Dyes and Pigments 127 (2016) 45–58

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis and properties of bipolar derivatives of 1,3,5-triazine and carbazole

T. Matulaitis [a], N. Kostiv [a], J.V. Grazulevicius [a, *], L. Peciulyte [a], J. Simokaitiene [a], V. Jankauskas [b], B. Luszczynska [c], J. Ulanski [c]

[a] *Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254, Kaunas, Lithuania*
[b] *Department of Solid State Electronics, Vilnius University, Sauletekio al. 9, LT-10222, Vilnius, Lithuania*
[c] *Department of Molecular Physics, Lodz University of Technology, Lodz, Poland*

ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form
30 October 2015
Accepted 2 November 2015
Available online 22 November 2015

Keywords:
Triazine
Carbazole
Photoluminescence
Solvatochromism
Hole mobility
Theoretical study

ABSTRACT

Three new bipolar star-shaped derivatives of 2,4,6-triphenyl-1,3,5-triazine containing carbazolyl groups were designed, synthesized and characterized. All the materials possess high thermal stability and high glass transition temperatures ranging 97–226 °C. Photophysical study of the dilute solutions and neat films of the synthesized compounds was performed. Lippert–Mataga plots revealed linear dependence of Stokes shifts on the orientation polarizability for all the compounds. The dilute solutions of the triazine derivatives exhibited high photoluminescence quantum yields reaching 0.85, while for the neat films photoluminescence efficiency of 0.20–0.33 was observed. Ionization potentials of the solid layers of carbazole-triazine adducts estimated by photoelectron spectroscopy were found to be in the range of 5.49–5.97 eV. Hole drift mobility of the materials well exceeded the magnitude of 10^{-3} $cm^2\ V^{-1}\ s^{-1}$ at an electric field of $6.4 \cdot 10^5$ V/cm. The selected compounds were tested as light emitting materials in organic light emitting diodes based on host-guest systems.

1. Introduction

Organic conjugated materials have received great attention in recent decades in optoelectronic and electronic applications such as organic light-emitting diodes (OLEDs), organic solar cells, organic field effect transistors because of their potentially low cost and possibility of easy fabrication of the devices [1–4]. Recently, growing interest has been focused on the search of the materials with bipolar charge-transporting properties for the application in OLEDs [5,6]. Using bipolar materials for the preparation of emitting layers, enhanced performances and operational stability were demonstrated [7]. The utilization of bipolar materials also offers the possibility to achieve efficient and stable single-layer OLEDs, which are highly desirable because of simplification of the manufacturing process and reduction of the production costs [8].

The most widely adopted strategy to obtain bipolar materials is to incorporate D–A combinations into the same molecule, facilitating injection and transport of both holes and electrons [7,9,10]. Incorporation of electron-donating and electron-withdrawing moieties into a light-emitting material may promote the emission efficiency because of an extended π-conjugation. However, this might bring about a huge bathochromic effect. Therefore, one of the major challenges in developing bipolar blue emitters with D–A structures is preventing the red-shift in the emission while maintaining or even increasing their photoluminescence quantum yield.

Compared to other donors, carbazole is useful in the generation of short-wavelength absorption and emission, as it is weaker π-donor than aromatic amines [11]. Bipolar hosts with carbazole as the donor moiety usually possess higher triplet energy than their counterparts with triphenylamino group. The triplet energy of carbazole (T_1 = 3.19 eV) is higher than that of triphenylamine (T_1 = 3.04 eV) [12]. Moreover, carbazole is a fully aromatic moiety providing high thermal, chemical and environmental stability [13]. It can be easily substituted with a wide variety of functional groups [14–16].

Triazine has an electron affinity larger than those of other typical electron-deficient heteroaromatic compounds (e.g., pyridine, pyrimidine) [17–19]. Due to this reason, triazine has been frequently incorporated into the backbone of conjugated compounds to improve their electron-injection and electron-transportation

---

[*] Corresponding author. Tel.: +370 37 300193; fax: +370 37 300152.
E-mail address: juozas.grazulevicius@ktu.lt (J.V. Grazulevicius).

http://dx.doi.org/10.1016/j.dyepig.2015.11.001
0143-7208/© 2016 Published by Elsevier Ltd.

abilities [20–22]. In addition, derivatives of triazine exhibit good thermal stability [19]. Rigid skeleton of 2,4,6-triphenyl-1,3,5-triazine ensures high symmetry. Compounds containing triazine unit as electron-accepting center and carbazolyl or diphenylamino peripheral units linked through π-conjugated bridges showed aggregation induced emission and two-photon absorption properties [23].

In this paper we report on the synthesis of new star-shaped compounds containing both donor (carbazole) and acceptor (2,4,6-triphenyl-1,3,5-triazine) moieties linked through various linking bridges. We describe the results of optical, photophysical, electrochemical and computational studies which were carried out in order to study structure-properties relationship of these hybrid materials.

2. Experimental

2.1. Materials

Trifluoromethanesulphonic acid, copper iodide, *bis*-(triphenylphosphin)-palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), triphenylphosphine (PPh_3), trimethylsilylacethylene, triethylamine (Et_3N), tetrabutilammoniumhydrosulfate (TBAHS), 1-bromohexane, 1 M tetrabutylammoniumfluoride (n-Bu_4NF) solution in THF, 4-iodobenzonitrile, aluminium trichloride (anhydrous), 18-crown-6, copper, sodium sulfate, 9*H*-carbazole, potassium iodide, potassium iodate, 2-chloro-2-methylpropane, acetic acid, sodium hydroxide, potassium carbonate were purchased from Sigma–Aldrich and used as received. Poly(N-vinyl carbazole) (PVK) and 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) were also obtained from Aldrich. The solvents, i.e. toluene, chloroform, ethyl acetate, *n*-hexane, diethyl ether, methanol, acetone, acetonitrile, (Penta), dichloromethane (Poch), *o*-dichlorobenzene (Sigma–Aldrich) were dried and distilled according the conventional procedures [24].

2.2. Instrumentation

Nuclear magnetic resonance spectra of deuterated chloroform solutions of the synthesized compounds were recorded with a "Varian Gemini-2000" (300 MHz (^{1}H), 75.4 MHz (^{13}C)) spectrometer. All the data are given as chemical shifts in δ (ppm), multiplicity, integration down field from $(CH_3)_4Si$ as the internal standard. Mass spectra (MS) were obtained on "Waters ZQ 2000". Elemental analysis data were obtained on a EuroEA Elemental Analyzer. Infrared (IR) spectra were recorded using "Perkin Elmer Spectrum GX II FT–IR System". The spectra of the solid compounds were recorded in the form of KBr pellets.

UV–Vis spectra of 10^{-4} M solutions of the compounds were recorded in quartz cells using Perkin Elmer Lambda 35 spectrometer. Photoluminescence (PL) spectra of 10^{-5} M solutions of the compounds were recorded using Edinburgh Instruments' FLS980 Fluorescence Spectrometer. Thin solid films for recording of UV–VIS and PL spectra were prepared by drop casting 2 mg/ml solutions of the compounds in toluene on the pre-cleaned quartz substrates. Fluorescence quantum yields (η) of the solutions and of the solid films were estimated using the integrated sphere method [25]. An integrating sphere (Edinburgh Instruments) coupled to the FLS980 spectrometer was calibrated with two standards: quinine sulfate in 0.1 M H_2SO_4 and rhodamine 6G in ethanol. Each quantum yield measurement was repeated 5 times and the error corridor was estimated. Fluorescence decay curves of the samples were recorded using a time-correlated single photon counting technique utilizing the nF920 Nanosecond Flashlamp as an excitation source. The phosphorescence spectra were recorded at 77 K for the solid solutions of the compounds (1 wt%) in Zeonex polymer matrix using nanosecond gated luminescence measurements (from 400 ps to 1 s) using a high energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA). A model liquid nitrogen cryostat (Janis Research) was used for the experiment. The blue-edge highest energy peak in the phosphorescence spectrum was taken for the $T^1 \rightarrow S^0$ transition.

Differential scanning calorimetry (DSC) measurements were carried out with a TA Instruments "DSC Q100" calorimeter. The samples were heated at a scan rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a "Mettler TGA/SDTA851e/LF/1100". The samples were heated at a rate of 20 °C/min.

Ionization potentials (IP^{EP}) of the films of the synthesized compounds were measured by electron photoemission in air by the earlier reported procedure [26]. The materials were dissolved in chloroform and coated onto Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of MKM layer was not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, this layer is conductive enough to avoid charge accumulation on it during the measurements. The measurement method was, in principle, similar to that described in literature [27]. The samples were illuminated with monochromatic light from the quartz monochromator. The negative voltage of −300 V was applied to the sample substrate. The counter-electrode with a slit for illumination was placed at ~5 mm distance from the sample surface. The counter-electrode was connected to the input of electrometer for the photocurrent measurement. The $I^{0.5} = f(h\nu)$ dependence was plotted. The linear part of this dependence was extrapolated to the $h\nu$ axis and the value was determined as the photon energy at the interception point. We evaluate the ionization potential measurement error as 0.03 eV.

Cyclic voltammetry (CV) measurements were carried out with a glassy carbon working electrode in a three-electrode cell using a μ-Autolab Type III (EcoChemie, Netherlands) potentiostat. Platinum wire and $Ag/AgNO_3$ (0.01 mol/l in acetonitrile) were used as counter and reference electrodes, respectively, and Bu_4NBF_6 in dichloromethane (0.1 M) was used as electrolyte. The data were collected using GPES (General Purpose Electrochemical System) software. Electrochemical measurements were conducted at room temperature at a potential rate of 100 mV/s. The reference electrode was calibrated versus ferrocene/ferrocenium redox couple. The solid state ionization potential energy (I_p^{CV}) was estimated from the onset oxidation potential by using the relationship $I_p^{CV} = 4.8 + E_{ox}$, where the potential is related to that of ferrocenium/ferrocene. The electron affinity (EA^{SS}) values were obtained from the reduction potential using the approximation $EA^{CV} = 4.8 + E_{red}$.

Charge drift mobility measurements were performed by a xerographic time-of-flight (XTOF) method [28,29]. The samples for the charge mobility measurements were prepared as described earlier [30]. The samples for the measurements were prepared by drop-casting 10 mg/ml solutions of the compounds in $CHCl_3$ onto cleaned ITO coated glass substrate. After casting the cells were heated at 70 °C for 5 min. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 1 ns, wavelength 337 nm). After photo excitation of the sample with a short light impulse, the rate of potential discharge in the XTOF measurements has a plateau region. The transit time was determined from the kink point in the transient photocurrent curves. The transit time t_{tr} with the surface potential (U_0) at the moment of illumination indicates the passage of holes through the entire thickness of the films (d) and enables determination of the hole mobility as $\mu = d^2/U_0 \cdot t_{tr}$. The experimental setup consists of a delay generator Stanford Research DG 535 and a digital storage oscilloscope Tektronix TDS754C.