



# Spectroelectrochemical characterization of conducting polymers from star-shaped carbazole-triphenylamine compounds



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## ARTICLE INFO

### Article history:

Received 20 October 2014

Received in revised form 11 December 2014

Accepted 15 December 2014

Available online 17 December 2014

### Keywords:

carbazole

triphenylamine

conducting polymers

UV-Vis-spectroelectrochemistry

ESR-spectroelectrochemistry

## ABSTRACT

In the field of materials for optoelectronic applications much attention is paid to the derivatives of triphenylamine and carbazole. We report on the electrochemical and spectroelectrochemical properties of two conductive polymers prepared by electropolymerization of two compounds containing either carbazole or triphenylamine moieties. Electrochemical, UV Vis- and EPR-spectroelectrochemical tools were used to study the properties of the polymers. 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

In the field of organic materials for electronics several prevailing trends can be identified. One of the most widely investigated groups of organic electroactive materials is represented by carbazole derivatives that are known as effective luminescent or electroluminescent materials, good hole transporting materials, or photoconductors [1,2]. Due to totally flat structure and large enough band gap of the biphenyl unit carbazole exhibit bluish photo- or electroluminescence [1–3]. The properties of carbazole-based compounds can be easily modified by introduction of new groups to many positions. For instance, the class of 3,6-linked carbazole derivatives was found to be very interesting for electrochemical and phosphorescence applications, 2,7-linked carbazoles showed promising electrochromic properties in the visible range [3–16], while the substitution at N-9 position was mainly used for the modification of solubility or thermal properties [17], and less frequently for the modification of conjugation length and the related properties [18–21].

Recently much attention was also paid to triaryl amines. Triaryl amines exhibit high oxidizability combined with high stability of the corresponding radical cations which together make

them very good hole transporting species. Many of the compounds referred to, have triphenylamine (TPA) units in the molecule, being either as a core or as peripheral groups [22–36]. TPA derivatives have been widely used as hole injecting or hole transporting materials in optoelectronic devices, as well as electrochromic or photoluminescent and electroluminescent materials [27–34]. More complex systems with bis(triarylamine) unit were reported to exhibit strong NIR electrochromism due to intervalence charge transfer [35,37]. In the presented paper we report on electrochemical and spectroscopic properties of two electropolymers obtained in electrochemical polymerization process of two compounds 4,4',4''-tris(9-carbazolyl) triphenylamine [38] (TNCPA) and tri(9-ethylcarbazol-3-yl) amine (TCA), bearing both carbazole and triphenylamine moieties. In TNCPA three carbazole moieties are linked through their nitrogen atoms to para-positions of each ring of TPA moiety. TCA on the other hand is a compound in which three carbazole moieties are connected to form TPA core.

## 2. EXPERIMENTAL

TNCPA was purchased from Sigma Aldrich and was used as received; TCA was synthesized according to the procedure similar to that described in the literature [39].

*Tri(9-ethylcarbazol-3-yl) amine (TCA)* ( $C_{42}H_{36}N_4$ , FW = 596 g/mol)

Tris-(dibenzylideneacetone) di-palladium(0) (Pd2(dba) 3, 0.008 g, 0.04 mmol) and tri-tert-butylphosphine ((t-Bu) 3P,

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0.034 g, 0.04 mmol) were dissolved under argon in 10 ml of dry toluene and stirred for 10 min at room temperature (preformation of the catalyst). Then the mixture of 3-amino-9-ethylcarbazole (0.56 g, 5.8 mmol), 3-iodo-9-ethylcarbazole (0.2 g, 1.0 mmol) and sodium tert-butoxide (0.56 g, 5.8 mmol) in 20 ml of dry toluene (30 ml) were added. The reaction mixture was heated at 90 °C for 8 h. After cooling, the reaction mixture was diluted with ethyl acetate and the organic phase was washed with water and brine. After being dried over MgSO<sub>4</sub> and filtered, the solvent was removed and the residue was purified twice by column chromatography using hexane/ethylacetate (5/1) as eluent. It was recrystallized from eluent.

Yield of TCA (yellow amorphous powder) 36%, (0.2 g). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>), δ (m. d.): 0.93 (t, 9H, J=7.4 Hz, -CH<sub>3</sub>), 3.69–3.79 (m, 6H, -N-CH<sub>2</sub>), 7.27–7.36 (m, 4H, Ar), 7.41–7.58 (m, 10H, Ar), 7.78–7.95 (m, 7H, Ar). IR (KBr), (ν/cm<sup>-1</sup>): 3049 (C–H,Ar); 2979, 2931 (C–H,Aliph); 14805, 1468 (C=C,Ar); 1378, 1344, 1305 (C–N). MS(ACPI+, 20 V), m/z (%): 596 ([M+H]<sup>+</sup>, 100).

Electrochemical measurements were carried out using CH Instruments 660 C potentiostat. The experiments were carried out in the conventional three electrode system. Platinum disc of 1 mm dia. was used as the working electrode, Pt wire served as the counter electrode, whereas Leakless Miniature Ag/AgCl Electrode (Model ET072 from eDAQ Pty Ltd) was used as a reference. Additionally in each experiment the reference electrode potential was monitored using ferrocene as a standard. All cyclic voltammetry measurements were carried out at the scan rate of 0.1 V/s at room temperature in the solutions that were purged with Ar for 10 min prior to each experiment. A typical sample concentration was 1 mM in the dried dichloromethane solution containing 0.2 M of Bu<sub>4</sub>NPF<sub>6</sub> (Aldrich, 98% purity).

UV-Vis spectroelectrochemical measurements were done with AutoLab PGSTAT 20 electrochemical complex and Ocean Optics QE6500 and NIRQuest apparatus. In spectroelectrochemical experiments the ITO/quartz transparent electrode was used in the cuvette-type cell. The EPR vs. potential measurements were carried out using Joel JES-FA 200 EPR instrument and AutoLab

PGSTAT 20 potentiostat in tube-type three electrode cell with 0.3 mm dia. Pt working electrode.

Fluorescence spectra were recorded using Hitachi F-2500 instrument. Fluorescence quantum yields of the solutions were estimated versus reference which were 9,10-diphenylanthracene in cyclohexane or anthracene in ethanol. The results were verified by using the integrating sphere (Avantes AvaSphere-80 coupled with Avantes Fiber optic CCD spectrometer and Hitachi F-2500 spectrofluorimeter light source). The integrating sphere method was also used for the estimation of the fluorescence quantum yields of the films.

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

### 3. RESULTS

Fig. 1a shows the structures of the compounds that were used for electropolymerization. Both compounds can be considered as derivatives of both carbazole (Cz) and triphenylamine (TPA). In TNCPA three carbazole moieties are linked via N-9 position to para-position of each ring of triphenylamino group. TCA on the other hand is a compound in which three carbazole moieties are connected to form TPA core. Fig. 1b shows the optimized geometries of the investigated compounds, with spin densities. The structure of TPA is not flat. The rings are twisted by 41.5 degrees with respect of each other [40]. QC calculations gave the same value for TPA moiety in TNCPA and 47 degrees in TCA; torsion angle between each ring of TPA and Cz rings in TNCPA were found to be ca. 30 degrees, which seems to be sufficient for the partial orbital overlapping and developing of conjugation in the whole molecule.

#### 3.1. Electrochemistry

The electrochemical characteristics of both compounds and of their polymers were studied by cyclic voltammetry. Both the

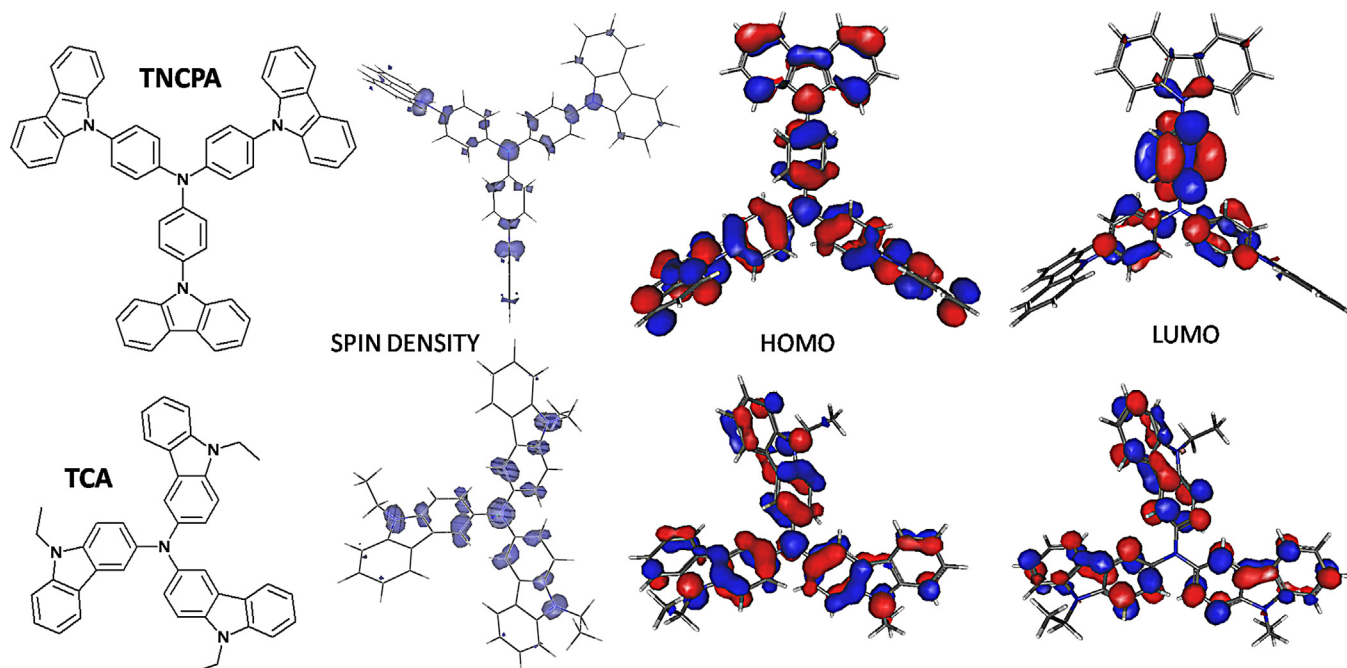


Fig. 1. Structures of investigated compounds, their optimized geometry with spin density profile and HOMO and LUMO levels.

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