

# Ab Initio Prediction of the Emission Color in Phosphorescent Iridium(III) Complexes for OLEDs

Filippo De Angelis,<sup>†</sup> Fabrizio Santoro,<sup>‡</sup> Mohammad K. Nazeruddin,<sup>§</sup> and Vincenzo Barone<sup>\*‡</sup>

*Istituto CNR di Scienze e Tecnologie Molecolari (ISTM), c/o Dipartimento di Chimica, ISTM-CNR, Perugia, via Elce di Sotto 8, I-06123, Perugia, Italy, Istituto CNR per i Processi Chimico-Fisici (IPCF), Via Moruzzi 1, I-56124, Pisa, Italy, and Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland*

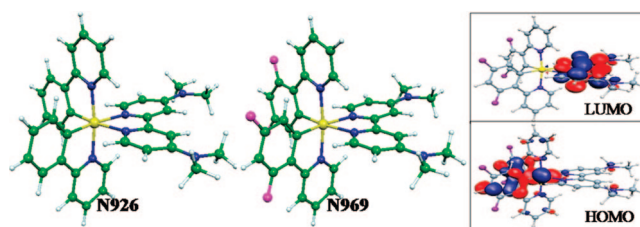
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We performed fully first principles quantum mechanical calculations of the ground and excited state geometries and harmonic vibrational frequencies of two prototype cationic Ir(III) complexes showing high emission quantum efficiencies. Thanks to recent theoretical advances, we have been able for the first time to simulate their vibrationally resolved emission spectra. Our results, in good agreement with the experiment, allow us to calculate the CIE coordinates and therefore the emission color of this important class of emitters for OLEDs and LECs.

Ir(III) cyclometalated complexes are attracting wide spread interest because of their unique photophysical properties and application as emitters in organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs).<sup>1–3</sup> The success of these complexes is related to their high stability, emission color tunability, and strong spin-orbit coupling, which sharply increases the efficiency of radiative transitions.<sup>4</sup> When applied in light-emitting devices, these characteristics translate into effective harvesting of both singlet and triplet excitons, thus pushing the device external quantum efficiency up to about 19%.<sup>1</sup>

OLED and LEC emitters should present sharp colors in the red, green, and blue region, exhibiting at the same time very high phosphorescence quantum yields. In mixed ligand cationic Ir(III) complexes of the type  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$ , with (C<sup>∧</sup>N) cyclometalating and (N<sup>∧</sup>N) bipyridine or phenanthroline ligands, the two type of ligands can be almost independently functionalized, thus achieving the desired color by selective tuning of the HOMO and LUMO energies.<sup>5,6</sup> Moreover, the use of cationic complexes, bearing drifting counterions, allows the use of a simplified device architecture.<sup>3b</sup>

Prediction of the electronic and optical properties of Ir(III) emitters by computer simulations would allow the “in silico” design and screening of new complexes, thus significantly reducing the synthetic and characterization time. Several investigations on cationic Ir(III) complexes have recently appeared, in which calculations of the vertical emission energies have been reported.<sup>6</sup> While these electronic structure calculations allowed in some cases to directly compare calculated transition energies with experimental emission maxima,<sup>6a</sup> no information could be obtained about the shape and intensity distribution of the emission spectrum, which ultimately determines the color



**Figure 1.** Optimized structures of the N926 and N969 complexes and isodensity plots of the HOMO and LUMO for N969. Yellow, Ir; purple, F; blue, N; green, C; white, H atoms.

perceived by the human eye. To overcome this limitation, one needs to move beyond a purely electronic picture and to be able to simulate vibrationally resolved emission spectra.

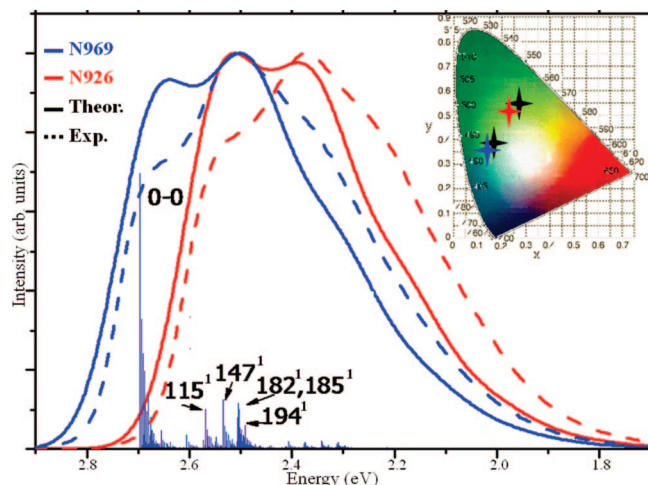
Thanks to recent theoretical developments,<sup>7</sup> in this study we document that this kind of simulation is now possible for such large systems as the two Ir(III) cationic complexes,  $[\text{Ir}(\text{2-phenylpyridine})_2(4,4'\text{-dimethylamino-2,2'-bipyridine})]^+$ , N926, and  $[\text{Ir}(\text{2,4-difluorophenylpyridine})_2(4,4'\text{-dimethylamino-2,2'-bipyridine})]^+$ , N969, see Figure 1, for which color tuning in the green–blue region of the spectrum with quantum yields exceeding 80% has been recently reported by some of us.<sup>5c,6a</sup> We present two main achievements: (i) the prediction of spectral shapes in close agreement with experiment and (ii) a quantitative description of the emission spectral shift and shape for the two species, which support the predictive power of the adopted methodology. We perform DFT calculations on the ground singlet  $S_0$  and first triplet  $T_1$  excited states of the two complexes, characterizing the excited state geometries and harmonic vibrational frequencies, and including solvation effects. Electronic structure calculations are carried out by the Gaussian 03 program package<sup>8</sup> using the B3LYP and PBE0 functionals,<sup>9</sup> along with the SDD basis set for all atoms and the corresponding pseudopotential for Ir.<sup>10</sup> Test calculations were also performed with the larger c-pVDZ basis set on F, N, C, and H atoms, maintaining the same SDD basis set and pseudopotential for

\* Corresponding author. E-mail: baronev@unina.it.

<sup>†</sup> Università di Perugia.

<sup>‡</sup> Istituto CNR per i Processi Chimico-Fisici.

<sup>§</sup> Swiss Federal Institute of Technology.



**Figure 2.** Calculated (solid lines) and experimental (dashed lines) emission spectra for N969 (blue) and N926 (red), along with calculated stick-spectrum for N969 (blue vertical lines). The calculated (blue/red stars) and experimental (black stars) CIE coordinates for N969 and N926 are also shown. Vibrational contributions are labeled by  $n^x$ , where  $x$  indicates the quanta deposited on normal mode  $n$  and the modes not explicitly mentioned are in their ground state ( $x = 0$ ).

the metal atom.  $T_1$  borrows emission intensity towards  $S_0$  through the spin-orbit coupling with close-lying singlet excited states, mainly from the bright  $S_2 \rightarrow S_0$  transition.<sup>6a</sup> As a consequence, the lineshape of the vibrationally resolved phosphorescence spectra can be suitably calculated within the Franck–Condon (FC) approximation. The reported spectra are computed exactly in the harmonic approximation, considering the geometric displacements, the frequency changes and the Duschinsky mixing between the ground and excited states.

These challenging calculations, requiring in principle evaluation of a huge number of multidimensional FC integrals, of the order of  $10^{25}$ , are made possible by exploiting the method proposed by some of us,<sup>7</sup> in which the manifold of possible final states is partitioned into classes  $C_n$  depending on the number  $n$  of simultaneously excited normal modes, and an effective strategy allows selecting of the relevant contributions for each class.<sup>7</sup> The calculations are performed by the *FCclasses* code.<sup>7e</sup>

The main differences between the structures of  $S_0$  and  $T_1$  involve the Ir–N(bipyridine) and the linking C–C bond lengths of the bipyridine ligand, see Supporting Information. Both distances are shortened by about 0.05 Å upon excitation from  $S_0$  to  $T_1$ , as a consequence of population in  $T_1$  of the  $S_0$  LUMO, a  $\pi^*$  orbital localized on the substituted bipyridine, see Figure 1. In vacuo the B3LYP excitation energy between the ground vibrational states of  $S_0$  and  $T_1$  ( $E_{0-0}$ ) amounts to 2.34 and 2.45 eV for N926 and N969, respectively. The corresponding  $\Delta$ SCF adiabatic electronic excitations (AEE, i.e., the differences between the energies of  $T_1$  and  $S_0$  minima), 2.45 and 2.59 eV, are slightly larger than the  $E_{0-0}$  values, since the weakening of bonding interactions in the excited state lowers the zero-point vibrational energy of  $T_1$  compared to  $S_0$ . The  $\Delta$ SCF AEE are comparable to the corresponding TD-DFT adiabatic excitation energies.<sup>6a</sup> Solvation effects<sup>11</sup> lead to small changes in the investigated properties, the  $E_{0-0}$  of N969 being increased by just 0.05 eV. The PBE0 functional provides a slightly larger  $E_{0-0}$  for N969 in vacuo (2.53 eV).

We report in Figure 2 a comparison between the emission spectra of N969 and N926 calculated in vacuo at the B3LYP/SDD level and the corresponding experimental data in aceto-

nitrile solution.<sup>6a,12</sup> In this manuscript, we focus on emission color rather than on absolute intensities and hence on the spectral lineshapes; for a better comparison of the latter, the spectra in Figure 2 are normalized so to have maximum peaks with equal heights. Reproduction of absolute intensities depends on the accurate evaluation of spin-orbit couplings and of the transition dipole moments from  $S_0$  to the excited singlet states  $S_n$  coupled by spin-orbit to  $T_1$  and is beyond the scope of the present investigation. The experimental spectra show a broad two-peak shape as a consequence of the inhomogeneous broadening induced by the polar solvent. To simulate the spectral broadening, we use a Gaussian convolution with FWHM of 0.16 eV. The calculated spectrum has been blue-shifted by 0.24 eV for better comparison with the experiment. Apart from this shift, the agreement between theory and experiment is good, and the main experimental spectral features are accurately reproduced but for a slight overestimation of the intensity of the  $E_{0-0}$  transition. The energy shift of the calculated spectrum could be possibly reduced by using improved DFT functionals<sup>13</sup> (see also the Supporting Information), different electronic structure methods,<sup>14</sup> or more extended basis sets. In this latter case, it is noteworthy that for N969 the use of the larger cc-pVDZ basis set for the H, C, N, and F atoms leads to comparable geometry displacements between the  $T_1$  and  $S_0$  equilibrium structures as those computed by the SDD basis set, increasing however the  $\Delta$ SCF AEE from 2.59 to 2.69 eV and  $E_{0-0}$  from 2.45 to 2.58 eV, thus slightly improving the agreement with experiment.

In Figure 2, the assignment of the most relevant vibrational contributions to the spectra is reported, with normal modes sorted in order of increasing frequency. The bluest phosphorescence peak is due to the 0-0 transition and to progressions along low-frequency modes, see the Supporting Information. It is noteworthy that the 0-0 stick band is significantly blue-shifted with respect to the band peak position (by 0.06 eV) so that the computed  $E_{0-0}$  and the experimental peak-maximum can not be directly compared, a feature that only a vibrationally-resolved analysis could highlight. The low-energy peak of the phosphorescence spectrum has main contributions from modes 181, 182, 185, and 194 respectively, all describing collective stretches of the bipyridine rings, coupled to some bendings involving the H's of dimethyl-amino substituents. This finding is related to the localization of the excitation on the bipyridine ligand, and reflects the structural displacements from  $S_0$  to  $T_1$  discussed above. Contributions to the spectral shape between the two main peaks come from modes 147 and 115, mainly involving the bipyridine ligand.

Figure 2 shows that the same blue-shift and broadening used for N969 allow a satisfactory reproduction of the experimental emission spectrum of N926. In particular, both theory and experiment show a decreased ratio between the first and second peak intensities (by 0.91) going from N969 to N926, which can be traced back to the larger nuclear displacements taking place in N969 upon excitation.

Most notably, having accurately calculated the band shape, we can provide a computational estimate of the CIE color coordinates for the investigated complexes. To this end, we numerically calculate the spectral overlap integral with the standard CIE Red, Green and Blue color matching functions.<sup>15</sup> With reference to data in Figure 2, our calculations lead to 0.19:0.34:0.47 CIE coordinates for N969, to be compared to experimental values of 0.21:0.39:0.41. Apart from the red-shifted  $E_{0-0}$  transition, which we correct by shifting the calculated spectrum, the main discrepancy between computations and experiments is the overestimation of the blue-wing intensity

and slight underestimation of the red-wing intensity (see Figure 2), which leads to a too large content of blue color in the calculated spectrum compared to experiment (0.47 and 0.41, respectively). Furthermore, it is apparent that our calculations quantitatively reproduce the difference in CIE coordinates between N969 and N926 complexes and hence the different emission color. This is a major result of our work, highlighting the predictive capability of the underlying computational model.

In conclusion, an integrated approach based on a DFT description of geometric and electronic structures together with a reliable treatment of vibrational contributions allows us to nicely simulate the phosphorescence spectra of complex organometallic systems. The quantitative reproduction of the complexes emission color makes this approach a valuable tool for the “in silico” design of new related species with pre-determined emission properties.

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**Supporting Information Available:** Complete ref 8. Geometrical structures. Stick bands and their assignments for N926 and N969. Spectra convergence tests. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) (a) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *J. Appl. Phys.* **2001**, *90*, 5048. (b) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4.
- (2) (a) Slinker, J.; Bernards, D.; Houston, P. L.; Abruna, H. D.; Bernhard, S.; Malliaras, G. G. *Chem. Commun.* **2003**, 2392. (b) Rudmann, H.; Shimida, S.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 4918.
- (3) (a) Bernhard, S.; Barron, J. A.; Houston, P. L.; Abruna, H. D.; Ruglovsky, J. L.; Gao, X.; Malliaras, G. G. *J. Am. Chem. Soc.* **2002**, *124*, 13624. (b) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. *J. Am. Chem. Soc.* **2004**, *126*, 2763.
- (4) (a) Ohsawa, Y.; Sprouse, S.; King, K. A.; DeArmond, M. K.; Hanck, K. W.; Watts, R. J. *J. Phys. Chem.* **1987**, *91*, 1047. (b) Garces, F.O.; King, K. A.; Watts, R. J. *Inorg. Chem.* **1988**, *27*, 3464.
- (5) (a) Lowry, M. S.; Hudson, W. R.; Pascal, R. A., Jr.; Bernhard, S. *J. Am. Chem. Soc.* **2004**, *126*, 14129. (b) Lowry, M. S.; Bernhard, S. *Chem. Eur. J.* **2006**, *12*, 7970. (c) Nazeeruddin, M. K.; Wegh, R. T.; Zhou, Z.; Klein, C.; Wang, A.; De Angelis, F.; Fantacci, S.; Grätzel, M. *Inorg. Chem.* **2006**, *45*, 9254.
- (6) (a) De Angelis, F.; Fantacci, S.; Evans, N.; Klein, C.; Zakeeruddin, S. M.; Moser, J.-E.; Kalyanasundaram, K.; Bolink, H.; Grätzel, M.; Nazeeruddin, M. K. *Inorg. Chem.* **2007**, *46*, 5989. (b) Dragonetti, C.; Falcicola, L.; Mussini, P.; Righetto, S.; Roberto, D.; Ugo, R.; De Angelis, F.; Fantacci, S.; Sgamellotti, A.; Ramon, M.; Muccini, M. *Inorg. Chem.* **2007**, *46*, 8533.
- (7) (a) Santoro, F.; Improta, R.; Lami, A.; Bloino, J.; Barone, V. *J. Chem. Phys.* **2007**, *126*, 084509. (b) Santoro, F.; Improta, R.; Lami, A.; Bloino, J.; Barone, V. *J. Chem. Phys.* **2007**, *126*, 169903. (c) Santoro, F.; Improta, R.; Lami, A.; Bloino, J.; Barone, V. *J. Chem. Phys.* **2008**, *128*, 224311. (d) Santoro, F.; Improta, R.; Lami, A.; Barone, V. *J. Chem. Phys.* **2007**, *126*, 184102. (e) Santoro, F. *F Cclasses*, a Fortran 77 code: to obtain the code, visit <http://village.ipcf.cnr.it>.
- (8) Frisch, M. J.; Gaussian 03; see the Supporting Information for complete reference.
- (9) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
- (10) Fuentealba, P.; Preuss, H.; Stoll, H.; v. Szentpaly, L. *Chem. Phys. Lett.* **1989**, *89*, 418.
- (11) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comp. Chem.* **2003**, *24*, 669.
- (12) The experimental data in the wavelength domain have been transformed to the frequency domain (see the Supporting Information) according to Karunakaran, V.; Senyushkina, T.; Saroja, G.; Liebscher, J.; Ernsting, N. P. *J. Phys. Chem. A* **2007**, *111*, 10944.
- (13) Brancato, G.; Rega, N.; Barone, V. *Phys. Rev. Lett.* **2008**, *100*, 107401.
- (14) Bloino, J.; Biczysko, M.; Crescenzi, O.; Barone, V. *J. Chem. Phys.* **2008**, *128*, 244105.
- (15) Beck, M. E. *Int. J. Quantum Chem.* **2004**, *101*, 683.

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