Blue Phosphorescent Iridium(III) Complex. A Reaction Path on the Triplet Potential Energy Surface

Gabin Treboux,* Junji Mizukami, Masayoshi Yabe, and Shinichiro Nakamura
Mitsubishi Chemical Group, Science and Technology Research Center Inc.,
1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502

(Received July 23, 2007; CL-070783; E-mail: 6305945@cc.m-kagaku.co.jp)

The potential energy surfaces associated with the triplet electronic state of the Ir(ppz)$_3$ and Ir(ppy)$_3$ cyclometalated complexes, respectively, are calculated using density functional theory [where ppz = 1-phenylpyrazolyl-*N*,C2′, ppy = 2-phenylpyridyl]. Both surfaces present a metal-to-ligand charge-transfer energy minimum and a ligand-field energy minimum, connected by a chemical path involving only the rotation of one pyrazolyl or pyridyl group. Unlike Ir(ppy)$_3$, the lowest energy minimum of Ir(ppz)$_3$ is the ligand-field state.

Since the seminal work of Tang and VanSlyke,[1] a great deal of research activity has been devoted to the development of electroluminescent organic light-emitting devices (OLEDs). Owing to their energy conversion efficiency and high-throughput manufacturability, OLEDs have tremendous potential for full-color flat-panel display applications. The energy conversion efficiency depends critically on the nature of the molecules responsible for the current-to-photon conversion. OLEDs using phosphorescent molecules have been shown to harvest 100% of the excitons generated by electrical injection, which constitutes a fourfold increase in efficiency compared to that achievable using fluorescent molecules.[2] For display applications, the development of green- and red-emitting complexes satisfying technological requirements was completed several years ago. One of the leading green-emitting materials is the facial isomer of Ir(ppy)$_3$ (ppy = 2-phenylpyridyl). This complex was used in an OLED component giving an internal quantum efficiency close to 100%.[3] The development of the remaining blue-emitting phosphorescent complex has proved to be more problematic and is still fraught with difficulties.[4–7] In a simplistic one-electron scenario, a cyclometalated triplet state can be built according to two different schemes. In the first scheme, one electron is promoted to a ligand π^* orbital. This scheme is characteristic of a π–π^* and/or a metal-to-ligand charge transfer. In the second scheme, one electron is promoted to a metal e_g orbital. In this letter, these two schemes are denoted ^{3}MLCT and ^{3}LF, respectively. One major challenge lies in the selection of suitable ligands able to form a complex with sufficiently large MLCT transition energies to obtain a blue phosphorescence. Such an approach inevitably raises the MLCT state to a region very close to or even higher than the LF state thus limiting the phosphorescence of the complexes[8] since the ^{3}LF state is a nonradiative deactivation channel.

Clearly, modeling tools that could assist in the design of these complexes would be useful. Remarkable predictions of the ground state properties of cyclometalated complexes have been generated using density functional theory.[4–7] Unrestricted density functional theory permits the analysis of the triplet state properties and the calculation of energy variation as a function of the geometric changes, i.e., the potential energy surface (PES). Unrestricted calculations were reported for several complexes, including Ir(ppy)$_3$,[9] the validity of which has been confirmed experimentally.[10] In this letter, we give a comparative analysis of the PESs of the lowest triplet state of *fac*-Ir(ppz)$_3$ (ppz = 1-phenylpyrazolyl-*N*,C2′) and *fac*-Ir(ppy)$_3$. Calculations were carried out using the density functional B3LYP. The first set of calculations used 6-31G basis sets and a LANL2DZ core potential.[11] In the second set of calculations, a polarization function was added to the atom of the ligands and a SDD core potential[12] was used. Both sets of calculations gave qualitatively similar results. The calculations were performed using the Gaussian package.[13] During the searches for both minima and transition structures, the geometries were fully optimized without geometric constraints. The QST2 algorithm was employed for the location of the transition structures. The cartesian coordinates of the energy minima and of the transition states are given in the Supporting Information section. For each PES the octahedral isomer, represented schematically in Figure 1, is taken as the energy reference, i.e., E_o = zero.

With the optimized geometry of the *fac*-Ir(ppy)$_3$ octahedral isomer as a starting point, we analyzed, the energy variation associated with the rotation of a phenyl group or a pyridyl group of one ligand. The rotation of the phenyl destroys one Ir–C bond while the rotation of the pyridyl destroys one Ir–N bond. A 90°-rotation of the phenyl while keeping the pyridyl fixed increased the energy by 35 kcal/mol (clockwise), and 37 kcal/mol (anticlockwise). A 90°-rotation of the pyridyl while keeping the phenyl ring fixed increased the energy by 7 kcal/mol (clockwise), and 12 kcal/mol (anticlockwise). The calculations show that the rotation of the pyridyl requires much less energy than the corresponding rotation of the phenyl. The calculation also highlights a feature well documented in photochemistry, that is, the triplet state PES is significantly flatter than the ground state PES. On the ground state PES, similar clockwise rotations of the phenyl and pyridyl increased the energy by 89 and 29 kcal/mol, respectively.

The energy variation associated with the rotation of the pyridyl was small. This prompted us to analyze this rotation further. Without applying geometric constraints, we identified a structure with a rotated pyridyl group. The analysis of the hessian matrix confirms that this structure corresponds to an energy minimum. This isomer, represented schematically in Figure 1, is referred hereafter as open isomer Its energy is 5.1 kcal/mol. The energy barrier between the octahedral and open isomers is 6.6 kcal/mol.

Using the same procedure, we analyzed the triplet state PES of *fac*-Ir(ppz)$_3$. Rotation of the phenyl group or pyrazolyl group on one ligand corresponds to an energy of 24 kcal/mol and −6 kcal/mol, respectively. The negative energy associated with

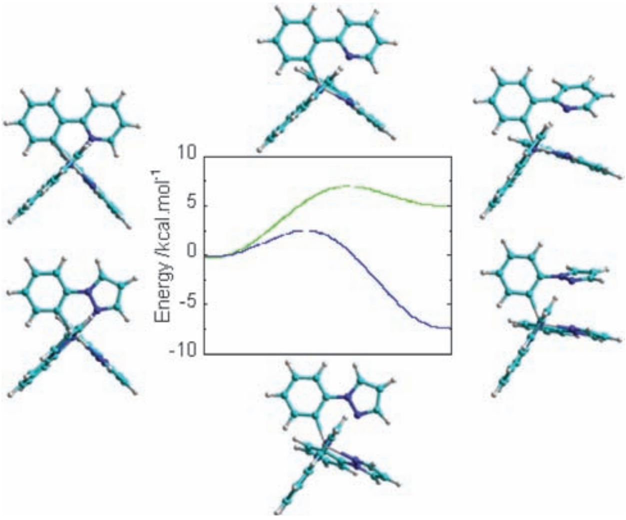

Figure 1. Schematic representation of the triplet state PES of *fac*-Ir(ppy)$_3$ (green curve) and *fac*-Ir(ppz)$_3$ (blue curve) complexes. The octahedral isomers correspond to the energy minima located on the left. The open isomers correspond to the energy minima located on the right. The transition structures, presented in the center of the figure, correspond to the energy extrema. The carbon, nitrogen, and hydrogen atoms are represented in cyan, blue, and white, respectively. The iridium atom is located at the center of the complex.

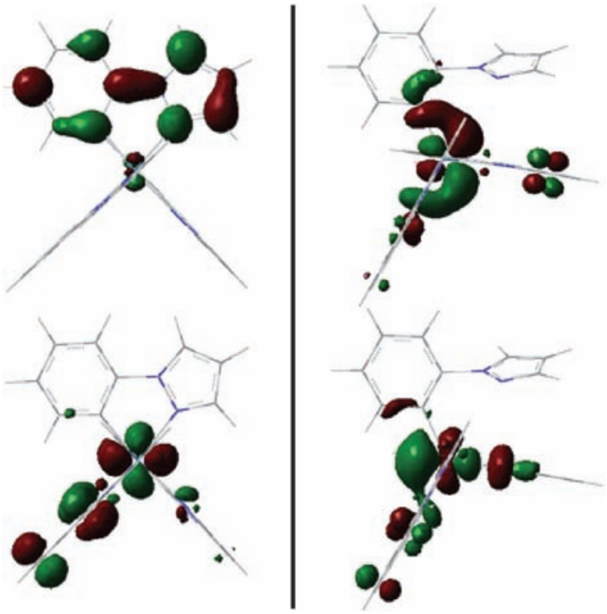

Figure 2. Contour plots of the low (bottom) and high (top) energy orbitals forming the triplet state of the octahedral (left) and open isomers (right) of *fac*-Ir(ppz)$_3$. Each orbital contains one electron.

the rotation of the pyrazolyl indicates that this rotation stabilizes the complex. Without applying geometric constraints, we identified an energy minimum with a rotated pyrazolyl group. The energy of this open isomer is −7.0 kcal/mol. The energy barrier between the octahedral and open isomers is 2.0 kcal/mol. While the rotation of the pyrazolyl is small in the transition state, the distance between the iridium atom and the nitrogen atom takes a value of 2.9 Å. This Ir–N bond length is significantly larger than the Ir–N bond length of 2.2 Å found in the other two ligands.

The orbitals forming the triplet state of the Ir(ppz)$_3$ octahedral and open isomers are represented in Figure 2. The orbitals of the Ir(ppy)$_3$ isomers, not represented here, are similar. The precise assignation of the respective characters of MLCT and LC is complicated by the presence of a strong metal–ligand mixing in the orbital, but qualitatively, the octahedral isomer corresponds to a ^{3}MLCT electronic state, while the open isomer corresponds to a ^{3}LF electronic state. The phosphorescence of *fac*-Ir(ppy)$_3$ and *fac*-Ir(ppz)$_3$ is well-established experimentally.[14] *fac*-Ir(ppy)$_3$ is a robust green-emitting complex presenting a strong phosphorescence at 77 K and at room temperature. *fac*-Ir(ppz)$_3$ is a blue-emitting complex which, in contrast to *fac*-Ir(ppy)$_3$, presents a strong phosphorescence at 77 K but no phosphorescence at room temperature. Given the fact that *fac*-Ir(ppz)$_3$ has an octahedral geometry in the ground state, a vertical excitation from the singlet state would reach the octahedral isomer on the triplet PES. Because this octahedral isomer has an ^{3}MLCT electronic state, the calculations are in line with a phosphorescence at low temperature. The calculations, predicting a facile conversion from the octahedral isomer to the open isomer, provide an explanation for the disappearance of the phosphorescence of *fac*-Ir(ppz)$_3$ at a higher temperature.

References

1 C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
2 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151.
3 C. Adachi, M. A. Baldo, S. R. Forrest, M. E. Thompson, *Appl. Phys. Lett.* **2000**, *77*, 904.
4 Md. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Graetzel, *J. Am. Chem. Soc.* **2003**, *125*, 8790.
5 J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. Christopher Thomas, J. C. Peters, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 1713.
6 C.-H. Yang, S.-W. Li, Y. Chi, Y.-M. Cheng, Y.-S. Yeh, P. T. Chou, G.-H. Lee, C.-H. Wang, C.-F. Shu, *Inorg. Chem.* **2005**, *44*, 7770.
7 Y.-Y. Lyu, Y. Byun, O. Kwon, E. Han, W. S. Jeon, R. R. Das, K. Char, *J. Phys. Chem. B* **2006**, *110*, 10303.
8 K. Koike, N. Okoshi, H. Hori, K. Takeuchi, O. Ishitani, H. Tsubaki, I. P. Clark, M. W. George, F. P. A. Johnson, J. J. Turner, *J. Am. Chem. Soc.* **2002**, *124*, 11448.
9 P. J. Hay, *J. Phys. Chem. A* **2002**, *106*, 1634.
10 J. Breu, P. Stossel, S. Schrader, A. Starukhin, W. J. Finkenzeller, H. Yersin, *Chem. Mater.* **2005**, *17*, 1745.
11 P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
12 D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chem. Acta* **1990**, *77*, 123.
13 J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. C. M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98 (Revision A.7)*, Gaussian, Inc., Pittsburgh, PA, **2001**.
14 T. Karatsu, E. Ito, S. Yagai, A. Kitamura, *Chem. Phys. Lett.* **2006**, *424*, 353.

Published on the web (Advance View) October 13, 2007; doi:10.1246/cl.2007.1344