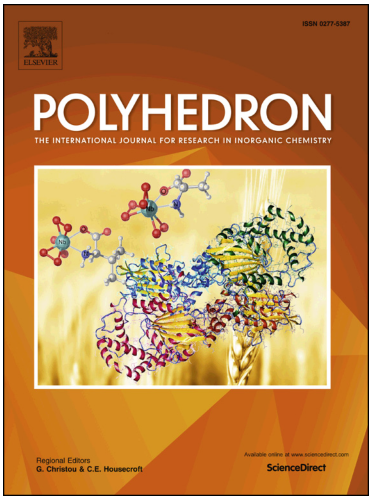

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PII: S0277-5387(17)30647-2
DOI: https://doi.org/10.1016/j.poly.2017.10.006
Reference: POLY 12869

To appear in: *Polyhedron*

Received Date: 26 September 2017
Accepted Date: 7 October 2017

Please cite this article as: J.M. Junquera-Hernández, J. Escobar, E. Ortí, Electronic nature of the emitting triplet in $SF_5$-substituted cationic Ir(III) complexes, *Polyhedron* (2017), doi: https://doi.org/10.1016/j.poly.2017.10.006

# Electronic nature of the emitting triplet in $SF_5$-substituted cationic Ir(III) complexes

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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 $[Ir(C\^{}N)_2(dtBubpy)]^+$ (dtBubpy = 4,4'-di-tert-butyl-2,2'-bipyridine), that incorporate 2-phenylpyridine (**1**, **2**) and 1-phenylpyrazole (**3**, **4**) cyclometallating C^N ligands functionalized with $SF_5$ groups. The goal is to investigate the effect that the inclusion of $SF_5$ 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^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^N ligands ($^3LC_{C\^{}N}$) and the introduction of the $SF_5$ 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 $^3LC_{C\^{}N}$ states and the lowest-energy triplet involves the diimine N^N ligand ($^3LC_{N\^{}N}$). Theoretical calculations therefore predict that the electronic nature of the lowest-lying triplet drastically changes in passing from the unsubstituted complex ($^3MLCT$) to complexes **1** and **2** ($^3LC_{C\^{}N}$) and to complexes **3** and **4** ($^3LC_{N\^{}N}$). These changes help to rationalize