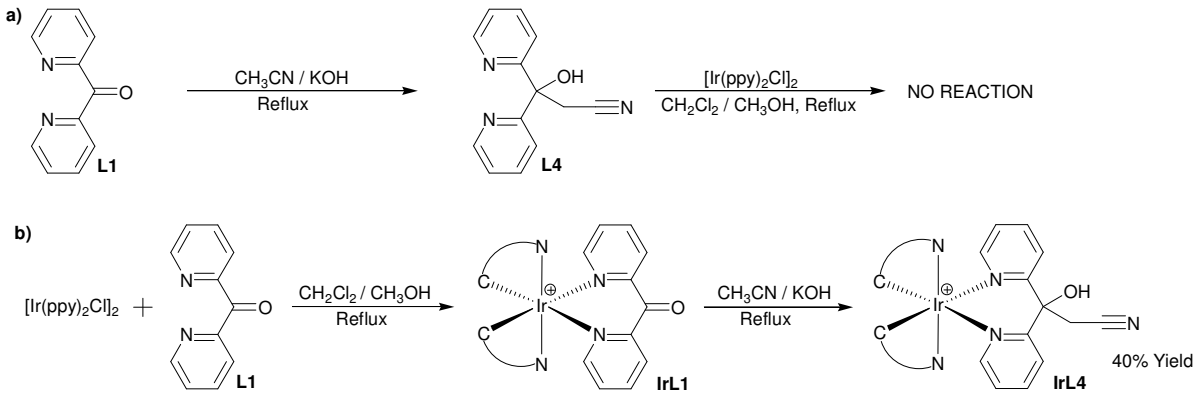

Scheme ESI1 Sketch of the synthetic pathways to **IrL4**

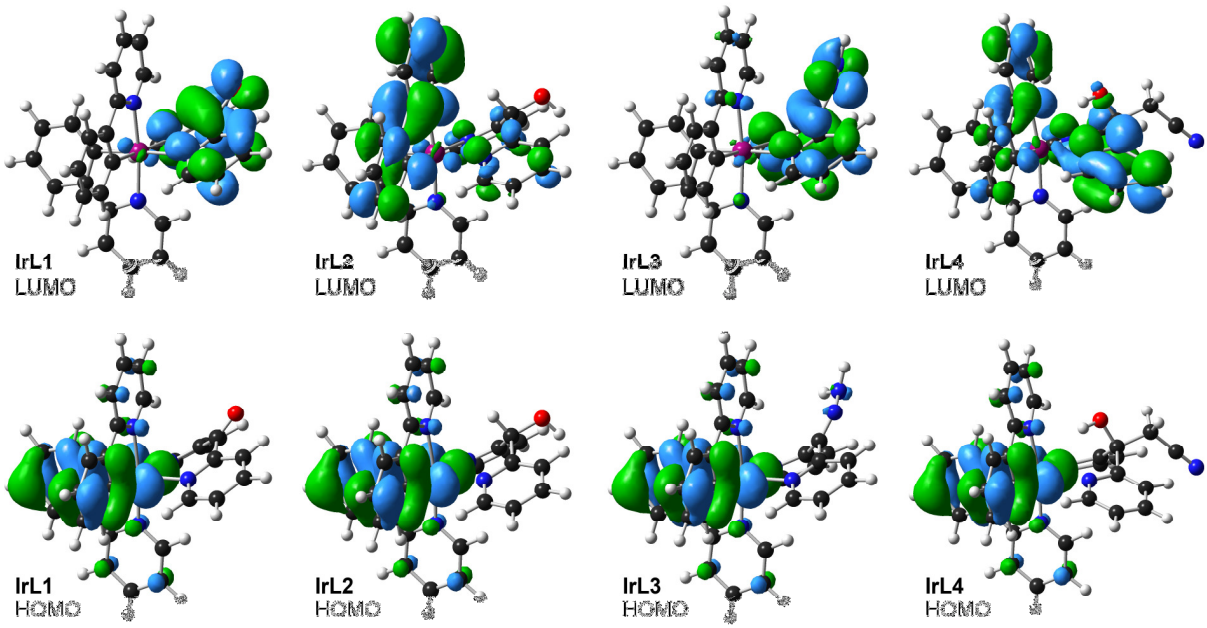

Fig. ESI1 Frontier orbitals for complexes **IrL1–IrL4**

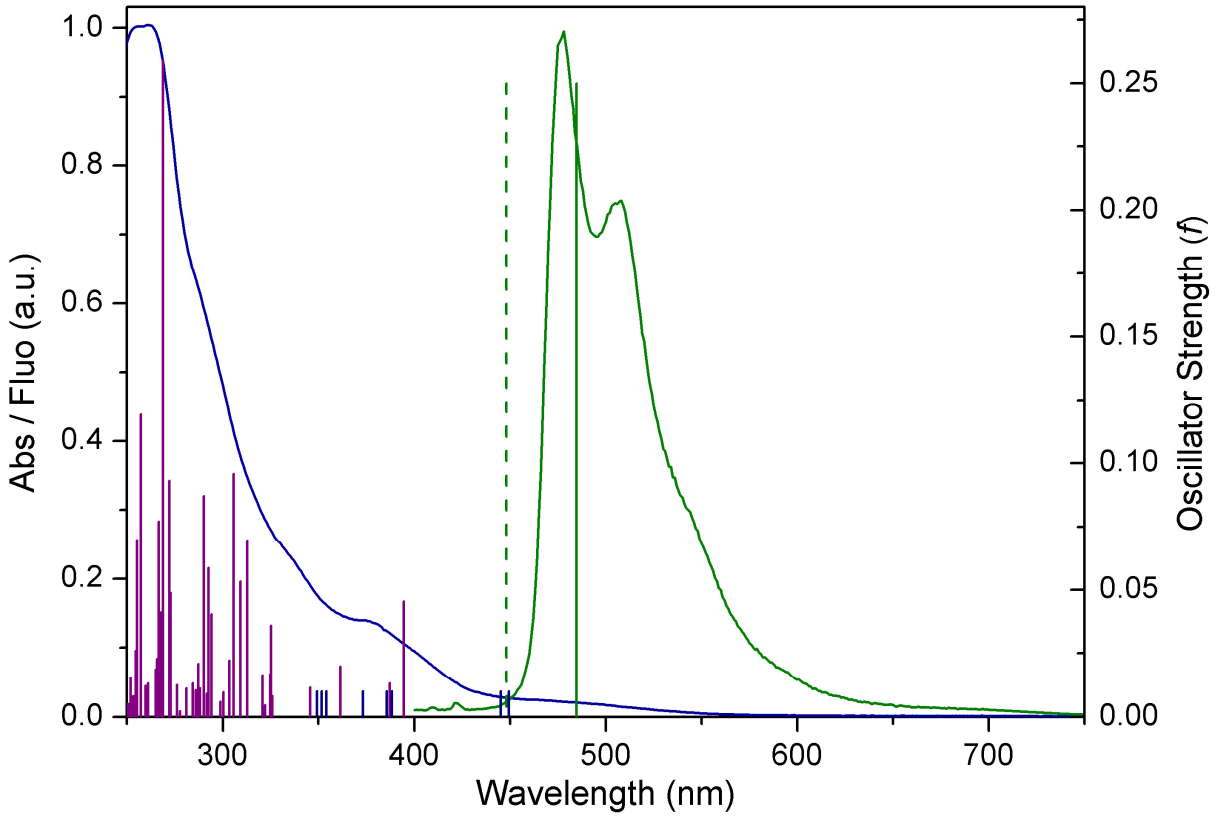

Fig. ESI2 Experimental absorption (blue line) and emission (green line) spectra, calculated singlet (purple bars) and triplet (blue bars) excited state transitions, and estimated emission energy using ΔSCF (dashed green bar) and TD-DFT (solid green bar) approaches, of complex **IrL2** in acetonitrile.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

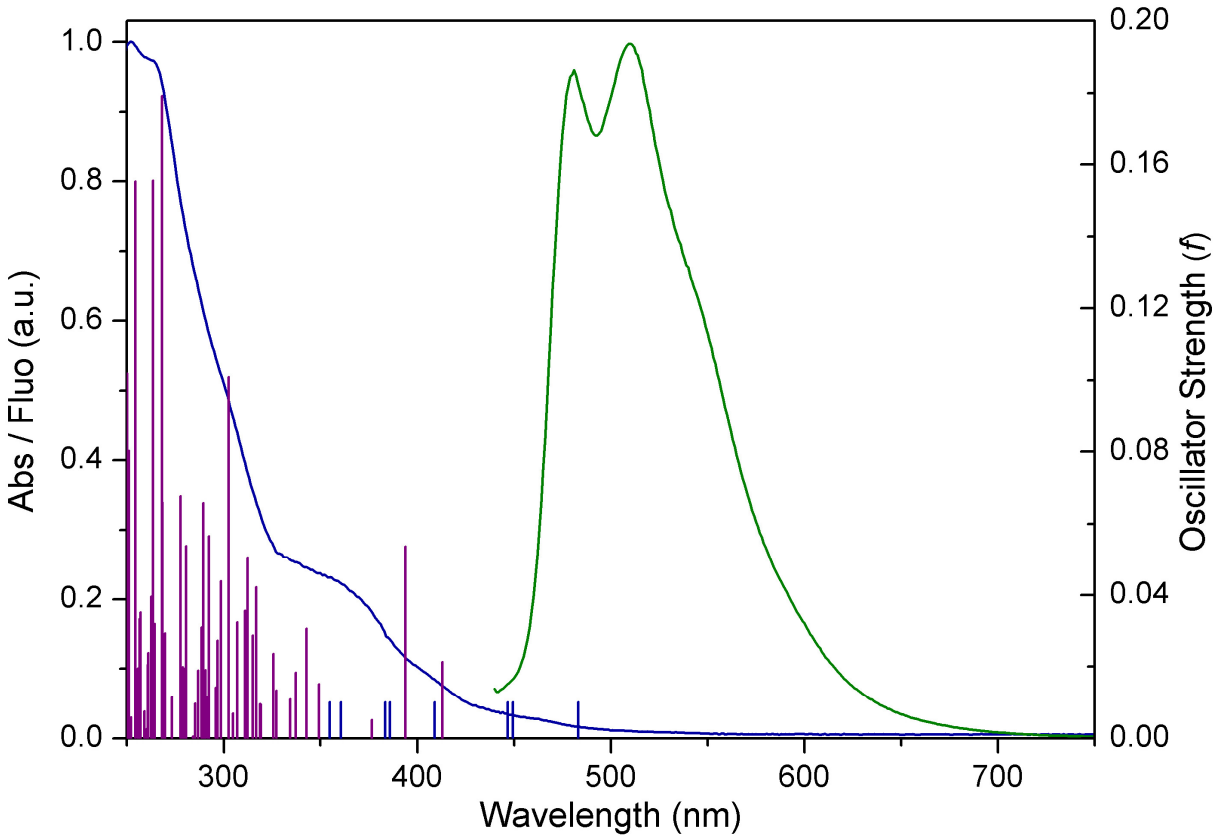

Fig. ESI3 Experimental absorption (blue line) and emission (green line) spectra, calculated singlet (purple bars) and triplet (blue bars) excited state transitions of complex **IrL3** in acetonitrile. The vertical bar height of singlet transitions is equal to the oscillator strength, while the other bars have arbitrary intensity to indicate their position

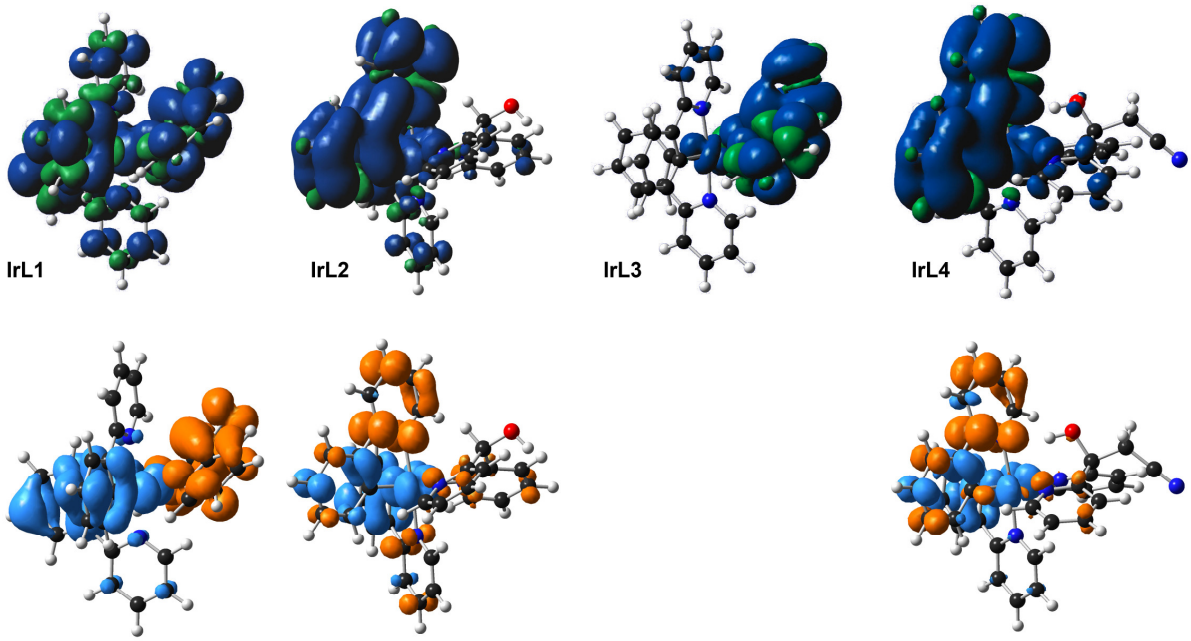

Fig. ESI4 Top: contour plots of the spin density of the lowest-lying triplet-state geometry of **IrL1**–**IrL4** (isovalue=0.004), bottom: electron density difference maps (EDDMs) of the lowest energy singlet-triplet electronic transition of **IrL1**, **IrL2**, and **IrL4** in their lowest-lying triplet state geometries. Blue indicates a decrease in charge density, while orange indicates an increase