Invited paper

Synthesis and properties of twin derivatives of triphenylamine and carbazole

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A B S T R A C T

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′-thiodibenzenthiol 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.

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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
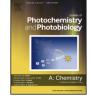
quenching. In addition, it is required that the triplet energy of the host is higher than that of the emitter in order to prevent energy back transfer from the phosphorescent guest to the host. Such materials are characterized by confined conjugated systems. Due to the high triplet energies, wide band 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 thiodibenzenthiol, 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

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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

^{1}H and ^{13}C NMR spectra were recorded using Bruker 700 MHz Avance III [700 MHz (^{1}H), 175 MHz (^{13}C)] spectrometer at room temperature. All the data are given as chemical shifts in δ (ppm). (CH$_3$)$_4$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 cm^2 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 tetrabulthylammonium perchlorate (TBAP; 0.1 M) 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 $E^{Fc}_{1/2}$ = 0.216 V/Ag: Ag$^+$.

The ionization potentials ($I_{p(EP)}$) 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 6517 B 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) (ε∼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 $\mu = d^2/U\,t_t$. 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′-thiodibenzenthiol (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.

2.4. 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′-thiodibenzenthiol (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′-thiodibenzenthiol (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). ^{1}H NMR (700 MHz, CDCl$_3$), δ (ppm): 2.91 (t, J = 8.3 Hz, 4H, S-CH$_2$), 3.17 (t, J = 8.3 Hz, 4H, Ar-CH$_2$), 7.00–7.06 (m, 8H, Ar), 7.07–7.11 (m, 12H, Ar), 7.22–7.30 (m, 16H, Ar). ^{13}C NMR (175 MHz, CDCl$_3$), 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-CH$_2$), 35.0 (Ar-CH$_2$).MS (APCl$^+$, 20 V), m/z (%) = 793 ([M+H]$^+$, 100). Elemental analysis. Calcd for C$_{52}$H$_{44}$N$_2$S$_3$ (%): C 78.75, H 5.59, N 3.53, S 12.13; found (%): C 78.63, H 5.69, N 3.64.