Novel Star-Shaped Triphenylamine-Based Molecular Glasses and Their Use in OFETs

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Six novel star-shaped compounds with a triphenylamine core and carbazole or fluorene sidearms have been synthesized by Suzuki cross-coupling. The star-shaped molecules are able to form molecular glasses. They were characterized regarding their thermal, optical, and electrochemical properties. The new compounds were tested as organic semiconductors in solution processed organic field-effect transistors (OFETs). Mobilities of 3×10^{-4} cm^2/(V s), high on/off ratios of up to 10^5, and low threshold voltages were obtained. The new materials show very small hysteresis and an exceptionally high stability under ambient conditions.

1. Introduction

Among organic materials, vitrification was regarded for a long time to be mainly a privilege of polymers. Today a large number of amorphous low molar mass materials, so-called organic glasses, are known. Especially those with conjugated π-electron systems have attracted the interest of many research groups.[1,2] Due to their remarkable electronic and optical properties, such amorphous compounds have a high potential as materials in optoelectronic devices. In fact, molecular glasses are widely used in photocopiers,[3] laser printers, and organic light-emitting diodes (OLEDs).[4]

In electronic and optoelectronic devices organic materials are usually used as thin films. From molecular glasses such films can be prepared both from solution, e.g. drop casting, spin coating, and ink jet printing,[5] or by vapor deposition from the gas phase. Compared to polymers, amorphous molecular materials have a number of advantages. Molecular glasses are monodisperse compounds and therefore can be highly purified by column chromatography or sublimation. This is very important for optoelectronic materials since a small amount of impurities is often detrimental for the electrical properties, e.g., the charge carrier mobility.

In the past, we have studied a number of organic glasses with star-shaped architectures.[6−10] We found that star-shaped molecules with three sidearms have excellent glass-forming properties.[8,9] Amorphous phases from such molecules showed excellent long-term stability under ambient conditions, which means that the tendency to crystallize is very low. The glass transitions of these compounds are at sufficiently high temperatures to allow their application in electronic devices.

An upcoming field of application is organic electronics where π-conjugated molecular glasses are used as active material in organic field-effect transistors (OFETs). In this paper we describe the synthesis of six novel star-shaped molecules with a triphenylamine core and carbazole or fluorene sidearms. The molecules are shown in Chart 1. Compounds **13**−**16** form molecular glasses which have been successfully tested as semiconductors in OFETs.

2. Results and Discussion

Synthesis of the Carbazole and Fluorene Sidearms and the Triphenylamine Core. Monofunctional carbazoles and fluorenes were used as sidearms for our star-shaped molecules (Scheme 1). Bromination of carbazole with Br_2 usually leads to a variety of brominated carbazole compounds. Due to the electronic structure of the carbazole molecule, the activated 3- and 6-positions are substituted first. By using only 1 equiv of bromine and careful control of the reaction temperature at 0 °C it is possible to obtain 3-bromocarbazole (**1**) in good yield.

The synthesis of 2-bromocarbazole (**2**) is more complicated. In this case, the bromine has to be introduced before the carbazole skeleton is generated. For this purpose we used the ring-closure reaction of 4-bromo-2′-nitrobiphenyl, which has been reported elsewhere.[11]

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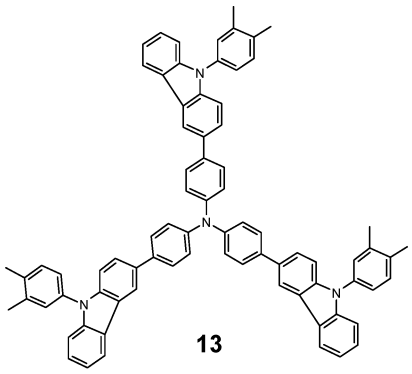
Chart 1. Structures of the Star-Shaped Molecules



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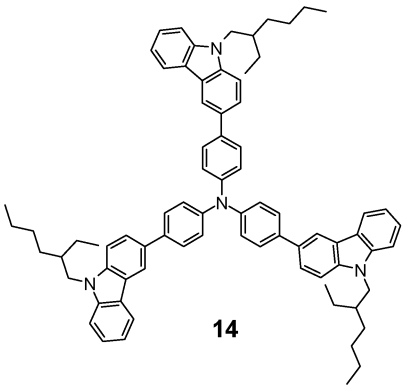

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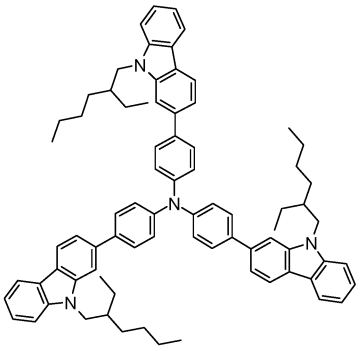

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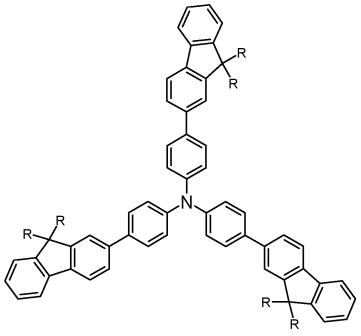
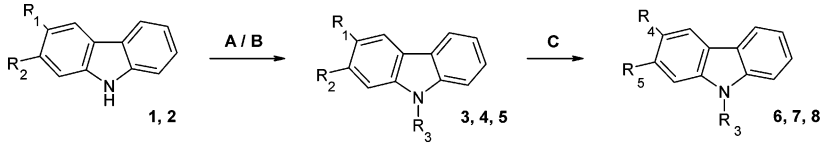


16 a-c

	R
16 a	ethyl
16 b	butyl
16 c	hexyl

Scheme 1. Synthesis of the Carbazole and Fluorene Sidearms



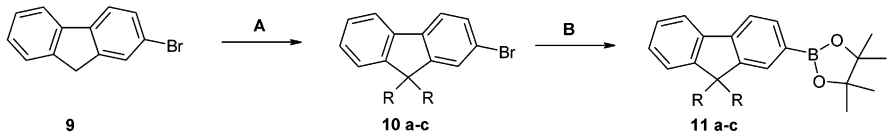
1, 2 **3, 4, 5** **6, 7, 8**

A = 2-ethyl-hexylbromide, acetone, KOH-powder, PTC, reflux, 12 h

B = 4-Iodo-1,2-dimethyl-benzene, trans-cyclohexane-1,2-diamine, CuI, DMF, toluene, K_2CO_3, 115 °C, 2.5 h

C = n-BuLi, THF (abs.), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C, 12 h

	R_1	R_2	R_3	R_4	R_5
1	Br	H	---	---	---
2	H	Br	---	---	---
3	H	Br	ethyl-hexyl	---	---
4	Br	H	ethyl-hexyl	---	---
5	Br	H	3,4-dimethyl-phenyl	---	---
6	---	---	ethyl-hexyl	borolane	H
7	---	---	ethyl-hexyl	H	borolane
8	---	---	3,4-dimethyl-phenyl	borolane	H



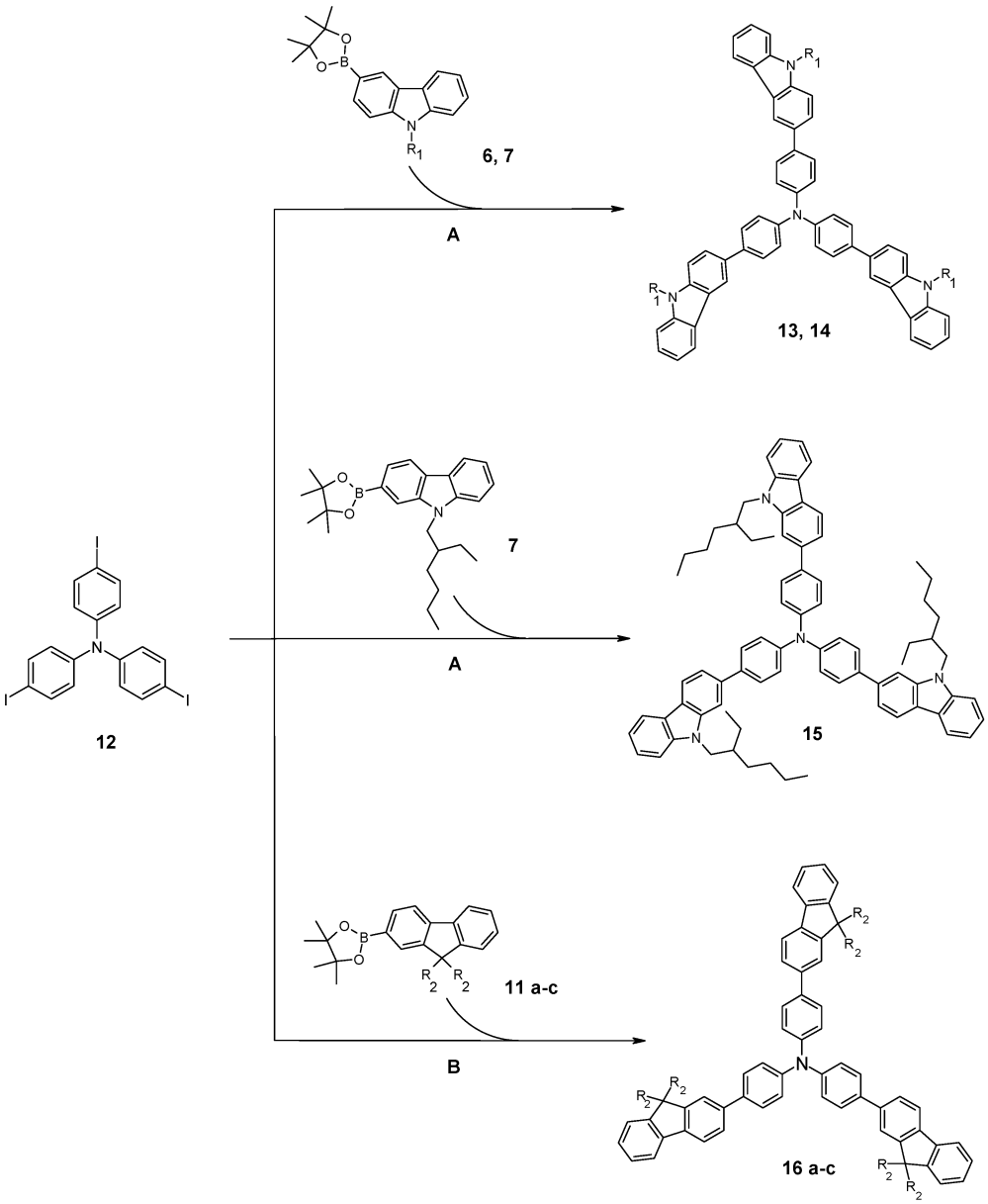
9 **10 a-c** **11 a-c**

A = alkyl bromide, 50% NaOH, PTC, DMSO, 80 °C, 16 h

B = n-BuLi, THF, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C, 12 h

10 / 11	R
a	ethyl
b	butyl
c	hexyl

Scheme 2. Synthesis of the Star-Shaped Compounds 13−16 by Suzuki Cross-Coupling



A = $P(o\text{-}tol)_3$, $Pd(OAc)_2$, toluene, 2N K_2CO_3, PTC, 60 °C, 2 h

B = $Pd(PPh_3)_4$, toluene, 2N K_2CO_3, PTC, 50 - 80 °C, 1 d

	R_1		R_2
13	3,4-dimethyl-phenyl	**16a**	ethyl
14	ethyl-hexyl	**16b**	butyl
		16c	hexyl

In the next step, the bromocarbazoles **1** and **2** were N-alkylated with 2-ethylhexyl bromide in order to achieve solubility and good film-forming properties of the target compounds (Chart 1). For the synthesis of the phenyl-substituted carbazole derivative **5**, 3-bromocarbazole (**1**) was N-phenylated with 4-iodo-1,2-dimethylbenzene and CuI in a modified Goldberg reaction.[12]

The bromocarbazoles **3**−**5** were then converted to the corresponding borolane compounds **6**−**8**, respectively. Compounds **3**−**5** were first lithiated at −78 °C and then reacted with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

The alkylations of commercially available 2-bromofluorene (**9**) were carried out in a two-phase system of dimethyl sulfoxide (DMSO) and 50% NaOH according to a literature procedure.[13] Subsequently the fluorene compounds **10a**−**c** were converted to the borolanes **11a**−**c** in the same way as described for the carbazoles.

All the molecular glasses described in this paper have a triphenylamine core. Therefore, triphenylamine was iodinated with KI/KIO_3 in a mixture of glacial acid and water under reflux to yield tris(4-iodophenyl)amine (**12**).[14]

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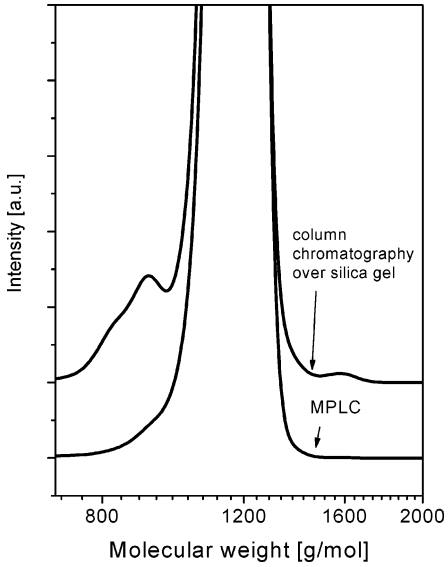

Figure 1. Magnified section of SEC chromatograms of **16b** after conventional column chromatography and after MPLC (lower curve). Eluent: THF, calibration with oligostyrene standards.

Preparation of the Star-Shaped Compounds. The key step of our synthesis is a trifold Suzuki cross-coupling reaction, which was carried out in a two-phase system of toluene and aqueous potassium carbonate. Due to the different reactivity of the sidearms, two different catalyst systems were chosen. For the more reactive fluorene sidearms, the reactivity of $Pd(PPh_3)_4$ is sufficient, whereas for the carbazoles a more reactive combination of $Pd(OAc)_2$ and P(*o*-tol)$_3$ was used. (Scheme 2).

The target compounds **13**−**16** were first purified by column chromatography on silica gel. Size exclusion chromatography (SEC) measurements with a column set suitable for the separation of oligomers revealed that the materials still contained small amounts of impurities (Figure 1). Since materials for applications in organic electronics must exhibit a very high purity, we decided to carry out further purification by medium-pressure liquid chromatography (MPLC, for details see Experimental Section). With that method, the star-shaped compounds **13**, **14,** and **16a**−**c** were obtained in a very high purity. Compound **15** was purified by preparative thin-layer chromatography. As an example, Figure 1 shows the SEC chromatogram of **16b** before and after purification by MPLC. It can be seen that after the first purification using column chromatography some byproducts are still present. After MPLC purification no impurities are detected in the magnified SEC scan.

Table 1. Thermal Characteristics of the Star-Shaped Molecules 13−**16**

	T_{dec}[a] (°C)	T_g[b] (°C)	T_m[b] (°C)
13	495	167	
14	413	68	
15	424		223
16a	407	118	248[c]
16b	384	96	
16c	392	57	

[a] Onset of decomposition determined by TGA: heating rate, 10 K/min; N_2 atmosphere. [b] Determined by DSC: scan rate, 10 K/min; N_2 atmosphere; second run. [c] Melting point was only detected during the first heating; the compound vitrified on cooling to room temperature with 10 K/min.

Properties of the Star-Shaped Molecules. The thermal properties were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA experiments in nitrogen atmosphere revealed that all of the novel star-shaped molecules exhibit a high thermal stability up to 495 °C (**13**) (Table 1).

DSC measurements showed that the two carbazole-containing molecules **13** and **14** and the fluorene compounds **16a**−**c** form molecular glasses with glass transition temperatures (T_g) between 57 and 167 °C. It is interesting that **14** (carbazole linked in 3-position to the core) forms a molecular glass (T_g = 68 °C), whereas **15** (carbazole building block linked in 2-position to the core) crystallizes upon cooling and shows a melting point (T_m) at 223 °C. Nevertheless, amorphous films are also obtained from **15** when the material is processed from solution.

The absorption and fluorescence spectra of **14**, **15** and **16a** are presented in Figure 2. It turns out that the longest wavelength absorption of the fluorene-2-yl compound **16a** and the carbazole-2-yl compound **15** are very similar (Table 2). Furthermore, the emission spectra of **15** and **16a** are also

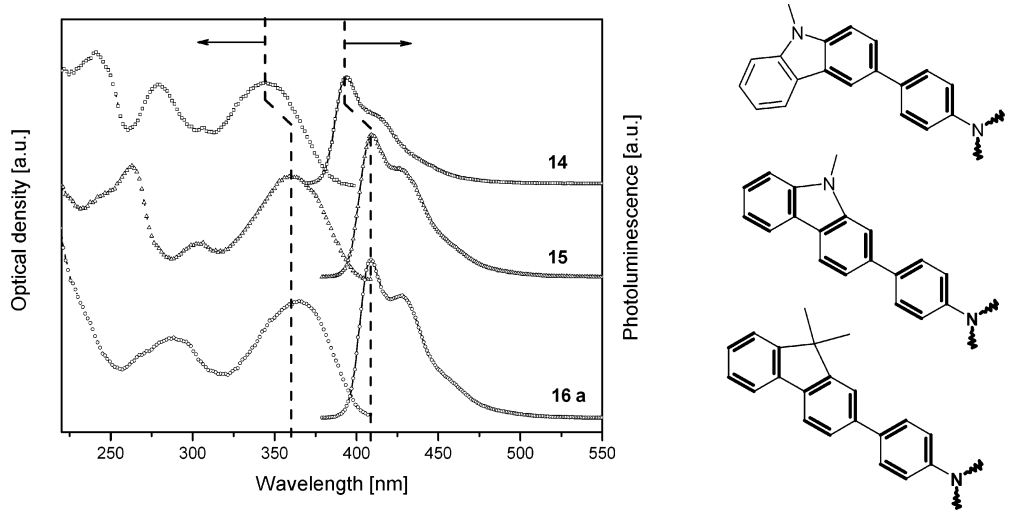

Figure 2. Comparison of the absorption and fluorescence spectra of star-shaped compounds with 2-/3-linked carbazole and fluorene sidearms. Absorption spectra were measured from 10^{-6} M THF solutions. The fluorescence spectra were taken from 10^{-4} M THF solutions (excitation wavelength, 350 nm). Right: schematic of the conjugated segments in **14**, **15** and **16a**.

Table 2. Optical Properties of the Star-Shaped Molecules

	λ_{abs}[a] (nm)	$\lambda_{max,flu}$[b] (nm)	λ_{ae}[c] (nm)
13	348	405	390
14	344	394	385
15	360	409	398
16a	365	408	401
16b	365	408	401
16c	365	408	401

[a] Longest wavelength absorption maximum, measured in 10^{-6} M THF solution. [b] Fluorescence spectra measured in 10^{-4} M THF solution: excitation wavelength, 350 nm. [c] Absorption edge.

Table 3. Oxidation Potentials and HOMO and LUMO Values of the Star-Shaped Molecules 13−16

	Ox_1 vs Ag/Ag^+[a] (V)	Ox_2 vs Ag/Ag^+[a] (V)	reversible	HOMO (eV)	ΔE[b] (eV)	LUMO (eV)
13	0.27	0.66	yes	−5.0	3.2	−1.8
14	0.30	0.52	yes	−5.0	3.2	−1.8
15	(0.44)	(0.59)	no	(−5.2)	3.1	(−2.1)
16a−c	0.50	1.04	yes	−5.2	3.1	−2.1

[a] CV measured in CH_2Cl_2 solution with $TBAPF_6$ and ferrocene/ferrocenium. [b] Optical gap taken from the absorption spectra.

almost identical. In the case of the carbazole-3-yl compound **14**, the absorption and fluorescence maxima are shifted to shorter wavelengths.

The conjugated system is best represented by a benzidine-like structure in the star-shaped compounds, where the carbazole sidearms are linked in the 3-position, whereas in the 2-linked compounds **15** and **16a**, the conjugation is extended over a terphenyl-like structure (Figure 2).

The electrochemical stability of the star-shaped compounds was examined by cyclic voltammetry (CV). All measurements were carried out at 25 °C in CH_2Cl_2 solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte with a glassy carbon working electrode. The oxidation potentials were measured vs Ag/AgCl as the reference electrode. The experiments were calibrated with the standard ferrocene/ferrocenium redox system. Taking −4.8 eV as the HOMO level for the ferrocene redox system,[17] the HOMO values of the star-shaped molecules were calculated. The LUMO values were obtained from the optical gap (ΔE), which in turn can be calculated from the absorption edge (refer to Table 2). The results of the CV measurements are shown in Table 3.

To check if the new compounds are electrochemically stable, 10 subsequent redox cycles were measured. The fluorene-containing compounds **16a−c** do not show any change during the 10 measurements. Two fully reversible oxidations at about 0.5 and 1.0 V are detected. HOMO values of −5.2 eV were calculated for **16a−c**. The carbazole-based molecules **13** and **14** also showed reversible oxidations during the 10 redox cycles. Only compound **15**, in which the carbazole units are connected in the 2-positions to the triphenylamine core, is electrochemically unstable. We suppose that the electron-rich and therefore highly activated 3- and 6-positions of the carbazole rings in **15** are very sensitive toward electrochemical oxidation, which may lead to dimerization reactions.[18] Since the 3- and 6-positions in fluorenes are not activated, **16a−c** exhibit fully reversible

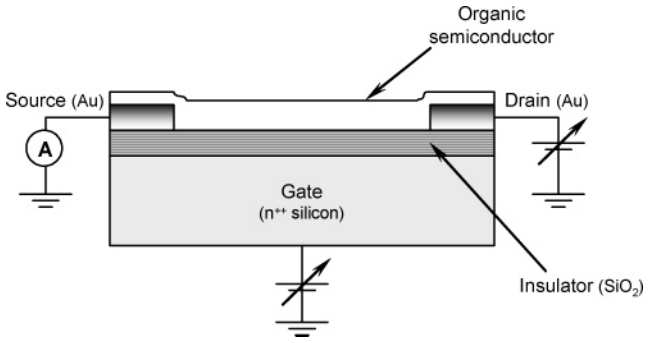

Figure 3. Schematic of the organic field-effect transistors.

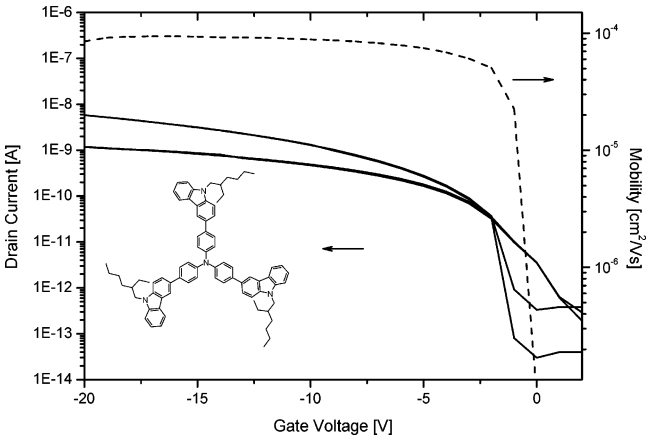

Figure 4. OFET characteristics of **14**. The drain potentials were −20 and −2 V in the upper and lower traces, respectively (solid lines). The dashed curve shows the mobility values (for $V_D = -2$ V).

oxidations. In contrast to the electrochemically unstable compound **15**, the carbazole-containing molecules **13** and **14** in which the carbazole rings are linked in the 3-position to the triphenylamine core exhibit a reversible redox behavior. As already described with the optical spectra, we attribute this to the fact that the "chromophore" in **13** and **14** is a benzidine-like structure, whereas in the case of **15** it is more like an amino-substituted terphenyl. This leads to a smaller activation of the 6-positions in **13** and **14** compared to **15** and hence to a higher electrochemical stability. For the electrochemically stable compounds **13** and **14** HOMO values of −5.0 eV were determined.

Material Screening in OFET Devices. Today, aromatic amines are frequently used as xerographic materials and in OLEDs,[3,19] whereas reports on their use as semiconducting material in OFETs are seldom. Only very recently triarylamine oligomers have been used in organic field-effect transistors, and high field-effect mobilities combined with exceptionally high stabilities have been reported.[20]

The transistor architecture we have used for testing our new materials is shown in Figure 3.[21] The drain current was measured as a function of the gate bias (forward sweep from +5 to −20 V/backward sweep from −20 to +5 V). The

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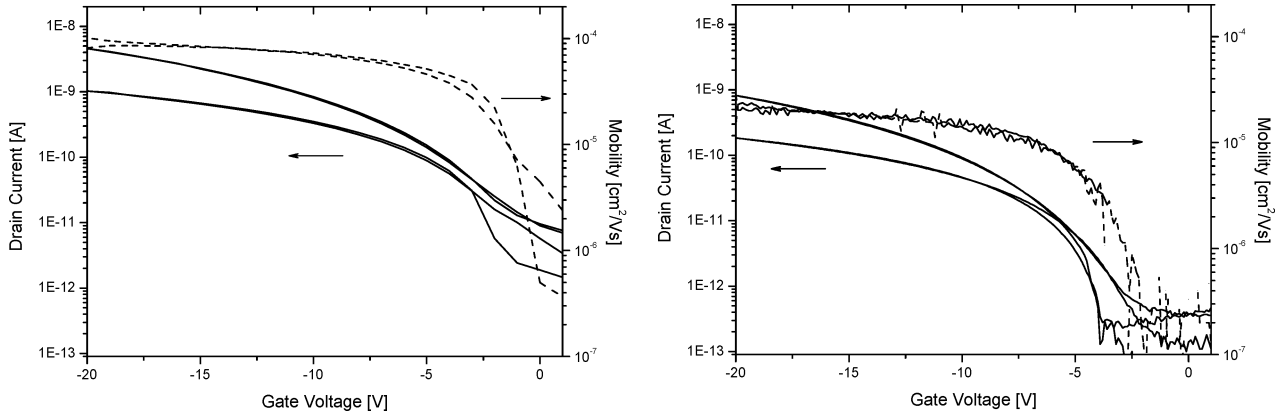

Figure 5. Transfer characteristics of **13**. The drain potentials were −20 and −2 V in the upper and lower traces, respectively (solid lines). The transistor shows only very small hysteresis in the forward/backward sweeps. The dashed curve shows that the mobility (calculated from eq 1) reaches its maximum almost directly after turning on the FET device. Left: freshly prepared device. Right: device performance after storage under ambient conditions and daylight for 4 months.

Table 4. Properties of the OFET Devices

	onset[a] (V)	μ_{FET}[b] ($cm^2\ V^{-1}\ s^{-1}$)	I_{on}/I_{off}[c]
13	−3	1×10^{-4}	10^3
14	−2	1×10^{-4}	10^4
15d	−5	3×10^{-4}	10^4
16b	−1	1×10^{-4}	10^5

[a] Determined at a drain potential of −2 V. [b] Mobility calculated using eq 1. [c] On/off ratio calculated from the drain currents at gate voltages of 0 and −20 V and $V_D = -20$ V. [d] Amorphous film processed from solution.

devices were tested with two fixed drain potentials of −2 and −20 V, respectively.

The mobility was calculated from the gate sweep according to the following equation:[22]

$$\mu_{FET} = (L/WC_iV_D)\,(\partial I_D/\partial V_G) \quad (1)$$

where L is the channel length, W is the channel width, C_i is the capacitance of the insulator per unit area, V_D is the drain voltage, I_D is the drain current, and V_G is the gate voltage. All measurements were performed in air.

The transfer characteristics of an OFET prepared from the carbazole-containing molecular glass **14** is presented in Figure 4. Compound **14** exhibits a field-effect mobility of 10^{-4} $cm^2\ V^{-1}\ s^{-1}$, an on/off ratio of 10^4, and a very low turn-on voltage of about −2 V. The results of the transistor measurements with the other molecular glasses are summarized in Table 4. It turns out that the three carbazole-containing compounds (**13**−**15**) and the fluorene glass **16b** all have field-effect mobilities in the range of 10^{-4} $cm^2\ V^{-1}\ s^{-1}$. Their on/off ratios vary from 10^3 for **13** to 10^5 for **16b**. Since both the carbazole glasses **13**−**15** and the fluorene glass **16b** have HOMO levels between −5.0 and −5.2 eV, holes are efficiently injected from the gold electrodes, which leads to very low onset voltages between −1 and −5 V.

A very important property of organic materials to be used in OFETs is their stability under ambient conditions. A field-effect transistor from the star-shaped compound **13** was stored for 4 months under ambient conditions and light in the laboratory and then tested again, with no observed change in the onset voltage or on/off ratio. Only the field-effect mobility dropped to a value of 2×10^{-5} $cm^2\ V^{-1}\ s^{-1}$. The transistor characteristics of **13** before and after storage are presented in Figure 5.

3. Conclusions

We have synthesized six novel star-shaped molecules with a triphenylamine core and tested them in organic field-effect transistors. By using alkylfluorenes and N-alkylated or N-phenylated carbazole units as sidearms of the novel molecular glasses, we obtained electrochemically stable materials with a high solubility in common organic solvents and good film-forming properties. The materials were highly purified by medium-pressure liquid chromatography (MPLC). We have tested the new materials as semiconductors in solution-processed organic field-effect transistors. Compounds **13**−**15** and **16b** exhibit mobilities in the range of 10^{-4} $cm^2\ V^{-1}\ s^{-1}$. The highest mobility of 3×10^{-4} $cm^2/(cm^2\ V^{-1}\ s^{-1})$ was obtained in a device prepared from **15**. Probably the most promising result is the very good long-term stability of the OFETs under ambient conditions. The fact that the molecular glasses can be easily processed from solution helps to simplify device preparation.

We have shown that the triphenylamine-based molecular glasses, both with carbazole and fluorene sidearms, are well-suited as semiconductors in organic FETs. We believe that improvements in surface treatment and the use of insulators with a low dielectric constant[20] may lead to a further increase of the field-effect mobility and thus make the materials attractive for applications in organic electronics.

4. Experimental Section

Material Synthesis. All chemicals and reagents were used as received from Aldrich. Tetrahydrofuran (THF) and toluene were distilled over potassium before use. The synthesis of 2-bromocarbazole (**2**) has been reported elsewhere.[11]

Synthesis of the Sidearms. *3-Bromocarbazole (1).* To a solution of 33.5 g (0.2 mol) of carbazole in 800 mL of pyridine, a mixture of 10.3 mL (0.2 mol) of bromine in 30 mL of pyridine was added slowly from a dropping funnel at 0 °C. After the addition was completed, the reaction mixture was stirred for 2 h at 0 °C. The pyridine was removed by distillation, and 300 mL of water, 60 mL of ethanol, and 5 mL of HCl were added to the residue. The

(22) Brown, A. R.; Jarrett, C. P.; de Leeuw, D. M.; Matters, M. *Synth. Met.* **1997**, *88*, 37.

mixture was heated to reflux and stirred vigorously for 20 min. After cooling to room temperature, the residue was separated, dissolved in toluene, and filtered over neutral aluminum oxide. Recrystallization from toluene yielded 32.11 g (65%) of 3-bromocarbazole (**1**) as white powder. ^{1}H NMR (250 MHz, DMSO-d_6; ppm): δ 7.15 (t, 1H), 7.43 (m, 4H), 8.12 (d, 1H), 8,33 (d, 1H), 11.40 (s, 1H). ^{13}C NMR (62.5 MHz, DMSO-d_6; ppm): δ 110.9, 111.2, 113.2, 119.3, 120.5, 121.0, 121.8, 123.1, 125.8, 128.2, 138.7, 140.5. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3404, 1753, 1622, 1600, 1469, 1445, 1332, 1240, 1109, 1054, 879, 724. Mass spectrum: *m*/*z* ([M$^+$]) 245/247.

*3-Bromo-9-(2-ethylhexyl)carbazole (**4**).* To a solution of 3 g (12 mmol) of 3-bromocarbazole (**2**) in 30 mL of acetone, 1.35 g (24 mmol) of KOH powder, 4.26 mL (24 mmol) of 2-ethylhexyl bromide, and 0.2 g of tetrabutylammonium hydrogen sulfate as phase-transfer catalyst were added. The reaction mixture was heated to reflux for 12 h before the solvent was evaporated. The residue was poured into water and extracted with diethyl ether. The organic layer was washed with water and dried over Na_2SO_4 before the solvent was evaporated. The crude product was purified by column chromatography on silica gel with hexane:ethyl acetate (10:1) as eluent, yielding 3.86 g (85%) of 3-bromo-9-(2-ethylhexyl)carbazole (**4**) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.87 (t, 3H), 0.91 (t, 3H), 1.20−1.49 (m, 8H), 1.95 (septet, 1H), 4.01 (m, 2H), 7.15 (m, 1H), 7.23 (dd, 1H), 7.28 (m, 1H), 7.37 (m, 1H), 7.42 (d, 1H), 7.84 (d, 1H), 7.96 (d, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 11.3, 14.4, 23.4, 24.8, 29.1, 31.3, 39.6, 47.9, 108.7, 109.4, 119.6, 119.7, 120.9, 121.7, 122.9, 122.2, 122.7, 126.4, 141.4, 142.1. IR (NaCl; $\tilde{\nu}$ (cm^{-1})): 3063, 2958, 2929, 2871, 1624, 1591, 1472, 1451, 1437, 1322, 1246, 1218, 1126, 721. Mass spectrum: *m*/*z* ([M$^+$]) 357/359.

2-Bromo-9-(2-ethyl-hexyl)carbazole (**3**) was prepared according to the same procedure.

*3-Bromo-9-(3,4-dimethylphenyl)carbazole (**5**).* The reaction mixture consisting of 3-bromocarbazole (**2**) (1 g, 4 mmol), 0.25 mL (4 mmol) of *trans*-cyclohexane-1,2-diamine, 0.7 mL (5.0 mmol) of 4-iodo-1,2-dimethylbenzene, 1.3 g (9.2 mmol) of K_2CO_3, 76 mg (0.4 mmol) of CuI, 30 mL of dimethylformamide (DMF), and 15 mL of toluene was stirred under argon at 115 °C. After 2.5 h the mixture was poured into 300 mL of water and was extracted three times with hexane:ethyl acetate (4:1). The organic layer was washed with water and concentrated sodium thiosulfate solution and filtered over neutral aluminum oxide. After the solvent was evaporated, the crude product was purified by column chromatography on silica gel using hexane:ethyl acetate (16:1) as eluent to yield 2.5 g (50%) of 3-bromo-9-(3,4-dimethylphenyl)carbazole (**5**) as a white solid. ^{1}H NMR (250 MHz, DMSO-d_6; ppm): δ 2.24 (s, 3H), 2.26 (s, 3H), 7.24 (m, 3H), 7.33 (m, 2H), 7.40 (m, 2H), 7.50 (m, 1H), 8.27 (m, 1H), 8.47 (m, 1H). ^{13}C NMR (62.5 MHz, DMSO-d_6; ppm): δ 21.3, 22.4, 110.1, 111.4, 112.5, 120.1, 120.4, 122.2, 125.0, 126.48, 126.53, 128.5, 134.4, 136.1, 139.7, 141.3. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3056, 2958, 2866, 1515, 1467, 1446, 1364, 1325, 1270, 1231, 1054, 746. Mass spectrum: *m*/*z* ([M$^+$]) 349/351.

*9-(2-Ethylhexyl)-2-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-carbazole (**7**).* A 1.5 g amount (4.2 mmol) of 2-bromo-9-(2-ethylhexyl)carbazole (**4**) were dissolved in 50 mL of absolute THF under argon. The solution was cooled to −78 °C before 2.9 mL (4.6 mmol) of *n*-BuLi (1.6 M solution in hexane) was added dropwise. The reaction mixture was stirred for 20 min before 1.0 mL (5.0 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 was carried out by column chromatography on silica gel with hexane:acetic ester (20:1) as eluent. The reaction yielded 1.12 g (66%) of 9-(2-ethylhexyl)-2-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)carbazole (**7**) as yellowish oil. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.80 (t, 3H), 0.83 (t, 3H), 1.12−1.37 (m, 8H), 1,32 (s, 12H), 2.02 (m, 1H), 4.12 (m, 2H), 7.14 (m, 1H), 7.32 (d, 1H), 7.40 (m, 1H), 7.61 (dd, 1H), 7.79 (s, 1H), 8.02 (d, 1H), 8.05 (d, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 11.0, 14.1, 23.0, 24.4, 25.0, 28.6, 30.8, 39.3, 47.2, 83.8, 109.1, 115.4, 118.6, 119.5, 120.7, 122.6, 124.8, 125.2, 126.1, 140.5, 141.3. IR (NaCl; $\tilde{\nu}$ (cm^{-1})): 3053, 2961, 2859, 1623, 1561, 1476, 1360, 1330, 1141, 964,. Mass spectrum: *m*/*z* ([M$^+$]) 405.

*9-(2-Ethylhexyl)-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-carbazole (**6**).* The synthesis was carried out as described before for **7**.The reaction yielded 80% of **6** as yellowish oil. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.87 (t, 3H), 0.91 (t, 3H), 1.20−1.49 (m, 8H), 1,41 (s, 12H), 2.07 (m,1H), 4.18 (m, 2H), 7.26 (m, 1H), 7.38−7.42 (m, 2H), 7.47 (m, 1H), 7.93 (d, 1H), 8.15 (d, 1H), 8.62 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 11.3, 14.4, 23.4, 24.7, 25.3, 29.2, 31.3, 39.7, 47.8, 83.9, 108.7, 109.4, 119.5, 120.9, 122.9, 124.5, 125.9, 128.1, 132.4, 141.3, 143.5. IR (NaCl; $\tilde{\nu}$ (cm^{-1})): 3042, 3013, 2972, 2855, 1623, 1596, 1458, 1429, 1354, 1223, 1073, 963, 863, 747. Mass spectrum: *m*/*z* ([M$^+$]) 405.

*9-(3,4-Dimethylphenyl)-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)carbazole (**8**).* The synthesis was carried out as described before for **7**.The reaction yielded 86% of **8** as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 1.32 (s, 12H), 2.32 (s, 3H), 2.34 (s, 3H), 7.17−7.26 (m, 7H), 7.76 (d, 1H), 8.10 (d, 1H), 8.56 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 24.9, 31.4, 83.6, 109.3, 109.9, 120.1, 120.4, 123.0, 123.4, 125.8, 126.6, 126.7, 127.7, 132.3, 134.7, 141.2, 143.1, 150.6. IR (NaCl): $\tilde{\nu}$ (cm^{-1}): 3042, 2972, 2867, 1623, 1595, 1481, 1428, 1353, 1301, 1233, 1141, 1073, 962, 863, 748. Mass spectrum: *m*/*z* ([M$^+$]) 397.

*2-Bromo-9,9-diethylfluorene (**10a**).* A 10 g amount (41 mmol) of the commercially available 2-bromofluorene (**9**) were dissolved in 85 mL of DMSO. To the solution 0.85 g of triethylbenzylammonium chloride and 0.85 g of tetra-*n*-butylammonium chloride were added as phase-transfer catalysts. After the addition of 50 mL of 25 N NaOH solution, 16.8 mL (230 mmol) of bromoethane was added. The reaction mixture was stirred at 100 °C. After 12 h, water was added until the two phases mixed. The solution was extracted with diethyl ether, washed with water, and dried with Na_2SO_4 before the solvent was evaporated. The crude product was purified by column chromatography on silica gel with hexane:ethyl acetate 15:1 as eluent, yielding 12 g (97%) of 2-bromo-9,9-diethylfluorene (**10a**) as white crystals. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.32 (t, 6H), 2.00 (q, 4H), 7.30 (m, 3H), 7.45 (m, 2H), 7.55 (m, 1H), 7.66 (m, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 8.4, 32.6, 56.4, 119.7, 121.7, 122.9, 126.2, 127.0, 127.4, 129.9, 140.4, 140.5, 149.4, 152.1. Mass spectrum: *m*/*z* ([M$^+$]) 300/302. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3059, 2960, 2910, 2847, 1440, 1375, 1256, 1130, 1003, 874, 731.

*2-Bromo-9,9-dibutylfluorene (**10b**).* The synthesis for **10b** was carried out as described before for **10a**. The reaction yielded 91% **10b** as white powder. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.55 (m, 4H), 0.67 (t, 6H), 1.03 (m, 4H), 1.95 (m, 4H), 7.33 (m, 3H), 7.44 (m, 2H), 7.55 (m, 1H), 7.63 (m, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 13.8, 23.0, 25.9, 40.1, 55.3, 119.7, 120.9, 121.0, 122.9, 126.2, 126.9, 127.4, 129.9, 140.0, 140.1, 150.3, 152.9. Mass spectrum: *m*/*z* ([M$^+$]) 356/358. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3059, 2960, 2910, 2874, 1440, 1375, 1256, 1130, 1003, 874, 731.

*2-Bromo-9,9-dihexylfluorene (**10c**).* Compound **11c** was prepared according to the procedure described above for **10a**. The reaction yielded 93% **10c** as colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$;

ppm): δ 0.55 (m, 4H), 0.67 (t, 6H), 1.00−1.21 (m, 12H), 1.94 (m, 4H), 7.32 (m, 3H), 7.45 (m, 2H), 7.54 (m, 1H), 7.67 (m, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 14.0, 22.6, 23.6, 29.6, 31.5, 40.3, 55.3, 119.7, 120.9, 121.0, 122,9, 126.1, 126.9, 127.4, 129.9, 140.0, 140.1, 150.3, 153.0. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3063, 3024, 2954, 2856, 1599, 1465, 1442, 1405, 1377, 1132, 1062, 876. Mass spectrum: *m*/*z* ([M^+]) 412/414.

*2-(9,9-Diethylfluoren-2-yl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**11a**).* An 8 g amount (26.6 mmol) of **10a** was dissolved in 100 mL of absolute THF under argon. The solution was cooled to −78 °C before 11.7 mL (29.2 mmol) of *n*-BuLi (2.5 M solution in hexane) was added dropwise. The reaction mixture was stirred for 20 min before 6.5 mL (31.9 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 12 h before it was poured into ice water. The solution was extracted with diethyl ether, the organic phase washed with brine and dried with Na_2SO_4 before the solvent was evaporated. Purification was carried out by column chromatography on silica gel with hexane: acetic ester (10:1) as eluent. The reaction yielded 7.3 g (79%) of 2-(9,9-diethylfluoren-2-yl)-4,4,5,5-tetramethyl[1,3,2]-dioxaborolane (**11a**) as white solid. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.29 (t, 6H), 1.38 (s, 12H), 2.05 (m, 4H), 7.33 (m, 3H), 7.69 (d, 1H), 7.71 (m, 1H), 7.73 (d, 1H), 7.79 (dd, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 8.5, 24.9, 32.6, 56.1, 83.7, 118.9, 120.0, 122.9, 126.7, 127.5, 128.0, 128.9, 133.7, 141.3, 144.5, 149.0, 152.4. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3064, 3038, 2999, 2926, 2875, 1608, 1456, 1418, 1356, 1141, 831. Mass spectrum: *m*/*z* ([M^+]) 348.

*2-(9,9-Dibutylfluoren-2-yl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**11b**).* Compound **11b** was prepared according to the same procedure as that described for **11a**. The reaction yielded 72% **11b** as white solid. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.52 (m, 4H), 0.65 (t, 6H), 1.05 (m, 4H), 1.39 (s, 12H), 1.98 (m, 4H), 7.27−7.37 (m, 3H), 7.70 (d, 1H), 7.72 (m, 1H), 7.74 (d, 1H), 7.81 (dd, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 13.8, 23.0, 24.9, 25.9, 40.1, 55.0, 83.7, 118.9, 120.1, 122.9, 126.6, 127.5, 128.0, 128.8, 133.7, 140.9, 144.1, 149.8, 151.3. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3031, 2964, 2928, 1611, 1419, 1357, 1145, 741. Mass spectrum: *m*/*z* ([M^+]) 404.

*2-(9,9-Dihexylfluoren-2-yl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**11c**).* Compound **11c** was prepared according to the same procedure as that described for **11a**. The reaction yielded 75% **11c** as colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.60 (m, 4H), 0.75 (t, 6H), 1.00−1.13 (m, 12H), 1.38 (s, 12H), 1.97 (m, 4H), 7.27−7.36 (m, 3H), 7.70 (d, 1H), 7.72 (m, 1H), 7.75 (d, 1H), 7.81 (dd, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 13.9, 22.6, 23.6, 24.9, 29.6, 31.5, 40.2, 55.1, 83.7, 118.9, 120.1, 122.9, 126.6, 127.4, 128.0, 128.8, 133.7, 140.9, 144.1, 149.9, 151.3. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3051, 2977, 2955, 2927, 1610, 1570, 1456, 1354, 1145, 963, 741. Mass spectrum: *m*/*z* ([M^+]) 460.

Synthesis of the Core Molecule. *Tris(4-iodophenyl)amine (**12**).* To a mixture of triphenylamine (12.3 g, 50 mmol) and potassium iodide (16.6 g, 100 mmol), 200 mL of glacial acetic acid and 20 mL of water were added. The reaction mixture was refluxed under argon until a clear, yellow solution was obtained. A 21.4 g amount of KIO_3 (100 mmol) was added in small portions, and the mixture was refluxed for 1 h. Thereafter 20 mL of water was added to precipitate the crude product. The residue was filtered off, dissolved in toluene, and washed several times with concentrated sodium thiosulfate solution. The organic layer was then washed with water and dried over Na_2SO_4 and the solvent evaporated. Recrystallization from ethyl acetate yielded 28.7 g (92%) of tris(4-iodophenyl)amine (**12**) as light brown crystals. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 6.81 (d, 6H), 7.54 (d, 6H). ^{13}C NMR (63.5 MHz, $CDCl_3$; ppm): δ 86.6, 126.0, 138.4, 146.4. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 1574, 1483, 1312, 1283, 1058, 1003, 815, 709, 509. Mass spectrum: *m*/*z* ([M^+]) 623.

Synthesis of the Star-Shaped Molecules. *Tris-{4-[9-(3,4-dimethylphenyl)carbazol-3-yl]phenyl}amine (**13**).* A 0.27 g amount (0.43 mmol) of **12** and 3.2 equiv of **8** (0.55 g, 1.38 mmol) were dissolved in 15 mL of toluene. 8 mL of a 2 M K_2CO_3 solution and 10 mg of trimethylbenzylammonium chloride were added before the reaction mixture was degassed by three subsequent freeze/thaw cycles. Thereafter 5.8 mg (2.6×10^{-5} mol) of $Pd(AcO)_2$ and 23.7 mg (7.8×10^{-5} mol) of tri-*o*-tolylphosphine were added under argon. The mixture was stirred for 10 h at 75 °C before it was poured into ice water, extracted with diethyl ether, and dried with Na_2SO_4. After evaporation of the solvent the product was purified by column chromatography on silica gel with hexane:toluene (3:2) as eluent. Finally the product was purified a second time with MPLC. Hexane:tetrahydrofuran (15:1) was used as eluent at a pressure of 18 bar. The reaction yielded 0.28 g (62%) of tris{4-[9-(3,4-dimethylphenyl)carbazol-3-yl]phenyl}amine (**13**) as white solid. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 2.32 (d, 18H), 7.17−7.38 (m, 27H), 7.60 (m, 9H), 8.10 (m, 3H), 8.28 (m, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 18.5, 18.9, 108.9, 117.2, 118.7, 119.3, 122.3, 122.7, 123.4, 123.5, 124.0, 124.9, 126.9, 127.3, 129.9, 131.8, 134.2, 135.0, 137.3, 139.4, 140.5. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3027, 2919, 2854, 1601, 1506, 1474, 1287, 1254, 1160, 1012, 883, 744. $\lambda_{max,abs}$ (10^{-6} M THF solution), 348 nm; $\lambda_{max,flu.}$ (10^{-4} M THF solution), 405 nm. Mass spectrum: *m*/*z* ([M^+]) 1052. Isotopic clusters of M^+ [g/mol] (rel intens): 1052 (100%), 1053 (89%), 1054 (39%), 1055 (12%), 1056 (3%). Anal. Calcd for $C_{78}H_{60}N_4$ (1053.4): C, 88.94; H, 5.74; N, 5.32. Found: C, 89.14; H, 5.96; N, 4.99.

*Tris{4-[9-(2-ethylhexyl)carbazol-3-yl]phenyl}amine (**14**).* The synthesis was carried out as described for star-shaped compound **13**. MPLC-purification was carried out with hexane:toluene (3:1) as eluent at a pressure of 20 bar yielding 58% of **14** as white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm): 0.80(t, 9H), 0.85(t, 9H), 1.11−1.41(m, 24H), 2.01(m, 3H), 4.10(m, 6H), 7.15(m, 6H), 7.32(m, 6H), 7.39(m, 6H), 7.61(m, 9H), 8.07(d, 3H), 8.25(m, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm): 11.4, 14.5, 23.5, 24.9, 29.3, 31.5, 39.9, 47.9, 109.5, 109.6, 118.8, 119.2, 120.8, 123.4, 123.7, 124.7, 125.2, 126.1, 128.3, 132.2, 140.7, 141.8. IR (KBr): $\tilde{\nu}$ (cm^{-1}): 3055, 3028, 2955, 2926, 1627, 1600, 1514, 1488, 1476, 1315, 1218, 1155, 745. $\lambda_{max,abs.}$ (10^{-6} M THF solution) 344 nm; $\lambda_{max,flu.}$ (10^{-4} M THF solution) 394 nm. Mass spectrum: *m*/*z* ([M^+]): 1076. Isotopic clusters of M^+[g/mol] (rel int.): 1076(100%), 1077(90%), 1078(40%), 1079(12%), 1080(3%). Anal. Calcd for $C_{78}H_{87}N_4$ (1077.6): C, 86.94; H, 7.86; N, 5.20. Found: C, 86.40; H, 7.96; N, 5.59.

*Tris{4-[9-(2-ethylhexyl)carbazol-2-yl]phenyl}amine (**15**).* The synthesis was carried out as described for star-shaped compound **13**. In this case the product (**15**) was purified by preparative thin-layer chromatography (TLC) with hexane:CH_2Cl_2 (5:2) as eluent yielding 52% **15** as white solid. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.79 (t, 9H), 0.86 (t, 9H), 1.16−1.36 (m, 24H), 2.05 (m, 3H), 4.14 (d, 6H), 7.16 (m, 3H), 7.27 (m, 6H), 7.33−7.43 (m, 9H), 7.51 (s, 3H), 7.61 (m, 6H), 8.01−8.07 (m, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 11.4, 14.4, 23.5, 24.8, 29.2, 31.4, 39.8, 47.8, 107.3, 109.4, 118.5, 119.3, 120.6, 120.9, 122.2, 123.0, 124.9, 125.9, 128.7, 137.1, 138.8, 141.8, 142.0, 147.1. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3061, 3031, 2957, 2927, 1599, 1515, 1456, 1317, 1287, 744. $\lambda_{max,abs}$ (10^{-6} M THF solution), 360 nm; $\lambda_{max,flu}$ (10^{-4} M THF solution), 409 nm. Mass spectrum: *m*/*z* ([M^+]) 1076. Isotopic clusters of M^+ [g/mol] (rel intens): 1076 (100%), 1077 (90%), 1078 (40%), 1079 (12%), 1080 (3%). Anal. Calcd for $C_{78}H_{87}N_4$ (1077.6): C, 86.94; H, 7.86; N, 5.20. Found: C, 87.02; H, 7.44; N, 5.54.

*Tris[4-(9,9-diethylfluoren-2-yl)phenyl]amine (**16a**).* A 1.0 g amount (1.58 mmol) of **12** and 2.2 g (6.32 mmol) of **11a** were dissolved in 16 mL of toluene. 10 mL of a 2 M Na_2CO_3 solution and 10 mg of trimethylbenzylammonium chloride were added before the reaction mixture was degassed by three subsequent freeze/thaw cycles. After that, 40 mg (3.5×10^{-5} mol) of tetrakis-(triphenylphosphine)palladium [$Pd(PPH_3)_4$] were added under argon. The mixture was stirred for 24 h at 85 °C before it was poured into ice water, extracted with diethyl ether, and dried with Na_2SO_4. After evaporation of the solvent the product was purified by column chromatography on silica gel with hexane:tetrahydrofuran (15:1) as eluent. Finally the product was purified by MPLC. Hexane: tetrahydrofuran (30:1) was used as eluent at a pressure of 20 bar. The reaction yielded 0.95 g (66%) of tris[4-(9,9-diethyl-fluoren-2-yl)phenyl]amine (**16a**) as yellowish solid. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.37 (t, 18H), 2.10 (q, 12H), 7.27−7.37 (m, 15H), 7.56−7.63 (m, 12H), 7.75 (m, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 8.6, 32.8, 56.1, 119.6, 119.9, 121.0, 122.9, 124.4, 125.5, 126.8, 126.9, 127.9, 136.0, 139.4, 140.5, 141.2, 146.7, 150.1, 150.6. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3032, 2962, 2918, 1598, 1513, 1451, 1321, 1284, 821, 737. $\lambda_{max,abs}$ (10^{-6} M THF solution), 365 nm; $\lambda_{max,flu}$ (10^{-4} M THF solution), 408 nm. Mass spectrum: *m*/*z* ([M^+]) 905. Isotopic clusters of M^+ [g/mol] (rel intens): 905 (100%), 906 (78%), 907 (30%), 908 (7%), 909 (2%). Anal. Calcd for $C_{69}H_{63}N$ (906.3): C, 91.45; H, 7.01; N, 1.55. Found: C, 91.26; H, 6.98; N, 1.76.

*Tris[4-(9,9-dibutylfluoren-2-yl)phenyl]amine (**16b**).* The synthesis was carried out as described for star-shaped compound **16a**. MPLC made with hexane:tetrahydrofuran (30:1) as eluent at a pressure of 18 bar yielding 80% of **16b** as white solid. ^{1}H NMR (250 MHz, $CDCl_3$; ppm): δ 0.63 (m, 12H), 0.66 (t, 18H), 1.09 (m, 12H), 2.01 (m, 12H), 7.29−7.37 (m, 15H), 7.60 (m, 12H), 7.75 (m, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$; ppm): δ 13.8, 23.1, 26.0, 40.3, 55.0, 119.7, 119.9, 120.9, 122.9, 124.4, 125.5, 126.8, 126.9, 127.9, 136.1, 139.4, 140.1, 140.8, 146.7, 150.9, 151.4. IR (KBr; $\tilde{\nu}$ (cm^{-1})): 3055, 3031, 2955, 2927, 1599, 1483, 1451, 1320, 740. $\lambda_{max,abs}$ (10^{-6} M THF solution), 365 nm; $\lambda_{max,flu}$ (10^{-4} M THF solution), 408 nm. Mass spectrum: *m*/*z* ([M^+]) 1073. Isotopic clusters of M^+ [g/mol] (rel intens): 1073 (100%), 1074 (93%), 1075 (43%), 1076 (12%), 1077 (2%). Anal. Calcd for $C_{81}H_{87}N$ (1074.6): C, 90.54; H, 8.16; N, 1.30. Found: C, 90.23; H, 8.28; N, 1.33.

*Tris[4-(9,9-dihexylfluoren-2-yl)phenyl]amine (**16c**).* The synthesis was carried out as described for star-shaped compound **16a**. MPLC was made with hexane:tetrahydrofurane (35:1) as eluent at a pressure of 20 bar yielding 73% of **16c** as white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm): 0.69(m, 12H), 0.76(t, 18H), 1.06−1.16(m, 36H), 2.00(m, 12H), 7.23(m, 15H), 7.57−7.64(m, 12H), 7.74(m, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm): 14.0, 22.6, 23.7, 29.7, 31.5, 40.4, 55.1, 119.6, 119.9, 120.9, 122.8, 124.4, 125.5, 126.7, 126.9, 127.9, 136.1, 139.4, 140.1, 140.8, 146.7, 150.9, 151.4. IR (KBr): $\tilde{\nu}$ (cm^{-1}): 3032, 2953, 2926, 1599, 1483, 1465, 1451, 1320, 739. $\lambda_{max,abs.}$ (10^{-6} M THF solution) 365 nm; $\lambda_{max,flu.}$(10^{-4} M THF solution) 408 nm. Mass spectrum: *m*/*z* ([M^+]): 1241. Isotopic clusters of M^+[g/ mol] (rel int.): 1241(95%), 1242(100%), 1243(52%), 1244(18%), 1245(5%), 1246(2%). Anal. Calcd for $C_{93}H_{111}N$ (1242.9): C, 89.87; H, 9.00; N, 1.13. Found: C, 90.03; H, 8.59; N, 1.37.

The purity of all star-shaped compounds was additionally checked by SEC using a column set suitable for separation of oligomers with THF as eluent.

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 $Si(CH_3)_4$. 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 (MS) were recorded with a Finnigan MAT 8500 (70 eV) spectrometer. 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 SEC system for oligomers (analytical columns, cross-linked polystyrene gel (Polymer Laboratories); length, 2 × 60 cm; width, 0.8 cm; particle size, 5 μm; pore size, 100 Å; eluent, THF (0.5 mL/min, 80 bar); polystyrene standard). The system included a Waters 410 differential refractometer and a Waters 486 UV detector (254 nm). 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.

Device Fabrication and Testing. The organic field-effect transistor devices were prepared on heavily doped n^{2+} silicon wafers as gate contact on top of which an insulating layer of silicon dioxide was thermally grown. Gold was evaporated and photolithographically patterned to form the source and drain contacts.[22] The devices were completed by deposition of the starburst molecules which functioned as the organic semiconducting material. The films were prepared by using the drop casting technique. The average film thickness of the semiconductor layer was about 150 nm. For dissolving the triphenylamine-based compounds, toluene or methylene chloride were used as solvent. The electrical measurements were carried out either in air or under vacuum (10^{-4} Torr) using a Hewlett-Packard semiconductor parameter analyzer Agilent 4155C. The reported transistors had a ring configuration with a channel length of 40 μm and a channel width of 1000 μm.

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