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Self-Encapsulation of Poly-2,7-fluorenes in a Dendrimer Matrix

Dirk Marsitzky, Robert Vestberg, Paul Blainey, Beverly T. Tang, Craig J. Hawker, and
Kenneth R. Carter*

Contribution from the IBM Almaden Research Center, NSF Center for Polymeric Interfaces and
Macromolecular Assemblies, 650 Harry Road, San Jose, California 95120-6099

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Abstract: The synthesis and characterization of complex dendritic, rigid rod poly-2,7-fluorene homopolymers and copolymers via a macromonomer approach is reported. Several 2,7-dibromofluorene monomers containing benzyl ether dendrons (generations 1, 2, and 3) in the 9,9'-position of the fluorene ring were prepared and employed in condensation polymerizations to yield both homopolymers and copolymers with diethylhexylfluorene. Fluorescence measurements of the materials reveal extensive conjugation along the polymer backbone. The determination of the solid-state PL spectra and quantum efficiencies showed that there is an apparent optimum size of the dendritic side groups with the [G-2]-derivatives showing high reactivity with associated site isolation of the conjugated chain. AFM analysis and DSC results confirmed that the hybrid polymers and copolymers did not show any sign of a microphase-separated morphology. First EL-results demonstrated that the homopolymers have higher turn-on voltages than the corresponding copolymers.

Introduction

Electroluminescent organic polymers have transitioned in the recent years from being pure scientific curiosities to materials of commercial interest.¹ An important issue under investigation is the development of efficient and stable blue-emitting materials.^{2,3} In this area the stepladder polymer poly-2,7-(9,9-dialkyl)-fluorene (2,7-PF) has attracted a great deal of attention because of its chemical and thermal stability and the possibility to vary the properties of the resulting polymer via the substitution pattern of the 9-position of the fluorene unit.⁴⁻¹⁵ The problems encountered with polymeric rodlike blue emitters in general are

their tendency to aggregate and form excimers leading to blue-green emission and fluorescence quenching.^{16,17} Concepts

(1) Part of this increased focus is indicated by the growing number of companies performing research and attempting to commercialize products in this area, e.g., IBM, Covion, Philips, Dow Chemicals, DuPont, Kodak, Xerox, Pioneer, CDT, UniAx, etc.

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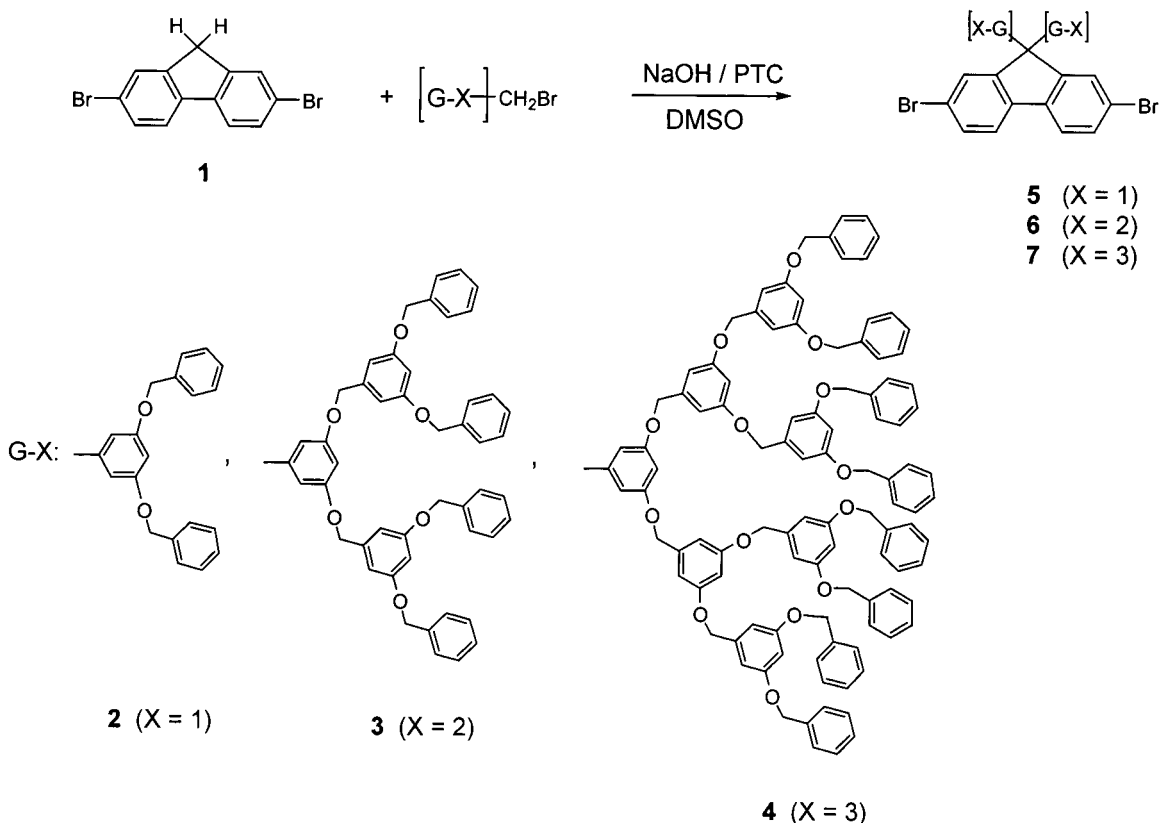
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Scheme 1. Synthesis of the Macroinitiators 5–7

applied to avoid this detrimental π -aggregation behavior include the statistical copolymerization of 2,7-dibromofluorene with suitable comonomers,⁶ the use of bulky side chains as solubilizers, and the incorporation of dendritic endgroups.¹² Dendritic side-chain functionalization of several conjugated polymer systems has been reported, namely poly(*p*-phenylenevinylene),¹⁸ poly(*p*-phenyleneethynylene),¹⁹ poly(thiophene),²⁰ poly(triacetylene)²¹ and poly(*p*-phenylene).^{22–24} The attachment of polyether dendrons to lanthanide complexes has been shown by Fréchet *et al.* to improve the luminescence properties of these complexes both in solution and solid state. The observed enhancement of luminescence activity of the dendron-functionalized La³⁺-complexes was attributed to both an “antenna effect”, the transfer of energy from the ligand to the core, and a “shell effect”, the site isolation of the La³⁺-cores leading to decreased rate of self-quenching.²⁵ While this manuscript was in review, a report by Müllen *et al.* appeared which described the combination of a conjugated polymer with a first-generation polyphenylene dendron. They particularly investigated the shielding effect provided by different phenylene side groups to avoid aggregation.²⁶

We wished to explore the utility of incorporation of side-chain dendrons in a thermo-oxidatively stable blue-emitting

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polymer of commercial interest, 2,7-PF.²⁷ Our motivation for the synthesis of these novel hybrid materials was 3-fold: first, the dendrons serve as excellent solubilizers due to their highly branched structure, and second, they envelope and protect the polymer rods from aggregation and degradation. A third aspect includes the possibility to fine-tune the charge-transport properties via statistical or alternating copolymerization with other 2,7-dibromofluorene derivatives. Here we report the results of the homo- and copolymerization of the macromonomers **5**, **6**, and **7**, the determination of the optical properties of the resulting dendritic 2,7-PFs and the corresponding copolymers as well as the AFM investigation and the first results of the electroluminescent properties evaluation of these novel materials.

Results and Discussion

In general, two different synthetic routes can be applied to yield dendron-functionalized homopolymers: the first route utilizes a polymer backbone with anchor groups to either convergently or divergently attach a dense sequence of dendrons (grafting-onto route). The second route utilizes monomers already carrying dendrons which are subjected to polymerization or polycondensation (macromonomer route). We selected the macromonomer route to circumvent the intrinsic problems of the grafting-onto procedure, for example achieving complete coverage of the polymer backbone with dendrons and purifying the product.

The macromonomers **5–7** were designed in a way to, (1) ensure a certain shielding behavior of the polyfluorene backbone by choosing sufficiently large dendrons while (2) not shielding the reaction site of the transition-metal-mediated polycondensation reactions. A third aspect of the monomer design involves the potential dilution of the electroluminescent properties of 2,7-

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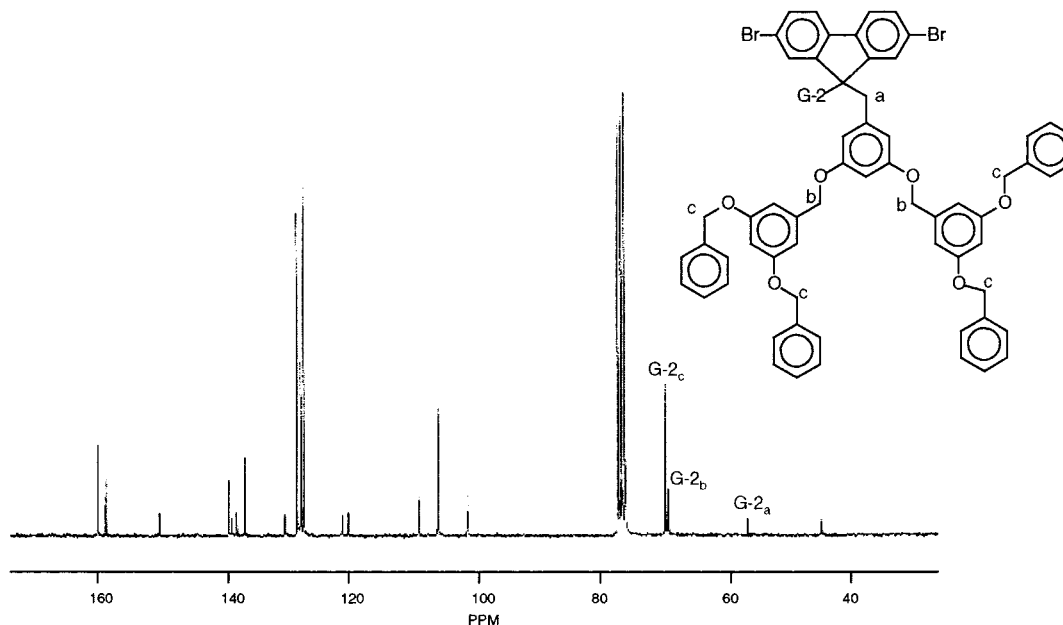
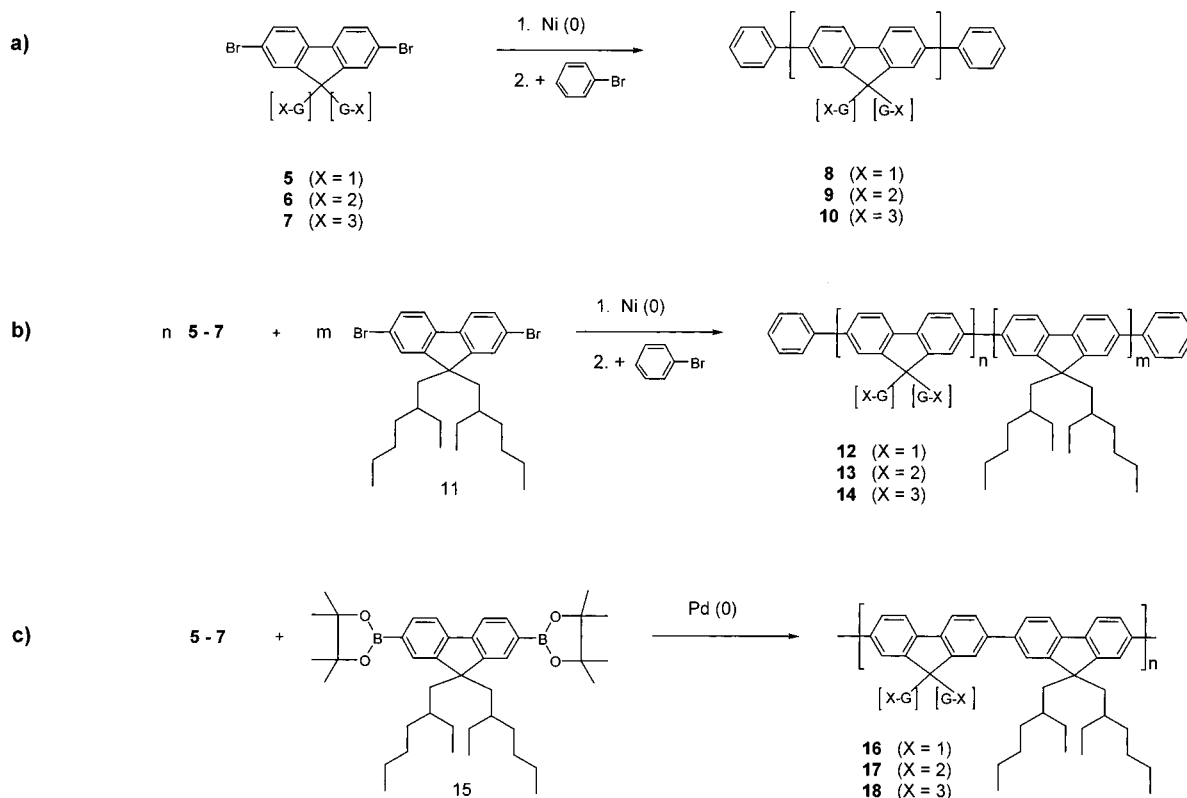


Figure 1. ^{13}C NMR spectrum (125 MHz, CDCl_3) and structure of **6**.

Scheme 2. Synthesis of the Dendrimer–Polyfluorene Hybrid Materials **8–10**, **12–14**, and **16–18**



PF by incorporating a large wt % of dendrimer. As one can see, the correct choice of dendrimer size is dependent on the subtle interplay of a number of different issues.

The monomers **5–7** were synthesized by selective nucleophilic substitution reactions (S_N) of the 9,9'-position of **1** with the respective dendrons **2–4** (see Scheme 1).²⁷ The benzyl bromide-functionalized dendrons **2–4** were synthesized according to established literature procedures.²⁸ The S_N reaction proceeded with high yield (84–91% after purification) and gave the macromonomers **5–7** as confirmed by ^1H - and ^{13}C NMR analysis (see Figure 1).

The macromonomers were then subjected to a Yamamoto-type polymerization²⁹ (Scheme 2a) utilizing bis(cyclooctadiene)-nickel(0), 2,2'-bipyridine, and cyclooctadiene in a toluene/DMF mixture followed by chain termination with bromobenzene. The polymerization of macromonomer **5** proceeded smoothly and yielded after workup the 2,7-PF **8** carrying [G-1]-dendrons as side groups. The larger second-generation macromonomer **6** did not polymerize using the same reaction parameters (concentration of monomer, amount of reactive coupling reagent, temperature) as used in the literature for other 2,7-dibromofluorene

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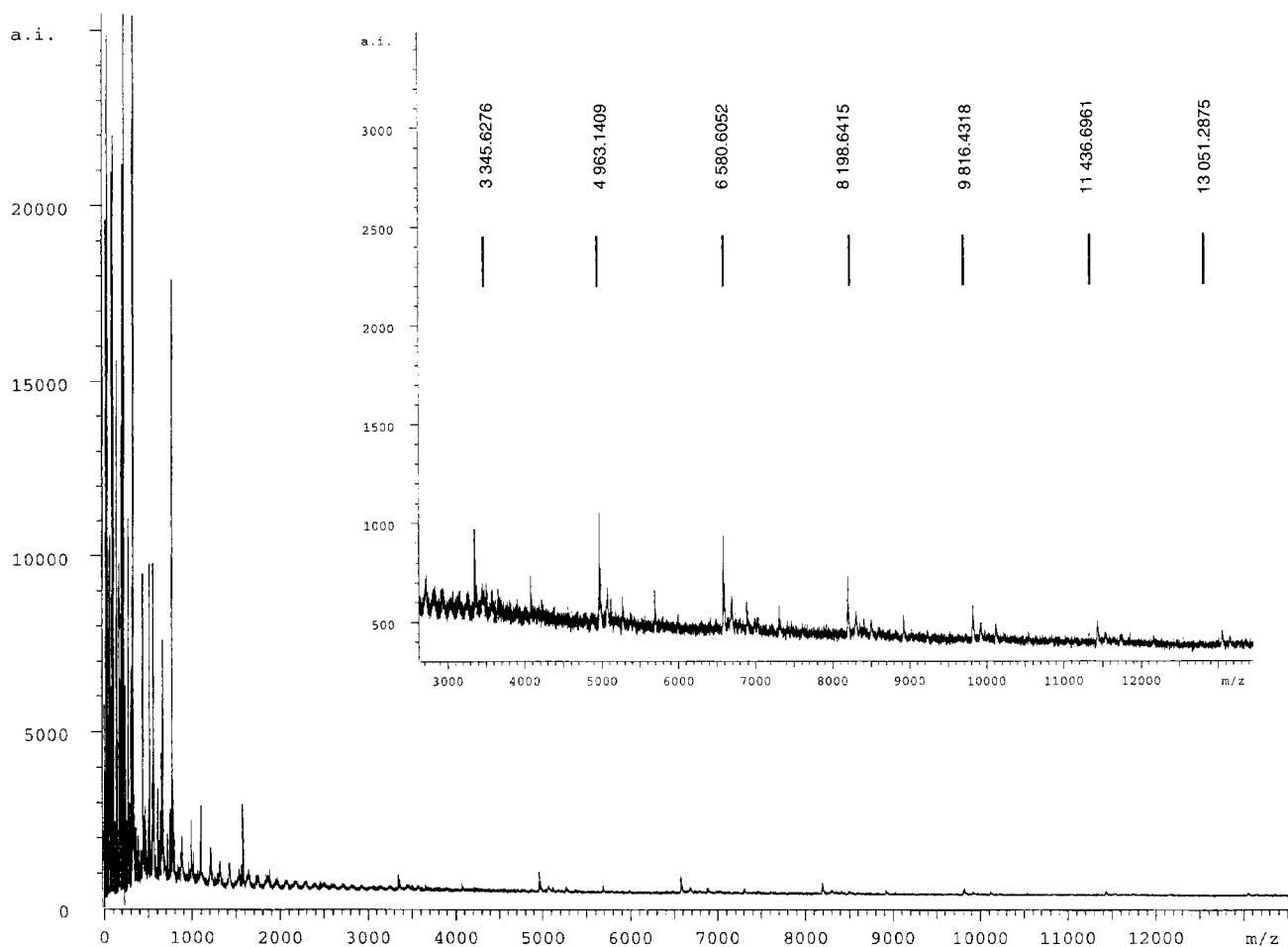


Figure 2. MALDI-TOF spectrum of **9b**.

derivatives.⁵ Since it is known from the palladium(0)-mediated synthesis of dendron-functionalized poly-*p*-(phenylene)s (PPP) that the concentration of the macromonomers plays an important role in respect to the polymerization results, we increased the concentration of **6**.^{22–24} The resulting polymer **9a** was obtained as a white solid and showed good solubility in common organic solvents such as toluene and THF (maximum solubilities range from 15 to 20 mg/mL solvent).

The molecular weight of the material was determined using gel permeation chromatography (GPC) calibrated with polystyrene standards to be $M_n = 6240$ g/mol. The molecular weight determination of conjugated, rigid rod-type polymers using relative methods such as GPC calibrated with coil-like polystyrene standards, however, is known to only give an estimation of the actual molecular weight.³⁰ This is even more true for the conjugated polymer–dendrimer hybrid materials studied here. A further increase of the monomer concentration to the saturation limit led to only a small incremental increase of the molecular weight of 2,7-PF **9** (see Table 1). The polymerization of **7** was also conducted using the highest possible macromonomer concentration; however, it yielded only a low-molecular weight sample of 2,7-PF **10**, reflecting the sterically crowded reaction site of **10** carrying two bulky [G-3]-dendrons.

The molecular weight of the dendron-functionalized PFs **8–10** were also examined by MALDI-TOF mass spectrometry. The oligomeric 2,7-PFs **9a**, **9b**, and **10** with low polydispersities could be analyzed using a 1,8,9-trihydroxyanthracene (= dithranol) matrix and silver-trifluoroacetate as cationization

Table 1. Molecular Weight (M_n in g/mol, GPC, THF, Polystyrene Calibration) and Polydispersity Index (PDI), Monomer Concentration (c_M in wt %), Decomposition Temperature (T_D after 5% Weight Loss in °C) and Optical Properties (λ_{max} , λ_{em} , and Φ_F) in Solution (THF, Φ_F : Toluene) of the Dendronized 2,7-PFs **8–10**

	M_n /PDI	c_M	T_D	T_G	$\lambda_{max}/\lambda_{em}$	Φ_F
8	51 400/2.01	5.3	320	94	388/414	0.78
9a	6200/1.44	7.7	340	50	370/408	0.97
9b	9300/1.66	9.3	360	50	380/411	1.0
10	4400/1.11	9.5	320	10	340/391	0.41

agent (see Figure 2). The signal intensities in all cases were quite low, allowing only a qualitative analysis of the molecular weight. All derivatives **9–10** show up to four peaks per repeat unit due to endgroup variations and fragmentation reactions caused by absorption of laser energy by these high band-gap materials.^{31,32} The G-1-functionalized 2,7-PF **8** could not be analyzed, probably due to a combination of factors, its high molecular weight (51 400 g/mol), and high polydispersity ($D = 2.01$). Despite the oligomeric nature and the low polydispersities of the alternating copolymers **16–18** these dendron-functionalized 2,7-PFs could not be analyzed by MALDI-TOF analysis.

The statistical copolymerization of macromonomers **4–6** with 2,7-dibromo-9,9-(bis-2'-ethylhexyl)fluorene **11** (Scheme 2b) was also performed via the nickel(0)-mediated Yamamoto-polymerization (feed ratio 1:1) with the aim of synthesizing high-

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Table 2. Molecular Weight (M_n in g/mol, GPC, THF, Polystyrene Calibration) and Polydispersity Index (PDI), Incorporation Ratio (via ^1H NMR Analysis), Decomposition Temperature T_D (at 5% Weight Loss in $^\circ\text{C}$) and Optical Properties (λ_{max} , λ_{em} , and Φ_F) in Solution (THF, Φ_F : Toluene) of the Statistical Copolymers **12–14**

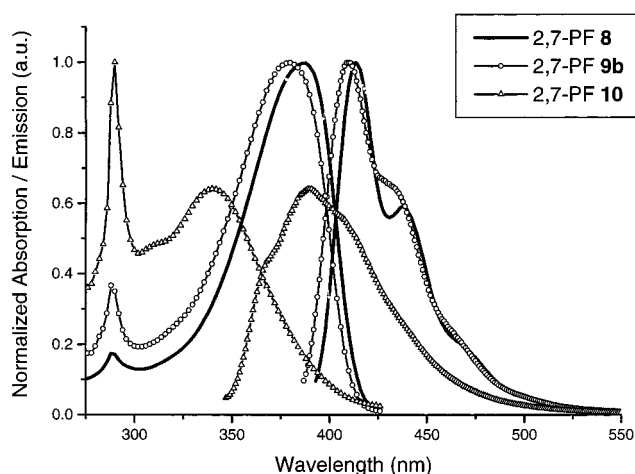
	M_n /PDI	$m:n$ (NMR)	T_D	T_G	$\lambda_{\text{max}}/\lambda_{\text{em}}$	Φ_F
12	62 800/2.22	1:1.5	350	73	384/411	0.69
13	26 200/2.33	1:0.9	290	48	383/411	0.92
14	68 300/2.21	1:0.07	320	51	385/411	0.76

Table 3. Molecular Weight (M_n in g/mol, GPC, THF, Polystyrene Calibration) and PDI, Monomer Concentration (c_M in wt %), Decomposition Temperature (T_D in $^\circ\text{C}$), Glass Transition Temperature T_G (in $^\circ\text{C}$) and Optical Properties (λ_{max} , λ_{em} , and Φ_F) in Solution (THF, Φ_F : Toluene) of the Dendronized 2,7-PFs **15–17**

	M_n /PDI	c_M	T_D	T_G	$\lambda_{\text{max}}/\lambda_{\text{em}}$	Φ_F
15	3900/1.46	22	340	78	372/411	0.53
16	16 300/2.46	26	370	50	388/419	1.0
17	11 900/1.65	20	360	49	374/410	0.84

molecular weight polymers with excellent film-forming properties. The monomer concentrations of the copolymerization reactions were comparable to the homopolymerization reactions. All copolymerizations proceeded smoothly, and the resulting copolymers were obtained after several washing steps and reprecipitations as high-molecular weight materials (see Table 2) showing excellent solubility in a variety of organic, apolar solvents. The incorporation ratio of the dendron-functionalized fluorenes was checked by comparing the relative ^1H NMR signal intensities of the 2'-ethylhexyl resonances ($\delta = 0.39\text{--}1.01$) with the α -benzyl ether signals ([G-1] $\delta = 3.42$; [G-2] $\delta = 3.32$; [G-3] $\delta = 3.19$). The results (Table 2) show that copolymer **12** ($M_n = 62\,800$ g/mol) is slightly enriched with respect to the [G-1]-functionalized fluorene (incorporation 1:1.5), copolymer **13** ($M_n = 46\,600$ g/mol) nearly displays the expected incorporation ratio (1:0.9), while the incorporation ratio of [G-3]-functionalized fluorene **7** in **14** ($M_n = 68\,300$ g/mol) is quite low (1:0.07). We assume, that the reactivity of **5** carrying the less bulky and more polar [G-1]-benzyl ether dendrons in the side chain is slightly higher than that of **11**, leading to a slightly preferred incorporation of **5** in the resulting copolymer. The reactivity of the macromonomer **6**, bearing dendrons of generation 2 in the side chains, on the other hand, is almost the same as that of 2,7-dibromofluorene **11**, resulting in a conformity of incorporation and feed ratio. In contrast, the reaction site of macromonomer **7** with the bulky [G-3]-dendrons as solubilizing groups, however, is very crowded, leading to a low incorporation ratio in the copolymer **14**.

For the synthesis of alternating copolymers consisting of 9,9-bis(ethylhexyl)fluorene and the corresponding dendronized fluorenes, **5–7**, we utilized the palladium(0)-mediated Suzuki polycondensation³³ in the two-phase system THF and 2 N potassium carbonate solution at 90 $^\circ\text{C}$ (see Scheme 2c). The synthesis of **15** was performed according to an established literature procedure.^{34,35} All alternating copolymerizations were again carried out with a minimum amount of solvent. The molecular weight of the alternating copolymers as determined by GPC are shown in Table 3. Surprisingly the alternating copolymer **16** carrying the [G-1]-dendrons shows the same degree of polymerization as **18**, $D_p = 3$, corresponding to six coupled fluorene units which contain the sterically crowded

**Figure 3.** UV/vis- and PL spectra ($\lambda_{\text{exc.}} = \lambda_{\text{max}}$) of the dendron-functionalized 2,7-PFs **8–10** in solution (THF).

[G-3]-dendron. The [G-2]-macromonomer **6**, however, gave the highest degree of polymerization under the conditions employed with respect to catalyst choice, solvents, and reaction temperatures and unoptimized Suzuki-reaction parameters ($D_p = 8$).

The thermal properties of the conjugated materials **8–18** were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All materials exhibit excellent thermal stability up to 300 $^\circ\text{C}$ (see Tables 1–3). Only one T_g was detected for each of the copolymers with no evidence of two-phase behavior. The glass transitions of the dendron-functionalized 2,7-PFs **8–18** decline with increasing size of the attached dendrons and increasing amount of dendrimers (see Tables 1–3).

PL- and EL-properties. All dendron-functionalized 2,7-PFs **8–10**, **12–14**, and **16–18** exhibit good solubility in common organic solvents such as chloroform, THF, and toluene and show bright blue fluorescence in solution. The absorption spectrum of **8** resembles a superposition of the [G-1]-UV spectrum ($\lambda_{\text{max}} = 288$ nm) and a high-molecular weight 2,7-PF spectrum ($\lambda_{\text{max}} = 388$ nm)⁴ while the fluorescence spectrum of **8** ($\lambda_{\text{exc.}} = 388$ nm) represents principally the optical properties of the 2,7-PF backbone ($\lambda_{\text{em}} = 414$ nm, see Figure 3). The absorption and emission data of **9a**, **9b**, and **10** are in the same range as those reported for the respective 2,7-PF oligomers^{10,15} and indicate that the attached dendrons of generation 2 and 3 at the 9-position of the fluorene monomer units do not inhibit conjugation along the polymer main chain (see Table 1). The optical properties of the statistical copolymers in solution (see Table 2) are dominated by the conjugated backbone and are identical to high-molecular weight polyfluorenes carrying alkyl chains as solubilizers. The absorption and emission characteristics of the lower-molecular weight alternating copolymers **16** and **18** resemble those reported for fluorene oligomers up to six repeat units.¹⁰ The alternating 2,7-PF **17**, however, has passed the effective conjugation length of 11 repeat units (for fluorescence) and emits blue light at the same wavelength as high-molecular weight 2,7-PFs.

The PL quantum yields (Φ_F) of the 2,7-PFs **8–10**, **12–14**, and **16–18** in solution (toluene) were measured in comparison to 9,10-diphenylanthracene ($\Phi_F = 1.0$)³⁶ and range from 0.41 to 1.0 (see Tables 1–3). These PL efficiency values are comparable to many laser dyes in solution³⁷ and are exception-

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Table 4. Thin-Film Absorption and Emission ($\lambda_{\text{max}} = \lambda_{\text{em}}$) Data of the Dendronized 2,7-PFs after Thermal Treatment (30 min at 100 °C) as Well as PL-Quantum Efficiencies (Relative to Poly-2,7-9,9-dioctylfluorene)

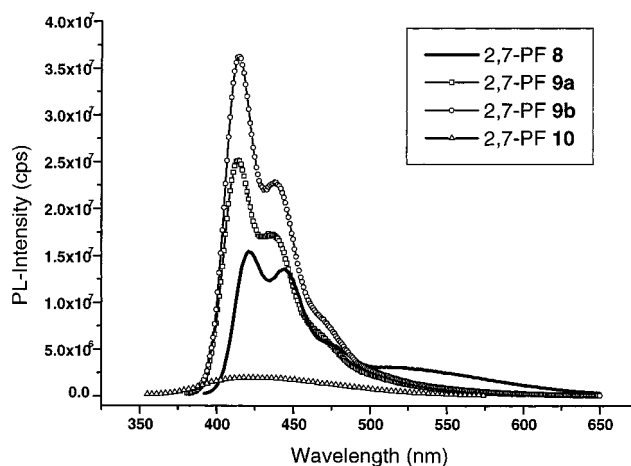
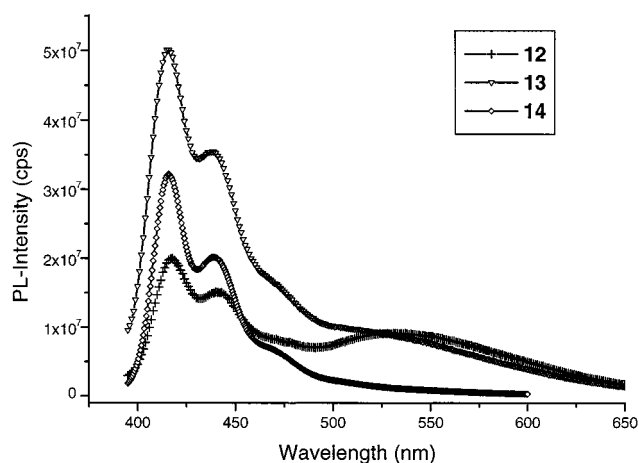
	absorption (nm)	emission (nm)	PL-QE (ϕ_F)
8	388	421, 446, 522	0.25
9a	372	416, 438	0.66
9b	382	418, 438	0.98
10	345	419 (broad)	0.15
12	388	417, 440, 533	0.29
13	388	415, 438	0.46
14	388	416, 449	0.35
16	380	415, 438, 523	0.12
17	388	419, 440	0.73
18	380	414, 436	0.56

ally high for the derivatives **9a**, **9b**, **13**, and **16** compared to the Φ_F values reported for 2,7-PF homopolymers (e.g., poly-2,7-[9,9-(3,6-dioxahexyl)-fluorene]: $\Phi_F = 0.77$)⁴ as well as copolymers ($\Phi_F = 0.36$ – 0.79).⁵

To evaluate the potential of these materials as the emissive layer in blue LEDs, the thin film photoluminescence was examined (Figures 3–5). The UV- and fluorescence data of the homopolymers **8**–**10** and the copolymers **14**–**16** and **16**–**18** are summarized together with the photoluminescence quantum efficiencies in Table 4. The films were prepared by spin-coating the polymers from *p*-xylene solutions ($c = 15$ mg/mL) for 60 s at 1500 rpm on quartz substrates. All thin-films were thermally annealed (30 min at 100 °C) well above their glass-transition temperatures since it has been shown by real-time IR-analysis, that the temperature in operating LED devices can reach up to 86 °C.³⁸

An AFM study by Friend et al. revealed that the morphology present in polyfluorene blends can greatly affect the electrooptical properties of the blend films.³⁹ Our AFM investigation of the 2,7-PFs **8**–**10**, **12**–**14**, and **16**–**18**, however, did not reveal any macroscopic order or nanophase separation in the dendron-containing materials, and they were not significantly different from other polyfluorene samples examined. AFM of polymer films only probes the surface of the film so that nanoscopic features embedded within the polymer film cannot be strictly ruled out.

The PL spectrum of the [G-1]-2,7-PF **8** still exhibits a tail in the long-wavelength region (540 nm) (probably caused by excimer formation since the absorption spectrum does not change) even though this tail is much less pronounced than in films of thermally treated films of 2,7-PF derivatives carrying straight alkyl chains as solubilizing groups. The [G-2]-2,7-PFs **9a** and **9b**, however, showed no additional band in the long-wavelength region (see Figure 4). The [G-3]-functionalized 2,7-PF **10** displayed only a weak and broad fluorescence spectrum in the solid state which is probably due the poor optical quality of the spin-coated films. The solid-state PL spectra of the statistical copolymers **12**–**14** after thermal treatment are shown in Figure 5. The copolymer **12** exhibits a broad additional band at 542 nm attributed to excimer formation (no change of absorption spectrum before and after annealing), an effect which is less pronounced in the PL spectrum of **13**. Only the copolymer **14** with the fluorene-G-3 incorporated does not show any sign of aggregate and excimer formation—an astonishing result when regarding the low incorporation of the [G-3]-macromonomer in the copolymer **14**. In the case of the alternating copolymers

**Figure 4.** Solid-state PL spectra of **8**–**10** ($\lambda_{\text{exc.}} = \lambda_{\text{max}}$). Films were prepared by spin-coating (CHCl_3 , $c = 15$ mg/mL, 2000 rpm) and drying at 100 °C for 30 min.**Figure 5.** Solid-state PL spectra of **12**–**14** ($\lambda_{\text{exc.}} = \lambda_{\text{max}}$). Films were prepared by spin-coating from *p*-xylene solutions ($c = 15$ mg/mL, 2000 rpm) and drying at 100 °C for 30 min.

16–**18** only **16**, containing the small [G-1]-dendron exhibits the broad excimer-band at 540 nm, the alternating copolymers **17** and **18** emit both deep blue light even after thermal treatment (see Figure 6).

The fluorescence quantum yields (ϕ_F) of these films (see Table 4) were generated by comparing the fluorescence intensity of polymers **8**–**10** with that of a sample of poly-2,7-(9,9-dioctylfluorene) excited at 384 nm ($\phi_F = 0.55$).⁴⁰ Even though this relative method has to be considered an estimate (e.g., different absolute PL-QE values for poly-2,7-9,9-dioctylfluorene are given in the literature⁴¹) it gives a first impression of the PL performance of these materials compared to those for 2,7-PFs with straight alkyl chains. We observed that the quantum yield of the [G-1]-2,7-PF **8** ($\phi_F = 0.25$) has dropped significantly compared to that of the 2,7-PF standard. This low quantum yield is probably due to the aggregated nature of the conjugated backbone leading to excimer emission and fluorescence quenching. The PL-QE of the [G-2]-2,7-PF **9a** ($\phi_F = 0.66$), however, is higher than that of the standard, while the higher molecular weight derivative, **9b** ($\phi_F = 0.98$), shows an exceptionally high

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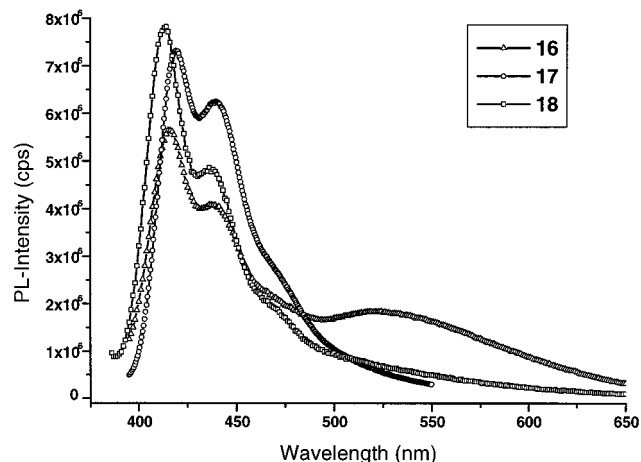


Figure 6. Solid-state PL spectra of **15–17** ($\lambda_{\text{exc.}} = \lambda_{\text{max}}$). Films were prepared by spin-coating from *p*-xylene ($c = 15 \text{ mg/mL}$, 2000 rpm) and drying at 100°C for 30 min.

quantum efficiency. The reason for the decreased PL efficiency of the shorter derivative **9a** compared to **9b** might be the better optical quality of the spin-coated film of **9b**. The low ϕ_F of **10** (0.15) is probably due to the low degree of polymerization of the [G-3]-functionalized 2,7-PF leading to crystallization phenomena and fluorescence quenching. The PL-efficiencies of the copolymers, **12–14** and **16–18**, show trends similar to those of the homopolymers **8–10**. The materials that incorporate the small [G-1]-dendron all exhibit relatively high aggregation and excimer formation tendencies and thus possess relatively low photoluminescence yields (**12**, $\phi_F = 0.29$; **16**, $\phi_F = 0.12$). The [G-2]-functionalized 2,7-PF copolymers, however, exhibit the highest PL-efficiencies (**13**, $\phi_F = 0.46$; **17**, $\phi_F = 0.73$) relative to their [G-1]- and [G-3]-analogues. The PL-efficiency of the [G-3]-functionalized statistical copolymer **14** ($\phi_F = 0.35$) is lower than that of the standard 2,7-PF, while the PL-efficiency of the alternating copolymer **18** ($\phi_F = 0.56$) is in the same range as that of the 2,7-PF reference.

Light-emitting diode structures from the dendron-functionalized 2,7-PF homopolymers **8**, **9b** as well as from the [G-2]-functionalized statistical and alternating copolymers **13** and **17** were prepared in the device configuration indium–tin-oxide (ITO)/PEDOT (= poly-2,5-(3,4-ethylenedioxy)-thiophene)/2,7-PF **8**, **9b**, **13**, or **17** / Ca/Al. The fabrication process was accomplished by spin-coating the first hole-transport layer PEDOT onto the commercially available glass–ITO substrates. Then the respective materials **8**, **9b**, **13**, or **17** were deposited by spin-coating from *p*-xylene solutions ($c = 10 \text{ mg/mL}$, film-thickness $\approx 40 \text{ nm}$) followed by stepwise evaporation of the calcium/aluminum cathode onto the EL-active layer. The diodes with the [G-1]- and [G-2]-functionalized 2,7-PF homopolymers **8** and **9b** started to emit blue light around 16 V. The LEDs built from copolymers **13** and **17**, however, showed considerably lower turn-on voltages of 4.5 and 6 V, respectively. These diodes were more stable than those made of the 2,7-PF derivatives **8** and **9b**. However, all devices possessed short functional lifetimes, which may be attributed to the thin EL-layers (ca. 35–40 nm compared to usual 80–120 nm in 2,7-PF LEDs⁴²) in combination with the unoptimized diode structure used. It should be noted that we were unable to reproducibly obtain high-quality thin films of the polymers when spun on the ITO/PEDOT substrates, leading to shorts and diode failure.

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Conclusions

In summary, we report the synthesis and characterization of complex dendritic, rigid-rod homopolymers and copolymers, in which site isolation of the fluorescent poly-2,7-fluorene backbone is achieved by self-encapsulation in a dendritic matrix. A macromonomer approach was followed, and several 2,7-dibromo-fluorene monomers containing benzyl ether dendrons (generation 1, 2, and 3) in the 9,9'-position of the fluorene ring were prepared. These macromonomers were employed in condensation polymerizations to yield both—homopolymers (**8–10**) and copolymers with diethylhexylfluorene (**12–14**, **16–18**). The solution- and solid-state fluorescence data revealed extensive conjugation along the polymer backbone. Interestingly, we discovered that there was an apparent optimum size of the dendritic side groups, in respect to PL quantum efficiency, with the [G-2]-derivatives showing high reactivity with associated chain isolation. This leads to aggregation-free solid-state spectra and high PL quantum efficiencies. AFM analysis and DSC results confirmed that these hybrid copolymers—polymers did not show any signs of a microphase-separated morphology. Attempts to optimize the EL properties when tested in standard device configurations are currently in progress.

Experimental Section

Materials. The compounds 2,7-dibromofluorene, benzyl(triethyl)-ammoniumchloride, hexylbromide, 2,2'-bipyridine, and 1,5-cyclooctadiene were purchased from Aldrich and used without further purification. The Yamamoto coupling reagent bis(1,5-cyclooctadiene)nickel(0) was purchased from Strem and handled under inert atmosphere. The solvents were dried according to standard procedures. The 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(2'-ethylhexyl)-fluorene (**15**) were prepared according to already published reaction protocol.^{13,34,35} All other materials were purchased from Aldrich and used as received. All reactions were carried out under an argon atmosphere.

Characterization. The ¹H- and ¹³C NMR spectra were recorded on a Bruker AF 250 MHz spectrometer. TGA measurements of the dendron-functionalized 2,7-PFs were performed under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ using a Perkin-Elmer TGS-2 instrument. The polymer molecular weights were determined using a Waters 150-C gel permeation chromatography instrument calibrated with polystyrene standards. The optical properties were investigated with a Hewlett-Packard 8452A diode array spectrophotometer and an SA Instruments FL3-11 fluorimeter. The solution PL quantum yields (Φ_F) were determined by excitation of the respective polymer solutions (toluene) at λ_{max} and comparison with the solution emission of the 9,10-diphenylanthracene ($\Phi_F = 1.0$).³⁶ The solid-state fluorescence efficiencies were measured by comparison of the fluorescence of the respective dendron-functionalized 2,7-PF films on quartz substrates (film thickness: 40–70 nm) with that of a standard poly-2,7-(9,9-dioctylfluorene) sample ($M_n = 52\,000 \text{ g/mol}$, PDI = 2.4) spin-coated from *p*-xylene solution onto quartz (film thickness: 50 nm).⁴⁰ The analysis of the film thickness was performed using an Alpha-Step 200 from Tencor Instruments. The MALDI-TOF measurements were carried out with a Reflex I mass spectrometer (Bruker, Bremen, Germany), equipped with a 337 nm nitrogen laser. The spectra were recorded in the linear mode with the Bruker HIMAS detector at an acceleration voltage of 30 kV. The mass spectrometer was calibrated externally with polystyrene standards (PSS, Mainz, Germany). The matrix 1,8,9-trihydroxyanthracene (dithranol) (Aldrich) and the analytes were dissolved in THF and mixed at a mole ratio of approximately 1:500 (analyte:matrix).

Synthesis of the [G-1]-, [G-2]-, and [G-3]-dendrons 2–4. The dendrons 2–4 were synthesized according to well-known literature procedures by Hawker et al.²⁸

General Procedure for the Synthesis of Macromonomers 5–7. 2,7-Dibromofluorene (1 g, 3.09 mmol), the phase-transfer catalyst benzyl(triethyl)ammoniumchloride (0.22 g, 0.07 mmol) and the respec-

tive dendron **2–4** (6.8 mmol) were dissolved in 90 mL of DMSO. The solution was degassed three times and purged with argon. Then 5 mL of a 50 wt % solution of NaOH were added via a syringe, and the reaction mixture was stirred for 4 h. After the reaction was quenched with the addition of 50 mL of water, 100 mL of dichloromethane were added and the phases were separated. The aqueous phase was extracted twice with dichloromethane, and the combined organic phases were dried over MgSO₄. After removal of the solvent the residue was chromatographed using silica gel and a hexane/ethyl acetate solvent mixture (2:1).

9,9-Bis[(3,5-bis(benzyloxy)benzyloxy)methyl]-2,7-dibromofluorene 5: yield 2.62 g (91%); ¹H NMR (250 MHz, CDCl₃) δ 3.22 (s, 4 H), 4.72 (s, 8 H), 5.91 (t, *J* = 2 Hz, 2 H), 6.29 (t, *J* = 2 Hz, 4 H), 7.21–7.58 (m, 26 H); ¹³C NMR (68 MHz, CDCl₃) δ 45.4, 57.2, 70.0, 101.5, 109.3, 120.6, 121.4, 127.3, 127.8, 128.1, 128.5, 130.5, 137.0, 138.2, 139.0, 150.5, 159.0.

9,9-Bis[(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-methyl]-2,7-dibromofluorene 6: yield 4.67 g (85%); ¹H NMR (250 MHz, CDCl₃) δ 3.17 (s, 4 H), 4.65 (s, 8 H), 4.99 (s, 16 H), 5.88 (t, *J* = 2 Hz, 4 H), 6.26 (t, *J* = 2 Hz, 2 H), 6.52 (t, *J* = 2 Hz, 4 H), 6.58 (d, *J* = 2 Hz, 8 H), 7.26–7.51 (m, 46 H); ¹³C NMR (68 MHz, CDCl₃) δ 45.3, 57.2, 69.8, 70.1, 101.5, 101.6, 106.2, 109.3, 120.5, 121.4, 127.5, 128.0, 128.1, 128.6, 130.4, 136.9, 138.2, 139.0, 139.5, 150.5, 158.8, 160.1.

9,9-Bis[(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-benzyloxy)-methyl]-2,7-dibromofluorene 7: yield 9.01 g (84%); ¹H NMR (250 MHz, CDCl₃) δ 3.14 (s, 4 H), 4.63 (s, 8 H), 4.90 (s, 16 H), 4.97 (s, 32 H), 5.89 (d, *J* = 4 Hz, 4 H), 6.29 (t, *J* = 2 Hz, 2 H), 6.48–6.65 (m, 36 H), 7.26–7.50 (m, 86 H); ¹³C NMR (68 MHz, CDCl₃) δ 45.2, 57.2, 68.0, 70.0, 70.1, 101.5, 101.7, 106.3, 106.4, 109.3, 120.5, 121.5, 125.5, 127.5, 127.9, 128.0, 128.6, 130.4, 136.8, 138.3, 138.9, 139.3, 139.4, 150.4, 158.8, 160.0, 160.2.

General Procedure for the Synthesis of the Dendron-Functionalized 2,7-PFs 8–10 and 12–14. A Schlenk tube containing 2 mL of degassed toluene, 1 mL of degassed DMF, bis(1,5-cyclooctadiene)-nickel(0) (100 mg, 3.64 mmol), 2,2'-bipyridine (60 mg, 3.84 mmol), and 1,5-cyclooctadiene (0.04 mL, 3.84 mmol) was heated under argon to 80 °C for 20 min. The respective monomers (0.12 mmol), dissolved in 0.75 mL of degassed toluene, were added to the above solution via a syringe, and the polymerization was maintained at 80 °C for 72 h. Then 1.5 mL of bromobenzene was added to remove residual bromine endgroups, and the reaction mixture was stirred for additional 3 h at 80 °C. After the reaction 50 mL of toluene was added, and the solution was washed three times with EDTA (aq). The organic solution was concentrated, and the polymer was precipitated from an equivolume mixture of methanol and acetone. Finally the polymer was dried at 50 °C under vacuum.

Poly-9,9-bis[(3,5-bis(benzyloxy)benzyloxy)methyl]-2,7-fluorene 8: yield 215 mg (52%); ¹H NMR (250 MHz, CDCl₃) δ 3.25 (s, b, 4 H), 4.57 (s, b, 8 H), 6.04–6.33 (b, 4 H), 7.13–7.32 (m, 2 H), 7.35–7.51 (m, 26 H); UV-vis (THF) λ_{max} = 388 nm.

Poly-9,9-bis[(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-methyl]-2,7-fluorene 9: yield 148 mg (54%); ¹H NMR (250 MHz, CDCl₃) δ 3.24 (s, b, 4 H), 4.42 (s, b, 8 H), 4.60–4.77 (b, 16 H), 5.82–5.90 (b, 2 H), 6.32–6.41 (b, 16 H), 7.14–7.50 (m, 46 H); **9a:** UV-vis (THF) λ_{max} = 370 nm; **9b:** UV-vis (THF) λ_{max} = 380 nm.

Poly-9,9-bis[(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-benzyloxy)-methyl]-2,7-fluorene 10: yield 180 mg (45%); ¹H NMR (250 MHz, CDCl₃) δ 3.14 (s, b, 4 H), 4.27–4.93 (m, 56 H), 5.79 (b, 4 H), 6.25–6.55 (m, 38 H), 7.15–7.41 (m, 86 H); UV-vis (THF) λ_{max} = 340 nm.

Poly-9,9-bis[(3,5-bis(benzyloxy)benzyloxy)methyl]-co-9,9-bis[2'-(ethyl)hexyl]-2,7-fluorene 12: yield 250 mg (90%); ¹H NMR (250

MHz, CDCl₃) δ 0.48–1.05 (m, b, 30 H), 1.82–2.01 (s, b, 4 H), 3.42 (s, b, 4 H), 4.41–4.65 (m, b, 8 H), 6.00–6.08 (m, b, 4 H), 6.55 (s, b, 2 H), 6.94–7.89 (m, b, 26 H); UV-vis (THF) λ_{max} = 384 nm.

Poly-9,9-bis[(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-methyl]-co-9,9-bis[2'-(ethyl)hexyl]-2,7-fluorene 13: yield 200 mg (76%); ¹H NMR (250 MHz, CDCl₃) δ 0.39–0.95 (m, b, 30 H), 1.89–2.10 (s, b, 4 H), 3.32 (s, b, 4 H), 4.41–4.96 (m, b, 24 H), 5.95–6.07 (b, 6 H), 6.27–6.59 (m, b, 12 H), 7.11–7.55 (m, b, 46 H); UV-vis (THF) λ_{max} = 383 nm.

Poly-9,9-bis[(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-methyl)-co-9,9-bis[2'-(ethyl)hexyl]-2,7-fluorene 14: yield 175 mg; ¹H NMR (250 MHz, CDCl₃) δ 0.53–0.93 (m, b, 30 H), 1.92–2.10 (s, b, 4 H), 3.19 (s, 4 H), 4.62 (s, b, 8 H), 4.79–4.89 (m, b, 48 H), 6.08 (s, w, 4 H), 6.47–6.57 (m, b, 38 H), 7.19–7.27 (m, b, 80 H), 7.42–7.61 (m, b, 6 H); UV-vis (THF) λ_{max} = 385 nm.

General Procedure for the Synthesis of Alternating 2,7-PF-Copolymers 16–18. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-bis(2'-ethylhexyl)fluorene (0.17 mmol), 0.17 mmol of the respective macromonomers **5–7**, and 5 mol % tetrakis(triphenylphosphine)palladium(0) were dissolved in a nitrogen atmosphere in 1.2 mL of degassed THF in a two-neck Schlenk-flask equipped with a reflux condenser. K₂CO₃ (0.75 mL of a 2 M solution) was added via a syringe, and the reaction mixture was degassed and purged with nitrogen three times. The two-phase system was then heated under vigorous stirring for 36 h at 95 °C. The workup included adding 10 mL of toluene and water, separating the phases and washing the organic phase three times with water. The organic phase was concentrated and precipitated in an excess of a 10:1 mixture of methanol:acetone. The precipitate was collected by filtration, intensively washed with acetone, and dried in a vacuum to afford the alternating copolymers as pale yellow powders.

Poly-9,9-bis[(3,5-bis(benzyloxy)benzyloxy)methyl]-alt-9,9-bis[2'-(ethyl)hexyl]-2,7-fluorene 16: yield 148 mg (75%); ¹H NMR (250 MHz, CDCl₃) δ 0.42–0.89 (m, 30 H), 1.83–1.99 (s, b, 4 H), 3.27–3.35 (m, 4 H), 4.56–4.64 (m, 8 H), 5.95–6.04 (m, 4 H), 6.29 (s, b, 2 H), 7.08–7.32 (m, b, 20 H), 7.48–7.64 (m, b, 6 H); UV-vis (THF) λ_{max} = 372 nm.

Poly-9,9-bis[(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-methyl]-alt-9,9-bis[2'-(ethyl)hexyl]-2,7-fluorene 17: yield 283 mg (82%); ¹H NMR (250 MHz, CDCl₃) δ 0.38–0.82 (m, b, 30 H), 1.82–1.97 (s, 4 H), 3.36–3.50 (s, b, 4 H), 4.56 (s, b, 8 H), 4.84 (s, b, 16 H), 6.06 (s, 4 H), 6.29 (s, 2 H), 6.44–6.49 (m, b, 12 H), 7.18–7.54 (m, 46 H); UV-vis (THF) λ_{max} = 388 nm.

Poly-9,9-bis[(3,5-bis(3,5-bis(3,5-bis(benzyloxy)benzyloxy)benzyloxy)-benzyloxy)-methyl]-alt-9,9-bis[2'-(ethyl)hexyl]-2,7-fluorene 18: yield 390 mg (90%); ¹H NMR (250 MHz, CDCl₃) δ 0.37–0.89 (m, b, 30 H), 1.82–2.01 (s, b, 4 H), 3.41 (b, 4 H), 4.50–4.95 (m, b, 56 H), 5.85 (b, 2 H), 6.02 (b, 4 H), 6.39–6.59 (m, b, 36 H), 7.12–7.32 (m, b, 80 H), 7.37–7.68 (m, 6 H); UV-vis (THF) λ_{max} = 374 nm.

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