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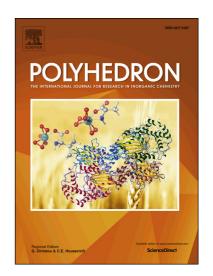
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Electronic nature of the emitting triplet in SF₅-substituted cationic Ir(III) complexes

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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 SF₅ groups. The goal is to investigate the effect that the inclusion of SF₅ 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-toligand charge transfer (MLCT) triplet described by the HOMO \rightarrow 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 SF₅ 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 $(^3LC_{N^{\wedge}N})$. Theoretical calculations therefore predict that the electronic nature of the lowestlying triplet drastically changes in passing from the unsubstituted complex (3MLCT) to complexes 1 and 2 ($^3LC_{C^{\circ}N}$) and to complexes 3 and 4 ($^3LC_{N^{\circ}N}$). These changes help to rationalize

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