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Electronic nature of the emitting triplet in SF<sub>5</sub>-substituted cationic Ir(III) complexesJosé M. Junquera-Hernández<sup>a</sup>, Javier Escobar<sup>a</sup>, Enrique Ortí<sup>a,\*</sup><sup>a</sup> Instituto de Ciencia Molecular, Universidad de Valencia, 46100 Burjassot (Valencia), Spain

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## Abstract

A theoretical density functional theory study has been performed on a family of cationic iridium (III) complexes of the form [Ir(C<sup>^</sup>N)<sub>2</sub>(dtBubpy)]<sup>+</sup> (dtBubpy = 4,4'-di-tert-butyl-2,2'-bipyridine), that incorporate 2-phenylpyridine (**1**, **2**) and 1-phenylpyrazole (**3**, **4**) cyclometallating C<sup>^</sup>N ligands functionalized with SF<sub>5</sub> groups. The goal is to investigate the effect that the inclusion of SF<sub>5</sub> groups in *meta* (**1**, **3**) and *para* position (**2**, **4**) with respect to the Ir–C bond has on the electronic nature of the emitting triplet state and the emission wavelength. The attachment of the electron-withdrawing groups induces the stabilization of the molecular orbitals localized on the C<sup>^</sup>N ligands and, in particular, of the highest-occupied molecular orbital (HOMO). This stabilization enlarges the energy gap between the HOMO and the lowest-unoccupied molecular orbital (LUMO), and shifts to higher energies the metal-to-ligand charge transfer (MLCT) triplet described by the HOMO → LUMO excitation. As a consequence, a triplet state of ligand-centered (LC) nature becomes the lowest-energy triplet excited state for all the four complexes. For complexes **1** and **2**, the state is centered on the C<sup>^</sup>N ligands (<sup>3</sup>LC<sub>C<sup>^</sup>N</sub>) and the introduction of the SF<sub>5</sub> groups in *para* causes a greater effect than their insertion in *meta*. Substitution of the pyridine ring by a pyrazole ring in complexes **3** and **4** destabilizes the <sup>3</sup>LC<sub>C<sup>^</sup>N</sub> states and the lowest-energy triplet involves the diimine N<sup>^</sup>N ligand (<sup>3</sup>LC<sub>N<sup>^</sup>N</sub>). Theoretical calculations therefore predict that the electronic nature of the lowest-lying triplet drastically changes in passing from the unsubstituted complex (<sup>3</sup>MLCT) to complexes **1** and **2** (<sup>3</sup>LC<sub>C<sup>^</sup>N</sub>) and to complexes **3** and **4** (<sup>3</sup>LC<sub>N<sup>^</sup>N</sub>). These changes help to rationalize

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