

Synthesis and properties of twin derivatives of triphenylamine and carbazole

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Abstract

Synthesis as well as thermal, optical, photophysical, and electrochemical properties of new carbazole and triphenylamine twin derivatives with high triplet energies are reported. The synthesized compounds exhibit ability of glass formation. Their glass transition temperatures are in the range of 32 – 37 °C. The triphenylamine and carbazole derivatives absorb electromagnetic irradiation in the range of 200 – 360 nm with the band gaps of 3.71 and 3.44 eV, respectively. DFT calculations show that HOMO and LUMO orbitals of compounds are localized separately on the substituents and central 4,4'-thiodibenzenthioi unit, respectively. The synthesized twin derivatives have triplet energies of 2.72 and 2.76 eV. The electron photoemission spectra of the films of the synthesized compounds reveal ionization potentials of 5.54 and 5.61 eV.

1. Introduction

Organic semiconductors are currently used in different (opto)electronic devices such as organic light-emitting diodes (OLED), photovoltaic cells, field-effect transistors, lasers [1-7]. The

development of inexpensive, reliable and effective organic electroluminescent materials is one of the hottest research area of organic optoelectronics. The efficient OLEDs are mainly based on phosphorescent transition metal complexes. With phosphorescent emitters the theoretical limit of the internal quantum efficiency is 100% as a result of their harvesting of both singlet and triplet excited states [8]. One of the reasons why the efficiency of phosphorescent materials is less than the theoretical one is the concentration quenching effect which results in the decrease of the photoluminescence quantum efficiency of the emitting material and hence can lead to the decrease of the external quantum efficiency of phosphorescent OLEDs [9]. To avoid self-quenching it is necessary to dope the emitters into an appropriate host. The ability to form stable amorphous films guarantees that the emitter is uniformly dispersed in the host to minimize the concentration quenching. In addition, it is required that the triplet energy of the host is higher than that of the emitter in order to prevent energy back transfer from the phosphorescent guest to the host. Such materials are characterized by confined conjugated systems. Due to the high triplet energies, wide band gaps, efficient charge transport and excellent thermal stability, derivatives of carbazole and triphenylamine are widely used in the design of host materials for emitting layers of OLEDs [10-14]. In addition, these compounds are relatively inexpensive. They can be prepared from easily available raw materials. However, low-molar-mass glasses often suffer from poor morphological stability, and facile crystallization, which limit their use in OLEDs. To prevent this problem compounds with higher molecular weight, which do not readily crystallize, are required. The synthesis of twin molecules from vinylcarbazole or vinyltriphenylamine linking them the fragment of thiodibenzethiol, thus preventing conjugation between the chromophores was the main synthetic strategy. The limited conjugation between the chromophores is the precondition of high triplet energy. The attachment of carbazole or triphenylamine moieties to the linkages with the limited conjugation improve ability of the compounds to form morphologically stable solid amorphous layers [15-18].

In this work we report on the synthesis and properties of two new carbazole and triphenylamine twin derivatives with electronically separated chromophores. The derivatives were prepared by thiol-ene click reactions [19,20]. The ecologically friendly nature of the coupling reaction (which eliminate the use of toxic and expensive metal catalysts or organometallic reagents) is an attractive feature that simplifies both the reaction processing and the product isolation. Even though it is possible to synthesize a wide variety of organic compounds by employing inexpensive copper(I)-catalyzed reactions [21,22], traces of copper may still remain at ppm levels in the product after purification and affect the optoelectronic characteristics of the obtained compounds.

2. Experimental

2.1 Instrumentation

^1H and ^{13}C NMR spectra were recorded using Bruker 700 MHz Avance III [700 MHz (^1H), 175 MHz (^{13}C)] spectrometer at room temperature. All the data are given as chemical shifts in δ (ppm). $(\text{CH}_3)_4\text{Si}$ (TMS, 0 ppm) was used as an internal standard. The courses of the reactions were monitored by thin layer chromatography (TLC) using Silicagel 60 F254 plates and developed with I_2 or UV radiation. Silica gel (grade 60, 63–200 mesh, 60 Å, Fluka) was used for column chromatography. Melting points of the compounds were determined using Electrothermal Mel-Temp melting point apparatus. Mass (MS) spectra were recorded on a Waters ZQ (Waters, Milford, MA). Elemental analysis was performed with an Exeter Analytical CE-400 Elemental. Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q200 thermal analyser at a heating rate of 10 °C/min under nitrogen flow. Thermogravimetric analysis (TGA) was performed on a TGA Q50 apparatus.

Absorption spectra of the dilute tetrahydrofuran (THF) solutions were recorded on Perkin Elmer Lambda 35 spectrometer. Room temperature fluorescence spectra (PL) of the synthesized compounds were taken by Perkin Elmer LS 55 spectrometer. For these measurements, the dilute solutions of the investigated compounds were prepared by dissolving them in a spectral grade THF at 10^{-5} M concentration. The phosphorescence spectra of dilute solution in THF (10^{-5} M) were recorded at 77 K by Edinburgh Instruments FLS980.

The cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The working electrode was a glassy carbon of 0.12 cm² surface. The reference electrode and the counter electrode were Ag/Ag⁺ 0.01 M and Pt wire respectively. The solutions with the concentration of 10^{-3} M of the compounds in argon-purged dichloromethane with tetrabutylammonium perchlorate (TBAP; 0.1M) as electrolyte were used for the CV measurements. The CV curves were drawn versus Fc/Fc⁺ as internal reference where the potential of the redox system $E_{1/2}^{\text{Fc}} = 0.216$ V/Ag : Ag⁺. The ionization potentials ($I_{p(\text{EP})}$) of the solid samples of the synthesized compounds were measured by the electron photoemission in air method as reported earlier [23a,b]. The measurement error is evaluated as 0.03 eV. The samples for the measurements were prepared by dissolving compounds in THF and by casting on ITO coated glass plates. The samples were illuminated with the monochromatic light when the negative voltage of -300 V was supplied to ITO. The counter-electrode was placed at the distance of 3 mm from the sample surface and was connected to the

input of the 6517B Keithley electrometer for the photocurrent measurement. An energy scan of the incident photons was performed while increasing the photon energy $h\nu$. In this scan direction, no electrons were emitted until $h\nu$ exceeded the ionization potential of the layer [24].

The charge carrier mobility (μ) measurements were carried by the time of flight method (TOF) as reported earlier [25-27]. The sandwich-like cells (ITO/compound/Al) were fabricated for the measurements. First, the layers of the compounds were prepared by drop casting their solutions in THF onto cleaned ITO coated glass substrate. Finally, electrode Al (80 nm) was evaporated at 15 Å/s. The thickness of thin layers was measured using the method of carrier extraction in linearly increasing voltage (CELIV) ($\epsilon \sim 3.5$) [28]. The charge carriers were generated at the layer surface by illumination with pulses of Nd:YAG laser (pulse duration was 25 ps, wavelength 355 nm). The transit time was determined from the kink point in the transient photocurrent curves. The transit time t_t with the applied bias (V) indicates the passage of holes through the entire thickness of the cell (d) and enables determination of the hole mobility as $\mu = d^2/U \cdot t_t$. The experimental setup consisted of a delay generator Stanford Research DG 535 and a digital storage oscilloscope Tektronix TDS754C.

2.2 Computational details

The theoretical calculations were performed in the frame of density functional theory (DFT) employing the B3LYP functional with Gaussian 09 program [29-31]. The 6-31G(d,p) basis set was utilized for all calculations. The spectroscopic properties and of the molecules were calculated by means of the method of time dependent density functional theory (TDDFT) [32,33]. Up to 40 excited states were calculated and the theoretical absorption bands were obtained by considering a band half-width at half-maximum 0.15 and 0.3 eV. Natural transition orbital (NTO) calculations were carried out to understand the nature of selected excited-states [34].

2.3 Materials

Triphenylamine (TPA), phosphorus(V) oxychloride (POCl_3), triphenylmethylphosphonium bromide, potassium *tert*-butoxide (*t*-BuOK), 4,4'-thiodibenzenthiole (TBT) were purchased from Aldrich and used without further purification. Triphenylamine-4-carbaldehyde (F-TPA) [35], 4-vinyltriphenylamine (V-TPA) [34], 9-ethylcarbazole-3-carbaldehyde (F-CZ) [36], 9-ethyl-3-vinylcarbazole (V-CZ) [36] were prepared according to the published procedures.

General procedure for the synthesis of TBT-2TPA and TBT-2CZ

A mixture of vinyl derivative (V-TPA or V-CZ, 2.2 equiv.) and 4,4'-thiodibenzthiol (TBT, 1.0 equiv.) in dichloromethane was stirred for 1 h under argon atmosphere at room temperature. Then the solvent was distilled and the crude product was purified by column chromatography.

Di(4-(2-(4-(N,N-diphenylamino)phenyl)ethyl)thio)phenylsulfide (TBT-2TPA) was prepared according to the general procedure from 4-vinyltriphenylamine (V-TPA, 1.6 g, 5.9 mmol) and 4,4'-thiodibenzthiol (TBT, 0.5 g, 2.0 mmol). The crude product was purified by column chromatography on silica gel using hexane/dichloromethane (8/1) as an eluent. The target compound was obtained as white powder (fw=792 g/mol) in 38% yield (0.37 g). ¹H NMR (700 MHz, CDCl₃), δ (ppm): 2.91 (t, *J* = 8.3 Hz, 4H, S-CH₂), 3.17 (t, *J* = 8.3 Hz, 4H, Ar-CH₂), 7.00 – 7.06 (m, 8H, Ar), 7.07 – 7.11 (m, 12H, Ar), 7.22– 7.30 (m, 16H, Ar). ¹³C NMR (175 MHz, CDCl₃), δ (ppm): 147.9, 146.3, 136.0, 134.4, 133.1, 131.5, 129.6, 129.3, 129.2, 124.4, 124.0, 122.6, 35.1 (S-CH₂), 35.0 (Ar-CH₂). MS (APCI⁺, 20 V), *m/z* (%) = 793 ([M + H]⁺, 100). Elemental analysis. Calcd for C₅₂H₄₄N₂S₃ (%): C 78.75, H 5.59, N 3.53, S 12.13; found (%): C 78.63, H 5.69, N 3.64.

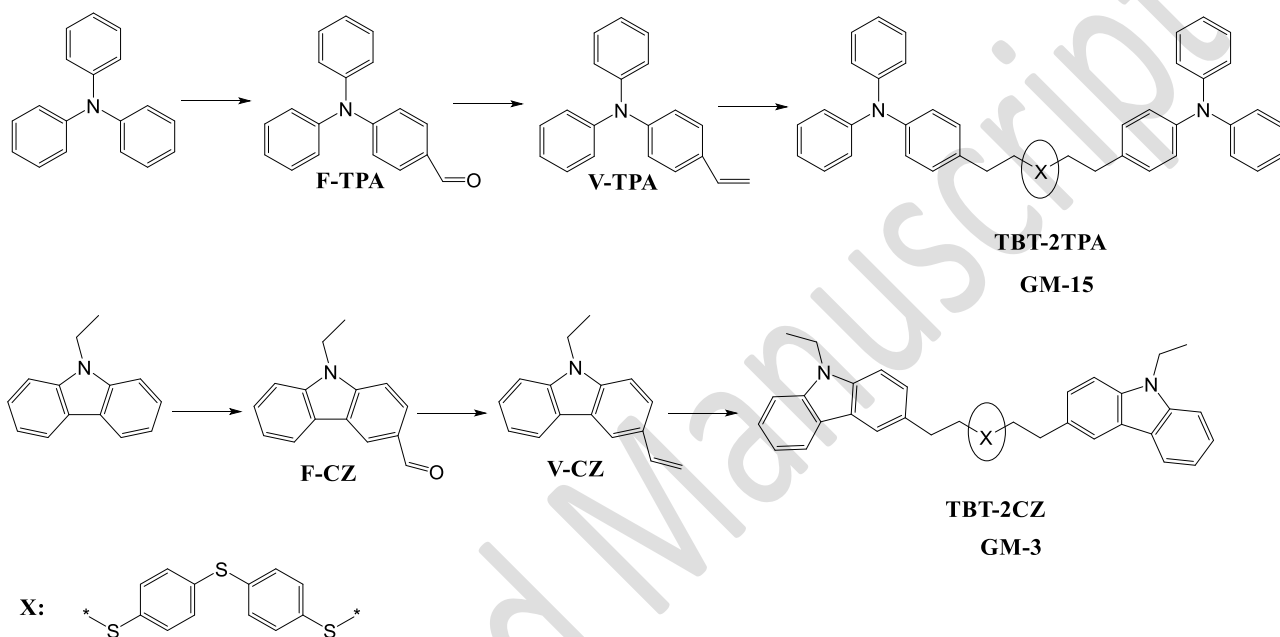
Di(4-(2-(9-ethylcarbazol-3-yl)ethyl)thio)phenylsulfide (TBT-2CZ) was prepared according to the general procedure from 9-ethyl-3-vinylcarbazole (V-CZ, 1.0 g, 4.48 mmol) and 4,4'-thiodibenzthiol (TBT, 0.31 g, 2.06 mmol). The crude product was purified by column chromatography on silica gel using hexane/acetone (6/1) as an eluent. The target compound was obtained as yellow powder (fw=692 g/mol) in 15% yield (0.13 g). ¹H NMR (70 MHz, CDCl₃), δ (ppm): 1.46 (t, *J* = 7.2 Hz, 6H, CH₃), 3.15 (t, *J* = 8.2 Hz, 4H, S-CH₂), 3.29 (t, *J* = 8.3 Hz, 4H, Ar-CH₂), 4.38 (q, *J* = 7.3, 4H, N-CH₂), 7.14–7.53 (m, 18H, Ar), 7.95 (s, 2H, Ar), 8.10 (d, *J* = 7.7 Hz, 2H, Ar), 8.12 (d, *J* = 7.8 Hz, 2H, Ar). ¹³C NMR (175 MHz, CDCl₃), δ (ppm): 140.3, 138.9, 136.2, 133.0, 132.6, 131.5, 130.6, 130.4, 129.6, 126.3, 125.7, 123.1, 122.7, 120.4, 120.1, 118.7, 108.5, 37.6 (N-CH₂), 35.8 (S-CH₂), 35.7 (Ar-CH₂), 13.8 (CH₃). MS (APCI⁺, 20 V), *m/z* (%) = 693 ([M + H]⁺, 100). Elemental analysis. Calcd for C₄₄H₄₀N₂S₃ (%): C 76.26, H 5.82, N 4.04, S 13.88; found (%): C 76.12, H 5.91, N 4.08.

3. Results and discussion

3.1 Synthesis

TBT-2TPA and **TBT-2CZ** were synthesized by thiol-ene reaction as illustrated in Scheme 1. Aldehydes **F-TPA** and **F-CZ** were obtained under the conditions of the Vilsmeier reaction [35,36]. Compounds **V-TPA** and **V-CZ** were prepared by Wittig reaction of the corresponding aldehydes in

the presence of methyltriphenylphosphonium bromide and potassium *tert*-butoxide. The reactions of vinyl derivatives (**V-TPA** or **V-CZ**) and 4,4'-thiodibenzenthionol (**TBT**) in dichloromethane yielded twin the molecules (**TBT-2TPA** and **TBT-2CZ**). The chemical structures of the synthesized compounds were confirmed by ^1H NMR, ^{13}C NMR, mass spectrometries, and elemental analysis. **TBT-2TPA** and **TBT-2CZ** were readily soluble in common organic solvents like dichloromethane, chloroform, THF, acetonitrile, toluene.



3.2 Thermal properties

The thermal stability and morphological changes of the synthesized compounds were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The glass transition (T_g) and 5% weight loss (T_{10}) temperatures of the derivatives are summarized in Table 1. T_{10} for the twin molecules is observed at 290 °C, which is slightly lower to those of the common carbazole and triphenylamine based compounds reported in the literature, such as 4,4'-bis(9-carbazolyl)biphenyl derivatives [37,38] (310–365 °C) or triphenylamine-based derivatives with different side groups (300 to 349 °C) [39]. For the fabrication of devices, the temperatures of vacuum evaporation of **TBT-2TPA** and **TBT-2CZ** have to be considerably lower than T_{10} for avoiding of thermal degradation of the compounds. The recent study showed that impurities in organic materials decreased the lifetime of OLEDs even if the impurities did not contribute to the emission [40]. TGA curves of the derivatives are shown in Fig. 1a. Two-stages are observed in the thermal degradation of the synthesized compounds. The first step is apparently due to the degradation of the linkage

moiety. The onset of the second step for **TBT-2TPA** and **TBT-2CZ** is observed at approximately the same temperature (355 °C) which corresponds to the temperature of the onset of the thermal degradation of carbazole [41] and triphenylamine [42] moieties.

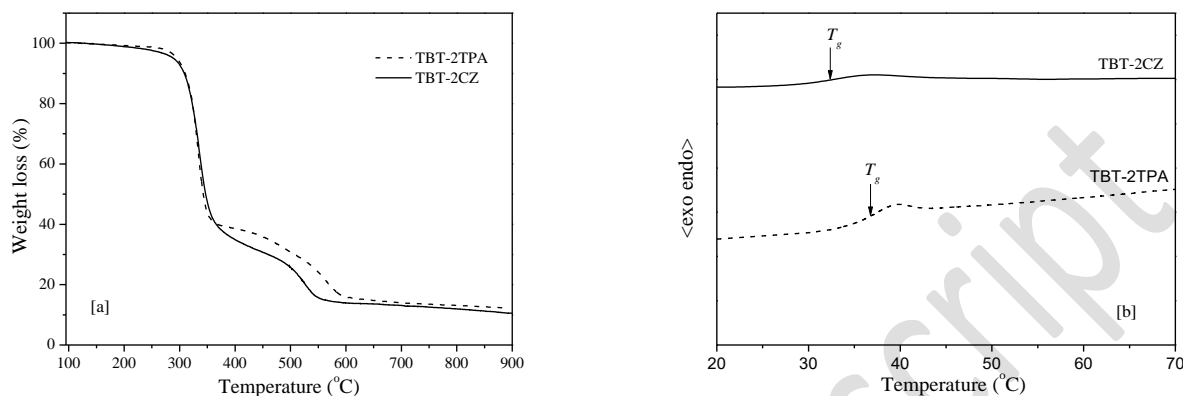


Fig. 1. [a] TGA curves and [b] DSC curves (second heating scan) of **TBT-2TPA** and **TBT-2CZ** (heating rate 10 °C/min, N₂ atmosphere)

Both the synthesized compounds were isolated as amorphous materials and only glass transitions were observed in their DSC scans at 37 and 32 °C, respectively, and no peaks due to crystallization and melting appeared. Cooling down and following repeated heating revealed only glass transitions (Fig. 1b).

Table 1. Thermal characteristics of **TBT-2TPA** and **TBT-2CZ**.

| Compound | TBT-2TPA | TBT-2CZ |
|-----------------|----------|---------|
| T_g^a (°C) | 37 | 32 |
| T_{ID}^b (°C) | 290 | 290 |

^aDetermined by DSC, scan rate 10 °C/min, N₂ atmosphere. ^b5% weight loss temperature determined by TGA, heating rate 10 °C/min, N₂ atmosphere.

3.3 Geometrical structures and frontier orbitals

The theoretical optimized geometries of the twin derivatives of triphenylamine- and carbazole are shown in Fig. 2. The propeller-like triphenylamine moieties have dihedral angles between phenyl ring planes and C-N-C bonds of 41° – 43° in **TBT-2TPA**. In the structures of both compounds **TBT-2TPA** and **TBT-2CZ** benzene rings of 4,4'-thiodibenzenthio linker and substituents linked through an alkyl chain are parallel to each other.

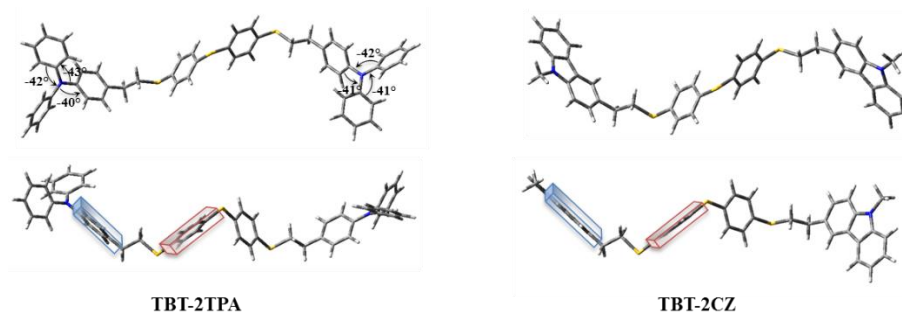


Fig. 2. Theoretical geometrical structures of **TBT-2CZ** and **TBT-2TPA** (B3LYP/6-31G(d,p) level)

Theoretical calculations revealed that the 4,4'-thiodibenzenthioi linker with alkyl chain in the synthesized compounds **TBT-2TPA** and **TBT-2CZ** interrupt the conjugation between analogous moieties. (Fig. 3) Therefore, the HOMO is localized on only one triphenylamine fragment, whereas the HOMO delocalization on both carbazole moieties is an artefact due to the over delocalization effect inherent to several DFT functionals. As expected, the LUMO is distributed on the central 4,4'-thiodibenzenthioi unit. The small electron contribution of ethyl unit in HOMO and LUMO is associated with the hyperconjugation effect between σ bonds with adjacent π orbital [43].

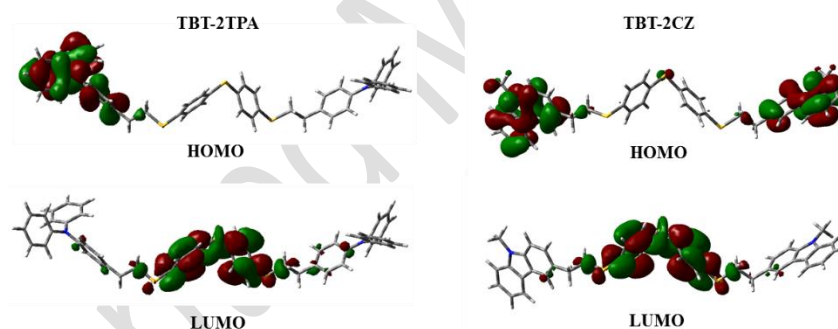


Fig. 3. Frontier orbitals of **TBT-2CZ** and **TBT-2TPA** (B3LYP/6-31G(d,p) level)

3.4 Optical and photophysical properties

The optical and photophysical characteristics of the compounds are summarized in the Table 2. Fig. 4a displays the room temperature absorption spectra of 10^{-4} M THF solutions of **TBT-2TPA** and **TBT-2CZ**. The spectra of pure triphenylamine (TPA) and 9-ethylcarbazole (CZ) compounds are given for the comparison. Dilute THF solutions of the synthesized triphenylamine and carbazole-based derivatives absorb electromagnetic radiation up to 360 nm. The positions of absorption bands of **TBT-2CZ** and **TBT-2TPA** are almost identical compared to those of CZ and TPA, respectively. The theoretical absorption spectra of these compounds are presented in Fig. 4b. It can be observed

that the experimental and the theoretical approaches produce different trends for the lowest energy bands of triphenylamine- and carbazole-based compounds. Indeed, the weak lowest energy band in the experimental spectra of **TBP-2CZ** is redshifted with respect to **TBT-2TPA**, whereas the opposite can be observed from the theoretical spectra. The origin of this disagreement might reside in combined effects: (i) solute-solvent interactions, carbazole is more prominent to these interactions as compared to triphenylamine due to its planar geometry, and (ii) B3LYP functional overestimates the effective conjugation length giving slight redshift of excitation energy of TPA and **TBT-2TPA** [44]. Due to the donor-acceptor architecture, the band gaps of **TBT-2TPA** (4.00 eV) and **TBT-2CZ** (4.44 eV) are lower than those of TPA (4.65 eV) and CZ (4.69 eV) (Table S1) [45]. Therefore, the experimental lowest energy bands of twin derivatives are shifted to longer wavelengths with respect of that of the corresponding model compounds.

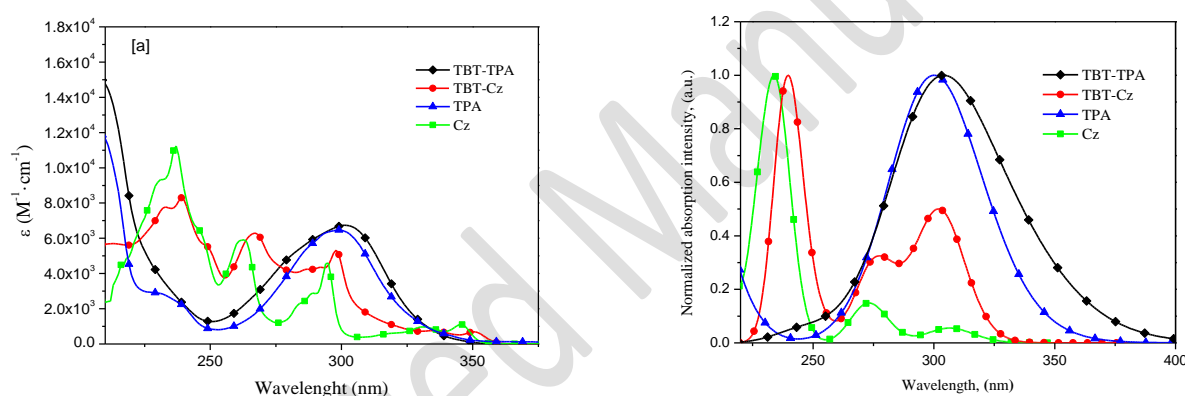


Fig. 4. [a] Experimental and [b] theoretical UV absorption spectra of **TBT-2TPA**, **TBT-2CZ**, TPA and CZ ($\lambda_{\text{ex}} = 310$ nm)

In order to characterize electron transitions, induced by absorption of electromagnetic radiation, the theoretical absorption spectra of analysed compounds were investigated (Fig. S1, Fig. S2, Fig. S3, Table S2). Based on the theoretical results, the lowest energy absorption bands of **TBT-2TPA** and **TBT-2CZ** are attributed to the combination of electronic transitions towards various excited states. The transitions $S_0 \rightarrow S_1$, $S_0 \rightarrow S_9$ for **TBT-2TPA** and $S_0 \rightarrow S_3$ for **TBT-2CZ**, with largest oscillator strengths, are the dominant transitions which characterize the lowest energy absorption bands. In order to identify the nature of transitions, the corresponding NTO were calculated. The hole and electron localizations in the compounds received from NTOs are shown in Fig. 5. According to these results, the lowest energy absorption band at 301 nm ($S_0 \rightarrow S_1$, $S_0 \rightarrow S_9$) of compound **TBT-2TPA** can be characterized as the charge transfer (CT) transition between the triphenylamine donor

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part and the 4,4'-thiodibenzenthioi acceptor linker. In the case of **TBT-2CZ**, the lowest energy absorption band at 351 nm ($S_0 \rightarrow S_3$) is dominated by the donor \rightarrow acceptor CT transition, also containing some contribution from the local acceptor excitations. The lowest transition $S_0 \rightarrow S_1$ for **TBT-2CZ** exhibits small oscillator strength, therefore it is hidden and does not appear as a separate band (Fig. S1 and Table S2). The NTO results indicate that the lowest transition in **TBT-2TCZ** is associated with the local electronic excitations in carbazole fragment (Fig. 5), involving HOMO-1, HOMO \rightarrow LUMO+1 transitions (Table S2).

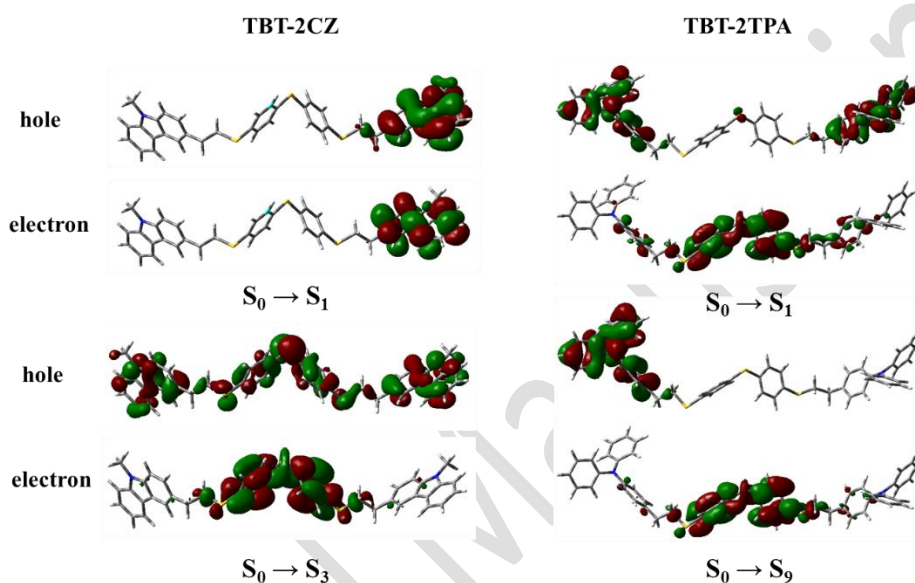


Fig. 5. Natural transition orbitals corresponding to hole- and electron localizations corresponding to selected excited states of compounds **TBT-2TPA** and **TBT-2CZ 2** (TD-B3LYP/6-31G(d,p) level)

The bands of fluorescence spectra of **TBT-2TPA** and **TBT-2CZ** are shifted towards long wavelength region in comparison with those of TPA or CZ, with Stokes shifts ranging from 23 to 70 nm. The TPA-based compounds exhibit larger Stokes shifts as compared to CZ-based compound, probably due to the larger geometrical deformations happening in the TPA moiety.

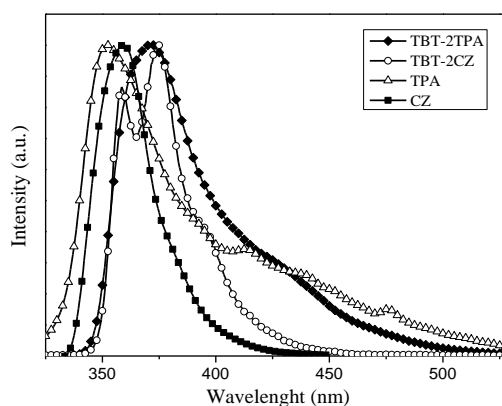


Fig. 6. Fluorescence spectra of the dilute THF solutions of **TBT-2TPA**, **TBT-2CZ**, TPA and CZ ($\lambda_{\text{ex}} = 310\text{nm}$)

For the possible application of compounds **TBT-2TPA** and **TBT-2CZ** as host materials for the phosphorescent emitters the triplet energies are of major interest. For efficient phosphorescence from triplet guests in a host matrix, the triplet energy $\Delta E(T_1-S_0)$ of a host must be larger than that of a guest to facilitate exothermic energy transfer from a host to a guest and to prohibit reverse energy transfer from a guest back to a host [8,46].

Phosphorescence spectra of the solutions of **TBT-2TPA** and **TBT-2CZ** in THF were recorded at 77 K by applying delay time of 100 μs after excitation. The triplet energies estimated from the first phosphorescence emission peak were found to be 2.72 and 2.76 eV for **TBT-2TPA** and **TBT-2CZ**, respectively. These values are higher than that of common blue phosphorescent emitter iridium(III)bis[(4,6-difluorophenyl)-pyridinato- $N,C^{2'}$]picolinate (FIrpic, $E_T=2.65$ eV) [46]. Consequently, efficient energy transfer from the host materials to the FIrpic dopant is expected, indicating that **TBT-2TPA** and **TBT-2CZ** can be suitable as the host materials for blue OLEDs.

Table 2. Optical and photophysical characteristics of **TBT-2TPA**, **TBT-2CZ**, TPA and Cz.

| Compound | TBT-2TPA | TBT-2CZ | TPA | Cz |
|---|----------|---------------|------|---------------|
| $\lambda_{\text{ab.max}}^{\text{a}}$ (nm) | 301 | 298, 337, 351 | 299 | 294, 335, 346 |
| $\lambda_{\text{ab.teor}}^{\text{b}}$ (nm) | 305 | 239, 275, 302 | 300 | 233, 273, 308 |
| $\lambda_{\text{fl.max}}^{\text{c}}$ (nm) | 371 | 357, 374 | 352 | 359 |
| $\lambda_{\text{phos.max}}^{\text{d}}$ (nm) | 449 | 455 | 408 | 409 |
| Stokes Shift (nm) | 70 | 23 | 53 | 13 |
| $E_g^{\text{opt e}}$ (eV) | 3.71 | 3.44 | 3.75 | 3.52 |

| | | | | |
|--------------|------|------|-------|-------|
| E_S^f (eV) | 3.34 | 3.31 | 3.52 | 3.45 |
| E_T^g (eV) | 2.72 | 2.76 | 3.04* | 3.03* |

^a Wavelengths of absorption peaks of solutions (10^{-5} M in THF). ^b Theoretical wavelengths of absorption peaks. ^c Wavelengths of fluorescence peaks of solutions (10^{-5} M in THF). ^d Wavelengths of phosphorescence peaks of solutions (10^{-5} M in THF, 77 K). ^e The optical band gaps E_g^{opt} estimated from the edges of absorption spectra. ^f Singlet energy estimated from the highest-energy fluorescence peak. ^g Triplet energy estimated from the highest-energy phosphorescence peak. ^{*} The values taken from the literature [47,48].

3.5 Electrochemical and photoelectrical properties

To elucidate the energetic conditions for energy and electron transfer in dilute solutions, the ionization potentials and electron affinities were established by cyclic voltamperometry (CV). The measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1M tetrabutylammonium perchlorate (TBAP) as electrolyte, Ag/AgNO₃ as the reference electrode and a Pt wire counter electrode. The experiments were calibrated with the standard ferrocene/ferrocenium redox system [49]. The electrochemical characteristics are summarized in Table 2. The CV curves of **TBT-2TPA** and **TBT-2CZ** are shown in Fig. 7. In the first redox cycle the oxidation of **TBT-2TPA** started at 0.73 V (Table 3) and resulted in the formation of cation radicals. As the CV scans continued, a new oxidation peak appeared at 0.63 V. A possible explanation can be related to the oxidation of new compounds formed after the initial CV cycle. Indeed, further to the first oxidation cycle, the cation radicals reacted with each other or with the neutral molecules, leading to the formation of dimmers. The dimmers are more easily oxidized than TPA moieties [50]. The intensity of this peak increased gradually with the number of continued scans. Furthermore, during the each CV cycle, **TBT-2TPA** exhibited consequently two reduction peaks in the region of 0.55 – 0.80 V, which can be ascribed to the reduction of the oxidized species present in the solution.

TBT-2CZ exhibited the similar electrochemical behaviour (Fig. 7). The oxidation of **TBT-2CZ** started at 0.68 V in the first cycle, which was somewhat lower than the corresponding value observed for **TBT-2TPA** (Table 3). **TBT-2CZ** exhibited two oxidation peaks in the region of 0.30 – 0.8 V by continued scanning, one of which was absent in the first cycle. It seems that the carbazole moieties were oxidized in the first scan, followed by irreversible formation of new carbazolyl compound [51].

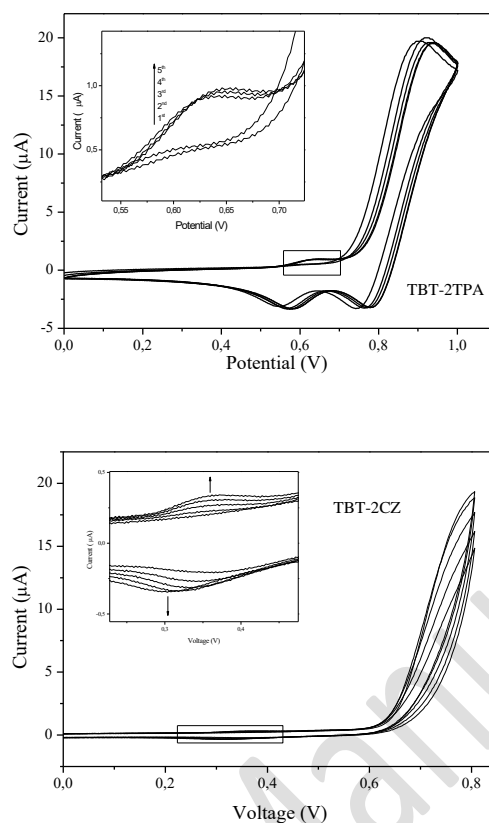


Fig. 7. Cyclic voltammograms of **TBT-2TPA** and **TBT-2CZ** in argon-purged dichloromethane solution (scan rate of 50 mV s^{-1})

Taking 4.8 eV [52] as the ionization potential ($I_{p(CV)}$) value for the ferrocene redox system related to the vacuum level, the $I_{p(CV)}$ values of **TBT-2TPA** and **TBT-2CZ** were estimated and were found to be 5.39 and 5.48 eV , respectively (Table 3). With the band gap (E_g^{opt}) values obtained from the absorption spectra, the electron affinity ($E_{A(CV)}$) values of 1.68 and 2.04 eV were estimated for **TBT-2TPA** and **TBT-2CZ** respectively.

In the design and fabrication of organic devices, it is very important to have energy levels of the materials used [53]. The solid-state ionization potentials ($I_{p(EP)}$) of organic materials are usually estimated by ultraviolet photoelectron spectroscopy (UPS) in deep vacuum [54,55]. For organic materials which possess $I_{p(EP)}$ lower than 6.0 eV (the value related to absorbance of oxygen) $I_{p(EP)}$ can be estimated by UPS in air [56,57]. Taking into account the potential application of the studied compounds in organic devices, the ionization potentials $I_{p(EP)}$ of the solid layers of the compounds were also estimated by photoelectron emission spectrometry in air. The results are presented in Fig. 8 and Table 3. In the agreement with the CV results, $I_{p(EP)}$ of triphenylamine-based compound (**TBT-2TPA**) was found to be slightly higher than that of carbazole derivative (**TBT-2CZ**). Having © 2018. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

$I_{p(EP)}$ of 5.54 and 5.61 eV and the optical band-gap energy of ca. 3.71 and 3.44 eV, the electron affinity ($E_{A(EP)}$) of 1.83 and 2.17 eV was calculated by a formula $E_{A(EP)}=I_{p(EP)}- E_g^{opt}$ for **TBT-2TPA** and **TBT-2CZ**. The energy levels $I_{p(EP)}$ and $E_{A(EP)}$ are related to the values of HOMO of -5.54 and -5.61 eV and LUMO of -1.83 and -2.17 eV, respectively. These values should be taken into account in the case of application of **TBT-2TPA** and **TBT-2CZ** in solid-state devices.

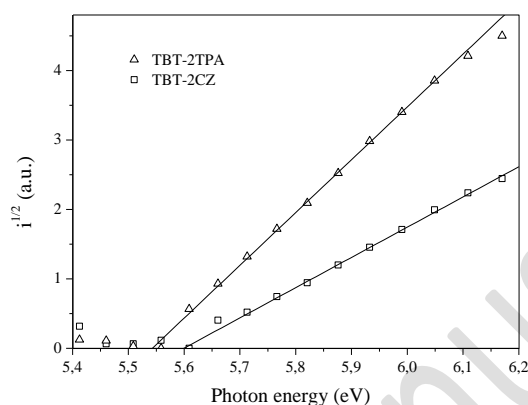


Fig. 8. Electron photoemission spectra of the layers of **TBT-2TPA** and **TBT-2CZ** recorded in air at 25 °C

Table 3. Electrochemical and photoelectrical characteristics of TBT-2TPA and TBT-2CZ.

| Compound | E_{onset} (V) | $I_{p(CV)}^a$ (eV) | $E_{A(CV)}^b$ (eV) | $I_{p(EP)}^c$ (eV) | μ_o^d ($\text{cm}^2/\text{V}\cdot\text{s}$) | μ^e ($\text{cm}^2/\text{V}\cdot\text{s}$) |
|----------|--------------------|-----------------------|-----------------------|-----------------------|--|--|
| TBT-2TPA | 0.73 | 5.39 | 1.68 | 5.54 | - | - |
| TBT-2CZ | 0.68 | 5.48 | 2.04 | 5.61 | 2.8×10^{-9} | 2.3×10^{-7} |

^a Ionization potentials $I_{p(CV)}$ and ^belectron affinities $E_{A(CV)}$ were estimated by cyclic voltamperometry according to $I_{p(CV)} = 4.8 + E_{onset}$ and $E_{A(CV)} = I_{p(CV)} - E_g^{opt}$. ^c Ionization potentials $I_{p(EP)}$ of the solid samples were measured by electron photoemission spectrometry. ^d Zero field mobility in the films of the synthesized compounds molecularly doped in bisphenol Z polycarbonate (PC-Z). ^e Hole mobility value in the films of the synthesized compounds molecularly doped in PC-Z) at electric field $E = 1.5 \times 10^6$ V/cm.

Time-of-flight technique was used to characterize hole drift mobilities in the films of the synthesized compounds. To run TOF, we have prepared non-doped layers of **TBT-2TPA** and **TBT-2CZ** by thermal evaporation of the compounds. Next, the top Al electrode was deposited. However, the quality of Al electrode was not sufficient, most probably, due to low glass transition temperatures of 37 and 32 °C for **TBT-2TPA** and **TBT-2CZ**, respectively. This result shows that **TBT-2TPA** and **TBT-2CZ** can not be used for the preparation non-doped layers in organic devices, but the compounds can be used as dopants depending on future device design. In addition, the TOF

technique was used to characterize hole drift mobilities in the films of the synthesized compounds molecularly doped in polymeric host bisphenol Z polycarbonate (PC-Z). Because of the relatively low solubility of **TBT-2TPA** in PC-Z we were not able to prepare the solid solutions of high enough concentration for the time-of-flight measurements. Only **TBT-2CZ** showed good enough solubility for the preparation of 50 wt.% solid solution in PC-Z. The solid solution of **TBT-2CZ** in PC-Z demonstrated hole drift mobility of $2.3 \times 10^{-7} \text{ cm}^2/\text{V}\cdot\text{s}$ at electric field $E= 1.5 \times 10^6 \text{ V/cm}$ (Table 3). Hole drift mobility of the order of $10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ can be predicted for amorphous films of the pure compounds.

4. Conclusions

Carbazole and triphenylamine twin derivatives with high triplet energies were synthesized by thiol-ene click reactions. The molecular structures allow the synthesized compounds to exist in solid amorphous state with high enough thermal stability. The glass transition temperatures of the synthesized compounds were observed at 37 and 32 °C. Results obtained by means of TDDFT calculations showed charge transfer character in the excited state of the carbazole- and triphenylamine-based derivatives. The triplet energies of the solid samples of the compounds were found to be 2.72 and 2.76 eV. The electron photoemission spectra of the films of the compounds revealed ionization potentials of 5.54 and 5.61 eV. Meanwhile, the cyclic voltammetry measurements showed slightly lower ionization potentials of 5.39 and 5.48 eV. Hole drift mobility in the solid solution of carbazole twin derivative in bisphenol Z polycarbonate reached $2.3 \times 10^{-7} \text{ cm}^2/\text{V}\cdot\text{s}$ at electric field of $1.5 \times 10^6 \text{ V/cm}$, as established by time-of-flight technique.

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