Frontier orbitals for **IrL2**, **IrL5**, **IrL6**, and **IrL8**; Experimental absorption and emission spectra of **IrL2**, **IrL6-Boc**, **IrL6-TFA**, and **IrL8**, together with calculated singlet and triplet excited state transitions, and estimated emission energy using ΔSCF and TD-DFT approaches (**IrL2**, **IrL6**, and **IrL8**); Contour plots of the spin density of the lowest-lying triplet-state geometry of **IrL2**, **IrL5**, **IrL6**, and **IrL8**; Lowest energy singlet-triplet electronic transition of **IrL5**, **IrL6**, and **IrL8** in their lowest-lying triplet state geometries. Energy diagram of frontier orbitals of complexes **IrL1**, **IrL2**, **IrL5**, **IrL6**, **IrL8, IrLNNH$_2$, IrLCN, and IrLOH**.

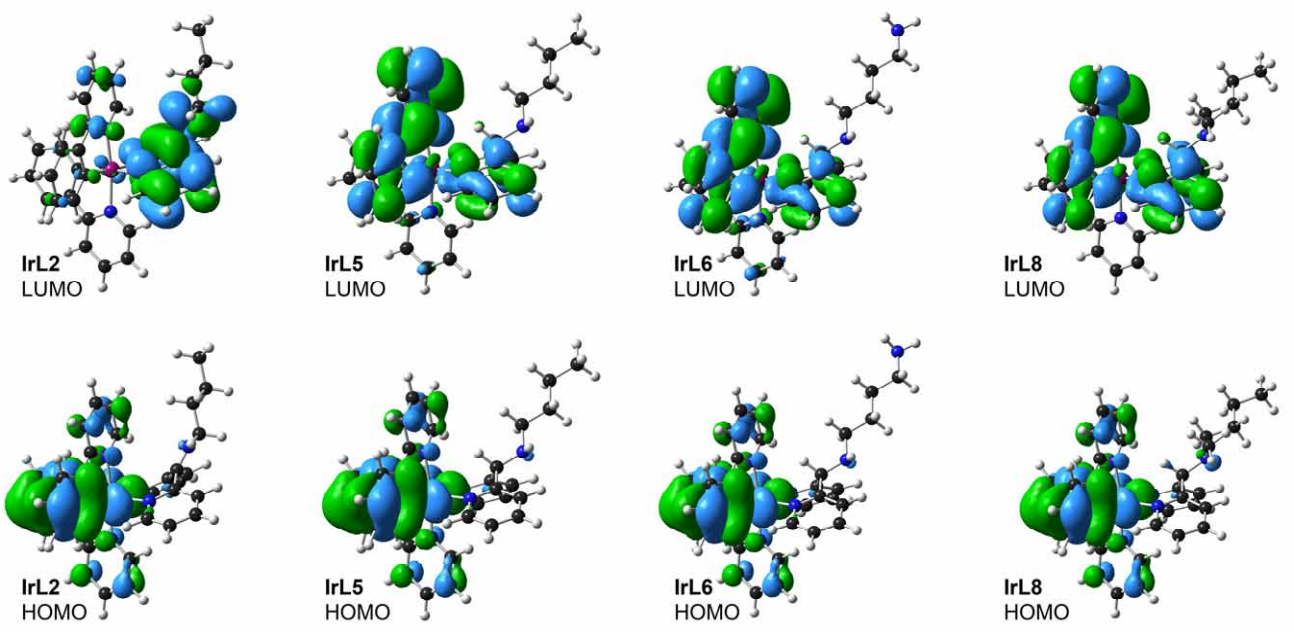


Fig. ESI1 Frontier orbitals for complexes **IrL2**, **IrL5**, **IrL6**, and **IrL8**

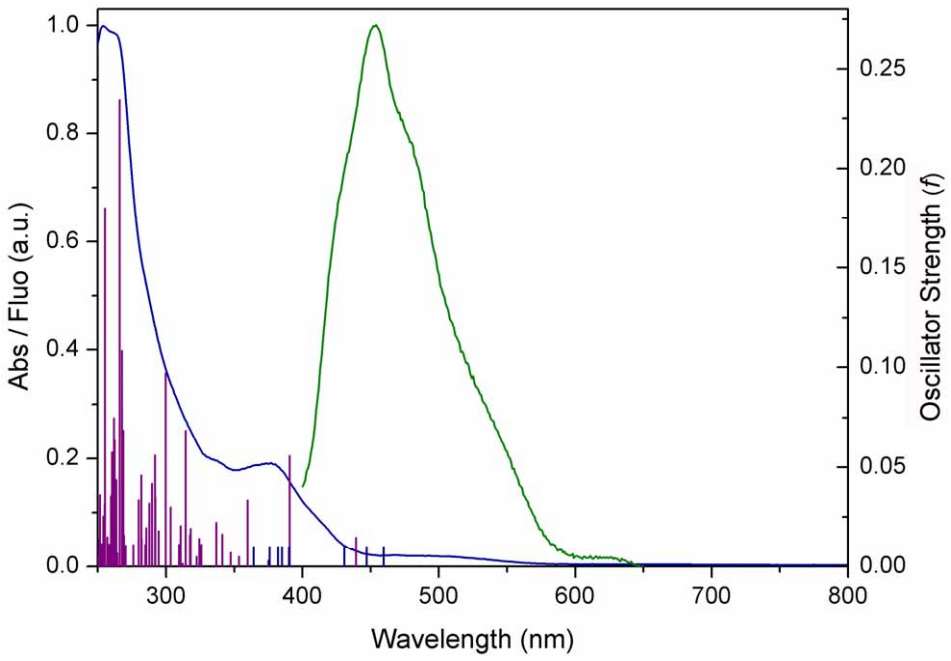


Fig. ESI2 Experimental absorption (blue line) and emission (green line) spectra, calculated singlet (purple bars) and triplet (blue bars) excited state transitions of complex **IrL2** in acetonitrile. The vertical bar height of singlet transitions is equal to the oscillator strength, while the other bars have arbitrary intensity to indicate their position

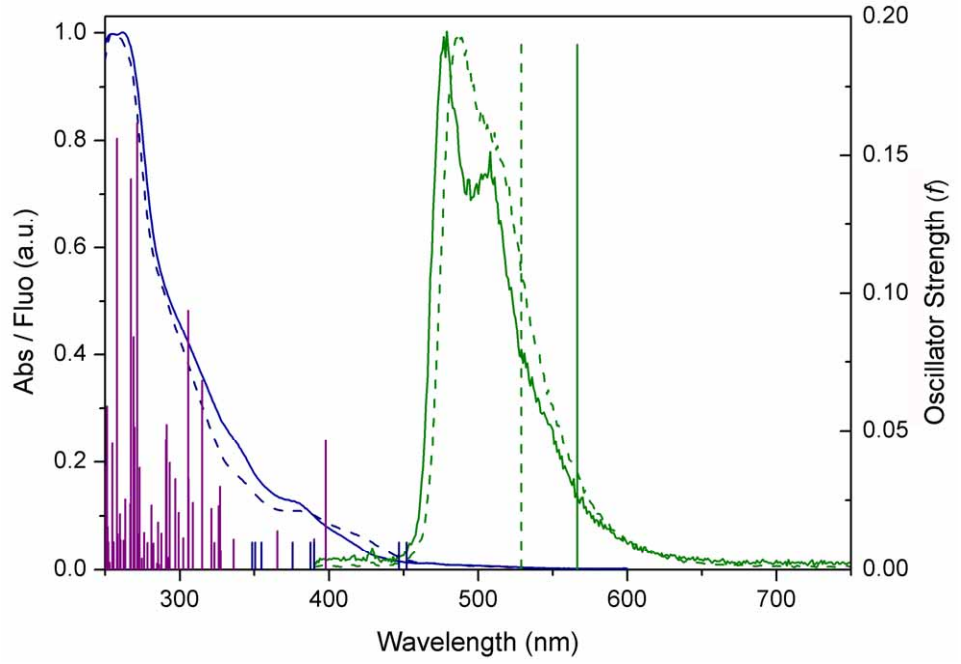


Fig. ESI3 Experimental absorption (blue line) and emission (green line) spectra of **IrL6-Boc** (solid) and **IrL6-TFA** (dashed) in acetonitrile. Calculated singlet (purple bars) and triplet (blue bars) excited state transitions, and estimated emission energy using ΔSCF (dashed green bar) and TD-DFT (solid green bar) approaches, of complex **IrL6** in acetonitrile. The vertical bar height of singlet transitions is equal to the oscillator strength, while the other bars have arbitrary intensity to indicate their position

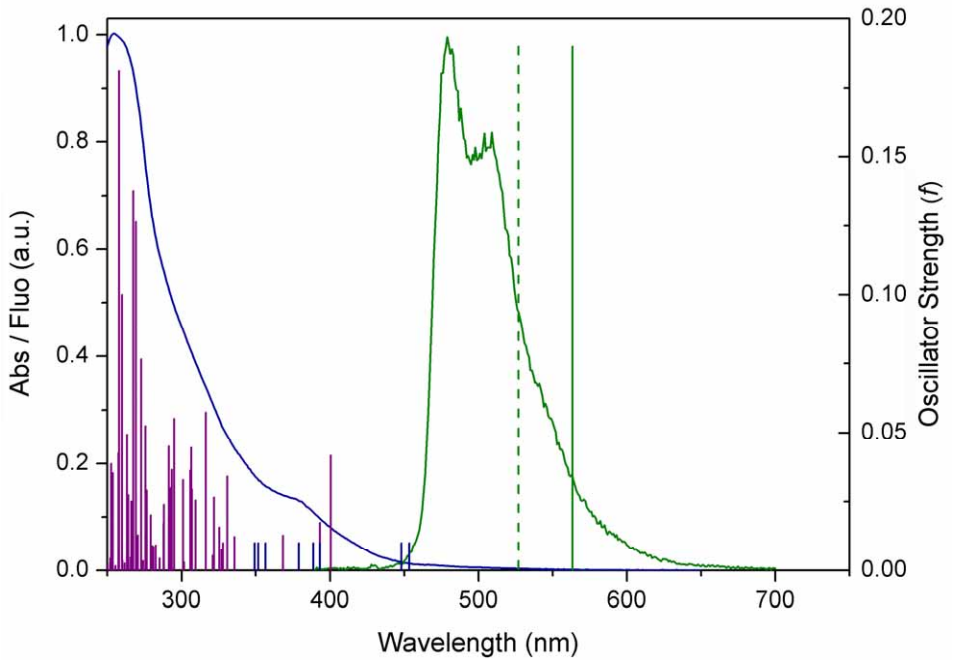


Fig. ESI4 Experimental absorption (blue line) and emission (green line) spectra, calculated singlet (purple bars) and triplet (blue bars) excited state transitions, and estimated emission energy using ΔSCF (dashed green bar) and TD-DFT (solid green bar) approaches, of complex **IrL8** in acetonitrile. The vertical bar height of singlet transitions is equal to the oscillator strength, while the other bars have arbitrary intensity to indicate their position

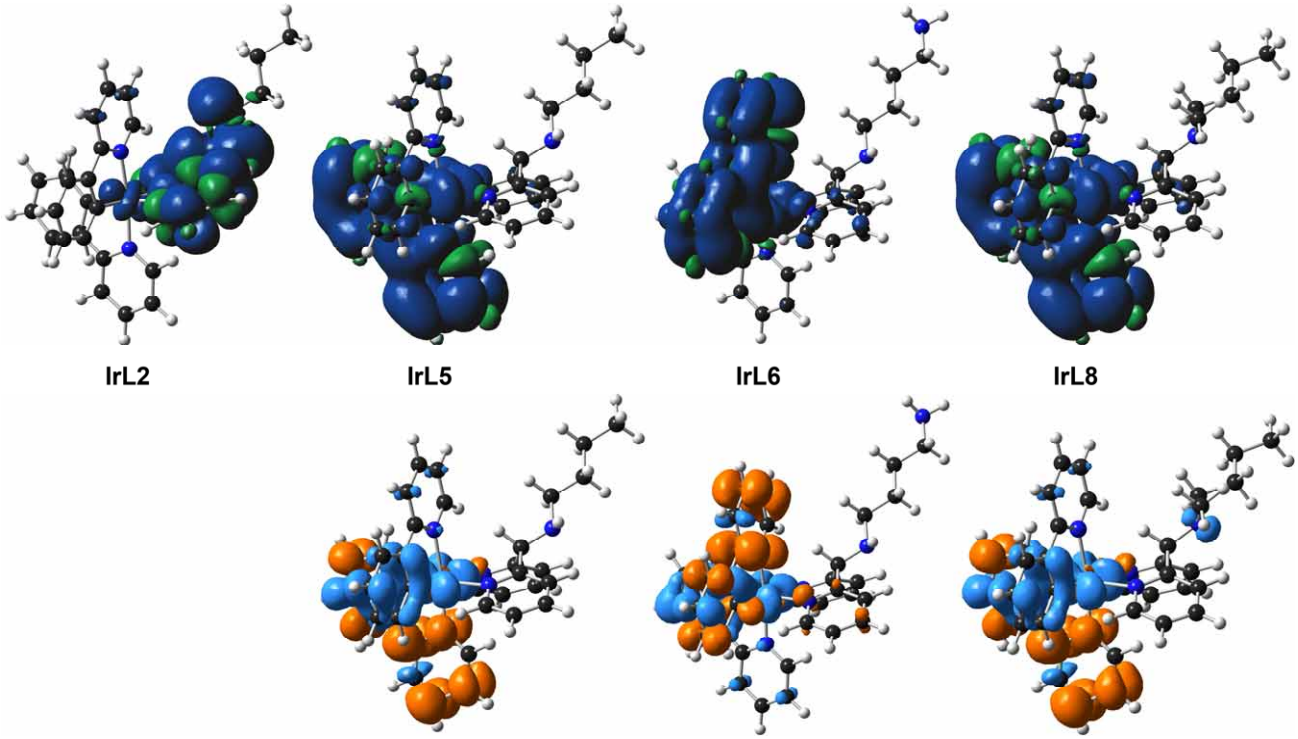
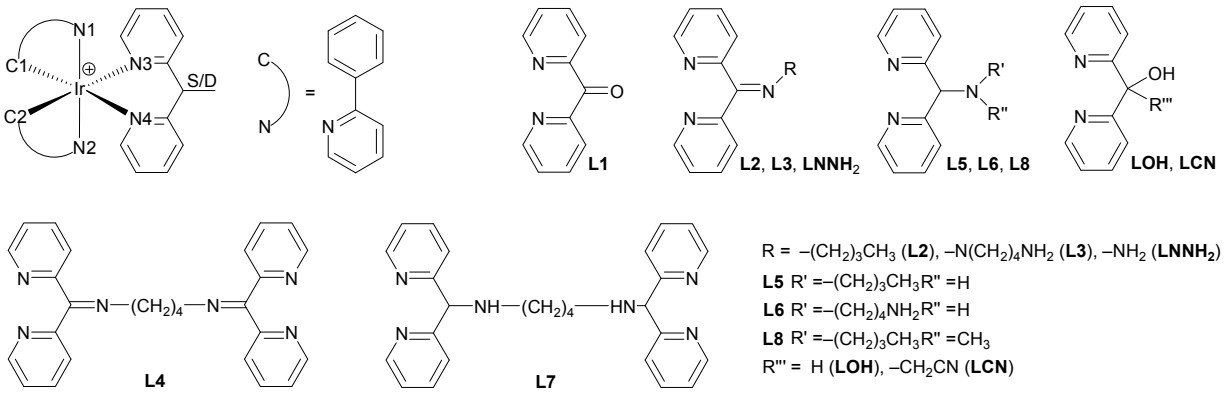


Fig. ESI5 Top: contour plots of the spin density of the lowest-lying triplet-state geometry of **IrL2**, **IrL5**, **IrL6**, and **IrL8** (isovalue=0.004), bottom: electron density difference maps (EDDMs) of the lowest energy singlet-triplet electronic transition of **IrL5**, **IrL6**, and **IrL8** in their lowest-lying triplet state geometries. Blue indicates a decrease in charge density, while orange indicates an increase



Scheme ESI1

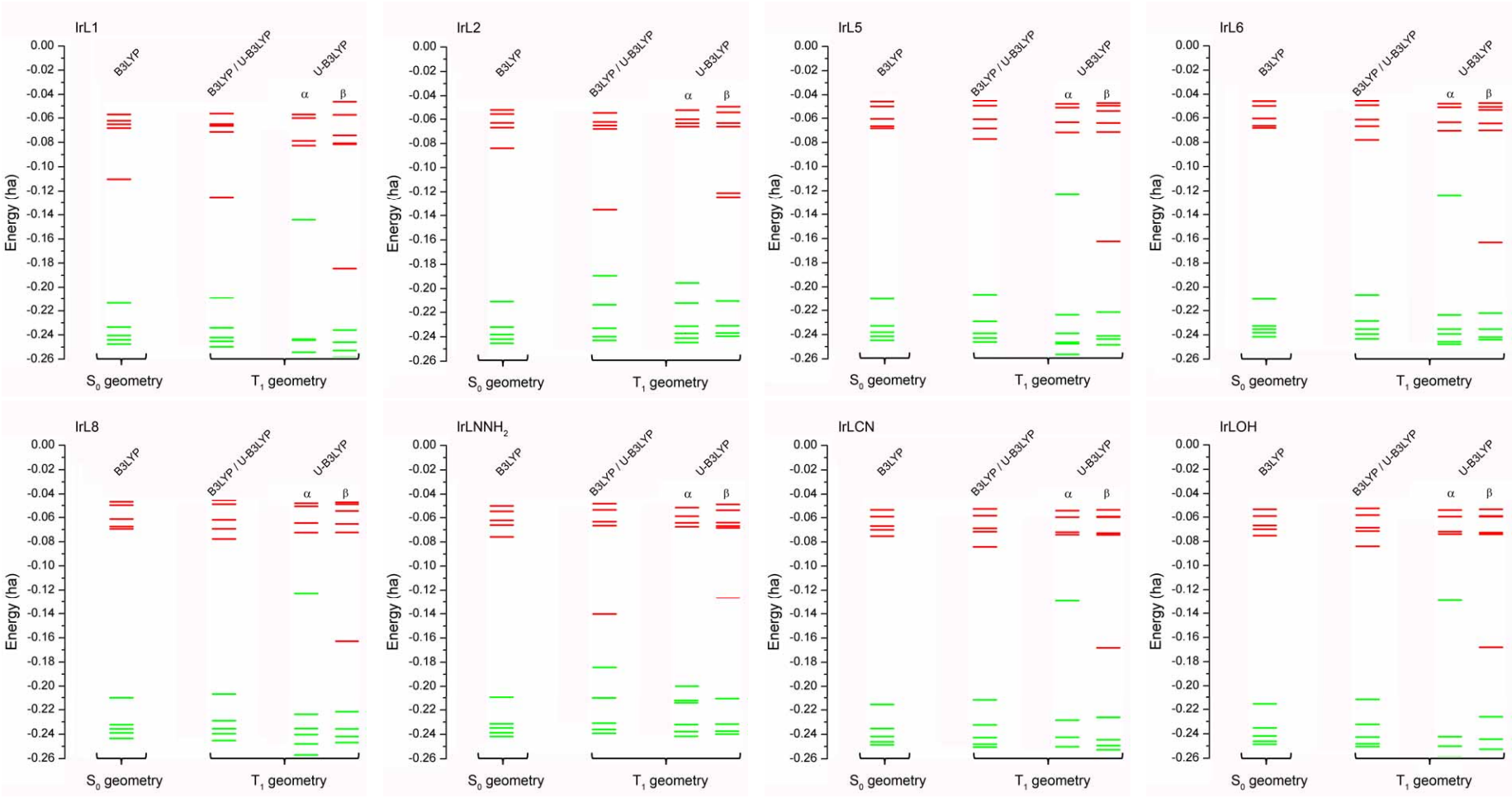


Fig. ESI6 Diagram of occupied (green) and unoccupied (red) frontier orbitals of complexes **IrL1**, **IL2**, **IrL5**, **IrL6**, **IrL8**, **IrLNNH$_2$**, **IrLCN**, and **IrLOH**. Calculated at the ground-state (S_0) and lowest-lying triplet-state (T_1) geometries, with restricted (B3LYP) and unrestricted (U-B3LYP) DFT methods