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Esther Scheler[a]; Peter Strohriegl[a]
[a] Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany

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Synthesis of oligofluorenes by endcapping

ESTHER SCHELER and PETER STROHRIEGL*
Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany

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An efficient one-step synthesis of 9,9-di(2-ethylhexyl)-2,7-fluorene oligomers via an endcapping reaction is reported. Controlled endcapping demands a full conversion of functional groups and thus the Yamamoto reaction was chosen as the aryl–aryl coupling method. SEC analysis showed that the endcapping is complete. The molecular weights were adjusted in the range from 1300 to 3800 g mol^{-1} by different amounts of endcapper. The mixtures exhibit broad mesophases and the transition temperatures strongly increase with molecular weight. In the series of oligomers reported here, clearing temperatures between 57°C and over 360°C could be realized.

1. Introduction

Among conjugated polymers known today, poly(9,9-dialkylfluorenes) have achieved much attention as efficient blue light-emitting materials [1, 2]. Besides the strong blue emission, polyfluorenes exhibit a thermotropic liquid crystalline (LC) phase which allows a facile orientation of the polymer into large monodomains [3]. Such a parallel orientation of the polyfluorene chains directly leads to the emission of polarized light in organic light-emitting diodes (OLEDs) [4, 5, 6]. In addition to polyfluorene homopolymers, the orientation of polyfluorene copolymers like poly(9,9-dioctylfluorene-*alt*-bithiophene) (F8T2) has been carefully investigated and used to increase the carrier mobility in organic field-effect transistors (OFETs) [7].

One major problem concerning the orientation of polyfluorenes is the high temperature necessary for the orientation in the LC phase. Poly[9,9-di(2-ethylhexyl)-fluorene] (PF2/6) exhibits a nematic phase only at temperatures above 169°C. The clearing temperature (T_c) can not be detected due to the decomposition of the material [2]. Thus, orientation experiments at such high temperatures have to be carried out under carefully controlled inert conditions since the polyfluorenes are sensitive towards oxidation to the corresponding 9-fluorenones, which leads to an undesirable green shift of the fluorescence [2, 8, 9, 10]. It was proven by several experiments that this green shift results from intra- or intermolecular energy transfers from the fluorene to the fluorenone moieties [11].

In addition to high molecular weight polyfluorenes, low molecular mass fluorene model compounds with up to 12 fluorene units have been described [12, 13, 14]. In a series of fluorene model compounds with 2-ethylhexyl substituents the glass transition temperatures (T_g) rise from 22°C for the tetramer to 42°C for the heptamer [15]. Above T_g, a nematic phase is observed for all model compounds from the tetramer onwards. The clearing temperatures rise from 64°C for the tetramer to 246°C for the heptamer. Cyclic voltammetry was used to investigate the electrochemical properties of this homologous series and it was demonstrated that an increasing number of fluorene units leads to an increase of reversibly accessible oxidation states [16]. Furthermore the optical properties of the model compounds were studied in detail and extrapolated to an ideal polymer chain [17, 18]. A lot of insight into the physical properties of fluorene polymers comes from the investigation of a homologous series of model compounds and it could be shown that the nematic phase of the tetramer, pentamer and hexamer are below 200°C and allow a facile orientation in the LC phase without the risk of oxidation reactions. Nevertheless the synthesis of these monodisperse compounds is a time consuming procedure, which comprises a large number of synthetic steps [15].

For the limitation of the molecular weight of a growing polymer chain, endcapping with a monofunctional monomer is a well known method. As a consequence, well defined end groups can be introduced and the number of ill defined groups at the chain end (e.g. bromine) can be reduced drastically.

PF2/6 endcapped with triphenylamine moieties has already been described in the literature [19]. The

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*Corresponding author. Email: peter.strohriegl@uni-bayreuth.de

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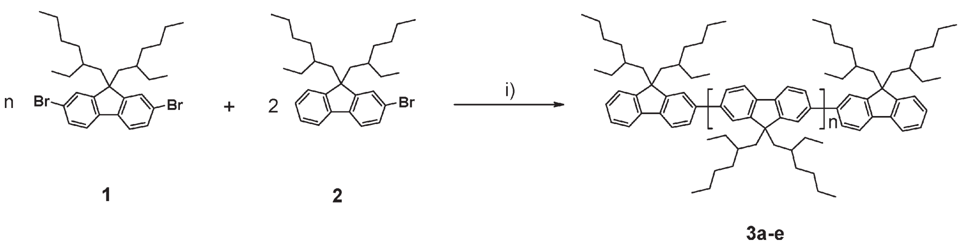

Scheme 1. Synthesis of oligo[9,9-di(2-ethylhexyl)fluorene-2,7-diyl] via endcapping reaction; (i) dry DMF/dry toluene/2,2′-bipyridyl/COD/Ni(COD)$_2$.

molecular weight of PF2/6 varied from 122 000 g mol^{-1} to 12 000 g mol^{-1} by increasing the amount of triphenylamine endcapper. The LC phases of the polyfluorene are not altered by the endcapper in this molecular weight range [19].

Another study dealt with the influence of the molecular weight of PF2/6 on its thermotropic alignment [20, 21]. Low molecular weight materials with M_n<10 000g mol^{-1} were found to exhibit only a nematic mesophase, whereas high molecular weight compounds (M_n>10 000 g mol^{-1}) showed nematic as well as hexagonal phases. These two LC phases were investigated by X-ray scattering and the orientation of the different PF2/6s on polyimide was described in detail.

In this paper we describe the synthesis and characterization of polydisperse oligo[9,9-di(2-ethylhexyl)fluorene-2,7-diyl]s in the low molecular weight range between 1300 and 3800 g mol^{-1}. The Yamamoto reaction was chosen as the aryl–aryl coupling method. By this simple synthetic strategy large amounts of well-defined oligomers can be made in a single step. The resulting oligomers exhibit nematic phases at moderate temperature, which allows a controlled alignment without decomposition processes taking place. Both T_g and T_c were determined and compared with monodisperse model compounds from the literature [15].

2. Results and discussion

2.1. *Synthesis*

The polydisperse oligofluorenes **3a–3e** were obtained via the one-step reaction shown in scheme 1. The monomers **1** and **2** were synthesized by alkylation of 2,7-dibromofluorene and 2-bromofluorene, respectively, as described in the literature [22]. The Yamamoto reaction of the bifunctional monomer **1** and the monofunctional endcapper **2** leads to the oligomeric mixtures **3a–3e** with different molecular weights. The coupling was performed using Ni(COD)$_2$ and 2,2′-bipyridyl in a mixture of dry DMF and dry toluene [23]. The chemical structure was validated by ^{1}H NMR and ^{13}C NMR spectroscopy.

The molecular weights of the fluorene oligomers **3a–3e** were determined by SEC and are shown in table 1.

The number average molecular weight of the oligomers decreases from 3800 g mol^{-1} to 1300 g mol^{-1} with increasing amounts of endcapper. The molecular weight distributions of **3a–3e** are shown in figure 1; for a simplified assignment, the SEC scan of an independently synthesized trimer (n=1) is also shown. The peak next to the trimer at M_n=780 g mol^{-1} can be assigned to the dimer (n=0), the signal at 1500 g mol^{-1} corresponds to the tetramer (n=2) and higher molecular weight

Table 1. Molecular weights and degrees of polymerization of **3a–3e**.

Sample	Ratio **1/2**	M_n (SEC)^a /g mol^{-1}	M_w (SEC)^a /g mol^{-1}	P_n (SEC)
3a	5:1	3800	4900	9.7
3b	2:1	2500	3100	6.4
3c	3:2	2000	2450	5.0
3d	1:1	1500	2000	4.0
3e	1:2	1300	1500	3.3

^{a}Oligofluorene calibration (for explanation see text).

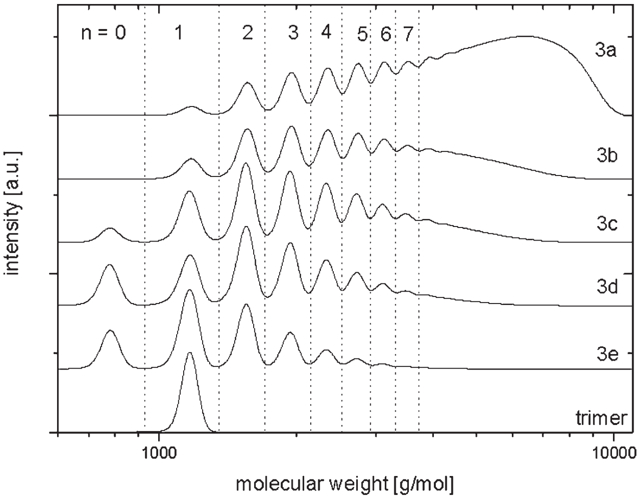

Figure 1. SEC scans of the oligomers **3a–3e** (oligofluorene calibration) and an independently synthesised trimer; n refers to scheme 1.

oligomers can be assigned up to the nonamer (n=7). With an increasing amount of bifunctional monomer **1** the intensity of high molecular weight part increases and in mixture **3a** the polymeric part becomes dominant. Each SEC scan shows only one homologous series of oligomers, which indicates that no side products were formed in the Yamamoto coupling.

For the molecular weight calibration the SEC scans depicted in figure 1 have been used. From MALDI-TOF measurements we know that the peaks assigned in figure 1 are the oligomers in which both sides are endcapped. Since the exact molecular weights of these oligomers are known, we set up a calibration curve for the oligofluorenes (figure 2). From this plot it becomes evident that for molecular weights between 700 and 2000 $\mathrm{g\,mol^{-1}}$ the results from PS (polystyrene) and oligofluorene calibration are similar. For molecular weights above 2000 $\mathrm{g\,mol^{-1}}$ the real molecular weights are lower than calculated from polystyrene calibration. For the highest molecular weight oligomer **3a** with M_n=3800 $\mathrm{g\,mol^{-1}}$ the polystyrene calibration would give an overestimation of 1200 $\mathrm{g\,mol^{-1}}$ compared to the oligofluorene calibration. This is in accordance with literature results [2]. They showed in a combined SEC/LS (light scattering) experiment that in the case of high molecular weight polyfluorene the molecular weights are overestimated by a factor of 2.7 if a polystyrene calibration is used [24]. This is explained by the semi-rigid character of the polyfluorene backbone. In the low molecular weight region below 2000 $\mathrm{g\,mol^{-1}}$ the polystyrene chain cannot be described as random coil which explains that the molecular weights determined by oligofluorene and polystyrene calibration are similar.

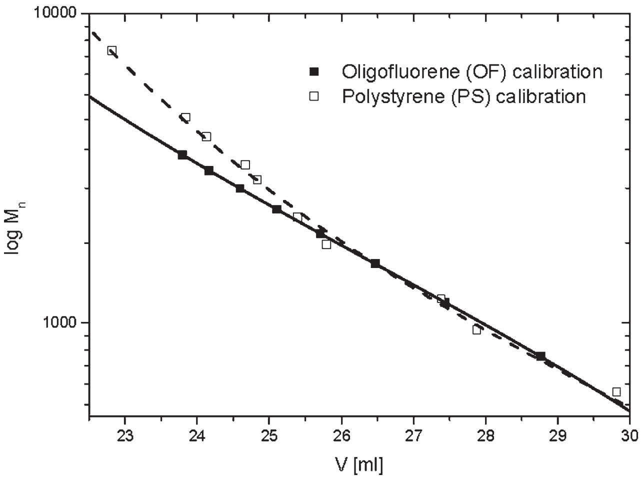

Figure 2. Oligofluorene and polystyrene calibration curves; the lines correspond to the 3$^\mathrm{rd}$ order polynomial fits of the experimental data points.

2.2. *Optical properties*

Figure 3 shows the UV–vis spectra of the fluorene oligomers. The data are given in table 2. With an increasing molecular weight, the absorption maximum λ_max shifts to higher wavelengths from **3e** to **3a**. For comparison the absorption spectrum of high molecular weight poly[9,9-di(2-ethylhexyl)-2,7-fluorene-diyl] is also shown in figure 3.

From the absorption edge, the optical band gap can be calculated (table 2). The absorption edges increase with increasing molecular weight from 406 to 421 nm. This corresponds to a decrease of the optical band gap from 3.05 eV for **3e** with a molecular weight of 1300 $\mathrm{g\,mol^{-1}}$ to 2.94 eV for polyfluorene.

Figure 4 shows a typical emission spectrum and reveals the strong blue fluorescence. The most intense transition at 414 nm is assigned to the $S_{1,0}$–$S_{0,0}$ transition and further well resolved vibronic progressions are the $S_{1,0}$–$S_{0,1}$ (437 nm) and $S_{1,0}$–$S_{0,2}$ (463 nm) transitions. The energy differences between the peaks at 414 and 437 nm is 1272 $\mathrm{cm^{-1}}$ and between 437 and

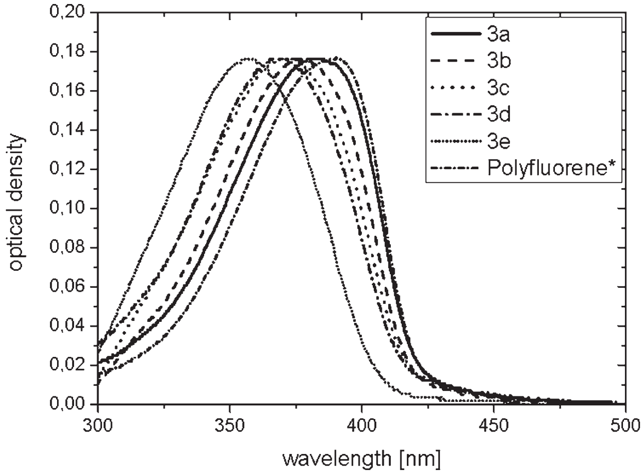

Figure 3. Normalized UV–vis spectra of thin films of **3a–3e** and poly[9,9-di(2-ethylhexyl)-2,7-fluorene-diyl] *M_n=20 000, M_w=48 000, synthesised via Yamamoto coupling.

Table 2. Absorption maxima, band edges and optical band gaps, ΔE, of **3a–3e**.

Sample	λ_max/nm	λ_AE/nm	ΔE/eV
3e	357	406	3.05
3d	368	416	2.98
3c	372	418	2.97
3b	377	418	2.97
3a	382	420	2.95
polyfluorene[a]	389	421	2.94

[a] M_n=20 000 $\mathrm{g\,mol^{-1}}$, M_w=48 000 $\mathrm{g\,mol^{-1}}$.

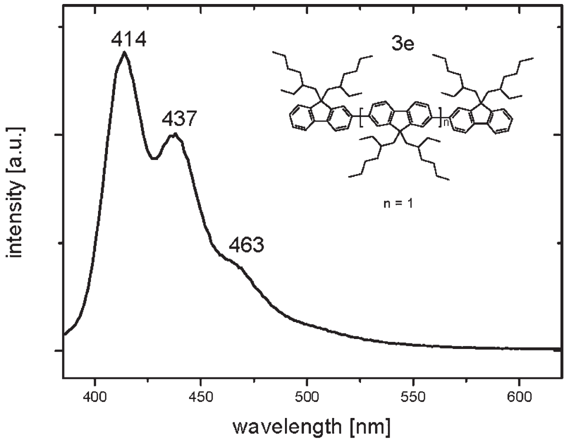

Figure 4. Fluorescence spectrum of a 20 nm thick film of **3e**.

463 nm is 1285 cm^{-1} and correspond to signals in the IR spectrum.

2.3. *Thermal properties*

The glass transition temperatures were obtained by differential scanning calorimetry (DSC) and rise from 2°C for **3e** up to 34°C for **3b** (see table 3). The glass transition of **3a** as well as the clearing temperatures of **3a–3e** could not be detected by the DSC instrument and were therefore determined with polarization microscopy. All mixtures except **3e** exhibit nematic mesophases and the typical Schlieren textures were observed (figure 5). From the SEC scans in figure 1 it is clear that **3e** mainly consists of the trimer and it is known that fluorene trimers do not exhibit LC phases [15]. However it has been shown that a reduction of the length of the alkyl chain in the 9-position of the fluorene from C_8 to C_1 and the introduction of *n*-octyl or *n*-hexadecyl lateral side groups leads to the formation of smectic phases [25].

The lowest clearing temperature of 57°C was observed for **3d** and the highest clearing point of 250°C for **3b**. The mixture **3a** with the highest molecular weight of 3800 gmol^{-1} exhibits a nematic phase up to decomposition at 360°C. Thus, we were able to show that by varying the amount of endcapper the nematic mesophase of the fluorene oligomers **3a–3e** can be shifted in a broad temperature range.

Figure 6 shows a plot of glass transition (T_g) and isotropic–nematic transition (T_{in}) temperatures versus $1/P_n$ for **3b–3e**. Both transition temperatures follow an almost linear dependence. The transition temperatures of monodisperse fluorene model compounds [15] are

Table 3. Glass transition temperatures and isotropic–nematic transition temperatures of **3a–3e**.

Sample	T_g/°C ^{a}	T_{in}/°C ^{b}
3a	n.d.	>360
3b	34	250
3c	22	150
3d	16	57
3e	2.0	n.d.

[a]Determined by DSC, heating rate 20 K min^{-1}. [b]Determined by polarization microscopy upon cooling with a rate of 0.1°C min^{-1}.

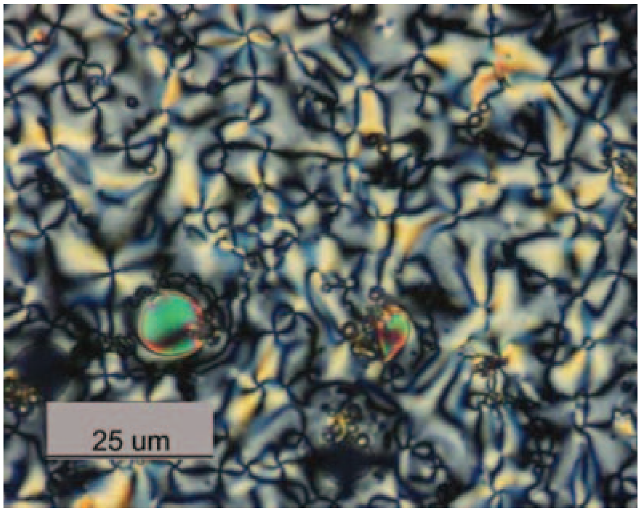

Figure 5. Nematic Schlieren texture of **3c** observed upon cooling at 0.1°C min^{-1} between crossed polarizers; picture taken at 140°C.

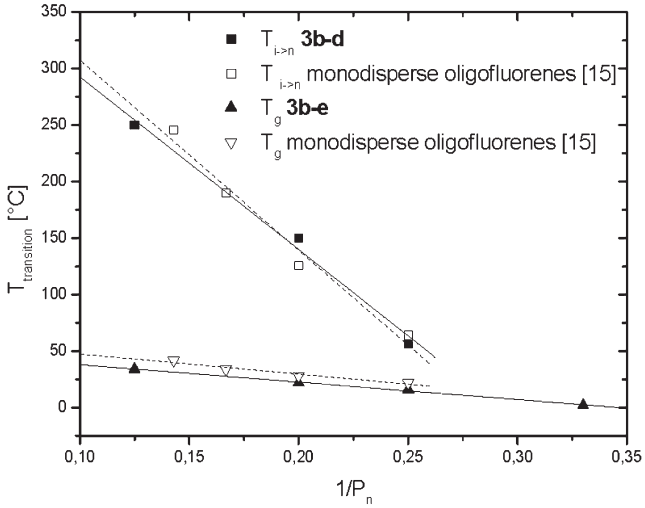

Figure 6. Glass transition temperature T_g and clearing temperature T_c versus reciprocal degree of polymerization for **3b–3e**. The transition temperatures of monodisperse oligomers [15] are also shown. The full and dotted lines represent the linear regressions, the full lines refer to the data points of **3b–3e** and dotted lines refer to the monodisperse fluorene model compounds.

also displayed (open signs) and a good agreement between monodisperse and polydisperse oligomers can be observed. The glass transition temperatures of the monodisperse samples are slightly higher than those for the polydisperse ones. The linear regression provides a T_g for the ideal polymer (with $P_n \rightarrow \infty$) of 53°C for the polydisperse fluorenes and 65°C for the monodisperse ones. The linear regression of the clearing temperatures leads to a value of >440°C for high molecular weight polyfluorene. In practice this value cannot be achieved due to decomposition starting at 360°C.

3. Conclusion

We have developed an efficient one-step synthesis of polydisperse fluorene oligomers **3a–3e**. SEC analysis showed that the endcapping process is efficient and the molecular weights could be adjusted in the range from 1300 g mol^{-1} to 3800 g mol^{-1} by varying the amount of monofunctional endcapper.

The thermal behaviour was determined using DSC and polarization microscopy. The glass transition temperatures vary between 2°C for the lowest molecular weight mixture and 34°C. Samples **3a–3d** exhibit liquid crystalline phases and their clearing temperatures rise from 57°C to more than 360°C. The comparison of the thermal behaviour of the polydisperse oligomers **3a–3e** with the monodisperse counterparts reported in reference [15] showed a good conformance. Thus, the simple and efficient one-step synthesis using a monofunctional endcapper enables us to tailor both the glass transition and the clearing temperature of oligofluorenes. In a forthcoming paper we will report the synthesis of analogous oligofluorenes with acrylate end groups and the formation of micron-sized patterns by photopolymerization.

4. Experimental

4.1. *General*

^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer in $CDCl_3$ at 250 MHz with tetramethylsilane as reference. The molecular weights were determined by a Waters size exclusion chromatography (SEC) system for oligomers (analytical columns: cross-linked polystyrene gel, length 2 × 60 cm, width 0.8 cm, particle size 5 μm, pore size 100 Å, eluent THF (0.5 ml min^{-1}, 80 bar), oligofluorene calibration). UV–vis absorption spectra were recorded on a HITACHI U-3000 spectrophotometer and the fluorescence spectra on a SHIMADZU RF-5301 PC spectrofluorometer with 90° detection. Absorption and emission spectra were obtained at ambient temperature from thin films spin coated (1500 rpm, 0.5 wt %) from xylene solutions on cleaned glass substrates. The liquid crystalline behaviour was examined by a polarization microscope Nikon Diaphot 300 with a Mettler FP 90 hot stage from films that were obtained by drop casting from CH_2Cl_2 solutions. For differential scanning calorimetry measurements (DSC) a Perkin-Elmer DSC-7 apparatus was used.

Absolute toluene and DMF were used as purchased from FLUKA. The catalyst $Ni(COD)_2$ was used as purchased from ABCR. 1,5-Cyclooctadiene and 2,2′-bipyridyl were used as received from Aldrich.

The synthesis of the monomers **1** and **2** (see scheme 1) has been reported elsewhere [22].

4.2. *Synthesis of the oligo[9,9-di(2-ethylhexyl)-2,7-fluorene-diyl]s (3a–3e, see table 4)*

The synthesis of the mixture **3a** with a molar ratio of the bifunctional monomer **1** to the endcapper **2** of 5:1 is described below in detail.

A schlenk flask was charged with 1.26 g (4.58 mmol) nickeldicyclooctadiene, 0.56 ml (4.58 mmol) cyclooctadiene, 0.715 g (4.58 mmol) 2,2′-bipyridyl and 25′ml dry DMF under argon. The mixture was degassed by three freeze–thaw cycles before it was heated to 80°C for 30 min while stirring. Dibromofluorene (**1**) (0.74 g, 1.35 mmol) and monobromofluorene (**2**) (0.13 g, 0.27 mmol) were mixed in a separate flask. Dry toluene (60 ml) was added and the mixture was degassed by three freeze–thaw cycles. Subsequently, the monomer mixture was added to the catalyst mixture using a cannula. The reaction mixture was stirred under argon at 80°C for five days in the dark. Afterwards, it was poured into 240 ml MeOH/HCl(conc.) 1:1 and stirred at room temperature for 2 h. The organic phase was separated from the HCl phase which was then washed with ether. The combined organic phases were washed with water and the solvent was evaporated. The crude product was filtered over a small alumina (neutral) column using toluene as eluent, then washed five times with alkaline EDTA solution (5%), reprecipitated twice

Table 4. Molar amounts for monomer **1** and endcapper **2**, yields and molecular weights of oligofluorenes **3a–3e**.

Sample	Ratio[a] **1/2**	n_A[b] /mmol	n_B[c] /mmol	Yield /%	M_n (SEC)[d] /g mol^{-1}
3a	5:1	1.35	0.27	87	3800
3b	2:1	1.89	0.95	61	2500
3c	3:2	1.77	1.18	73	2000
3d	1:1	0.18	0.18	76	1500
3e	1:2	1.18	2.36	92	1300

[a] Monomer **1**/endcapper **2**. [b] Monomer **1**. [c] Endcapper **2**. [d] Determined by SEC in THF with oligofluorene calibration.

from THF into MeOH and dried in vacuum yielding 0.551 g (87%) of **3a** as pale yellow powder. ^{1}H NMR (250 MHz, $CDCl_3$). δ (ppm): 7.5–7.9 (m, 5H), 7.3–7.45 (m, 1H), 1.9–2.25 (m, 4H), 0.4–1.1 (m, 30H). ^{13}C NMR (250–MHz, $CDCl_3$). δ (ppm): 151.7, 141.6, 140.8, 126.5, 123.5, 120.6, 55.5, 45.0, 35.2, 34.5, 28.7, 27.6, 23.2, 14.5, 10.8. IR (KBr) (cm^{-1}): 2957, 2921, 2855 (CH stretch); 1457 (aromatic ring vibration); 1377 (CH deformation); 813 (CH aromatic).

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