

# MODELLING OF EXCITED-STATE PROPERTIES OF NOVEL PHOSPHORESCENT IRIIDIUM COMPLEXES

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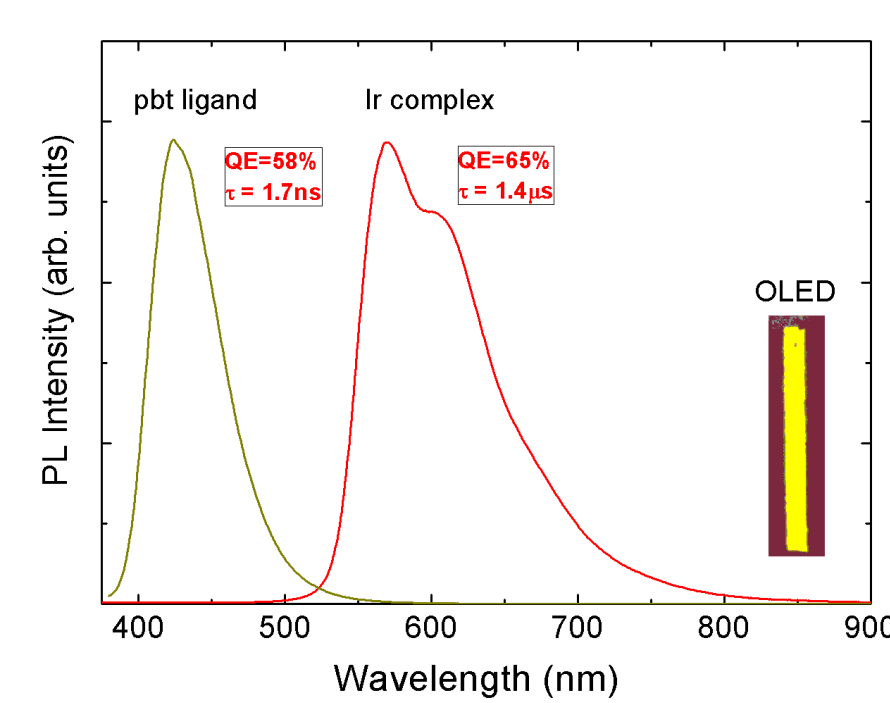
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## Overview

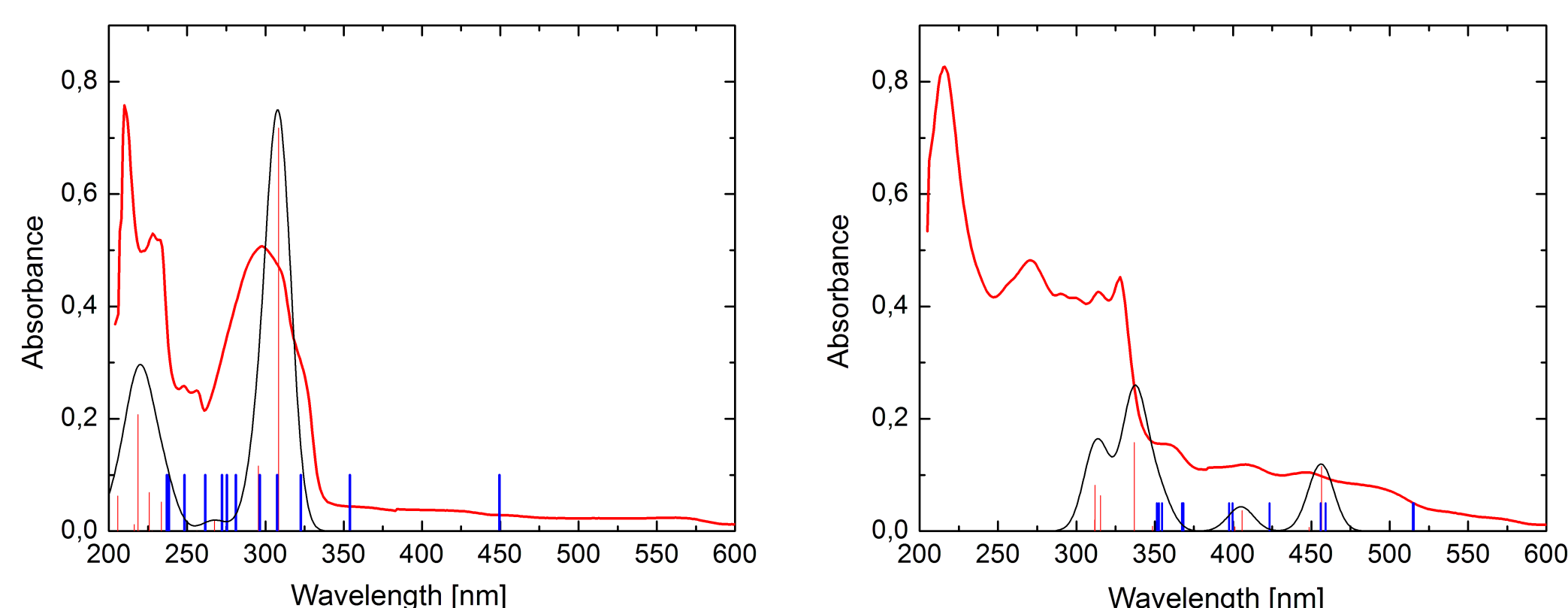
Organic light-emitting diodes (OLEDs) are among the most promising light sources for modern electronic devices and lighting systems [1], especially those that make use of special properties exclusive to the organic semiconducting materials, such as transparency or flexibility. Organic devices also have potential to be scaled down to the dimensions of a single molecule (few nm to tens of nm), which makes them suitable prospects for the next miniaturization phase. OLEDs are usually made of several layers of different organic materials, each layer having a specific function. Molecular complexes containing heavy metal atom, such as Pt or Ir, are regarded as one of the most promising materials for light-emitting layer of OLEDs because of their high efficiency and wavelength tunability [2,3]. Theoretical and experimental research of such compounds is therefore crucial in development of OLED devices.

Here we present results based on quantum-chemical calculations of structural and electronic properties of bis(2-phenylbenzothiazole)-iridium-acetylacetonate ((pbt)<sub>2</sub>Ir(acac)) molecular complex and its derivatives. Molecular structure and excited-state properties of the compounds are determined using several computational models; the results are compared between the models and to the experimental data. The calculations were performed using *Gaussian03* and *GAMESS-US* programs. The molecular structure of the compounds was optimized using density functional theory (DFT) with B3LYP functional and cc-pVDZ/6-31G(d,p) valence basis sets (effective core potential basis set lanl2DZ was used to describe iridium atom), as well as model core potential approach with triple-zeta valence basis set (MCP-TZP, as implemented in *GAMESS-US*). Singlet and triplet excitation properties were obtained using TD-DFT approach.

## Absorption and luminescence spectra

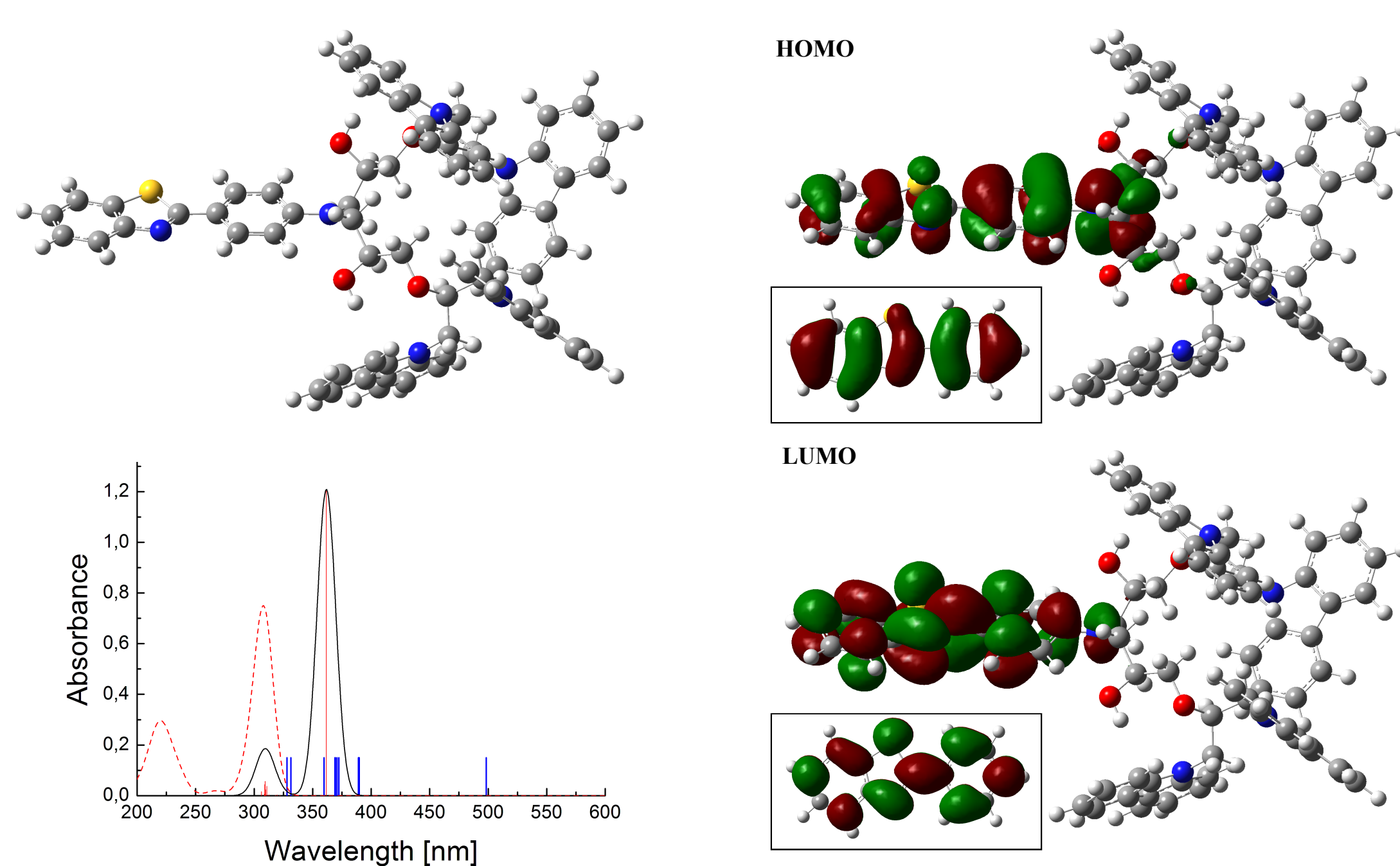


Experimental photoluminescence spectra of pbt ligand and Ir complex



Electronic excitations of pbt ligand (left) and (pbt)<sub>2</sub>Ir(acac) complex (right). Singlet states (red lines), triplet states (blue lines), theoretical absorption spectrum (black curve) and experimental data (red curve) are shown

## Properties of 4-carbazole pbt ligand (V-520)

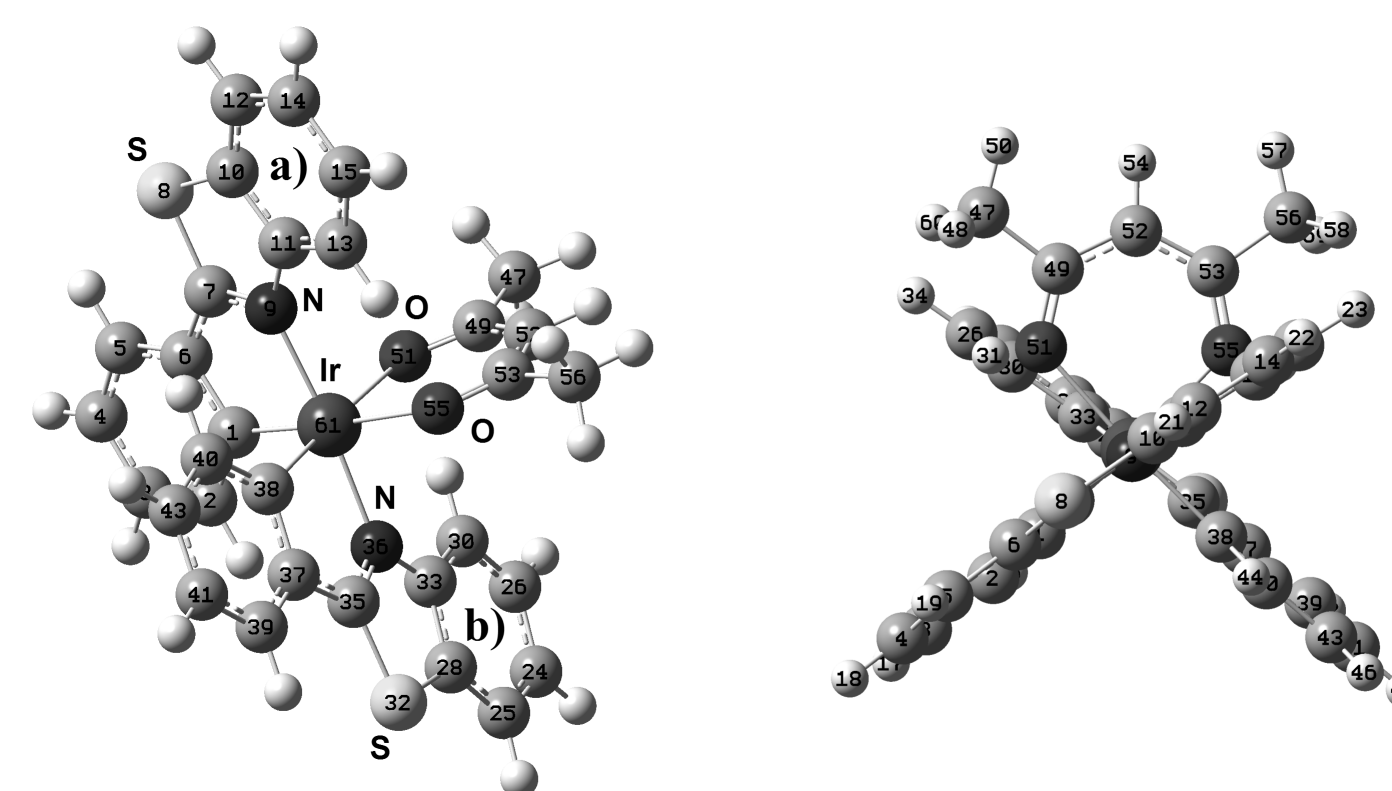


Molecular structure, electronic excitations (bottom left) and HOMO/ LUMO orbitals (right) of 4-carbazole pbt ligand. Singlet states (thin red lines), triplet states (thick blue lines), theoretical absorption spectrum (solid black line) and spectrum of pbt ligand (dashed red line) are shown in excitation graph. Respective orbitals of separate pbt ligand are pictured in boxes next to V-520

## References:

- [1] C. W. Tang, S. A. Vanslyke, *Appl. Phys. Lett.*, **51**, 913 (1987)
- [2] C. Jiang, W. Yang, J. Peng, *Adv. Mater.*, **16**, 537 (2004)
- [3] S. Lamansky, P. Djurovitch, D. Murphy, *J. Am. Chem. Soc.*, **123**, 4304 (2001)
- [4] K. Šviderek, P. Paneth, *J. Phys. Org. Chem.*, **22**, 845 (2009)

## Molecular structure of pbt ligand and (pbt)<sub>2</sub>Ir(acac) complex

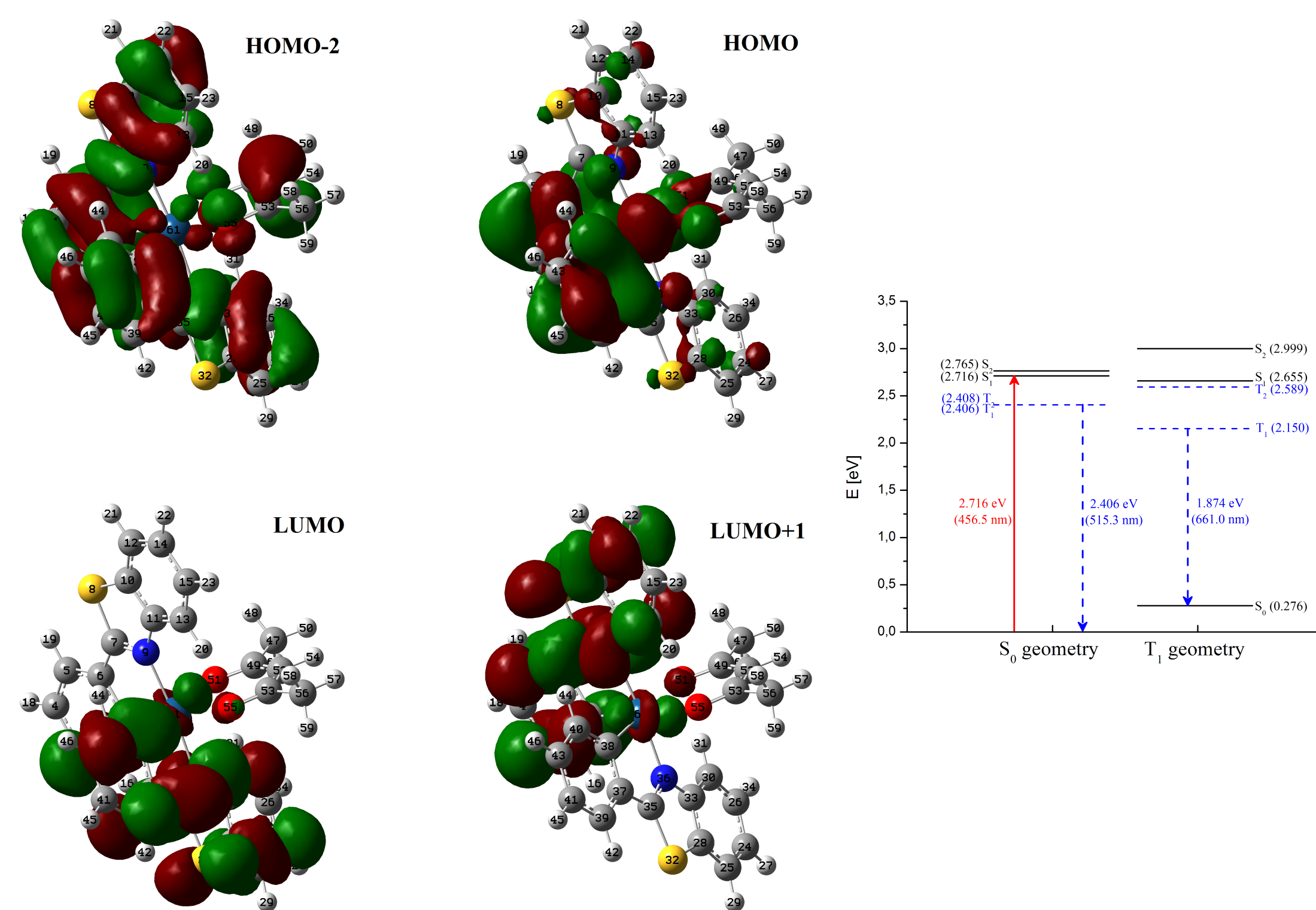


Molecular structure of (pbt)<sub>2</sub>Ir(acac) complex. Two 2-phenylbenzothiazole (pbt) ligands are marked a) and b). Similar structures are reported in theoretical studies of related materials [4]

	Separate	V-520	Complex, S <sub>0</sub> geometry		Complex, T <sub>1</sub> geometry	
			ligand a	ligand b	ligand a	ligand b
C <sub>1</sub> -S <sub>1</sub>	1,7517	1,7522	1,7599	1,7604	1,7718	1,7592
C <sub>1</sub> -S <sub>2</sub>	1,7905	1,7994	1,7512	1,7521	1,7724	1,7488
C <sub>1</sub> -N <sub>1</sub>	1,3006	1,3009	1,3264	1,327	1,4091	1,3245
C <sub>1</sub> -C <sub>2</sub>	1,4696	1,4596	1,4422	1,4418	1,388	1,4457
C <sub>1</sub> -C <sub>3</sub>	1,4076	1,4079	1,4266	1,4267	1,4668	1,4249
N <sub>1</sub> -C <sub>2</sub> -S <sub>1</sub>	114,69	114,47	114,2	114,17	112,75	114,26

Calculated bond distances and angles for 2-phenylbenzothiazole as separate compound, with added carbazole groups (V-520) and as part of (pbt)<sub>2</sub>Ir(acac) complex. Bond lengths are given in Å, angles in degrees

## Energy states and excitations of (pbt)<sub>2</sub>Ir(acac) complex



Lowest energy levels of (pbt)<sub>2</sub>Ir(acac) complex at S<sub>0</sub> and T<sub>1</sub> geometries (right) and selected molecular orbitals of (pbt)<sub>2</sub>Ir(acac) complex at S<sub>0</sub> geometry (green and red colors represent positive and negative sign of wavefunction). Red arrow represents singlet excitation at S<sub>0</sub>, blue arrows – triplet excitations at S<sub>0</sub> and T<sub>1</sub>

## Results

The optimized geometries are in good correspondence to the results of theoretical studies of similar compounds, and the absorption spectra agree fairly well with the experimental data (*Absorption and luminescence spectra*). Influence of the polarization continuum solvent model (PCM) to the calculation results was also tested; solvent effects were found to have an impact on excitation properties, while changes in molecule geometry were insignificant for these complexes.

The results of calculations of the lowest-lying singlet and triplet excited states indicate that both excitations are strongly linked to HOMO-LUMO electron transition between iridium atom and one of the two pbt ligands. Because of the identical ligands, the excitation spectrum in the S<sub>0</sub> geometry exhibits pairs of states with very similar excitation energies; however, this symmetry is broken in the T<sub>1</sub> geometry (*Energy states and excitations of (pbt)<sub>2</sub>Ir(acac) complex*). Experimental phosphorescence spectrum with well-resolved vibronic structure indicates ligand-centered character of transitions, which is in line with results of DFT calculations.

Geometry optimization and excited states calculations of the extended ligand with additional carbazole groups and the resulting Ir complex were also carried out to assess the effect of carbazole groups to the wavefunction character of the lowest excited states of the complex. It is shown that wavefunction character in the lowest excited states is not affected by addition of the charge transporting groups (*Properties of 4-carbazole pbt ligand (V-520)*); this is consistent with experimental observations.

