Polyfluorenes with Polyphenylene Dendron Side Chains: Toward Non-Aggregating, Light-Emitting Polymers

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Abstract: A polyfluorene **12** has been prepared in which bulky polyphenylene dendrimer substituents suppress formation of long wavelength emitting aggregates, thus giving a polymer with pure blue emission. Absorption- and emission spectra and molecular modeling confirm that the bulky dendrimer side chains do not cause extra torsion between the fluorene units. New polyfluorenes with 9,9-diaryl substituents have been prepared to determine the minimum size of substituent necessary for aggregation suppression. An LED using **12** has been demonstrated to produce blue emission with onset voltages below 4 V.

Introduction

The development of blue-light emitting polymers has been the subject of intense academic and industrial research directed toward the fabrication of full color organic displays. Poly-*p*-phenylene (PPP) **1** and its derivatives have the large HOMO−LUMO energy gaps required for obtaining blue emission.[1,2] However, as yet, no organic polymer fully meets the desired criteria of long-term stability, high efficiency, and bright blue emission that are essential for commercially viable light emitting diodes (LEDs). The realization of electrically pumped organic laser devices is becoming feasible with conjugated materials[2b] if they are intrinsically stable and able to carry high electrical current densities. To synthesize well-defined PPPs, solubilizing groups have been attached to the phenylene repeating units.[3] The introduction of such side chains however, dramatically reduces the conjugation between the phenylene units with a resultant hypsochromic shift of the emisssion wavelength. One of the great advantages of polytetrahydropyrene (PTHP) **2**,[4] polyfluorene (PF) **3**,[5,6] poly-2,8-indenofluorene (PIF) **4**,[7] and ladder-type PPP (LPPP) **5**[8] in comparison to soluble PPPs is their ability to introduce solubilizing side chains without hampering the conjugation within the aromatic π-system (Scheme 1).

Scheme 1. Blue-Emitting Materials: Poly-*p*-phenylene (PPP) **1**, Polytetrahydrophenanthrene (PTHP) **2**, Polyfluorene (PF) **3**, 2,8-Polyindenofluorene (2,8-PIF) **4**, Ladder-Type Poly-*p*-phenylene (LPPP) **5**
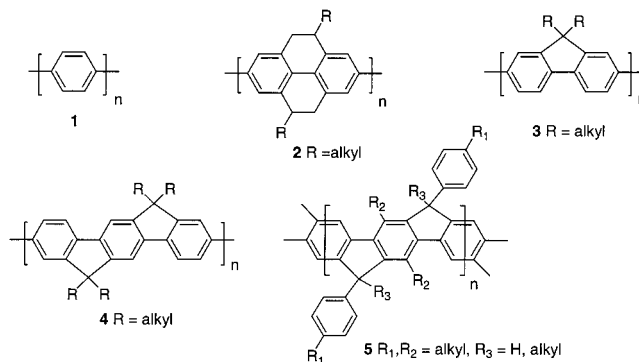
Although these polymers exhibit remarkably high photoluminescence quantum efficiencies as well as good thermal and chemical stability, their utility in electroluminescence (EL) devices is restricted by their tendency to form aggregates either during annealing or passage of current, leading to red-shifted and less efficient emission.[9−11] To minimize their tendency to aggregate, several statistical copolymers of **2**[12] and **5**[9] with various conjugated and nonconjugated monomers have been prepared. However, aggregate formation could not be fully prevented in these copolymers.

Miller et al.[13] have used semiflexible poly(benzyl ether) (Fréchet-type)[14] dendrimers as endcapping reagents in the Ni-

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(0)-mediated polymerization of 2,7-dibromo-9,9-dihexylfluorene to suppress aggregate formation in the resultant polymers. It was demonstrated that for polymers carrying fourth generation dendrimers intermolecular π-stacking and consequent aggregate formation were inhibited, but as yet there have been no devices reported using these polymers. In contrast to Fréchet-type dendrimers, polyphenylene (Müllen-type) dendrimers[15,16] are both shape-persistent and chemically stable. Therefore, they exclude π-stacking at lower dendritic generations than the Fréchet type. Their three-dimensional shielding ability has been demonstrated using perylene dyes as the core molecule.[17]

The idea of combining the encapsulation of a linear polymeric emitter with a dendritic structure led us to synthesize **12**, a 2,7-PF which carries in the side chain polyphenylene dendrons that not only serve as solubilizing groups but also permit spatial control of the polymer chain and hinder aggregation. To determine the minimal steric requirements for prevention of aggregation, we also prepared materials bearing side chains with varying degrees of bulk.

Results and Discussion

To synthesize the polymer **11** two different approaches were envisaged. Since the Diels−Alder reaction of tetracyclopenta-dienone with acetylene proceeds quantitatively, one might synthesize the precursor polymer **9** that could then be dendronized in a polymer-analogous step, although complexation of Ni(0) with the ethynyl groups might limit the reaction.[18,19] Alternatively, one could first synthesize the dendritic monomer **11** via the reaction of tetraphenylcyclopentadienone with the diacetylene **10** and then polymerize it under Ni(0)-mediated (Yamamoto) conditions. In this case the bulky substituents at the 9-position might limit the degree of polymerization.[20]

The reaction of 2,7-dibromofluorene **6** with 4-iodobenzyl bromide with sodium hydoxide as base and benzyltrimethyl-ammonium chloride as phase-transfer catalyst[21] produced the diaddition product **7** in 73% yield. A selective Pd(0)-mediated Hagihara−Sonogashira coupling[22] of **7** with trimethyl- or triisopropylsilylacetylene afforded the desired 2,7-dibromo-9,9-di(4-trimethylsilylethynylbenzyl)fluorenes **8** in good yields. Unfortunately, due to the interaction of the acetylene groups with the Ni(0), neither polymers nor oligomers of **8a** could be obtained from the Yamamoto polymerization. Using the much bulkier triisopropyl-substituted **8b** gave only oligomers with up to five repeat units in very low yield (Scheme 2).

Consequently the dendrimer forming Diels−Alder reaction had to be performed before the polymerization step. Deprotection of **8a** with potassium carbonate in methanol−THF produced an almost quantitative yield of the diacetylene **10**. The Diels−Alder reaction of **10** with tetraphenylcyclopentadienone in

Scheme 2. Synthesis of the Precursor Polymer **9**[a]
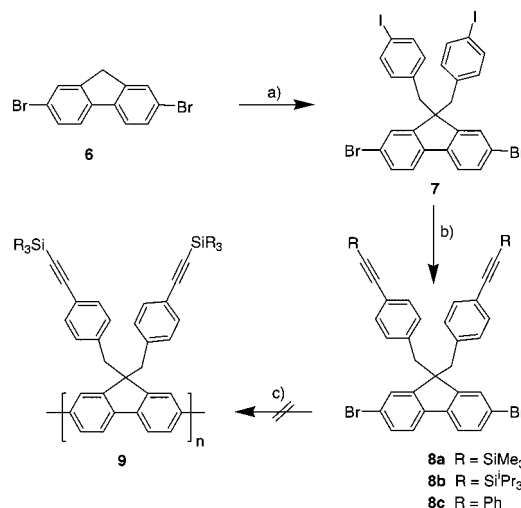
[a] a) NaOH (50%), 1-bromomethyl-4-iodo-benzene, benzyl trimethyl-ammonium chloride, DMSO, 2 h, rt, 73 %; b) RC₂H, Pd(PPh₃)₂Cl₂, Cu(I)I, THF, triethylamine, rt, 4 d, **8a**: 69 %, **8b**: 72 %, **8c**: 75%; c) Ni(cod)₂, cyclooctadiene (cod), 2,2′-bipyridyl, DMF, toluene, 3 d, 80°.

Scheme 3. Synthesis of the Shielded Polyfluorene **12**a[a]
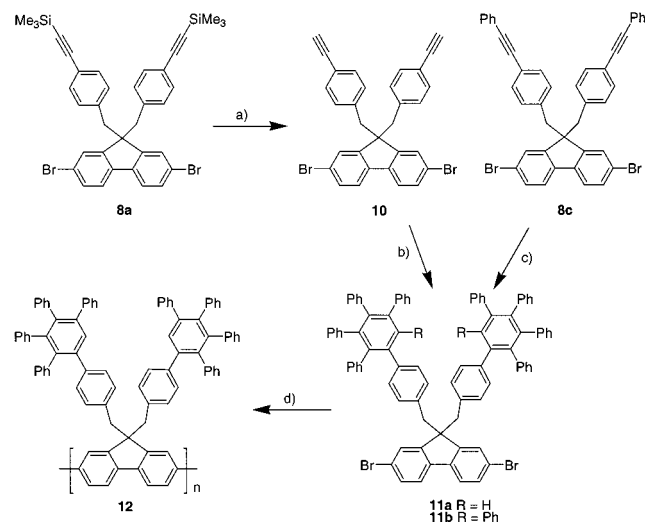
[a] a) K₂CO₃, THF, MeOH, 3 h, rt, 98 %; b) tetraphenylcyclopenta-dienone, o-xylene, 12 h, reflux, 82 %; c) tetraphenylcyclopentadienone, o-xylene, 5 d, reflux, 85 %; d) Ni(cod)₂, cod, 2,2′-bipyridyl, DMF, toluene, 3 d, 80 °C, bromobezene, 12 h, 80°, 75%.

reflushing o-xylene gave the monomer **11a** in 82% yield (Scheme 3). Coupling of **7** with phenylacetylene gave the bisdiarylacetyl-ene **8c** (72%), which reacted with tetraphenylcyclopentadienone to give the hexaphenyl monomer **11b** in 85% yield. The polymerization of **11a** occurred with Ni(0) under Yamamoto conditions for 3 days. To remove any remaining bromine endgroups, bromobenzene was added, and the mixture was allowed to react for an additional 12 h.. The resulting polymer **12** exhibits good solubility in toluene, benzene, and chlorinated organic solvents and shows excellent film-forming properties. Polymerization of **11b** did not proceed under these conditions.

Gel permeation chromatography (GPC) analysis (toluene, polystyrene standards) of **12** shows a monomodal distribution with a weight-average molecular weight (M_w) of 1.6 × 10⁵ g/mmol and a number-average molecular weight (M_n) of 4.6 × 10⁴ g/mmol (PD = 3.6), corresponding to 42 repeat units. However, it is well established that GPC misrepresents the M_n value of rigid rod polymers.[4] Bradley et al. determined an

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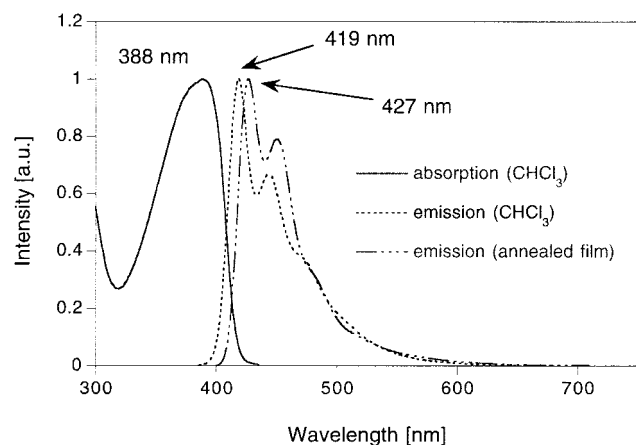
Figure 1. Absorption and emission spectra of polymer **12**.

overestimation factor of 2.7 for poly(9,9-dioctylfluorene) by comparing the M_n values of light scattering with those of the GPC.[23]

Thermogravimetric analysis (TGA) shows the excellent thermal stability of the polymer **12**. Initial weight loss (5%) was observed at 400 °C, with the main decomposition occurring at 426 °C (50%). Differential scanning calorimetry (DSC) exhibits only a phase transition at 248 °C. As polarizing optical microscopy shows no evidence for a thermotropic liquid crystalline phase, we attribute this to a glass transition. This result stands in contrast to the behavior of the octyl and ethylhexyl substituted polyfluorenes which show liquid crystal-line phases with transition temperatures at 156 and 167 °C, respectively.[24,25] The absence of a thermotropic phase and the high T_g are caused by the rigid pentaphenylbenzene groups and indicate the effective supression of the orientation in the polymer main chain.

The UV−vis spectrum of the polymer **12** in chloroform solution exhibits an absorption maximum at 387 nm, while the fluorescence spectrum ($\lambda_{exc} = 380$ nm) displays a vibronic fine-structure with two sharp bands at 419 and 443 nm (Figure 1). The value for absorption and emission maxima of the shielded PF **12** are similar to those for the alkyl substituted PF. This implies that the bulky groups in the 9-position do not increase the torsion angle in the conjugated polymer backbone. Such a limitation in conjugation would cause a hypsochromic shift in the absorption and emission spectra as has been demonstrated for copolymers of unsubstituted and 2,5-dihexyl substituted PPP.[26−28] The emission maximum ($\lambda_{exc} = 380$ nm) of a drop-casted film of the polymer **12** is only 6 nm bathochromically shifted in comparison to the wavelength of the dissolved polymer and does not show any sign of aggregate formation. In comparison the films prepared via spin coating of poly(9,9-dioctylfluorene) solution in chloroform by Bradly et al. exhibit two vibronic peaks at 427 and 448 nm, followed by a long featureless tail extending into the red.[11] The emission spectra from the film of polymer **12** did not change even after thermal

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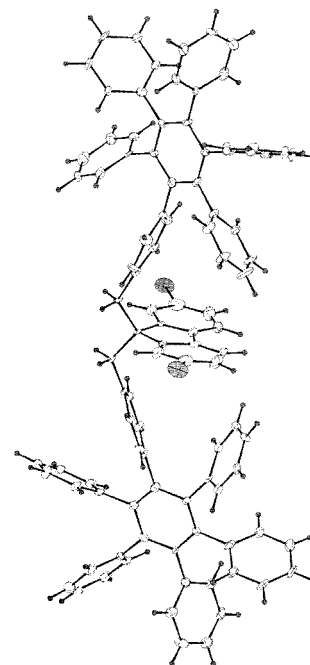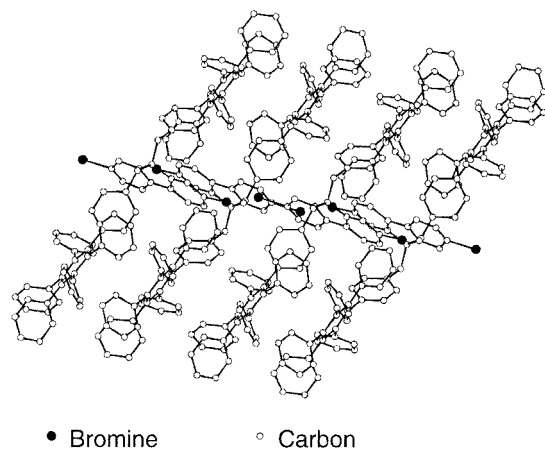
Figure 2. ORTEP diagram of **11b** determined by X-ray.

treatment at 100 °C for 24 h. Thermal treatment of poly(9,9-dioctylfluorene) causes an even higher bathochromic shift of the emission wavelengths (430, 452, 487, 520, and a shoulder at 560 nm).[11] The absorption and emission spectra of **12** did not change even after addition of methanol to the chloroform solution (chloroform/methanol: 1/1). These results indicate that the steric impact of the dendritic substituents suppresses the intermolecular π-stacking of the polymer without undesired blue-shifts in the emission spectra.

By contrast, in the first reported combination of dendrimers with conjugated polymers by Schlüter et al.,[29] who employed Fréchet-dendrons as side chains on PPP to prepare macrocyl-inders that formed micelles, vesicles, or membranes, the sterically demanding dendritic side chains led to strong torsion about the phenyl−phenyl bonds. Such increased torsional strains have been avoided by Aida et al.[30] and by Bao et al.[31] who made copolymers of poly(phenylene ethynylene) (PPE) and poly(phenylene vinylene) (PPV), respectively, with the dendritic side chains attached only to every second phenylene unit. In these cases, although no evidence of increased phenylene−phenylene torsion was seen, the aggregation was also not totally suppressed.

The packing of polymer **12** in the solid state was found to be amorphous by X-ray diffraction experiments, with two broad correlation peaks being observed at $d = 4.4$ Å (average C−C intermolecular distance) and 7.3 Å (average interchain dis-tance).[32] To better examine the steric effects of the dendrimer side chains in the solid state, the crystal structure of the hexaphenyl monomer **11b** was obtained. Single-crystals of **11b** were obtained by slow evaporation of chloroform from methanol−chloroform solution. The monomer builds up cocrystals with chloroform. Figure 2 shows the ORTEP plot of **11** accomplished by X-ray diffraction at 150 K.[32] The hexaphenylbenzene groups stand perpendicular to the fluorene unit. Therefore, the conceived polymer backbone is efficiently shielded by the dendritic side groups (Figure 3).

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(32) See Supporting Information.

● Bromine   ○ Carbon

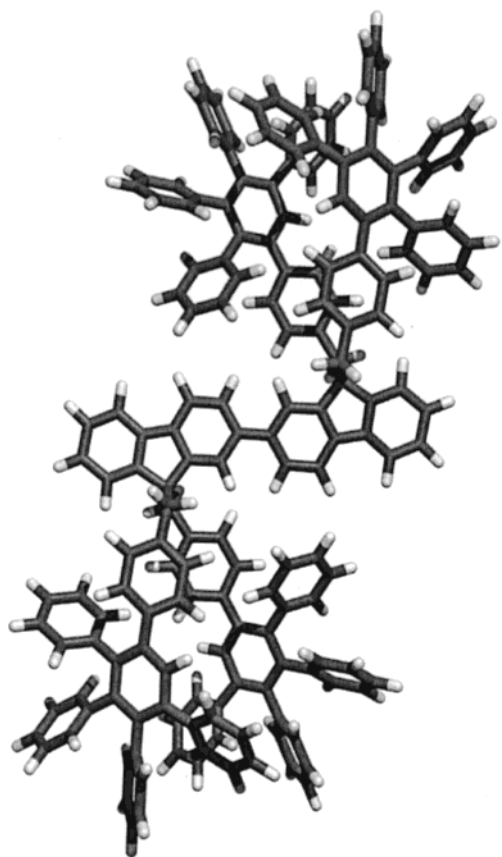**Figure 3.** Crystal structure of **11b** determined by X-ray.

Figure 4. Calculated structure of the dimer.

The structure of the monomeric fluorene building unit (**12**, *n* = 1) has been optimized using the MM2 (MM+) force field, as implemented in HyperChem 5.1 (Hypercube Inc.)*. A force field method was preferred over the application of quantum mechanics methods due to the prohibitively large number of atoms in the dendritic molecule. The minimized structure of the monomer was employed to build up the dimer of **11a**. After rotation around the bond connecting both fluorene units, several conformers were obtained. Figure 4 represents the conformer with the lowest energy, containing two twisted fluorene units with a torsion angle of 12° and dendrons in anti position from each another. The lowest-energy conformers for higher oligomers (tetramer, octamer) were obtained by connecting the required numbers of the lowest-energy dimer units and subsequent energy minimization of the resulting oligomers. The calculated structure for the octamer is shown in Figure 5.

Furthermore, MM+ minimization performed on an alkyl-substituted PF dimer and trimer indicated torsion angles of 15° along the polymer backbone. By contrast, reported calculations on the quantum mechanics level HF, 6-31G for unsubstituted fluorene dimer and trimer revealed a torsion angle in the range of 40°,[33a] but these results cannot be directly compared with ours, as different methods were used. Our calculated torsion angles are consistent with the observed absorption and emission spectra, as larger torsion angles would lead to a blue-shift in the absorption and emission maxima of **12** compared with other polydialkylfluorenes.[33b]

To further model the effects of the dendron side chains on the packing of the polymer chains, the properties of well-defined oligomers will need to be studied. To this end we have synthesized a dimer **19** (Scheme 4). Reaction of 2-bromofluorene **13** and 4-iodobenzylbromide under phase-transfer conditions gave the dialkylated product **14** in 83% yield. Hagihara−Sonogashira coupling with trimethylsilylacetylene followed by hydrolysis with potassium carbonate gave a mixture of the desired diacetylene **16** (60%) and the triacetylene **17** (15%) which were readily separated by chromatography on silica. The Diels−Alder reaction of **16** with tetraphenylcyclopentadiene proceeded smoothly to give the bisdendronised-mono-bromo-fluorene **18** in 85% yield. This material should be useful as a bulky endcapping reagent and in the synthesis of oligomers. Nickel(0) coupling of **18** gave the dimer **19** in 81% yield. Attempts are underway to obtain a crystal structure of **19** for comparison with the calculated structure.

The benzyl linkages in polymer **12** are potentially susceptible to photooxidation, thus introducing oxygenated functionality into the polymer, which is known to be the major cause of polymer degradation and device failure in conjugated polymer based LEDs.[2a] Also, it is not clear that the effective shielding of the backbone requires so bulky a substituent. To this end we have investigated the effects of introducing smaller substituents lacking benzyl protons into the 9-position. It was decided to prepare the poly(9,9-diarylfluorene)s **20**. The synthetic route to **20** is shown in Scheme 5. Treatment of methyl 4,4′-dibromobiphenyl-2-carboxylate **22**[34] with 2 equiv of phenyllithium gave the carbinol **23a** (70%) which was ring-closed with sulfuric acid in acetic acid to give 2,7-dibromo-9,9-diphenylfluorene **24a** in 89% yield. Yamamoto nickel(0) coupling of **24a** gave the desired poly(9,9-diphenyl-2,7-fluorene) **20a** in high yield. However, the polymer proved to be totally insoluble in all organic solvents tried. Soxhlet extraction over 5 days with toluene gave a small (10% of total mass) soluble fraction which from the mass spectrum was a mixture of the pentamer and tetramer. The UV−vis and fluorescence spectra showed maxima at 368 nm for absorption and at 415 and 435 for emission in toluene solution. Klärner and Miller[35] report emission maxima in THF solution of 425 and 434 nm for the tetramer and pentamer of 9,9-dihexylfluorene, while Lee and Tsutsui[36] report an emission maximum of 435 for the tetramer in chloroform solution. A MALDI-TOF analysis of the insoluble bulk material (details to be published separately[37]) shows a mass range from 1900 to 8000 Da, corresponding to degrees of polymerization

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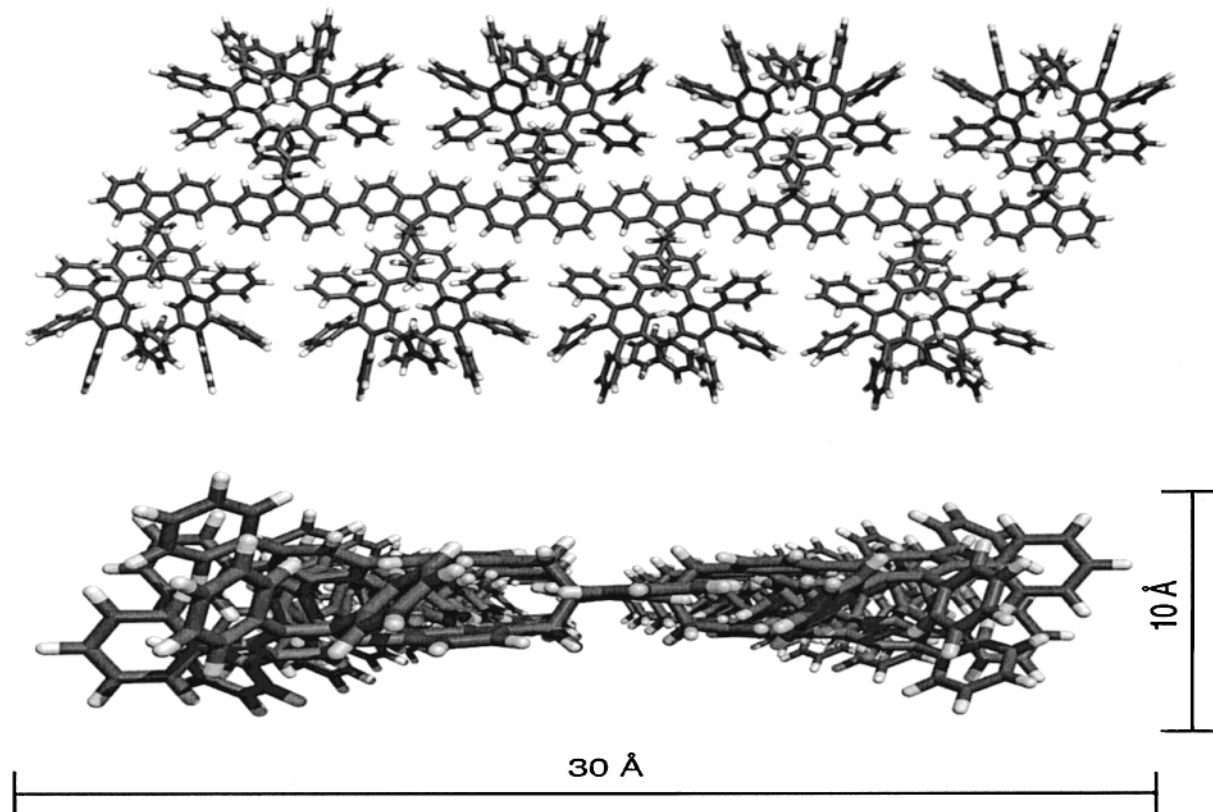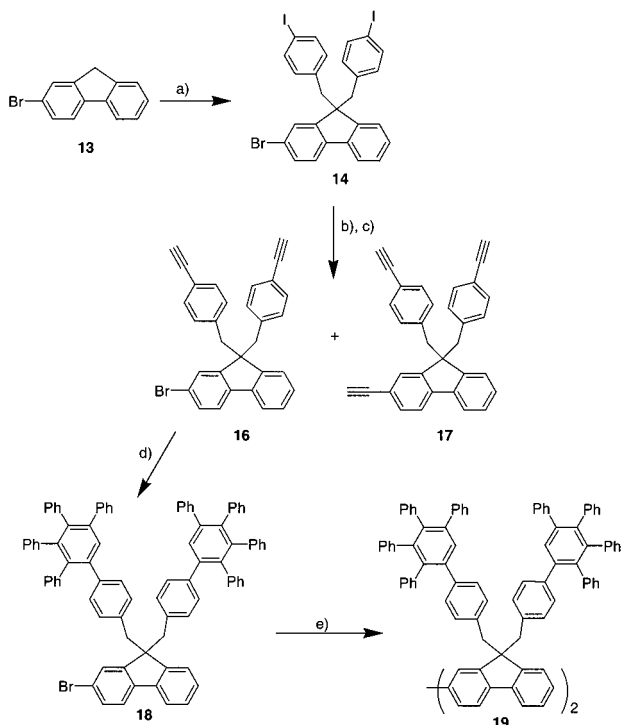
Figure 5. Calculated structure of the octamer.

Scheme 4. Synthesis of the Dimer **19**[a]

[a] a) NaOH (50%), 1-bromomethyl-4-iodo-benzene, tetrabutylammonium chloride, DMSO, 19 h, rt, 83 %; b) TMS−acetylene, Pd(PPh₃)₂Cl₂, Cu(I)I, THF, triethylamine, rt, 70 h; c) K₂CO₃, THF, MeOH, 4 h, rt, **16** (60%), **17** (15%); d) tetraphenylcyclopentadienone, *o*-xylene, 39 h, reflux, 85 %; e) Ni(cod)₂, cyclooctadiene (cod), 2,2′-bipyridyl, DMF, toluene, 46 h, 80°, 81%.
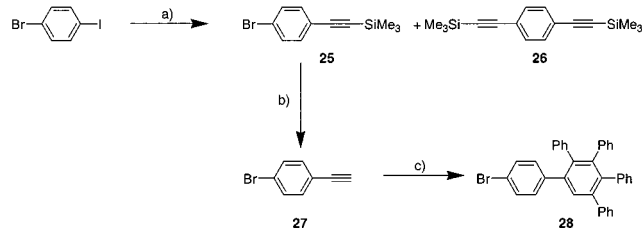
of up to 25 units. This suggests that the end of the polymer chain continued to be reactive even when it was no longer in solution. TGA showed **20a** to be extremely stable with less than

Scheme 5. Synthesis of Poly(diarylfluorene)s **20**[a]
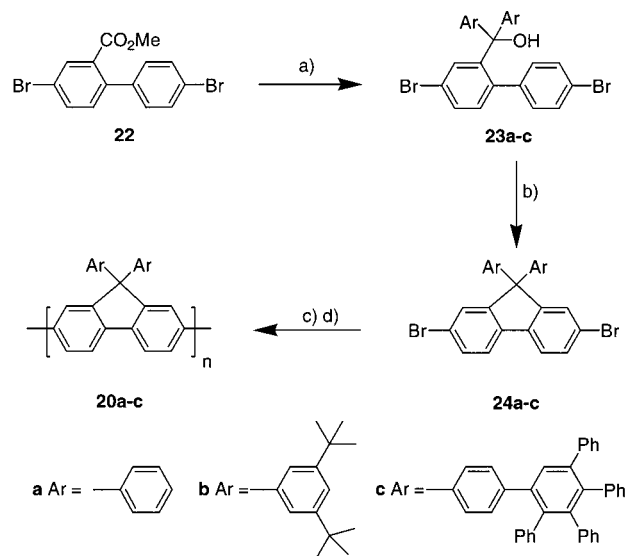
[a] a) 2 ArLi, THF, −78° to rt, 18 g, **23a** (94%); **23b** (79%); **23c** (69%); b) HOAc, H₂SO₄, 100°, 1 h, **24a** (89%); **24b** (73%); **24c** (82%); c) Ni(cod)₂, cyclooctadiene (cod), 2,2′-bipyridyl, DMF, toluene, 1−3 d, 80°; d) PhBr, 1 d, 80°.

5% weight loss up to 500° and major weight loss (10%) occurring only at 520°. DSC performed up to 250° showed no phase transitions. Obviously, introduction of solubilizing substituents onto the aromatic rings is required to give solubility. Reaction of **22** with 2 equiv of the lithium derived from 3,5-bis(*tert*-butyl)bromobenzene gave the carbinol **23b** (77%) which was ring-closed with acid to give 2,7-dibromo-9,9-di(3,5-bis-*tert*-butylphenyl)fluorene **24b** in 73% yield. Polymerization of **24b** by the Yamamoto method for 24 h, followed by endcapping with bromobenzene, gave the desired polymer **20b** which was

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Scheme 6. Synthesis of the Bromodendron **28**[a]

[a] a) TMS−acetylene, Pd(PPh$_3$)$_2$Cl$_2$, Cu(I)I, THF, triethylamine, rt, 18 h, **25** (91%), **26** (7%); b) K$_2$CO$_3$, THF, MeOH, 5 h, rt, 78%; c) tetraphenylcyclopentadienone, *o*-xylene, 19 h, reflux, 78 %.

soluble in chloroform, dichloromethane, toluene, and THF. GPC showed a weight-averaged molecular weight of 11 300 Da with a polydispersity of 1.84. This material was also very thermally stable with a 10% mass loss between 250 and 490 °C, followed by a loss of 30% between 490 and 550 °C. DSC performed up to 250 °C showed no phase transitions. The absorption maximum for **20b** in chloroform solution was at 382 nm, while the fluorescence spectrum (λ_{exc} = 370 nm) shows two sharp bands at 416 and 439 nm. The fluorescence spectrum for a film dropcast from chloroform showed a slight bathochromic shift, with maxima at 423 and 445 nm and a small tail into the yellow. After annealing at 100 °C for 24 h, however, the intensity of emission from the longer-wavelength region (500−600 nm) of the spectrum increased. Although the aggregation appears to be much weaker than for poly(9,9-dialkylfluorene)s, it is clear that the bis(di-*tert*-butylphenyl) substituents are insufficiently bulky to completely suppress aggregation. Consequently, we prepared the polymer **20c** with dendronised substituents. Hagihara−Sonogashira coupling of 1-bromo-4-iodobenzene with a slight excess of trimethylsilylacetylene for 18 h, gave largely the monoaddition product **25**[22c] (91%), which was separated from the diadduct **26**[22b] (7%) by chromatography on silica. Hydrolysis of **25** with potassium carbonate in methanol gave 4-bromophenylacetylene **27**[22c] (78%). The Diels−Alder reaction with tetraphenylcyclopentadienone produced the bromodendron **28** in 78% yield (Scheme 6). Lithiation and addition to **22** afforded the carbinol **23c** (69%) which was ring-closed to the desired monomer **24c** in 82% yield. Polymerization of this gave the desired polymer **20c** which was soluble in dichloromethane, chloroform, toluene, and THF. GPC in toluene revealed a weight-averaged molecular mass of 63 000, with a polydispersity of 1.28. This material showed exceptional themal stability with a less than 1% mass loss prior to the primary mass loss of 16% at 570°. DSC performed up to 250° again showed no phase transitions. The UV−vis spectrum in toluene exhibited an absorption maximum at 384 nm, while in the emission spectrum (λ_{exc} = 320 nm) there appeared a single maximum at 414 nm, with a shoulder at 432 nm. The solid-state fluorescence spectrum showed a small bathochromic shift with distinct maxima at 421 and 445 nm. No long wavelength emission was detected after annealing at 100 °C for 24 h. These results suggest that the minimum degree of side chain bulk required to avoid aggregation is intermediate between the bis(di-*tert*-butylphenyl) and bis-dendron substituents of **20b** and **20c** respectively. A more precise determination of the critical size criteria for aggregation suppression will require synthesis of polymers with side chains of intermediate size.

Photoinduced Absorption and Electroluminescence Measurements on the Polymer 12. Figure 6 shows the PL emission and PL excitation spectrum of poymer **12** in the solid state. The PL emision spectrum is characterized by a maximum at 2.9 eV (425 nm), and two resolved vibronic features at 2.7 (460
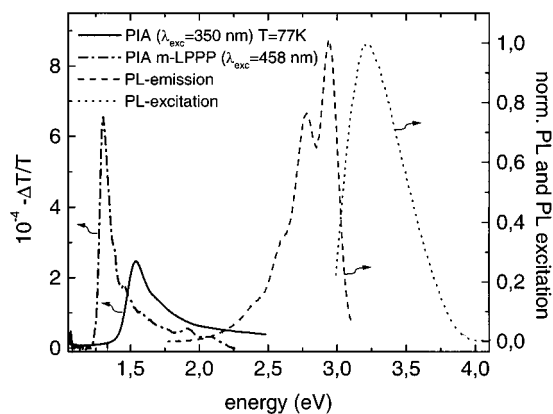

Figure 6. Photoluminescence emission (dotted line) and excitation (dashed line) spectra (T = 300 K) of a solid film of polymer 12 together with the photoduced absorption spectrum of polymer **12** (laser excitation = 350 nm) and the photoinduced absorption spectrum of a solid film of polymer **5** taken at 77 K.

nm) and 2.55 eV (487 nm). The absorption spectrum does not exhibit any vibronic replica but is composed of only one broad feature with a maximum at 3.2 eV (388 nm). Furthermore, it was found that the onset of the absorption feature is less steep than that of the emission feature. This is characteristic of many π-conjugated polymers and arises from the distribution of the effective conjugation lengths. The energy of the π−π* transition depends on the conjugation length; the distribution of energies broadens the absorption and obscures the vibronic structure of any particular segment.[38,39] By contrast PL emission only probes the lowest energetic sites. Hence, the combination of a large Stokes shift as observed for the polymer **12** and vibronic structure in the emission spectrum arises from exciton migration prior to fluorescence.[40]

The PIA spectrum of polymer **12** (Figure 6) reveals one broad feature at 1.6 eV (775 nm) which extends up to 2.5 eV (496 nm). By comparison, the PIA spectrum of polymer **5** (R$_1$ = C$_{10}$H$_{21}$, R$_2$ = C$_6$H$_{13}$, R$_3$ = H), which represents the planar limit of a polyfluorene system and thus has a very well-defined electronic structure due to the absence of rotational disorder, exhibits two distinct features at 1.3 eV (956 nm) and 1.9 eV (654 nm). From a comparison with doping and charge induced absorption measurements the feature at 1.3 eV was attributed to excited-state absorption of triplet excitons−a triplet−triplet transition ($T_1 \rightarrow T_n$)−and the band at 1.9 eV to a polaron P2 bands.[41a] Two bands are also seen in the PIA spectra of polyindenofluorenes **4**[41b] (1.5 and 2.1 eV−829 and 592 nm) and poly(9,9-dialkylfluorene)s **3**[41c] (1.65 and 2.1 eV−753 and 592 nm). Owing to its similarity we therefore attribute the PIA band at 1.6 eV for polymer **12** to a $T_1 \rightarrow T_n$ transition. The absence of a distinct strong polaronic absorption feature in the

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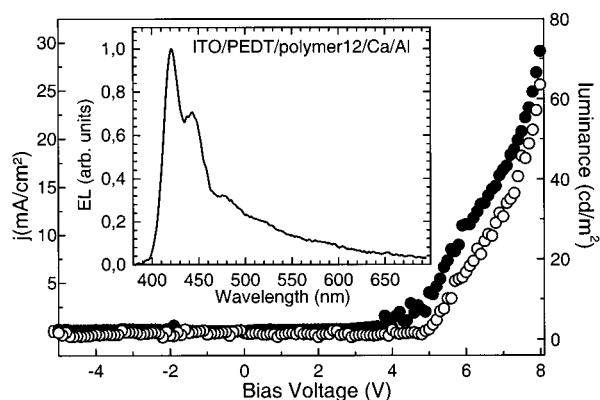
Figure 7. EL emission (inset), current−voltage (solid circles), and luminance−voltage (open circles) characteristics of a typical electroluminescence device [device area: 4 mm², device structure: glass/ITO/PEDT:PSS/polymer**12**/Ca/Al]; ITO: indium−tin-oxide, PEDT/PSS: poly(3,4-ethylenedioxythiophene/polystyrene sulfuric acid.

tail of the $T_1 \rightarrow T_n$ feature for **12** is yet another indication for the isolation of the polymer chains due to the bulky dendrimer side chains. In contrast to triplet excitons, which are intrinsically long-lived metastable states due to the forbidden transition to the ground state, polarons require extrinsic stabilization or trapping as provided by nonisolated polymer chains to be observed in continuous wave PIA experiments. We plan further thermally stimulated current experiments and photoluminescence detected magnetic resonance[41c] on **12** to determine the defect density and their energy level positions, as well as the interaction of these trapped states with singlet excitons.

Figure 7 depicts the EL spectrum (inset) and the current− voltage and luminance−voltage characteristics of an electrolu-

minescent device fabricated with polymer **12** as the active layer, ITO/PEDT:PSS for the anode and calcium (70 nm)/aluminum (300 nm) for the cathode. The average thickness of the polymer films was 100 nm, and of the PEDT:PSS layer was 60−70 nm, and the active area of the LEDs was 3 × 3 mm. The electroluminescence spectrum of **12** closely matches the PL spectrum (Figure 7), with an emission maximum at 420 nm (2.95 eV); some minor differences may be ascribed to the presence of the PEDT layer and consequent morphological differences. All measurements on the devices were undertaken in an argon atmosphere. The device stability and lifetimes have not been studied systematically, but all devices showed reproducible current/voltage characteristics and electroluminescence spectra with no sign of aggregation provided the driving voltage did not exceed ∼12 V. To test the effect of molecular weight on the efficiency of devices using **12**, we extracted the powder with cyclohexane for 100 h at room temperature to obtain a low-molecular weight fraction. Both this and the remaining high-molecular weight fraction were dissolved in toluene for spin-coating films. The devices using the high-molecular weight fraction were found to give more reproducible results. AFM pictures (Figure 8) of films of the two fractions cast from solution onto polished silicon wafers show that while the low-molecular weight fraction forms isolated particles of height about 40 nm embedded in polymer film islands (Figure 8a), the high-molecular weight fraction produces reproducibly homogeneous films with an average surface roughness of about 2 nm (Figure 8b). Due to the high ionization potential of polyfluorenes ($I_p \approx$ 5.8 eV) and thus a significant energy barrier of about 0.8 eV with ITO ($I_p \approx$ 5 eV) it is quite difficult to inject holes directly from ITO into polyfluorenes (PFs). Therefore a level matching
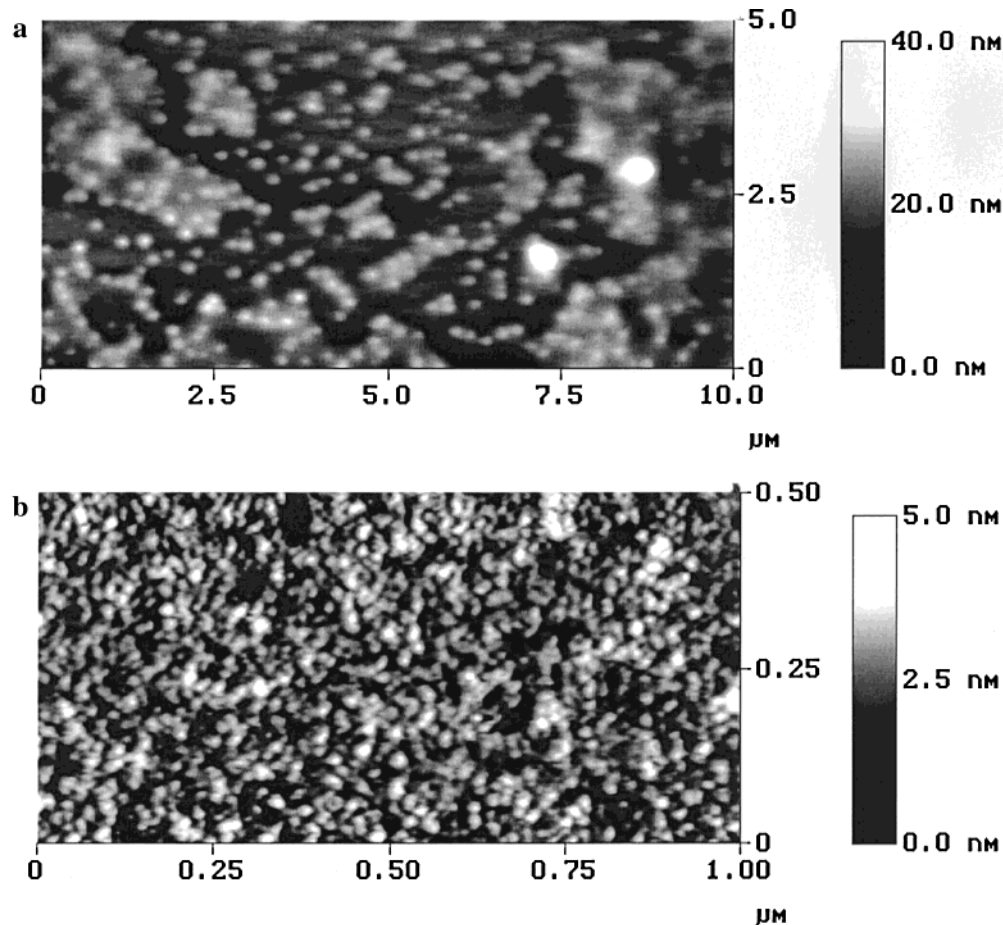

Figure 8. AFM pictures of (a) low-molecular weight, (b) high-molecular weight fractions of polymer **12** cast on polished silicon wafers.

layer (PEDT:PSS, Bayer BAYTRON *P*) was inserted between the ITO and the layer of **12**. Injecting electrons into PFs is much easier, since the work function of metals such as calcium differs by only a few tenths of an eV from the LUMO energy level. The onset of the electroluminescence emission was observed between 3 and 4 V. The maximum luminance for for bright blue emission as depicted in the inset of Figure 7 was found to be 400cd/m^2 at a driving voltage of $\sim$10 V. For this device we found the maximum efficiency to be $\sim$0.2 cd/A at a driving voltage of 7.5 V wih a current density of 22 mA/cm^2. This corresponded to a maximum power efficiency of 0.16 lm/W. These device related parameters are very similar to those found for other devices fabricated from polyfluorenes (PFO),[42] except that in our devices we typically found lower onset voltages. The onset voltage for EL in ITO/HTL/PFO/Ca devices is generally observed above 5 V.[42,43] However, if polyfluorene with sufficently high molecular weight is applied as the emission layer in ITO/PEDT:PSS/PFO/Ca-LEDs, onset voltages below 3 V can be obtained.[44] This is in agreement with the performance parameters of EL devices fabricated with our polymer **12**, proving that attaching the dendrimer side chains reduces the aggregation of the polymer chains without altering their electronic properties. Recently, Meerholz[45] has reported that poly(4,4′-methoxybithiophene) is an even better polymeric hole-injecting anode for polyfluorene-based LEDs than PEDT, and it is possible devices using this anode would show even better performances.

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Conclusions

In this paper we have established synthetic approaches to nonaggregating polyfluorenes **12** and **20c** using pentaphenylene dendrons as shielding and solubilizing groups and made some initial studies into their electronic properties. The emission spectra of the polymer films reveal the efficiency of the side chains in preventing π-stacking without causing undesirable blue-shifts in the absorption or emission spectra. Comparison of these polymers with others bearing slightly less bulky side chains has given some indication as to the minimum side chain size requirements for complete aggregation inhibition in py-fluorenes. The synthetic routes developed are capable of extension to give other materials with bulky, possibly function-alized, side chains, and to the synthesis of other polymers, for example, 2,8-PIF **4** with dendritic side chains.

Electroluminescent devices have been constructed using the dendronised polymer **12**, and their luminance and electrical characteristics have been found to be comparable with those of alkylated polyfluorenes. This further indicates that the suppres-sion of aggregation has been acheived without sacrificing the desirable properties of the polyfluorene backbone.

Supporting Information Available: Experimental section; UV−vis absorption and PL fluorescence spectra for polymers **20b** and **20c**; X-ray diffraction spectra for polymer **12** (PDF). An X-ray crystallographic file (CIF) for compound **11b**. This material is available free of charge via the Internet at http.//pubs.acs.org.

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