



Synthesis and characterization of 1,3,5-triphenylamine derivatives with star-shaped architecture



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ABSTRACT

In this work we report the synthesis, electrochemical and optical properties of five new, star shaped compounds containing both carbazole and triphenylamine moieties, further endcapped with thiophene or 3,4-ethylenedioxythiophene units. Electrochemical, UV–visible spectroscopy and fluorescence methods were employed to study the properties of these compounds as well as their electropolymers. The basic characteristics such as the band gaps, HOMO and LUMO values, absorption and emission maximum wavelengths of the monomers and the polymers are reported and discussed.

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1. Introduction

Star-shaped low molecular weight compounds that possess electroactive properties have been willingly applied in a variety of applications such as organic light emitting diodes (OLEDs), organic photovoltaics (OPVs) or organic field effect transistors (OFETs) [1–3]. Depending upon the core and functionalization of the peripheral units it is possible to obtain star-shaped molecules with different geometry and symmetry. A flat, inflexible central unit with rigid arms usually provides an overall 2D geometry, whereas non-planar centers provide a 3D architecture [1].

The structural orientation of the star-shaped molecules highly affects their photophysical and electrochemical properties. A lack of conjugation between the core and the peripheral arms can result in a large energy band gap and hence absorption and emission of light at shorter wavelengths. For this reason, carbazole and fluorene functionalized star-shaped molecules are often used in blue OLEDs

[2–4]. Flattening the structure through the introduction of the rigid core functionalized units that do not cause large steric hindrance or elongation of arms, result in a shift in absorption and emission spectra toward longer wavelengths [5,6]. Another approach for better control of HOMO and LUMO energy levels and hence the photophysical properties includes the introduction of both donor and acceptor type units as the core or peripheral units of the star-shaped molecules and thus shifting the spectra toward longer wavelengths [7,8]. Among advantages of molecules with 3D architecture is the possibility of obtaining an amorphous material (i.e. molecular glasses) due to non-planar molecular structure preventing packing of molecules and hence ready crystallization [9].

Tripheylamine (TPA) possesses a flexible structure, which together with bulky substituents enables some rotation in the star-shaped molecule, thus it is successfully applied in materials exhibiting aggregation induced emission enhancement (AIEE) [10,6]. TPA also easily undergoes oxidation and forms stable radical cations therefore it is commonly used as a hole transporting layer [11,12]. Carbazole, due to its quite large planar structure can cause some steric hindrance when functionalizing the TPA core and thus it can enlarge the 3D molecular structure. Moreover, carbazole exhibits good electron donating character and good hole

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transporting properties thus when substituted onto the TPA core can be considered as a promising p-type material [13,14].

Herein we present a series of star-shaped molecules with C3 symmetry (Fig. 1) for potential application in organic electronics. We have recently reported on the star-shaped derivatives with a benzene core decorated with carbazoles [15]. In this work benzene is replaced with TPA in order to compare how this new core affects the optical properties of the investigated star shaped molecules and their electrochemical characteristics. The TPA core is further functionalized with carbazole units end-capped with thiophene and 3,4-ethylenedioxythiophene (EDOT) units that are known to easily undergo electropolymerization. We report therefore electro-oxidation induced polymerization of the investigated oligomers and electrochemical and spectroelectrochemical characterization of the obtained high molecular weight polymeric species.

2. Synthesis

The star-shaped compounds with a TPA core were synthesized by Suzuki-Miyaura coupling between triphenylamine boronic acid pinacol ester and carbazolyl halides (Scheme 2). The triphenylamine boronic acid pinacol ester (4) was prepared by the bromination of triphenylamine with NBS followed by borylation using 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Carbazole derivatives were prepared by monoiodination or dibromination and followed by *N*-alkylation. Additional heterocyclic rings were coupled with dibromocarbazole via Stille coupling as shown in Scheme 1. Stille coupling obtained mono substituted products (4a/4b) using $\text{PdCl}_2(\text{PPh}_3)_2$ as the catalyst. Products were, however, obtained with a low yield of 20% after 72 h both when the reaction was carried out in both DMF and THF solution. The addition of cesium fluoride and copper(I) iodide as proposed by Mee *et al.* [16] reduced the reaction time to 2 h, however the yield of the product was still a low 17%. Addition of 2-(tributylstannyl) derivative in small portions throughout the whole reaction time allowed obtained the mono substituted product with 35% yield. The synthesized compounds were purified by column chromatography and characterized by ^1H NMR, ^{13}C NMR and MALDI TOF analysis. The data is in full compliance with expected chemical structures.

3. Results and discussion

3.1. Photophysical properties

The normalized absorption and emission spectra of the investigated TPA derivatives are shown in Fig. 2 and the optical

properties are gathered in Table 1. Absorption spectra of all molecules exhibit three intense peaks located in the UV range of the electromagnetic spectrum, with λ_{max} at 241, 282 and 347 nm for Ia and Ib; 264, 304 and 356 nm for IIa and IIb; 265, 317 and 346 nm for III respectively.

Comparing the spectra of all compounds one can see that the introduction of additional aromatic substituents increases the conjugation length but only to a certain extent. Introduction of thieryl units into the oligomer results in bathochromic shift of the two first peaks of approximately 20 nm. The absorption maximum of the last peak, and thus the absorption range is however shifted only by 10 nm. The bathochromic shift is a result of the increased effective conjugation length in IIa and IIb. The introduction of ethylenedioxythienyl units do not cause any bathochromic shift in the absorption maximum, which can be explained by larger steric hindrance and poor conjugation between carbazole and EDOT moieties. It seems that alkyl substituent at the nitrogen atom, have a negligible effect on the absorption and emission spectra. However if we compare appropriate pairs of compounds we can conclude that peaks of compounds with longer chains are always 2–4 nm blue shifted, proving a slight steric hindrance effect.

To obtain insight into the electronic spectra, TDDFT calculations were completed employing a B3LYP/6-31G(d) functional. Calculations were performed for molecules containing ethyl substituents at the carbazole instead of long alkyl chains to shorten the calculation time. Chosen results of calculations are shown in supplementary data.

The peak at 347 nm in the spectra of compounds Ia and Ib is mainly attributed to π - π^* transitions in well conjugated carbazole and TPA core (according to calculation the highest contribution in this band having transitions HOMO \rightarrow LUMO, HOMO \rightarrow LUMO+1,3,4). The peak at 286 nm is strongly attributed to transitions in which lone pair of nitrogen atoms (both from the carbazole moieties as well as the central nitrogen atom) are involved (highest contribution of transitions HOMO-3 \rightarrow LUMO, HOMO-4 \rightarrow LUMO+2, HOMO-6 and HOMO-5 \rightarrow LUMO+1). The absorption band at about 300 nm is also assigned to π - π^* transitions in carbazole moieties.

For compounds IIa and IIb the peak at 356 nm is attributed to π - π^* transitions in the highly conjugated core reaching TPA and carbazole and also π - π^* transitions covering the thiophene moieties (according to calculation the highest contribution in this band has transitions HOMO \rightarrow LUMO, LUMO+1,2,6,7). Between 300 and 325 nm there is a broad absorption band consisting of two overlapping bands with peaks at about 304 and 315 nm. The peak at 304 nm is strongly attributed to transitions in which lone pair of

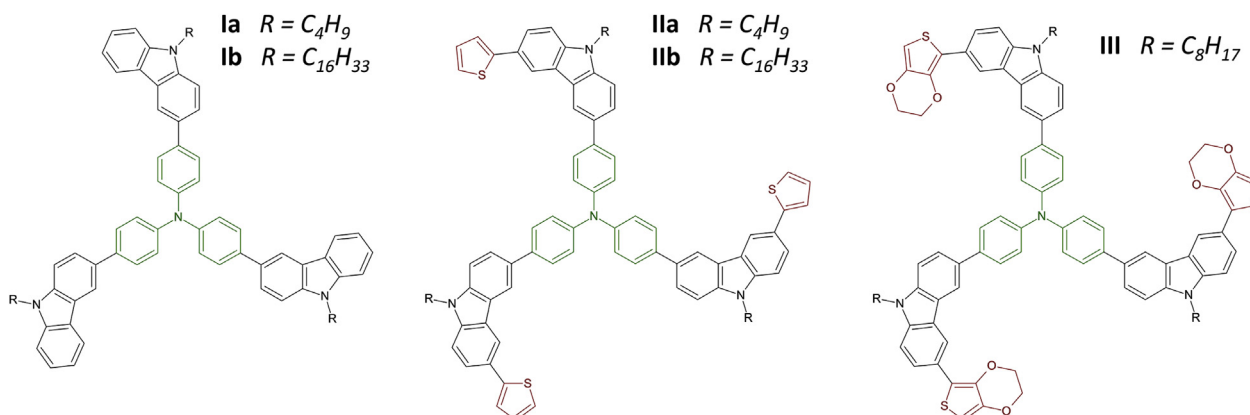


Fig. 1. Structures of investigated compounds with C3 symmetry.

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