

New diarylamino-phenyl derivatives of carbazole: Effect of substituent position on their redox, spectroscopic and electroluminescent properties



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ABSTRACT

Three new derivatives of carbazole were synthesized, namely two isomers disubstituted with diarylamino-phenyl groups in 2,7- and 3,6- positions (**C1** and **C2**) and diarylamino-phenyl symmetrically disubstituted with carbazole **C3**. All three compounds showed similar electrochemical behavior with one reversible redox couple, originating from the oxidation of the diarylamino-phenyl units to radical cations, followed by an irreversible anodic peak associated with the oxidation of the carbazole unit. The electrochemical results were supported by DFT calculations which predicted the same order of ionization potential values as experimentally found. Absorption and emission bands in the spectra of **C1** and **C3** were bathochromically shifted as compared to the corresponding bands in **C2**, again consistent with DFT calculations. **C1** showed a very high value of the photoluminescence quantum yield in THF solution, i.e. 90%. Moreover, the position of the emission band turned out to be solvent dependent and underwent a hypsochromic shift in toluene with simultaneous decrease of the photoluminescence quantum yield value to 68%. Blue light emitting **C1** was used as an electrolumiphore in a simple, guest/host-type single-layer light emitting diodes exhibiting luminance exceeding 1000 cd/m² and luminous efficiency of 0.7 cd/A.

1. Introduction

Carbazole derivatives constitute popular building blocks of several low and high molecular weight compounds exhibiting interesting electrochemical [1–4] and electrical transport [5–7] properties. For this reason they have been successfully used as components of electrochromic devices [8–11], active layers of field effect transistors [12–14], hole transporting materials in various electronic devices [15–18] *etc.* Photo- and electroluminescence of carbazole derivatives are other features of this family of compounds which are technologically promising. Therefore, carbazole unit-containing compounds have been successfully used as organic emitters [19–22], matrix materials for blue OLEDs [23–25] or electro donating units in molecules exhibiting the thermally activated delayed fluorescence (TADF) effect [26–29].

Each of the above listed applications requires the synthesis of compounds exhibiting different physical properties. Thus, low and high molecular weight carbazole derivatives used as hole transporting layer should exhibit high glass transition temperatures and good hole mobility. For derivatives considered as potential organic emitters high

values of the electroluminescence quantum yield are required. Matrix materials for blue OLEDs should, in turn, show high triplet energy as well as balanced charge injection. For TADF emitters small ΔE_{ST} values must be achieved due to well separated HOMO and LUMO levels. Tuning of all these properties is possible through appropriate functionalization of the carbazole unit either in its 2,7- or 3,6- positions.

In this paper we describe the studies on the effect of the type of substitution on redox photo- and electroluminescent properties of three new carbazole derivatives containing diarylamino-phenyl substituents. In two of them the central carbazole unit is differently disubstituted with diarylamino-phenyl (2,7- or 3,6- substitution). The third derivative studied consists of the central diarylamino-phenyl unit symmetrically disubstituted with carbazole moieties.

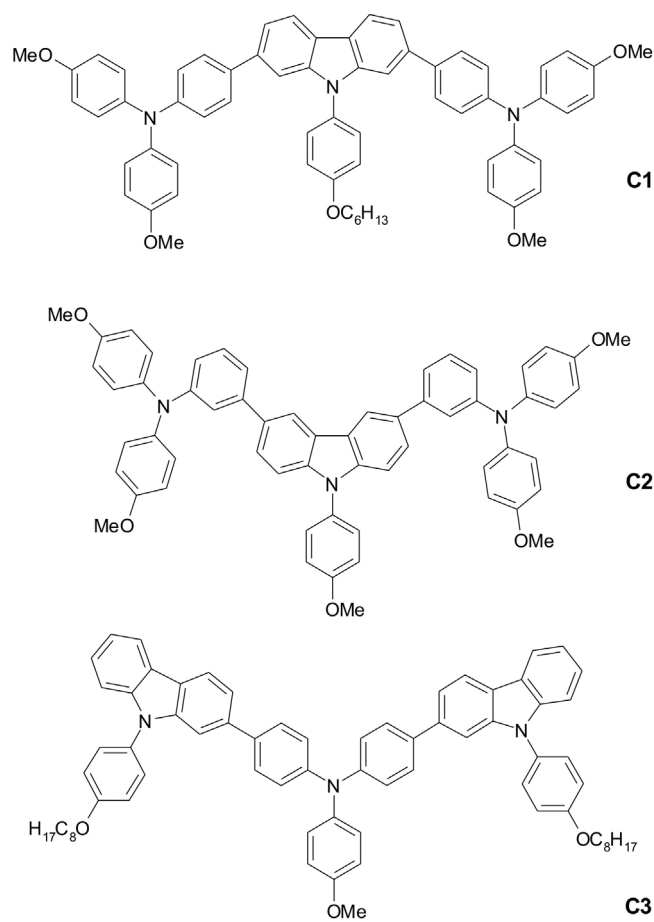
2. Results and discussion

2.1. Synthesis

The new synthesized carbazole derivatives are depicted in [Scheme](#)

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Scheme 1. Chemical structures of the studied aminophenyl carbazoles **C1–C3**. **C1**: 4,4'-(9-(4-hexyloxyphenyl)-9H-carbazole-2,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline), **C2**: 3,3'-(9-(4-methoxyphenyl)-9H-carbazole-3,6-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline), **C3**: (4-methoxy-*N,N*-bis(4-(9-(4-(octyloxyphenyl)-9H-carbazol-2-yl)phenyl)-aniline).

1.

The specific features of the applied synthetic strategy can be outlined as follows. Aminophenyl disubstituted carbazoles *i.e.* **C1** and **C2** were synthesized using Suzuki cross coupling (see Scheme 2). In the case of **C1** commercially available 2,7-dibromo derivative was used as a substrate, which was substituted with 4-hexyloxyphenyl at 9-carbazole position in a standard procedure. Thus, the reaction of 2,7-dibromocarbazole with 4-hexyloxy-1-iodobenzene in the presence of CuI and 1,2-diaminocyclohexane gave **1** with 62% yield. In the procedure of the preparation of **C2**, carbazole was first *N*-substituted with a 4-methoxyphenyl group using the same protocol as that applied in the case of the synthesis of **C1** (58% yield). The resulting product (**2**) was brominated with NBS to afford the 3,6-dibromo derivative **3** with 97% yield. Independently, 4-amino- and 3-aminophenyl boronic acid pinacol esters **S1** and **S2** were prepared (see Supplementary Material) with 69% and 59% yields, respectively. Palladium-catalyzed Suzuki coupling reactions between dibromocarbazole derivatives **1** and **3** and the corresponding borolanes **S1** and **S2** afforded the target products **C1** and **C2** with 55% and 64% yields, respectively.

C3 was synthesized in a four-step procedure (Supplementary Materials, Scheme S2). Anizidinediphenyl amine **4** was obtained with 92% yield in a Buchwald–Hartwig–type reaction using Pd(OAc)₂/t-Bu₃P as a catalyst. **4** was then brominated with NBS to give its dibromoderivative **5** with 91% yield. Suzuki-type coupling of **5** with commercially available carbazole boronate led to the dicarbazolamine derivative **6** (46% yield), which was finally *N*-substituted with 4-octyloxyphenyl in the presence of CuI/1,2-diaminocyclohexane to afford **C3** with 62% yield.

The detailed description of the synthesized target compounds as well as all their precursors together with their spectroscopic characterization and elemental analyses can be found in Supplementary Materials.

3. Electrochemical studies

Representative cyclic voltammograms of **C1–C3** are shown in Fig. 1. All three voltammograms reveal some common features, namely a reversible redox couple at lower potentials and an irreversible oxidation at higher potentials. The first one is associated with the diarylamine-phenyl oxidation to a radical cation. In the case of **C1** and **C2** both diarylaminephenyl substituents are oxidized at very similar potentials and these redox processes are manifested by some broadening of the anodic and cathodic peaks without the possibility of their resolution. In the case of **C3**, which contains only one triphenylamine unit undergoing oxidation, the peak of the first redox couple is narrower and separated by 70 mV, consistent with a one-electron redox process. The second redox process of predominantly irreversible (**C1**) or irreversible (**C2** and **C3**) nature has to be attributed to the oxidation of the carbazole moiety [30]. Electrochemical data derived from the chronovoltamperometric investigations are collected in Table 1.

As expected the redox properties of the investigated derivatives are dependent on the effective conjugation between both moieties constituting the molecule. Better conjugated 2,7- substituted derivative (**C1**) is easier to oxidize than its less conjugated isomer (**C2**). Diarylaminophenyl group in **C3** undergoes oxidation at higher potentials than in the case of **C1** and **C2** which probably is associated with a weak electron withdrawing effect of two aromatic rings of two carbazole moieties. In **C1** and **C2** diarylaminophenyl groups are in terminal positions and this effect must be less pronounced. In general, the oxidation of substituted diarylaminophenyl is very sensitive to the presence of electrodonating (accepting) groups in its closest vicinity. For example, in arylene bisimides disubstituted with diarylaminophenyl in their core, the potential of the substituent oxidation is shifted to higher potentials by *ca.* 350–400 mV as compared to **C1–C3** [31]. From the formal first oxidation potential it is possible to calculate the ionization potentials, IP, of **C1–C3** using the absolute potentials scale, *i.e.* expressing their values with respect to a vacuum level [32]. The obtained IP values, listed in Table 1, are relatively low as expected for conjugated molecules containing easily oxidizable arylamino moieties [33].

We were tempted to verify whether DFT calculations support these conclusions. At the early stage, the calculations were aimed at the equilibrium geometry elaboration since all three compounds could accommodate various possible conformations. At that point in all cases the geometry was constrained to C₂ symmetry point group and the calculations were performed without the alkoxy substituents. Then for the least energetic conformations –OMe groups were attached to simplify the calculations, which also removed the symmetry constraints and introduced C₁ symmetry. Then the geometries were re-optimized for neutral and charged species applying also the solvation model for IP and EA determination. The resulting HOMO/LUMO and IP/EA values along with respective E_g are collected in Table 2.

The data collected in Table 2 clearly demonstrate that the solvation changes the HOMO/LUMO levels, dropping down both values by *ca.* 0.2–0.3 eV. Since the changes are almost the same for HOMO and LUMO, the band gap, E_g, values determined in vacuum and in solution remain essentially the same. The calculated IP values are *ca.* 0.4 eV smaller than those derived from the cyclic voltammetry investigations, however, the trend remains the same (compare data in Tables 1 and 2). The calculated EA values are very low, consistent with the fact that all three compounds are easy to oxidize but very difficult to reduce. The calculations also clearly indicate that the 3,6-substituted derivative (**C2**) is less conjugated than the 2,7-substituted isomer (**C1**).

In Fig. 2 the frontier orbitals contours are presented. As it can be

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