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



PIGMENTS

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1. Introduction

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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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

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[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 starshaped 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].

Triphenylamine (TPA) possesses a flexible structure, which together with bulky substituents enables some rotation in the starshaped 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 2isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Carbazole derivatives were prepared by monoiodination or dibromiantion 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 PdCl₂(PPh₃)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, ¹³C 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 thienyl 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 $\pi-\pi^*$ transitions in the highly conjugated core reaching TPA and carbazole and also $\pi-\pi^*$ 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.



Scheme 1. Synthetic route for the preparation of carbazole halides. (i) NBS, DMF, 0.5 h (ii) NaH, C₈H₁₇Br/C₁₆H₃₃Br, DMF, 80 °C, 17 h (iii) 2-(tributylstannyl)thiophene/2-(tributylstannyl)ethylenodioxythiophene, CsF, CuI, PdCl₂(PPh₃)₂, DMF, 40 °C, 2 h.



Scheme 2. Synthetic route for the preparation of carbazolyltriphenylamines Ia/Ib, IIa/IIb, III. Reagents and conditions: Pd(PPh_3)_4, K_2CO_3, TBAB, toluene:H_2O (4:1), reflux, 92 h.



Fig. 2. Absorption and emission spectra of studied compounds in CH₂Cl₂.

Table 1Optical properties of compounds Ia, Ib, IIa, IIb and III.

| Compound | λabs [nm] | λem (λex) [nm] | Φ |
|----------|---------------|----------------|------|
| Ia | 241, 282, 347 | 415 (347) | 0.35 |
| Ib | 241, 280, 346 | 412 (347) | _ |
| IIa | 264, 304, 358 | 426 (356) | _ |
| IIb | 264, 304, 355 | 413 (356) | 0.58 |
| III | 265, 317, 346 | 414 (346) | 0.28 |

 λabs –maximum of absorbance, λem maximum of emission, λex – excitation wavelength, Φ – fluorescence quantum yield.

nitrogen atoms (both from carbazole moieties as well as central

nitrogen atom) are involved (highest contribution of transitions HOMO-2,HOMO-3 \rightarrow LUMO and HOMO-1 \rightarrow LUMO+1). The peak at 315 nm on the other hand is mainly attributed to π - π * transitions in carbazole and tiophene moieties (HOMO \rightarrow LUMO+2,3,4 transitions).

For compound III the broad absorption band with maximum at 346 nm comprises bands corresponding mainly to π - π * transitions in Cz-Edot and in Cz-TPA core (HOMO \rightarrow LUMO, LUMO+3,5,8). Bands corresponding to n- π * transitions occur at 317 nm (HOMO-1 \rightarrow LUMO+3, HOMO \rightarrow LUMO+3,9,10).

All compounds are fluorescent. Photoluminescence spectra in CH_2Cl_2 are collected on Fig. 2. Compounds Ia, Ib, Ilb and III have almost the same shape, with emission band extending from 370 to

500 nm, spectra of IIa is little red shifted. Peak maxima were found at 415 nm for Ia, 412 nm for Ib, 426 nm for IIa, 413 nm for IIb and 414 nm for compound III (samples excited with light of a wavelength of 347 nm for Ia and Ib, 356 nm for IIa and IIb and 346 nm for the III respectively). Quantum yields measured in toluene for derivatives end-capped with carbazole, thiophene and EDOT are 0.53, 0.58 and 0.28 for Ia, IIb and III respectively.

All spectra are evidently red shifted by approximately 60 nm when compared to carbazole, which is assumed to be the most emissive component in the investigated molecules. These starshaped compounds are also shifted 10 nm when compared to previously described analogic compounds with a benzene core [15,17]. This bathochromic shift proves the interaction between TPA and carbazole moieties. An additional shift in compound IIa, having thienyl units, is related to yet more increased effective conjugation length. Interestingly this effect isn't observed in the case of analogous compound with longer alkyl chain (IIb), nor in the compound containing the EDOT unit (III), which is probably due to steric hindrance.

3.2. Electrochemical properties

Electrochemical properties of the compounds were investigated using cyclic voltammetry (CV). All dyes undergo multistage oxidation. The character of the oxidation process is different for compounds terminated with carbazole units and for the ones terminated with thiophene/EDOT units. Ia and Ib undergo a three step oxidation in which the relative ratio of electrons involved in each step is approximately 1:1:2 (data from DPV analysis), while compounds IIa, IIb and III on the other hand undergo a two-step oxidation with relative charge 1:3.

Fig. 3 shows example voltammograms of Ia, IIa and III registered during oxidation at various potentials. On the CV of Ia, the first oxidation step is a reversible process (peak separation $\Delta_{pp} = 0.06$ V), which can be attributed to the oxidation of the triphenylamine core and formation of a stable radical cation, proposed previously by this group [18]. Further oxidation leads to the formation of reactive radicals in the carbazole moieties and dications are generated by their recombination (second and third peaks respectively). Oxidation to potentials above 0.9 V versus Fc/Fc⁺ (third peak on the cyclic voltammogram) initiates the oligomerization.

Analogously in the case of IIa the initial oxidation of Ib is accompanied by the formation of stable radical cations on the TPA unit. Further oxidation above 0.65 V is associated with oxidation of the three arms bearing carbazole and thiophene moieties and leads to the formation of dications and reactive radicals in thiophene. The increase of peak currents during the next voltammetric scans and the resulting formation of a conducting film on the working electrode is caused by the oligomerization process.

In case of compound III the oxidation begins at much lower potential, E_{onset} , approximately 0.15 V, with the peak found at 0.293 V. Already this first oxidation step is an irreversible process associated with rapid oligomerization. So low potential of oxidation and ease of oligomerization resembles behavior of pure EDOT which exhibits oxidation peak at 0.15 V [19].

Fig. 4 shows the multi-sweep cyclic voltammograms of all investigated compounds (black line) in Bu₄NBF₄/dichloromethane electrolyte and their electrodeposited films (red line) in monomer free Bu₄NBF₄/dichloromethane electrolyte. Corresponding anodic and cathodic peaks (Ea and Ec) occurs on CV at potential (versus Fc/Fc⁺) for Ia: Ea1/Ec1 = 0.314/0.288, Ea2/Ec2 = 0.731/0.655, Ea3 = 0.954 V, for Ib: Ea1/Ec1 = 0.421/0.349, Ea2/Ec2 = 0.786/0.720, Ea3 = 1.010 V, for IIa: Ea1/Ec1 = 0.267/0.200, Ea2 = 0.517 V, for IIb: Ea1/Ec1 = 0.360/0.296, Ea2 = 0.626 V, for III Ea1 = 0.293 V.

For most of the investigated compounds oxidation is followed by the consecutive oligomerization process, which is demonstrated by the appearance of new peaks in the next scans. Only for monomer lb, a polymer film didn't deposit well on the working electrode under applied conditions. It was most likely caused by the very good solubility of the formed oligomers in the electrolyte solution due to the attached long alkyl chains. This supposition was confirmed by the diffusion of a colorful species from the working electrode surface into the bulk electrolyte during cyclic voltammetric scans.

All obtained polymers exhibit slightly different electrochemical properties to those of the corresponding monomers. Poly-Ia undergoes a three step oxidation, with corresponding peaks found at potentials of Ea1/Ec1 = 0.279/0.283, Ea2/Ec2 = 0.612/0.506, Ea3/Ec3 = 0.992/0.915 V versus Fc/Fc⁺. In case of poly-Ib, four peaks are observed using CV, Ea1/Ec1 = 0.350/0.320, Ea2/Ec2 = 0.610/0.560, Ea3/Ec3 = 0.813/0.787, Ea3/Ec3 = 1.054/0.965 V.

Films of poly-IIa and poly-IIb exhibit three oxidation peaks. For poly-IIa peaks occur at Ea1/Ec1 = 0.287/0.284, Ea2/Ec2 = 0.638/0.548, Ea3/Ec3 = 1.073/0.985 V vs. Fc/Fc⁺, while for poly-IIb Ea1/Ec1 = 0.390/0.374, Ea2/Ec2 = 0.732/0.651, Ea3/Ec3 = 1.191/1.081 V.

CV of poly-III displays four peaks, Ea1/Ec1 = -0.232/-0.271, Ea2/Ec2 = -0.037/-0.130, Ea3/Ec3 = 0.305/0.258, Ea3/Ec3 = 0.943/0.877 V vs. Fc/Fc^+ . All received polymer films are stable under oxidation up to approximately. 1.3 V versus ferrocene.



Fig. 3. Cyclic voltammogram (CV) registered during electrochemical oxidation of oligomers Ia, IIa and III to various potentials. Potential sweep rate 0.1 V/s; 1 mM monomer solution in 0.1 M Bu4NBF4/CH₂Cl₂.



Fig. 4. Cyclic voltammograms of star-shaped derivatives: black lines demonstrate CV curves of compounds in 0.1 M Bu₄NBF₄/dichloromethane electrolyte and red lines display CV curves of electrodeposited polymers on a platinum working electrode in monomer free 0.1 M Bu₄NBF₄/dichloromethane electrolyte. Measurement conditions: scan rate 0.1 V/s; Ag/AgCl reference electrode calibrated against Fc/Fc+. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The electrochemical data were used to determine the energy of the HOMO levels. Each HOMO level was calculated using the oxidation onset potential according to the equation $HOMO = -(5.1 + Eox_{onset})$. The LUMO level, which is accompanied with the reduction process, couldn't be determined due the limitation of the supporting electrolyte. Subsequently this value was then calculated from the difference between the HOMO and the band gap, determined from the optical band gap (Eg_{opt}). The optical band gap was calculated from the Planck equation for photon energy. All parameters are displayed in Table 2.

3.3. Spectroelectrochemistry of polymers

Spectroelectrochemical properties of the electro-deposited carbazole containing polymer films were investigated by UV–vis–NIR analysis. The absorption spectra of polymers Ia, Ib, IIa, IIb, and III, on an ITO coated glass electrode, recorded as a function of increasing applied electrode potentials are shown in Fig. 5.

The oxidation process proceeds in a different way for each group of polymers.

In the case of Ia and Ib the absorption bands corresponding to the electro-deposited polymers, gradually decrease with the increasing applied voltage. At the same time during the doping



Fig. 5. Set of UV–vis absorption spectra of poly-Ia, lb, IIa, IIb and III thin films on an ITO electrode, recorded at gradually stepped potentials.

| Table 2 | |
|---------|--|
|---------|--|

Electronic properties of compounds Ia, Ib, IIa, IIb and III and their polymers.

| Compound | Monomer | | | Polymer | | |
|----------|------------------------|---------------------|------------------------|------------------------|---------------------|------------------------|
| | Eg _{opt} [eV] | $E_{\rm HOMO}$ [eV] | E _{LUMO} [eV] | Eg _{opt} [eV] | $E_{\rm HOMO}$ [eV] | E _{LUMO} [eV] |
| Ia | 3.15 | -5.34 | -2.19 | 2.31 | -5.27 | -2.96 |
| Ib | 3.14 | -5.39 | -2.25 | 3.07 | -5.28 | -2.21 |
| lla | 3.06 | -5.26 | -2.20 | 2.58 | -5.24 | -2.66 |
| IIb | 3.15 | -5.36 | -2.21 | 2.57 | -5.09 | -2.52 |
| III | 3.13 | -5.25 | -2.12 | 2.61 | -4.79 | -2.18 |

Electrochemical data of Ia, Ib, IIa, IIb, III obtained from cyclic voltammetry (Potentials vs Ag/AgCl calibrated against Fc/Fc⁺). $E_{HOMO} = -(Eoxonset+5.)$ where, $E_{LUMO} = E_{HOMO} + E_{g}$, Energy of band-gap calculated from UV-vis spectroscopy.

process new defined absorption bands appear at ca. 470 and beyond 900 nm. While further doping proceeds, these peaks slightly shift hypsochromically and later diminish. Simultaneously a new, broad absorption band grows in at approximately 700 nm. The absorption peak located at ca. 700 nm is apparently due to the formation of bipolarons, whereas the spectral bands appearing at lower and higher energy regions might be due to the formation of polaronic species [20,21].

Oxidation of poly-IIa, IIb and III occurs in a different way. During oxidation, two peaks representing two various polarons appear simultaneously at approximately 450 and 650 nm (and beyond 900 nm). When the applied potential is raised the bipolaron band increases in the range of 800-1000 nm. This observation might be explained by the formation of charged species such as two different polarons and later bipolarons. Potentials, at which bands corresponding to polarons and dipolarons appear, on the spectra are consistent with peak potentials in the cyclic voltammograms. As a result of p-doping, the color of the electrodeposited films changes from yellowish (in the undoped state) to black (in the fully oxidized state at app. 1.5 V potential) which implies that these polymeric films have potential for application in electrochromic devices. An example of this color change within electrodeposited films can be seen in Fig. 6 whereby photos of poly-IIa film on ITO in the neutral and oxidized state (yellowish and black respectively) are shown. Other compounds exhibit similar colors in neutral and oxidized forms.

3.4. Electronic properties of monomers vs polymers

The band gaps (Eg) of the materials films were calculated from the optical absorption edge and were significantly dependent upon chemical structure (see Table 2).

All monomers have similar Eg values which varies from 3.06 eV for compound IIa to 3.15 eV for Ia and IIb. From these values it appears that the Eg is mainly determined by the carbazole –triphenylamine core. In almost all cases after polymerization the Eg value decreased significantly, providng evidence of the increase in conjugation length. The most significant decrease in Eg is observed for poly-Ia, where the Eg is equal to 2.31 eV (versus 3.15 eV for the monomer). Interestingly, in the case of its analog structure Ia, which differs by the alkyl chain length attached to the carbazole, the Eg decreases the least, reaching 3.07 eV (versus



Fig. 6. The photo showing a film of poly-IIa on ITO in the neutral state i.e. undoped (left) and the fully oxidized state, at a potential approx. 1.5 V (right).

3.14 eV for the monomer). This unusual behavior is probably caused by steric hindrances that also cause difficulties in polymerization.

Both compounds with carbazole-thiophene linkages reach similar Eg 2.58 and 2.57 eV for poly-IIa and poly-IIb respectively. The Eg value of III monomer equals to 3.13 eV and after polymerization this value decreases to 2.61 eV.

4. Experimental

4.1. Methods

The structure of the synthesized compounds were analyzed with NMR at 600 MHz for ¹H NMR and 151 MHz for ¹³C NMR on a Varian 600 MHz System spectrometer or at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR on an 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 without additional matrix.

Electrochemical measurements were carried out using a CH Instruments 660C potentiostat. The experiments were carried out in the conventional three electrode system. Briefly, a platinum disc of 1 mm diameter was used as the working electrode, Pt wire served as the counter electrode, and Ag wire was used as a pseudoreference. Additionally, in each experiment the reference electrode potential was monitored using ferrocene as an internal standard. All cyclic voltammetry measurements were carried out at the scan rate of 0.1 V/s at room temperature. All solutions were purged with Ar for 10 min prior to each experiment. A typical sample concentration was 1 mM in the dried dichloromethane containing 0.2 M of Bu₄NBF₄ (Aldrich, 98% purity).

UV—vis spectroelectrochemical measurements were completed with an AutoLab PGSTAT 20 electrochemical complex, Ocean Optics QE6500 and NIRQuest apparatus. In spectroelectrochemical experiments an ITO/quartz transparent electrode was used in the cuvette-type cell.

Fluorescence spectra were recorded using Jobin Yvon Horiba Spectrofluorimeter Fluoro Max-3. Fluorescence quantum yields (Φ_f) were determined using a comparison method using 9,10 diphenylanthracene (0.95 in ethanol) as the solution standard [22]. The reference and unknown samples were prepared with their absorbance maxima reading less than 0.1 in order to reduce internal filter effects. Samples were deoxygenated in a clean degassing cell, immediately prior to measurement of the fluorescence emission. The emission spectrum of each sample was corrected for detector efficiency before data analysis.

The quantum-mechanical calculations were performed for both investigated compounds using density functional theory (DFT) using U-B3LYP/6-31G level of theory and basic set; calculations were performed on Gaussian software using the PL-Grid infrastructure.

4.2. Materials

Carbazole, triphenylamine, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and other synthetic materials were purchased from Sigma-Aldrich and used as received. 3-Iodo-9*H*-carbazole was synthesized according to the procedure described by Tucker [23]. 3,6-dibromo-9*H*-carbazole was prepared according to the procedure described by Cheng-Hsiu Ku et al. [24]. Alkylated carbazoles were prepared by previously reported procedures [15]. Tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine was prepared according to the procedure described by Cremer *et. al* [25]. Solvents were used without further purification except from DMF (HPLC grade) which was dried with 4 Å molecular sieves prior to use. Toluene Rotidry was taken for the coupling reactions. Column chromatography was performed using silica gel 60 (0.040–0.063 mm) purchased from Merck.

4.2.1. 3-Bromo-9-hexadecyl-6-(thiophen-2-yl)-9H-carbazole (4a)

3,6-Dibromo-9-hexadecyl-9*H*-carbazole 5 (5.0 g, 9.1 mmol) was dissolved in anhydrous DMF (100 mL) and purged with nitrogen. Cesium fluoride (2.8 g, 18 mmol), copper(I) iodide (0.17 g, 0.91 mmol) and PdCl₂(PPh₃)₂ (0.32 g, 0.46 mmol) were then added to the reaction mixture. 2-(tributylstannyl)thiophene (3.4 g, 9.1 mmol) was added dropwise to the reaction mixture for 2 h at 40 °C, while stirring. The reaction mixture was stirred for a further 30 min until the 2-(tributylstannyl)thiophene substrate was completely consumed (progress of reaction was monitored by TLC (n-hexane: CHCl₃ 5:1, v/v)). The reaction mixture was poured into water (200 mL), extracted with CH₂Cl₂ (4 × 40 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under diminished pressure and the residue was purified by silica gel packed column (hexane: CHCl₃ 5:1, v/v) to an afford light yellow solid (1.8 g, yield: 35%).

¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, J = 1.8, 0.6 Hz, 1H), 8.22–8.21 (m, 1H), 7.72 (dd, J = 8.4, 1.6 Hz, 1H), 7.53 (dd, J = 8.8, 2.0 Hz, 1H), 7.36 (dd, J = 8.8, 1.6 Hz, 1H), 7.32 (dd, J = 3.6, 1.2 Hz, 1H), 7.26–7.23 (m, 2H), 7.09 (dt, J = 6.0, 3.0 Hz, 1H), 4.23 (t, J = 7.2 Hz, 2H), 1.87–1.79 (m, 2H), 1.38–1.17 (m, 10H), 0.89–0.81 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 145.40, 140.19, 139.49, 128.55, 128.00, 126.10, 124.97, 124.47, 123.82, 123.22, 122.21, 122.16, 117.94, 111.78, 110.29, 109.22, 43.31, 31.75, 29.31, 29.13, 28.92, 27.24, 22.58, 14.04.

4.2.2. 3-Bromo-6-(3,4-ethylenedioxythiophen-2-yl)-9-octyl-9H-carbazole (4b)

3,6-Dibromo-9-octyl-9*H*-carbazole 5 (2.0 g, 4.6 mmol) was dissolved in anhydrous DMF (45 mL) and purged with nitrogen. Cesium fluoride (1.4 g, 9.2 mmol), copper(I) iodide (90 mg, 0.46 mmol) and PdCl₂(PPh₃)₂ (0.16 g, 0.23 mmol) were added to the reaction mixture.

2-(Tributylstannyl)-3,4-(ethylenedioxy)thiophene (2.0 g, 4.6 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 stannyl derivative substrate was consumed (TLC: n-hexane: CHCl₃ 5:2, v/v). The reaction mixture was poured into water (100 mL), extracted with CH₂Cl₂ (4 × 30 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under diminished pressure and the residue was purified by silica gel packed column (n-hexane: CHCl₃ 5:2, v/v) to an afford light yellow solid (0.84 g, yield: 37%).

¹H NMR (400 MHz, CDCl₃) δ 8.37 (d, J = 1.6 Hz, 1H), 8.24 (d, J = 1.6 Hz, 1H), 7.81 (dd, J = 8.6, 1.6 Hz, 1H), 7.52 (dd, J = 8.6, 1.6 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.26 (d, J = 8.6 Hz, 1H), 6.32 (s, 1H), 4.38–4.26 (m, 4H), 4.26–4.21 (m, 2H), 1.86–1.82 (m, 2H), 1.31–1.22 (m, 10H), 0.91–0.84 (m, 3H).

 13 C NMR (101 MHz, CDCl₃) δ 142.30, 139.61, 139.45, 137.11, 128.36, 125.14, 124.64, 124.63, 123.28, 122.07, 118.39, 111.64, 110.23, 109.02, 99.63, 96.48, 64.81, 64.58, 43.29, 31.75, 29.31, 29.12, 28.90, 27.23, 22.58, 14.11.

4.3. General procedure for the preparation of Ia/Ib, IIa/IIb and III

Tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) amine (0.10 g, 0.16 mmol) and corresponding aryl halide (3a, 3b or 3-lodo-9*H*-carbazole) (4,5 eq.) were dissolved in solvent mixture of toluene (20 mL) and H₂O (5 mL). Powdered anhydrous potassium carbonate (1.4 g, 100 mmol) and tetrabutylammonium bromide (10 mg, 0.03 mmol) were added and the reaction mixture was purged with nitrogen for 10 min and degassed. Next

tetrakis(triphenylphosphine)palladium(0) (18 mg, 0.016 mmol) was added to the reaction mixture. The reaction mixture was refluxed for 92 h under nitrogen, cooled to r.t. and poured onto water (50 mL). The resulting mixture was extracted with CH₂Cl₂ (4 × 20 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography (n-hexane: toluene 3:1 v/v for lb and Ia, n-hexane: CH₂Cl₂ 5:3 v/v for IIa, n-hexane: CH₂Cl₂ 2:1 v/v for IIb and n-hexane: CH₂Cl₂ 1:1 v/v and CH₂Cl₂ for III were used as eluents).

4.3.1. Tris{4-[9-butyl-9H-carbazol-3-yl]phenyl}amine Ia (57 mg, 39%)

¹H NMR (600 MHz, acetone-*d*6) δ 8.35 (d, J = 1.2 Hz, 3H), 8.14–8.11 (m, 3H), 7.68 (dd, J = 8.5, 1.8 Hz, 3H), 7.67–7.64 (m, 6H), 7.52 (d, J = 8.5 Hz, 3H), 7.46 (d, J = 8.5 Hz, 3H), 7.36–7.33 (m, 3H), 7.19–7.16 (m, 6H), 7.11–7.08 (m, 3H), 4.34 (t, J = 7.2 Hz, 6H), 1.80–1.72 (m, 6H), 1.33–1.28 (m, 6H), 0.83 (t, J = 7.4 Hz, 9H).

¹³C NMR (151 MHz, acetone-*d*6) δ 149.00, 143.64, 142.51, 139.23, 134.19, 130.46, 128.43, 127.26, 127.07, 126.03, 125.58, 123.01, 121.45, 120.74, 112.02, 111.78, 45.12, 33.71, 22.82, 15.92. MALDI-TOF-MS *m*/*z* calcd for C₆₆H₆₀N₄, 909,21; found, 908.2.

4.3.2. Tris{4-[9-hexadecyl-9H-carbazol-3-yl]phenyl}amine Ib (83 mg, yield: 38%)

¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 3H), 8.14 (d, J = 7.6 Hz, 3H), 7.72 (d, J = 8.2 Hz, 3H), 7.66 (d, J = 8.0 Hz, 6H), 7.50–7.43 (m, 6H), 7.41 (d, J = 8.2 Hz, 3H), 7.36–7.30 (m, 6H), 7.25–7.21 (m, 3H), 4.30 (t, J = 7.0 Hz, 6H), 1.93–1.85 (m, 6H), 1.43–1.14 (m, 78H), 0.87 (t, J = 6.8 Hz, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 140.89, 139.75, 131.84, 128.99, 127.95, 125.70, 124.85, 124.50, 123.35, 123.00, 120.40, 118.81, 118.42, 110.37, 108.87, 108.78, 43.22, 31.92, 29.70, 29,69, 29.67, 29.66, 29.65, 29.61, 29.58, 29.52, 29.43, 29.36, 29.03, 27.34, 22.69, 14.11. MALDI-TOF-MS *m/z* calcd for C₁₀₂H₁₃₂N₄, 1414,17; found, 1414.96.

4.3.3. Tris{4-[9-butyl-6-(thiophen-2-yl)-9H-carbazol-3-yl]phenyl} amine IIa (78 mg, yield: 42%)

¹H NMR (600 MHz, acetone-*d*6) δ 8.59 (d, J = 1.6 Hz, 3H), 7.83–7.78 (m, 15H), 7.64 (d, J = 8.5 Hz, 3H), 7.62 (d, J = 8.5 Hz, 3H), 7.48 (dd, J = 3.6, 1.1 Hz, 3H), 7.38 (dd, J = 5.1, 1.1 Hz, 3H), 7.32–7.29 (m, 6H), 7.13 (dd, J = 5.1, 3.6 Hz, 3H), 4.47 (t, J = 7.2 Hz, 6H), 1.93–1.88 (m, 6H), 1.48–1.36 (m, 6H), 0.95 (t, J = 7.4 Hz, 9H).

¹³C NMR (151 MHz, acetone-*d*6) δ 149.03, 148.15, 143.17, 143.02, 139.06, 134.48, 130.72, 130.47, 128.41, 127.64, 127.08, 126.78, 126.32, 126.12, 126.01, 124.71, 121.09, 120.31, 112.29, 45.27, 33.74, 22.81, 15.92. MALDI-TOF-MS *m*/*z* calcd for C₇₈H₆₆N₄S₃, 1155,58; found, 1154.9.

4.3.4. Tris{4-[9-hexadecyl-6-(thiophen-2-yl)-9H-carbazol-3-yl] phenyl}amine IIb (0.11 g, 40%)

¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, J = 1.6 Hz, 3H), 7.84–7.78 (m, 12H), 7.66 (d, J = 8.6 Hz, 6H), 7.63 (d, J = 8.6 Hz, 3H), 7.48 (dd, J = 3.6, 1.1 Hz, 3H), 7.38 (dd, J = 5.1, 1.1 Hz, 3H), 7.32 (d, J = 8.6 Hz, 6H), 7.12 (dd, J = 5.1, 3.6 Hz, 3H), 4.48 (t, J = 7.2 Hz, 6H), 1.96–1.92 (m, 6H), 1.43–1.16 (m, 78H), 0.86 (m, 9H). MALDI-TOF-MS m/z calcd for C₁₁₄H₁₃₈N₄S₃, 1660,54; found, 1661.83.

4.3.5. Tris{4-[9-octyl-6-(3,4-ethylenedioxythiophen-2-yl)-9H-carbazol-3-yl]phenyl}amine III (0.11 g, yield: 45%)

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 1.6 Hz, 3H), 8.28 (d, J = 1.2 Hz, 3H), 7.75 (dd, J = 8.6, 1.6 Hz, 3H), 7.66 (dd, J = 8.8, 1.6 Hz, 3H), 7.60 (d, J = 8.4 Hz, 6H), 7.47 (d, J = 8.4 Hz, 3H), 7.38 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 6H), 6.21 (s, 3H), 4.25 (m, 18H), 1.85–1.77 (m, 6H), 1.37–0.93 (m, 30H), 0.82–0.76 (m, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 146.34, 142.26, 140.09, 139.81, 136.93, 136.48, 131.99, 127.97, 124.99, 124.71, 124.57, 124.45, 124.41, 124.21, 123.43, 123.22, 118.75, 118.67, 118.30, 114.01, 108.98, 108.86, 96.24, 64.78, 64.56, 43.27, 31.76, 29.35, 29.14, 29.02, 27.28, 22.65, 14.07. MALDI-TOF-MS *m/z* calcd for C₉₆H₉₆N₄O₆S₃, 1498,01; found, 1494.4.

5. Conclusions

The synthetic route and properties of a series of star-shaped carbazole-triphenylamine derivatives containing various substituents on the carbazole nitrogen atom have been displayed and discussed. UV-vis and fluorescence studies have shown only slight changes in the optical properties depending on the groups appended to the carbazoles as well as the length of the alkyl chains attached. All compounds exhibited strong fluorescence approximately red shifted when compared to carbazole. The chemical structure very strongly influenced the electrochemical properties of investigated compounds. These differences included not only the potential of oxidation but also in polymerization. All compounds were successfully polymerized, producing electroactive oligomers. The thin films of the resulting polymers were investigated by means of UV-vis-spectroelectrochemistry. The spectroelectrochemical investigation proved the existence of both radical cations and dications in all polymers even at high doping level. All polymers exhibit similar electrochromic effects giving color changes from yellowish in the neutral form to almost black in the oxidized form what makes them promising candidates for electrochromic displays. Moreover, good luminescent properties and the capacity of tuning their electrochemical characteristic renders oligomers for application in OLED field.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.05.030.

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