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Synthesis and Characterization of New Carbazolocarbazoles: Toward π-Extended *N*-Fused Heteroacenes

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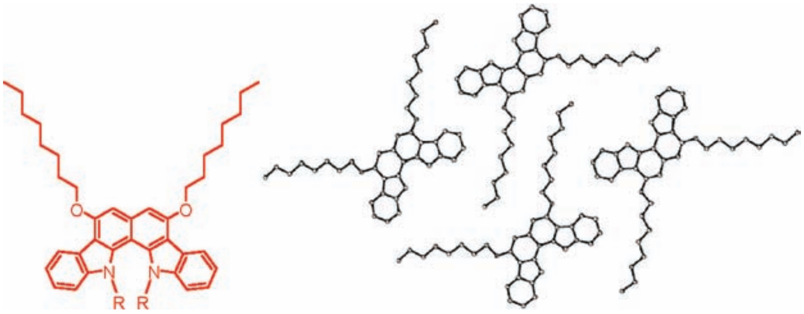
ABSTRACT



A regiospecific route has been developed for the synthesis of carbazolo[1,2-*a*]carbazole. The synthetic strategy is based on the use of appropriately tetrasubstituted naphthalene. Optical and electrochemical characterization of the fused heteroaromatic system reveals that this optically transparent heteroacene, with a low-lying HOMO, might be used as an organic material.

The application of conjugated polymers[1] and small molecules to the fabrication of electronic devices has become a promising and intense research topic in the recent past. Synthetic motivation lies in the search for novel π-conjugated materials with enhanced electronic properties. In this regard, acenes and heteroacenes[2] have attracted much interest as efficient semiconductors, among which pentacene illustrates the most studied example.[3] Nevertheless, in order to overcome the solubility and stability drawbacks of pentacene, the integration of heteroatoms into the fused polyaromatic framework has been successfully proved. The syntheses of several families of heteroacenes have been described in the literature, where sulfur,[4] nitrogen,[5] silicon,[6] selenium,[7] or a combination of these and other heteroatoms[8] have been integrated in fused structures.

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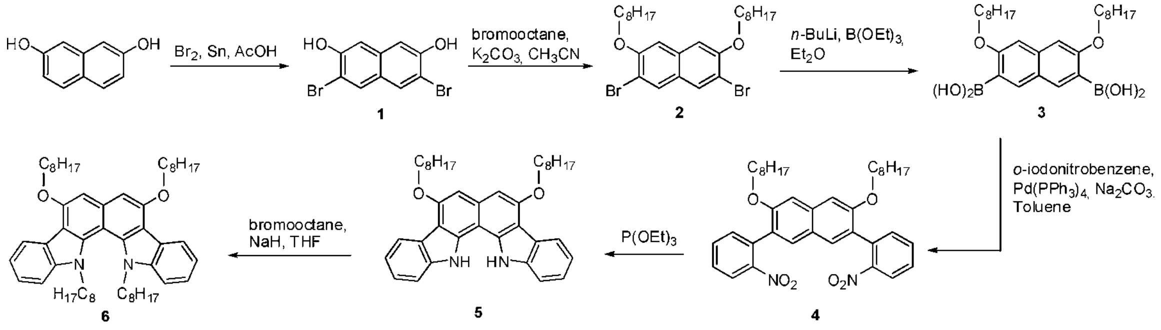
Scheme 1. Synthesis of Carbazolo[1,2-*a*]carbazole Derivatives



Regarding the nitrogen-based compounds, carbazole polymers and copolymers have long been used in optoelectronic devices due to their good conducting properties.[9] Indolocarbazole and diindolocarbazole derivatives (Figure 1),[10] either as small molecules or included in a polymer structure,[11] have also shown good performance as organic semiconductors. Excellent results have been reported for p-type field effect transistors with indolocarbazole derivatives.[12]

It has been established that an increase in the conjugation length of a molecule should result in an improvement of the charge mobility since better intermolecular interactions should have a beneficial effect on the nanomorphology of the molecular material. Herein we present the first synthesis and characterization of the hexacyclic carbazolo[1,2-*a*]carbazole system (Figure 1). Although the structure of carbazolocarbazole was first reported in 1965,[13] these heteroaromatic compounds have not received much attention, probably due to the lack of a convenient synthetic approach.

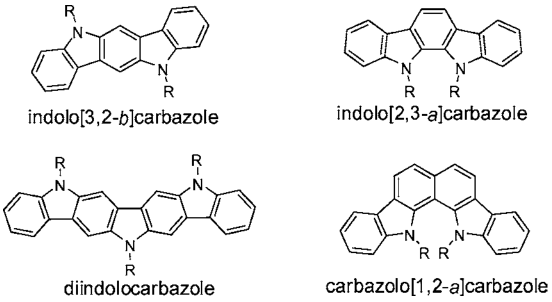


Figure 1. Carbazole-based N-heteroacenes.

The syntheses of heteroacenes are usually affected by the absence of regioselectivity which leads to the isolation of mixtures of different isomers. If those regioisomers cannot be separated, this might adversely influence the morphology of the deposited material and subsequently its charge transport ability. Therefore, the design of synthetic pathways which evolve toward isomerically pure materials is desirable. Our synthetic strategy (Scheme 1) is based on the use of conveniently tetrasubstituted naphthalenes as starting materials. The appropriate location of the substituents will allow a selective regiochemical development. Halogenation of 2,7-dihydroxynaphthalene was carried out as described in the literarture[14] to obtain 3,6-dibromo-2,7-dihydroxynaphthalene, **1**, with excellent selectivity.

The alkylation of the hydroxyl groups was achieved through a reaction with bromooctane in the presence of potassium carbonate. Bromo substituents in **2** were converted in good yield to the corresponding boronic acids **3** by treatment with *n*-butyllithium and triethyl borate. A double Suzuki−Miyaura cross coupling was then carried out between the diboronic acid and *o*-iodonitrobenzene to obtain compound **4**. Finally, due to the protective function of the octyloxy groups, a nitrene insertion through a Cadogan reaction is regiospecifically oriented to positions 4 and 5 of the naphthalene unit to obtain 5,8-dioctyloxycarbazolo[1,2-*a*]carbazole, **5**, with an 85% yield. The versatility of this route would enable the use of adequately substituted aromatic

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rings to be coupled with the naphthalene unit to ultimately yield substituted carbazolocarbazoles. These compounds could then be used in the synthesis of polymer materials.

The important role that alkyl substituents may play in organic materials is commonly assumed. These chains might induce both an enhancement of the solubility for solution processability of the molecule and an improvement of its morphology by noncovalent-induced ordering. In this regard, the synthetic route, which has just been described, includes the incorporation of those alkyl chains. Moreover, the structure of carbazolocarbazole allows the introduction of two more lipophilic substituents through the N-alkylation of **5** with bromooctane to isolate compound **6**. Due to the angle formed by the nitrogen exocyclic bonds, the steric hindrance of those groups results in the detection of atropoisomerism in the ^{1}H NMR spectrum of **6** since the peaks corresponding to the methylene groups, which are closer to the nitrogen atom, appear as nonisochronous protons.

Nevertheless, it is worth mentioning that it has been recently demonstrated, for indolo[3,2-*b*]carbazole derivatives, that N-alkyl chains might not have much influence on the semiconducting performance of the organic molecule, as long as its morphology might be controlled by other substituents in the skeleton.[12d]

All of the products have been characterized by ^{1}H NMR, ^{13}C NMR, and mass spectrometry.

Thermal stability of compounds **5** and **6** was studied by thermogravimmetric analysis (TGA) under nitrogen atmosphere. TGA revealed that samples did not show any significant mass loss up to 345 and 334 °C for compounds **5** and **6**, respectively.

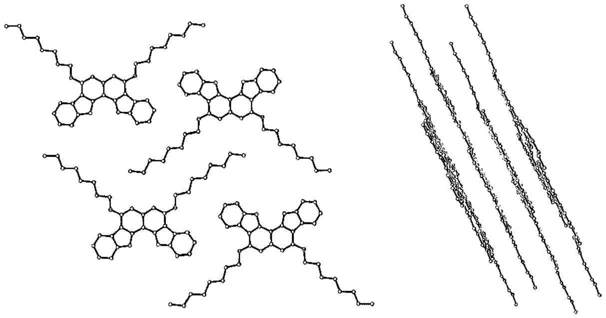

Figure 2. Crystal packing of **5** within the same plane (left) and in parallel planes (right). Hydrogen atoms have been omitted for the sake of clarity.

A single crystal for X-ray diffraction analysis could be grown by slow diffusion of methanol into a solution of **5** in dichloromethane. A completely flat structure is confirmed for the cabazolo[1,2-a]carbazole **5** (Figure 2). Even though molecules are packed in parallel planes, these planes are staggered and no $\pi-\pi$ stacking can be observed between adjacent planes. Nevertheless, aliphatic chains can interact with the aromatic system in the parallel plane through $C-H\cdots\pi$ contact (2.821−2.830 Å). As expected, the packing of molecules within the same plane is governed by fully extended alkyl−alkyl chain interaction, which shows a $C-H\cdots C$ contact distance of 2.846 Å. Additionally, aromatic CHs can also interact with the aliphatic chain of a neighbor molecule to stabilize the packing within the same plane. A perfectly flat arrangement is observed since all the molecules remain in the plane and no deviation is observed across the extended packing pattern. This arrangement could favor charge transport over the plane.

The optical properties of the carbazolocarbazoles were studied by absorption and emission spectroscopy (Figure 3). These properties were evaluated at different concentrations to prove that they were concentration independent and no aggregation effects took place in solution (see the Supporting Information). The UV−vis spectra of **5** showed well-resolved structured bands corresponding to different $\pi-\pi^*$ transitions, all below the visible range. The absorption spectrum was not very sensitive to the solvent polarity, except for the spectra recorded in DMSO, in which a 4 nm bathocromic shift could be detected. Interestingly, compound **6**, which shows a very similar pattern in the absoption spectrum, is red-shifted when compared to **5**. An optical HOMO−LUMO gap of 3.25 and 3.11 eV for compounds **5** and **6**, respectively, was determined from the absorption spectra onset in dichloromethane solution.

The emission spectra also showed the vibrational structure of the molecule with two peaks and a pronounced shoulder (Figure 3). The energy of the radiative transitions in compounds **5** and **6** did not show a significant solvent dependence either. Only a short 4 nm red shift was again determined in DMSO solution compared to the rest of the tested solvents. This is ascribed to the stabilization of the excited state, which is favored by the higher dipole moment and dielectric constant of DMSO. As happened for the absoption spectra, a noticeable red-shift was also detected in the emission of **6** when compared to **5**. Besides, as expected for rigid fluorophores, narrow (6 nm) Stokes shifts were observed. Interestingly, an increase in the luminescence intensity was detected upon increasing the viscosity of the solvent due to a decrease in the probability of the nonradiative processes. Quantum yield values were determined in ethanol solution at room temperature. Both compounds **5** and **6** displayed the same emissive efficiency (0.34) in spite of the structural differences produced by the two N-alkyl chains in **6**.

Conversely, time-resolved experiments, which were recorded in dichloromethane solution, revealed different decay patterns for both carbazolocarbazoles **5** and **6**. Whereas compound **5** showed a better fit for a double-exponential decay, N-alkylated derivative **6** showed a monoexponentially attenuated fluorescence (see the Supporting Information).

Electrochemical characterization was carried out by cyclic voltammetry in dichloromethane solution (see Table 1 and the Supporting Information). A reversible single wave voltammogram was registered for both compounds **5** and **6** with half-peak potentials of $E_{1/2} = 616$ mV and $E_{1/2} = 645$ mV, respectively. The oxidation of the studied carbazolo[1,2-*a*]carbazoles corresponded to a one electron process, as could

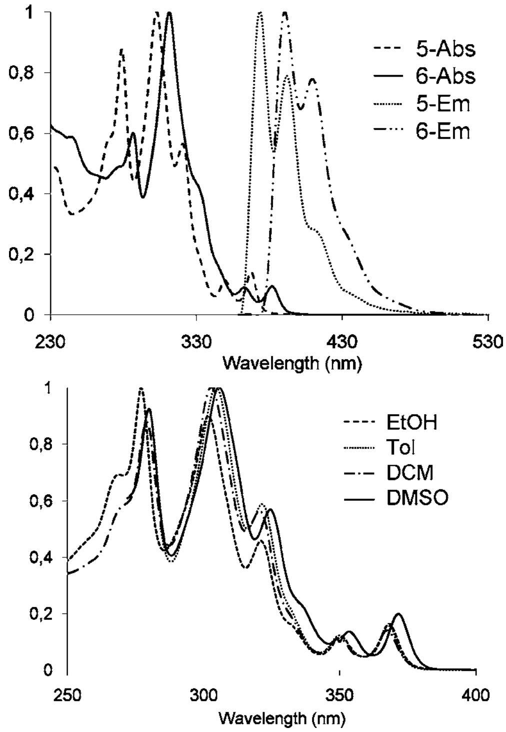

Figure 3. (Top) Normalized absorption and emission spectra of **5** and **6** in CH_2Cl_2 (10^{-5} M). (Bottom) Solvent effect (ethanol, toluene, dichloromethane, and dimethyl sufoxide) on normalized absorption spectra of **5**.

Table 1. Optical and Electrochemical Characterization

compd	**5**	**6**
$\lambda_{\mathrm{abs\ max}}$ (nm)/ε (M^{-1} cm^{-1})[a]	367/9317	382/7497
E_{gap} (eV)[b]	3.25	3.11
$E_{1/2}$ (V)[c]	0.72	0.74
LUMO (eV)	−2.10	−2.26
HOMO (eV)[d]	−5.35	−5.37
Φ_f[e]	0.34	0.34
τ_f (ns)[f]	$\tau_1 = 2.99$ $\tau_2 = 4.84$	7.36

[a] Recorded in dichloromethane (10^{-5} M) at room temperature. [b] Determined from the absorption spectra onset. [c] Calculated from the anodic and cathodic peaks in cyclic voltammetry ($E_{pa} + E_{pc}$)/2, CH_2Cl_2 (10^{-3} M) at room temperature, $TBAPF_6$ (0.1 M), scan speed: 0.1 V/s, SCE reference electrode, Pt working electrode. [d] Calculated from $E_{\mathrm{HOMO}} = -(4.7 + E_{\mathrm{ox\ onset}})$. [e] Determined in ethanol at room temperature using anthracene as reference. [f] Calculated in CH2Cl2 (10^{-5} M) at room temperature, $\lambda_{\mathrm{exc}} = 372$ nm, χ^2(**5**) = 0.98 and χ^2(**6**) = 1.11, error <7%.

be confirmed by normal pulse voltammetry. An estimation of the HOMO energy relative to the vacuum level was obtained from the oxidation onset, HOMO (**5**) = −5.35 eV and HOMO (**6**) = −5.37 eV. The LUMO energies could then be approximated by adding the energy of the optical gap to the HOMO energies, LUMO (**5**) = −2.10 eV and LUMO (**6**) = −2.26 eV. These LUMO energies can give an idea of the magnitude of the negative reduction potentials which could not be determined within the solvent window of our electrochemical experiments. The reversibility of cyclic voltammetry can be intepreted as a good sign of the stability of the radical cation of carbazolocarbazole.

In summary, we have developed a new synthetic route for the preparation of carbazolo[1,2-*a*]carbazole derivatives. X-ray diffraction shows a well-ordered arrangement of carbazolocarbazoles packed in parallel planes. Photochemical and electrochemical studies have been carried out to characterize the energies of the HOMO and LUMO orbitals which participate in charge-transfer processes. The low energy of HOMO orbitals, which can contribute to a higher stability toward oxidation, joined to the transparency of these compounds, resulting from the wide HOMO−LUMO gap, might make them applicable to organic electronics. The integration of these molecules into an electronic device is currently underway, and results will be reported in due course.

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Note Added after ASAP Publication. The name of indolo[2,3-*a*]carbazole was incorrectly named in the version published ASAP on June 15, 2010; the corrected version was published on the Web on July 9, 2010.

Supporting Information Available: Experimental details, ^{1}H NMR and ^{13}C NMR spectra, absorption and emission spectroscopy analysis, X-ray data, and electrochemical studies.This material is available free of charge via the Internet at http://pubs.acs.org.

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