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A new carbazole-based helically chiral architecture: Synthesis and physical properties

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Abstract- A short and efficient synthesis leading to a new helically chiral heptacyclic system, containing a carbazole unit, was achieved *via* a Knoevenagel condensation-photocyclization strategy. The optical properties of the carbazole-based material were investigated by UV-visible absorption and photoluminescence spectroscopy and an emission in the visible region was observed. From the cyclic voltammetry analysis, the electrochemical band gap of the target organic material was estimated to be 2.38 eV indicating that it might be a good candidate for electron-injection hole-blocking layers in organic light-emitting diodes.

Keywords: Chirality, Azahelicenes, Carbazole, Fused-rings, Knoevenagel condensation, Photocyclization.

Helicenes have been investigated since 1956 as aromatic molecules in which the *ortho*-condensed ring system gives rise to a helical structure.[1] Thirty years later, numerous studies on the synthesis and physico-chemical properties of helicenes have been published.[2] More recently, helicenes have sparked interest due to the use of their intrinsic properties (e.g. chirality, strong rotatory power) in various fields such as catalysis,[3] non-linear optics,[4] circulary polarized luminescence[5] and organic light-emitting materials.[6] Besides typical carbohelicenes composed of an all-carbon ring framework, heterohelicenes incorporating one or more heteroaromatic units in the skeleton have also gained increasing attention due to their additional propreties.[7] Pyridohelicenes, as a kind of typical azahelicenes, are prime examples.[8] However, the pyrrole-alternatives have been rarely focused on.[9] That is partially because pyrrolohelicenes, with a low number of fused aromatic rings (<6), are supposed to be stereochemically less stable resulting from the small overlap at the terminal aromatic nuclei.[10]

The classical oxidative photocyclization of stilbene derivatives has been optimized and widely applied. However, many helicene derivatives consisting of fused aromatic rings, including benzene,[11] thiophene,[12] benzothiophene,[13] pyridine,[8] quinoline[14] and phosphindole[15] have previously been reported. To the best of our knowledge, few examples of helicenes in which a large π-conjugated polycyclic aromatic hydrocarbon (PAH) core such as carbazole, have been used to obtain helical structures. In an independent study, Katz and co-workers[16] reported the synthesis of the azahelicenebisquinone **1** in nonracemic form (Fig. 1). Later, Nozaki[17] reported the synthesis of aza[7]helicene **2** *via* Pd-catalyzed coupling reactions. Recently, Liu and co-workers[18] described the synthesis of the carbazole-based diaza[7]helicene **3** and aza[6]helicene **4** through ‘‘3+3’’ and “3+2” approaches respectively, and described their application as a deep-blue emitter in an organic light-emitting diode (OLED). More recently, our research group successfully prepared novel pentacyclic helicene **5** containing a carbazole unit, using an oxidative intramolecular photocyclization through a “3+1” approach.[19] More recently, Bedekar and co-workers[20] have synthesized the carbazole derived aza[7]helicene **6**. This class of helicene, with a carbazole framework, could open new possibilities for the utilization of *N*-containing helicenes in OLEDs and could also have potential applications in other organic electronic fields. For these reasons, there is interest to extend our approach to higher helicene frameworks containing the carbazole core. Moreover, we selected carbazole as a starting material because it has excellent fluorescence features[21] and carbazole derivatives are commonly used as fluorescence probes/sensors.[22]

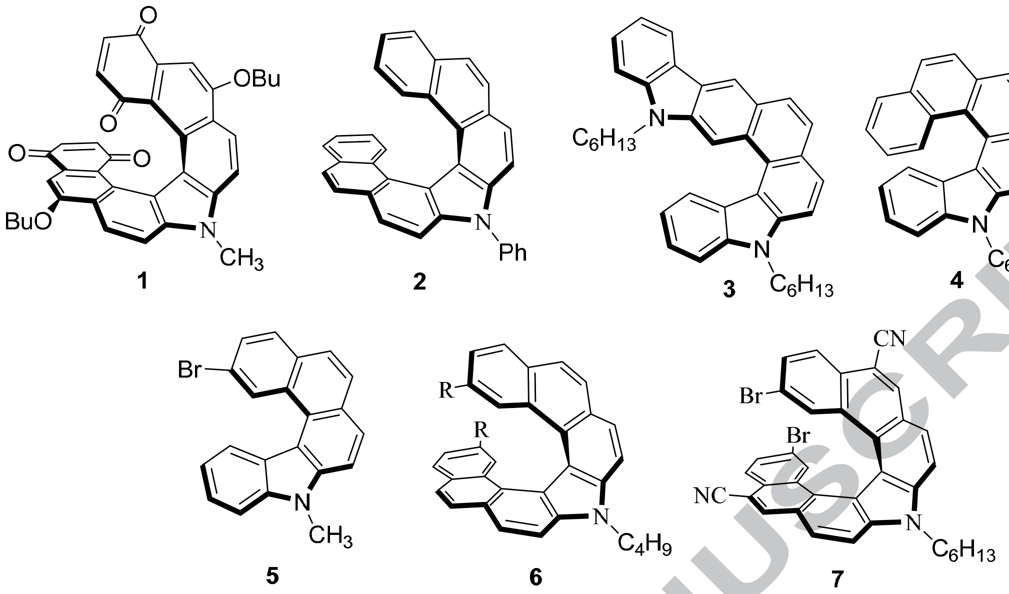
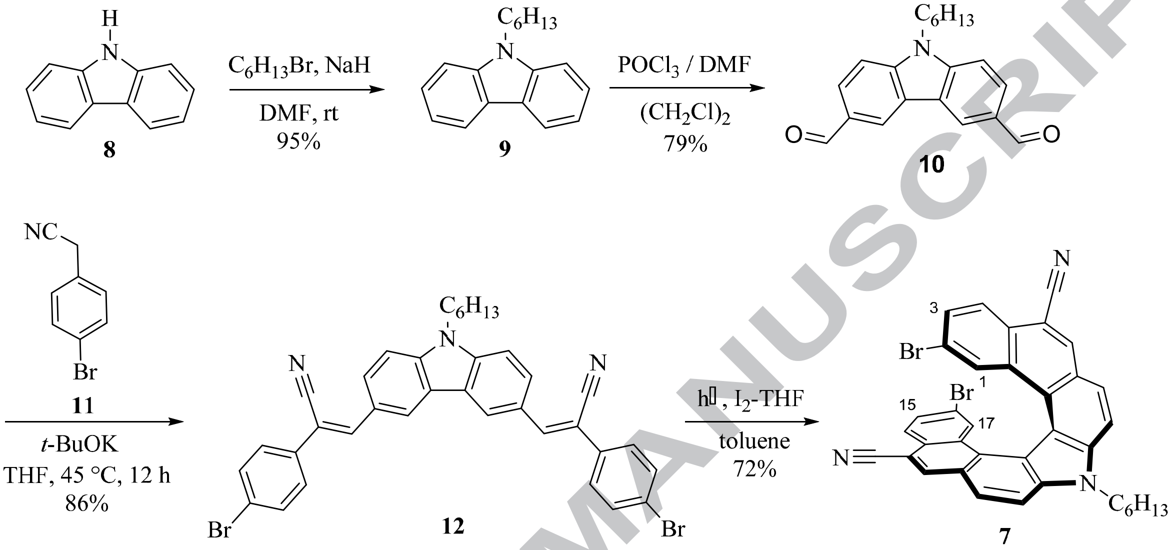


Figure 1. Chemical structures of azahelicenes **1-7**.

Herein, we report an efficient synthetic strategy towards a new symmetric carbazole-based heptahelicene **7** bearing two bromine atoms and two cyano groups at selected positions on the aromatic rings. The cyano groups could increase the solubility of the helicene derivative and improve its optical properties. Our synthetic strategy to construct the target functionalized heptahelicene **7** was based on a Knoevenagel condensation, followed by an oxidative photocyclization.

The synthesis of the helically chiral heptacyclic framework **7** was performed as shown in Scheme 1. To ensure good solubility of the final organic π-conjugated material in common organic solvents, we chose to incorporate a flexible aliphatic chain onto the carbazole unit. Thus, the commercially available tricyclic ring system, 9-*H*-carbazole (**8**), was reacted with hexylbromide in DMF to produce *N*-hexylcarbazole (**9**) in 95% yield. The latter was converted into *N*-hexylcarbazole-3,6-dicarbaldehyde (**10**) in 79% yield *via* a Vilsmeier-Haack reaction.[23] Compound (**10**) underwent double Knoevenagel condensation with 4-bromophenylacetonitrile (**11**), using potassium *tert*-butoxide as a base, in THF by heating at 45 °C for 12 hours to afford 3,6-bis(*p*-bromo-α-cyanostyryl)-9-hexylcarbazole (**12**) in 86% yield.[24]

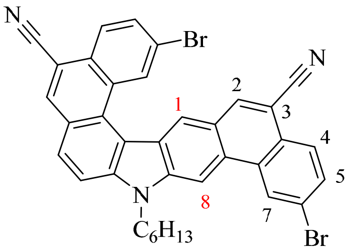
In order to obtain the helically chiral heptahelicene **7**, bis-cyanovinylene **12** was subjected to a double photocyclization using a 500 W high-pressure mercury immersion lamp. Photolysis was performed on a dilute solution (2.10^{-1} g/L) for approximately 6 hours, in the presence of stoichiometric iodine as an oxidizing agent, in one litre mixture of toluene and THF (95:05) at room temperature. THF was used as a hydrogen iodide scavenger and also to increase the solubility of alkene **12**.[25] The heptacyclic helicene **7** was obtained as a pure yellow solid in 72% yield, after purification by column chromatography.[26]



Scheme 1. Synthetic route to the helically chiral heptacyclic system **7**.

The helicene **7** obtained was characterized by NMR spectroscopy and HRMS, and was found to show good solubility in common organic solvents including dichloromethane, chloroform, toluene, ethyl acetate and tetrahydrofuran. The product was highly stable in air and to light. In the ^{1}H NMR spectrum, it displayed typical patterns for the H-1/17 and H-3/15 protons of the helicene moiety: high field signals at δ = 7.14 (J = 1.8 Hz) and 7.42 ppm (J_1 = 8.7 Hz, J_2 = 1.8 Hz) for H-1/17 and H-3/15, respectively (Scheme 1).

No other regioisomer was isolated from the reaction mixture, indicating that the ring closure of alkene **12** had occurred from the opposite side of the tricyclic moiety. Importantly, the anthracene-like derivatives **13** and **14** (Fig. 3) were not formed during the cyclization step, as these regioisomers would be expected to display characteristic signals for both H-1 and H-8 at low field in the ^{1}H NMR spectrum.[27]



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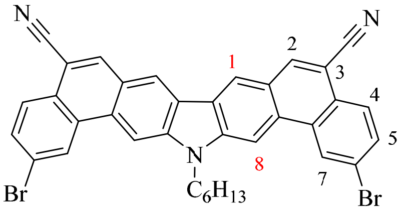

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Figure 3. Chemical structures of the anthracene-like derivatives **13** and **14**.

The optical properties of the heptahelicene derivative **7** were investigated using UV-Vis absorption and photoluminescence (PL) spectroscopy at room temperature (Table 1). The UV-Vis absorption spectra were recorded using a dilute solution of **7** in dichloromethane (1×10^{-5} M). As shown in Figure 4, the UV-Vis spectra were characterized by several structured bands between 250 nm and 425 nm. Specifically, the absorption spectrum of compound **7** contained one maxima (266 nm), four medium peaks (308, 332, 347 and 362 nm), and two minima (398 and 415 nm). The absorption bands in the range of 250-350 nm are associated with π-π* and n-π* electronic transitions, while the absorption peaks at the longer wavelength region (375-425 nm) can be ascribed to the intramolecular charge transfer (ICT) transition (π-π* transition) from the *N*-hexylcarbazole unit as an electron donor to the electron withdrawing cyano group and are similar to the characteristic vibration patterns of other helicene derivatives.[20,28] Moreover, the optical energy band gap $E_{g\text{-}op}$, calculated from the absorption band edge of the UV-Vis absorption spectra, is approximately 2.82 eV.

Upon excitation, a dilute solution (*ca.* 1×10^{-6} M) of compound **7** in dichloromethane at room temperature, the material showed two main emissions in the green region at 507 nm and 540 nm with a shoulder peak at 467 nm. This emission behaviour is similar to that observed for other aza[7]helicenes.[28]

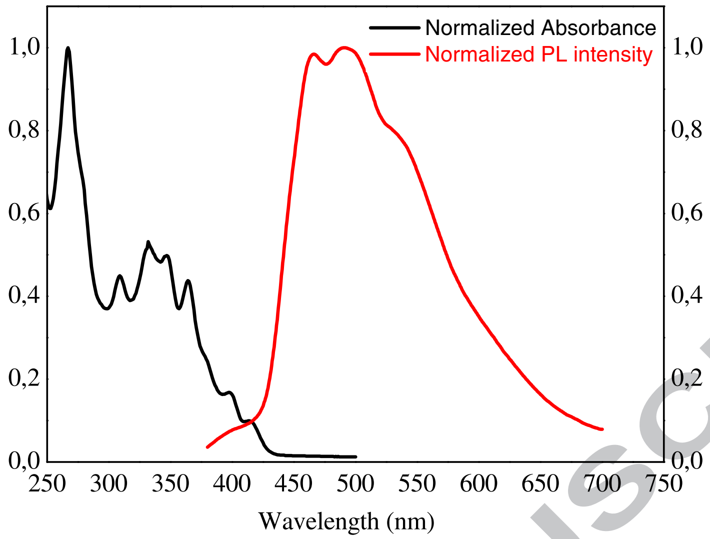

Figure 4. UV/Vis absorption (black line) and PL spectra (red line) of heptahelicene **7** in dilute dichloromethane.

Table 1.
Photophysical properties of helicene **7**.

	Absorption			Photoluminescence	
	$\lambda_{max}^{abs\ a}$ (nm)	λ_{onset} (nm)	$E_{g\text{-}op}{}^{b}$ (eV)	$\lambda_{ems}{}^{c}$ (nm)	FWHM^{d} (nm)
Helicene **7**	266	433	2.86	491	132

[a] Absorption maxima measured in a dichloromethane solution (5 x 10^{-5} mol.L^{-1}) at room temperature.
[b] The optical gap (E_g-$_{op}$) was estimated from the onset point of the absorption spectra: $E_{g\text{-}op} = 1240/\lambda_{onset}$.
[c] Emission maxima measured in a dichloromethane solution (5 x 10^{-6} mol.L^{-1}) at room temperature.
[d] Spectrum full width at half maximum.

Next, we investigated the electrochemical characteristics of the helicene **7** by cyclic voltammetry (CV) using ferrocene (Fc/Fc$^+$) as the internal standard with a scan rate of 100 mV.s^{-1} at room temperature. This material was scanned both positively and negatively, separately, in 0.10M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous dichloromethane at room temperature. As shown in the cyclic voltammogram in Figure 5, compound **7** exhibits irreversible anodic and cathodic peaks, the onset of oxidation ($V_{onset\text{-}ox}$) was found to occur at 1.45 V and the onset of reduction ($V_{onset\text{-}red}$) was at -0.93 V (vs SCE). According to an empirical method,[29] and by assuming that the energy level of the ferrocene/ferrocenium couple was 4.8 eV below the vacuum level, the HOMO and LUMO energy levels were calculated as follows:

E_{HOMO} (ionization potential) = – ($V_{\mathrm{onset\text{-}ox}} - V_{\mathrm{FOC}} + 4.8$)

E_{LUMO} (electron affinity) = – ($V_{\mathrm{onset\text{-}red}} - V_{\mathrm{FOC}} + 4.8$)

$E_{\mathrm{g\text{-}el}} = (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})$ eV

Where V_{FOC} is the ferrocene half-wave potential (0.494 V), $V_{\mathrm{onset\text{-}ox}}$ is the oxidation onset and $V_{\mathrm{onset\text{-}red}}$ is the material reduction onset, all measured versus (Ag/AgCl). The calculated E_{LUMO}, E_{HOMO} and $E_{\mathrm{g\text{-}el}}$ values are summarized in Table 2. The lowest unoccupied molecular orbital (LUMO) was 3.37 eV, while the highest occupied molecular orbital (HOMO) was 5.75 eV, giving electrochemical band gaps of 2.38 eV. The difference between the optical and electrochemical band gap of 0.48 eV is attributed to the interface barrier between the electrode and the helicene, and the exciton binding energy.[30]

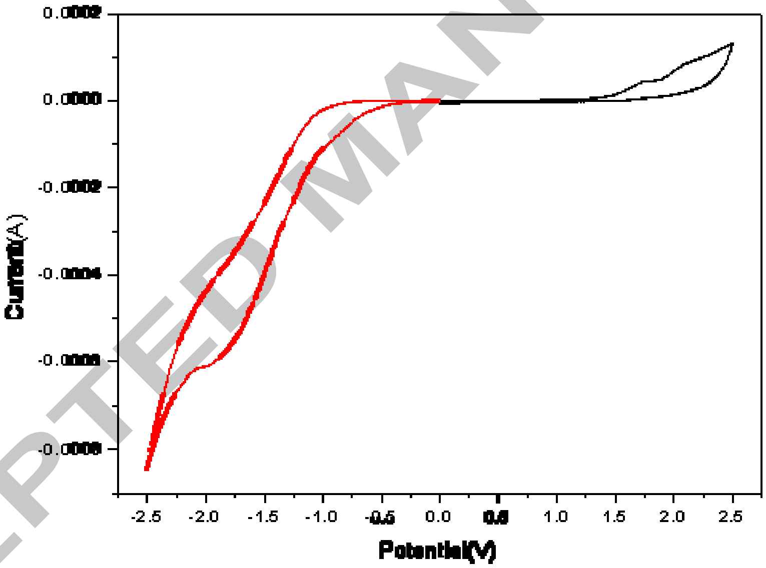

Figure 5. Cyclic voltammogram of azahelicene **7** in 0.1 M (n-Bu)$_4$NBF$_4$/dichloromethane at a scanning rate of 100 mVs^{-1}.

Table 2.
Electrochemical properties of helicene **7**.

Compound	$V_{\mathrm{onset\text{-}ox}}$ (V)	$V_{\mathrm{onset\text{-}red}}$ (V)	E_{HOMO} [a] (eV)	E_{LUMO} [b] (eV)	$E_{\mathrm{g\text{-}el}}$ [c] (eV)
Helicene **7**	1.45	-0.93	-5.75	-3.37	2.38

[a] Calculated from the oxidation potential.
[b] Calculated from the reduction potential.
[c] Band gap was calculated from the difference between HOMO and LUMO.

In summary, we have developed a straightforward method for the preparation of a carbazole-fused heptahelicene **7**, from readily available 9-*H*-carbazole in four steps with an overall yield of 46% under mild conditions. The photophysical and electrochemical behaviors of the helicene were also studied. This material showed relatively high electron affinity and may be a good candidate for electron-injection hole-blocking layers. Work in this field and resolution of the heptacyclic helicene are currently in progress.

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24. *Experimental procedure for diarylethene **12***: A solution of 9-hexylcarbazole-3,6-dicarbaldehyde **10** (1.5 g, 4.85 mmol) and 4-bromophenylacetonitrile **11** (2.10 g, 10.7 mmol) in dry THF (30 mL) was placed in a two-necked flask, fitted with a septum, which was degassed and purged with argon three times. To this solution was added a stoichiometric amount of potassium *tert*-butoxide (2.64 g, 23.5 mmol) and the mixture was stirred vigorously for 12 hours at 45 °C. After cooling, the mixture was poured into MeOH. The precipitate was collected using a sintered glass filter, washed with MeOH, and dried under vacuum. The purification of **12** was accomplished by chromatography on a silica gel column using CH_2Cl_2 as eluent to provide a bright yellow solid (2.75 g, yield = 86 %); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, J = 7.2 Hz, 3H), 1.30-1.36 (m, 6H), 1.90-1.86 (m, 2H), 4.29 (t, J = 7.2 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.50-7.60 (m, 8H), 7.65 (s, 2H), 8.15 (d, J = 8.4 Hz, 2H), 8.60 (d, J = 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 13.97, 22.48, 26.86, 28.90, 31.42, 43.54, 106.90, 109.60, 118.53, 122.66, 122.91, 123.01, 125.43, 127.10, 127.57, 132.11, 133.84, 142.12, 142.98; HRMS (MALDI-TOF) Calcd for $C_{36}H_{29}Br_2N_3$ $[M]^+$: 663.0728. Found: 663.0733.

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26. *Experimental procedure for the photocyclization reaction*: To a solution of alkene **12** (200 mg, 0.30 mmol) in 1 L of toluene/THF (95:05) was added a stoichiometric amount of I_2. The solution was irradiated using a falling-film photoreactor and a high-pressure Hg-vapor lamp (500 W, Hanovia). The reaction was monitored by TLC. Following completion, the solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel with cyclohexane/CH_2Cl_2 (80:20) to give helicene **7** as a pale yellow solid (144 mg,

72%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, J = 7.2 Hz, 3H, Me), 1.29-1.44 (m, 6H), 2.04-2.11 (m, 2H), 4.78 (t, J = 7.2 Hz, 2H), 7.14 (d, J = 1.8 Hz, 2H), 7.42 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 8.7 Hz, 2H), 8.17 (d, J = 8.7 Hz, 2H), 8.54 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 14.04, 22.56, 27.05, 29.85, 31.54, 44.19, 105.96, 111.60, 115.68, 118.15, 118.72, 125.21, 126.04, 127.08, 127.83, 127.87, 129.56, 129.96, 130.65, 135.47, 141.12; HRMS (MALDI-TOF) Calcd for $C_{36}H_{25}Br_2N_3$ $[M]^+$: 659.0415. Found: 659.0422.

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Graphical abstract

A new carbazole-based helically chiral architecture: Synthesis and physical properties

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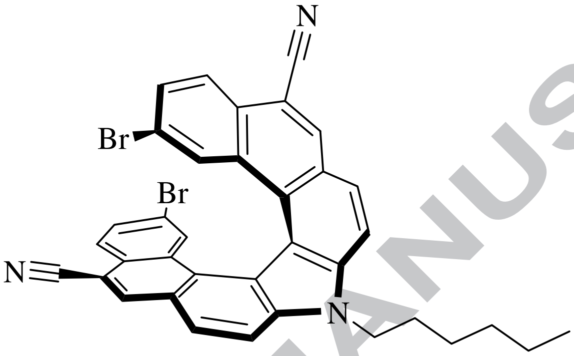

Highlights

- A photochemical approach leading to a new carbazole-based heptahelicene
- The optical properties of the carbazole-based material were investigated
- The electrochemical band gap of the target helicene was estimated to be 2.38 eV