

Energy transfer between exciplex-type excited states and inorganic nanoparticles for use in two-color organic/inorganic hybrid light-emitting diodes

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In the present work we show for the first time double-channel emission from organic exciplexes coupled to inorganic nanoparticles. The process is demonstrated for yellow-green emission in light-emitting diodes based on organic exciplexes hybridized with perovskite-type dispersed BaZrO₃ nanoparticles. Such double-channel emission provides broadening of the electroluminescence spectrum and, therefore, a soft yellow-green emission color of the device that is harmless to the human eye. We have successfully realized an energy transfer from the exciplexes between the tris(4-carbazoyl-9-ylphenyl)amine and 4,7-diphenyl-1,10-phenanthroline molecules to the spherical-shaped BaZrO₃ nanoparticles sporadically deposited on the organic interface. The fabricated device exhibits high current efficiency values of 3.88 Cd/A, maximum brightness of 3465 cd/m² (at 15V), and external quantum efficiency of about 1.26%. In order to estimate the efficiency of the energy transfer from the

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exciplex to the BaZrO₃ nanoparticles we have applied the Förster model for the dipole-dipole energy transfer accounting for the mutual overlap of the exciplex emission spectrum and the absorption spectrum of the BaZrO₃ nanoparticles.

During recent time hybrid organic-inorganic light-emitting devices (LEDs) based on quantum dots (QDs) and organic/inorganic hybrid perovskites have attracted great attention¹⁻³ along with pure organic (OLEDs)⁴ and inorganic (LEDs)⁵ devices. Such hybrid LEDs combine the main advantages of OLEDs, like flexibility and widescreen display, with LEDs which provide high brightness and narrow emission wavelengths that are tunable throughout the visible region. Among the hybrid organic/inorganic perovskite-type materials the $\text{CH}_3\text{NH}_3\text{PbI}_3$ compound demonstrates the best emissive characteristics.¹ However, its practical implementation in LED technology is significantly limited by its environmental toxicity.⁸ Moreover, one of the main challenges in optimizing high-tech organic/inorganic LEDs is to find efficient ways for charge injection into the radiative core. This requires sophisticated multi-stage methods for the synthesis of organic/inorganic hybrid materials.

Structurally disordered semiconductors like perovskite titanates and zirconates can be even more efficient than the crystalline ones taking into account the cost of manufacturing.⁹ Many of these solid-state substances provide highly efficient PL in the short-wavelength part of the visible spectrum at room temperature.¹⁰ Barium zirconate is an alkaline-earth perovskite material which is very promising for electroceramics.¹⁰⁻¹² The BaZrO_3 (BZO) semiconductor in doped and pure forms provides good thermal resistance and conductivity, showing green-blue emission which has been explained by a structurally disordered vacancy.^{10,13} This led us to the idea of using BZO as the emissive material in LEDs. While it is too difficult to activate directly the emission of BZO due to the very high excitation energy (more than 4 eV), it is more easy to use sensitizers to activate the BZO emission. It is preferable that such a sensitizer should possess simultaneous co-emission together with BZO that provides a broadening of the electroluminescence spectrum and a soft emission color of the device that is harmless to the human eye.

In the present work we propose to use environment-friendly BZO perovskite ceramics as a guest green-emissive dopant for a host formed by a highly efficient blue exciplex at the interface of tri(9-hexylcarbazol-3-yl)amine (TCTA) and 4,7-diphenyl-1,10-phenanthroline (Bphen).^{14,15} It should be noted, that exciplex-type OLEDs are characterized by the high values of the external quantum efficiency parameter due to the intramolecular spin up-conversion from the non-luminescent triplet state to the fluorescent singlet state (thermally activated delayed fluorescence, TADF) that serves as a key for high performance OLEDs.¹⁵⁻¹⁸ It was shown recently that exciplexes can be used as hosts for a highly efficient yellow and red fluorescent device^{17,19,20} as well as for the blue phosphorescent OLEDs.²¹ In this case an energy transfer from the exciplex to dopants was shown to be very efficient

without energy loss.²¹ The long-range exciplex emission has been observed recently in spatially separated electron-donating and electron-accepting molecules across ultra-thick spacer layers.²²

The BaZrO₃ nano-powder (<50 nm particle size), tris(4-carbazoyl-9-ylphenyl)amine (TCTA) and 4,7-diphenyl-1,10-phenanthroline (Bphen) were purchased from Aldrich. In this work we have used the step-by-step technique for deposition of different organic layers and metal electrodes onto precleaned ITO-coated glass substrate under a vacuum of 10⁻⁵ Torr for fabrication of LEDs. For analysis of the surface by SEM besides the ITO-coated glass substrate we used also the silicon substrates. Inorganic BZO interlayer was formed by the fast heating method of the BZO nanopowder in the melting pot up to temperature of 1600°C, the lowest melting point of the powder.¹¹

In the present work we have fabricated three types of light-emitting devices of the following structures:

ITO/TCTA(30nm)/Ca(50nm)/Al(200nm) (device A),

ITO/TCTA(30nm)/Bphen(30nm)/Ca(50nm)/Al(200nm) (device B),

ITO/TCTA(30nm)/BZO interlayer/Bphen(30nm)/Ca(50nm)/Al(200nm) (device C)

We have used the technique of the step-by-step deposition of different organic layers on the metal electrodes. The pure organic layers of TCTA and Bphen were vacuum deposited as well, but the molecular mixture TCTA:Bphen (50:50) was spin-coated onto clean quartz substrate. Continuous film of BZO was prepared onto the clean quartz substrate by the usage of the same method for the photoluminescence studies performance.

Since Ca is highly reactive and corrodes quickly in the ambient atmosphere, the Ca layer topped with 200 nm aluminum (Al) layer was used as the cathode. The active area of the obtained devices was 3x2 mm².

The density current-voltage and luminance-voltage characteristics were measured using a semiconductor parameter analyzer (HP 4145A) in the air without passivation immediately after the formation of the device. The brightness measurements were performed using a calibrated photodiode.²³ The electroluminescence spectra were recorded with an Ocean Optics USB2000 spectrometer.

Photoluminescence spectra were recorded with the Edinburgh Instruments FLS980 spectrometer at room temperature using a low repetition rate µF920H Xenon Flash lamp as the excitation source. A Hitachi SU-70 scanning electron microscope was used for SEM studies. Room temperature exciplex spectrum and exciplex quantum yield of the solid films

of the mixtures TCTA:BPhen were recorded utilizing an Edinburgh Instruments FLS980 spectrometer. Exciplex quantum yields were recorded using integrated sphere calibrated with two standards quinine sulfate in 0.1 M H₂SO₄ and rodamine 6G in ethanol. A 450 W xenon lamp and a monochromator were used for the excitation of studied films at 350 nm. For these measurements, the solid films of the mixtures TCTA:BPhen (1:1) were prepared from THF solutions of the TCTA and BPhen by two-steps spin coating at 1500 rpm for 20 s and 2000 rpm for 120 s using a spincoater SPIN150 and drying at room temperature under Nitrogen atmosphere during 20 min.

The PL spectrum of solid BZO film at room temperature is shown in Figure 1. Three bands with maxima at 372 nm, 386 nm, 538 nm and weak shoulder near 410 nm are observed (Fig.1). This spectrum is similar to the known PL emission profile of BZO^{10,11} and is typical for a multiphonon and multilevel process for a system in which relaxation occurs by several paths, involving the participation of numerous states inside the band gap of the material. According to Refs.^{24,25} this behavior is related to the structural disorder of BZO and confirms the presence of additional electronic levels in the forbidden band gap controlled by [ZrO₅·V_O^{*}]-[ZrO₆] complex clusters.²⁴

As follows from the SEM data (Fig. S1)²⁹ the inorganic BZO phase in the device C represents the insertions of spherical-shape nanoparticles with the diameter less than 50 nm at the TCTA/Bphen interface. The electroluminescence spectra of the device C shown in Figure 2 is characterized by two main emission bands at 490 and 540 nm. The shoulder at 490 nm (Fig. 2) corresponds to the emission from TCTA electromers that is supported by the absence of this band in the PL spectrum of TCTA film and by the occurrence of this band in the EL spectrum of the single-layer device A (Fig. 3).

The band with maximum 540 nm (Fig. 2) completely coincides with the fluorescence spectrum of the BZO film and is responsible for the structural disorder of BZO.^{10,24} The absence of the exciplex emission band (460 nm) in the hybrid device was somewhat unexpected¹⁵ (Fig. 2), because such emission may occur even at large space separations between the exciplex-forming donor and acceptor molecules.²² It is evident that in the present case we deal with energy transfer from the exciplex to the inorganic counterpart (Fig. 4). To our knowledge, this is the first reported example of energy transfer between the exciplex-type excited states and inorganic nanoparticles. However, the similar phenomenon of energy transfer between the exiplexes and organic acceptors has been described in some recent publications (unfortunately without theoretical interpretation).²⁶

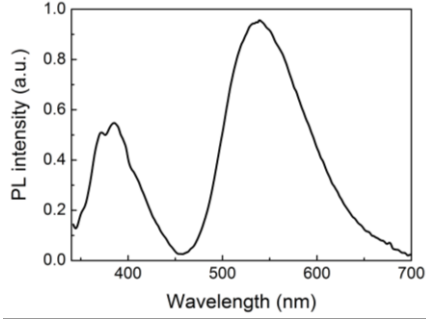


FIG. 1. Photoluminescence spectrum of the pure continuous BaZrO₃ solid film

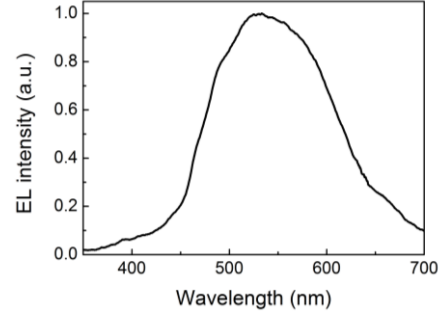


FIG. 2. EL spectrum of the device C.

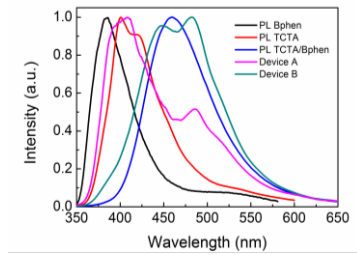


FIG. 3. PL spectra of the TCTA, Bphen and TCTA/Bphen solid films as well as EL spectra for devices A and B.

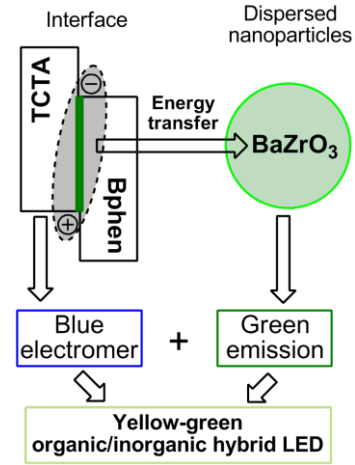


FIG. 4. Principle of the electroluminescence for the device C.

In the present study we have utilized the classical Förster mechanism²⁷ for the estimation of energy transfer efficiency between the TCTA/Bphen exciplexes (donor) and the BZO nanoparticles (acceptor) *via* the nonradiative dipole-dipole coupling. Considering the fact that both donor and acceptor species possess energetically close blue and green fluorescence, respectively, and also taking into account that a significant wave function overlap between the donor and acceptor is rather improbable, we have concluded that the Förster model of dipole-dipole energy transfer can be applied in this case.²⁸

According to the Förster theory, the rate constant k_{ET} for the energy transfer between the donor and acceptor can be given by the following equation:^{27,28}

$$k_{ET} = \frac{1}{\tau_D} \left(\frac{R_0}{R} \right)^6, \quad (1)$$

where τ_D is the fluorescence lifetime for the free donor species (79.1 ns for the TCTA/Bphen exciplexes¹⁵), R is the distance between donor and acceptor, R_0 is the Förster radius (so-called critical radius). The R_0^6 term can be estimated as follows:

$$R_0^6 = \frac{9 \cdot 10^3 Q_0 (\ln 10) k^2 J}{128 \pi^5 n^4 N_A}, \quad (2)$$

where Q_0 is the luminescence quantum yield of the donor species (in our case Q_0 for the TCTA/Bphen exciplex emission equals 7%), k^2 is the dipole orientation factor (2/3 for an arbitrary orientation of donor and acceptor species), n is the refractive index of the medium (assumed to be equal ~1.5), N_A is Avogadro constant, and J is the overlap integral (Fig. 5) between the PL spectrum of donor (TCTA/Bphen exciplex) and absorption spectrum of the acceptor (BZO nanoparticles) which is equal to $9.2 \cdot 10^7 \text{ nm}^4/(\text{M} \cdot \text{cm})$.

The J integral has been calculated by the following equation:

$$J = \int f_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda, \quad (3)$$

where $f_D(\lambda)$ is the normalized donor emission spectrum, $\varepsilon_A(\lambda)$ is the acceptor molar absorption coefficient. If we know the Förster radius we can estimate the efficiency of the Förster-type energy transfer varying the distance R between donor and acceptor counterparts:

$$E_{ET} = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6} \quad (4)$$

Using the Eqn. 2 we have calculated the Förster radius to be 3.1 Å for which the efficiency of energy transfer should be equal to 50%.²⁸ Varying the intermolecular distance in the range from 3.1 to 10 Å we observe a sharp increasing of the rate constant and energy transfer efficiency with increasing R . As it can be seen from Figure 6 the Förster-type energy transfer in the TCTA/Bphen – BZO system is the most efficient in the short range of donor-acceptor distances and varies from 50% (at R_0) to 17% (at $R=4$ Å). At higher distances the energy transfer efficiency is very low (only 1% at 7 Å and $8 \cdot 10^{-2}$ % at 10 Å).

The most detrimental impact on E_{ET} originates certainly from the very low PL quantum yield of the TCTA/Bphen exciplexes. The change of PL quantum yield from 7% to 40% (for example) gives an increasing Förster radius, from 3.1 Å to 4 Å, and therefore E_{ET} should be higher at the large distances of 4-6 Å which correspond to the usual intermolecular separation between the organic exciplexes and guest molecules.^{18,23} Therefore, this could be the possible pathway to improve the efficiency of energy transfer: to use the exciplexes with the higher values of PL quantum yield and also with the blue-shifted emission spectrum in

order to increase the overlap integral between the absorption spectrum of BZO and the PL spectrum of the exciplex.

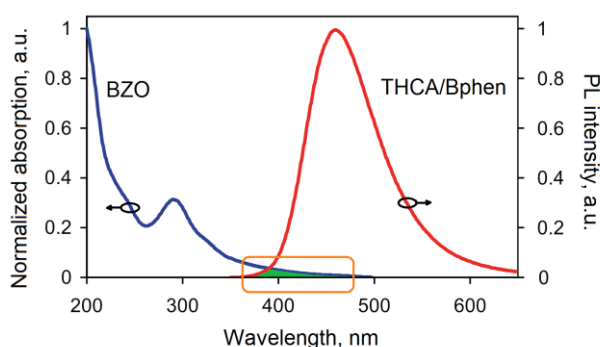


FIG. 5. Overlap between the absorption spectrum of a continuous BZO film and PL spectrum of the TCTA/Bphen exciplexes. The green area (in orange square) corresponds to the overlap integral J .

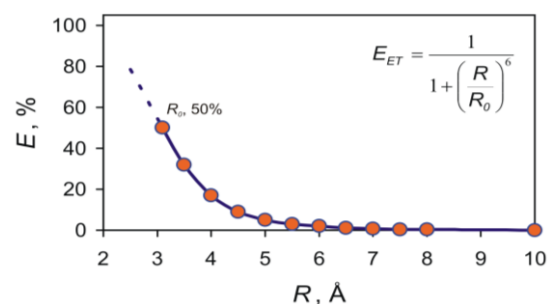


FIG. 6. Dependence of the Förster-type energy transfer efficiency on the distance between the interacting BZO and TCTA/Bphen species.

As follows from Table 1 and Fig. S2²⁹ the device exhibits high current efficiency values of 3.88 cd/A, with a maximum brightness of 3465 cd/m² (at 15V), and external quantum efficiency of about 1.26 %. The efficiency of the fabricated hybrid LED is not so high compared with other known exciplex-based OLEDs¹⁶ or phosphorescent OLEDs,²¹ however, it corresponds to the level of typical fluorescent OLEDs. As we have mentioned earlier the possible strategy to increase the efficiency of such hybrid LED is the enhancement of the charge transfer efficiency between the donor exciplex excited state and accepting BZO nanoparticle by the modulation of the critical distance between the interacting dipoles (in the framework of the Förster model). Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (x, y) of the hybrid device C were found to be (0.33, 0.41), corresponding to yellow-green emission color (Figure S3²⁹).

Table 1. The EL characteristics of the fabricated device C.

Device	Von (V)	Max. brightness (cd/m ²)	Max. current efficiency (cd/A)	Max. power efficiency (lm/W)	Max. external quantum efficiency (%)	1000 Cd/m ²		
						Current efficiency (cd/A)	Power efficiency (lm/W)	External quantum efficiency (%)
ITO/TCTA/BZO interlayer/Bphen/Ca/Al	6.60	3465	3.88	1.52	1.26	2.76	0.83	0.9

Summing up, a novel hybrid organic/inorganic light emitting device has been fabricated by step-by-step vacuum deposition. As emissive system we have used a blue TCTA/Bphen exciplex with sporadically deposited nanodispersed BaZrO₃ co-emitters at the TCTA/Bphen interface. The fabricated device is characterized by a bright yellow-green electroluminescence which originates from the emission of the TCTA electromers and the BaZrO₃ nanoparticles while the TCTA/Bphen exciplex emission remains unobserved. The dual emission phenomenon corresponds to an energy transfer from the TCTA/Bphen exciplexes to the BaZrO₃ nanoparticles. To our knowledge this is the first example of energy transfer between the exciplexes and inorganic nanoparticles in LEDs. Applying the Förster model for the energy transfer we conclude that the main source of efficiency loss of the device is the very low photoluminescence quantum yield of the exciplex emission. As a result, the efficiency of energy transfer strongly increases with the increase of distance between the donor (TCTA/Bphen exciplex) and the acceptor (BaZrO₃) species. We believe, that future development in the field of organic-inorganic LEDs can lead to new branches of low cost and non-toxic LEDs with simplified structures that could form the background to achieve commercial success of hybrid LEDs.

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²⁹ See supplementary material for the additional experimental details (SEM and current-voltage characterization), charge transfer rate constants (k_{ET}) for the different R values and chemical structures of TCTA and Bphen compounds