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Synthesis and characterization of novel conjugated bisindenocarbazoles

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Abstract—We present the synthesis of five new bisindenocarbazoles with different alkyl substituents. The synthesis starts from 2,7-dibromocarbazole and leads to the bisindenocarbazoles **6–10** in five steps with an overall yield of about 50%. By substitution of the core with different alkyl chains in the last step of the synthesis, the morphology of the bisindenocarbazoles can be varied from crystalline materials to molecular glasses. The bisindenocarbazoles are electrochemically stable and exhibit a strong, saturated blue emission with a quantum yield of 63% in solution.

1. Introduction

Fused aromatics like pentacene and rubrene are attractive materials for organic electronics. Both pentacene single crystals[1] and thin, polycrystalline pentacene films exhibit carrier mobilities above 1 cm^2/Vs in organic field effect transistors (OFETs).[2] Single crystalline rubrene shows carrier mobilities up to 15 cm^2/Vs in OFETs.[3] In addition, rubrene has been used as efficient yellow dopant in organic light emitting diodes (OLEDs).[4]

Besides pure hydrocarbons like pentacene, materials containing fused heterocycles have attracted increasing interest as materials for organic electronics during the last years. For example, indolo- and bisindolocarbazoles have been synthesized and successfully tested in OFETs.[5–8]

In this paper, we present the synthesis of five new bisindenocarbazoles, a class of fused heterocycles that has not yet been described in the literature. We have developed a new and versatile strategy for the preparation of these materials, which makes it possible to introduce different alkyl substituents to the core in the very last step of the synthesis. This allows us to tailor the properties of this new class of materials. For example, **6** with four small methyl substituents in the 1- and 1′-positions is highly crystalline, whereas **7** with two butyl and two methyl groups is an amorphous molecular glass.

Keywords: Bisindenocarbazole; Carbazole; Suzuki cross coupling.
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2. Results and discussion

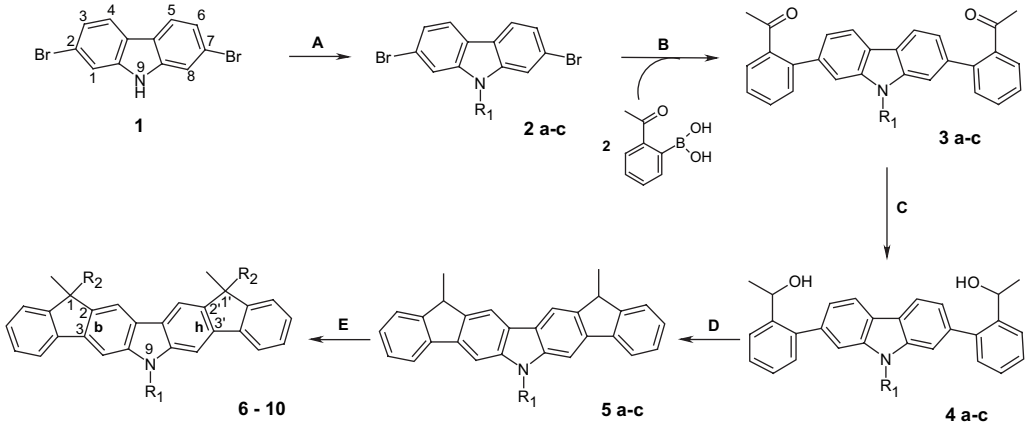
2.1. Preparation of the bisindenocarbazoles

Scheme 1 shows the synthetic route to the new bisindenocarbazoles. The preparation of 2,7-dibromocarbazole (**1**) and the *N*-alkylated carbazole monomers (**2a–c**) has been reported elsewhere.[9–13]

For phenylation (**B**) of the *N*-alkyl carbazoles **2a–c** in positions 2 and 7, the Suzuki cross coupling reaction was chosen, as it is an excellent tool for unsymmetrical aryl–aryl couplings.[14] 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 Suzuki coupling of 2-acetylphenylboronic acid and *N*-alkylated 2,7-dibromocarbazoles **2a–c**, a mixture of $Pd(OAc)_2$ and P(*o*-tol)$_3$ was used as catalyst. Excellent yields of up to 91% of **3a–c** were achieved. In the next step, the keto groups were reduced to the corresponding secondary alcohols **4a–c** by reaction with lithium triethyl borohydride (super-hydride) in abs THF. In the case of bisindenocarbazoles, the reduction with super-hydride solution works fast and quantitatively.

The ring closure reaction of **4a–c** to the bisindenocarbazoles **5a–c** was carried out with boron trifluoride etherate as Lewis-acid catalyst in dichloromethane at room temperature. Ring closure occurs exclusively in the 3- and 6-positions of the carbazole, which are highly activated.

Finally, different alkyl side chains can be introduced to the planar bisindenocarbazole core with *n*-BuLi and the



2a,b: A = alkyl bromide, acetone, KOH, PTC, 70 °C, 5 h

2c: A = Me_2SO_4, acetone, 10N KOH, 50 °C, 30 min

B = $P(otol)_3$, $Pd(OAc)_2$, 2N KOH, toluene, PTC, 90 °C, 2 h

C = lithium triethylborohydride, THF, 0 °C, 1 h

D = BF_3*$O(C_2H_5)_2$, CH_2Cl_2, RT, 30 min

E = 1.6 M n-BuLi, alkyl bromide, THF, -78 °C, 1 h

compd	R_1	R_2
2-5a	*sec*-butyl	---
2-5b	2-ethylhexyl	---
2-5c	methyl	---
6	*sec*-butyl	methyl
7	*sec*-butyl	n-butyl
8	*sec*-butyl	ethyl
9	2-ethylhexyl	ethyl
10	methyl	ethyl

Scheme 1. Synthesis of bisindenocarbazoles with different alkyl substituents.

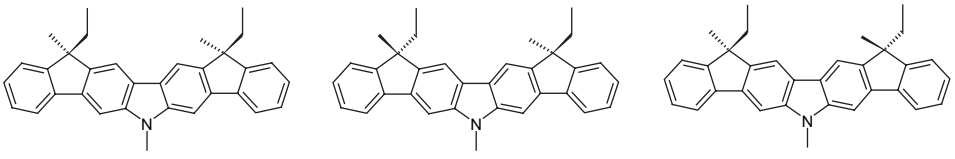
corresponding alkyl halide. The alkylation of bisindenocarbazoles in the very last step is a big advantage of this synthetic approach. As we will show in the next paragraphs, the morphology and the thermal properties of the target molecules can be tailored by adding alkyl groups of different lengths without changing the optical and electrical properties.

The bisindenocarbazoles **6–10** are mixtures of stereoisomers. Compound **6** is a mixture of two enantiomers, **7–9** have three stereocenters and hence eight enantiomers and four diastereomers. Compound **10** with two stereocenters in the 1- and 1′-positions is a mixture of two enantiomers and two diastereomers. Only in the case of **10** we were able to separate the two diastereomers by medium pressure liquid chromatography (MPLC). The first fraction is the *meso* form with (*R*,*S*)-configuration. The second fraction consists of the (*R*,*R*)- and (*S*,*S*)-enantiomers (Scheme 2). The (*R*,*R*/*S*,*S*)- and (*R*,*S*)-isomers are formed in a ratio of 2:1. The melting points of the two isomers differ by 19 °C. The (*R*,*S*)-isomer melts at 292 °C and the (*R*,*R*/*S*,*S*) racemate melts at 273 °C. In contrast, it was not possible to separate the bisindenocarbazoles **7–9**, which are a mixture of four diastereomers. Therefore, the NMR and thermal data refer to the isomeric mixtures.

All bisindenocarbazoles show good solubility in common organic solvents (e.g., THF, toluene, chloroform). The structures of the bisindenocarbazoles were confirmed by IR, ^1H and ^{13}C NMR, mass spectrometry, and elemental analysis. The synthetic procedures and the analytical data of all compounds are given in Section 4.

2.2. Thermal properties

The thermal properties of the bisindenocarbazoles were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and are summarized in Table 1. TGA experiments in nitrogen showed that the bisindenocarbazoles **6–10** start to sublime at temperatures above 260 °C. Between 300 and 350 °C, quantitative weight



(R,S)-isomer of **10** *(S,S)*-isomer of **10** *(R,R)*-isomer of **10**

Scheme 2. Different isomers and configurations of **10**.

Table 1. Thermal properties of the bisindenocarbazoles **6–9**

Compd	T_g [°C][a]	T_m [°C][a]	T_{subl} [°C][b]
6	—	265	310
7	106[c]	—	320
8	103[c]	250[c,d]	305
9	74[c]	164[c]	330
10 (*R*,*S*)	—	292	260
10 (*R*,*R*/*S*,*S*)	—	273	260

[a] Determined by DSC, scan rate 10 K/min, second run, N_2 atmosphere.
[b] Onset of sublimation determined by TGA, heating rate 10 K/min, N_2 atmosphere.
[c] T_g and T_m refer to mixtures of four diastereomers.
[d] Melting point only detected in the first heating cycle.

loss was detected in all cases. The fact that the molecules can be sublimed quantitatively at ≈320 °C at normal pressure allows to prepare high quality films of the materials by vapor deposition.

DSC measurements clearly show how the morphology of the molecules can be tailored by changing the alkyl side groups. Compound **6** with four methyl substituents in the 1- and 1′-positions is crystalline (T_m=265 °C), whereas **7** with two butyl and two methyl side chains is amorphous and exhibits only a glass transition at 106 °C. In contrast to **6**, which recrystallizes upon cooling, the ethyl/methyl-substituted molecule **8** can be transferred into a glassy state upon cooling in the DSC experiment. Melting point of **8** is only observed in the first heating cycle at 250 °C. In the second and third run only the glass transition at 103 °C is detected. In the bisindenocarbazole **9**, the *N*-*sec*-butyl substituent of the central carbazole unit is replaced by a longer 2-ethylhexyl chain. This leads to a low glass transition temperature of 74 °C and melting point at 164 °C.

In the case of **10**, we were able to separate the two diastereomers. Both the (*R*,*R*/*S*,*S*)- and (*R*,*S*)-isomers of **10** are crystalline and melt at 273 and 292 °C, respectively. Upon cooling, both compounds show recrystallization in the DSC experiment. The mixture of the two diastereomers is also crystalline. In contrast to the two pure isomers, the mixture does not recrystallize upon cooling but forms a glass, which recrystallizes during the subsequent heating cycle. This shows that the mixture has a higher tendency to form a molecular glass than the pure diastereomers.

2.3. Optical properties

As expected, identical UV–vis spectra are obtained from the bisindenocarbazoles. The change of the alkyl side chains has no influence on the absorption of the bisindenocarbazole chromophore. The absorption and fluorescence spectra of **6** (Fig. 1) are representative for the bisindenocarbazoles **6–10**. The absorption maximum is at 380 nm. The bisindenocarbazoles exhibit a strong, saturated blue fluorescence with an emission maximum at 410 nm. The small Stokes shift of 6 nm is typical for the rigid structure of the bisindenocarbazoles.[15]

The fluorescence spectrum of **6** shows characteristic vibronic structures. The separation between the peaks at 388 and 410 nm is 1382 cm^{-1}, and between 410 and the shoulder at 435 nm is 1461 cm^{-1}. These values correspond

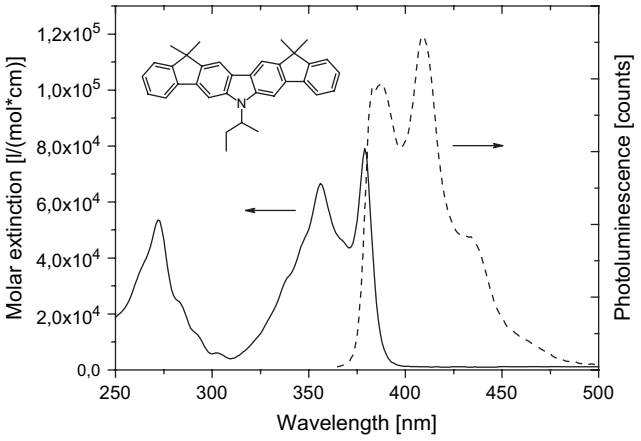


Figure 1. Absorption and fluorescence spectra of the bisindenocarbazole **6**. The absorption spectra were taken from 10^{-5} M cyclohexane solutions and the fluorescence spectra from 10^{-6} M cyclohexane solutions with an excitation wavelength of 350 nm.

to two discrete carbazole skeleton vibrations in the IR-spectrum.

In order to estimate the fluorescence quantum yield (Φ_f) of the bisindenocarbazoles, the fluorescence of **6** was compared with the well known blue laser dye Exalite 428 [7,7″-bis(4-*tert*-amylphenyl)-9,9,9′,9′,9″,9″-hexapropyl-2,2′:7′,2″-terfluorene]. Exalite 428 has a quantum efficiency of 90% in cyclohexane solution.[16] Solutions (10^{-5} M) of **6** and Exalite 428 in cyclohexane were prepared and diluted to an optical density of ≈0.1 in order to minimize self-absorption.[17] From these solutions, fluorescence spectra were taken and by integration, a fluorescence quantum yield of 63% was calculated for **6**.

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 versus Ag/AgCl as the reference electrode.[18] The CV curve of **6** (Fig. 2) shows one oxidation peak at 0.60 V, which is fully reversible. Repeated oxidation and reduction cycles had no influence on the CV curve. The same results are obtained for other bisindenocarbazoles **7–10**. This is a proof for the electrochemical stability of the new bisindenocarbazoles. It has been reported that the electrochemical oxidation of compounds based on 2,7-linked carbazoles is not fully reversible and that such materials undergo dimerization reactions in the activated 3- and 6-positions of the carbazole rings.[6,10] The high electrochemical stability of the bisindenocarbazoles **6–10**, in which these positions are blocked by ring closure, strongly supports this argument and shows that the activated 3- and 6-positions in 2,7-linked carbazole compounds have to be blocked in order to obtain electrochemically stable materials.

The HOMO levels of the bisindenocarbazoles **6–10** can be estimated from the CV measurement. For this purpose, the CV was calibrated with the standard ferrocene/ferrocenium

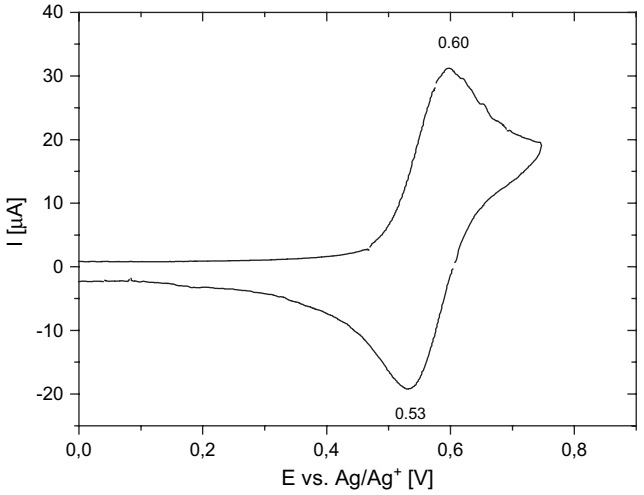


Figure 2. CV measurement of **6**, measured at 25 °C at a scan rate of 50 mV/s versus Ag/Ag^+ in acetonitrile with $TBAPF_6$ as supporting electrolyte.

redox system. Taking −4.8 eV as HOMO level for the ferrocene redox system,[19] HOMO values of −5.3 eV were obtained. With an optical band gap of 3.2 eV, calculated from the absorption edge at 391 nm, LUMO values of −2.1 eV are calculated for compounds **6–10**.

3. Conclusions

In conclusion, we have developed a new versatile synthetic route to conjugated bisindenocarbazoles. The title compounds **6–10** are obtained in five steps from 2,7-dibromocarbazole **1** with an overall yield of 50%. By substitution with a variety of alkyl substituents in the very last step of the synthesis, their morphology can be varied from highly crystalline materials (**6**) to amorphous molecular glasses (**7**). The compounds sublime quantitatively at temperatures around 320 °C and excellent films can be prepared by evaporation. In CV experiments, the bisindenocarbazoles showed a high electrochemical stability. This is in contrast to the 2,7-carbazole trimers, which have been reported before.[10] These trimers show irreversible electrochemical oxidation due to dimerization reactions in the highly activated 3- and 6-positions of the carbazole ring. In the bisindenocarbazoles **6–10**, the reactive 3- and 6-positions in the central carbazole unit are blocked by the ring closure. From CV measurements and optical band gap, HOMO levels of −5.3 eV and LUMO values of −2.1 eV were calculated. All bisindenocarbazoles **6–10** exhibit a strong, saturated blue emission with a quantum yield of 63% in solution and will be tested as blue dopants in organic light emitting diodes in the near future.

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. Conventional mass spectra (MS) were recorded with a Finnigan MAT 8500 (70 eV) with a MAT 112S Varian. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TAS-409 at a heating rate of 10 K/min under N_2. For differential scanning calorimetry measurements (DSC), Perkin–Elmer DSC-7 apparatus was used (heating/cooling rate: 10 K/min). Cyclic voltammetry measurements (CV) 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. Tetrahydrofuran (THF) was distilled over potassium before use. The synthesis of 2,7-dibromocarbazole (**1**) and *N*-alkylated 2,7-dibromocarbazoles (**2a–c**) has been reported elsewhere.[9–13]

4.2. 2,7-Bis-(2-acetylphenyl)-9-*sec*-butyl-carbazole (3a)

2,7-Dibromo-9-*sec*-butyl-carbazole (**2a**) (1.3 g, 3.5 mmol) and 2-acetylphenylboronic acid (1.3 g, 7.7 mmol) were dissolved in 45 ml of toluene. A 2 M solution of K_2CO_3 (25 ml) and 0.2 g of trimethylbenzylammonium chloride was added. The reaction mixture was degassed by three freeze/thaw cycles before 31.3 mg (0.14 mmol) $Pd(OAc)_2$ and 127.0 mg (0.42 mmol) tri-*o*-tolylphosphine ($P(o\text{-tol})_3$) were added under argon. The mixture was stirred for 15 h at 90 °C before it was poured into ice water and extracted with diethyl ether. After evaporation of the solvent, the product was purified by column chromatography on silica gel with hexane/THF (6:1) as eluent yielding 1.42 g (89%) of **3a** as a colorless solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.71(t, 3H), 1.58 (d, 3H), 1.86 (s, 6H), 1.95 (m, 1H), 2.21 (m, 1H), 4.53–4.67 (m, 1H), 7.20 (m, 2H), 7.37 (m, 4H), 7.52 (m, 6H), 8.13 (d, 2H). MS (70 eV): m/z=459 (M^+).

4.3. 2,7-Bis-(2-acetylphenyl)-9-(2-ethylhexyl)-carbazole (3b)

Compound **3b** was prepared according to the procedure described above (yield: 91%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.78–0.87 (m, 6H), 1.12–1.40 (m, 8H), 1.48 (s, 6H), 2.07 (m, 1H), 4.16 (m, 2H), 7.17 (d, 2H), 7.34 (m, 6H), 7.36 (m, 2H), 7.70 (d, 2H), 8.14 (d, 2H). MS (70 eV): m/z=515 (M^+).

4.4. 2,7-Bis-(2-acetylphenyl)-9-methyl-carbazole (3c)

Compound **3c** was prepared according to the procedure described above (yield: 83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 1.99 (s, 6H), 3.88 (s, 3H), 7.24 (d, 1H), 7.27 (d, 1H), 7.40 (m, 2H), 7.39–7.48 (m, 2H), 7.54–7.58 (m, 6H), 8.16 (d, 2H). MS (70 eV): m/z=417 (M^+).

4.5. 2,7-Bis-[2-(2-hydroxyethylphenyl)-9-*sec*-butyl]-carbazole (4a)

Compound **3a** (0.37 g, 0.80 mmol) was dissolved in 25 ml abs THF. The solution was flushed with argon and cooled to 0 °C before 2.3 ml (2.40 mmol) of 1 M lithium triethyl borohydride solution in THF (super-hydride) was added

slowly. The reaction mixture was stirred at 0 °C for 1 h and 15 ml of an aqueous NH_4Cl solution was added. Thereafter, the reaction batch was poured into 150 ml water and extracted with diethyl ether. The organic layer was washed with water and the solvent was removed. The product was purified by column chromatography on silica gel with hexane/ethyl acetate (1.5:1) as eluent yielding 0.35 g (95%) of **4a** as a colorless solid. ^{1}H NMR (250 MHz, DMSO): δ (ppm) 0.74 (t, 3H), 1.29–1.33 (m, 6H), 1.67 (m, 3H), 2.01 (m, 1H), 2.24 (m, 1H), 4.93 (m, 3H), 5.14 (m, 2H), 7.20 (d, 2H), 7.35–7.51 (m, 6H), 7.68 (d, 2H), 7.73 (d, 2H), 8.29 (d, 2H). MS (70 eV): m/z=463 (M^+).

4.6. 2,7-Bis-[2-(2-hydroxyethylphenyl)-9-(2-ethylhexyl)]-carbazole (4b)

Compound **4b** was prepared according to the procedure described above (yield: 96%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.71–0.88 (m, 6H), 1.14–1.46 (m, 11H), 1.49 (d, 3H), 2.07 (m, 1H), 4.16 (d, 2H), 5.09 (m, 2H), 7.17 (d, 2H), 7.36–7.49 (m, 8H), 7.71 (d, 2H), 8.12 (d, 2H). MS (70 eV): m/z=519 (M^+).

4.7. 2,7-Bis-[2-(2-hydroxyethylphenyl)-9-methyl]-carbazole (4c)

Compound **4c** was prepared according to the procedure described above (yield: 98%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 1.45 (d, 6H), 3.90 (s, 3H), 5.10 (q, 2H), 7.18 (d, 1H), 7.35–7.40 (m, 6H), 7.43–7.51 (m, 3H), 7.73 (d, 2H), 8.15 (d, 2H). MS (70 eV): m/z=421 (M^+).

4.8. 1,1′-Dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-*sec*-butyl-carbazole (5a)

To a solution of 0.1 g (0.22 mmol) **4a** in 10 ml dichloromethane, 0.1 ml (0.65 mmol) boron trifluoride etherate was added. The mixture was stirred for 30 min at room temperature before 15 ml ethanol and 20 ml water were added. The reaction batch was extracted with dichloromethane, washed with water, and dried with Na_2SO_4 before the solvent was evaporated. Purification by column chromatography on silica gel with hexane/THF (3:1) as eluent yielded 83 mg (92%) of **5a** as colorless solid. ^{1}H NMR (250 MHz, DMSO): δ (ppm) 0.81 (t, 3H), 1.64 (d, 6H), 1.80 (d, 3H), 2.12 (m, 1H), 2.49 (m, 1H), 4.10 (q, 2H), 5.05 (m, 1H), 7.35–7.46 (m, 4H), 7.64 (d, 2H), 8.12 (d, 2H), 8.21 (s, 2H), 8.39 (d, 2H). MS (70 eV): m/z=427 (M^+).

4.9. 1,1′-Dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-(2-ethylhexyl)-carbazole (5b)

Compound **5b** was prepared as described above (yield: 90%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.84 (m, 6H), 1.51–1.46 (m, 8H), 1.49 (d, 6H), 2.05 (m, 1H), 3.96 (q, 2H), 4.86 (m, 2H), 7.33–7.44 (m, 4H), 7.60 (d, 2H), 8.10 (d, 2H), 8.19 (s, 2H), 8.35 (d, 2H). MS (70 eV): m/z=483 (M^+).

4.10. 1,1′-Dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-methyl-carbazole (5c)

Compound **5c** was prepared as described above (yield: 88%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 1.56 (d, 6H), 4.13 (q, 2H), 4.51 (s, 3H), 7.32–7.40 (m, 4H), 7.55 (d, 2H), 7.72 (s, 2H), 7.86 (d, 2H), 8.20 (s, 2H). MS (70 eV): m/z=385 (M^+).

4.11. 1,1′-Di-*n*-butyl-1,1′-dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-*sec*-butyl-carbazole (7)

Compound **5a** (60 mg, 0.14 mmol) was dissolved in 15 ml THF (abs) under argon. The solution was cooled to −78 °C before 0.19 ml (0.3 mmol) *n*-BuLi (1.6 M solution in hexane) was added slowly. After 15 min stirring, 0.2 ml (0.4 mmol) 1-bromobutane was added. The solution was allowed to warm to room temperature and stirred for another hour before it was poured into 50 ml ice water. The reaction batch was extracted with diethyl ether, the organic phase was washed with water, and the solvent was evaporated. Purification was carried out by column chromatography on silica gel with hexane/THF (10:1) as eluent. In addition, **7** was purified by MPLC with hexane/THF (15:1) at a pressure of 18 bar. The reaction yielded 51 mg (75%) of **7** as white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.62 (m, 9H), 0.87 (t, 4H), 1.01–1.10 (m, 4H), 1.51 (m, 6H), 1.74 (d, 3H), 1.96–2.17 (m, 5H), 2.28–2.47 (m, 1H), 4.76 (m, 1H), 7.27–7.37 (m, 6H), 7.69 (s, 2H), 7.76 (d, 2H), 8.01 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 12.2, 14.3, 19.6, 23.5, 26.9, 28.1, 28.6, 41.8, 50.4, 53.6, 114.1, 119.9, 123.2, 123.3, 123.6, 127.1, 127.3, 128.5, 141.2, 143.7, 153.4. IR (Si-wafer): $\tilde{\nu}$ (cm^{-1}) 3011, 2958, 2972, 1488, 1452, 1378, 1342, 1240, 740. MS (70 eV): m/z=539 (M^+). Anal. Calcd for $C_{40}H_{45}N$ (539.8): C, 89.00; H, 8.40; N, 2.59. Found: C, 89.09; H, 8.31; N, 2.58.

4.12. 1,1-Dimethyl-1′,1′-dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-*sec*-butyl-carbazole (6)

Compound **6** was prepared according to the procedure described for **7**. For alkylation, iodomethane was used (yield: 70%). Compound **6** was purified by MPLC with hexane/THF (10:1) at a pressure of 18 bar. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.90 (t, 3H), 1.61 (m, 12H), 1.78 (d, 3H), 2.05–2.21 (m, 1H), 2.35–2.53 (m, 1H), 4.81 (m, 1H), 7.28–7.49 (m, 6H), 7.82 (s, 2H), 7.89 (d, 2H), 8.15 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 12.2, 19.6, 26.8, 28.5, 46.5, 53.6, 101.4, 114.0, 120.8, 123.1, 123.7, 127.4, 132.1, 137.6, 140.3, 145.3, 154.9. IR (Si-wafer): $\tilde{\nu}$ (cm^{-1}) 3014, 2961, 2926, 1489, 1452, 1377, 1342, 1241, 740. MS (70 eV): m/z=455 (M^+). Anal. Calcd for $C_{34}H_{33}N$ (455.7): C, 89.63; H, 7.30; N, 3.07. Found: C, 89.56; H, 7.33; N, 3.12.

4.13. 1,1′-Diethyl-1,1′-dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-*sec*-butyl-carbazole (8)

Compound **8** was prepared according to the procedure described for **7**. For alkylation, bromoethane was used. Compound **8** was purified by MPLC with hexane/THF (15:1) at a pressure of 18 bar (yield: 80%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.41 (m, 6H), 0.90 (m, 3H), 1.58 (s, 6H), 1.78 (d, 3H), 2.05–2.22 (m, 5H), 2.34–2.41 (m, 1H), 4.78 (m, 1H), 7.26–7.41 (m, 6H), 7.78 (s, 2H), 7.82 (d, 2H), 8.05 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 9.0, 11.8, 19.2, 27.3, 28.2, 34.1, 50.4, 53.2, 113.7, 115.0, 119.4, 122.9, 124.1, 126.4, 138.3, 141.0, 142.9, 152.6. IR (Si-wafer): $\tilde{\nu}$ (cm^{-1}) 3049, 2963, 2929, 1488, 1452, 1378,

1342, 1240, 741. MS (70 eV): m/z=483 (M^+). Anal. Calcd for $C_{36}H_{37}N$ (483.7): C, 89.39; H, 7.71; N, 2.90. Found: C, 89.54; H, 7.69; N, 2.85.

4.14. 1,1′-Diethyl-1,1′-dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-(2-ethylhexyl)-carbazole (9)

Compound **9** was prepared according to the procedure described for **7**. For alkylation, **5b** was treated with bromoethane. Compound **9** was purified by MPLC with hexane/THF (20:1) at a pressure of 18 bar (yield: 76%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.33 (m, 6H), 0.80–0.96 (m, 6H), 1.18–1.48 (m, 8H), 1.52 (s, 6H), 1.98–2.16 (m, 5H), 4.20 (m, 2H), 7.21–7.39 (m, 6H), 7.58 (s, 2H), 7.75 (d, 2H), 7.98 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 7.8, 9.8, 12.9, 21.8, 23.4, 26.0, 27.6, 29.8, 32.9, 38.2, 46.5, 49.2, 98.6, 112.5, 118.2, 121.6, 125.6, 125.7, 137.3, 139.7, 141.8, 151.4. IR (Si-wafer): $\tilde{\nu}$ (cm^{-1}) 3046, 2960, 2928, 1491, 1460, 1354, 1330, 1265, 739. MS (70 eV): m/z=539 (M^+). Anal. Calcd for $C_{40}H_{45}N$ (539.8): C, 89.00; H, 8.40; N, 2.59. Found: C, 89.03; H, 8.46; N, 2.59.

4.15. 1,1′-Diethyl-1,1′-dimethyl-bisindeno[3,2-*b*:2′3′-*h*]-9-methyl-carbazole (10)

Compound **10** was prepared according to the procedure described for **7**. For alkylation, **5c** was treated with bromoethane. Compound **10** was purified by MPLC with hexane/THF (25:1) at a pressure of 18 bar (yield: 76%). In case of **10**, it was possible to separate the two isomers by this technique. The (*R*,*S*)-isomer (200 mg) and (*S*,*S*/*R*,*R*)-isomer (400 mg) were obtained after vacuum freeze drying.

(R,S)-isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.28–0.45 (m, 6H), 1.59 (s, 3H), 1.88 (s, 3H), 2.15 (q, 2H), 2.29–2.45 (m, 1H), 2.51–2.68 (m, 1H), 4.32 (s, 3H), 7.28–7.44 (m, 6H), 7.71–7.76 (m, 2H), 7.78 (d, 1H), 7.86 (d, 1H), 8.05 (s, 1H), 8.17 (d, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 9.41, 27.74, 27.83, 28.04, 34.19, 34.48, 50.96, 52.91, 100.29, 112.33, 113.82, 119.56, 119.80, 119.94, 122.35, 123.30, 123.994, 124.64, 127.21, 127.30, 127.35, 127.39, 132.41, 139.34, 139.64, 140.47, 141.22, 141.29, 142.38, 144.25, 152.96. IR (Si-wafer): $\tilde{\nu}$ (cm^{-1}) 3049, 2962, 2923, 1495, 1457, 1378, 1307, 1225, 743. MS (70 eV): m/z=441 (M^+). Anal. Calcd for $C_{33}H_{31}N$ (441.6): C, 89.75; H, 7.08; N, 3.17. Found: C, 89.54; H, 6.95; N, 3.20.

(S,S/R,R)-isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 0.37–0.40 (m, 6H), 1.63 (s, 6H), 2.08–2.16 (m, 4H), 4.00 (s, 3H), 7.30–7.45 (m, 6H), 7.69 (s, 2H), 7.85 (d, 2H), 8.06 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm) 9.42, 27.79, 29.82, 34.56, 50.50, 99.81, 114.22, 119.94, 123.20, 123.26, 127.34, 139.08, 141.36, 142.07, 143.59, 152.96. IR (Si-wafer): $\tilde{\nu}$ (cm^{-1}) 3050, 2961, 2920, 1494, 1458, 1349, 1307, 1264, 739. MS (70 eV): m/z=441 (M^+). Anal. Calcd for $C_{33}H_{31}N$ (441.6): C, 89.75; H, 7.08; N, 3.17. Found: C, 89.73; H, 7.09; N, 3.09.

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