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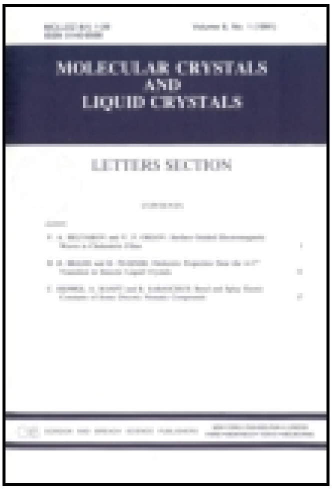

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Experimental and Theoretical Study of Electroluminescence Spectra of the Light-Emitting Devices Based on Zinc Complexes of Amino-Substituted Ligands

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Experimental and Theoretical Study of Electroluminescence Spectra of the Light-Emitting Devices Based on Zinc Complexes of Amino-Substituted Ligands

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The electroluminescence spectra of the light-emitting devices based on two zinc complexes of amino-substituted ligands Zn(DFP-SAMQ)$_2$ and Zn(PSA-BTZ)$_2$ are studied. The intrinsic and exciplex bands are observed in the spectra, the relation between them being strongly dependent on the material of a hole-transporting layer. A quantum-chemical study of the spectral properties of these complexes and the light-emitting devices based on them using the PBE density functional method is made. To model the spectra of a device, the spectra of the adduct containing one molecule of the zinc complex and one molecule of the hole-transporting material are calculated. The accordance between the experimental and theoretical data is observed.

Keywords Electroluminescence; exciplex; quantum-chemical calculations; PBE method; zinc complexes

Introduction

Recently, we have shown that the light-emitting devices based on zinc complexes of amino-substituted ligands exhibit long-wavelength bands in their electroluminescence spectra in addition to the intrinsic bands of zinc complexes [1–4]. These additional long-wavelength bands are due to the exciplex formation between the zinc complex molecules and the molecules forming the hole-transporting layer. The relation of the intrinsic and exciplex bands is strongly dependent on the material and the thickness of the hole-transporting layer. Triarylamine derivatives seem to be the most proper materials for the exciplex formation [1–4].

In this work, we have studied the electroluminescence spectra of the light-emitting devices based on two zinc complexes: bis[8-(3,5-difluorophenyl) sulphanylamino-quinoline]zinc, Zn(DFP-SAMQ)$_2$ and bis[2-(2-phenylsulphanylamino) phenyl]benzothiazole, Zn(PSA-BTZ)$_2$. The oligomer of triphenylamine oligo(4,4′-(4″-methyl)triphenylamine) (PTA) [5] and well-known N,N′di(1-naphthalenyl)-N,N′-diphenyl-1,1′biphenyl-4,4′-diamine (NPD) were used as hole-transporting materials. For a better

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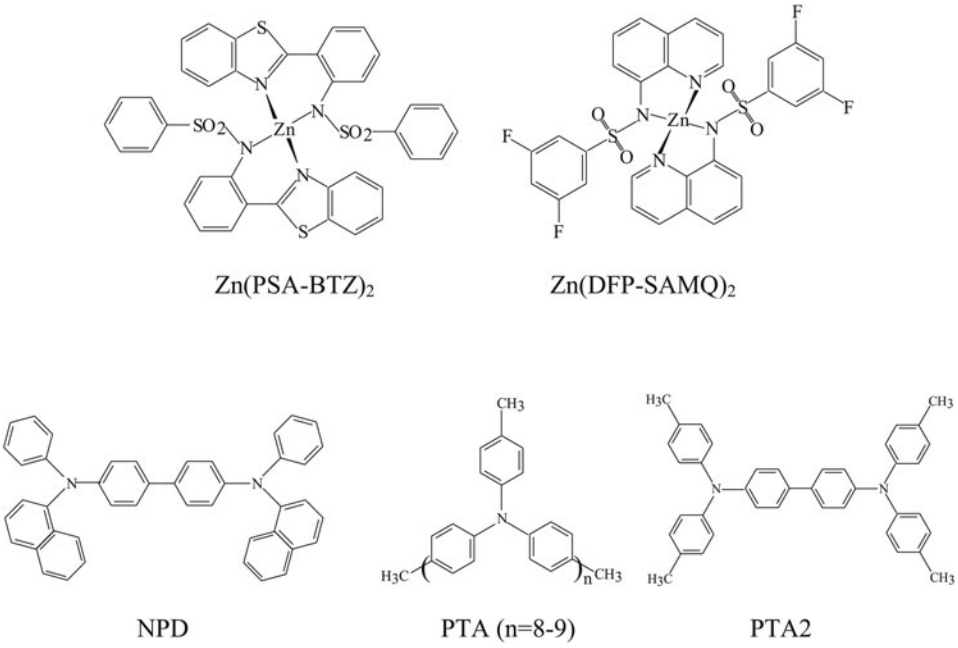
*Correspondence author: kaplunov@icp.ac.ru understanding of the nature of exciplex bands in the electroluminescence spectra, we made a quantum-chemical study of these complexes and the light-emitting devices based on them using the PBE density functional method. To model the electronic structure of a device, we performed the quantum chemical calculation the adduct containing one molecule of the zinc complex and one molecule of the hole-transporting material.



Scheme 1. Molecular structure of studied materials.

Methods

Methods of preparing the electroluminescent devices and measuring the EL and PL spectra are described elsewhere [1–4].

Quantum chemical calculations were performed using the PBE non-empirical density functional [6] and the extended basis H [5s1p/3s1p] C,N,O,F [5s5p2d/3s3p2d] Zn [9s9p8d/5s5p4d] for the SBK pseudopotential [7]. All the calculations were performed using the PRIRODA software package [8–9] with the aid of the facilities of the Joint supercomputer center of the Russian Academy of Sciences. The optimization of the geometry of the molecules under study was made for lower energy singlet (S_0) and, in some cases, for triplet (T_1) electronic states. For the energy minima obtained, we verified the absence of the imaginary frequencies of normal vibrations. The atomic charges were calculated in the frames of the Mulliken approximations. In the calculation of the energies of electronic excited states and the oscillator strengths of optical transitions to the ground state, we used the time-dependent density functional formalism TD-DFT. Up to 25 excited states were considered in this calculation. For a smooth representation of results for the calculated positions of transitions and excited states, a Gaussian line shape with a half-width of 10 nm was used.

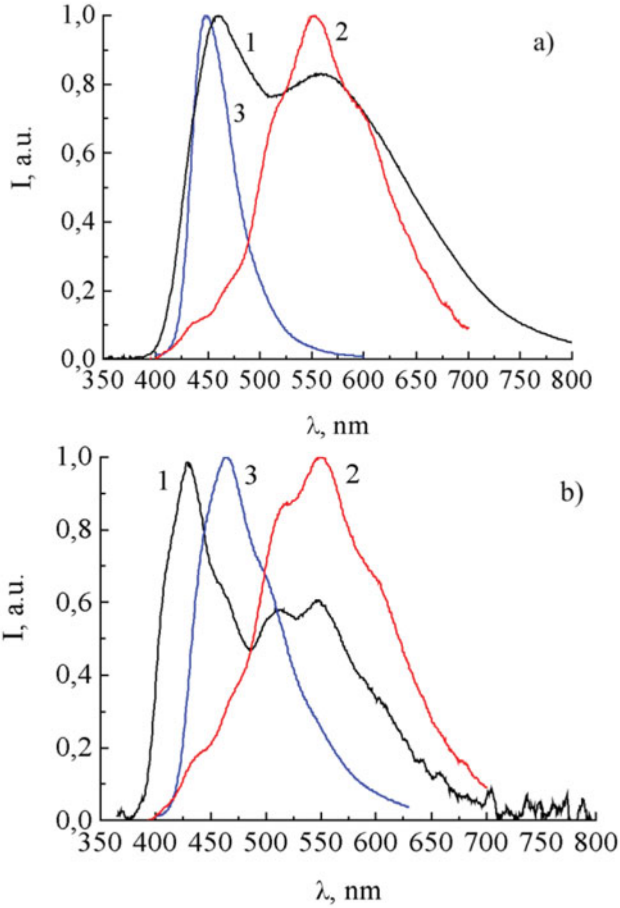


Figure 1. (a): 1 - the EL spectrum of the device ITO/PTA/NPD/Zn(PSA-BTZ)$_2$/Al:Ca; 2 – the EL spectrum of the device ITO/PTA/Zn(PSA-BTZ)$_2$/Al:Ca; 3 – the PL spectrum of Zn(PSA-BTZ)$_2$ powder. (b): 1 - the EL spectrum of the device ITO/NPD/Zn(DFP-SAMQ)$_2$/Al:Ca; 2 – the EL spectrum of the device ITO/PTA/Zn(DFP-SAMQ)$_2$/Al:Ca; 3 – the PL spectrum of Zn(DFP-SAMQ)$_2$ powder.

Results and Discussion

The chemical structures of the molecules under study are given below in Scheme 1. The oligomer molecule PTA normally contains about 8-9 monomer elements [5]. The quantum chemical calculations of the adduct of PTA and zinc complex were performed using a model molecule PTA2 which is a dimeric analog of PTA.

The EL Spectra

Typical EL spectra of the devices based on (PSA-BTZ)$_2$ and Zn(DFP-SAMQ)$_2$ complexes are shown in Fig. 1 together with the PL spectra of (PSA-BTZ)$_2$ and Zn(DFP-SAMQ)$_2$ powders. For the devices which contain NPD contacting with a zinc complex in the hole transporting layer, the EL spectra exhibit two bands: the first in the region of 450 nm and

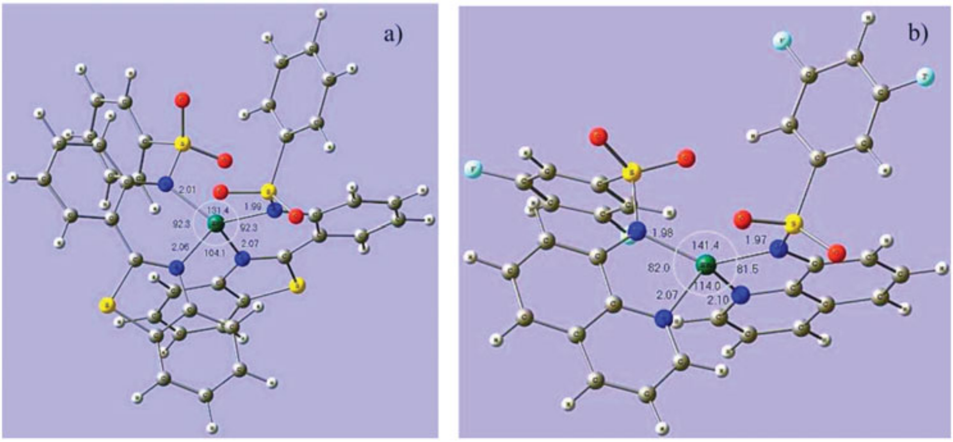


Figure 2. Optimized coformations of Zn(PSA-BTZ)$_2$ (a) and Zn(DFP-SAMQ)$_2$ (b) complexes.

the second in the region of 550 nm. The short-wavelength bands are due to the intrinsic emission of the zinc complexes (and are close to the PL spectra of corresponding zinc complex powder), and the long-wavelength bands are due to the formation of the exciplex between the molecule of a zinc complex and the molecule of the material of a hole-transporting layer [1–4]. It should be noted that the intrinsic EL band is observed only for devices with NPD as a hole-transporting material, and the strong dependence of the intensity of this band on the NPD layer thickness is observed [1–4]. When PTA is the material of a hole transporting layer contacting with the zinc complex layer, only the long-wavelength exciplex band is observed [1–4].

Quantum Chemical Calculations

Preliminary, the geometry of the molecules under study was optimized. Optimized conformations of Zn(PSA-BTZ)$_2$ and Zn(DFP-SAMQ)$_2$ complexes and of PTA2 and NPD molecules are shown in Figs. 2 and 3. In the optimized structure of the Zn(PSA-BTZ)$_2$ complex, the lengths of Zn-N bonds are 2.06 and 2.07 Å for coordination bonds with nitrogen atoms in heterocycles and some shorter values 2.01 and 1.99 Å for the bonds with nitrogen atoms of sulphanylamino groups. For the Zn(DFP-SAMQ)$_2$ complex, the corresponding values (2.07, 2.10 Å and 1.98, 1.97 Å) are practically the same. This is in consistency with the known experimental data for zinc complexes with nitrogen-containing heterocycles [10–12], where the values of the Zn-N coordination bonds with a nitrogen atom in heterocycles are in the region of 2.06-2.17 Å. These data coincide also well with the results of the previous quantum chemical calculation of the Zn(DFP-SAMQ)$_2$ complex by the b3LYP method [13], where corresponding values of Zn-N bond lengths are 2.118 and 1.981 Å.

The optimized structures of adducts of PTA2 and Zn(PSA-BTZ)$_2$ and Zn(DFP-SAMQ)$_2$ complexes are shown in Fig. 4. The optimized structures of adducts of NPD and Zn(PSA-BTZ)$_2$ and Zn(DFP-SAMQ)$_2$ complexes, which have typical close van-der-Waals contacts between components, are shown in Fig. 5. The ZnN bond lengths in the zinc complexes included in the adducts are close to those of the free complexes, and there are negligible changes of valence angles. Dipole moments of the adducts Zn(PSA-BTZ)$_2$·PTA2

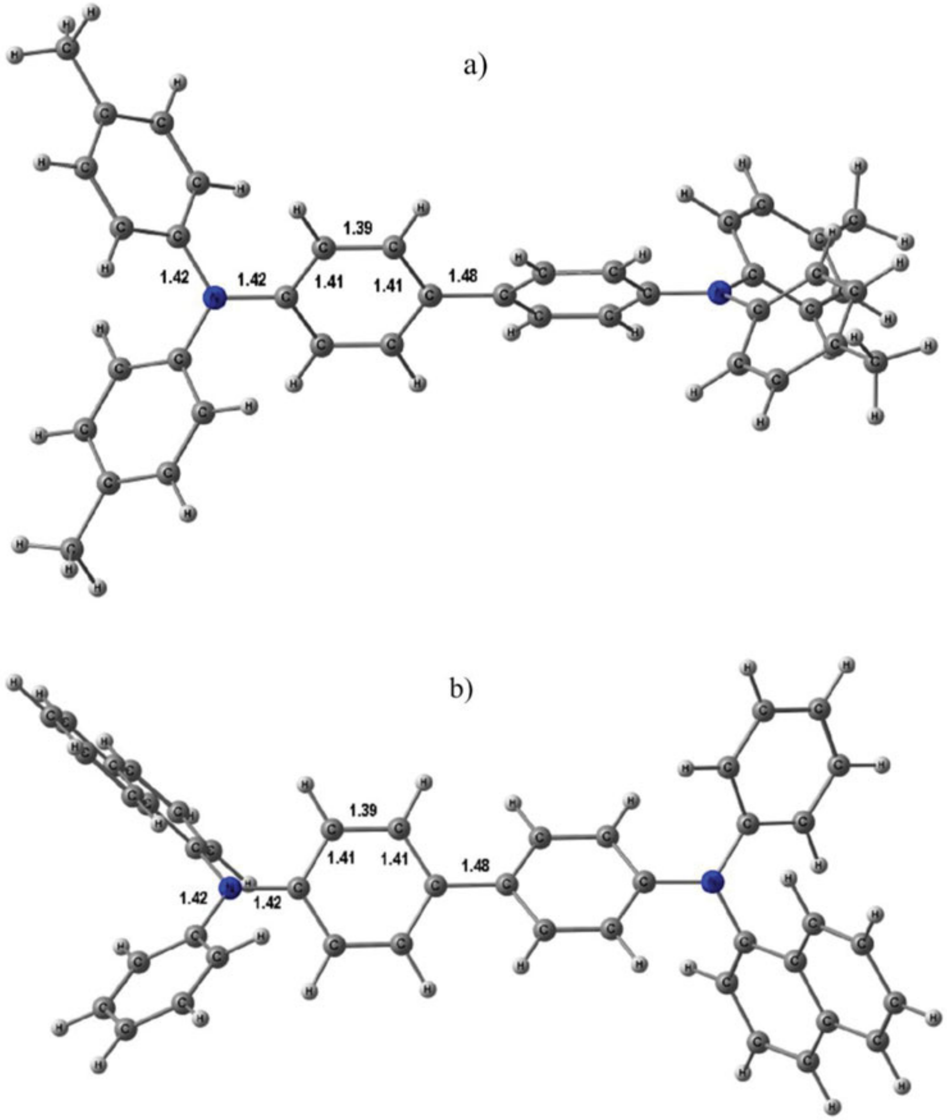


Figure 3. Optimized conformations of PTA2 (a) and NPD (b) molecules.

(6.62 D) and Zn(DFP-SAMQ)$_2$·PTA2 (8.90 D) are close to the dipole moments of the corresponding complexes, 5.81 D and 9.17 D. The dipole moment of PTA2 is about zero, which indicates a rather small charge transfer in the ground states of the adducts. A similar picture was found for the NPD adducts.

We have calculated Kohn–Sham highest occupied and lowest unoccupied energy levels, which are approximately equal to positions of HOMO and LUMO for the zinc complexes, for PTA2 and NPD, as well as for the adducts of PTA or NPD and the zinc complexes. Figure 6 shows the scheme of energy levels for standard EL devices based on the zinc complexes and PTA or NPD as a hole-transporting layer. The calculated energies of HOMO

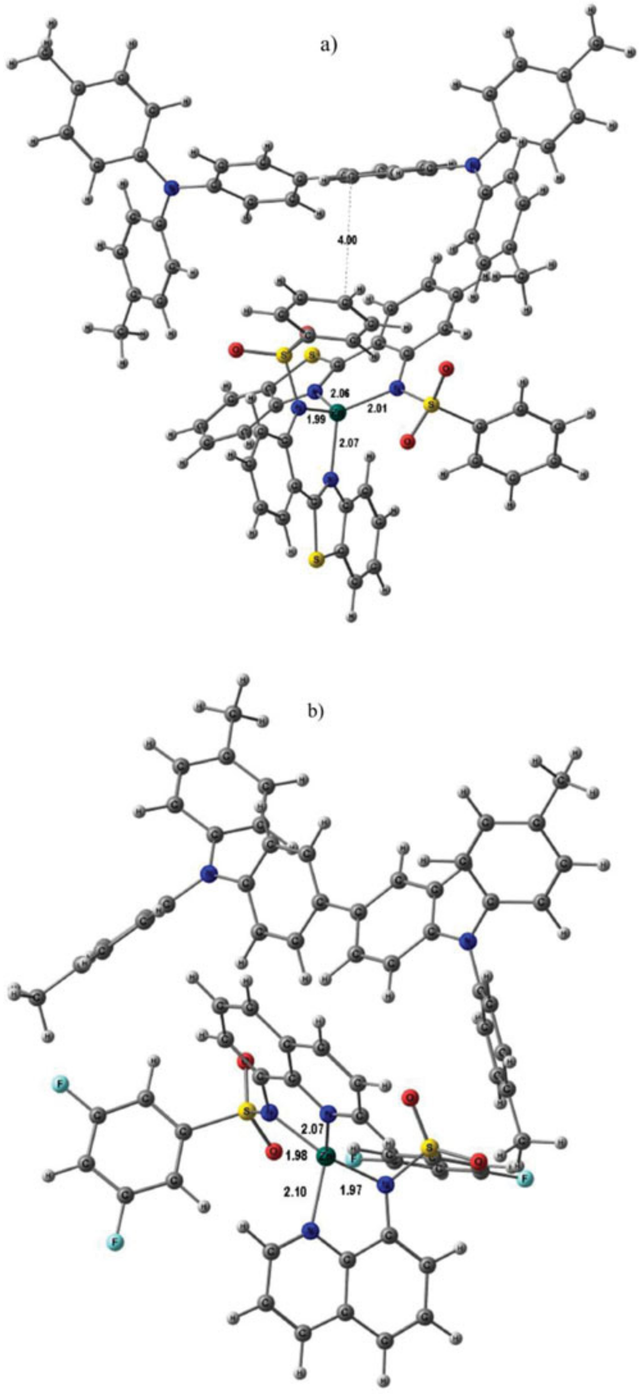


Figure 4. Optimized structures of adducts of PTA2 and Zn(PSA-BTZ)$_2$ (a) and of PTA2 and Zn(DFP-SAMQ)$_2$ (b).

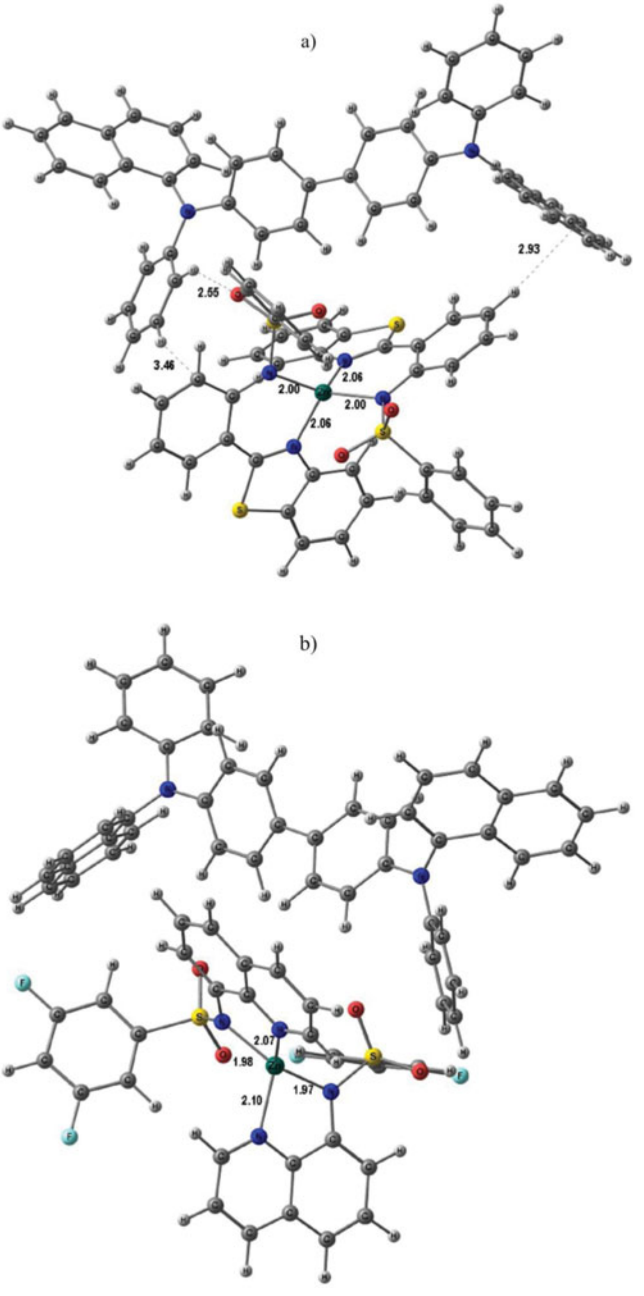


Figure 5. Optimized structures of adducts of NPD and Zn(PSA-BTZ)$_2$ (a) and of NPD and Zn(DFP-SAMQ)$_2$ (b).

and LUMO are shown together with the known work functions of Al and ITO. For NPD, the calculated LUMO energy of 2.25 eV is close to the experimental value 2.3-2.4 eV [14–16] and the calculated HOMO energy of 4.41 eV is slightly less than the experimental value 5.1-5.5 eV [14–16]. HOMO for NPD consists of two degenerated levels.

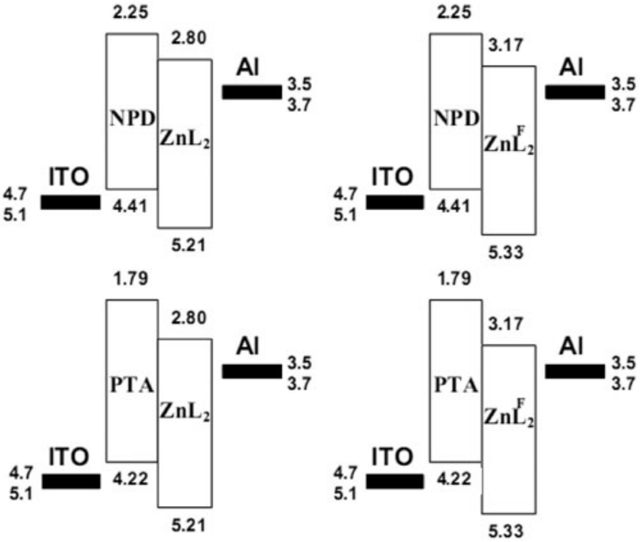


Figure 6. Scheme of energy levels (L = PSA-BTZ, L^F = DFP-SAMQ).

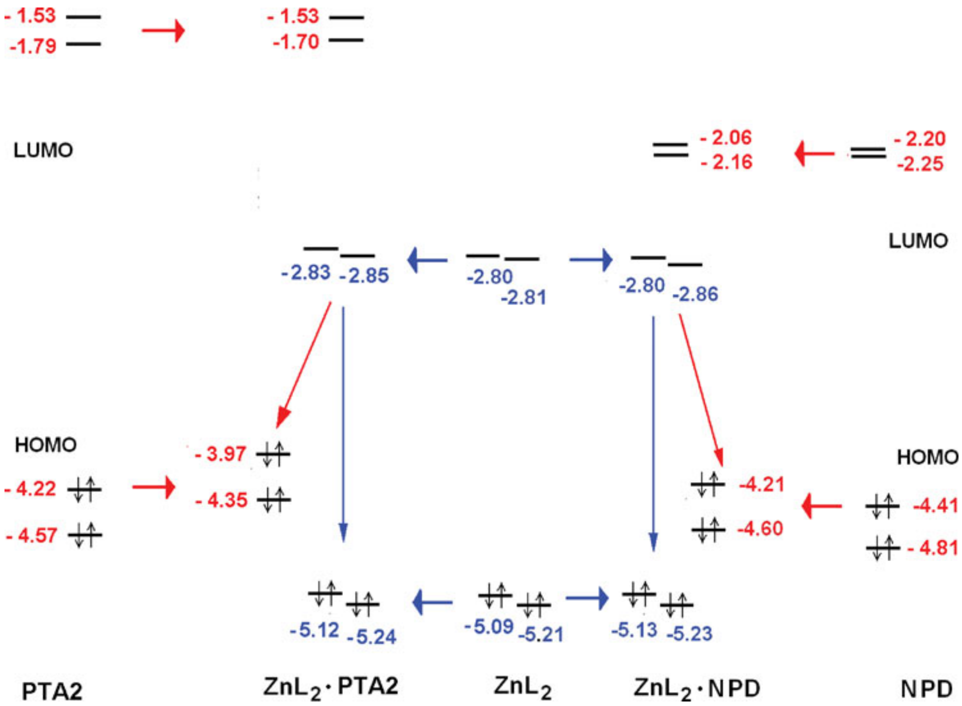


Figure 7. Scheme of electronic levels of ZnL_2, L = PSA-BTZ, complex, PTA2, NPD and their adducts. Vertical arrows indicate electronic transitions.

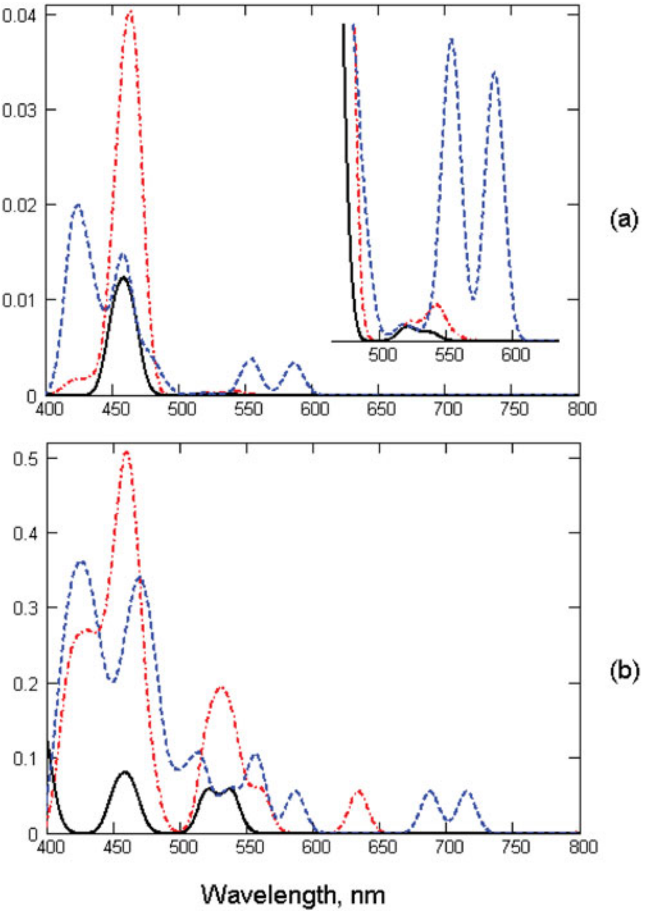


Figure 8. Calculated absorption spectra (a) and densities of excited states (b): Zn(PSA-BTZ)$_2$, (solid line) Zn(PSA-BTZ)$_2$ – PTA2 adduct, (dash-dot line) Zn(PSA-BTZ)$_2$ – NPD adduct (dot line)

Figure 7 shows the typical scheme of energy levels and electronic transitions for the adduct Zn(PSA-BTZ)$_2$ complex with PTA2 and NPD. For the complex, HOMO consists of two closely positioned levels originating from the two ligands with energy splitting due to the interaction with a Zn atom. For the adduct, HOMO consists of four splitted levels, two of them originate from HOMO of the zinc complex and the other two originate from HOMO and HOMO-1 of the amine component. This leads to a possibility of two types of electronic transitions from the excited state to the ground state: a) high-energy (short-wavelength) transition to the energy levels originating from the zinc complex, which may be considered as the intrinsic transitions of the zinc complex; b) low-energy (long-wavelength) transition to the energy levels originating from NPD, which may be considered as the exciplex transition. There is a noticeable difference in the positions of LUMO in PTA2 (−1.79 eV) and NPD (−2.25 eV). It results in a qualitative distinction in the ordering of excited states of NPD and PTA2 adducts. In the first case, the levels originated from LUMOs of the components are adjacent. But, in the second case, there are a lot of levels of excited states (−2.02, −1.76 and 1.76 eV) localized on the complex.

Figure 8a shows the calculated absorption spectra of Zn(PSA-BTZ)$_2$ and of the adducts Zn(PSA-BTZ)$_2$/PTA2 and Zn(PSA-BTZ)$_2$/NPD. The calculated absorption spectrum of Zn(PSA-BTZ)$_2$ contains two most intensive bands about 350 and 460 nm which may be compared to the experimental values of 310 and 390 nm [17]. For the adducts, the experimental absorption spectra cannot be measured because of the extremely small thickness of the interface of a zinc complex and a hole transporting layer.

From Fig. 8a, it is seen that the adduct formation lead to an enhancement of the optical transitions, but it is rather different for PTA2 and NPD amines. In the first case, there is only almost the four-time increase of the 460-nm band. But in the second case, this band is practically the same, whereas strong new bands appear as satellites at higher and lower wavelengths. It is more clearly seen in the distribution of the densities of excited states in Fig. 8b. As for the qualitative difference between EL spectra of the systems based on PTA (presumably exciplex band) and NPD (comparable bands of intrinsic and exciplex emission), it may be caused by several factors. In the electroluminescence device, the excited state is formed due to the electron transport in the zinc complex layer and the hole transport in the amine layer. It is hard to model this process, but we note that, according to the calculated densities of excited states in the PTA case, there is a higher probability of the formation of states corresponding to a lower energy (peak at 525 nm in Fig. 8b). This corresponds to the observed enhancement of the exciplex emission in EL spectra. Moreover, the overall line width of satellite emission (from 500 nm to 650 nm) well corresponds to the observed more narrow EL band for the ITO/PTA/Zn(PSA-BTZ)$_2$/Al:Ca device. In the NPD case, the calculated additional excited states of the adduct are spread in the region from 500 to 725 nm, which also corresponds well to the wider exciplex EL band for the ITO/NPD/Zn(PSA-BTZ)$_2$/Al:Ca device.

Conclusion

To model the spectra of the light-emitting devices based on zinc complexes of amino-substituted ligands, the spectra of the adduct containing one molecule of the zinc complex and one molecule of the hole-transporting material are calculated using the PBE density functional method. The calculated scheme of energy levels and electronic transitions for the adduct gives an opportunity to interpret the observed emission spectra containing the intrinsic bands of the zinc complex and exciplex bands originating from the interaction of a zinc complex molecule and a molecule of the hole-transporting material.

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