# Synthesis and Photophysical Properties of 3,6-Diphenyl-9-hexyl-9*H*-carbazole Derivatives Bearing Electron Withdrawing Groups

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**Summary.** 3,6-Diphenyl-9-hexyl-9*H*-carbazole derivatives bearing electron withdrawing groups, such as the formyl or the nitro-group in 4-positions of the phenyl substituents, were prepared and characterized. Their photophysical properties were evaluated and compared with those of the unsubstituted counterpart 3,6-diphenyl-9-hexyl-9H-carbazole. The electron withdrawing groups bearing compounds exhibited considerable red shifts of the absorption and the emission maxima. While 3,6-di(4-nitrophenyl)-9-hexyl-9H-carbazole emitted in the orange region of the visible spectrum with its emission maximum peaking at 585 nm, 3,6-di(4-formylphenyl)-9-hexyl-9H-carbazole gave a pure blue emission with a luminescence quantum yield of 95% peaking at 450 nm. Observed features were explained using quantum mechanical calculations and organic light emitting diodes using the formylphenyl substituted compound as emissive layer were built demonstrating the practical applicability of this class of compounds.

**Keywords.** Dyes; Heterocycles; Fluorescence spectroscopy; Absorption spectra; Density functional theory.

### Introduction

In the last decade, amorphous and film-forming carbazole derivatives have attracted much attention as molecular electronic materials [1] due to their good hole-transporting capability, high charge carrier mobility, and intense luminescence. Additionally, carbazoles exhibit high thermal, morphological, and chemical stability. The carbazole unit can be easily functionalized at its 3- and 6-positions and can be covalently attached to other organic moieties via the 9 position, greatly improving their thermal stability or glassy-state durability [2]. Thus, carbazole derivatives are finding applications in a variety of fields, such as organic light-emitting diodes (OLEDs) [3], organic photorefractive materials [4], organic field effect transistors (OFETs) [5], photoconductors [6], and as two-photon absorption dyes for the photodeposition of silver [7]. For instance, the simple 9-alkyl-9H-carbazole has been used as charge transporting plasticizer of photorefractive systems [8] and 3.6-disubstituted carbazoles have been investigated as charge transporting, electroluminescent host materials for OLEDs [9]. In most applications, 3,6disubstituted carbazole derivatives are used, because these materials are readily accessible starting from 3,6-dihalogenated precursor compounds. Additionally, 2,7-disubstituted carbazole derivatives have attracted considerable interest [10], but progress in this field is somewhat hampered by the tedious synthesis procedures like the *Cadogan* cyclization [11] needed to prepare the corresponding 2,7-dihalocarbazole precursors.

Although numerous OLED materials have been developed, ongoing design of new carbazole based compounds is a main issue in synthetic chemistry in

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order to improve efficiencies, brightness, and lifetimes of optoelectronic devices [12]. For green and red electrophosphorescent devices, promising hostguest systems are well-established [3a]. It is, however, still a challenge to find suitable host materials for triplet-state blue-light emitters [13] due to the fact that commonly used host molecules do not have sufficiently high triplet energies and, hence, do not prevent reverse energy transfer from the guest back to the host [14]. Thus, host materials with triplet energies greater than 2.75 eV are required [15]. A further challenge comprises stable blue light emitting chromophores for OLEDs. Although polyfluorenes (PF) are well known materials for blue light-emitting diodes, they suffer from the drawback that they are liable to oxidation on the 9-position of fluorene, leading to a drastic loss in quantum yield and the appearance of low-energy emission ("Keto-defect") [16].

In this work, we focused on the functionalization of the 3- and 6-position of carbazole with differently substituted phenyl groups in order to provide larger conjugated entities and, in particular, to tune the photophysical properties by incorporation of electron withdrawing groups (EWGs) in the *para*-position of these phenyl substituents. In this way, a push-pull chromophore, based on the carbazole's nitrogen and the EWG is created. Although donor-acceptor functionalized molecules have received considerably attention in, *e.g.*, two photon absorption dyes [17], the use of EWGs such as the formyl or nitro group in electroactive materials is not particularly common [18].

#### **Results and Discussion**

Starting from 3,6-dibromocarbazole, 3,6-dibromo-9hexyl-9H-carbazole (1) was obtained by a standard alkylation reaction using 1-bromohexane as the alkylation reagent and NaOH as the base [19]. Target molecules 3,6-diphenyl-9-hexyl-9H-carbazole (2), 3,6-di(4-formylphenyl)-9-hexyl-9*H*-carbazole (3), and 3,6-di(4-nitrophenyl)-9-hexyl-9H-carbazole (4) (cf. Scheme 1) were prepared via Suzuki crosscoupling reactions of 1 with phenylboronic acid, 4-formylphenylboronic acid, and 4-nitrophenylboronic acid pinacol ester. A standard protocol using  $[Pd(PPh_3)_4]$  as the catalyst in a mixture of toluene, ethanol, and water and Na<sub>2</sub>CO<sub>3</sub> as the base was used [20]. Compound 2 was obtained in acceptable yield of 63% upon purification by column chromatography and subsequent washing with hot *n*-pentane. In case of 3 and 4 yields were distinctly lower because of the need to separate by-products with similar retention indices. Compounds 3 and 4 were isolated in 31 and 44% yield. Similar difficulties of the removal of by-products were recently resolved by using the alternative catalyst bis(dicyclohexylamine) palladium acetate (DAPCy), ethanol as the solvent, and KOH as base [21]. However, in the present cases the above mentioned catalytic system failed. In all cases, only yields below 10% could be obtained. Park et al. reported the synthesis of 9-alkyl-3,6-diphenyl-9H-carbazole derivatives via a nickel catalyzed cross-coupling reaction of 3,6-dibromo-9-alkyl-9H-



Scheme 1

carbazole derivatives with the phenyl *Grignard* reagent [22] and obtained yields of 75-78%. This synthesis route is certainly an alternative for the preparation of **2**, but cannot be directly adopted for the synthesis of **3** and **4**.

Additionally, 3,6-di-(4-hydroxymethylphenyl)-9hexyl-9H-carbazole (5) was prepared by reduction of the two aldehyde functionalities in 3 with  $LiAlH_4$ in THF in a yield of 61%. Compounds 2–5 were characterized by elemental analysis, <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$ NMR as well as IR spectroscopy. NMR data were in accordance with the proposed structures and did not exhibit any special features. IR spectra of 2, 3, and 4 are characterized by strong absorptions features peaking at 1602, 1599, and  $1513 \text{ cm}^{-1}$ , which are caused by an asymmetrical skeleton vibration of the carbazole and the phenyl moieties [23]. Derivative 3 featured further characteristic peaks at 1697 and  $1482 \,\mathrm{cm}^{-1}$ , which were assigned to a CHO stretching vibration and a breathing mode of the pyrrole core of the carbazole. In the nitro-group featuring compound characteristic signals peaked at 1588 and  $1337 \,\mathrm{cm}^{-1}$ . These signals were assigned to an inplane bending vibration of the nitrogen atom of the nitro group and to the NO<sub>2</sub> stretching vibration. Furthermore, thermal properties of 2-5 were determined using combined DSC/TGA experiments. Thermal stability is of particular interest, since it is a crucial issue for device lifetime [24] and is needed when thermal evaporation processes are employed. While 2 showed a melting point at 123°C, the melting points of 3 and 4 were found at higher temperatures of 169 and 234°C. Compound 5, on the other hand, started to decompose at low temperatures of about 50°C as evidenced by the DSC as well as by the TGA curve. The other compounds exhibited thermal stability well above their melting points. As a measure for the thermal stability, the temperature at a weight loss of 5% was chosen. The corresponding values are 326°C for 2, 386°C for 3, 346°C for 4, and 94°C for 5. Figure 1 illustrates the results, which reveal favourable thermal properties for 2, 3, and 4, but which disqualifies 5 for the envisaged application in OLEDs.

To determine the photophysical properties of the compounds under investigation, UV-Vis absorption and photoluminescence (PL) measurements were performed in diluted solutions of  $CHCl_3$  (in case of **2**–**4**) and *THF* (in the case of **5**) at room temperature under ambient conditions. Results are presented in



Fig. 1. TGA thermograms of compounds 2–5

Table 1 and Fig. 2. To assign the various features in the UV-Vis spectra, we performed time dependentdensity functional theory calculations using the hybrid *B3LYP* exchange-correlation functional together with a SV(P) split valence polarised basis set. In order to cross-check the predictions made by TD-DFT, ZINDO calculations have been performed on **2**, based on the DFT-optimized geometry. Results of the calculations are presented in Table 2 and *Kohn-Sham* orbitals are shown in Fig. 3.

Compound 2 exhibits its main absorption feature with a maximum at 4.16 eV (298 nm), which is assigned to excitation into  $S_3$  dominated by a combination of HOMO  $\rightarrow$  LUMO +1 and HOMO-1  $\rightarrow$ LUMO transitions (cf. Fig. 3); The shoulder found experimentally around 3.8 eV (see Fig. 2) is attributed to an excitation into  $S_2$  (containing also predominantly HOMO  $\rightarrow$  LUMO + 1 and HOMO - 1  $\rightarrow$ LUMO contributions), for which a significantly smaller oscillator strength is obtained. The two occupied orbitals are delocalized over the whole molecule with stronger contributions on the carbazole. The LUMO is fully localized there and the LUMO + 1 and LUMO + 2 have their dominant contributions on the phenyls, which will later turn out to be crucial, when discussing substitution effects. For both features, the calculations overestimate the transition energy by about 0.2 eV.

This is also the case for  $S_0 \rightarrow S_1$ , which we tentatively associate with the experimental features around 3.5 eV (assigned to an electronic excitation and its vibronic replica). This would mean a serious underestimation of the corresponding oscillator strength in the simulations, which we do observe both in the ZINDO as well as in the TD-DFT calculations; the small oscillator strength associated with excitation into  $S_1$  is insofar surprising as based on the symmetry of the involved orbitals, a pure HOMO  $\rightarrow$ LUMO transition (which is the most dominant contribution for this excitation) is allowed. Therefore, the small oscillator strength has to be related to the influence of other contributions, which is more obvious for the ZINDO-calculations, where the HOMO  $\rightarrow$  LUMO (CI-coefficent: 0.54) derived tran-

**Table 1.** Absorption  $(\lambda_{abs})$  and emission wavelengths  $(\lambda_{em})$  as well as molar coefficients of extinction ( $\varepsilon$ ) and luminescence quantum yields ( $\Phi$ ) in solution of **2**, **3**, and **4** (recorded in CHCl<sub>3</sub>) and **5** (recorded in *THF*)

Compound	$\frac{\lambda_{\rm abs}/\rm nm}{(\varepsilon/10^{-3}M^{-1}\rm cm^{-1})}$	$\frac{\lambda_{\rm em}}{\rm nm}$	$\Phi/\%$	
2	298 (42.6), 350 (4.1), 364 (2.6)	395	$3\pm 2$	
3	315 (33.7), 362 (32.1)	450	$94\pm 5$	
4	298 (15.9), 363 (25.0), 390 (23.2)	585	$26 \pm 10$	
5	301 (41.8), 347 (3.3), 363 (2.1)	397	$3\pm 2$	

sition dipole is largely cancelled by other contributions from other excited determinants. Here, for example, transitions from HOMO-1 to LUMO + 1 and LUMO + 5 (CI: 0.29 and 0.20, respectively) as well as from HOMO-2 to LUMO + 1 and LUMO +



Fig. 2. Absorption and emission spectra of 2, 3, 4, and 5 recorded in solution



Fig. 3. Kohn-Sham orbitals of 2, 3, and 4 and their absolute energies in eV

7 (CI: -0.17 and 0.12, respectively) are also characterized by relatively large coefficients [25].

The UV-Vis spectra of **3** and **4** differ significantly from **2**, while that of **5** is very similar. The latter is not surprising, considering that the conjugation between the  $\pi$ -electron system and the OH groups is broken by the CH<sub>2</sub> linkers. The spectral signatures of **3** and **4**, however, deserve further attention.

Compound **3** exhibits two clearly separated absorption maxima with similar extinction coefficients at 3.94 eV (315 nm) and 3.43 eV (362 nm), which are both shifted to lower energies compared to the main peak in **2**. This trend is fully reproduced by the calculations, where the lowest energy peak is associated with an excitation into  $S_1$  (largely HOMO  $\rightarrow$  LUMO), while the higher peak is a superposition of absorption into  $S_6$  (largely HOMO  $-1 \rightarrow$  LUMO + 1) and  $S_7$  (HOMO  $-1 \rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO + 2).

The effect of the acceptor substituents is best seen in the molecular orbitals in Fig. 3. Both the shapes as well as the energies of the occupied orbitals are only weakly affected by the formyl group (stabilization by about 0.4 eV). The same is true for the LUMO of **2**, which is not surprising considering its localization on the carbazole. In contrast to that, the LUMO + 1 and LUMO + 2 of 2 are much more affected by the substitution. The former is stabilized by 1.2 eV and the latter even by nearly 1.4 eV rendering the corresponding orbitals the new LUMO and LUMO + 1 in 3. This is fully consistent with the strong contributions of these on the phenyl substituents. In fact, the substitution results in a stronger localization of these two unoccupied orbitals in the vicinity of the acceptor groups. Also the red-shift in the absorption spectra and the fact that the HOMO  $\rightarrow$  LUMO dominated excitation becomes strongly optically allowed in 3 (in contrast to 2) is simply a consequence of the different nature and strong stabilization.

The fluorescence spectra recorded for 2–5 are shown in Fig. 2. The spectral position of the emission maximum is distinctly dependent on the substituent of the phenyl groups. While the parent 2 exhibited its emission maximum at 395 nm (3.14 eV), a red-shift towards 450 nm (2.76 eV) in case of 3 and towards 585 nm (2.12 eV) in case of 4 was observed (It is well known that the nitro group is a much stronger acceptor than an aldehyde. A convenient measure is for example the empirically determined *Hammett*-parameter, which is considerable larger for NO<sub>2</sub> ( $\sigma_p = 0.78$ ) than for CHO ( $\sigma_p = 0.42$ ) [26]).

**Table 2.** B3LYP/SV(P) and ZINDO calculated  $S_0 \rightarrow S_n$  transition energies (*E*), corresponding wavelengths ( $\lambda_{abs,calc}$ ), and oscillator strengths (*f*) for the most relevant excited states in **2**, **3**, and **4** in their ground-state equilibrium conformations. The last column lists the dominant contributions to the excited states as computed by TD-DFT

Compound	State	$\lambda_{\rm abs,calc} (E)/\rm nm (eV)$	f	Contributions $(c^2 \cdot 100/\%)$
2	$S_1$	332 (3.73)	0.01	$H \rightarrow L (90.7)$
	$S_2$	310 (4.00)	0.21	$H \rightarrow L + 1$ (80.9), $H-1 \rightarrow L$ (17.6)
	$S_3$	284 (4.37)	0.85	$H-1 \rightarrow L$ (64.3), $H \rightarrow L+1$ (15.4)
2 (ZINDO)	$S_1$	332 (3.73)	0.03	$H-2 \rightarrow L+1$ (5.5), $H-1 \rightarrow L+1$ (16.3), $H-1 \rightarrow L+5$ (8.2),
				$H \rightarrow L$ (58.9)
	$S_2$	3.02 (4.10)	0.15	$H-6 \rightarrow L$ (5.5), $H-1 \rightarrow L$ (46.7), $H-1 \rightarrow L+2$ (7.7), $H \rightarrow L+7$ (9.4)
	$S_3$	291 (4.26)	0.82	$H-1 \rightarrow L+2$ (7.6), $H \rightarrow L+1$ (69.7)
3	$S_1$	368 (3.37)	0.52	$H \rightarrow L$ (98.1)
	$S_2$	346 (3.58)	0.12	$H \to L + 1 \ (94.4)$
	$\overline{S_6}$	317 (3.91)	0.25	$H-1 \to L+1$ (92.4)
	$S_7$	311 (3.99)	0.28	$H-1 \rightarrow L$ (61.1), $H \rightarrow L + 2$ (33.0)
	$S_8$	283 (4.38)	0.28	$H-1 \rightarrow L+2$ (75.7), $H \rightarrow L+5$ (10.5)
4	$S_1$	398 (3.11)	0.42	$H \rightarrow L (98.9)$
	$S_2$	380 (3.27)	0.12	$H \to L + 1$ (98.6)
	$\overline{S_4}$	342 (3.62)	0.13	$H-1 \to L+1$ (97.4)
	$S_7$	332 (3.85)	0.13	$H \rightarrow L + 2$ (71.1), $H-1 \rightarrow L$ (15.6)
	$S_9$	289 (4.29)	0.20	$H-2 \rightarrow L+1$ (35.8), $H-1 \rightarrow L+2$ (25.8), $H-10 \rightarrow L+1$ (12.2),
	-			$H-9 \to L (11.9)$
	$S_{15}$	267 (4.46)	0.14	$H \rightarrow L + 3$ (42.5), $H-3 \rightarrow L$ (15.5), $H \rightarrow L + 4$ (11.4),
				$H-4 \rightarrow L+1 \ (11.0)$

**Table 3.** B3LYP/SV (P) calculated lowest energies (*E*), emission wavelength ( $\lambda_{em,calc}$ ), and oscillator strength (*f*) for the lowest lying excited state of **2**, **3**, and **4** in their TD-DFT optimized *S*<sub>1</sub> equilibrium geometries

Compound	$\lambda_{\rm em, calc}/\rm nm~(E/eV)$	f	
2	358 (3.47)	0.01	
3	411 (3.01)	0.39	
4	468 (2.65)	0.14	

Photoluminescence quantum yields for all studied compounds were determined and results are presented in Table 1. While 2, 4, and 5 exhibited low to medium quantum yields, 3 offered bright blue emission with  $94 \pm 5\%$  guantum yield. This can be well correlated with the computed oscillator strengths of the first vertical transition of the  $S_1$  optimized geometries (see Table 3). It is also a striking feature of the spectra that the Stokes shift of 4 is larger than that of **3** by 61% (1.06 and 0.65 eV). This is qualitatively reproduced by our calculations, which predict a 77% larger change of the transition energies for 4 than for **3** when comparing the  $S_0 \rightarrow S_1$  transitions for  $S_0$ and  $S_1$  equilibrium geometries. Interestingly, for the  $S_1$ geometry of 4 a breaking of the pseudo- $C_2$  symmetry is observed. The absolute values of the Stokes shifts are, however, severely underestimated (0.36 eV for 3)and 0.46 eV for 4).

The electroluminescent (EL) properties of 3 were investigated because of the high PL quantum yield and the favourable blue emission maximum of this compound. For this purpose, an EL device using 3



Fig. 4. Bias/electroluminescence characteristics and normalized electroluminescence spectra at different voltages for OLEDs prepared from 3

was fabricated in a multilayer architecture on an indium-tin-oxide (ITO) covered glass substrate acting as a transparent anode followed by a spin-coated poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (*PEDOT:PSS*) film. Compound **3** was spincoated as emissive layer and finally a Ca electrode capped with an Al layer was deposited.

The obtained electroluminescence spectra are shown in the inset of Fig. 4. As representative examples, the data for operation at 8.0, 10.0, 13.0, and 16.0 V are shown. At these operating voltages, an EL maximum at 465 nm was observed, resulting in a pure and bright blue emission of the device. Compared to the PL spectrum of 3, the EL maximum is slightly red-shifted (450 vs. 465 nm). The luminance-voltage characteristic of the device ITO/ *PEDOT:PSS*/3/Ca/Al is also given in Fig. 4. The onset voltage was approximately 7.5 V and luminance intensities of  $\sim 60 \text{ cd m}^{-2}$  were obtained at a driving voltage of 11 V. Although this confirms the applicability of **3** as a blue-light emitting material in OLEDs, it should be noted that the herein presented data were obtained from a non-optimized device structure.

#### Conclusion

The preparation of carbazoles bearing 4-formyl and 4-nitro-substituted phenyl rings was achieved by Suzuki cross-coupling reactions of 3,6-dibromo-9hexyl-9H-carbazole with the corresponding boronic acid derivatives. Resulting EWG bearing 3,6-diphenyl-9-hexyl-9H-carbazole derivatives exhibited pronounced red shifts of their absorption and emission properties when compared to the parent compound 3,6-diphenyl-9-hexyl-9H-carbazole. The electronic effects of the EWGs on the photophysical properties of the compounds were described using quantum mechanical calculations. 3,6-Di(4-formylphenyl)-9-hexyl-9H-carbazole showed particularly interesting photophysical properties, exhibiting an emission maximum peaking at 450 nm and a luminescence quantum yield of 95% in solution. The capability of this derivative to act as the emissive layer in OLEDs was confirmed.

#### Experimental

Unless otherwise noted, materials were obtained from commercial sources (Aldrich, Fluka or Lancaster) and were used without further purification. 3,6-Dibromo-9-hexyl-9H-carbazole (1) was prepared according to the publication of Liu et al. [19]. Solvents for reactions were freshly distilled over appropriate drying agents prior to use. Reactions were carried out under inert atmosphere of Ar using standard Schlenk techniques. <sup>1</sup>H NMR spectra were recorded on a Varian INOVA 500 MHz Spectrometer at 500 MHz, <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 125 MHz. Assignment of the peaks was done by DEPT and COSY NMR spectroscopy. Solvent residual peaks were used for referencing the NMR-spectra to the corresponding values given in literature [27]. FT-IR spectra were obtained from films on NaCl windows with a Perkin Elmer Spectrum One and a DTGS-detector. Elemental analyses (C and H) were conducted for the novel compounds 2-5 with results that were found to be in good agreement ( $\pm 0.3\%$ ) with the calculated values. UV-Vis absorption spectra were recorded on a Cary 50 Bio UV-Vis Spectrophotometer, fluorescence spectra on a Perkin Elmer Luminescence Spectrometer LS50B. PL quantum yields were measured using a Shimadzu RF-5301PC Spectrofluorimeter (corrected for its spectral response) and Perkin Elmer Lambda 9 UV/VIS/NIR Spectrophotometer using quinine sulfate dihydrate in  $0.1 N H_2 SO_4$  as standard [28]. Combined differential scanning calorimetry/ thermogravimetric analysis measurements were performed with a Polymer Laboratories simultaneous thermal analyzer STA 625. The experiments were carried out in aluminum pans with a heat rate of 10°C/min in a nitrogen flow of approximately 35 cm<sup>3</sup>/min. Organic light emitting devices (OLEDs) were fabricated on glass substrates covered with transparent indium-tin-oxide (ITO), acting as anode in a commonly used sandwich structure (ITO/PEDOT:PSS/3/Ca/Al). First, the samples were cleaned in an ultrasonic bath for ten minutes in isopropanol followed by 10 min in toluene. Subsequently, they were etched for 10 min in oxygen plasma. Then poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin cast under ambient conditions (approximate thickness 50 nm). The samples were annealed in a vacuum oven at a temperature of 150°C for at least 60 min, followed by cooling to room temperature over 40 min. 3 was spin-coated from CHCl<sub>3</sub> solutions with a concentration of 8 mg/cm<sup>3</sup>. Calcium top electrodes and an aluminum capping layer were evaporated in an evaporation chamber located in an argon glove box. Devices were tested under inert atmosphere of argon. Device characteristics were recorded using a customized setup. While current/voltage characteristics were measured using a Keithley 236 Source Measure Unit, a photodiode mounted in an integrating sphere and connected to a Keithley 181 Nanovoltmeter was used to measure the emission intensity. To obtain luminance values (for devices operated in cw-mode), the set-up was calibrated using a Luminance Meter LS100 (Minolta) near the maximum emission intensity. Electroluminescence spectra were obtained with a DB401-UV CCD detector (Andor) mounted on an Oriel Multispec grid spectrometer. The spectral sensitivity was calibrated with an Ocean Optics LS-1-CAL tungsten-halogen lamp. Calculations have been performed using (time dependent)-density functional theory. The exchange-correlation hybrid functional B3LYP [29] together with a SV(P) double valence basis set was employed as implemented in the

TURBOMOLE 5.7 package [30]. B3LYP has been reported to correctly reproduce the ordering of states [31], and was recently very successful in explaining the optical properties of various classes of molecules [32], even when small basis sets were used. For geometry optimizations, no symmetry constraints were employed in order to prevent any bias of the results. For all converged geometries, a vibrational analysis was performed (i) to ensure that a minimum on the respective potential energy surface has been reached and (ii) to assign the measured IR spectra. TD-DFT results were supported using Zerner's Intermediate Neglect of Differential Overlap (ZINDO) method as implemented in the Gaussian03 package [33], with a CI active space of 25 occupied and 25 unoccupied orbitals. The transition and Kohn-Sham orbital energies are all given for the ground state equilibrium geometries for absorption and for  $S_1$ -excited state optimized geometries for emission.

#### 3,6-Diphenyl-9-hexyl-9H-carbazole (2, C<sub>30</sub>H<sub>29</sub>N)

3,6-Dibromo-9-hexyl-9H-carbazole (100.4 mg, 0.25 mmol), 105 mg phenylboronic acid (0.86 mmol), and 136 mg Na<sub>2</sub>CO<sub>3</sub> (1.28 mmol) were dissolved in a mixture of 4 cm<sup>3</sup> degassed toluene,  $0.5 \text{ cm}^3$  EtOH and  $1 \text{ cm}^3$  H<sub>2</sub>O. After heating the reaction mixture to  $90^{\circ}$ C,  $20 \text{ mg} \text{ Pd}(\text{PPh}_3)_4$  (0.02 mmol, 8 mol%) was added and the mixture was stirred for 20 h. Water  $(10 \text{ cm}^3)$  and  $10 \text{ cm}^3 Et_2O$  were subsequently added. The water layer was separated and extracted with  $3 \times 10 \text{ cm}^3 Et_2O$ . The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica (cy:ee =10:1) sampling the band at  $R_f = 0.86$  (cy:ee = 3:1). Subsequent washing of the residue with hot n-pentane afforded a white microcrystalline powder, which was dried in vacuum. Yield: 61.7 mg (63%); mp 123°C; <sup>1</sup>H NMR (500 MHz, *CDCl*<sub>3</sub>):  $\delta = 8.38$  (s, 2H, *carb*<sup>4,5</sup>), 7.75–7.74 (d, 4H,  ${}^{3}J_{HH} = 7.3$  Hz,  $ph^{2,6}$ ), 7.61–7.60 (d, 2H,  ${}^{3}J_{HH}$ =7.6 Hz,  $carb^{2,7}$ ), 7.51–7.48 (m, 6H, ph<sup>3,5</sup>, carb<sup>1,8</sup>), 7.37–7.35 (m, 2H, ph<sup>4</sup>), 4.37–4.34 (t, 2H, hex<sup>1</sup>), 1.94-1.91 (p, 2H, hex<sup>2</sup>), 1.37-1.30 (m, 6H, hex<sup>3,4,5</sup>), 0.90–0.88 (t, 3H, hex<sup>6</sup>) ppm; <sup>13</sup>C NMR (125 MHz, *CDCl*<sub>3</sub>):  $\delta = 142.2$ , 140.5 (4C,  $carb^{3.6}$ ,  $ph^1$ ), 132.5 (2C,  $carb^{8a,9a}$ ), 128.9 (4C,  $ph^{3.5}$ ), 127.4 (4C,  $ph^{2.6}$ ), 126.6 (2C,  $ph^4$ ), 125.5 (2C,  $carb^{4.5}$ ), 123.6 (2C,  $carb^{4.4b}$ ), 119.1 (2C,  $arb^{4.2}$ ), 100.2 (2C) (2C, carb<sup>2,7</sup>), 109.2 (2C, carb<sup>1,8</sup>), 43.5 (1C, hex<sup>1</sup>), 31.8 (1C, hex<sup>4</sup>), 29.2 (1C, hex<sup>2</sup>), 27.2 (1C, hex<sup>3</sup>), 22.7 (1C, hex<sup>5</sup>), 14.2 (1C, hex<sup>6</sup>) ppm; IR (Film on KBr):  $\bar{\nu} = 2954$  (w), 2927 (m), 1600 (m), 1477 (s), 1436 (w), 1352 (w), 1283 (w), 1267 (w), 1155 (w), 809 (w), 762 (s), 697 (m)  $\text{cm}^{-1}$ ; UV-Vis (CHCl<sub>3</sub>):  $\lambda_{abs} = 298 \text{ nm} \ (\varepsilon = 42600 M^{-1} \text{ cm}^{-1}); \text{ fluorescence (CHCl_3):}$  $\lambda_{\rm em} = 395 \, \rm nm.$ 

#### 3,6-Di-(4-formylphenyl)-9-hexyl-9H-carbazole (**3**, C<sub>32</sub>H<sub>29</sub>NO<sub>2</sub>)

3,6-Dibromo-9-hexyl-9*H*-carbazole (300.5 mg, 0.73 mmol), 384 mg 4-formylphenylboronic acid (2.56 mmol) and 390.9 mg Na<sub>2</sub>CO<sub>3</sub> (3.69 mmol) were dissolved in a mixture of 8 cm<sup>3</sup> degassed toluene, 1 cm<sup>3</sup> *Et*OH and 2 cm<sup>3</sup> H<sub>2</sub>O. After heating the reaction mixture to 90°C, 60 mg Pd(P*Ph*<sub>3</sub>)<sub>4</sub> (0.05 mmol, 7 mol%) was added and the mixture was stirred for 20 h. H<sub>2</sub>O

 $(20 \text{ cm}^3)$  and  $20 \text{ cm}^3 Et_2O$  were subsequently added. The water layer was separated and extracted with  $3 \times 30 \text{ cm}^3 Et_2O$ . After drying the combined organic layers over Na<sub>2</sub>SO<sub>4</sub> and evaporation of the solvent the resulting residue was purified by column chromatography on silica (cy:ee = 8:1) sampling the band at  $R_f = 0.24$  (cy:ee = 5:1). The product was further purified by washing with hot *n*-pentane six times to give a yellow solid. Yield: 103.9 mg (30.9%); mp 169°C; <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):  $\delta = 10.08$  (s, 2H, CHO), 8.45 (s, 2H,  $carb^{4,5}$ ), 8.00–7.99 (d, 4H,  ${}^{3}J_{HH} = 8.0$  Hz,  $ph^{3,5}$ ), 7.91–7.90 (d, 4H,  ${}^{3}J_{HH} = 7.8 \text{ Hz}, ph^{2.6}$ ), 7.82–7.80 (d, 2H,  ${}^{3}J_{HH} = 8.5 \text{ Hz}, carb^{2.7}$ ), 7.54–7.52 (d, 2H,  ${}^{3}J_{HH} = 8.5 \text{ Hz}, carb^{1.8}$ ), 4.39-4.36 (t, 2H, hex<sup>1</sup>), 1.95-1.92 (p, 2H, hex<sup>2</sup>), 1.37-1.30 (m, 6H, hex<sup>3,4,5</sup>), 0.90–0.87 (t, 3H, hex<sup>6</sup>) ppm; <sup>13</sup>C NMR  $(125 \text{ MHz}, CDCl_3): \delta = 192.1 (2C, CHO), 148.1 (2C, ph^1),$ (125 km2, cbC  $t_{3,6}^{3,6}$ ), 132.7 (2C, carb<sup>3,6</sup>), 134.7, 131.1 (4C, carb<sup>8,a,9a</sup>, ph<sup>4</sup>), 130.5 (4C, ph<sup>3,5</sup>), 127.7 (4C, ph<sup>2,6</sup>), 125.8 (2C, carb<sup>4,5</sup>), 123.7 (2C, carb<sup>4,4b</sup>), 119.5 (2C, carb<sup>2,7</sup>), 109.7 (2C, carb<sup>1,8</sup>), 43.6 (1C, hex<sup>1</sup>), 31.7 (1C, hex<sup>4</sup>), 29.2 (1C, hex<sup>2</sup>), 27.1 (1C, hex<sup>3</sup>), 22.7 (1C, hex<sup>5</sup>), 14.2 (1C, hex<sup>6</sup>) ppm; IR (Film on KBr):  $\bar{\nu} = 2926$  (m), 2854 (w), 2731 (w), 1697 (s), 1599 (s), 1563 (w), 1482 (s), 1390 (w), 1353 (w), 1308 (m), 1273 (m), 1215 (m), 1171 (s), 837 (w), 804 (m), 719 (w)  $cm^{-1}$ ; UV-Vis (CHCl<sub>3</sub>):  $\lambda_{abs} = 362 \text{ nm}$  ( $\varepsilon = 32100 M^{-1} \text{ cm}^{-1}$ ); fluorescence (CHCl<sub>3</sub>):  $\lambda_{em} = 450 \text{ nm}$ .

## 3,6-Di-(4-nitrophenyl)-9-hexyl-9H-carbazole (4, $C_{30}H_{27}N_3O_4$ )

To a mixture of 3,6-dibromo-9-hexyl-9H-carbazole (200.4 mg, 0.49 mmol), 4-nitrophenylboronic acid pinacol ester (425.9 mg, 1.71 mmol) and Na<sub>2</sub>CO<sub>3</sub> (260 mg, 2.44 mmol) was added a mixture of  $8 \text{ cm}^3$  degassed toluene,  $1 \text{ cm}^3$  EtOH, and  $2 \text{ cm}^3$ H<sub>2</sub>O. After heating the reaction mixture to 90°C, 40 mg  $Pd(PPh_3)_4$  (0.03 mmol, 6 mol%) was added and the mixture was stirred for 20 h.  $H_2O$  (15 cm<sup>3</sup>) and 15 cm<sup>3</sup> Et<sub>2</sub>O were subsequently added. The water layer was separated and extracted with  $3 \times 20 \text{ cm}^3$  Et<sub>2</sub>O. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica (cy:ee = 15:1 to 10:1) sampling the band at  $R_f = 0.57$  (cy:ee = 3:1). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> and methanol gave an orange solid. Yield: 106.9 mg (44.3%); mp 234°C; <sup>1</sup>H NMR (500 MHz, *CDCl*<sub>3</sub>):  $\delta = 8.43$  (s, 2H,  $\begin{array}{l} carb^{4.5}, 8.34-8.33 \text{ (d, 4H, }^{3}J_{HH} = 8.8 \text{ Hz}, ph^{3.5}), 7.88-7.86 \\ (d, 4H, \, ^{3}J_{HH} = 8.8 \text{ Hz}, ph^{2.6}), 7.81-7.79 \text{ (d, 2H, }^{3}J_{HH} = 8.5 \text{ Hz}, carb^{2.7}), 7.56-7.54 \text{ (d, 2H, }^{3}J_{HH} = 8.5 \text{ Hz}, carb^{1.8}), 4.40-4.37 \\ \end{array}$ (t, 2H,  $hex^1$ ), 1.95–1.92 (p, 2H,  $hex^2$ ), 1.37–1.30 (m, 6H,  $hex^{3,4,5}$ ), 0.90–0.87 (t, 3H,  $hex^6$ ) ppm; <sup>13</sup>C NMR (125 MHz,  $\begin{array}{l} \text{(125 MHZ,} \\ \text{(DCCl}_3): \delta = 148.5, 146.7 \ (4C, ph^4, ph^1), 141.5 \ (2C, carb^{3.6}), \\ 130.4 \ (2C, carb^{8a,9a}), 127.8 \ (4C, ph^{2.6}), 126.0 \ (2C, carb^{4.5}), \\ 124.5 \ (4C, ph^{3.5}), 123.7 \ (2C, carb^{4a,4b}), 119.8 \ (2C, carb^{2.7}), \\ 110.0 \ (2C, carb^{1.8}), 43.8 \ (1C, hex^1), 31.8 \ (1C, hex^4), 29.2 \ (1C, hex^{4}), \\ 124.5 \ (4C, ph^{3.5}), 123.7 \ (2C, carb^{4a,4b}), 119.8 \ (2C, carb^{2.7}), \\ 110.0 \ (2C, carb^{1.8}), 43.8 \ (1C, hex^1), 31.8 \ (1C, hex^4), 29.2 \ (1C, hex^{4}), \\ 124.5 \ (4C, ph^{3.5}), 123.7 \ (2C, carb^{4a,4b}), \\ 110.0 \ (2C, carb^{1.8}), 43.8 \ (1C, hex^1), 31.8 \ (1C, hex^4), 29.2 \ (1C, hex^{4}), \\ 124.5 \$ hex<sup>2</sup>), 27.2 (1C, hex<sup>3</sup>), 22.8 (1C, hex<sup>5</sup>), 14.3 (1C, hex<sup>6</sup>) ppm; IR (Film on KBr):  $\bar{\nu} = 2923$  (s), 2853 (m), 1588 (s), 1513 (s), 1477 (m), 1380 (w), 1337 (s), 1306 (w), 1275 (w), 1246 (w), 1185 (w), 1111 (w), 856 (w), 804 (w), 755 (m), 689 (w) cm<sup>-1</sup>; UV-Vis (CHCl<sub>3</sub>):  $\lambda_{abs} = 390 \text{ nm} \ (\varepsilon = 23200 M^{-1} \text{ cm}^{-1}); \text{ fluo-}$ rescence (CHCl<sub>3</sub>):  $\lambda_{em} = 585$  nm.

#### *3*,6-*Di*-(4-hydroxymethylphenyl)-9-hexyl-9H-carbazole (**5**, C<sub>32</sub>H<sub>33</sub>NO<sub>2</sub>)

Compound 3 (50.2 mg, 0.11 mmol) was dissolved in  $3 \text{ cm}^3$ absolute THF and cooled to 0°C under inert atmosphere of argon. LiAlH<sub>4</sub> (0.436 cm<sup>3</sup>, 0.44 mmol, 1.0 M in THF) was added drop wise by which the reaction mixture turned cloudy. The reaction mixture was allowed to warm to room temperature and was stirred for further 4h. After cooling to 0°C, excess LiAlH<sub>4</sub> was hydrolyzed by careful, drop wise addition of 10% HCl (0.5 cm<sup>3</sup>). Extraction with  $Et_2O$  (3×) from a saturated NaHCO<sub>3</sub> solution and drying over Na<sub>2</sub>SO<sub>4</sub> gave a pale yellow solid after removing the solvent under reduced pressure. The product was purified by column chromatography on silica (*cy:ee* = 1:1) sampling band at  $R_f = 0.15$ (cy:ee = 1:1) and washing with hot *n*-pentane. Yield: 30.8 mg (61.0%); mp not observed, decomposition starting at 50°C; <sup>1</sup>H NMR (500 MHz, *CDCl*<sub>3</sub>):  $\delta = 8.70$  (s, 2H, *carb*<sup>4,5</sup>), 7.93–7.88 (m, 6H, *carb*<sup>2,7</sup>, *ph*<sup>2,6</sup>), 7.79–7.78 (d, 2H,  ${}^{3}J_{HH} =$ 5.6 Hz,  $carb^{1.8}$ ), 7.60 (d, 4H,  ${}^{3}J_{HH} = 2.4$  Hz,  $ph^{3.5}$ ), 4.82 (s, 4H,  $CH_2OH$ , 4.62–4.61 (t, 2H,  $hex^1$ ), 1.94–1.91 (p, 2H,  $hex^2$ ), 1.37–1.30 (m, 6H,  $hex^{3,4,5}$ ), 0.90–0.88 (t, 3H,  $hex^6$ ) ppm; <sup>13</sup>C NMR (125 MHz, *CDCl*<sub>3</sub>):  $\delta$  = 142.5, 142.3, 142.2 (6C,  $ph^1$ ,  $ph^4$ ,  $carb^{3,6}$ ), 133.8 (2 C,  $carb^{8a,9a}$ ), 128.9 (4C,  $ph^{3,5}$ ), 128.4 (4C,  $ph^{2,6}$ ), 126.8 (2C,  $carb^{4,5}$ ), 125.4 (2  $b^{4a,4b}$ , 120.4 (2C,  $carb^{2,7}$ ), 111.3 (2C,  $carb^{1,8}$ ), 65.4 (2C, CH<sub>2</sub>OH), 44.6 (1C, hex<sup>1</sup>), 33.3 (1C, hex<sup>4</sup>), 30.9 (1C, hex<sup>2</sup>), 28.4 (1C, hex<sup>3</sup>), 24.2 (1C, hex<sup>5</sup>), 15.2 (1C, hex<sup>6</sup>); UV-Vis (*THF*):  $\lambda_{abs} = 301 \text{ nm}$  ( $\varepsilon = 41800 M^{-1} \text{ cm}^{-1}$ ); fluorescence (*THF*):  $\lambda_{em} = 397$  nm.

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state description is 90% HOMO  $\rightarrow$  LUMO, but in this context it has to be kept in mind that such percentage values are proportional to the square of the coefficients with which certain configurations enter the description of certain excited states, while the transition dipole to a certain state is linearly proportional to the sum of the transition dipoles to the individual configurations times their coefficients. Moreover, these coefficients are not normalized! *I.e.*, the sum of the norms of the coefficients is typically larger than 1 and only their squares are normalized. This means that also in the TD-DFT calculations other excitations will make appreciable contributions to the transition dipole, which has to be held responsible for the very small oscillator strength of  $S_1$ 

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