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Structure-properties relationship of the derivatives of carbazole and 1,8-naphthalimide: Effects of the substitution and the linking topology

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ABSTRACT

Nine compounds having electron-accepting 1,8-naphthalimide and electron-donating carbazole moieties were synthesized employing palladium-catalyzed C—N and C—C coupling reactions and characterized by the thermal methods, absorption and emission spectrometry, electrochemical and photoelectrical tools. The synthesized compounds possess high thermal stability with the 5% weight loss temperatures being in the range of 351–476 °C. Most of the synthesized compounds are capable of glass formation with glass transition temperatures ranging from 30 to 87 °C. The cyclic voltammetry measurements showed that the solid state ionization potentials values of the carbazole and 1,8-naphthalimide derivatives range from 5.46 eV to 5.76 eV and the electron affinities values range from −3.04 eV to −2.92 eV. Dilute solutions of the 3- and 3,6-naphthalimide-substituted derivatives of carbazole in polar solvents were found to emit in the green region with quantum yields ranging from 0.66 to 0.83, while in the solid state fluorescence quantum yields were found to be in the range of 0.01–0.45. ((E)-9-(((*N*-(2-ethylhexyl)-1,8-naphthalimide)-4-yl)ethenyl)-9*H*-carbazole) exhibited efficient fluorescence in the solid state with quantum yield as high as 0.45. The effects of the linking topology of the chromophores and of the incorporated alkyl substituents on the thermal, optical, and photoelectrical properties of the synthesized donor-acceptor compounds are analyzed. The impact of the ground state intramolecular twisting of the carbazole and naphthalimide moieties induced by the substituents resulting in significant variation in the rates of radiative and nonradiative excitation deactivation is revealed.

1. Introduction

Conjugated compounds containing both donor and acceptor moieties have been extensively synthesized and studied because of their potential applications in electronics and optoelectronics [1–3]. The unique structure of donor-acceptor molecules allows their optical and electrochemical properties to be tuned finely over a wide range by appropriate chemical modification of the donor and acceptor moieties [4]. The further progress in the design and synthesis of the compounds containing both donor and acceptor moieties depend to the great extent on the understanding the structure-property relationship of such compounds.

Derivatives of 1,8-naphthalimide are widely used for various applications [5,6]. They were utilized in such fields as colouration and brightening of polymers [7], as laser active media [8,9], fluorescent markers in biology [10], anticancer agents [11], analgesics in medicine [12], fluorescence switchers and sensors [13–16], as electron-transporting and emitting materials in light emitting diodes [17–19]. They were also used in liquid crystal displays [20] and as ion probes [21–23]. Derivatives of 1,8-naphthalimide derivatives generally have high electron affinity due to the existence of an electron-deficient centre [24] and display good electron-transporting or hole-blocking capabilities.1,8-Naphthalimide moiety can be easily functionalized [25]. By introducing different electron-donating substituents at C-4 position of 1,8-naphthalimide moiety the emission color of the compounds can be readily tuned from near infrared to pure blue [26–29].

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Carbazole-based compounds are known for their intense blue luminescence and electroluminescence [30,31]. Carbazole derivatives are prefereable due to their rigid plane and good hole-transporting properties [32]. Carbazole derivatives, consisting of large planar aromatic systems possess enhanced thermal stability [33–35]. Furthermore, carbazole moiety can easily be functionalized at its C-3 and C-6 [36], as well as at C-2 and C-7 [37] or *N*-positions [38], allowing the fine-tuning of the electro-optical properties of the molecules [39,40]. Many reported carbazole-based materials are equipped with substituents at its C-3 and C-6-positions to enhance morphological and electrochemical stability [41]. Recently, a series of carbazole derivatives with donor-acceptor structures was reported as efficient emitting materials for organic devices [42–44]. Such carbazole derivatives have a great potential for the application as host materials in organic light emitting diodes [45], therefore the molecular design and synthesis of new carbazole derivatives with donor-acceptor structure need to be further developed by the structural modification in order to improve the properties and to establish the relationship between structures and properties.

In this paper we present the synthesis by stepwise palladium-catalyzed C–N and C–C coupling reactions of a series of acceptor-donor-(acceptor) compounds having electron-accepting 1,8-naphthalimide moieties linked to electron-donating carbazole species functionalized at three different positions (C-3, C-6 and N-9). One of the aims of this work was to explore the effects of the linking topology of the chromophores and the nature of alkyl substituents introduced at the carbazole nitrogen on the thermal, optical, photophysical and photoelectrical properties of the compounds. Basing on the results of the density-functional modeling and detailed studies of the optical and photophysical properties of the compounds embedded in various surrounding media the impact of the conformational changes of the singly bonded carbazole-naphthalimide systems is elucidated and its impact on the nonradiative and radiative excited state deactivation is discussed.

2. Experimental methods

2.1. Instrumentation

Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were obtained using a Varrian Unity Inova (300 MHz (^{1}H), 75.4 MHz (^{13}C)). All the data are given as chemical shifts in δ (ppm), multiplicity, integration downfield from $(CH_3)_4Si$. Mass (MS) spectra were obtained on a Waters ZQ 2000 (Milford, USA). Elemental analysis was performed with an Exeter Analytical CE-440 Elemental Analyser. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. DSC measurements were carried out using a Perkin–Elmer DSC-7 series thermal analyzer at a heating rate 10 °C/min under nitrogen flow. TGA measurements were performed on a METTLER TOLEDO TGA/SDTA 851^e. Melting point (m.p.) of the material was determined using Electrothermal Mel-Temp apparatus. Ionization potentials (IP_{EP}) were established by electron photoemission technique in air [46]. The samples for the measurements were prepared by dissolving the compounds in THF and by coating onAl plates precoated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer [47]. Electrochemical investigation was carried out using Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The solutions of the synthesized compounds with the concentration of 10^{-5} M were used for cyclic voltamperometry (CV) measurements. The experiments were calibrated with the standard ferrocene/ferrocenium redox system [48].

Charge drift mobility measurements were performed using charge extraction by linearly increasing voltage (CELIV) method [49,50]. For the CELIV measurements the samples in configuration ITO/compound/Al with the thickness of layers organic compound of 100–200 nm and an active area of 7 mm^2 were prepared. The layers from 10 mg/mL THF solutions of the compounds were spin coated onto glass/ITO substrates at 1000 rpm. Glass/ITO substrates were sonicated in acetone, deionized water, and isopropanol for 10 min before use. Al electrode of 60 nm of was thermally evaporated at 10 Å/s at a pressure below $5\cdot10^{-5}$ mbar using a mask, to obtain three top contact pixels. The light pulse was used to photogenerate the charge carriers by exciting layers of compounds through the ITO layer. The charge carriers were generated by illumination with pulses of Nd:YAG laser (pulse duration was 25 ps, wavelength 355 nm). The experimental setup consisted of a delay generator Tektronix AFG 3011 and a digital storage oscilloscope Tektronix DPO 4032.

Absorption spectra of the dilute solutions of the investigated compounds were recorded by UV-Vis-NIR spectrophotometer Lambda 950 (Perkin Elmer). Fluorescence of dilute solutions, compounds embedded in polystyrene (PS) matrix and of the neat films was excited at a 365 and 420 nm wavelengths from 150 W xenon arc lamp light source passed through a monochromator and measured using back-thinned CCD spectrophotometer PMA-11 (Hamamatsu). For these measurements, the dilute solutions of the investigated compounds were prepared by dissolving them in a spectral grade solvent at 10^{-6} M concentration. The PS films with the dispersed compounds with concentration of 1 wt% were prepared by mixing the dissolved compounds and PS in THF and casting the solutions on quartz substrates in an ambient air. The drop-casting from THF solutions (1×10^{-3} M) was also employed to prepare the neat films of the compounds. Fluorescence quantum yields (QY) of the solutions were estimated by using integrated sphere method [51]. Integrating sphere (Sphere Optics) coupled to the CCD spectrometer via optical fiber was also employed to measure η of the neat films. Fluorescence transients of the samples were measured using a time-correlated single photon counting system PicoHarp 300 (PicoQuant) utilizing semiconductor diode laser (repetition rate 1 MHz, pulse duration 70 ps, emission wavelength 375 nm) as an excitation source.

2.2. Materials

4-Bromo-1,8-naphthalic anhydride and 2-ethylhexylamine were purchased from TCI. Tri-*o*-tolylphosphine and 9*H*-carbazole were purchased from Fluka and Reakhim respectively. 1-Iodomethane, 1-bromobutane, 2-ethylhexylbromide, *n*-BuLi (2.5 mol L^{-1} in hexane), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) and *N*-bromosuccinimide (NBS), palladium acetate(II) ($Pd(OAc)_2$), 18-crown-6, *N*-vinylcarbazole, triethylamine, copper were obtained from Aldrich. The solvent, i.e. dimethylformamide (DMF, Lachema) was dried by distillation over CaH_2. THF was dried and distilled over sodium and benzophenone. Dichloromethane (POCH), ethyl acetate and *n*-Hexane (Penta) were purified and dried using the standard procedures [52]. All other reagents and solvents were used as supplied.

3,6-Dibromocarbazole (**1a**) [53] (m.p. 207–208 °C, lit. [54] m.p. 209–210 °C), 3-bromocarbazole (**1b**) [55] (m.p. 192–193 °C, lit. [54] m.p. 197–198 °C), 3,6-dibromo-9-methyl-9*H*-carbazole (**2a**) [56] (m.p. 136–137 °C, lit. [56] m.p. 141 °C), 3,6-dibromo-*N*-butylcarbazole (**2b**) [57] (m.p. 71–72 °C, lit. [58] m.p. = 74–75 °C), 3,6-dibromo-9-(2-ethylhexyl)carbazole (**2c**) [59] (colorless oil), 3-bromo-9-methylcarbazole (**2d**) [53] (m.p. 74–75, lit. [56] m.p. = 78–79 °C), 3-bromo-9-butylcarbazole (**2e**) [60] (colorless