Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Sonntag, Martin and Strohriegl, Peter(2007) 'Synthesis of a novel liquid crystalline bisindenocarbazole derivative', Liquid Crystals, 34: 1, 49 — 57
To link to this Article: DOI: 10.1080/02678290601036225
URL: http://dx.doi.org/10.1080/02678290601036225

Liquid Crystals, Vol. 34, No. 1, January 2007, 49–57

Synthesis of a novel liquid crystalline bisindenocarbazole derivative

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(*Received 7 July 2006; accepted 18 August 2006*)

In this paper we describe the synthesis of four new bisindenocarbazole derivatives, prepared by selective bromination of bisindenocarbazole in the 7- and 7′-positions, followed by Suzuki crosscoupling with alkyl-substituted phenyl, biphenyl and fluorene units. From this new class of fused aromatics a liquid crystalline derivative is reported for the first time. The bisindenocarbazole with two 4-hexylphenyl side groups exhibits a broad nematic phase between 180 and 250°C, whereas the other derivatives are crystalline or form molecular glasses. All bisindenocarbazoles exhibit high thermal stabilities above 300°C and show excellent electrochemical stability. HOMO and LUMO levels of −5.4 eV and −2.3 eV, respectively, were determined by cyclic voltammetry and optical spectroscopy. The bisindenocarbazoles display a strong blue fluorescence with up to 56% quantum yield in solution.

1. Introduction

Over recent years the development of new organic semiconductors has seen major advance. Among these materials, fused aromatics such as pentacene and rubrene have received special attention due to their high charge carrier mobilities. In single crystals of pentacene [1] and rubrene [2] mobilities up to $15\,cm^2\,V^{-1}\,s^{-1}$ have been demonstrated. In recent years, fused heterocycles such as indeno- and indolo-carbazoles with improved stability towards oxidation have also been synthesized [3–6]. Polycrystalline thin films were obtained by evaporation of selected indolocarbazole derivatives on heated substrates. In these microcrystalline films charge carrier mobilities up to $0.1\,cm^2\,V^{-1}\,s^{-1}$ were achieved in organic field-effect transistors [5, 6]. In polycrystalline films the mobility strongly depends on the film morphology, e. g. the grain size and packing of the micro crystals, and therefore is very sensitive towards the deposition conditions.

An alternative approach to well ordered thin films is the formation of large monodomains by liquid crystals (LCs). The molecules can be aligned in the LC phase at elevated temperatures. The orientation is then frozen-in either by quenching the LC phase to room temperature or by photopolymerization of liquid crystalline compounds with photoreactive groups, to give what are known as reactive mesogens. High mobilities in discotic liquid crystal phases from 2,3,6,7,10,11-hexahexylthiotriphenylene were reported by Haarer *et al*. in 1999. Photoinduced charge carrier mobilities up to $0.1\,cm^2\,V^{-1}\,s^{-1}$ were obtained in the helical columnar mesophase [7]. Müllen and co-workers have reported the synthesis of discotic hexabenzocoronene derivatives. In these materials, carrier mobilities up to $1\,cm^2\,V^{-1}\,s^{-1}$ were determined by a pulse-radiolysis time-resolved microwave conductivity technique [8, 9]. Besides discotic materials, rod-like calamitic molecules can also form highly ordered mesophases with high carrier mobilities. In the crystal G phase of a α,ω-dialkylterthiophene, mobilities of $2\times10^{-2}\,cm^2\,V^{-1}\,s^{-1}$ for both holes and electrons were reported by Hanna and Funahashi [10]. The orientation of calamitic LC phases has also been used to make organic field effect transistors with high charge carrier mobilities. Here liquid crystalline fluorene-bithiophene copolymers such as F8T2 [11] have been used, as well as low molar mass oligothiophenes [12, 13] and reactive mesogens [14].

A second field in which ordered LC phases have been successfully applied are organic light emitting diodes. In this case, polyfluorenes exhibiting nematic mesophases were used to generate linearly polarized light [15–19].

Recently we have reported the synthesis of bisindenocarbazoles which form a new class of fused heterocycles. By the introduction of different alkyl side chains the thermal properties of the bisindenocarbazoles can be tailored from crystalline materials to amorphous molecular glasses [20]. In this paper we report the synthesis of the first rod-like bisindenocarbazole derivative exhibiting a nematic mesophase.

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290601036225

2. Results and discussion

2.1. *Preparation of the bisindenocarbazole derivatives*

We recently reported the synthesis of novel electroactive bisindenocarbazoles from which, depending on the alkyl substituents, both crystalline materials and amorphous molecular glasses are obtained [20]. In order to prepare a liquid crystalline bisindenocarbazole, the core molecule has to be extended by the introduction of aromatic side groups in order to increase the length of the molecule. For this purpose the bisindenocarbazole was first brominated in the 7- and 7′-positions. After that it was possible to substitute the dibromobisindenocarbazole with different aromatic substituents via a Suzuki crosscoupling. The synthesis of the bisindenocarbazole **1** is reported elsewhere [20]. In order to obtain the new building block **2**, the core molecule **1** had to be reacted with two equivalents of bromine. Kodomari *et al.* reported that aromatic hydrocarbons such as naphthalene and phenanthrene can easily be halogenated by alumina-supported copper(II) halides to give mono- or di-halogenated products [21]. By using this technique they were also able to brominate fluorene selectively in the 2- and 7-positions with high yields. We have adopted this method for the selective bromination of the bisindenocarbazole **1**. The halogenation was carried out with copper(II) bromide supported on alumina in carbon tetrachloride (scheme 1). The selective bromination of the bisindenocarbazole in the 7- and 7′-positions was proven by mass spectroscopy and 2-dimensional NMR spectroscopy.

Our approach to liquid crystalline bisindenocarbazoles was to react the novel building block **2** with different aromatic side groups. For this purpose we used the Suzuki crosscoupling reaction as it is a versatile method for unsymmetrical aryl–aryl couplings [22]. We coupled the brominated bisindenocarbazole **2** with alkylated phenyl, biphenyl and fluorene side groups. The preparation of the aromatic borolanes for the Suzuki crosscoupling is shown in scheme 2.

4,4′-Dibromo-biphenyl (**3**) and 2,7-dibromo-9,9-dimethylfluorene (**6**) were monoalkylated by reaction with one equivalent of *sec*-BuLi followed by the addition of 1-bromohexane. The alkylation proceeds statistically and non-, mono- as well as di-alkylated products are formed. Nevertheless yields of almost 50% were achieved with this synthetic approach after purification by column chromatography.

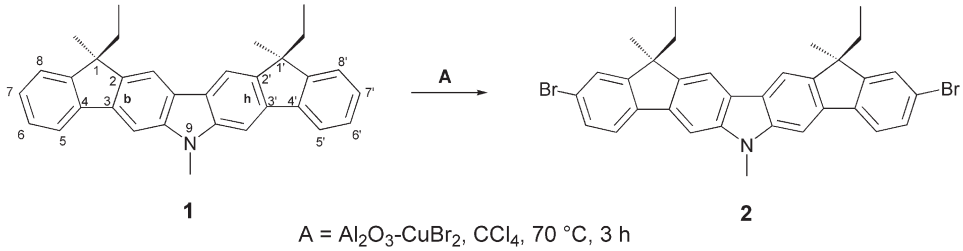
Step B in scheme 2 describes the synthesis of the borolane compounds **5**, **8**, **10** and **12**, which were used for the following Suzuki crosscoupling reactions. For the borolane syntheses the starting compounds **4**, **7**, **9** and **11** were reacted with *n*-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in dry THF. The aromatic borolanes **5**, **8**, **10** and **12** were coupled to the 7,7′-dibromobisindenocarbazole **2** using the Suzuki reaction. The reactions were carried out in a two-phase system of toluene and aqueous potassium carbonate, with trimethylbenzylammonium chloride as phase-transfer catalyst (scheme 3). Mixtures of $Pd(OAc)_2$ and $P(o\text{-tol})_3$ were used as catalyst.

In the Suzuki reactions, yields up to 85% were achieved after the purification of **13**–**16** by medium pressure chromatography (MPLC). The bisindenocarbazole derivatives **13**–**16** show excellent solubility in common organic solvents (e.g. THF, toluene, chloroform), which facilitates purification and processing of the compounds. The structures of the novel compounds were confirmed by IR, ^1H and ^{13}C NMR, mass spectrometry and elemental analysis. The synthetic procedures and analytical data for all compounds are given in §4.

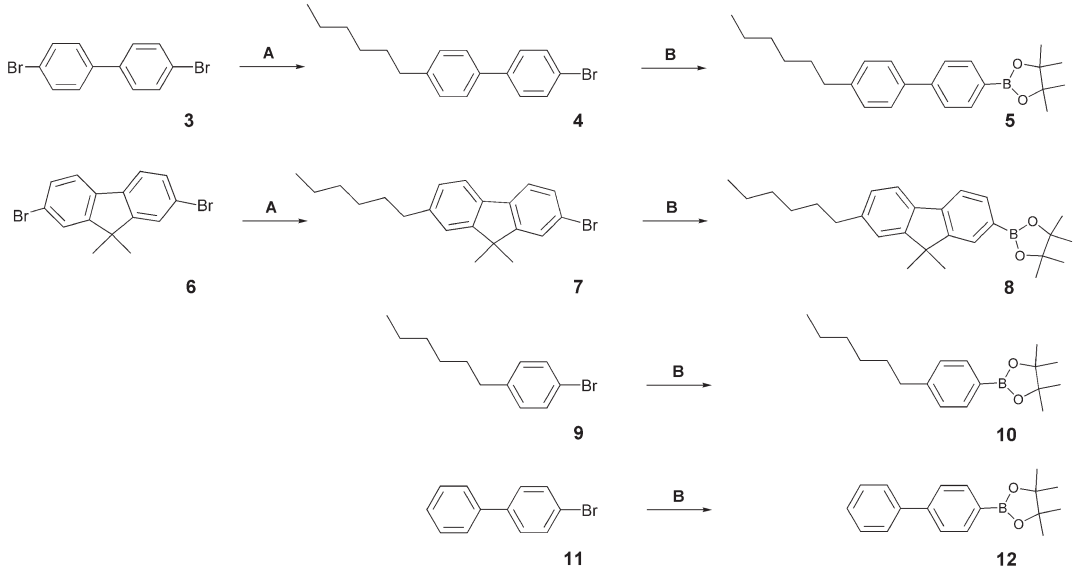
2.2. *Thermal properties*

The thermal properties of the bisindenocarbazole derivatives **13**–**16** were determined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and with small angle X-ray scattering (SAXS).

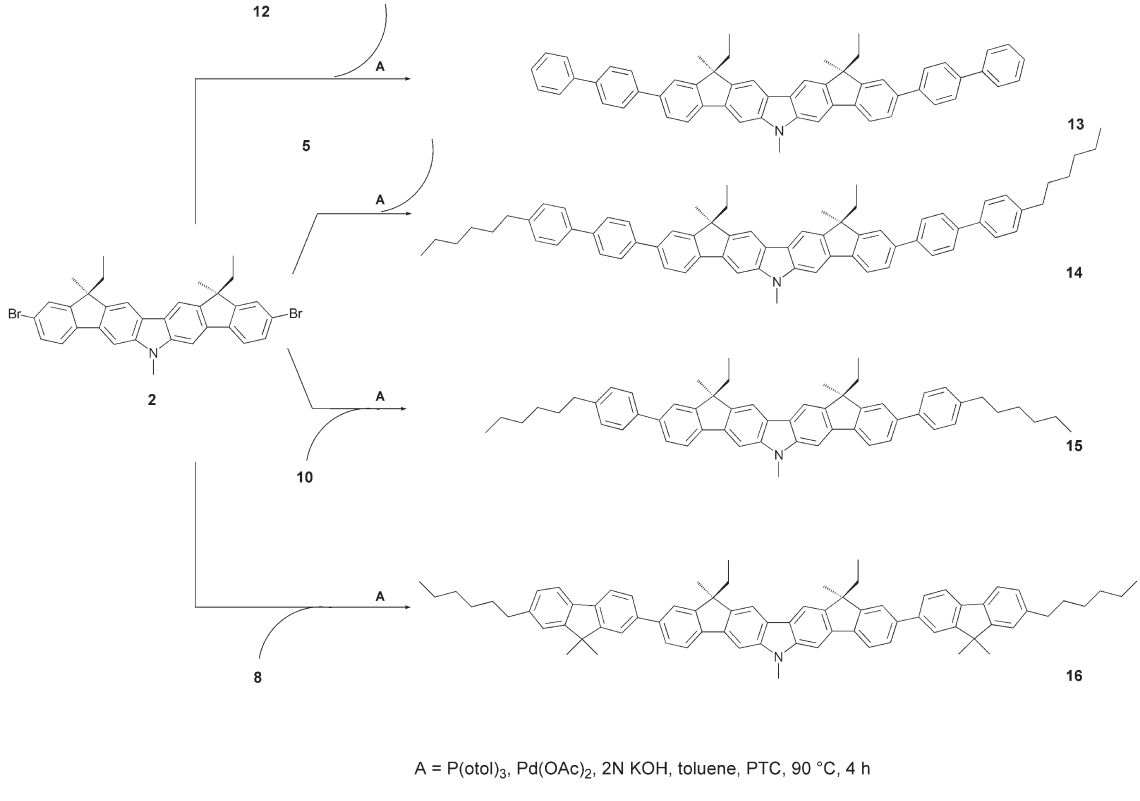
We found that compound **15** with the 4-hexylphenyl side groups shows a liquid crystalline phase. Above 180°C a nematic mesophase is observed by POM, up to a clearing temperature of 251°C. On cooling, the typical



Scheme 1. Synthesis of 7,7′-dibromo-(1*R*,1′*S*)-diethyl-(1*S*,1′*R*)-dimethylbisindeno[3,2-b:2′3′-h]-9-methylcarbazole. Note that the (*R*,*S*)-isomer of **1** was used as starting material.



Scheme 2. Synthesis of the borolane-functionalized side groups for Suzuki crosscoupling.



Scheme 3. Preparation of the bisindenocarbazole derivatives **13**–**16** by Suzuki crosscoupling.

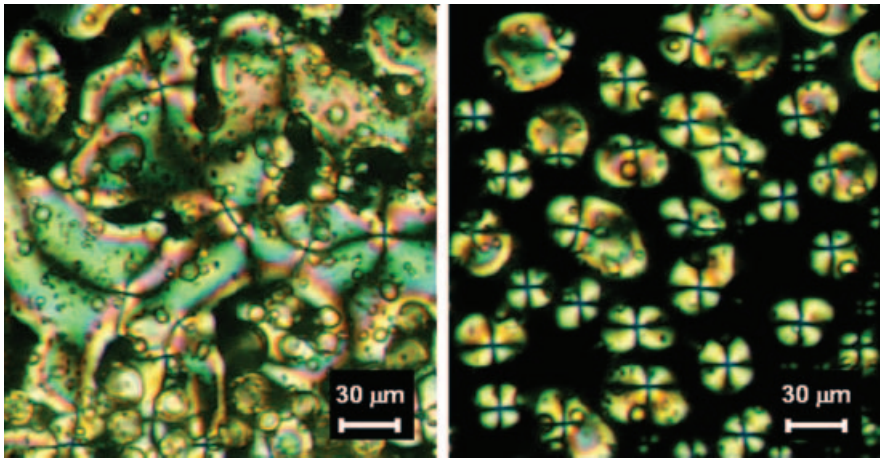


Figure 1. Polarizing microscopy images of **15** on heating to 220°C (left) and on cooling at 248°C (right) under crossed polarizers.

schlieren texture of the nematic mesophase appears at 250°C and crystallization starts at about 165°C. Polarizing microscope images are shown in figure 1. In the DSC measurement **15** exhibits a melting transition at around 180°C with an enthalpy of 12.4 kJ mol^{-1}, and recrystallization at 165°C (8.1 kJ mol^{-1}) on cooling. Further analysis by SAXS confirmed the existence of a nematic LC phase. The X-ray diffractogram of **15** in the nematic phase at 220°C is shown in figure 2. In the small angle region a Bragg peak is observed from which an average end-to-end distance of 34.5 Å at 220°C can be calculated. This distance is a little shorter than the calculated length of the extended molecules (*c.* 36 Å) which is consistent with a slightly tilted arrangement of the rigid rod-like bisindenocarbazole molecules in the nematic mesophase. From the broad wide angle Bragg peak a spacing of 5.6 Å is obtained. This peak reflects the average side-to-side distance of the rod-like molecules and is a typical value for a nematic LC phase.

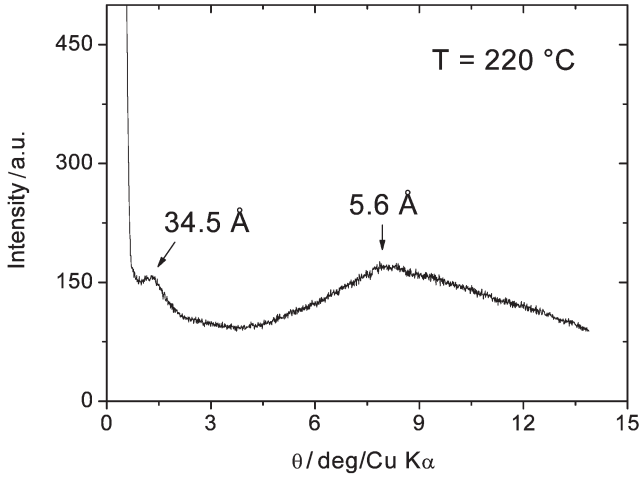


Figure 2. X-ray diffractogram of the bisindenocarbazole derivative **15** at 220°C.

The bisindenocarbazole derivatives with larger aromatic substituents show a different phase behaviour. Compound **14** with the alkylated biphenyl and **16** with fluorene side groups form molecular glasses with glass transition temperatures (T_g) of 103 and 105°C, respectively. In contrast, **13** with the non-alkylated biphenyl substituents is crystalline and melts at 331°C with decomposition. The melting point of **13** was determined by coupled dynamic thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

TGA demonstrated the high thermal stability of the novel bisindenocarbazole derivatives. At a heating rate of 10 K min^{-1} decomposition of the novel materials starts above 300°C in a nitrogen atmosphere.

2.3. *Optical properties*

The absorption and fluorescence spectra of the bisindenocarbazole derivatives **13**–**16** are shown in figures 3 and 4. For comparison, the absorption spectrum of the parent bisindenocarbazole **1** is also shown in figure 3. The spectra of **14** with the 4-hexylbiphenyl and **16** with the fluorene substituents are very similar to the spectrum of **1**. This means that there is almost no conjugation between the bisindenocarbazole core and the fluorene or biphenyl side groups. In the case of **15** with the hexylphenyl substituents the situation is markedly different. The long wavelength absorption at 395 nm is the strongest peak and has a redshift of 16 nm compared with the bisindenocarbazole **1**, which means that in **15** the conjugation of the bisindenocarbazole core is somewhat extended to the phenyl substituents. Until now we cannot explain the differences in the absorption spectra of **15** compared with **14** and **16**. But it is striking that among the four bisindenocarbazole

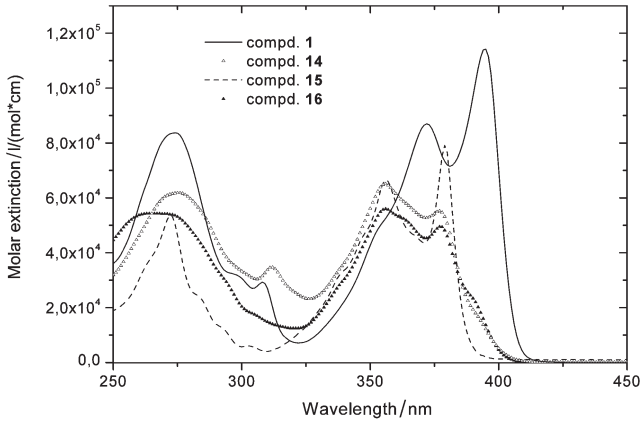


Figure 3. Absorption spectra of the bisindenocarbzole **1** and of its derivatives **14**, **15** (liquid crystalline) and **16**. All absorption spectra were taken from 10^{-5} M cyclohexane solutions.

derivatives presented in this paper only **15** with the 4-hexylphenyl substituents shows a liquid crystalline mesophase, while **13** is highly crystalline and **14** and **16** form molecular glasses.

The new bisindenocarbazole molecules show a strong blue fluorescence. The maxima of emission of all four compounds are very similar and are at about 400 nm. The combined absorption and fluorescence spectra of **15** are presented in figure 4. The results of the optical characterization are summarized in table 1. The small Stokes shift of all four compounds is typical for the rigid structure of the bisindenocarbazole derivatives [23]. Among the four substituted bisindenocarbazoles, **15** which exhibits a nematic mesophase has the smallest Stokes shift of 8 nm. For comparison, the planar bisindenocarbazole core compound **1** exhibits a Stokes shift of only 6 nm [20]. The derivatives with the larger substituents like the alkylated fluorenes **16**, apparently become more flexible. Compared with **15**, the Stokes shift of **16** has increased to 26 nm (table 1).

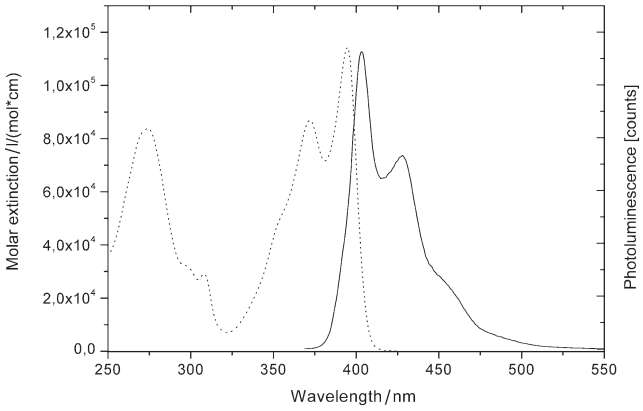


Figure 4. Absorption and fluorescence spectra of bisindenocarbazole **15**. The absorption spectrum was obtained from a 10^{-5} M cyclohexane solution and the fluorescence spectrum from a 10^{-6} M cyclohexane solution with an excitation wavelength of 395 nm.

In order to estimate the fluorescence quantum yield (Φ_f) of the bisindenocarbazole derivatives, the fluorescence of **13**–**16** was compared with the well known laser dye Exalite 428 [7,7″-bis(4-*t*-amylphenyl)-9,9,9′,9′,9″,9″-hexapropyl-2,2′:7′2″-terfluorene], which has a quantum efficiency of 90% in cyclohexane solution [24]. In order to minimize self-absorption it is necessary to measure the fluorescence from highly diluted solutions [25]. For the estimation of Φ_f, cyclohexane solutions of Exalite 428 and **13**–**16** with an optical density of 0.1 were prepared. From these solutions fluorescence spectra were recorded and by integration, the fluorescence quantum yield was calculated. With 56%, the biphenyl-substituted bisindenocarbazole derivative **13** gave the highest quantum efficiency (table 1).

2.4. *Electrochemical properties*

The electrochemical stability of the bisindenocarbazoles 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 [26]. Ten sequential redox cycles were measured to check the redox stability of the novel bisindenocarbazole derivatives **13**–**16**. The CV curve of **15** (figure 5) shows one quasireversible oxidation peak at 443 mV. Repeated oxidation and reduction cycles did not change the redox potential, which is evidence for the electrochemical stability of the material. Compounds **14**–**16** show identical behaviour in the CV experiments.

Taking −4.8 eV as the HOMO level for the ferrocene/ferrocenium redox system, HOMO values of about −5.4 eV were calculated for the bisindenocarbazole

Table 1. Optical properties of the bisindenocarbazole derivatives.

Compound	λ_{abs}/nm[a]	$\lambda_{max,flour}$/nm[b]	λae/nm[c]	Stokes shift/nm	Φ_f/%[d]
1	379	385	394	6	63
13	378	397	403	19	56
14	378	397	403	19	54
15	395	403	408	8	49
16	374	400	400	26	34

[a]Longest wavelength absorption maximum, measured in 10^{-5} M cyclohexane solution. [b]Fluorescence spectra taken from 10^{-6} M cyclohexane solution. [c]Absorption edge. [d]Fluorescence quantum yield (for details see text).

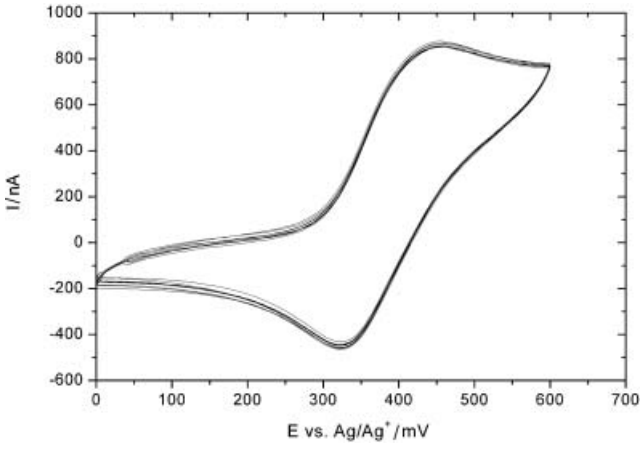


Figure 5. Cyclic voltammetry curve of **15**, measured in dichloromethane at 25°C at a scan rate of 50 mV s^{-1} vs. Ag/Ag^+ with $TBAPF_6$ as supporting electrolyte. In order to check the electrochemical stability 10 sequential redox cycles were carried out.

derivatives **13**–**16** [27]. With a band gap (ΔE) of 3.1 eV, taken from the absorption spectra, LUMO values of −2.3 eV were estimated for the new bisindenocarbazole compounds. The different aromatic side arms have no distinct influence on the electrochemical properties of the novel materials.

3. Conclusions

We have presented the synthesis of four new bisindenocarbazole derivatives which were prepared by selective bromination of bisindenocarbazole in the 7- and 7′-positions followed by Suzuki crosscoupling reactions with alkylated phenyl, biphenyl and fluorene groups. From this new class of fused aromatics a liquid crystalline derivative is reported for the first time. The phenyl-substituted bisindenocarbazole **15** exhibits a broad nematic phase between 180 and 250°C. In contrast to **15**, the other bisindenocarbazole derivatives are crystalline (**13**) or form amorphous molecular glasses (**14**, **16**). All target molecules exhibit high thermal stabilities to above 300°C and show excellent electrochemical stability in CV experiments. HOMO and LUMO levels of −5.4 and −2.3 eV, respectively, were determined for the novel bisindenocarbazoles. They display a strong blue fluorescence with quantum yields up to 56% in solution.

4. Experimental

4.1. *General*

^{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. Mass spectra (MS) were recorded with a Finnigan MAT 8500 (70 eV) with a MAT 112S Varian. TGA was performed on a Perkin Elmer TAS-409 at a heating rate of 10 K min^{-1} under N_2. For DSC measurements a Perkin-Elmer Diamond DSC apparatus was used (heating/cooling rate: 10 K min^{-1}). Polarizing microscopy was carried out with a Nikon Diaphot 300 equipped with a Linkam hot stage. X-ray analysis was carried out with a Huber/Seifert Iso-Debyeflex 3003, using a Guinier diffractometer system (Cu K_α: 15,418 Å) with a sealed tube for temperature-dependent measurements. Cyclic voltammetry measurements were performed with a glassy carbon working electrode (0.2 mm) in a three-electrode potentiostat configuration from EG&G Princeton Applied Research.

All chemicals and reagents were used as received from Aldrich. Neutral alumina was purchased from ICN Biomedicals (MP Alumina N, Akt. I). Carbon tetrachloride was received from Merck. Tetrahydrofuran (THF) was distilled over potassium before use. The synthesis of (1*R*,1′*S*)-diethyl-(1*S*,1′*R*)-dimethylbisindeno[3,2-b:2′3′-h]-9-methylcarbazole (**1**) is reported elsewhere [20]. 4,4′-Dibromo-biphenyl (**3**) was purchased from Aldrich and 2,7-dibromo-9,9-dimethylfluorene (**6**) was prepared as described in the literature [28].

4.2. *Preparation of Alumina-supported copper(II) bromide [21]*

To a solution of copper(II) bromide (10 g) in distilled water (30 ml), neutral alumina (20 g) was added at room temperature. The water was evaporated at 80°C under reduced pressure with a rotary evaporator. The resulting reagent was dried under high vacuum at 100°C for 24 h and afterwards stored under argon.

4.3. *Synthesis of the bisindenocarbazole building block: 7,7′-dibromo-(1R, 1′S)-diethyl-(1S, 1′R)-dimethylbisindeno[3,2-b:2′3′-h]-9-methylcarbazole (2)*

A mixture of bisindenocarbazole **1** (0.38 g, 0.86 mmol), Al_2O_3-$CuBr_2$ (2.9 g) and carbon tetrachloride (80 ml) was stirred at 70°C for 3 h. The product mixture was filtered and the spent reagent washed with dichloromethane (30 ml) before the solvents from the combined filtrate were evaporated under reduced pressure. Purification by column chromatography on silica gel with hexane/THF (10/1) as eluant yielded 0.4 g (78%) of

2 as a pale yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 0.32–0.43(m, 6H), 1.61(s, 6H) 2.15(q, 4H), 3.93(s, 3H), 7.48(dd, 2H, J=8.0 Hz and J=1.5 Hz), 7.53(d, 2H, J=1.5 Hz), 7.64(s, 2H) 7.68(d, 2H, J=8.0 Hz), 8.04(s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm) 8.93, 27.23, 29.41, 34.05, 50.88, 99.55, 113.95, 120.82, 120.89, 123.05, 126.27, 130.03, 137.72, 139.92, 141.77, 142.90, 154.73. MS (70 eV): m/z=597/599/601 (M^+). Anal: calcd for $C_{33}H_{29}Br_2N$ (599.4), C 66.13, H 4.88, N 2.34; found, C 66.11, H 4.87, N 2.36%.

4.4. *Preparation of the side groups*

4.4.1. 4′-Bromo-4-hexylbiphenyl (4). 4,4′-Dibromobiphenyl (2.5 g, 8 mmol) were dissolved in 40 ml abs. THF under argon. The solution was cooled to −78°C before 6.25 ml (8.1 mmol, 0.52 g) *sec*-BuLi (1.3M solution in hexane) were added slowly. After stirring for 5 min, 1-bromohexane (1.2 ml, 8.2 mmol) was added. The solution was allowed to warm to room temperature and stirred for 12 h before it was poured into 50 ml ice water. The reaction mixture was extracted with diethyl ether, the organic phase washed with water and dried over Na_2SO_4 and the solvent evaporated. Purification by column chromatography on silica gel with hexane/THF (50/1) as eluant yielded 1.25 g (49%) of **4** as a colourless solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm): 0.89(t, 3H), 1.26–1.45(m, 6H), 1.60–1.71(m, 2H), 2.63(t, 2H), 7.37–7.48(m, 4H), 7.50–7.59(m, 4H). MS (70 eV): m/z=317 (M^+).

4.4.2. 2-Bromo-7-hexyl-9,9-dimethylfluorene (7). This was prepared according to the procedure described for **4**, yielding 47% of **7**. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 0.88(t, 3H), 1.19–1.35(m, 6H), 1.47(s, 6H), 1.65(m, 2H), 2.67(t, 2H), 7.13(dd, 1H), 7.21(s, 1H), 7.42(dd, 1H), 7.54(m, 3H). MS (70 eV): m/z=357 (M^+).

4.4.3. 2-(4′-Hexyl-biphenyl-4-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (5). 4′-Bromo-4-hexylbiphenyl (**4**) (0.85 g, 2.7 mmol) was dissolved in absolute THF under argon. The solution was cooled to −78°C and 1.9 ml (3.0 mmol) *n*-BuLi (1.6M solution in hexane) added dropwise. The reaction mixture was stirred for 10 min, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.8 ml, 4.0 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h before pouring into ice-water. The solution was extracted with diethyl ether, the organic phase washed with brine and dried with Na_2SO_4 and the solvent removed. Purification by column chromatography on silica gel with hexane/THF (15/1) as eluant yielded 0.78 g (80%) of **5** as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 0.88(t, 3H), 1.25–1.35(m, 8H), 1.36(s, 12H), 2.64(t, 2H), 7.24–7.27(m, 2H), 7.54(d, 2H), 7.60(d, 2H), 7.87(d, 2H). MS (70 eV): m/z=364 (M^+).

4.4.4. 2-(7-Hexyl-9,9-dimethylfluoren-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (8). This was prepared according to the procedure described for **5**; yield 74%. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 1.38(m, 3H), 1.24–1.35(m, 8H), 1.38(s, 12H), 1.49(s, 6H), 2.68(t, 2H), 7.16(d, 1H), 7.26(s, 1H), 7.67(d, 2H), 7.81(d, 1H), 7.86(s, 1H). MS (70 eV): m/z=404 (M^+).

4.4.5. 2-(4-Hexylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (10). This was prepared according to the procedure described above for **5**. Purification by column chromatography on silica gel with hexane/THF (20/1) as eluant yielded 85% of **10** as a colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm): 0.86(t, 3H), 1.18–1.26(m, 8H), 1.33(s, 12H), 2.62(t, 2H), 7.20(d, 2H), 7.73(d, 2H). MS (70 eV): m/z=288 (M^+).

4.4.6. 2-Biphenyl-4-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (12). Again, prepared according to the procedure described above for **5**. Purification by column chromatography on silica gel with hexane/THF (10/1) as eluant yielded 76% of **12** as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 1.36(s, 12H), 7.42–7.45(m, 3H), 7.62(d, 4H), 7.89(d, 2H). MS (70 eV): m/z=280 (M^+).

4.4.7. 7,7′-Di(biphenyl-4-yl)-(1*R*,1′*S*)-diethyl-(1*S*,1′*R*)-dimethylbisindeno[3,2-b:2′3′-h]-9-methylcarbazole (13). 7,7′-Dibromobisindenocarbazole **2** (0.1 g, 0.17 mmol) and the borolane **12** (0.1 g, 0.37 mmol) were dissolved in 25 ml toluene. A 2M K_2CO_3 solution (6 ml) and trimethylbenzylammonium chloride (0.1 g) were added. The reaction mixture was degassed by three freeze/thaw cycles before 1.7 mg (7.3×10^{-6} mol) of palladium(II) acetate and 6.7 mg (2.2×10^{-5} mol) of tri-*o*-tolylphosphine were added under argon. The mixture was stirred for 4 h at 90°C, then poured into ice water, extracted with diethyl ether and dried with Na_2SO_4. After evaporation of the solvent, the crude product was purified by MPLC with hexane/THF (20/1) as eluant at a pressure of 18 bar; 98 mg (77%) of **13** was obtained as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 0.45(t, 6H), 1.64(s, 6H), 2.18(q, 4H), 2.94(s, 3H), 6.31(d, 2H), 6.91(t, 2H), 7.16(t, 2H), 7.37(t, 4H), 7.47(d, 4H), 7.55(d, 4H), 7.72–7.77(m, 8H), 8.16 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm) 9.33, 27.14, 36.37, 109.21, 112.99, 117.51, 120.95, 122.87, 123.15, 123.28, 126.82, 127.40, 127.55, 127.93, 129.28, 131.41, 131.56, 138.22, 140.75, 141.52, 144.13, 153.30. MS (70 eV): m/z=745 (M^+). IR (KBr):$\tilde{\nu}$ (cm^{-1}) 2960, 2921,

2850, 1635, 1486, 1398, 1341, 1008, 749. Anal. calcd for $C_{57}H_{47}N$ (746.0), C 91.77, H 6.35, N 1.88; found, C 91.69, H 6.28, N 1.92%.

4.4.8. 7,7′-Di(4′-hexyl-biphenyl-4-yl)-(1*R*,1′*S*)-diethyl-(1*S*,1′*R*)-dimethylbisindeno[3,2-b:2′3′-h]-9-methylcarbazole (14). Compound **14** was prepared by Suzuki crosscoupling according to the procedure described for **13** and purified by MPLC with hexane/THF (25/1) at a pressure of 18 bar; yield 81%. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 0.38–0.47(m, 6H), 0.90(t, 6H), 1.27–1.42(m, 16H), 1.59–1.68(m, 6H), 2.17(q, 4H), 2.62(t, 4H), 2.92(s, 3H), 6.31(d, 2H), 6.88–6.95(m, 2H), 7.14–7.20(m, 2H), 7.30(s, 2H), 7.34–7.40(m, 4H), 7.52–7.57(m, 4H), 7.66(d, 4H), 7.73(d, 4H), 8.15(s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm) 9.34, 14.49, 23.00, 27.97, 28.06, 29.35, 31.88, 32.13, 34.75, 36.00, 49.96, 112.94, 120.96, 122.82, 123.20, 123.30, 126.81, 127.19, 127.32, 129.33, 131.35, 131.50, 137.58, 137.86, 138.05, 140.65, 141.71, 142.82, 144.12, 153.30. MS (70 eV): m/z=913 (M^+). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 2959, 2925, 2854, 1497, 1457, 1342, 1006, 748. Anal: calcd for $C_{69}H_{71}N$ (914.3), C 90.64, H 7.83, N 1.53; found, C 90.40, H 7.74, N 1.79%.

4.4.9. 7,7′-Di(4-hexylphenyl)-(1*R*,1′*S*)-diethyl-(1*S*,1′*R*)-dimethylbisindeno[3,2-b:2′3′-h]-9-methylcarbazole (15). Compound **15** was prepared according to the procedure described for **13** and purified by MPLC with hexane/THF (30/1) at a pressure of 18 bar; yield 79%. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 0.33–0.41(m, 6H), 0.83(t, 6H), 1.18–1.32(m, 10H), 1.49–1.65(m, 12H), 2.09(q, 4H), 2.56(t, 4H), 3.89(s, 3H), 7.18(d, 4H), 7.50–7.57(m, 8H), 7.61(s, 2H), 7.79(d, 2H), 8.00(s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm) 8.01, 13.10, 21.63, 26.42, 28.04, 28.38, 30.51, 30.75, 33.21, 34.63, 49.62, 98.37, 112.77, 118.73, 120.39, 121.77, 124.90, 125.96, 127.82, 137.40, 138.01, 138.95, 138.99, 140.74, 140.93, 142.53, 152.15. MS (70 eV): m/z=761 (M^+). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 2959, 2926, 2854, 1559, 1495,1345, 1260, 841. Anal: calcd for $C_{57}H_{63}N$ (762.1), C 89.83, H 8.33, N 1.84; found, C 89.72, H 8.29, N 1.95%.

4.4.10. 7,7′-Di(7-hexyl-9,9-dimethylfluoren-2-yl)-(1*R*,-1′*S*)-diethyl-(1*S*,1′*R*)-dimethylbisindeno[3,2-b:2′3′-h]-9-methylcarbazole (16). Compound **16** was prepared according to the procedure described for **13** and purified by MPLC with hexane/THF (30/1) at a pressure of 18 bar; yield 85%. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm) 0.37(m, 6H), 0.89(t, 6H), 1.33(m, 10H), 1.46(s, 12H), 1.58(m, 12H), 2.16(q, 4H), 2.66(t, 4H), 3.70(s, 3H), 7.13(dd, 2H), 7.20(s, 2H), 7.39(dd, 2H), 7.51–7.55(m, 6H), 7.68–7.73(m, 6H), 7.81(s, 2H), 8.14(s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm) 9.35, 14.48, 23.01, 27.62, 28.10, 29.41, 29.48, 32.17, 34.67, 36.71, 47.10, 47.34, 50.04, 112.84, 120.30, 122.83, 123.28, 124.29, 125.51, 126.59, 126.70, 126.91, 127.23, 127.67, 129.83, 136.85, 137.01, 137.45, 139.37, 141.49, 143.00, 143.23, 153.28, 154.55. MS (70 eV): m/z=993 (M^+). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 2958, 2923, 2854, 1457, 1340, 1253, 821, 746. Anal: calcd for $C_{75}H_{79}N$ (994.5), C 90.58, H 8.01, N 1.41; found, C 90.46, H 7.93, N 1.52%.

Acknowledgments

The authors would like to thank Andrea Jahreis for helping to prepare the starting materials, Andreas Timme for the SAXS measurement and Günter Lattermann for fruitful discussions. We are grateful to the Deutsche Forschungsgemeinschaft (SFB 481) and the BMBF (POLITAG programme) for financial support.

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