Tuning the photophysical, thermal properties and electronic energy levels in the triphenylamine derivatives by benzoylhydrazone architecture

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ABSTRACT

A novel of triphenylamine derivatives with more extended π-conjugated systems achieved by benzoylhydrazone architecture were synthesized under mild condition with high yields. The dependence of their photophysical, electrochemistry and thermal properties on their chemical structure is discussed. Compared with the N,N-di(4-methylphenyl)aniline, the thermostability of the five triphenylamine-based hydrozones is dramatically promoted. These compounds are stable up to 345 °C according to thermogravimetric analysis. The energy levels of the four compounds were finely tuned by introducing the electron-donating and -withdrawing groups to the triphenylamine core which are supported by the fluorescence spectra and transit fluorescence spectra of the compounds ($-H > -CH_3 > -Cl >$ Pyridine $> -NO_2$). Their multiple cyclic voltammetry study and density functional study suggest these materials to be promising hole-transport properties.

1. Introduction

In order to suit the large-scale manufacturing of the opto devices (electrophotography, organic light emitting diodes, solar cells, field effect transistors etc.), triphenylamine-based molecules of low-molar-mass have attracted much attention [1–14]. Triphenylamine-based hydrazones as hole-transport materials are motivated by their facile preparation, high solubility, electrode compatibility, good transparency in the visible region, high **LUMO** (lowest unoccupied molecular orbital) energy level, and modest **HOMO** (highest occupied molecular orbital) level [15,16]. Hydrazones are a class of molecules that contain the $-CH=N-$ functionality, which could enhance the charge carrier mobility by enlargement of the molecule of conjugated π-electrons. The study

on structure−property relationship reveals that the absorptivities/electronic excitation energies and the **HOMO**/**LUMO** energy levels are affected mainly by the extending conjugation length, planarity and dimensionality of the π-center architecture [17,18]. The other important factor influencing charge transport properties is the origin of the substituents in hydrazone molecules. On the other hand, the thermal, optical, and charge transport properties were influenced by the nature of the linking fragment and the structure of the triphenylamine-based molecular symmetry. Various moieties have been used in the design and synthesis of triphenylamine-based low-molar-mass hydrazones. Apparently, the incorporation into the molecules of the rigid phenyl, alkoxyphenyl or branched alkyl groups, which hinder the packing of molecules, decreases their ability to form glasses [19,20]. These hydrazones form glasses and their amorphous films could be prepared on substrates by casting from solutions. Furthermore, the energy levels of triphenylamine-based hydrazones can be varied in a relatively wide range by changing the length of the linking fragment and the substituent of the hydrazide moieties. Density functional theory (**DFT**) has been applied to explain electronic structures, electronic excitation mechanisms, and optical properties of the molecules [18,21,22]. In order to develop higher effective triphenylamine-

based materials, a serial of new triphenylamine derivatives with different benzoylhydrazone structure were synthesized, and their morphology, optical properties, thermal stability, electron structure and electrochemistry properties were discussed in this paper. In addition, theoretical calculation was applied to further demonstrate the effect of the crossing-section side groups on the electron structure of these compounds.

2. Experiment section

2.1. Materials

All chemicals and solvents were analytical grade and without further purification. N,N-di(4-methylphenyl)aniline(**TPA**), 4-[N,N-di(4-tolyl)amino] benzaldehyde(**R²-CHO**), 4-chlorobenzohydrazide, 4-methylbenzohydrazide, 4-nitrobenzoylhydrazine 4-pyridine-carboxylic hydrazide, benzoylhydrazine were prepared according to the literature [16,23–25]. Thin layer chromatography purification was carried out using silica gel purchased from Qingdao Haiyang Co.LTD, China.

2.2. Instrumentation

Melting points of all compounds were determined on X-6 binocular microscope (Beijing Tech. Instrument Co.LTD, Beijing, China), and the thermometer was not corrected. Infra-red spectra were obtained on Bio-rad Fts3000 spectrometer in the 4000–400 cm^{-1} range as KBr disks. ^{1}H and ^{13}C NMR spectra were performed using Bruker AC-P500 Instrument spectrometer at 400 MHz in DMSO-D$_6$ or CDCl$_3$, TMS was induced as internal standard. High-resolution mass spectrometry (HRMS) data were recorded on VG ZAB-HS mass spectrometer. X-ray diffraction data of single crystals were collected by a Bruker Smart 1000 CCD diffractometer. The structure was solved by direct methods and expanded by difference Fourier techniques with SHELXS-97 program [26]. Absorption spectra were measured with Helios Gamma UV–vis spectrophotometer. Steady-state fluorescence spectra were recorded with a Varian Cary Eclipse fluorospectropho-tometer. Fluorescence transients of the samples were recorded using a time-correlated single photon counting system HORIBA Jobin Yvon IBH instrument, 370 nm Nanoled utilized as pulsed excitation sources. Thermogravimetric (TG) analysis was investigated by TA Q500 Thermo gravimetric analyzer instrument. Differential scanning calorimetry (DSC) were carried out in a nitrogen atmosphere with a TA Instruments Q10 calorimeter at a heating rate of 5 °C/min. Cyclic voltammetry (CV) was carried out on a CHI7600 electrochemical workstation in CH$_2$Cl$_2$, using n-Bu$_4$NPF$_6$ as support electrolyte (10^{-1} M); scan rate: 50 mV s^{-1}. The electrochemical cell was equipped with three electrodes: a working electrode (plate Pt electrode), an auxiliary electrode (platinum wire electrode), and a reference electrode (SCE, a saturated calomel electrode).

2.3. Theoretical calculations

In order to investigate the electron distribution of the **HOMO** and **LUMO** energy levels of the four compounds, density functional theory (**DFT**) calculations were carried out through the Gaussian 03 program at the B3LYP/6-31tG(D) level [27].

2.4. Synthetic procedure for 4-(N,N-diphenylamino) benzaldehyde(**R²-CHO**)

N,N-dimethylformamide (2.74 g, 37.5 mmol) was added drop-wise to the mixture of **TPA** (2.27 g, 18.8 mmol) and phosphorous

oxychloride (POCl$_3$) (5.65 g, 22.5 mmol) at 25 °C. The reaction mixture was stirred and heated at 130 °C for 6 h. After cooling down to room temperature, the reaction mixture was poured into 50 mL cold water and extracted with chloroform (3 × 15 mL). The combined organic layer was dried with anhydrous MgSO$_4$, filtered. The purified compound **R²-CHO** was obtained by recrystallizing from diluted ethanol. Yield: 1.75 g (31.5%). Melting point: 96.3–97.5 °C. ESI-MS (m/z, [M + H]$^+$) = 302.4.

2.5. General synthetic procedure for compound **I**

Aryl carboxylic esters (**I**) was synthesized from aromatic acids and ethanol. Thionyl chloride (32 mmol) was added dropwise to a stirred mixture of aromatic acids (8 mmol) and ethanol (70 mmol) at room temperature. After the reaction had been refluxed for 6 h, most of the ethanol was removed. The residue solution was poured into cold water (20 mL) and extracted with ethyl acetate (3 × 15 mL). Then, the organic layer was washed successively with water (3 × 10 mL). The organic layer was dried over anhydrous sodium sulfate. After filtration, the solvent was removed under vacuum to give the Compound **I** with high yield, which was not further purified.

2.6. General synthetic procedure for compound **II**

A 5 mL absolute ethanol solution of hydrazine hydrate (80%) and Compound **I** (6 mmol) was refluxed for 4–6 h under severely stir-ring, the product being appeared as yellowish white solid. For purification of product, it was filtered and washed with 30 mL water and 30 mL ethanol pre-cooled by ice, and recrystallized from ethanol to yield the Compound **II** as white solid.

4-chlorobenzohydrazide (**II-1**): yield (91.3%). Melting point: 143.6–144.1 °C. ESI-MS (m/z, [M + H]$^+$) = 171.2.

4-methylbenzohydrazide (**II-2**): yield (92.1%). Melting point: 105.7–106.3 °C. ESI-MS (m/z, [M + H]$^+$) = 151.2.

4-nitrobenzoylhydrazine (**II-3**): yield (93.4%). Melting point: 189.9–190.2 °C. ESI-MS (m/z, [M + H]$^+$) = 182.2.

4-pyridinecarboxylic hydrazide (**II-4**): yield (95.1%). Melting point: 170.0–171.0 °C. ESI-MS (m/z, [M + H]$^+$) = 138.2.

Benzoylhydrazine (**II-5**): yield (91.6%). Melting point: 110.0–112.0 °C. ESI-MS (m/z, [M + H]$^+$) = 137.2.

2.7. General synthetic procedure for compound **III**

The Compound **I** (0.79 mmol) was dissolved in 10 mL of absolute ethanol. Then the mixture of **R²-CHO** (0.66 mmol), 10 μL acetic acid and 3 mL absolute ethanol was added dropwise at 70 °C. The mixture was refluxed for 5 h. The solvent was evaporated. The crude product was purified by flash chromatography (neutral Al$_2$O$_3$).

4-[N,N-di(4-tolyl)amino] benzaldehyde 4-chlorobenzoyl hydrazone (**III-1**): yield (91.3%). Melting point: 114.2–117.6 °C. IR(KBr, cm^{-1}): 3446 (ν –NH–), 3090, 3027, 2920, 1654, 1598, 1564, 1506, 1273, 817. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.79(d, 1H, J = 6.8 Hz), 7.71–7.69(q, 1H), 7.55–7.52(q, 2H), 7.49(s, 1H, –N=CH–),7.43(d, 2H, J = 7.6 Hz), 7.26(s, 1H), 7.10(d, 4H, J = 8.0 Hz), 7.01(d, 4H, J = 8.0 Hz), 6.94(d, 2H, J = 8.4 Hz), 2.33(s, 6H, –CH$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm): 153.8, 144.3, 139.3, 133.8, 130.9, 130.1, 129.1, 128.8, 125.6, 122.2, 120.2, 20.9. HR-ESI-MS (m/z, [M + H]$^+$) calcd. for C$_{28}$H$_{25}$ON$_3$Cl$^+$ 454.1681, found 454.1679.

4-[N,N-di(4-tolyl)amino] benzaldehyde 4-methyl benzoylhy-drazone (**III-2**): yield (89.4%). Melting point: 111.8–112.5 °C. IR(KBr, cm^{-1}): 3440 (ν –NH–), 3190, 3026, 2918, 1646, 1599, 1557, 1504, 1274, 815. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 8.10(s, 1H),