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Effect of linking topology on the properties of star-shaped derivatives of triazine and fluorene

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ABSTRACT

Three star-shaped molecules, having 2,4,6-triphenyl-1,3,5-triazine core and fluorene side arms linked through different linkages, were designed and synthesized. The obtained compounds were characterized by UV and fluorescence spectroscopies, differential scanning calorimetry, thermogravimetric analysis, cyclic voltammetry, time-of-flight and CELIV techniques. All the three star-shaped compounds possess high thermal stability with the temperatures of the onsets of thermal degradation around 400 °C and glass formation ability with close glass transition temperatures (56–61 °C). The synthesized compounds show broadband absorption with the absorption maxima of dilute solutions in the range of 350–382 nm. Dilute solutions of the fluorenyl-substituted derivatives of 2,4,6-triphenyl-1,3,5-triazine showed monomer fluorescence with fluorescence quantum yields ranging from 0.50 to 0.70. The theoretical DFT calculations showed that the geometry, optical and electrochemical properties of the synthesized star-shaped molecules depend on their linking topologies. Thus, completely flat star-shaped molecules, in which the donor and acceptor moieties are linked through the linking bridges having double and triple bonds, are characterized by smaller optical band gap and bathochromic shift compared to the derivative with twisted skeleton in which the chromophores are linked directly via single bond. The best charge-transporting properties were shown by the compound in which 2,4,6-triphenyl-1,3,5-triazine and 2-[9,9-bis(2-ethylhexyl)-9*H*-fluorene] moieties are linked via the linking bridges containing ethenyl linkages. Hole mobility of the amorphous layer of this compound reached 1.9×10^{-3} cm/V s at an electric field of 1.15×10^{6} V/cm.

1. Introduction

Organic charge-transporting materials are desirable for various optoelectronic and electronic applications including light-emitting diodes, solar cells, field-effect transistors [1,2]. 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 exited states and red-orange light from excited aggregates (excimers or electromers) formed in the solid state [4]. White electroluminescence resulting from simultaneous emission of monomers and electromers was observed with the star-shaped 1,3,5-tris[2-(9-ethylcarbazolyl-3)ethylene]benzene emitter [3].

Solution-processable blue-emitting organic glass-forming materials thin films of which can be obtained by spin coating or casting are particularly attractive. Both polymers and low-molar-mass molecular materials, such as dendrimers and star-burst molecules can be used for the solution processing [5]. In contrast to polymers, molecular glasses including dendritic ones possess well-defined and monodisperse molecular structures as well as superior chemical purity, what makes them more advantageous in comparison to polymers.

Molecules having 1,3,5-triazine as a core are gathering considerable interest because of their high thermal stability, interesting optical and electrochemical properties [6–9]. 1,3,5-Triazine unit possesses structural symmetry and high electron affinity, which makes it useful as electron-accepting building block for the design and synthesis of star-shaped and dendritic electroactive molecules.

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1,3,5-Triazine derivatives were reported as electron transporting hosts for the highly efficient green phosphorescent OLEDs [10]. Incorporation of a donor moiety, such as fluorene, into the molecules with electron-deficient triazine core gives an opportunity to obtain materials with interesting photophysical and photoelectrical properties and to decrease the optical band gaps. Moreover, alkylated donor moieties provide good solubility of the materials in common organic solvents, what simplifies preparation of the devices.

In this paper, we present the synthesis and comparative study of the properties of the series of star-shaped derivatives of 2,4,6-triphenyl-1,3,5-triazine and dialkyl fluorene, in which the chromophores are linked via the different bridges containing single, double, and triple bonds.

The influence of linking topologies on the properties of organic semiconductors is of great interest. It is known, that the emission color and charge transport can be controlled via the degree of conjugation [11]. Introduction of the phenylene unit induces blue-shift in the emission spectra, while units with prolonged conjugation induce red shifts [12]. Introduction of the triple bonds leads to less pronounced red-shifting of the absorption and emission spectra than introduction of the double bond [13]. Moreover, the relative planarity of the molecule affects the color of emission as more planar materials have more effective conjugation and thus smaller band gaps [14]. Twisting of the molecular skeleton results in blue-shift in the emission and decreases charge mobility [15]. All these peculiarities encouraged us to investigate in this work structure–property relationship of the triazine derivatives.

2. Experimental

2.1. Instrumentation

NMR spectra were recorded on a Varian Inova 300 and Bruker DRX 500P spectrometers and chemical shifts are reported in parts per million relative to solvent residue peek 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 MALDI-TOF method on Schimadzu Biothech Axima mass spectrometer. Elemental analysis was performed on the EuroEA Elemental Analyser. UV/vis and fluorescence 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. Fluorescence quantum yields were determined using Perkin Elmer Lambda 35 spectrometer and Perkin Elmer LS55 fluorescence spectrometer by the comparative method reported by Williams et al. [16]. Thermogravimetric analysis (TGA) was performed on Metter TGA/SDTA851e/LF/1100 apparatus at a heating rate of 20 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were done on 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 in the dry dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate ($TBAPF_6$) as the electrolyte at room temperature under nitrogen atmosphere. Each measurement was calibrated with the standard ferrocene/ferrocenium (Fc/Fc^+).

Charge drift mobility measurements were performed by a xerographic time-of-flight (XTOF) [17,18] and by charge extraction by linearly increasing voltage (CELIV) [19,20] methods. The samples for the XTOF measurements were prepared by drop casting of the solutions of the synthesized compounds in tetrahydrofuran (THF) on aluminum coated glass plates with the thickness of layer ranging from 3 to 7 μm [21]. After keeping for 1 h in the saturated atmosphere of THF at room temperature, the samples were heated at 70 °C for 1 h in a hot air oven. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 1 ns, wavelength 337 nm). The transit time t_t for the samples with the charge transporting material was determined by the kink on the curve of the dU/dt transient in log–log scale. The drift mobility was calculated by using the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness, and U_0 the surface potential at the moment of illumination.

For the CELIV measurements sandwich-like structures ITO/TRZs/Al with the thickness of layers **TRZ1**, **TRZ2** and **TRZ3** 330, 340 and 220 nm, respectively, and an active area of 7 mm^2 were prepared. The thickness of the layers was measured by CELIV technique [22]. The layers from 10 mg/ml THF solution of the compounds were formed by casting method onto clean ITO coated glass substrate within a glove box. Al was evaporated at 15 Å/s at a pressure below 5×10^{-5} mbar. The experimental setup consisted of a delay generator Tektronix AFG 3011 and a digital storage oscilloscope Tektronix DPO 4032. The mobility measurements were conducted in the dark box by applying a triangular voltage pulse to the samples. The charge carrier mobility was calculated by formula $\mu = 2d^2/At_{\max}^2$, where $A = U(t)/t$ is the voltage rise rate, t_{max} is the time for the current to reach its extraction maximum peak, d is the sample thickness.

The theoretical calculations were carried out using the Gaussian 09 quantum chemical package [23]. 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 CH_2Cl_2 solution. Absorption spectra were simulated from the oscillator strengths of singlet transitions calculated by the TD-DFT B3LYP/6-31G(d) method in vacuum.

2.2. Materials

The starting compounds i.e. 4-iodobenzonitrile, 4-(bromomethyl)benzonitrile, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile, 9*H*-fluorene-2-carbaldehyde, 2-bromo-9*H*-fluorene and the required chemicals, i.e. trifluoromethanesulphonic acid (CF_3SO_3H), 1-bromo-2-ethylhexane, potassium *tert*-butoxide (*t*-BuOK), triphenylphosphine (PPh_3), Aliquat 336, *tetrakis*-triphenylphosphine palladium ($Pd(PPh_3)_4$), *bis*-triphenylphosphine palladium dichloride ($Pd(PPh_3)_2Cl_2$), copper iodide (CuI), ethynyltrimethylsilane, tetrabutylammonium fluoride (n-Bu_4NF) solution in THF, sodium hydrosulfate ($NaHSO_4$), potassium carbonate (K_2CO_3), anhydrous sodium sulfate (Na_2SO_4) were purchased from Sigma–Aldrich and used as received.

9,9-Bis(2-ethylhexyl)-9*H*-fluorene-2-carbaldehyde (**3**) and 2-bromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene (**4**) were obtained by the reported procedures [24,25]. 2,4,6-Tris[4-(bromomethyl)phenyl]-1,3,5-triazine (**1**) (m.p.: 190–192 °C, lit. m.p.: 191–193 °C [26]), ({4-[bis{4-[(triphenylphosphoniumyl)methyl]phenyl}-1,3,5-triazin-2-yl]phenyl}methyl)triphenylphosphoniumtribromide [27] (**2**) (m.p.: 279–281 °C) and 2,4,6-tris(4-iodophenyl)-1,3,5-triazine (**8**) (m.p.: 377–379 °C, lit. m.p.: 378 °C [28]) were also prepared according to the known procedures [20,22].