

Spectral and Luminescent Properties and Electroluminescence of Polyvinylcarbazole with 1,8-Naphthalimide in the Side Chain

Alexander Kukhta · Eduard Kolesnik · Ivo Grabchev · Seher Sali

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Abstract A novel copolymer with moieties capable of charge transport and light emission on the basis of polyvinylcarbazole and 1,8-naphthalimide is synthesized. A bright and stable electroluminescence from single layered structure is observed. White light emission can be easily realized by tuning the content of naphthalimide moieties or a number of naphthalimide derivatives. Such approach can be considered as a common way to create single layered light-emitting devices with a stable white emission.

Keywords Polyvinylcarbazole · 1,8-naphthalimide · electroluminescence

Introduction

Organic light-emitting diodes (OLEDs) are very promising devices for manifold applications owing to their fast response, high brightness and efficiency, low driving voltage, wide viewing angle, light weight, etc. [1]. As opposite to low molecular weight OLEDs, polymer-based OLEDs can be much cheaper processed though they have lower luminescence quantum efficiency. Luminescent dyes are often used as additives to conducting polymer matrix to change emission spectrum, conductivity, etc. The matrix serves as a

kind of solvent preventing molecules from aggregation and increasing fluorescence quantum yield. Unfortunately, there are some problems with such a blend. For example, dye molecules are often “washed out” from the matrix. Moreover, the energy transfer from the matrix to dye molecule is not always possible and effective.

In order to escape these phenomena and to increase stability an approach consisting in the chemical bonding of the molecules to the polymer matrix can be used. As a matrix we used polyvinylcarbazole (PVK) which is not π -conjugated polymer, but exhibit rather high electrical conductivity and is widely used as a photoconductor. Electroluminescence of both pure PVK and its mixtures with different luminescent compounds were observed [2–4]. We proposed to copolymerize PVK with 1,8-naphthalimide derivative to obtain chemically bonded mixture. 1,8-Naphthalimide molecules were found to be very stable radiating in different parts of spectrum depending on substituents [5]. In the obtained polymer chain both carbazole and naphthalimide moieties are side bonded. This polymer is capable of luminescence and both hole (carbazole moiety) and electron (naphthalimide moiety) transport.

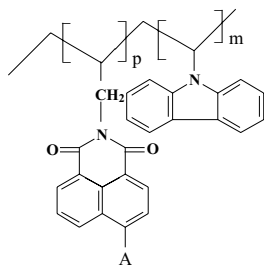
Experimental

This compound was synthesized from two compounds with a common chemical structure presented in Scheme 1, where A is NHCH_3 (compound I) and piperidino (compound II). The polymerization reaction was the following. Vinylcarbazole (1.0 g) and 4-aminosubstituted-*N*-allyl-1,8-naphthalimide (0.03 g) were dissolved in toluene (5 ml), followed by sufficient degassing by argon, adding dibenzoylperoxide (0.02 g), stirring the mixture at 80°C for 10 hr. After

A. Kukhta (✉) · E. Kolesnik
Institute of Molecular and Atomic Physics, NAS of Belarus,
70 Nezavisimosti Ave,
220072 Minsk, Belarus
e-mail: kukhta@imaph.bas-net.by

I. Grabchev · S. Sali
Institute of Polymers, Bulgarian Academy of Sciences,
Sofia, Bulgaria

Scheme 1



cooling, the copolymer was isolated by precipitation in acetone–ethanol mixture (1:1). The copolymer thus obtained having an intense yellow–green fluorescence was dissolved in chloroform and precipitated several times with ethanol in order to remove the non-reacted monomers. The precipitated copolymer was dried in vacuum at 40°C to a constant weight to obtain a random power polyvinylcarbazole copolymer dye (Poly(VC-co-dye)). The amount of dye incorporated into the polymer macromolecules was determined spectrophotometrically using a standard curve [6] is 1.7 wt % for dye **I** and 2.1 wt % for dye **II**. This value suggests that during polymerization, the activity of the monomer dye was much lower than the vinylcarbazole monomer units. Molecular weights and molecular weight distribution conform the formation of copolymers to molecular weight $M_w = (6.40\text{--}7.11) \times 10^3$ g/mol and $M_n = (2.45\text{--}2.55) \times 10^3$ g/mol. The double detection (refractive and visible at 420 nm) shows close value for the elution time in both chromatograms indicating also the presence of copolymer, which absorbs at about 420 nm. The polydispersity (M_w/M_n) of the copolymers is 2.61–2.79. The free radical copolymerization of vinylcarbazole with 4-aminosubstituted-*N*-allyl-1,8-naphthalimides (3 wt %) in toluene solution was investigated according to method described in [7].

The absorption spectra of the samples were recorded using “Cary 500 Scan UV-VIS-NIR” (Varian Ltd.) spectrophotometer with a quartz cell. Time-resolved transient absorption spectra were obtained using a special picosecond spectrophotometer on the basis of Ti-sapphire mode-locked laser with 4 ps pulses at a repetition rate of 10 Hz at time resolution of about 4 ps. The spectrometer provides pumping and supercontinuum probing pulses at different delays. The photoluminescence spectra were performed using “SFL-1211A” (Solar TII) spectrofluorimeter. The fluorescence quantum yield was determined using 3,6-diaminophthalimide as a standard (quantum yield = 0.60). The single-layered OLED was prepared by spin coating of the substance **I** (110 nm) onto ITO (indium tin oxide, 50 ohm/quadrat) precoated glass substrate rinsed previously in chloroform and acetone solutions and treated in oxygen plasma. The concentration of chloroform solution was 0.5 g/L. Aluminum cathode (200 nm) was deposited by thermovacuum evaporation.

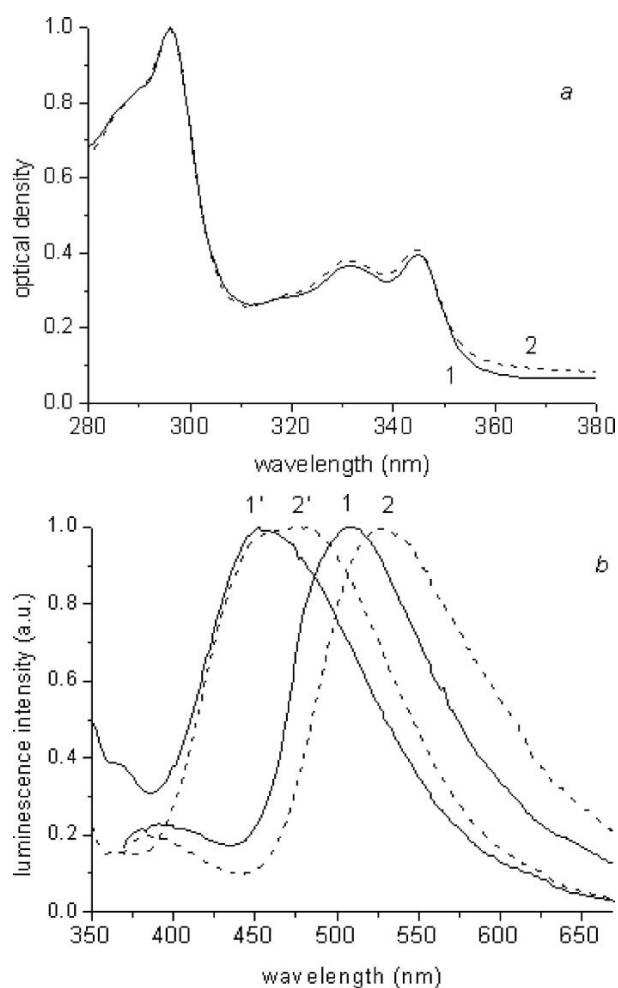


Fig. 1 Absorption (a) and fluorescence spectra (b) of chloroform solutions (1', 2') and thin films (1, 2) of compounds **I** (1) and **II** (2)

Results and discussion

Figure 1 shows that absorption spectra of thin films made of studied compounds are close to each other and to PVK that is connected with very low naphthalimide concentration. Fluorescence quantum yield for compound **I** is 22 and 17% for compound **II**. But the most bright emission at the same film thickness gives also compound **I** (approximately 10 times). Photoluminescence spectra for solutions and films are two centered and also close to each other though thin film spectra are red shifted owing to stronger intermolecular interaction in solid state. The band 391 nm of compound **I** corresponds to the emission of carbazole group. The band at 510 nm is much more intense and can be attributed to 1,8-naphthalimide moiety. The difference in intensity can be caused by the partial energy transfer from the polymer carbazole to 1,8-naphthalimide. The absorption spectrum of naphthalimide (the maximum is at about 400 nm) is overlapped with the fluorescence spectrum of carbazole (the maximum is at about 400 nm). The process

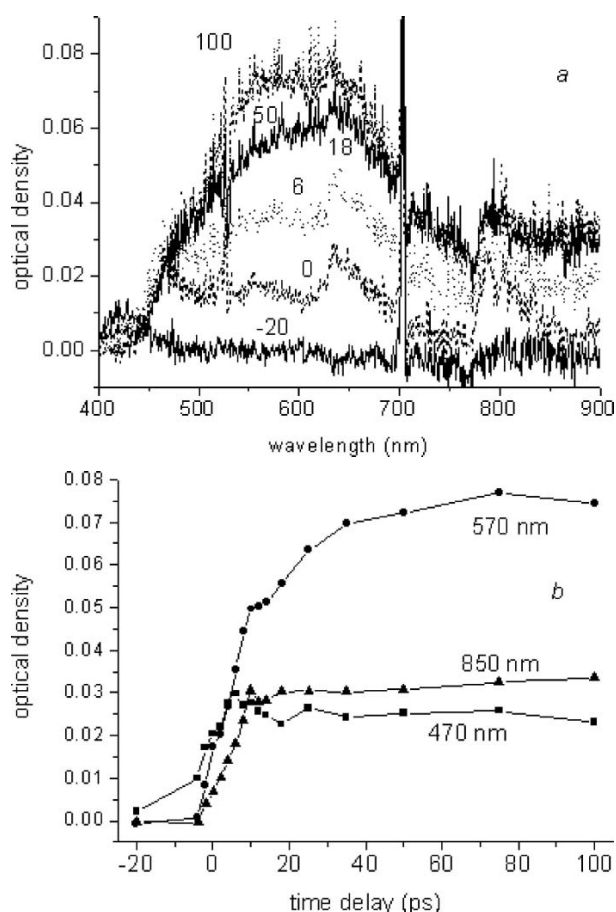


Fig. 2 Transient absorption spectra of toluene solution for compound **II** at different delays in ps (a). Dependence of increasing time of transient absorption at different characteristic registration wavelengths (b)

of energy transfer is also confirmed by the measured spectra and kinetics of the transient absorption in solutions for compound **I**. After excitation pulse a strong relaxation process with a characteristic time of 20–30 ps can be observed (Fig. 2) decreasing in absorption at about 420 nm and increasing at some longer characteristic wavelengths. Note that in such molecules a charge transfer from electron donating carbazole to electron accepting naphthalimide can also be occurred.

Electroluminescence spectrum and voltage–brightness characteristic measured under ambient conditions are presented in Fig. 3. Electroluminescent spectrum coincides with 1,8-naphthalimide fluorescence as opposite to photoluminescence. This is because in photoluminescence naphthalimide moiety emits light via energy transfer, but in electroluminescence direct charge interaction also contributes long-wave emission. The shape of electroluminescence spectrum is insensitive of the driving voltage. It is practically the same at 11 and 15 V. However, at lower naphthalimide concentrations it is possible to obtain luminescence of both naphthalimide and carbazole, i.e. white light. Apparently, the resulting luminescence spectrum is strongly dependent

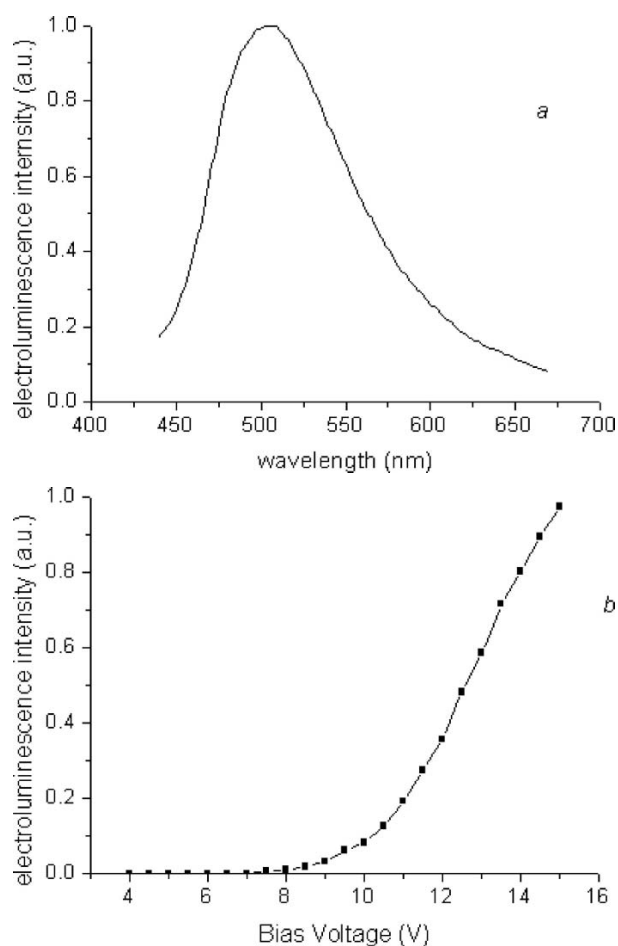


Fig. 3 Electroluminescence spectrum (a) and voltage brightness characteristic (b) for for single layer structure on the basis of compound **II**

on the relative concentration of radiating species and on the applied voltage. The threshold of electroluminescence for naphthalimide containing PVK (Fig. 3b) is about 3 V less than for pure PVK.

Conclusion

A novel copolymer with moieties capable of charge transport and light emission on the basis of polyvinylcarbazole and 1,8-naphthalimide is synthesized. A strong energy transfer from carbazole to naphthalimide moieties is occurred. A bright and stable electroluminescence from single layered structure is observed. The threshold of electroluminescence for naphthalimide containing PVK is about 3 V less than for pure PVK. Further studies of this problem is currently in progress.

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