



Electromodulation and magnetomodulation of exciton dissociation in electron donor (starburst amine) : electron acceptor (bathocuproine) system



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ABSTRACT

Electric field dependencies of electromodulated photoluminescence and photocurrents as well as the magnetic field effects on photocurrents, photovoltaic characteristics, electromodulated photoluminescence and photoluminescence have been investigated in vacuum evaporated films of m-MTDATA:BCP (4,4',4''-tris(N-(3-methylphenyl)-N-phenylamino)triphenylamine and bathocuproine) system. The electromodulation processes do remain in accordance with Onsager as well as with the Sano–Tachiya–Noolandi–Hong formalisms of electron–hole pair separation. While the electromodulated photocurrents are due to operation of both long-radius and short-radius e–h pairs, the electromodulated photoluminescence quenching is related to merely short-radius fraction of the e–h pairs involved in the exciplex creation process. The photocurrents, photovoltaic characteristics, photoluminescence and electromodulated photoluminescence are influenced by external magnetic field of the hyperfine coupling (HFC) scale which modulates the singlet–triplet intersystem crossing of long-radius e–h pairs.

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1. Introduction

The rapid increase in application of organic materials for manufacturing photovoltaic (PV) cells and electroluminescent (EL) diodes is nowadays accompanied by an intensive research in electrical and optical properties of organic thin films [1–3]. Among others, the charge recombination and exciton dissociation are the matter of exceptional interest since they are generally recognized as the basic electronic processes limiting the efficiency of organic EL and PV devices. These mechanisms in low-mobility organic materials are usually assumed to proceed via the intermediate stage of an electron–hole (e–h) pair of finite lifetime, but the knowledge on the subject is still far from complete. In particular, it is not known whether the same e–h pairs are involved in dissociation/recombination processes in the PV and EL devices which in turn addresses the issue of the intercarrier distance within these pairs [3]. An effective tool to resolve this problem is to trace the e–h distance by observation of influence of applied external electric and magnetic fields on the e–h pair dissociation and recombination products. In particular, under strong electric field the sample photocurrent and the electric-field assisted

photoluminescence quenching are investigated as a result of the Coulomb-bound e–h pair (exciton) dissociation. To develop the models of relevant mechanisms the Onsager approach to geminate recombination as well as the Langevin approach to the bimolecular recombination are typically used. The usage of magnetic field in turn makes it possible to probe effectively the different intercarrier distances in spin-correlated e–h pairs by investigation of magnetic field effects on photocurrent, photoluminescence and electroluminescence [3,4]. Essentially, if the spin coherence time of the e–h pairs is long enough and the electrostatic electron exchange interaction is sufficiently weak for efficient spin evolution to occur, the magnetic field-dependent intersystem crossing (ISC) between the singlet, ¹(e–h), and triplet, ³(e–h), pair spin states can take place [5]. This process does modulate the effectiveness of various e–h pair decay channels, hence the production of emissive states in the EL processes and the charge carrier population in the dissociation events in the PV devices [6–9]. It should be noted here that determination of the intercarrier distance and binding energy of the e–h pairs is essential for construction of exciton-dissociation models to optimize the efficiency of EL and PV devices. Indeed, sufficiently low electrostatic exchange energy of the e–h pairs allowing effective singlet–triplet spin mixing is required if the improvement of the electrofluorescent diodes over the pure spin

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statistic 25%-limit is considered using the reverse intersystem crossing (RISC) [10].

The origin of the magnetic field effects remains, however, under current debate (for recent reviews refer to Refs. [4,11]. Although the effects in weak magnetic fields are commonly interpreted in terms of the electron–hole conversion (EHP) model (see e.g. Refs. [7–9,12]), the trion model [4,13,14] as well as the bipolaron (BP) mechanism (see Refs. [15,16]), some experimental results obtained under strong magnetic fields cannot be rationalized in such a way. In particular, in Ref. [17] a simultaneous increase in fluorescence and phosphorescence in electrically excited layers of PhLPPP (phenyl-substituted derivative of the prototypical conjugated polymer ladder-type poly(*p*-phenylene) with trace concentrations of palladium atoms) under magnetic field intensity up to 8 T was reported which rejects any mechanisms involving the magnetic-field-driven conversion between the singlet and triplet spin pairs leading to the fluorescence intensity increase accompanied by the decrease in phosphorescence output or vice versa.

It is generally recognized that formation of intermolecular excited-state complexes (exciplex states) can take place as a result of charge transfer processes at the interface between the separate layers or mixed molecules of an organic hole transporter (electron donor, D, with lower ionization potential) and an organic electron transporter (electron acceptor, A, with larger electron affinity), one of them being excited [3,18]. The photoinduced electron transfer between D and A molecules promotes the intermolecular charge separation which is profitable in PV applications whereas the broadband emission from electrically induced exciplex states is favoured in development of new-generation sources of light. Therefore, the exciplex-based optoelectronic elements are nowadays the subject of intense studies with substantial effort aimed at fabrication of effective bifunctional, EL and PV, devices. For instance, the usage of m-MTDATA (4,4',4''-tris(N-(3-methylphenyl)-N-phenylamino)triphenylamine) and BCP (bathocuproine), respectively, as the electron donor and the electron acceptor to construct a PV/EL diode has been demonstrated with expectations of good performance applications [19], therefore, we decided to examine the exciton dissociation and charge recombination processes limiting the efficiency of such devices.

In this paper we investigate the vacuum-evaporated solid films of m-MTDATA:BCP system sandwiched between Al electrodes. The electric field dependencies of electromodulated photoluminescence and photocurrents as well as the magnetic field effects on photocurrents, photovoltaic characteristics, electromodulated photoluminescence and photoluminescence are analyzed to address the problem of the intercarrier distance of the e–h pairs involved in the relevant dissociation/recombination processes. An attempt has been undertaken to unveil the mechanisms responsible for spin-dependent processes underlying the observed magnetic field effects.

2. Experimental details

The quartz/Al/m-MTDATA:BCP[1:1]/Al sandwich structures were prepared as follows. Films of organic material mixture (for molecular structures of both compounds see Fig. 1a) were obtained by simultaneous thermal vacuum (5×10^{-3} Pa) deposition of the components from separate quartz crucibles onto quartz slides with previously evaporated semitransparent substrate electrodes. With temperatures of the crucibles adjusted to 270 °C for m-MTDATA and 175 °C for BCP the common average evaporation rate of ca. 15 nm/s was achieved to obtain the mixture films of controlled, ca. 1:1, mass ratio (the densities of both components are similar). The layer thicknesses were measured by means of a Tencor Alpha Step 500 Profiler. As results from the X-ray diffraction

measurements the obtained co-evaporated layers exhibit the quasi-amorphous structure [20]. Sandwich structures were formed by vacuum deposition of semitransparent counter-electrodes. Both metal films were evaporated at pressure of about 9×10^{-3} Pa giving optical transmittance of 5–20% in visible and next dried in air for ca. 10 min. The energy level diagram with the Fermi level of Al electrodes and frontier molecular orbital HOMO (highest occupied MO) and LUMO (lowest unoccupied MO) levels of m-MTDATA and BCP solid films are depicted in a flat band fashion in Fig. 1b. Note that the dark carrier injection ability of the electrodes into the solid mixture is rather poor due to high energy barriers both for the electron and hole injection. As usual for organic materials, the samples were stored in darkness and in ambient dried air atmosphere for several days before measurements. When necessary the electrical contacts between the sample electrodes and the relevant circuits were accomplished by drops of carbon-containing emulsion.

The absorption (ABS) spectra of system single components as well as component mixtures, both in the diluted and the solid phase, were recorded with the use of a Perkin Elmer, UV/VIS Lambda 10 spectrometer at fixed spectral line width of 2 nm. To obtain solutions the tetrahydrofuran (THF) was utilized as a solvent since its absorption spectrum does not coincide with the spectra of m-MTDATA and BCP. The photoluminescence (PL) spectra of all solutions and evaporated layers were in turn recorded with a Perkin Elmer, LS55B spectrofluorometer, also at fixed spectral width of excitation and emission lines being as high as 7.5 and 2.5 nm, respectively. Additionally, a Schott WG2 optical filter was used for the FL measurements of the BCP and m-MTDATA films, whereas for m-MTDATA:BCP ones a Corning 3-72 filter was applied. The spectral measurements were carried out with the spectral interval equal to 0.5 nm.

In the photoluminescence (PL) and photocurrent experiments a mercury lamp (Narva, HBO 200 W) or a xenon lamp (Osram, XBO 150W) followed by a Zeiss, SPM-2 monochromator was used as a source of sample illumination light. The photoluminescence of the m-MTDATA:BCP mixture layers was excited through the active electrode area of 0.2 cm² (mercury lamp, $\lambda_{\text{exc}} = 313$ nm) and the electric field-modulated photoluminescence (EML) was induced by a sinusoidally time-dependent field, $F(t) = F_0 \sin(\omega t)$ (at typical value of $\omega/2\pi = 175$ Hz), applied to the electrodes of the sample. The sample PL light was collected with a quartz lightguide followed by an Optometrics, SDMC1 monochromator together with a set of appropriate Schott and Corning cut-off glass filters and then its intensity was measured by an EMI, 9863QB photomultiplier tube driving a EG&G Princeton Applied Research, model 181 current preamplifier. To avoid effectively the undesirable detection of exciting light, the lightguide rod was placed behind the sample in a position out of the excitation light path, at the angle of 27° towards the layer plane (this angle was chosen arbitrary and has no special meaning). The voltage signal from the preamplifier consisted of a steady-state and alternating components corresponding to the field-modulated photoluminescence of the organic layer, $I(t)$, according to the Fourier series, $I(t) = \sum I_{n\omega}(t)$, ($n = 0, 1, 2, \dots$). The zeroth-order component, $I_{0\omega}$, was measured with a dc-voltmeter whereas the second harmonic, $I_{2\omega}(t)$, was extracted and measured using of a lock-in amplifier, EG&G Princeton Applied Research, model 5210 referenced by the PL-modulating signal. The point of interest in this EML experiment is the value of the ratio recorded as a function of the rms electric field strength, F_{RMS} , and excitation wavelength, here defined as

$$(2\omega)\text{EML} = \frac{I_{2\omega}}{I_{0\omega}} \quad (1)$$

where $I_{0\omega}$ denotes the steady-state Fourier component and $I_{2\omega}$ – the rms value of the second-order Fourier component of the

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