

QUANTUM-CHEMICAL CALCULATIONS OF NOVEL PHOSPHORESCENT IRIIDIUM COMPLEXES

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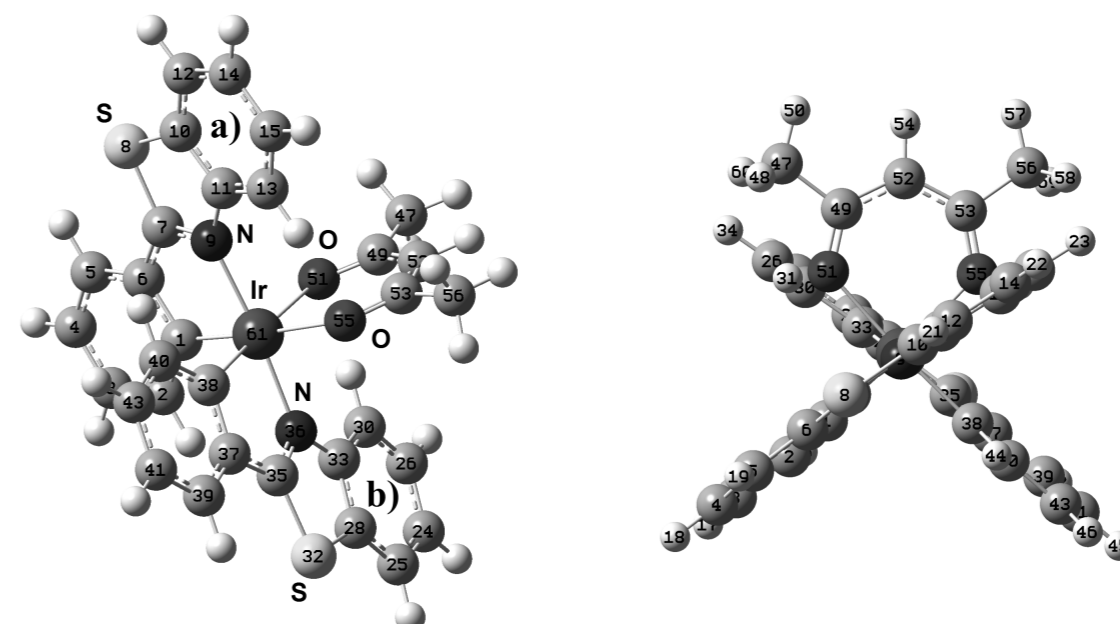
Overview

Organic light-emitting diodes (OLEDs) are one of the most promising light sources for modern electronic devices and lighting systems [1]. 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)₂Ir(acac)) molecular complex and its derivatives. Atomic structure and excitation 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.

Geometries of singlet and triplet energy minima of (pbt)₂Ir(acac) complex (S₀ and T₁) were optimized using DFT B3LYP functional with LanL2DZ effective core potential (ECP) basis set (for iridium atom) and 6-31G(d) valence basis set (for all other atoms). Separate optimizations were performed using IEF-PCM model for THF solvent and without solvent. Another model used for optimizations was model core potential approach with triple-zeta valence basis set (MCP-TZP).

Molecular structure of pbt ligand and (pbt)₂Ir(acac) complex

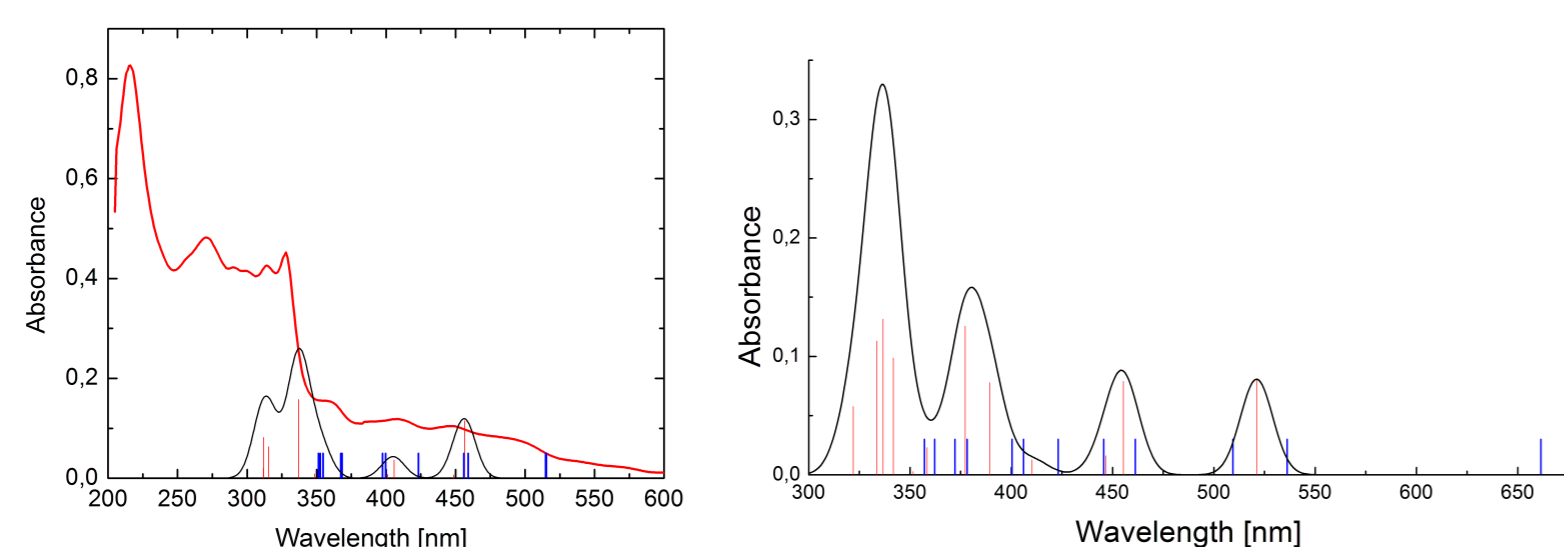


Molecular structure of (pbt)₂Ir(acac) complex. Two pbt ligands are marked a) and b). Similar structures have been observed in theoretical studies of related materials [4]

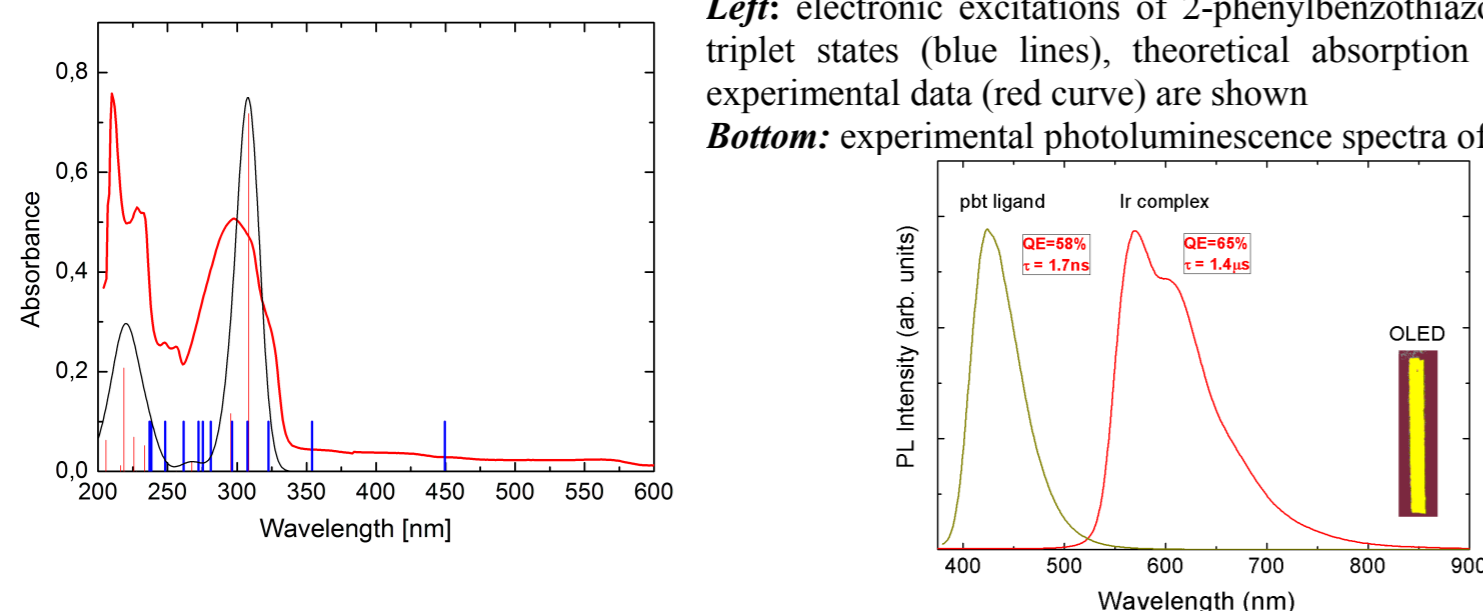
	Separate	V-520	Complex, S ₀ geometry		Complex, T ₁ geometry	
			ligand a	ligand b	ligand a	ligand b
C ₁₀ -S ₈	1.7517	1.7522	1.7599	1.7604	1.7718	1.7592
C ₇ -S ₈	1.7905	1.7994	1.7512	1.7521	1.7724	1.7488
C ₇ -N ₉	1.3006	1.3009	1.3264	1.327	1.4091	1.3245
C ₇ -C ₆	1.4696	1.4596	1.4422	1.4418	1.388	1.4457
C ₁ -C ₆	1.4076	1.4079	1.4266	1.4267	1.4668	1.4249
N ₉ -C ₇ -S ₈	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)₂Ir(acac) complex. Bond lengths are given in Å, angles in degrees

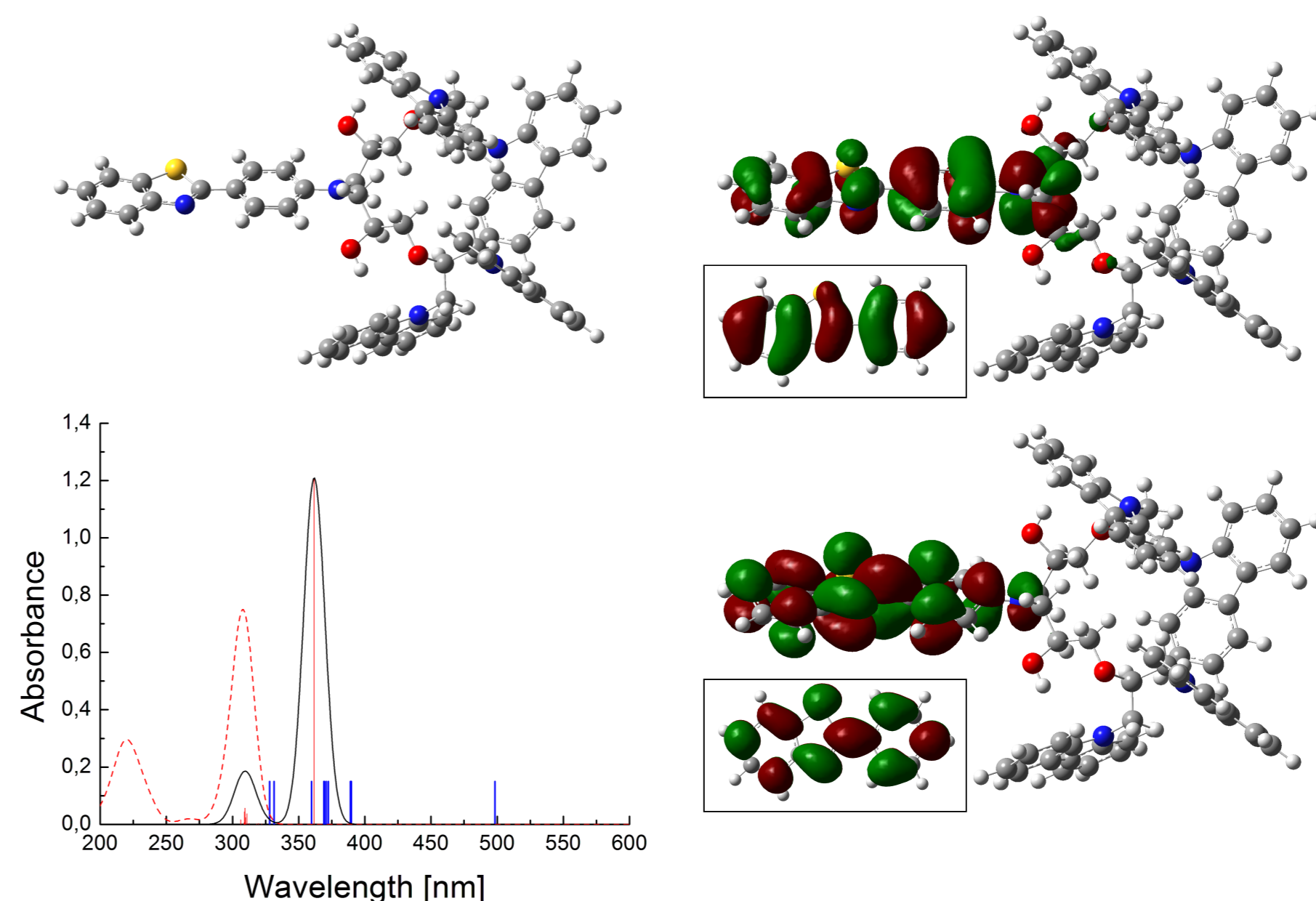
Absorption and luminescence spectra



Top: electronic excitations of (pbt)₂Ir(acac) complex at S₀ (left) and T₁ geometry (right).
Left: electronic excitations of 2-phenylbenzothiazole. Singlet states (red lines), triplet states (blue lines), theoretical absorption spectrum (black curve) and experimental data (red curve) are shown.
Bottom: experimental photoluminescence spectra of pbt ligand and Ir complex

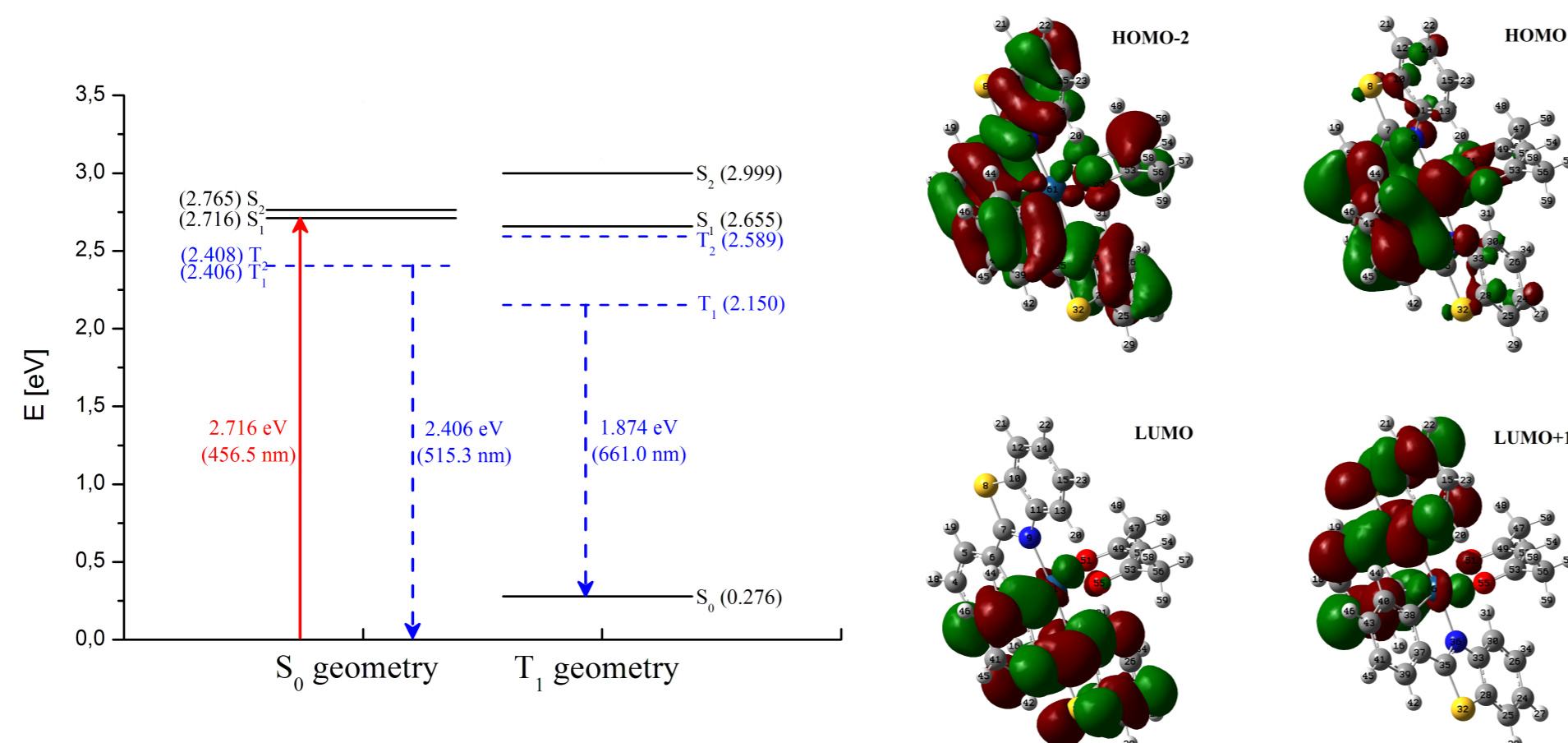


Properties of 4-carbazole pbt ligand



Left: molecular structure (top) and electronic excitations of 4-carbazole pbt ligand: singlet states (thin lines), triplet states (thick lines), theoretical absorption spectrum (solid line) and spectrum of pbt (dashed line). **Right:** HOMO (top) and LUMO (bottom) orbitals of pbt ligand (boxes) and 4-carbazole pbt ligand

Energy states and excitations of (pbt)₂Ir(acac) complex



Left: Lowest energy levels of (pbt)₂Ir(acac) complex at S₀ and T₁ geometries

Right: Selected molecular orbitals of (pbt)₂Ir(acac) complex at S₀ geometry (green and red colors represent positive and negative sign of wavefunction). Both lowest singlet and triplet excitations at S₀ geometry (red and thick blue lines in left graph) involve HOMO, LUMO and LUMO+1. At T₁ geometry slight deformation of the complex results in different energies for excitations to LUMO and LUMO+1, making one of the ligands preferential

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. 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 S₀ geometry exhibits pairs of states with very similar excitation energies; however, this symmetry is broken in the T₁ geometry. 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 performed using the DFT method. It is shown that wavefunction character in the lowest excited states is not affected by addition of the charge transporting groups.

Literature:

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