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Synthesis and properties of 1,3,5-tricarbazolylbenzenes with star-shaped architecture

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ABSTRACT

A series of star-shaped carbazole derivatives were prepared *via* Suzuki-Miyaura and Stille coupling procedures. Received monomers were characterized by UV-Vis spectroscopy, fluorescence spectroscopy and cyclic voltammetry in order to estimate their basic spectral, electrochemical and electronic properties important for wide scale of applications in organic electronics and photovoltaics. Experimental results were supported by DFT calculations. Synthesised compounds were also used as monomers in the electrodeposition of conjugated polymers. Spectroelectrochemical EPR and UV-Vis-NIR measurements were carried out in order to study the influence of structure on charge carrier formation.

1. Introduction

Steadily increasing progress in organic electronics, evidenced by the boost of devices based on π-conjugated organic materials, has led to intense research for materials of precisely defined and tailored properties [1]. A number of recent investigations have been focused upon the relationship between modification of the molecular structure and its influence on optical and electrochemical properties of the molecules [2–5]. One approach for tailoring a molecule's properties is the application of a different architecture: linear, star-shaped or branched. Star-shaped and branched architectures demonstrate several virtues in comparison with a linear one, inter alia, molecules exhibit better thermal stability if bulky substituents that ensure large steric hindrance are incorporated, thus facilitating glass formation and amorphous morphology. Limited fluorescence quenching in the solid state caused by close packing and π–π interactions characteristic for linear systems is also beneficial [1,6–8].

We have already reported the characterization, including cyclic voltammetry study as well as *in situ* UV-Vis spectroelectrochemical measurements, of a series of meta-substituted arylbenzenes (representing star-shaped architecture) that were electroactive and turned out to easily undergo electropolymerization creating stable, during multiple doping and dedoping cycles, thin films on an electrode surface [9,10]. Reported poly(arylbenzene)s based on thiophene, furan and EDOT linkages exhibited, however, limited applicability due to their insufficient solubility in common organic solvents. In order to meet commercial applications, materials suitable for solution processing methods are highly coveted [11].

Carbazole molecular moieties are widely employed for the synthesis of materials for optoelectronic applications since they exhibit strong electron-donating ability, very good hole-transporting properties and electrochemical and photochemical stability [12]. Carbazole itself exhibits blue fluorescence, thus compounds possessing carbazole units are frequently applied for the preparation of blue emitting devices [13–15]. Some carbazole derivatives are also known to form aggregates in water that can emit light more efficiently than their solutions, thus they are said to exhibit aggregation-induced emission enhancement (AIEE) [8,16], which is crucial for OLEDs applications. Other important research

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includes application of these molecules as organic sensitizer for organic solar cells [17,18].

In this report we present a series of symmetric 1,3,5-tricarbazolylbenzenes which were synthesized *via* Suzuki cross-coupling. The architecture of these compounds has been designed to combine the advantages of star-shaped and carbazole oligomeric materials for possible application as sensitizers for organic solar cells or electroluminescence materials for OLEDs.

Attachment of carbazole derivatives through their C3 carbon atom leaves the nitrogen atom of carbazole units unsubstituted. Its *N*-alkylation using alkyl halides of various chain lengths can be easily performed and ensures better solubility of the final monomers as well as of the oligomers formed by electrochemical oxidation. We incorporate the additional thiophene rings to better control the energy gap (Eg) by extending the conjugation length, as well as tuning the optical properties of the star-shaped carbazole based molecules.

We present here the photophysical and electrochemical properties of carbazolylbenzenes alongside with the theoretical calculations for these molecules.

2. Experimental section

2.1. Synthesis

2.1.1. Methods

NMR spectra were recorded at 600 MHz for ^1H NMR and 151 MHz for ^{13}C NMR on a Varian Mercury Plus 600 MHz spectrometer or at 400 MHz for ^1H and 100 MHz for ^{13}C NMR on a Agilent 400 MHz spectrometer; δ values are in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. MALDI-TOF spectra were recorded on a Shimadzu AXIMA Performance instrument with no additional matrix.

2.1.2. Materials

Carbazole, 1,3,5-tribromobenzene and 2,4,6-tribromophenol and other required materials were purchased from Sigma Aldrich and used as received. 3-Iodo-9*H*-carbazole (1) and 3,6-diiodo-9*H*-carbazole (4) were synthesized according to procedure described by Tucker [19].

Solvents were used without further purification except from THF which was distilled over sodium and dried with 4 Å molecular sieves prior to use. DMF (HPLC grade) was dried with 4 Å molecular sieves prior to use. Column chromatography was performed using silica gel 60 (0.040–0.063 mm) purchased from Merck.

2.1.3. General procedure for the preparation of alkylated carbazoles (**2** and **5**)

To the solution of mono-iodinated carbazole **1** (6 g, 20 mmol) or di-iodinated carbazole **4** (6 g, 14 mmol), in anhydrous DMF (70 ml), NaH (60 wt% in mineral oil) (1 eq.) and octyl bromide (1 eq.) were added. The reaction mixture was stirred at 80 °C overnight. After consumption of carbazole substrate (the reaction was monitored by TLC; *n*-hexane was used as the eluent) the reaction mixture was poured into water (200 ml), extracted with ethyl acetate (3 × 50 ml) and dried over anhydrous $MgSO_4$. The solvent was removed under diminished pressure and the residue was purified by column chromatography eluting with *n*-hexane to afford white solids (**2**, **5**).

2.1.4. 3-iodo-9-octyl-9H-carbazole (**2**); 7.6 g, yield: 91%

^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 1.6 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.68 (dd, J = 8.2, 1.6 Hz, 1H), 7.47 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.25–7.21 (m, 1H), 7.17 (d, J = 8.1 Hz, 1H), 4.24 (t, J = 7.3 Hz, 2H), 1.85–1.81 (m, 2H), 1.37–1.16 (m, 10H), 0.91–0.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.38, 139.55, 133.72, 129.15, 126.26, 125.33, 121.54, 120.47, 119.23, 110.70, 108.83, 81.08, 42.89, 31.87, 31.01, 22.68, 20.50, 14.10, 13.82.

2.1.5. 3,6-diiodo-9-octyl-9H-carbazole (**5**); 6.2 g, yield: 82%

^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 1.6, 2H), 7.70 (dd, J = 8.6, 1.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 4.21 (t, J = 7.1 Hz, 2H), 1.84–1.77 (m, 2H), 1.35–1.17 (m, 10H), 0.85 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.51, 134.50, 129.36, 123.99, 110.89, 81.62, 43.26, 31.74, 29.30, 29.11, 28.82, 27.21, 22.58, 14.04.

2.1.6. 3-iodo-9-octyl-6-(thiophen-2-yl)-9H-carbazole (**6**)

3,6-Diiodo-9-octyl-9*H*-carbazole **5** (2.12 g, 4 mmol) was dissolved in DMF (50 ml) and flushed with nitrogen. Cesium fluoride (1.21 g, 8 mmol), copper (I) iodide (0.04 g, 0.2 mmol) and $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol) were added to the reaction mixture. 2-(tributylstannyl)thiophene (1.5 g, 4 mmol) was added dropwise to the reaction mixture for 2 h at 40 °C. The reaction mixture was stirred for another 30 min until the 2-(tributylstannyl)thiophene substrate was consumed (progress was monitored by TLC (*n*-hexane: chloroform 5:1, v/v)). The reaction mixture was poured into water (140 ml), extracted with CH_2Cl_2 (4 × 30 ml) and dried over anhydrous Na_2SO_4. The solvent was removed under diminished pressure and the residue was purified by silica gel packed column to afford light yellow solid (0.68 g, yield: 35%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 1.6 Hz, 1H), 8.22 (d, J = 1.6 Hz, 1H), 7.72 (dd, J = 8.4, 1.6 Hz, 1H), 7.68 (dd, J = 8.8, 1.6 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.31 (dd, J = 3.6, 1.2 Hz, 1H), 7.25 (dd, J = 5.1, 1.2, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.09 (dd, J = 5.1, 3.6 Hz, 1H), 4.21 (t, J = 7.2 Hz, 2H), 1.84–1.80 (m, 2H), 1.37–1.16 (m, 10H), 0.87–0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.40, 139.99, 139.86, 134.08, 129.31, 127.99, 126.17, 125.25, 124.93, 123.81, 122.15, 121.96, 117.90, 110.89, 109.14, 81.39, 43.25, 31.75, 29.31, 29.12, 28.90, 27.23, 22.58, 14.04.

2.1.7. General procedure for the preparation of carbazolyl boronic acid pinacol esters (**3** and **7**)

3-Iodo-9-octyl-9*H*-carbazole **2** (4.05 g, 10 mmol) or 6-iodo-9-octyl-3-thienyl-9*H*-carbazole **6** (4.87 g, 10 mmol) was dissolved in anhydrous THF (100 ml). The solution was cooled to −78 °C and *n*-butyllithium (2.5 M in hexane, 5.2 ml, 13 mmol) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.12 ml, 30 mmol) was added in one portion. The resulting mixture was slowly warmed up to room temperature and stirred overnight. The mixture was poured into water (150 ml), extracted with CH_2Cl_2 (3 × 40 ml) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel packed column (*n*-hexane: ethyl acetate 10:1, v/v) to afford light yellow oil of **3** and blue oil of **7**.

2.1.8. 9-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**3**)

1.4 g, yield: 35%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.13 (d, J = 7.2 Hz, 1H), 7.91 (dd, J = 8.2, 0.8 Hz, 1H), 7.48–7.38 (m, 3H), 7.25–7.21 (m, 1H), 4.30 (t, J = 7.2 Hz, 2H), 1.91–1.81 (m, 2H), 1.40–1.37 (m, 12H), 1.35–1.23 (m, 10H), 0.90–0.84 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.61, 140.53, 132.08, 127.75, 125.56, 123.14, 122.60, 120.55, 119.16, 108.70, 108.05, 83.54, 43.10, 31.77, 29.36, 29.14, 28.92, 27.27, 26.93, 24.93, 22.58, 14.03.

2.1.9. 9-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(thiophen-2-yl)-9H-carbazole (**7**); 1.4 g, yield: 32%

^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.38 (d, J = 1.6 Hz, 1H), 7.93 (dd, J = 8.2, 1.0 Hz, 1H), 7.71 (dd, J = 8.4, 1.6 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 8.4, 1H), 7.32 (dd, J = 3.5, 1.1 Hz, 1H), 7.24 (dd, J = 5.1, 1.1 Hz, 1H), 7.09 (dd, J = 5.1, 3.5 Hz, 1H), 4.26 (t, J = 7.2 Hz,