4736 *Chem. Mater.* **2004,** *16,* 4736−4742

Novel 2,7-Linked Carbazole Trimers as Model Compounds for Conjugated Carbazole Polymers

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Received January 7, 2004. Revised Manuscript Received May 12, 2004

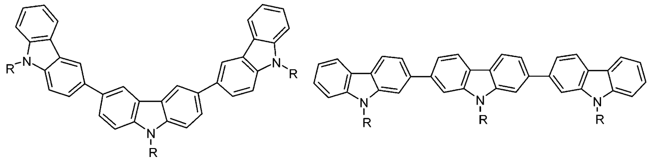
In this paper we present a new synthesis for *N*-alkylated 2,7-dibromocarbazoles, from which 2,7-linked carbazole trimers have been synthesized by Suzuki cross coupling. The compounds were characterized regarding their thermal, optical, and electrochemical properties and compared to analogous fluorene trimers, which also have been prepared by Suzuki reactions. The carbazole and fluorene trimers exhibit thermal stabilities of more than 300 °C and are able to form molecular glasses. Only one of the carbazole trimers is crystalline. Both carbazole and fluorene trimers exhibit a bright blue fluorescence with a maximum at 393 nm and show similar absorption characteristics. Cyclovoltammetric experiments revealed the electrochemical stability of the fluorene trimers. Their HOMO and LUMO levels are at −5.6 and −2.5 eV, respectively. In contrast to the fluorenes, the 2,7-linked carbazole trimers showed nonreversible oxidations in the CV experiments.

I. Introduction

Due to their extended p-electron systems conjugated polymers have attracted the interest of many researchers in recent years. Such conjugated systems are featured with some very interesting electronic and optical properties and have a high potential to be used as materials in organic light-emitting diodes (OLEDs),[1−3] field effect transistors,[4] photovoltaic devices,[5,6] and solid-state lasers.[7] As there is high commercial interest especially in the field of OLEDs rapid development has been made in this area in the past few years.

Over the years a large number of conjugated polymers based on aromatic building blocks have been prepared. In 1990 Friend et al. used poly(*p*-phenylenevinylene) (PPV) as the light-emitting polymer in an OLED for the first time.[8] A number of soluble PPV derivatives have meanwhile been synthesized[3] and commercialized.[9] Some years later alkylated polyfluorenes, which were developed by Dow Chemical in the early 1990s, were introduced as blue emitters for OLEDs.[2] Some fluorene homo- and copolymers exhibit liquid crystalline phases, which can be aligned and used in polarized OLEDs[10,11] as well as in organic field effect transistors with high mobilities.[12]

Chart 1. Molecular Structures of 3,6-Linked (Left) and 2,7-Linked (Right) Carbazole Trimers



Compared to the conjugated polymers described above, polycarbazoles have been much less studied. Several reports exist on the polymerization of 3,6-dihalogenated carbazoles, but there is only one paper which describes the formation of high-molecular-weight poly(*N*-alkyl-3,6-carbazoles).[13] Recently we have reported that besides the polymer a large amount of macrocycles are formed in this polymerization reaction.[14] In poly(3,6-carbazoles), the bond angle between two carbazole units is much smaller than 180°, and for that reason 3,6-linked polycarbazoles are not able to form liquid crystalline phases (Chart 1). In contrast, 2,7-substituted carbazoles should be ideal building blocks for rigid, rodlike molecules.

Making 2,7-substituted carbazole monomers is much more difficult, compared to 3,6-substituted compounds, since the 3- and 6-positions of the carbazole are activated by the nitrogen atom. All kinds of electrophilic substitution reactions will take place in these positions. In fact, only a few 2,7-substituted carbazole compounds

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10.1021/cm040142i CCC: $27.50

are known today. Leclerc et al. recently published a route for the synthesis of such molecules.[15–17] However, the monomer synthesis consists of several steps, and only moderate yields are obtained. Nevertheless, Patil et al. recently used this route for a new conjugated ladder-type polymer that contains 2,7-substituted carbazole moieties (LPPPC).[18]

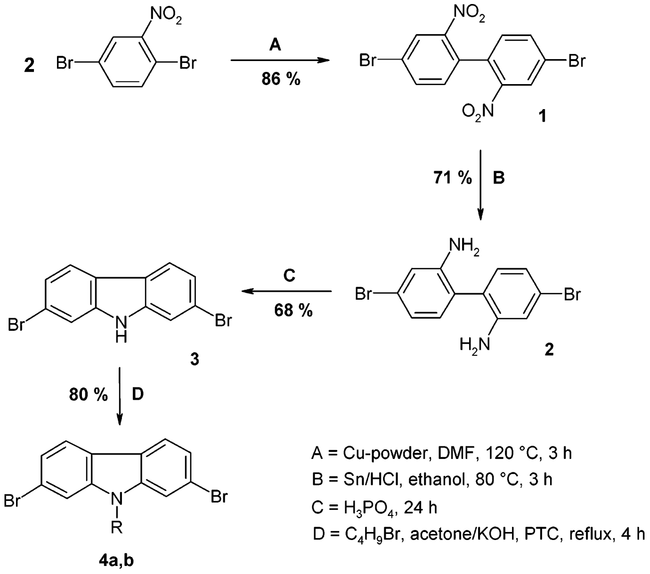
In this paper we present an improved synthesis for *N*-alkyl-2,7-dibromocarbazoles and *N*-alkyl-2-bromocarbazoles. From these two building blocks two different 2,7-linked carbazole trimers have been prepared via Suzuki cross coupling. For comparison, we have made fluorene trimers with identical alkyl substituents. The thermal, optical, and electrochemical properties of the new 2,7-linked carbazole trimers are compared to those of their fluorene counterparts.

II. Results and Discussion

Preparation of *N*-Alkylated Carbazole Trimers. Over the years, a large number of compounds containing 3,6-substituted carbazole rings have been synthesized and characterized, whereas only very few 2,7-linked carbazoles appear in the literature. The complex preparation of 2,7-substituted carbazoles might be the major reason for that. Recently Leclerc et al. published a five-step synthesis for *N*-octyl-2,7-diiodocarbazole with an overall yield of 14%.[17] In this paper we present an improved route for the preparation of *N*-alkylated 2,7-dibromocarbazoles. Our synthesis consists of four steps with a 42% yield of 2,7-dibromocarbazole. In the course of our studies, an improved route yielding 50% 2,7-dibromocarbazole[19] has been published.

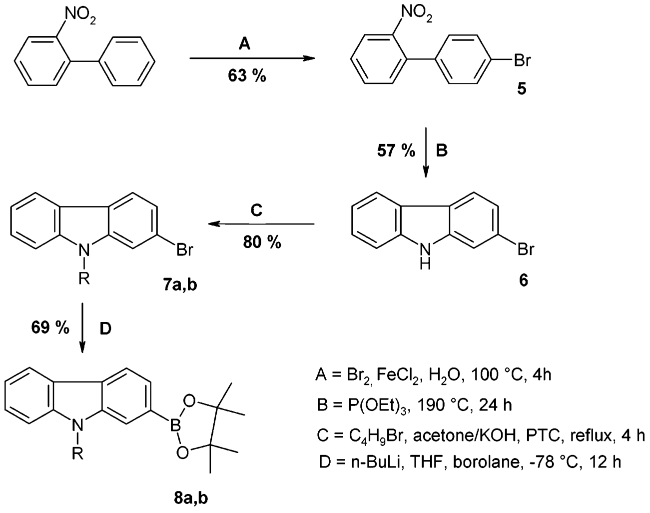
Chart 2 shows the synthesis of *N*-alkylated 2,7-dibromocarbazoles. The first step consists of an Ullmann coupling reaction of 2,5-dibromonitrobenzene with activated copper,[20,21] which yielded 86% **1**. Before the ring closure, the nitro groups had to be reduced to amines. The reduction was carried out with tin/HCl. The ring closure was made by heating the diamine **2** in concentrated H_3PO_4 to 190 °C for 24 h. The crude 2,7-dibromocarbazole was recrystallized to yield 68% **3**. A relatively high overall yield of 42% was achieved for 2,7-dibromocarbazole. In the next step the carbazole monomer was *N*-alkylated with *sec*-butyl bromide or isobutyl bromide, respectively. The reactions were carried out in acetone/KOH with tetrabutylammonium hydrogen sulfate as phase-transfer catalyst.

Chart 2. Synthesis of *N*-Alkyl-2,7-dibromocarbazoles



	R
4a	sec-butyl
4b	iso-butyl

Chart 3. Synthesis of 2-Bromocarbazole[22] and the Borolanes 8a and 8b



	R
7a / 8a	sec-butyl
7b / 8b	iso-butyl

The second building blocks for the carbazole trimers are borolanes from *N*-alkylated 2-bromocarbazoles. Steps A and B in Chart 3 show the synthesis of 2-bromocarbazole, which we have already described.[22] 4-Nitrobiphenyl was brominated in position 2′ using $FeCl_2$ as catalyst. The bromination was followed by a ring closure reaction in triethyl phosphite to obtain 2-bromocarbazole (**6**). The carbazole was *N*-alkylated with *sec*-butyl or isobutyl bromide in the same way as described for **4a** and **4b**. Step D in Chart 3 describes the synthesis of the borolanes **8a,b** that were used in the following Suzuki cross coupling reactions. For the borolane syntheses BuLi was added slowly at −78 °C to **7a/7b**, and the mixture was stirred for 15 min before 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The borolanes **8a** and **8b** were purified by column chromatography.

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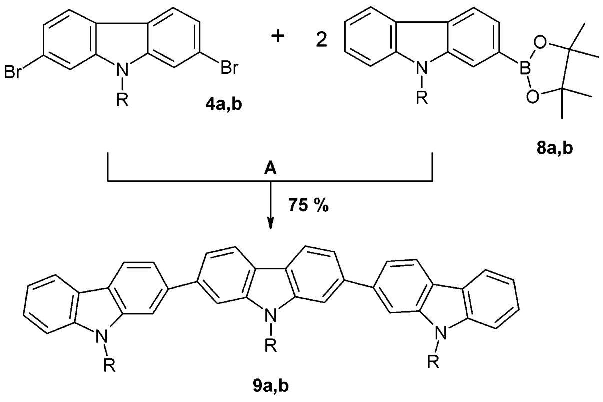
Chart 4. Synthesis of the Carbazole Trimers via Suzuki Cross Coupling Reaction



A = P(o-tol)$_3$, Pd(OAc)$_2$, toluene, aq. K$_2$CO$_3$, PTC, 50 °C, 12 h

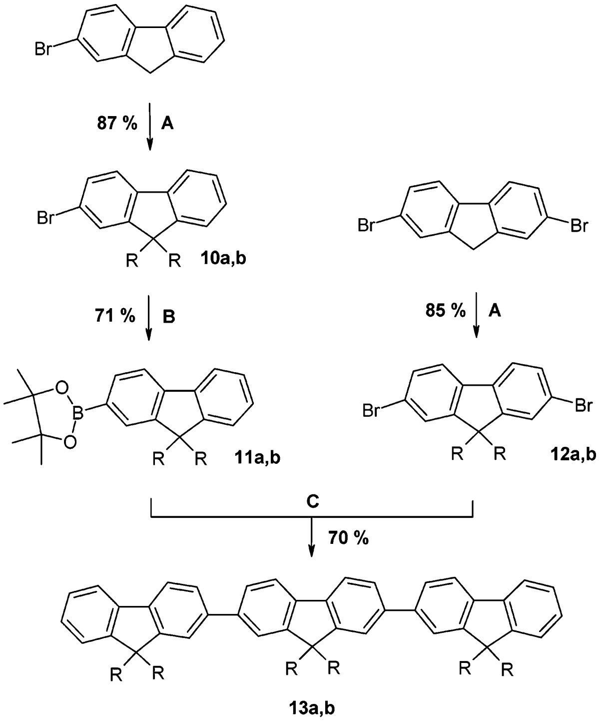
	R
4a / 8a / 9a	sec-butyl
4b / 8b / 9b	iso-butyl

We decided to use Suzuki cross coupling reactions for the preparation of the carbazole and fluorene trimers as it is known as an efficient tool for unsymmetrical aryl−aryl couplings. Chart 4 shows the Suzuki coupling reaction of 2,7-dibromo-9-alkylcarbazoles **4a**,**b** with 2-oxaborolanyl-9-alkylcarbazoles **8a**,**b**. The reactions were carried out in a two-phase system of toluene and aqueous potassium carbonate, with trimethylbenzylammonium chloride as phase-transfer catalyst (PTC). For the carbazole trimer syntheses we used a mixture of Pd(OAc)$_2$ and P(*o*-tol)$_3$ as catalyst. A relatively high yield of 75% was achieved for the *N*-*sec*-butyl-2,7-carbazole trimer (**9a**) after purification by medium-pressure liquid chromatography (MPLC). The synthesis of **9b** gave a yield of 70%.

Preparation of Dialkylated Fluorene Trimers. To compare the physical properties of the carbazole trimers **9a**,**b**, we prepared the analogous fluorene trimers with isobutyl and *sec*-butyl substituents. The synthetic route to the fluorene trimers is shown in Chart 5.

Three different reactions were used for their preparation. Reaction A is the alkylation of mono- and dibromofluorenes. The reactions were carried out in a two-phase system of DMSO and aqueous sodium hydroxide with an alkyl bromide, tetra-*n*-butylammonium chloride, and triethylbenzylammonium chloride as phase-transfer catalysts. The alkylfluorenes **10a**,**b** and **12a**,**b** were obtained with a yield of about 80%. In the second step borolanes **11a**,**b** were prepared from the monobromofluorenes (reaction B). The boronylations were carried out in the same way as described for the carbazoles **8a**,**b**. The key step in the synthesis of the fluorene trimers is a Suzuki cross coupling reaction (step C). We used the same conditions for coupling the alkylated dibromofluorenes **12a**,**b** with the fluorene borolanes **11a**,**b** as for the carbazole monomers except the catalyst system. In this case we used freshly prepared Pd(PPh$_3$)$_4$ as catalyst. Purification by MPLC yielded 72% fluorene trimer **13a**. An overview of the four different carbazole and fluorene trimers is shown in Chart 6.

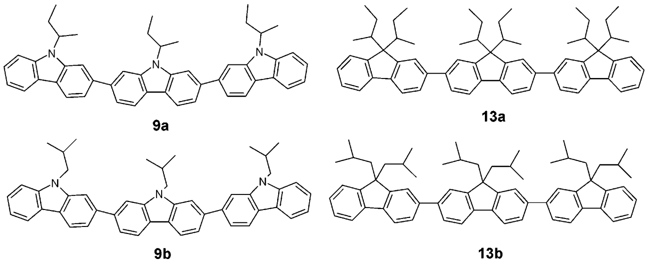
Chart 5. Synthetic Route to the Fluorene Trimers 13a and 13b



A = C$_4$H$_9$Br, 25 M NaOH, PTC, DMSO, 80 °C, 16 h
B = n-BuLi, THF, borolane, -78 °C, 12 h
C = Pd(PPh$_3$)$_4$, PTC, toluene, 2N K$_2$CO$_3$, 50 °C, 12 h

	R
10a / 11a / 12a / 13a	sec-butyl
10b / 11b / 12b / 13b	iso-butyl

Chart 6. Overview of the Carbazole (Left) and the Fluorene (Right) Trimers



Characterization. All trimers were characterized by IR, ^{1}H NMR, and mass spectroscopy. Purity was checked by gel permeation chromatography (GPC) with a column set suitable for the separation of oligomers. After purification by MPLC no impurities are visible in the GPC diagram. It turned out that MALDI-TOF mass spectrometry is an ideal tool for the investigation of model compounds such as the conjugated carbazole and fluorene trimers. In Figure 1, the MALDI spectrum of the fluorene trimer **13b** is shown. Only the M$^+$ peak at 831 Da is visible in the spectrum, which was taken from a sample that contains only **13b** and no matrix to assist ionization. Furthermore, the intensity of the laser beam was diminished to approximately 1% of its original energy. Since molecules such as the carbazole trimers **9a**,**b** and the fluorene trimers **13a**,**b** strongly absorb ionizing laser light of 337 nm and are able to form

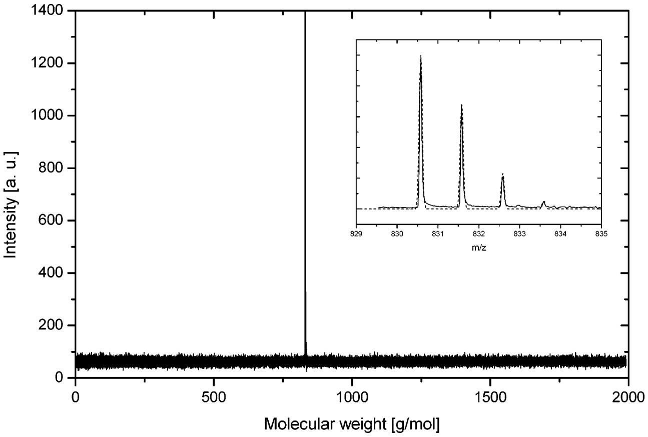


Figure 1. MALDI-TOF spectrum of fluorene trimer **13b**. The spectrum was taken without a matrix and with a laser intensity of only 1% of the original laser output. The inset shows the calculated (---) and the measured (—) isotope distributions of **13b**.

Table 1. Thermal Characteristics of the Fluorene and Carbazole Trimers

compd	T_g [a] (°C)	T_m [a] (°C)	T_{dec} [b] (°C)
9a	124		355
9b		285	330
13a	114		310
13b	73		315

[a] Determined by DSC, scan rate 10 °C/min, N_2 atmosphere. [b] Onset of decomposition determined by TGA, heating rate 10 °C/min, N_2 atmosphere.

extremely stable radical cations, no signals except that of the M^+ ion are visible. This makes MALDI-TOF a powerful tool for the analysis of model compounds and oligomeric mixtures.

Properties of the Trimers. Both fluorene trimers **13a**,**b** and the carbazole trimer with the *sec*-butyl side groups (**9a**) are soluble in common organic solvents such as tetrahydrofuran, toluene, acetone, and chloroform, whereas the carbazole trimer with isobutyl side groups (**9b**) became almost insoluble once it had crystallized after purification.

The thermal properties of the trimers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements. TGA shows that all trimers exhibit a high thermal stability (Table 1). In nitrogen decomposition starts above 300 °C. With an onset of decomposition at 355 °C the carbazole trimer **9a** with *sec*-butyl substituents shows the highest thermal stability of the four trimers. In general, the carbazole trimers have a slightly higher decomposition temperature than the fluorenes.

DSC measurements (Figure 2) show that both fluorene trimers **13a**,**b** and one carbazole trimer (**9a**) are able to form molecular glasses, whereas the carbazole trimer with isobutyl substituents (**9b**) is crystalline. In the DSC trace of the carbazole trimer with isobutyl side groups (**9b**) melting is observed at 285 °C. The peak at 170 °C in the cooling curves is probably due to crystallization of the compound. During the heating cycle another small exothermic peak appears, which we tentatively assign to recrystallization.

The carbazole trimer **9a** behaves totally differently. Only the glass transition at 124 °C can be seen in repeated DSC runs. The glass transition temperatures of the fluorene trimers **13a**,**b** range from 73 to 114 °C (Table 1). The different behavior of the two carbazole trimers shows that small changes in the chemical structure may lead to a dramatic change of the morphology. In the case of the carbazole trimers, the ability of **9a** to form a molecular glass and the possibility to prepare thin films from **9a** both by evaporation and from solution are highly desirable for applications in OLEDs and OFETs. Although the trimers have a rigid, rodlike architecture, no liquid crystalline phases can be seen in the DSC traces and in the polarizing microscope. Probably the trimers are not long enough to exhibit LC phases.

Both the carbazole and the fluorene trimers absorb light in the range from 300 to 380 nm. The absorption maxima are between 351 and 356 nm for all four compounds (Table 2). As an example, the UV–vis spectra of carbazole trimer **9a** and the fluorene trimer **13a** are shown in Figure 3. The molar extinction coefficients are very similar for the two different trimers (see Figure 3). This shows that the 2,7-linked carbazole trimers are highly conjugated molecules like their fluorene counterparts.

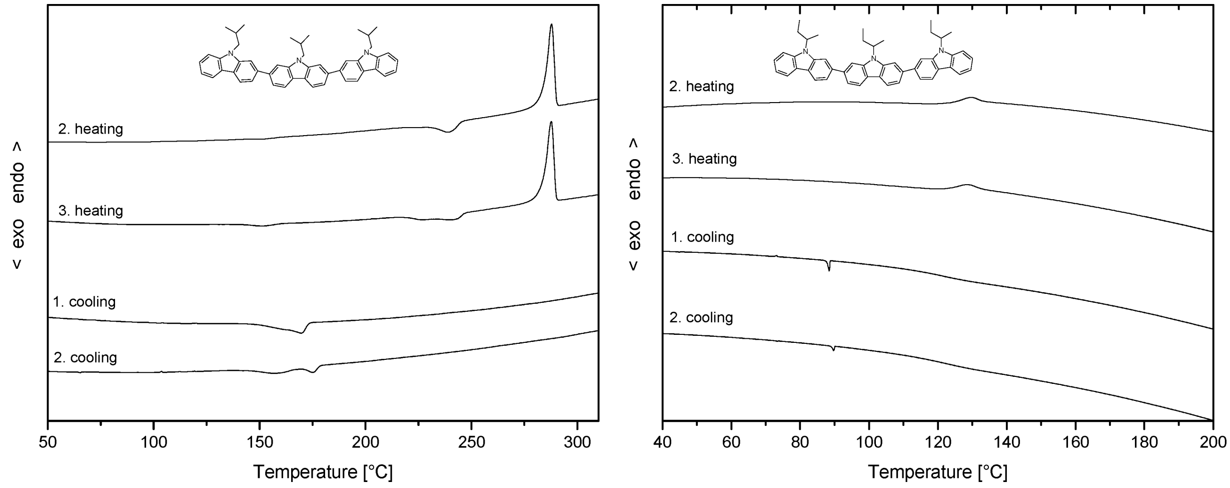


Figure 2. DSC curves of crystalline **9b** (left) and of glass-forming **9a** (right).

Table 2. Optical Properties of the Fluorene and Carbazole Trimers

compd	$\lambda_{\text{max,fluorescence}}$[a] (nm)	$\lambda_{\text{max,absorption}}$[b] (nm)	λ_{ae}[c] (nm)
9a	394.4	354	391
9b	394.6	356	390
13a	392.8	352	388
13b	391.6	351	390
3,6-linked carbazole trimer	420.2	307	340

[a] Fluorescence spectra measured in 10^{-5} M THF solution, excitation wavelength 345 nm. [b] Absorption spectra measured in THF solution. [c] Absorption edge.

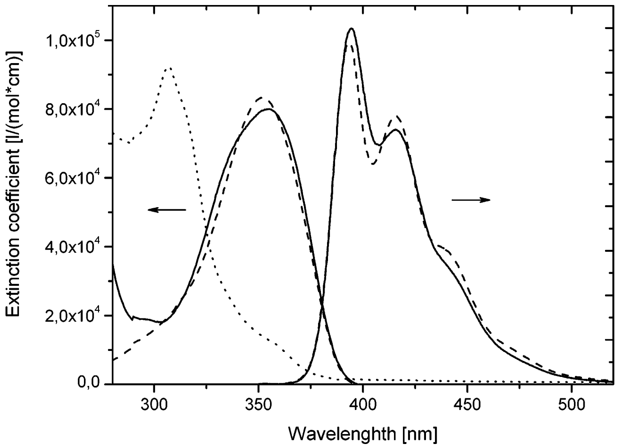
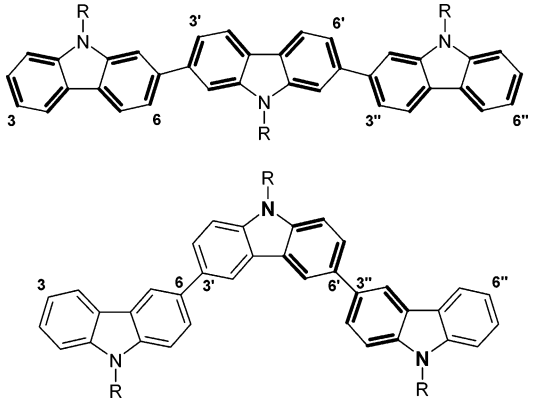


Figure 3. Absorption and fluorescence spectra of 10^{-5} M THF solutions of the carbazole trimer **9a** (—) and the fluorene trimer **13a** (---). For comparison, the absorption spectrum of 9,9′,9″-triethylhexyl[3,3′;6′,3″]tercarbazole (···) is shown. It was also taken from a 10^{-5} M THF solution.

Chart 7. Conjugation of Six Phenyl Rings in a 2,7-Linked Carbazole Trimer and Conjugation of Only Two Rings in the 3,6-Linked Trimer ("Meta" Linkage)



Recently we have published the synthesis of a 3,6-linked carbazole trimer[23] (Chart 7). For comparison the absorption spectrum is included in Figure 3. The 3,6-linked trimer has an absorption maximum at 307 nm which is 45 nm lower than the maximum of the 2,7-linked trimer **9a**.

In the 3,6-linked carbazole trimers there is no conjugation over large distances.[24] The conjugated segment can probably be best described as a substituted 1,4-diaminobiphenyl structure.[25] The different conjugated segments in the two carbazole trimers are shown in Chart 7.

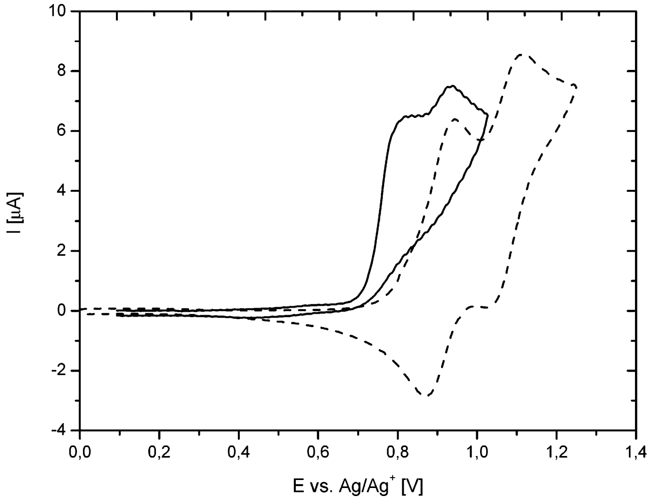


Figure 4. Cyclic voltammetric measurement of the carbazole trimer **9a** (—) and the fluorene trimer **13a** (---), measured at 25 °C at a scan rate of 50 mV/s vs Ag/Ag$^+$ in acetonitrile with TBAPF$_6$ as supporting electrolyte.

The fluorescence spectra of the carbazole and fluorene trimers are also included in Figure 3. The shape and the maxima of the fluorescence curves are almost identical for the 2,7-carbazole and the fluorene trimers. At 393 and 415 nm two maxima of fluorescence are detected. Like the fluorene trimers, the carbazoles **9a**,**b** exhibit a strong blue fluorescence, which is unusual for carbazole-containing compounds. The 3,6-linked carbazole trimer (Chart 7) shows only weak, pale blue fluorescence. Furthermore, the fluorescence spectra in Figure 3 show characteristic structures. In the case of **9a**, the separation between the peaks at 440 and 415 nm is 1369 cm^{-1}, and between 415 and 393 nm the separation is 1349 cm^{-1}. These values are close to those expected for a carbazole ring vibration.

The electrochemical stability of the trimers was examined by cyclic voltammetry (CV). All measurements were carried out at 25 °C in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) with a glassy carbon working electrode. The oxidation potentials were measured vs Ag/AgNO$_3$ as a reference electrode. The experiments were calibrated with the standard ferrocene/ferrocenium redox system. The CV curves of fluorene trimer **13a** and the carbazole compound **9a** are shown in Figure 4. **9b** could not be measured because of its insolubility.

The CV curve of the fluorene trimer **13a** shows two fully reversible oxidation peaks at 0.90 and 1.12 V. Repeated oxidation and reduction cycles did not change the redox potentials of the fluorene compounds. Taking −4.8 eV as the HOMO level for the ferrocene/ferrocenium redox system,[26] a HOMO of −5.7 eV was calculated for **13a** (Table 3). With the band gap (ΔE) from the absorption spectrum, a LUMO value of −2.5 eV is estimated for **13a**.

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Table 3. Oxidation Potentials and HOMO and LUMO Values of Carbazole and Fluorene Trimers

compd	E_{ox}(vs Ag$^+$) (V)	E_{ox}(vs Fc) (V)	HOMO (eV)	ΔE^a (eV)	LUMO (eV)
9a	0.62			3.2	
9b^b				3.2	
13a	0.90	0.055	−5.7	3.2	−2.5
13b	0.91	0.050	−5.7	3.2	−2.5
3,6-linked carbazole trimer	0.45	0.043	−5.2	3.7	−1.6

[a] Optical band gap taken from the absorption spectra. [b] No CV measurement possible due to low solubility.

Evaluation of CV measurements for the carbazole trimer **9a** leads to a completely different result. In the first redox cycle two oxidation peaks at 0.78 and 0.90 eV can be detected, but there are no corresponding reduction signals at all. Obviously the electrochemical oxidation of 2,7-linked carbazole compounds is not reversible, meaning that such compounds are not electrochemically stable. In the 3,6-linked carbazole trimer mentioned above, the oxidation is reversible as in the fluorene trimers **13a**,**b**. An explanation for the different electrochemical behavior of these compounds would be that in the case of the 2,7-linked carbazole trimers the radical cation is extended over the whole molecule (Chart 7). Due to the donor effect of the carbazole nitrogen, the 3,6/3′,6′- and 3″,6″-positions are highly activated and can undergo dimerization reactions.[15] In contrast, the conjugated system in the 3,6-substituted trimer is best represented by a benzidine-like structure (Chart 7). The corresponding radical cation is localized in this benzidine-like segment, and therefore, the 3- and 6″-positions are much less reactive compared to those of the 2,7-linked trimer. In contrast, the fluorene trimers **13a**,**b** are electrochemically stable since the 3- and 6-positions of the fluorene rings are not activated.

III. Conclusions

We have developed a new synthesis for *N*-alkylated 2,7-dibromocarbazoles. From these building blocks a series of 2,7-linked carbazole trimers and the corresponding fluorene trimers have been prepared. All compounds possess thermal stabilities of more than 300 °C. Three of the four trimers show glass-forming properties with glass transition temperatures in the range from 73 to 124 °C. The *N*-isobutyl-substituted carbazole trimer is crystalline with a melting point at 285 °C. The optical properties of the carbazole and fluorene trimers are very similar. They absorb light in the range from 300 to 380 nm and show a bright blue fluorescence. In electrochemical measurements the carbazole and the fluorene trimers behave differently. The fluorene trimers are electrochemically stable; the HOMO and LUMO energy levels are about −5.7 and −2.5 eV, respectively. The oxidation of the 2,7-linked carbazole trimers is irreversible.

Electrochemical stability can eventually be obtained by blocking the sensitive 3- and 6-positions of the carbazole units, which is the goal of our current work. Due to their high degree of conjugation and their bright blue fluorescence, stable 2,7-linked carbazole compounds should be interesting materials in OLEDs and OFETs.

IV. Experimental Section

Material Synthesis. All chemicals and reagents were used as received from Aldrich. Tetrahydrofuran (THF) and toluene were distilled over sodium before use. The synthesis of 2-bromocarbazole has been reported elsewhere.[22]

4,4′-Dibromo-2,2′-dinitrobiphenyl (1). A mixture of 2,5-dibromonitrobenzene (12 g, 43 mmol) and activated copper powder (8.6 g, 150 mmol) was stirred in 80 mL of DMF for 3 h at 120 °C. After cooling to room temperature, 150 mL of toluene was added. The mixture was stirred for a few minutes before the brown residue was filtered off. The organic layer was washed with water and brine, the solution dried over Na_2SO_4, and the solvent evaporated. Recrystallization from ethanol/toluene (4:1) yielded 7.3 g (85%) of **1** as a light brown solid (85%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.15 (d, 2H), 7.82 (dd, 2H), 8.38 (d, 2H). IR (KBr): ν (cm^{-1}) 3092 (aromatic CH), 1930, 1600 (NO_2), 1533, 1462, 1345, 1277, 1156, 1102, 1003. MS: *m/z* ([M$^+$]) 402.

4,4′-Dibromo-2,2′-diaminobiphenyl (2). While a mixture of **1** (2.0 g, 4.9 mmol), 10 mL of concentrated HCl, and 30 mL of ethanol was stirred, small portions of tin powder (2.4 g, 20.2 mmol) were added. The reaction mixture was heated to reflux for 3 h. The mixture was poured into 300 mL of cold water, and 2 M NaOH solution was added, until pH 8 was reached. The solution was extracted several times with diethyl ether. The organic layer was washed with water and dried with Na_2SO_4 and the solvent evaporated. The residue was purified by column chromatography on silica gel using methylene chloride/hexane (30:1) as the eluent to yield **2** (1.2 g, 72%) as a colorless solid. ^{1}H NMR (250 MHz, d_6-DMSO): δ (ppm) 4.99 (br, N−H, 4H), 6.80 (dd, 2H), 6.88 (d, 2H), 7.01 (d, 2H). IR (KBr): ν (cm^{-1}) 3419, 3390 (NH_2), 3284, 3183 (aromatic CH), 1630, 1577, 1551, 1494, 1476, 1407, 1297, 1284, 1255, 1080, 998, 861. MS: *m/z* ([M$^+$]) 342.

2,7-Dibromocarbazole (3). A mixture of **2** (0.7 g, 2.1 mmol) and 15 mL of concentrated H_3PO_4 was refluxed at 190 °C for 24 h. The crude product was filtered off and washed with water thoroughly. The residue was diluted with toluene and filtered over silica gel. After the solvent was evaporated, the product was recrystallized from toluene/hexane (10:1). Yield: 0.4 g (60%) of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.37 (dd, 2H), 7.58 (d, 2H), 7.88 (d, 2H), 8.09 (br, N−H). IR (KBr): ν (cm^{-1}) 3399 (NH), 1599 (carbazole), 1442 (carbazole), 1420, 1324, 1240, 1052, 998, 891, 857, 804. MS: *m/z* ([M$^+$]) 325.

2,7-Dibromo-9-*sec*-butylcarbazole (4a). A 1.8 g (5.5 mmol) sample of **3** was dissolved in 25 mL of acetone. The phase-transfer catalyst $[(C_4H_9)_4N]HSO_4$ (0.1 g, 0.3 mmol), 2-bromobutane (1.0 mL, 9.3 mmol), and KOH powder (0.5 g, 8.9 mmol) were added. The mixture was stirred and refluxed for 4 h. After the reaction was finished, the solvent was evaporated and the residue suspended in diethyl ether. The precipitate was filtered off and the organic phase washed with water and dried over Na_2SO_4 before the solvent was evaporated. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (8:1) as the eluent to yield **4a** (1.2 g, 57%) as a white solid. ^{1}H NMR (250 MHz, d_6-DMSO): δ (ppm) 0.65 (t, 3H), 1.55 (d, 3H), 1.95 (m, 1H), 2.15 (m, 1H), 4.85 (m, 1H), 7.32 (dd, 2H), 7.91 (d, 2H), 8.12 (d, 2H). IR (KBr): ν (cm^{-1}) 2957 (alkyl), 2872, 1584 (carbazole), 1477, 1452 (carbazole), 1379, 1329, 1268, 1217, 1132, 1110, 1056, 998, 954, 923. MS: *m/z* ([M$^+$]) 381.

The alkylation of 2,7-dibromocarbazole (**3**) and 2-bromocarbazole (**6**) with isobutyl bromide was carried out as described for compound **4a**.

2,7-Dibromo-9,9-di-*sec*-butylfluorene (12a). 2,7-Dibromofluorene (15 g, 46 mmol) was dissolved in 120 mL of DMSO. To this solution were added 1 g of triethylbenzylammonium chloride and 1 g of tetra-*n*-butylammonium chloride as phase-transfer catalyst. After the addition of 60 mL of a 25 N NaOH solution, 2-bromobutane (27.3 mL, 25 mmol) was added dropwise. The reaction mixture was stirred at 100 °C. After 16 h water was added until the two phases mixed. The solution was extracted with diethyl ether, the ether phase washed with water and dried with Na_2SO_4, and the solvent evaporated. After recrystallization from methanol, 10.8 g (54%) of a white powder was obtained. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.71−1.18 (m, 16H), 2.08 (m, 2H), 7.36−7.45 (m, 6H). IR

(KBr): ν (cm^{-1}) 3065, 2957, 2929 (alkyl), 1567, 1447 (fluorene), 1410, 1380, 1299, 1246, 1061, 1004, 905. MS: *m/z* ([M$^+$]) 437.

The alkylation of 2,7-dibromofluorene and 2-bromofluorene with isobutyl bromide was carried out as described for **12a**.

9-*sec*-Butyl-2-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)carbazole (8a). A 2 g (6,6 mmol) sample of 2-bromo-9-*sec*-butylcarbazole (**7a**) was dissolved in absolute THF under argon. The solution was cooled to −78 °C before 4.8 mL of *n*-BuLi (1.6 M solution in hexane) was added dropwise. The reaction mixture was stirred for 20 min, before 1.6 mL (7.9 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h before it was poured into ice−water. The solution was extracted with diethyl ether and the organic phase washed with brine and dried with Na_2SO_4 before the solvent was evaporated. Purification by column chromatography with hexane/acetic ester (15:1) as eluent yielded 1.6 g (70%) of white crystals. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.79 (t, 3H), 1.40 (s, 12H), 1.70 (d, 3H), 2.04 (m, 1H), 2.33 (m, 1H), 4.76 (m, 1H), 7.18 (t, 1H), 7.44 (m, 1H), 7.52 (d, 1H), 7.69 (d, 1H), 7.95 (s, 1H), 8.13 (m, 2H). IR (KBr): ν (cm^{-1}) 3080 (CH_3), 2982, 2948 (alkyl), 2884, 1621, 1561 (carbazole), 1477, 1438 (carbazole), 1361, 1325, 1271, 1255, 1141, 1079, 965, 926, 857, 822. MS: *m/z* ([M$^+$]) 349.

The borolane syntheses for **8b**, **11a**, and **11b** were carried out as described above.

Synthesis of the Trimers. *9,9′,9′′-Tri-sec-butyl[2,2′;7′,2′′]-tercarbazole (**9a**).* **4a** (0.34 g, 0.9 mmol) and **8a** (0.7 g, 2.1 mmol) were dissolved in 15 mL of toluene. A 2 M K_2CO_3 solution (5 mL) and 0.1 g of trimethylbenzylammonium chloride were added. The reaction mixture was degassed by three freeze/thaw cycles before 9 mg of $Pd(AcO)_2$ and 36.5 mg of tri-*o*-tolylphosphine were added under argon. The mixture was stirred for 16 h at 50 °C. The reaction mixture was poured into ice−water, extracted with diethyl ether, and dried with Na_2SO_4. After evaporation of the ether the product was purified by MPLC with a hexane/tetrahydrofuran mixture (4:1) as eluent. A 450 mg (75%) yield of **9a** was obtained as a white powder. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.86 (m, 9H), 1.76 (m, 9H), 2.05 (m, 3H), 2.41 (m, 3H), 4.80 (m, 3H), 7.15 (m, 1H), 7.29 (m, 1H), 7.45 (m, 2H), 7.61 (m, 6H), 7.80 (m, 4H), 8.21 (m, 6H). IR (KBr): ν (cm^{-1}) 3043, 2971 (alkyl), 2936, 2871, 1637, 1556 (carbazole), 1442 (carbazole), 1328, 1221, 994, 813, 746. MALDI-TOF MS: *m/z* 665. Anal. Calcd for $C_{48}H_{47}N_3$ (665.9): C, 86.58; H, 7.11; N, 6.31. Found: C, 85.58; H, 7.22; N, 7.05.

*9,9′,9′′-Triisobutyl[2,2′;7′,2′′]tercarbazole (**9b**)* was synthesized as described above. The compound started to crystallize after it had been purified by MPLC. Crystalline **9b** is almost insoluble in common organic solvents.

*9,9,9′,9′,9′′,9′′-Hexa-sec-butyl[2,2′;7′,2′′]terfluorene (**13a**)*. **12a** (3.1 g, 7.1 mmol) and 2-(9,9-di-*sec*-butylfluoren-2-yl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**11a**) (6.3 g, 15.4 mmol) were dissolved in 50 mL of toluene. A 2 M K_2CO_3 solution (31 mL) and 0.1 g of trimethylbenzylammonium chloride were added. The reaction mixture was degassed by three freeze/thaw cycles before 60 mg of $Pd[P(C_6H_5)_3]_4$ was added under argon. The reaction mixture was refluxed for 16 h before it was poured into ice−water and extracted with diethyl ether. The organic layer was dried with Na_2SO_4, the solvent evaporated, and the crude product purified by MPLC (eluent hexane/acetonitrile, 60:1). A 4.2 g (72%) yield of **13a** was obtained as a white powder. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.83 (m, 43H), 1.38 (m, 5H), 2.32 (m, 6H), 7.4−7.8 (m, 20H). IR (KBr): ν (cm^{-1}) 3059, 2962 (alkyl), 1463 (fluorene), 1449, 1379, 1343, 1253, 1156, 1089, 1003, 971. MALDI-TOF MS: *m/z* 831. Anal. Calcd for $C_{63}H_{74}$ (831.3): C, 91.03; H, 8.97. Found: C, 90.60; H, 9.05.

*9,9,9′,9′,9′′,9′′-Hexaisobutyl[2,2′;7′,2′′]terfluorene (**13b**)* was synthesized in the same way as described above.

The purity of all trimers was checked by GPC using a column set suitable for the separation of oligomers and by MALDI-TOF mass spectrometry.

Measurements. ^{1}H NMR spectra were recorded with a Bruker AC 250 (250 MHz) apparatus. All data are given as chemical shifts δ (ppm) downfield from the $Si(CH_3)_4$ peak. The IR spectra were recorded using a Bio-Rad Digilab FTS-40. The UV−vis spectra were recorded with a Hitachi U-3000 spectrophotometer. Emission spectra were obtained from a Shimadzu spectrofluorophotometer RF-5301PC. Conventional mass spectra were recorded with a Finnigan MAT 8500 (70 eV) with a Varian MAT 112S. A Bruker Reflex III apparatus with a high-mass detector was used to record the high-resolution MALDI-TOF mass spectra. TGA was performed on a Perkin-Elmer TAS-409 at a heating rate of 10 K/min under N_2. For DSC measurements a Perkin-Elmer DSC-7 apparatus was used (heating/cooling rate 10 K/min). The purity of the target compounds was checked with a Waters GPC system for oligomers. The system included a Waters 410 differential refractometer using THF as eluent and polystyrene standards. CV measurements were performed with a glassy carbon working electrode (0.2 mm) in a three-electrode potentiostat configuration from EG&G Princeton Applied Research.

Acknowledgment. We thank M. Lanzendörfer for the MALDI spectra and J. Ostrauskaite for the CV measurements. We are grateful to the BASF AG and the BMBF (POLITAG program) for financial support.

CM040142I