



Structure–property relationships of star-shaped blue-emitting charge-transporting 1,3,5-triphenylbenzene derivatives



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ABSTRACT

Three star-shaped derivatives of 1,3,5-triphenylbenzene bonded to fluorene moieties with various linking groups were designed and synthesized. The three dendritic compounds are characterized by high values of decomposition temperature (up to 434 °C) and form glasses with glass transition temperatures ranging from 55 to 75 °C. The star-shaped compounds emit light in the deep blue region (385–412 nm) and their solutions exhibit moderately high fluorescence quantum yields in the range of 0.40–0.54. The obtained molecules show relatively small values of the optical gaps ranging from 2.50 to 3.08 eV. The layers of the compounds exhibit hole mobility values in the range of $4.9 \cdot 10^{-4}$ – $2.4 \cdot 10^{-3}$ cm²/V s at electric field $1 \cdot 10^5$ V/cm. A comparative study of the experimentally estimated and theoretically calculated (DFT method) characteristics of the 1,3,5-triphenylbenzene showed that the geometry, optical and electrochemical properties of the star-shaped molecules depend on the degree of conjugation and the nature of the linking bridge.

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1. Introduction

Organic light-emitting diodes (OLEDs) are a promising solution for large-area, high-resolution flat panel displays and lighting sources [1]. They show promise to improve the efficiency of indoor lighting due to their low power consumption, high quantum efficiency, and potential low cost of manufacturing [2]. In recent years white organic light emitting devices (WOLEDs) have been attracting much interest [3]. Generation of white electroluminescence in WOLEDs involves simultaneous emission of light of the three primary colors (red, green and blue) or of two complementary colors (e.g. orange and blue). A convenient method to attain white light emission from a single compound is based on chemical species that simultaneously emit blue light from molecular excited states and red-orange light from excited aggregates (excimers or excromers) formed in the solid state [4]. However, the development of a blue emitter with high color purity, high efficiency, and a long lifetime is an extremely challenging research topic [5,6].

Historically, conjugated polymers have represented the main type of materials used in organic semiconductor applications. However, small molecules are alternatives to polymers that, in many cases, provide significant improvement in device efficiencies and performance [7]. Molecular glasses including dendritic ones possess well-defined and monodisperse molecular structures as well as superior chemical purity, features which are advantageous in comparison to polymers. Solution-processable blue-emitting, organic glass-forming materials thin films of which can be obtained by spin coating or casting are particularly attractive [8].

Molecules having 1,3,5-triphenylbenzene as a core are gathering considerable interest because of their high thermal stability, interesting optical and electrochemical properties [9,10]. The 1,3,5-triphenylbenzene unit possesses structural C₃ symmetry, as well as shifted molecular skeleton [11], which make it an excellent building block for the preparation of dendritic molecules with a wide energy gap and a high triplet energy level [12]. The above mentioned parameters are necessary for the achievement of the efficient blue emission. Apparently, incorporation of the fluorene moiety also facilitates blue emission [13], since it is known that fluorene-based conjugated oligomers can emit deep blue light with high efficiencies of both solutions and films [14,15].

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In this work we report on the synthesis of three star-shaped 1,3,5-triphenylbenzene –based molecules end-capped with alkylated fluorene moieties. The fluorophores in each molecule are connected via the different linkages containing single, double and triple bonds. We describe the results of optical, photophysical, electrochemical and computational studies which were carried out for better understanding of the structure–property relationship of the synthesized compounds.

2. Experimental

2.1. Instrumentation

NMR spectra were recorded on a Varian Inova 300 and chemical shifts are reported in parts per million relative to solvent residue peak as an internal standard. IR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum GX II FT-IR System. Mass spectra were obtained by the ESI-MS method on Esquire-LC 00084 mass spectrometer. Elemental analysis data were obtained on a EuroEA Elemental Analyser. UV/vis and photoluminescence spectra of 10^{-4} M solutions of the compounds were recorded in quartz cells using Perkin Elmer Lambda 35 spectrometer and Perkin Elmer LS55 fluorescence spectrometer respectively. Photoluminescence quantum yields were determined using Perkin Elmer Lambda 35 spectrometer and Perkin Elmer LS55 fluorescence spectrometer by the comparative method reported by William, Winfield and Miller [16]. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA851e/LF/1100 apparatus at a heating rate of 20 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were done on a DSC Q 100 TA Instrument at a heating rate of 10 °C/min under nitrogen atmosphere. Cyclic voltammetry (CV) measurements were carried out with a glassy carbon working electrode in a three electrode cell. The measurements were performed using Eco Chemie Company's AUTOLAB potentiostat "PGSTAT20" in the dry dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate (TBAPF₆) as the electrolyte at room temperature under nitrogen atmosphere. The results were collected using GPES (General Purpose Electrochemical System) software. The electrochemical cell comprised platinum wire with 1 mm diameter of working area as working electrode, Ag wire calibrated versus ferrocene/ferrocinium redox couple as a quasi-reference electrode and platinum coil as an auxiliary electrode. Cyclic voltamperometric measurements were conducted at 50 mV/s potential rate.

The ionization potentials (IP) of the layers of the synthesized compounds were measured by the electron photoemission method in air [17]. For the recording of the electron photoemission spectra the layers were prepared by drop casting from the solutions in tetrahydrofuran (THF) on cleaned indium tin oxide (ITO) coated glass substrates. The negative voltage of 300 V was applied to the sample substrate. The deep UV deuterium light source ASBN-D130-CM and CM110 1/8 m monochromator were used for illumination of the samples with the monochromatic light. A 6517B Keithley electrometer was connected to the counter-electrode for the photocurrent measurement, which was flowing in the circuit under illumination. An energy scan of the incident photons was performed while increasing the photon energy.

Charge drift mobility measurements were performed by a time-of-flight (TOF) method. The samples for the TOF measurements were prepared by drop casting of the solutions of the synthesized compounds in tetrahydrofuran (THF) on the pre-cleaned ITO coated glass plates with the thickness of a layer ranging from 1.12 to 1.45 μm [18]. The samples were heated at 70 °C for 20 min in a hot air oven. Next, 60 nm of aluminum was deposited using a mask by thermal evaporation under vacuum below $5 \cdot 10^{-5}$ mbar. The

sample area was of 0.7 cm² with 3 samples per substrate. The light pulse was used to photo generate the charge carriers by exciting layers of compounds through the ITO. For hole mobility measurements, the positive voltage was applied to the ITO electrode. A delay generator Tektronix AFG3011 was used to generate square pulse voltage with a pulsed third-harmonic Nd:YAG laser EKSPLA PL2140 working at a pulse duration of 25 ps and the wavelength of 355 nm. A digital storage oscilloscope Tektronix DPO4032 was used to record TOF transients of the layers of the synthesized materials. The transit time t_{tr} for the samples with the charge transporting material was determined by the kink on the curve of the transient in log–log scale. The drift mobility was calculated using the formula $\mu = d^2/Ut_{tr}$, where d is the layer thickness, and U is the surface potential at the moment of illumination.

The theoretical calculations were carried out using the Gaussian 09 quantum chemical package [19]. Full geometry optimizations of the compounds in their electronic ground state were performed with DFT using the B3LYP functional consisting of Becke's three parameter hybrid exchange functional combined with the Lee–Yang–Parr correlation functional with the 6-31G(d) basis set in vacuum. The energies of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals were obtained from single point calculations in the framework of DFT B3LYP/6-311G(d,p) approach for the CH₂Cl₂ solution. Absorption spectra were simulated from the oscillator strengths of singlet transitions calculated by the TD-DFT B3LYP/6-31G(d) method in vacuum. The vertical ionization potentials were calculated by the DFT B3LYP/6-311G(d,p) method in vacuum.

2.2. Materials

The starting compounds i.e. 1-(4-iodophenyl)ethanone, 2-bromo-9H-fluorene, 9H-fluorene-2-carbaldehyde, and the required chemicals, i.e. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 1-bromohexane, potassium *tert*-butoxide (*t*-BuOK), tetrachlorosilane (SiCl₄), *n*-butyllithium (*n*-BuLi) solution in hexane, triphenylphosphine (PPh₃), Aliquat 336, *tetrakis*-triphenylphosphine palladium (0) (Pd(PPh₃)₄), *bis*-triphenylphosphine palladium(II) dichloride (Pd(PPh₃)₂Cl₂), palladium(II) acetate (Pd(OAc)₂), tetra-*n*-butylammonium bromide (*n*-Bu₄NBr), copper iodide (CuI), ethynyltrimethylsilane, tetra-*n*-butylammonium fluoride (*n*-Bu₄NF) solution in THF, sodium hydrosulfate (NaHSO₄), potassium carbonate (K₂CO₃), anhydrous sodium sulfate (Na₂SO₄) were purchased from Sigma–Aldrich and used as received.

2-Bromo-9,9-dihexyl-9H-fluorene (**1**) and 9,9-dihexyl-2-vinyl-9H-fluorene (**4**) were obtained by the reported procedures [20]. 2-(9,9-Dihexyl-9H-fluorene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) was synthesized as described in the literature source [21]. 2-Vinyl-9H-fluorene (**3**) was prepared according to the known procedure [22]. ((9,9-Dihexyl-9H-fluorene-2-yl)ethynyl)trimethylsilane (**5**) was synthesized by the Sonogashira coupling reaction as described earlier [23]. 2-Ethynyl-9,9-dihexyl-9H-fluorene (**6**) was prepared as described in the literature [12,24]. 1,3,5-Tris(4-iodophenyl)benzene (**7**) was obtained by the reported method [25].

2.3. Synthesis

2.3.1. 2-((3,5-Bis(4-(9,9-dihexyl-9H-fluorene-2-yl)phenyl)phenyl)phenyl)-9,9-dihexyl-9H-fluorene (TPB1)

1,3,5-Tris(4-iodophenyl)benzene (**7**) (0.50 g, 0.73 mmol) and 2-(9,9-dihexyl-9H-fluorene-2-yl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**2**) (1.80 g, 3.91 mmol) were dissolved in toluene (20 ml). 2 M Aqueous potassium carbonate solution (1.21 g, 8.76 mmol, 4.36 mL) and Aliquat 336 (10 mg) were added before the reaction mixture was degassed by three subsequent freeze/thaw cycles. After that,

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