**	28740	81330	25380	24100	28650	25130	23870
tetramer **13**	27930	111500	24750	23470	27550	24390	23200
pentamer **14**	27400	141700	24450	23150	27030	23980	22940
hexamer **15**	27170	173000	24330	23040	26880	23810	22780
heptamer **17**	26880	200300	24270	23040	26810	23700	22730
polymer	26110	–	24100	22940	25910	23590	22570

[a] Since the resolution of the low-energy peak was too low at the temperature at which the data were recorded, only the ν_{max} values of the two high-energy components are given.

a linear fit, as shown in Figure 2. The polymer has a maximum absorption at 26110 cm^{-1} (383 nm);[3] hence, we can estimate an effective conjugation length of 14 repeat units from the plot in Figure 2, a figure that can be compared with the reported value of 12 for poly(9,9-bis(*n*-hexyl)fluorene-2,7-diyl).[11] The UV/Vis absorption spectra of thin films of the oligofluorenes on quartz substrates are practically identical to the solution data except for slight red-shifts in the absorption maxima, as listed in Table 1.

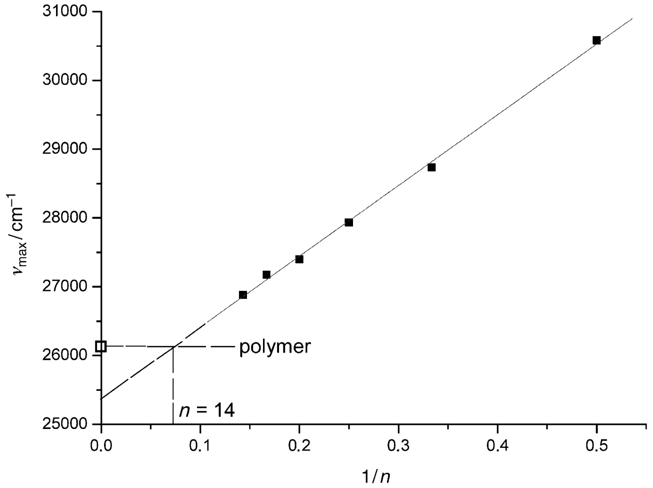


Figure 2. Plot of $\tilde{\nu}_{max}$ versus reciprocal degree of polymerization *n*.

Figure 3a shows the photoluminescence (PL) spectra of the oligomers from dimer **5** to heptamer **17** in chloroform with the same concentration of fluorene units (1.0×10^{-6} M), excited at the corresponding energy of maximum absorption. Similar to polyfluorenes, three well-resolved fluorescence bands are observed. They may be assigned to the 0–0, 0–1, and 0–2 intrachain singlet transitions.[22] The spectral position and the intensity of the PL maximum changes with the number of fluorene units, *n*. This is explained by the increase of effective conjugation from dimer **5** up to heptamer **17**. Notably, the relative intensity of the three emission bands also changes with *n*. The relative intensity of the 0–0 transition increases with *n*, while that of the 0–2 transition decreases. This may be related to an increase of the intrachain coupling interaction with the molecule's length.

Normalized solid-state PL spectra of oligofluorenes **5**, **6**, **13**, **14**, **15**, and **17** from thin films on a quartz plate excited at the absorption maxima are shown in Figure 3b and the key data are listed in Table 1. Relative to the PL spectra measured in solution, red shifts in the emission maxima are observed and the relative intensities of the 0–2 intrachain singlet transition increase in all cases. Most importantly, the green-band emission usually seen for the polymer[3] is absent for all of the oligomers (Figure 3b). Even upon high-temperature annealing (180 °C) in air, this green emission is still negligible for the oligomers. This result casts doubt on the widely discussed hypothesis that the green emission seen with varable intensity in polymer samples (Figure 3b) originates from excimer formation by interchain interaction. It is difficult to see why such interchain interactions should be suppressed in the case of oligomers if this explanation was true.

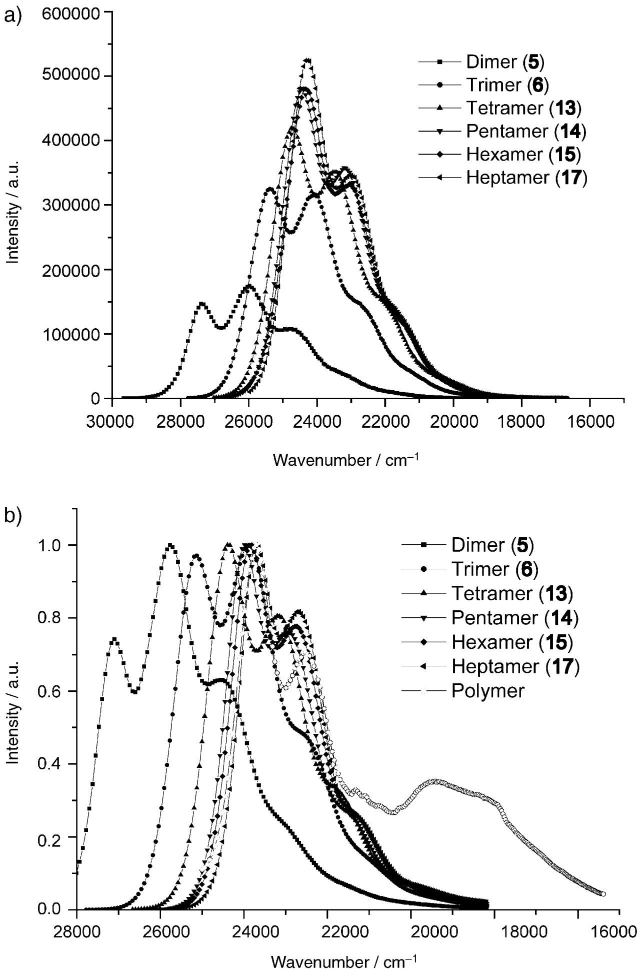


Figure 3. a) Fluorescence spectra of oligofluorenes (dimer to heptamer) in chloroform solution at room temperature at a fixed concentration of fluorene repeat units of 1×10^{-6} mole L^{-1}. b) Photoluminescence spectra of thin films of the oligofluorenes (dimer to heptamer). The spectrum for the polymer, also shown in this figure, was obtained for a sample annealed at 180 °C for 1 h in air.

Phase transition characteristics of oligofluorenes: The DSC traces shown in Figure 4 clearly exhibit the glass transition temperatures for all of the oligomers in the low-temperature range, followed by an endothermic transition for the tetramer **13**, pentamer **14**, hexamer **15**, and heptamer **17** as the temperature is increased. The latter transition is identified as the liquid-crystalline to isotropic transition from the polarized optical microscopy study. The Schlieren texture and the very small enthalpy value of the transition, as shown in Table 2, indicate that the liquid-crystal structure is probably of nematic character, but a further study on this topic is in progress.

The isotropization temperature T_{iso} of this liquid-crystalline to isotropic transition extrapolates to a hypothetical T_{iso}(Polymer) for $n\rightarrow\infty$ of 475 °C if plotted in the coordinates $T_{iso}=T_{iso}(n\rightarrow\infty)(1-KX_E)$ where X_E is the mole frac-

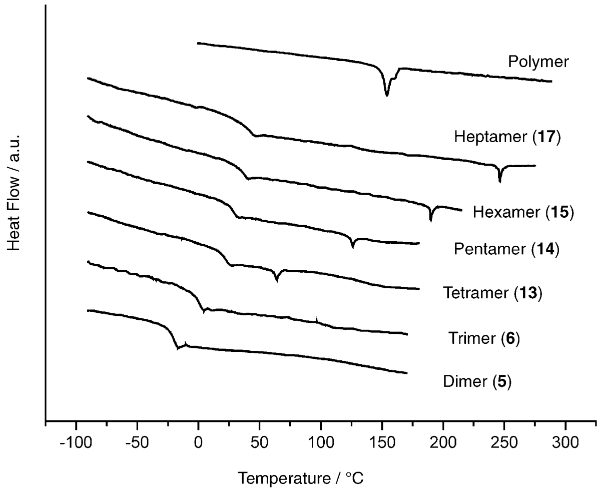


Figure 4. DSC traces for the oligofluorenes (dimer to heptamer; second heating at 10 °C min^{-1}). The DSC trace for the polymer is also shown for comparison.

tion of end groups and K is an empirical constant. This temperature is well above the decomposition range of the high polymer. In this regard, it is important to note that the polymer exhibits a well-known "melting" transition around 160 °C. Above 160 °C the polymer exists in a nematic liquid-crystal phase; below that temperature another solid phase is formed, the true nature of which is not yet understood. It may be of higher order smectic type but of such a rigidity of the packing that a transition to a glassy state is suppressed. Whether this substantial difference in the phase structure and nature of transitions has consequences for the electro-optical properties of these materials needs to be studied further.

The glass transition temperatures, listed in Table 2, tend to level off as the chain length increases and exhibit n^{-1} dependence of the type: $T_g = 64.0 - 174.7n^{-1}$.

Table 2. Summary of glass transition temperature (T_g), isotropization temperature (T_{iso}), and the enthalpy of isoptropization value (ΔH_{iso}) for the oligofluorenes.

Sample	T_g [K]	T_{iso} [K]	ΔH_{iso} [J g^{-1}]
dimer **5**	252	–	–
trimer **6**	274	–	–
tetramer **13**	295	337	0.50
pentamer **14**	301	399	0.47
hexamer **15**	307	463	0.71
heptamer **17**	315	519	0.74

Therefore, the extrapolated T_g for the polymer is estimated to be approximately 64 °C. The occurrence of this glass transition is difficult, if not impossible, to see in the DSC thermogram for the polymer (see Figure 4). This may be due to the above-mentioned differences of the liquid-crystal phases in the polymer and in the oligomers.

Conclusion

Oligofluorenes up to the heptamer can be synthesized on the hundred-milligram scale by a stepwise route involving Suzuki and Yamamoto coupling reactions. The synthesis of the boronates for the Suzuki coupling is based on the Pd-catalyzed transformation of aryl bromides into boronates, a process that avoids strongly basic aryl lithium intermediates. Therefore, this methodology has potential for the synthesis of oligofluorenes containing a variety of functional groups. The synthesis of mono- or dibrominated fluorenyl oligomers, which are essential for expanding of the chain length, is based on the much higher reactivity of aryl boronates over aryl bromides in the Pd-catalyzed cross-coupling reaction with aryl diazonium salts.

The pure oligomers as solid films do not show the undesired green-band emission characteristics of the polymer. Moreover, they are found to align more readily to form monodomains on various surfaces, as will be published elsewhere. The oligomers from tetramer to heptamer show a liquid-crystal phase with clearly defined isotropization temperatures; this allows extrapolation to the expected isotropization temperature of the polymer at around 475 °C, well above the thermal decomposition temperature. Most importantly, the oligofluorenes do not show the same high-order phase that the polymer exhibits below the melting temperature of approximately 160 °C. However, unlike the polymer, the oligomers do show a glass transition temperature which exhibits n^{-1} dependence and allows extrapolation to a hypothetical glass transition of the polymer at around 64 °C. As this glass transition refers to a freezing of a liquid-crystal phase not seen for the polymer, it is not too surprising that this phenomenon cannot be detected for the polymer.

Experimental Section

General remarks: Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140 °C). Tetrahydrofuran (THF) was distilled from potassium prior to use. Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX 250 or AC 300 spectrometers (250 and 300 MHz for ^{1}H, 62.5 and 75.48 MHz for ^{13}C). Chemical shifts are given in ppm, referenced to residual proton resonances of the solvents. Thin-layer chromatography was performed on aluminium plates precoated with Merck 5735 silica gel 60 F_{254}. Column chromatography was performed with Merck silica gel 60 (230 ± 400 mesh). Field desorption spectra were recorded on a VG ZAB 2-SE FPD machine. Differential scanning calorimetry was measured on a Mettler DSC 30 with a heating or cooling rate of 10 K min^{-1}. Polarization microscopy was performed on a Zeiss Axiophot apparatus with a nitrogen-flushed Linkam THM 600 hot stage. UV/Vis spectra were recorded at room temperature with a Perkin–Elmer Lambda 9 UV/Vis/NIR spectrophotometer. Photoluminescence spectra were obtained on a Spex Fluorolog II (212) apparatus. Optical properties of solid thin films were normally obtained for samples spin-coated on a quartz substrate from dilute chloroform solutions and dried under vacuum. Elemental analysis were performed by the University of Mainz. Melting points were measured with a Reichert hot-stage apparatus and are uncorrected.

2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene (1): 2-Ethylhexylbromide (38.73 g, 185.18 mmol, 35.74 mL) was added to a mixture of 2,7-dibromofluorene (25.0 g, 77.16 mmol) and triethylbenzylammonium chloride (0.878 g, 3.86 mmol, 5 mol %) in DMSO (125 mL) and 50 % aqueous

NaOH (31 mL). The reaction mixture was stirred at room temperature for 5 h. An excess of diethyl ether was added, the organic layer was washed with water, diluted HCl, and brine, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with *n*-hexane as the eluent (R_f = 0.78) and solidified from EtOH at −30 °C to give **1** as a white solid (36.21 g, 85.6 %): M.p. 45–54 °C; ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.57–7.43 (m, 6H), 1.94 (d, J = 5.35 Hz, 4H), 0.89–0.68 (m, 22H), 0.55–0.41 (m, 8H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 152.3, 139.1, 130.1, 127.4, 121.0, 55.3, 44.3, 34.6, 33.6, 28.0, 27.1, 22.7, 14.0, 10.3 ppm; MS (FD): *m/z*: 548.2 [M^+].

2-Bromo-9,9-bis(2-ethylhexyl)fluorene (3): Compound **3** was prepared according to the method used for **1** by using 2-ethylhexylbromide (43.3 g, 224.5 mmol, 39.9 mL), 2-bromofluorene (25.0 g, 102.0 mmol), triethylbenzylammonium chloride (1.16 g, 5.10 mmol, 5 mol %), DMSO (165 mL), and 50 % aqueous NaOH (41 mL). Purification by column chromatography over silica gel with *n*-hexane as the eluent (R_f = 0.72) gave **3** as a colorless liquid (43.14 g, 90.1 %): ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.70–7.26 (m, 7H), 1.97 (m, 4H), 0.90–0.43 (m, 30H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 152.8, 150.0, 140.3, 129.8, 127.3, 126.9, 124.0, 120.9, 120.4, 119.6, 55.1, 44.4, 34.6, 33.6, 28.0, 27.0, 22.7, 14.0, 10.4 ppm; MS (FD): *m/z*: 470.2 [M^+].

2,7-Bis(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2-yl)-9,9-bis(2-ethylhexyl)-fluorene (2): Under an argon atmosphere, **1** (2.43 g, 4.43 mmol), bis(pinacolato)diboron (4.05 g, 15.94 mmol), KOAc (2.60 g, 26.57 mmol), and $Pd(dppf)Cl_2$ (0.226 g, 0.266 mmol) were dissolved in DMF (40 mL) and heated to 60 °C overnight. After the reaction mixture was cooled to room temperature, water and diethyl ether were added. The aqueous phase was extracted with diethyl ether and the combined organic layers were dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with petroleum ether/dichloromethane (3:1) as the eluent (R_f = 0.34) and solidified from EtOH at −30 °C to give **2** as a white solid (2.60 g, 91.5 %): M.p. 85.5–87.6 °C; ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.84–7.69 (m, 6H), 2.00 (d, J = 5.3 Hz, 4H), 1.36 (s, 24H), 0.86–0.50 (m, 22H), 0.48–0.45 (m, 8H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 150.1, 143.9, 133.5, 130.4, 119.2, 83.5, 54.7, 44.0, 34.6, 33.5, 27.8, 27.2, 24.8, 22.7, 14.1, 10.3 ppm; MS (FD): *m/z*: 643.0 [M^+].

2-(4,4,5,5-Tetramethyl[1.3.2]dioxaborolan-2-yl)-9,9-bis(2-ethylhexyl)fluorene (4): Compound **4** was prepared according to the method used for **2** by using **3** (14.07 g, 30.0 mmol), bis(pinacolato)diboron (12.19 g, 48.0 mmol), KOAc (8.82 g, 90.0 mmol), and [$Pd(dppf)Cl_2$] (1.23 g, 1.5 mmol) in DMF (300 mL). Column chromatography over silica gel with petroleum ether/dichloromethane (4:1) as the eluent (R_f = 0.59) afforded **4** as an oily product (14.78 g, 95.5 %): ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.82–7.64 (m, 4H), 7.36–7.21 (m, 3H), 2.0–1.86 (m, 4H), 1.34 (s, 24H), 0.86–0.65 (m, 22H), 0.50–0.43 (m, 8H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 151.0, 149.5, 144.2, 141.1, 133.6, 130.3, 126.6, 124.1, 120.0, 118.8, 83.5, 54.8, 44.5, 44.1, 34.6, 33.5, 28.2, 27.8, 27.3, 26.8, 24.8, 22.7, 14.1, 10.5, 10.1 ppm; MS (FD): *m/z*: 516.7 [M^+].

9,9,9′,9′-Tetrakis(2-ethylhexyl)-2,2′-bifluorene (5): A mixture of **4** (5.17 g, 10.0 mmol) and **3** (4.69 g, 10.0 mmol) in toluene (50 mL) and 2 M aqueous Na_2CO_3 solution (25 mL, 50 mmol) was degassed by pump and freeze cycles (3 ×) and [$Pd(PPh_3)_4$] (0.577 g, 0.5 mmol) was added under argon. The solution was heated to reflux with vigorous stirring for 20 h. After the reaction mixture was cooled to room temperature, diethyl ether and water were added. The organic layer was separated and washed with diluted HCl and brine, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatograpy over silica gel with petroleum ether as the eluent (R_f = 0.47) to give **5** (7.08 g, 90.8 %): ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.73–7.80 (m, 4H), 7.57–7.64 (m, 4H), 7.25–7.44 (m, 6H), 2.04–2.14 (m, 8H), 0.49–0.88 (m, 60H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$):δ = 150.9, 150.6, 141.1, 140.4, 126.8, 126.3, 126.0, 124.1, 122.9, 119.6, 54.9, 44.5, 34.6, 33.8, 28.2, 26.9, 22.7, 14.0, 10.3 ppm; MS (FD): *m/z*: 779.4 [M^+]; elemental analysis: calcd for $C_{58}H_{82}$ (779.2): C 89.39, H 10.61; found: C 89.29, H 10.79.

9,9,9′,9′,9″,9″-Hexakis(2-ethylhexyl)-2,2′-7′,2″-terfluorene (6): Compound **6** was prepared according to the method used for **5** by using **2** (2.0 g, 3.12 mmol), **3** (4.40 g, 9.36 mmol), and [$Pd(PPh_3)_4$] (0.36 g, 0.31 mmol) in toluene (30 mL) and 2 M Na_2CO_3 aqueous solution (15.6 mL, 31.2 mmol) for 27 h. After cooling to room temperature, the mixture was diluted with ethyl acetate and the organic layer was washed with diluted HCl and brine, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with petroleum ether as the eluent (R_f = 0.22) to give **6** as a colorless viscous gum (2.32 g, 63.8 %): ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.83–7.73 (m, 6H), 7.61–7.66 (m, 8H), 7.44–7.25 (m, 6H), 2.13–2.05 (m, 12H), 0.90–0.49 (m, 90H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 151.2, 150.9, 150.6, 141.1, 140.4, 140.1, 126.8, 126.3, 126.0, 124.1, 122.9, 119.7, 119.6, 54.9, 44.6, 34.6, 33.8, 28.2, 27.1, 22.8, 14.0, 10.3 ppm; MS (FD): *m/z*: 1168.2 [M^+]; elemental analysis: calcd for $C_{87}H_{122}$ (1167.9): C 89.47, H 10.53; found: C 89.26, H 10.42.

2-Amino-7-bromo-9,9-bis(2-ethylhexyl)fluorene (7): Compound **7** was prepared according to the method used for **1** by using 2-ethylhexylbromide (7.78 g, 40.3 mmol, 7.2 mL), 2-amino-7-bromofluorene (5.0 g, 19.2 mmol), triethylbenzylammonium chloride (220 mg, 1 mmol, 5 mol %), DMSO (50 mL), and 50 % aqueous NaOH (3.8 mL). The reaction mixture was stirred for 2 h. Purification by column chromatography over silica gel with *n*-hexane/dichloromethane (6.5:3.5) as the eluent (R_f = 0.47, 0.44, and 0.38; the title product separated into three spots, due to the diaseteroisomers) gave **7** as a slightly yellow oily product (7.65 g, 82 %): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.46–7.37 (m, 4H), 6.70–6.63 (m, 2H), 3.81 (brs, 2H), 1.84–1.90 (m, 4H), 0.92–0.73 (m, 22H), 0.57–0.52 (m, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.5–152.4 (three peaks, 2 × C), 146.9–146.8 (three peaks), 141.4, 131.5–131.4 (three peaks), 129.8, 127.4–127.3 (three peaks), 120.9, 119.9, 118.7–118.5 (three peaks), 114.2, 110.9–110.8 (three peaks), 55.2, 44.9–44.8 (four peaks), 35.0, 33.9–33.7 (four peaks), 28.5–28.3 (four peaks), 23.2, 14.3, 10.6–10.4 (four peaks) ppm; MS (FD): *m/z*: 484.0 [M^+].

2-Bromo-9,9-bis(2-ethylhexyl)fluorenyl-7-diazonium tetrafluoroborate (8): A solution of **7** (3.48 g, 7.18 mmol) in CH_2Cl_2 (10 mL) was slowly added to $BF_3{\cdot}OEt_2$ (11.46 mmol, 1.42 mL) with stirring under an argon athmosphere at −10 °C. After 10 min, a solution of butyl nitrite (1.18 mL, 10.01 mmol) in CH_2Cl_2 (4 mL) was slowly added and the mixture stirred for additional 30 min at 0 °C. *n*-Pentane (200 mL) was added and the mixture was stored at −20 °C overnight. The precipitate was filtered off, washed with cold diethyl ether and dried in air to give **8** as a pale yellow solid (3.39 g, 81 %): ^{1}H NMR (300 MHz, [D_6]acetone): δ = 9.08 (m, 1H), 8.87 (m, 1H), 8.53 (m, 1H), 8.16 (m, 1H), 8.06 (s, 1H), 7.77 (m, 1H), 2.30–2.20 (m, 4H), 0.88–0.45 (m, 1H) ppm; ^{13}C NMR (75 MHz, acetone-d_6): δ = 156.6, 154.2–153.9 (three peaks), 153.8, 137.9–137.8 (three peaks), 134.6, 132.6–132.5 (three peaks), 129.5–129.4 (three peaks), 129.0–128.8 (three peaks), 126.7, 125.8, 123.7–123.6 (three peaks), 111.9–111.6 (three peaks), 57.6–57.5 (three peaks), 44.5–44.3 (four peaks), 35.9–35.8 (two peaks), 34.7–33.9 (three peaks), 28.9–28.5 (three peaks), 28.0, 23.4–23.3 (two peaks), 14.3–14.2 (two peaks), 10.7–10.3 (three peaks) ppm; decomposition temperature: 98 °C.

7-Bromo-9,9,9′,9′-tetrakis(2-ethylhexyl)-2,2′-bifluorene (9): A mixture of **4** (0.90 g, 1.74 mmol), **8** (1.12 g, 1.92 mmol), and $Pd(OAc)_2$ (40 mg, 0.178 mmol) in ethanol (30 mL) was heated to 60 °C for 1 h (no additional base was added). After cooling to room temperature, the mixture was diluted with diethyl ether and the organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with petroleum ether as the eluent (R_f = 0.49) to give **9** as an oily product (1.04 g, 70 %): ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.80–7.26 (m, 13H), 2.14–2.04 (m, 8H), 0.88–0.52 (m, 60H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 153.0, 151.0, 150.6, 141.0, 140.5, 140.1, 139.2, 129.9, 127.4, 126.8, 126.4, 126.0, 124.1, 122.9, 120.9, 120.3, 119.6, 54.9, 44.5, 34.6, 33.8, 28.2, 27.1, 22.7, 14.0, 10.3 ppm; MS (FD): *m/z*: 857.6 [M^+].

2-[9,9,9′,9′-Tetrakis(2-ethylhexyl)-7,2′-bifluoren-2-yl]-4,4,5,5-tetramethyl[1.3.2]dioxaborolan (10): Compound **10** was prepared according to the method used for **2** by using **9** (970 mg, 1.1 mmol), bis(pinacolato)diboron (450 mg, 1.8 mmol), KOAc (326 mg, 3.3 mmol), and [$Pd(dppf)Cl_2$] (45 mg, 0.055 mmol) in DMF (10 mL). Column chromatography over silica gel with *n*-hexane/CH_2Cl_2 (9:1) as the eluent (R_f = 0.12) gave **10** as an oily product (570 mg, 55.7 %): ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.86–7.73 (m, 6H), 7.65–7.60 (m, 4H), 7.41 (m, 1H), 7.36–7.27 (m, 2H), 2.09–2.04 (m, 8H), 1.35 (s, 12H), 0.88–0.49 (m, 90H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 152.8, 151.6, 151.3, 150.5–150.3, 144.6, 141.7, 141.1–140.6, 134.1, 131.1–130.9, 127.4, 127.0, 126.6–126.5, 124.8, 123.6–123.4, 120.8, 120.3–120.2, 119.4, 84.2, 55.6–55.5, 45.1–44.5, 35.4–35.3, 34.4–34.3, 28.8–28.5, 27.9–27.5, 25.3, 23.3, 14.5–14.4, 10.9–10.6 ppm; MS (FD): *m*/*z*: 904.2 [M^+].

7-Bromo-9,9,9′,9′,9″,9″-hexakis(2-ethylhexyl)-2,2′-7′,2″-terfluorene (11): Method A: Compound **11** was prepared according to the method used for **9** by using **10** (160 mg, 0.18 mmol), **8** (155 mg, 0.26 mmol), and $Pd(OAc)_2$ (4 mg, 0.018 mmol) in ethanol (10 mL). Column chromatography over silica gel with *n*-hexane as the eluent ($R_f=0.16$) gave **11** as a slightly yellow oily product (106 mg, 48 %): ^1H NMR (250 MHz, CD_2Cl_2): $\delta=7.84$–7.73 (m, 5 H), 7.64–7.57 (m, 10 H), 7.50–7.26 (m, 4 H), 2.12–2.05 (m, 12 H), 0.90–0.53 (br m, 90 H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta=153.0$, 151.2, 150.9, 150.6, 141.1, 140.8, 140.3, 140.1, 139.2, 129.9, 127.4, 126.8, 126.4, 126.1, 124.0, 123.0, 120.9, 120.3, 119.8, 55.0, 44.5, 34.7, 33.8, 28.2, 27.1, 22.7, 14.0, 10.3 ppm; MS (FD): *m*/*z*: 1248.4 [M^+].

Method B: Compound **11** was also prepared according to the method used for **5** by using **12** (4.9 g, 5.24 mmol), **4** (1.69 g, 3.27 mmol), and [$Pd(PPh_3)_4$] (0.189 g, 0.15 mmol) in toluene (16 mL) and 2 M aqueous Na_2CO_3 (15 mmol, 8.2 mL). The reaction took 16 h. After cooling to room temperature, the mixture was diluted with diethyl ether (200 mL) and the organic layer was washed with diluted HCl, brine, and water, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with hexane/dichloromethane (10:0.5) as the eluent ($R_f=0.42$) to give **11** (1.83 g, 45.0 %).

7,7′-Dibromo-9,9,9′,9′-tetrakis(2-ethylhexyl)-2,2′-bifluorene (12): Br_2 (3.15 g, 19.71 mmol) in CH_2Cl_2 (5 mL) was added to a solution of **5** (7.67 g, 9.85 mmol) in CH_2Cl_2 (20 mL) at room temperature. The solution was heated to reflux for 1.5 h. After the reaction mixture was cooled to room temperature, water and diethyl ether were added. The organic layer was washed with $Na_2S_2O_3$ solution, brine, and water, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was recrystallized from ethanol to give **12** as a white solid (8.24 g, 89.5 %): M.p. 71.5–72.8 °C; ^1H NMR (250 MHz, CD_2Cl_2): $\delta=7.78$–7.46 (m, 12 H), 2.08–2.03 (m, 8 H), 0.88–0.55 (m, 60 H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta=153.0$, 150.6, 140.6, 140.0, 139.4, 130.0, 127.4, 126.2, 123.0, 121.0, 120.4, 119.9, 55.2, 44.5, 34.7, 33.7, 28.1, 27.1, 22.7, 14.0, 10.3 ppm; MS (FD): *m*/*z*: 939.2 [M^+].

9,9,9′,9′,9″,9″,9‴,9‴-Octakis(2-ethylhexyl)-2,2′-7′,2″-7″,2‴-tetrafluorene (13): A schlenk tube was charged with $Ni(COD)_2$ (101.2 mg, 0.55 mmol), 2,2′-bipyridine (57.5 mg, 0.55 mmol), 1,5-COD (39.8 mg, 0.55 mmol), and DMF (3.0 mL) in a glove box. The mixture was stirred at 80 °C for 0.5 h and then **9** (0.32 g, 0.37 mmol) in toluene (11 mL) was added to the blue solution and stirred at 80 °C for 8 h. After cooling to room temperature, the mixture was diluted with diethyl ether. The organic layer was washed with diluted HCl, brine, and water, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with petroleum ether/dichloromethane (20:1) as the eluent ($R_f=0.61$) to afford **13** as a white waxy solid (151 mg, 52.6 %): ^1H NMR (250 MHz, CD_2Cl_2): $\delta=7.85$–7.75 (m, 8 H), 7.67–7.63 (m, 12 H), 7.45–7.26 (m, 6 H), 2.14–2.06 (m, 16 H), 0.90–0.50 (m, 120 H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta=151.2$, 150.9, 150.6, 141.1, 140.36, 140.1, 126.8, 126.4, 126.1, 124.1, 122.9, 119.7, 54.9, 44.4, 34.7, 34.0, 28.2, 27.1, 22.8, 14.0, 10.3 ppm; MS (FD): *m*/*z*: 1556.4 [M^+], 778.2 [M^{2+}]; elemental analysis: calcd for $C_{116}H_{162}$ (1556.5): C 89.51, H 10.49; found: C 89.22, H 10.35.

9,9,9′,9′,9″,9″,9‴,9‴,9⁗,9⁗-Decakis(2-ethylhexyl)-2,2′-7′,2″-7″,2‴-7‴,2⁗-pentafluorene (14): Compound **14** was prepared according to the method used for **5** by using **2** (124.5 mg, 0.194 mmol), **9** (664.7 mg, 0.776 mmol), and $Pd(PPh_3)_4$ (22.4 mg, 0.0194 mmol) in toluene (4 mL) and 1 M aqueous Na_2CO_3 (2.0 mL, 2.0 mmol). The reaction took 16 h. After cooling to room temperature, the mixture was diluted with diethyl ether and the organic layer was washed with diluted HCl and brine, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with petroleum ether/dichloromethane (10:0.8) as the eluent ($R_f=0.31$) to afford **14** as a white waxy solid (176.5 mg, 46.8 %): ^1H NMR (250 MHz, CD_2Cl_2):$\delta=7.85$–7.74 (m, 10 H), 7.67 (br m, 16 H), 7.45–7.26 (m, 6 H), 2.14–2.06 (m, 20 H), 0.92–0.50 (m, 150 H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta=151.2$, 150.9, 150.6, 141.1, 140.3, 140.1, 126.8, 126.3, 126.1, 124.1, 123.0, 119.8, 55.1, 44.5, 34.7, 34.0, 28.3, 27.1, 22.7, 14.0, 10.3 ppm; MS (FD): *m*/*z*: 1946.2 [M^+], 973.3 [M^{2+}]; elemental analysis: calcd for $C_{145}H_{202}$ (1945.1): C 89.53, H 10.47; found: C 89.41, H 10.35.

9,9,9′,9′,9″,9″,9‴,9‴,9⁗,9⁗,9⁗′,9⁗′-Dodecakis(2-ethylhexyl)-2,2′-7′,2″-7″,2‴-7‴,2⁗-7⁗,2⁗′-hexafluorene (15): Compound **15** was prepared according to the method used for **13** by using **11** (370.0 mg, 0.300 mmol) in toluene (10.0 mL) and $Ni(COD)_2$ (82.5 mg, 0.45 mmol), 2,2′-bipyridine (46.8 mg, 0.45 mmol), 1,5-COD (32.4 mg, 0.45 mmol), and DMF (2.5 mL). After cooling to room temperature, the mixture was diluted with diethyl ether and the organic layer was washed with diluted HCl and brine, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with hexane/dichloromethane (10/0.8) as the eluent ($R_f=0.24$) to afford **15** as a white solid (183.0 mg, 52.4 %): ^1H NMR (250 MHz, CD_2Cl_2): $\delta=7.86$–7.68 (m, 32 H), 7.45–7.26 (m, 6 H), 2.14–2.06 (m, 24 H), 0.90–0.50 (m, 180 H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta=151.2$, 150.9, 150.6, 141.1, 140.4, 140.2, 126.8, 126.3, 126.2, 124.1, 122.9, 119.8, 55.1, 44.6, 34.7, 34.0, 28.3, 27.1, 22.8, 14.0, 10.3 ppm; MS (FD): *m*/*z*: 2335.9 [M^+], 1166.9 [M^{2+}], 777.5 [M^{3+}]; elemental analysis: calcd for $C_{174}H_{242}$ (2333.8): C 89.55, H 10.45; found: C 89.32, H 10.36.

7,7″-Dibromo-9,9,9′,9′,9″,9″-hexakis(2-ethylhexyl)-2,2′-7′,2″-terfluorene (16): Compound **16** was prepared according to the method used for **9** by using **2** (0.80 g, 1.25 mmol), **8** (1.82 g, 3.13 mmol), and $Pd(OAc)_2$ (56 mg, 0.25 mmol) in ethanol (40 mL) at 60 °C for 2 h (no additional base was added). After cooling to room temperature, the mixture was diluted with diethyl ether and the organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with *n*-hexane as the eluent ($R_f=0.16$) to give **16** as an oily product (0.90 g, 54.4 %): ^1H NMR (300 MHz, CD_2Cl_2): $\delta=7.84$–7.76 (m, 4 H), 7.64–7.51 (m, 12 H), 7.48 (m, 2 H), 2.12–2.05 (m, 12 H), 0.90–0.54 (m, 90 H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=154.9$, 153.1, 152.5, 142.4–141.7, 141.1, 131.6, 129.3–129.1, 128.2–127.9, 124.7–124.5, 122.8, 122.3–122.1, 121.7, 57.1–56.9, 46.2–25.9, 36.5–36.4, 35.8–25.3, 30.0–29.7, 28.9, 24.6, 15.7–15.6, 12.0–11.9 ppm; MS (FD): *m*/*z*: 1324.2 [M^+].

9,9,9′,9′,9″,9″,9‴,9‴,9⁗,9⁗,9⁗′,9⁗′,9⁗″,9⁗″-Tetradecakis(2-ethylhexyl)-2,2′-7′,2″-7″,2‴-7‴,2⁗-7⁗,2⁗′-7⁗′,2⁗″-heptafluorene (17): Compound **17** was prepared according to the method used for **5** by using **16** (369.0 mg, 0.278 mmol), **10** (756.0 mg, 0.835 mmol), and [$Pd(PPh_3)_4$] (10 mg, 0.0087 mmol) in toluene (10 mL) and 2 M aqueous Na_2CO_3 (5.0 mL, 10.0 mmol). The reaction took 24 h. After cooling to room temperature, the mixture was diluted with diethyl ether and the organic layer was washed with diluted HCl and brine, then dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography over silica gel with *n*-hexane/CH_2Cl_2 (95:5) as the eluent ($R_f=0.1$) to afford **17** as a pale yellow solid (287.0 mg, 38.0 %): ^1H NMR (250 MHz, CD_2Cl_2): $\delta=7.86$–7.69 (m, 38 H), 7.45–7.26 (m, 6 H), 2.15–2.06 (m, 28 H), 0.92–0.50 (m, 210 H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta=151.2$, 150.9, 150.6, 141.1, 140.4, 140.2, 126.8, 126.1, 124.1, 123.0, 119.8, 119.6, 55.1, 44.5, 34.7, 34.1, 28.3, 27.1, 22.8, 14.0, 10.4 ppm; MS (FD): *m*/*z*: 2724 [M^+], 1362 [M^{2+}], 907 [M^{3+}]; elemental analysis: calcd for $C_{203}H_{282}$ (2722.4): C 89.56, H 10.44; found: C 89.43, H 10.38.

Synthesis of poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl): The polymer was prepared according to the well-known Yamamoto polycondensation[18] by using $Ni(COD)_2$ (1.1 g, 4 mmol), 2,2′-bipyridine (623 mg, 4 mmol), and 1,5-COD (441 mg, 4 mmol) as the coupling agents for dihaloaromatic compound **1** (953 mg, 1.74 mmol). The polymer was precipitated by adding the reaction mixture into a mixture of methanol/acetone/HCl (concentrated). The isolated polymer was dissolved in chloroform and reprecipitated in methanol. This procedure was repeated twice to give the polymer (480 mg, 75 %): GPC (polystyrene internal standard, THF): M_n 42 000, M_w 84 000.

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