Theoretical and experimental investigation of exciplex radiation in organic light emitting diode

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The electric current flow in the structure of an organic light-emitting diode (OLED) is accompanied by recombination of electrons and holes. Generally, the movement speed of electrons and holes (charge carriers, CCs) in organic materials is very different, therefore, additional layers are introduced for the balance of CC transport which have predominantly hole or electronic transport. In some cases, the material of the radiating layer can interact with the transport layer and form an excited complex (exciplex). The exciplex radiation lies in the long-wavelength region compared to the radiation of the radiating material itself [1, 2].

In the present work, the formation of the zinc complex ($Zn(DFP\ SAMQ)_2$) with the hole-transport material (NPD) exciplex is experimentally and theoretically studied in OLED structures. For this purpose, two OLED structures were created:

1) ITO / PEDOT: PSS / Zn ($DFP\text{-}SAMQ)_2$ / Ca / Al

2) ITO / PEDOT: PSS / NPD / $Zn(DFP\text{-}SAMQ)_2$ / Ca / Al,

where ITO is the transparent anode of tin oxide indium, Ca / Al is the cathode, PEDOT: PSS is a hole-injection and planarizing layer. OLED-structure 2 differs from the first one in that it contains the hole-transport layer of NPD molecules that form an exciplex with molecules of the zinc complex $Zn(DFP\text{-}SAMQ)_2$. A detailed method of preparation of substrates and creation of organic LEDs is described earlier [3].

Because the exciplex radiation lies in the long-wavelength region compared to the radiation of the NPD and $Zn(DFP\text{-}SAMQ)_2$ molecules, the formation of exciplexes can be experimentally detected by comparing the fluorescence spectra of structure 1 and 2. The electroluminescence spectra were experimentally obtained for both diodes.

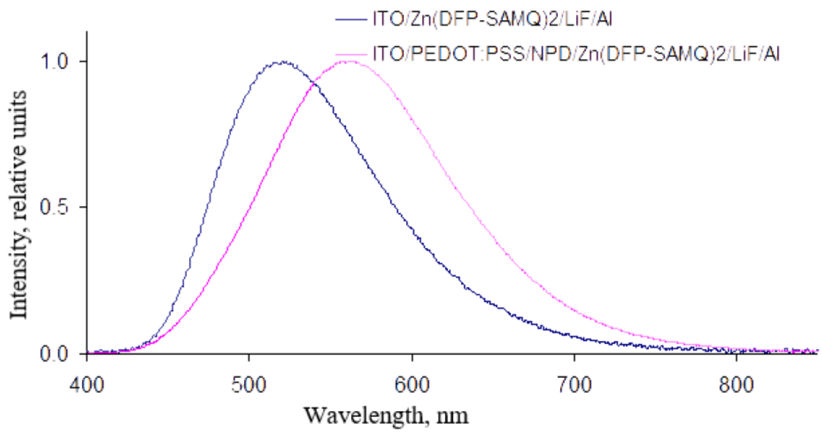

Figure 1: Electroluminescence spectra of OLED structures.

The electroluminescence band maximum of first OLED is located at 520 nm (19230 cm^{-1}). Due to the intense fluorescence, the NPD material can be used not only as a hole-transport when creating OLED devices, but also as a radiating layer [4]. In this case, the electroluminescence band of OLED lies in the region of 455 nm [4]. However, when $Zn(DFP\text{-}SAMQ)_2$ and NPD are used together in an OLED device (structure 2), the electroluminescence is in the long-wave region with a maximum at 560 nm (17860 cm^{-1}) and corresponds to the exciplex radiation.

Since the S1 state of the exciplex is of the nature of charge transfer, then, having performed quantum-chemical calculations of the S1 state nature of the complex of NPD and Zinc molecules, we can determine whether this complex is an exciplex. Using the geometry of molecules in the S1 state, supercomplexes with different Zn(DFP-SAMQ)$_2$ and NPD positions were built relative to each other. In total, 4 different complexes were studied. The energies of the singlet and triplet states of the supercomplexes were calculated and the nature of the exited states was determined and the radiation rate constants were obtained.

In supercomplex $1-3$, the contribution to the nature of S1-state consists of transition from the highest occupied molecular orbital (HOMO) to the lowest free molecular orbital (LUMO) (to state S1) is ~ 0.7 while HOMO is localized on the NPD molecule and LUMO is on one of the Zn ligands (DFP-SAMQ)$_2$. Thus, the S1 transition is charge transfer (CT) and supercomplexes $1-3$ can be referred to exciplexes. In supercomplex 4, the S1 state is formed by the intra-ligand transition and this supercomplex is not an exciplex.

Since exciplex is formed only at the boundary of the layers, the thickness variation of the Zn(DFP SAMQ)$_2$ layer allows to change the ratio of the emission bands of the zinc complex and exciplex, and expand the emission range of the LED increasing its color rendering index.

References

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