



Differently linked fluorene-carbazole triads for light amplification



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ABSTRACT

The impact of linking topology of fluorene-carbazole triads on amplified and spontaneous emission as well as on concentration quenching of emission and charge carrier mobility, *i.e.* on the properties essential for organic laser application, was investigated. Deep-blue-emitting triads featuring 2,7- substitution pattern and bulky alkyl moieties expressed high emission quantum yield (0.8–0.9) and low concentration quenching, which benefited in attaining large radiative decay rates ($\sim 10^9 \text{ s}^{-1}$) and rather low amplified spontaneous emission (ASE) threshold (down to 9 kW/cm^2) for compound concentrations up to 3 wt % in polymer matrix. Most of the triads expressed carrier drift mobilities close to $10^{-2} \text{ cm}^2/(\text{V}\cdot\text{s})$ in amorphous films pointing out efficient charge transport essential for reducing threshold current density for lasing. The impact of the position (central or side) of fluorene/carbazole moieties in the triad or the linking position (C-2 or C-3) of the side groups on the ASE threshold and carrier mobility was found to be of little significance. However, a huge advantage of 2,7- substitution pattern over 3,6- pattern for the triads in terms of ASE performance was demonstrated. Importantly, the obtained results suggested a possible trade-off between ASE threshold reduction and carrier mobility enhancement, which may hamper the realization of electrically-driven lasing in organic amorphous films.

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1. Introduction

The rapid development of conjugated organic materials initiated the work on multiple optoelectronic applications. The introduction of organic solid-state lasers could lead to numerous potential target applications in spectroscopy, chemical sensing and communication [1–3]. Currently, the idea of developing efficient electrically pumped organic laser is being pursued, nevertheless, no demonstration of such device has been reported yet, which is due to multiple challenges that are primarily related to electrical pumping. The high current densities required, excitation quenching due to presence of contacts, and most importantly, absorption by the injected charge carriers are the main issues related to the rather low charge carrier mobility of organic materials [4–8]. The issues could be overcome by designing new laser architectures (e.g. various optical resonator configurations or organic-inorganic hybrid structures)

and synthesizing novel molecular structures with desirable photophysical and electrical properties [3,9,10].

The combination of high charge carrier mobility and efficient light emission has proved to be difficult to achieve in organic semiconductors. High charge carrier mobility is achieved in the molecular films that facilitate intermolecular $\pi-\pi$ stacking, however π -electron system interactions arising between neighboring molecules (often *via* formation of aggregates or excimers) quench exciton luminescence, and thus, increase the threshold for amplified spontaneous emission (ASE). This suggests a possible trade-off between carrier transport and ASE properties, which need to be considered. To reduce the ASE threshold, several approaches that involve increasing the spacing between chromophores have been applied. These include utilization of bulky aliphatic spacers or complex molecular geometries (e.g. dendrimers or spiro-compounds) [11–13]. The most straight-forward way to eliminate concentration quenching is blending molecules with polymer host material. Unfortunately, diluting the material significantly reduces charge carrier mobility [14], and moreover adversely affects organic laser efficiency [8]. Nonetheless, this method is advantageous for

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determining the relation between ASE threshold and the molecular concentration in the low-loss waveguiding films.

In addition to superior optical and electrical properties molecular compounds must ensure high thermal stability and excellent film forming properties. In this regard, multifunctional compounds consisting of several bridged polycyclic aromatic moieties are considered to be promising raw material for the state-of-the-art light-emitting devices [15–17]. Two of the most exploited aromatic units constituting the multichromophoric systems are carbazole and fluorene, which, in fact, by proper substitution are capable of delivering multifunctional properties. For instance, carbazoles, known as classic hole transporters are also employed as light-emitting materials [18,19]. Meanwhile, fluorenes are known for their high fluorescence efficiency, high laser gain [20] as well as excellent thermal and oxidative stability [21]. Functionalization of carbazole and fluorene units *via* substitution at the 2,7-positions have demonstrated great potential for light-emitting device applications by yielding extended conjugation, enhanced emission efficiency, and, in some cases, bipolar charge carrier transport with electron and hole mobilities as high as 10^{-3} cm²/(V·s) [18,22,23]. More symmetrical, linear-shaped molecules with the emitting dipoles oriented in the plane of the active layer were found to be beneficial for enhanced light outcoupling from an OLED structure as well as for reduced ASE threshold [24–26]. Thus, highly efficient emitters also capable of efficiently transport charges could in turn facilitate development of electrically-pumped organic semiconductor lasers, which still remain a challenge.

To this end, aiming for compounds with efficient light amplification, the impact of linking topology of a series of fluorene-carbazole triads (molecular glasses) on ASE threshold and charge carrier mobility as well as on emission quantum yield, concentration quenching of emission and radiative decay rate was studied. In the study, the triads bearing 2,7- substitution pattern with C-2 linked side groups were mainly utilized as favoring extended π -conjugation, linear molecular shape (for controllable orientation), and thus, highly promising for efficient emission, charge transport, and consequently, for organic laser applications. A couple of compounds utilizing 2,7- and 3,6- substitution patterns with C-3 linked side groups were also investigated for comparison. The fluorene-carbazole triads were also designed to possess various alkyl moieties for investigating molecular packing effects on the concentration quenching and charge transport properties.

2. Experimental

2.1. Instrumentation

Proton and carbon nuclear magnetic resonance (¹H and ¹³C NMR) spectra were taken on Varrian Unity Inova (300 MHz (¹H), 75.4 MHz (¹³C)) spectrometer at room temperature. All the data are given as chemical shifts in δ (ppm), (CH₃)₄Si (TMS, 0 ppm) was used as an internal standard. The course of the reaction products was monitored by TLC Silica gel 60 F254 plates and developed with I₂ or UV light. Silica gel (grade 60, 63–200 mesh, 60 Å, Fluka) was used for column chromatography. Melting points were determined using Electrothermal Mel-Temp melting point apparatus. Mass (MS) spectra were recorded on a Waters ZQ (Waters, Milford, MA). Elemental analysis was performed with an Exeter Analytical CE-440 Elemental. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin–Elmer DSC-7 series thermal analyzer at a heating rate of 10 °C/min under nitrogen flow. Thermogravimetric TGA measurements were performed on a Mettler Toledo TGA/SDTA 851^c. Infrared (IR) spectra were recorded using Perkin Elmer Spectrum GX spectrometer. For solid compounds KBr pellets were used. Absorption spectra of the dilute THF solutions

were recorded on a UV–vis–NIR spectrophotometer Lambda 950 (Perkin–Elmer). Fluorescence of the investigated compounds in dilute THF solutions, polystyrene (PS) and neat films was excited by a 365 nm wavelength light emitting diode (Nichia NSHU590-B) and measured using a back-thinned CCD spectrometer PMA-11 (Hamamatsu). For these measurements, the dilute solutions of the investigated compounds were prepared by dissolving them in a spectral grade tetrahydrofuran (THF) at 1×10^{-5} M concentration. The PS films with the dispersed compounds with concentrations ranging from 0.06 to 10 wt % were prepared by mixing the dissolved compounds and PS in toluene solutions at appropriate ratios and casting the solutions on quartz substrates under ambient conditions. The neat films of the compounds were casted from 1×10^{-3} M THF solutions. Fluorescence quantum yields (Φ_F) of the solutions were estimated by comparing wavelength-integrated fluorescence intensity of the compound solutions with that of the reference. Quinine sulfate in 0.1 M H₂SO₄ with $\Phi_F = 0.53 \pm 0.023$ was used as a reference [27]. Φ_F were determined by selecting 340 nm excitation wavelength from a xenon lamp. Optical densities of the reference and sample solutions were kept below 0.05 to avoid reabsorption effects. Estimated quantum yields of the compound solutions were verified using the integrated sphere method [28]. An integrating sphere (Sphere Optics) coupled to the CCD spectrometer via optical fiber was also employed to measure Φ_F of the neat and PS films. Phosphorescence spectra of the compounds dispersed in polymer (PMMA) matrix at a concentration of 4.0 wt % were measured in a closed-cycle helium cryostat at 20 K temperature by utilizing time-gated intensified CCD camera iStar (Andor). Fluorescence transients of the samples were measured using a time-correlated single photon counting system PicoHarp 300 (PicoQuant), utilizing a semiconductor diode laser (repetition rate 1 MHz, pulse duration 70 ps, emission wavelength 375 nm) as an excitation source. Amplified spontaneous emission (ASE) measurements were carried out by exciting the films with a 40- μ m-wide laser stripe focused on the film surface near its freshly cleaved edge by using a cylindrical lens (the so-called thin excitation stripe geometry) [29,30]. Frequency-tripled (355 nm) Nd³⁺:YAG laser (EKSPILA) with a pulse duration of 5 ns and a repetition rate of 10 Hz was used as an excitation source. Excitation power density in the ASE measurements was varied by several orders of magnitude from 1 to 2000 kW/cm² to determine the ASE threshold. The same laser and excitation wavelength were used to test photostability of the compounds. Fluorescence microscopy of the compounds dispersed in PS matrix was carried out using fluorescence microscope BX51 (Olympus). Hole drift mobility was measured by xerographic time of flight technique [31,32]. The samples for the charge carrier mobility measurements were prepared as described elsewhere [33,34].

2.2. Materials

2-bromocarbazole [35], 4,4'-dibromo-2-nitrobiphenyl [36], 2,7-dibromocarbazole [36] and 2,7-dibromo-9-(2-ethylhexyl)carbazole (a) [36] were prepared according to the published procedures.

2,7-Bis(9H-carbazol-2-yl)-9-(2-ethylhexyl)carbazole (b). A dried 100-ml flask was charged with 2,7-dibromo-9-(2-ethylhexyl)carbazole (0.6 g, 1.36 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1 g, 3.4 mmol), tetrakis(triphenylphosphine)palladium dichloride (Pd(PPh₃)₂Cl₂) (100 mg, 0.136 mmol), and KOH (0.8 g, 13.6 mmol). The reaction vessel was vacuumed and filed with argon. Degassed THF (10 ml) and degassed water (1.5 ml) were added, and the reaction mixture was stirred at 80 °C for 24 h. The crude product was extracted into chloroform, and the organic phase was washed with water and dried over MgSO₄. The solvent was removed by rotary evaporation,

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