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► **To cite this version:**

Isabelle M. Dixon, Gauthier Boissard, Hannah Whyte, Fabienne Alary, Jean-Louis Heully. Computational Estimate of the Photophysical Capabilities of Four Series of Organometallic Iron(II) Complexes. *Inorganic Chemistry*, 2016, 55 (11), pp.5089-5091. 10.1021/acs.inorgchem.6b00223 . hal-01331155

**HAL Id: hal-01331155**

**<https://hal.science/hal-01331155>**

Submitted on 18 Feb 2020

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## Computational estimate of the photophysical capabilities of four series of organometallic iron(II) complexes.

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### ABSTRACT

In this study we examine a large range of organometallic Fe(II) complexes, aiming at identifying computationally the most promising ones in terms of photophysical properties. These complexes combine polypyridine, bis(phosphine) and carbon-bound ligands. DFT has allowed us to establish a comparative Jablonski diagram displaying the lowest singlet, triplet and quintet states. All the proposed FeN<sub>5</sub>C or FeN<sub>3</sub>P<sub>2</sub>C complexes unfavorably possess a lowest triplet state of MC nature. Among the FeN<sub>4</sub>C<sub>2</sub> and FeN<sub>2</sub>P<sub>2</sub>C<sub>2</sub> series, the carbene complexes display the least favorable excited state distribution, also having a low-lying <sup>3</sup>MC state. Validating our design strategy, we are now able to propose seven iron(II) complexes displaying a lowest excited state of <sup>3</sup>MLCT nature.

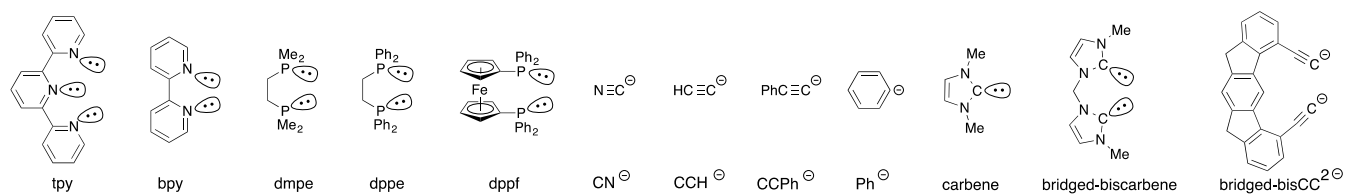
Despite recent efforts and progress, both experimentally and computationally, the quest for luminescent iron(II) complexes is still highly challenging. Aiming at expanding the lifetime of their charge transfer excited states, two opposite strategies have been followed: (i) to *increase* the ligand field strength through geometric<sup>1,2</sup> or electronic<sup>3-17</sup> modifications, and (ii) to *decrease* the ligand field strength through steric bulk, obtaining a quintet MC ground state that allows the straightforward population of a <sup>5</sup>MLCT state.<sup>18</sup> Recent studies have brought significant advances, particularly a 100-fold increase in the MLCT lifetime,<sup>3,6,9</sup> reaching 26 ps,<sup>10,18</sup> and efficient TiO<sub>2</sub> sensitization.<sup>5,7,9,14,15,17</sup> Both experimentally-driven and theoretically-driven studies confirm the promising status of certain classes of iron(II) complexes, particularly for photoinduced electron transfer.

Our contribution to the field is in the computational design of such complexes, using DFT to get a fast but reliable picture of the excited state distribution. Low-lying charge-transfer states are desired to bring photophysical properties such as luminescence or electron transfer, while high-lying metal-centered excited states are desired to avoid spin crossover processes and non radiative deactivation. In this respect, we have previously reported a series of mono- and bis(cyclometallated) iron(II) compounds, among which the charge neutral bis(6-phenyl-2,2'-bipyridine)Fe(II) was the most promising

candidate.<sup>12,13</sup> Willing to generalize the developed methodology to various families of organoiron(II) complexes, we are here evaluating the photophysical capabilities of several series of new compounds. The carbon ligands were chosen among the most classical ones in iron chemistry: cyanide, acetylide, carbene. In the complexes bearing two carbon ligands, these were placed in a *cis* configuration as it had been shown to be the most favorable one.<sup>11-13</sup> In the bridged case, the C-Fe-C angle was chosen to be around 90°. Ni(CO)<sub>3</sub>L complexes are classically used to study, both experimentally and computationally,<sup>19</sup> the M-L interaction through its repercussion on the CO stretching vibration. Such calculations allow a very fast estimation of the ligand's net donor power. A first evaluation of the electronic properties of the carbon ligands was performed on Ni(CO)<sub>3</sub>L model complexes, using the highest energy CO vibrational stretching as probe. This allows us to order the ligands according to their donating properties: CO ( $\nu_{\text{CO}}=2188\text{ cm}^{-1}$ ) < carbene (2115) < CN<sup>-</sup> (2088) < CCH<sup>-</sup> (2081) < CPh<sup>-</sup> (2075) < Ph<sup>-</sup> (2057).

The nitrogen ligands were classical polypyridines, serving as  $\pi$  acceptors to stabilize MLCT states. The initial idea behind this work was to replace bpy by a much stronger donating ligand, bis(dimethylphosphino)ethane (dmpe). For comparison, dppe and the more rigid dppf were also tested (although the ferrocenyl moiety of the dppf ligand can be expected to be detrimental for photophysics). In total 21 complexes were thus examined (Chart 1). Singlet, lowest triplet and lowest quintet states were optimized (see Supporting Information for the computational methodology). The nature of the excited states was identified and a comparative Jablonski diagram was built (Figure 1). To identify the most promising iron complexes, two major selection criteria come into play: (i) the <sup>5</sup>MC state should be sufficiently destabilized to be considered offside, and (ii) the complex should have a lowest triplet excited state of MLCT nature, in order to minimize its non radiative deactivation through population of a low-lying <sup>3</sup>MC state. Only one such example was reported experimentally.<sup>10</sup>

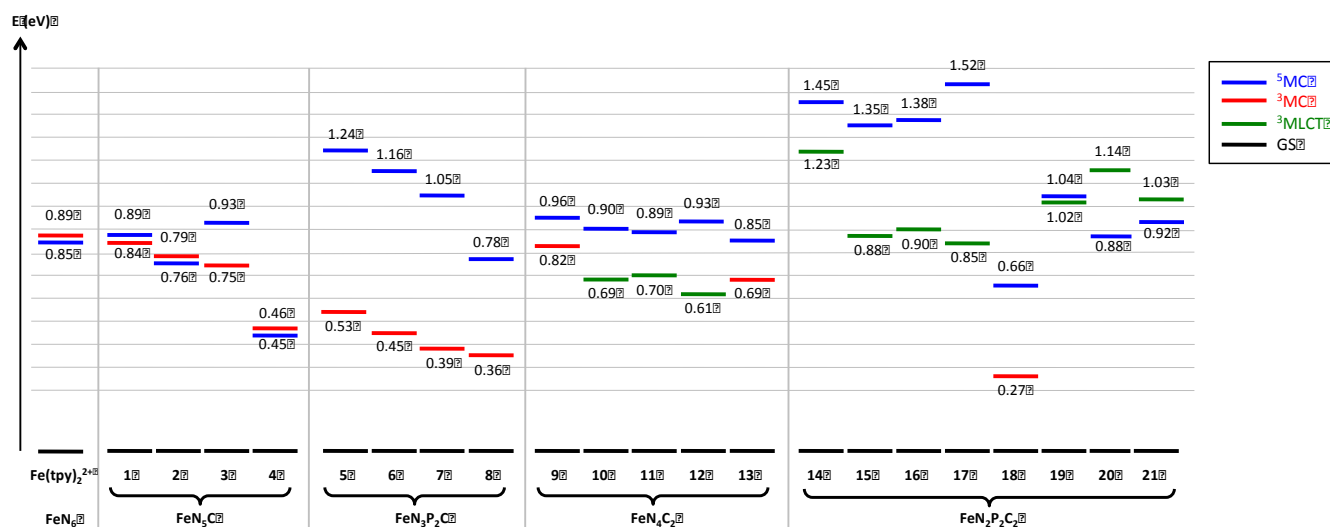
Chart 1. Ligands, Fe(II)L<sub>1</sub>L<sub>2</sub>L<sub>3</sub> complexes and abbreviations used in this study.



FeN <sub>5</sub> C series	L1 = tpy	L2 = bpy	L3 = CN <sup>-</sup> (1); CCH <sup>-</sup> (2); CPh <sup>-</sup> (3); carbene (4)
FeN <sub>3</sub> P <sub>2</sub> C series	L1 = tpy	L2 = dmpe	L3 = CN <sup>-</sup> (5); CCH <sup>-</sup> (6); CPh <sup>-</sup> (7); carbene (8)
FeN <sub>4</sub> C <sub>2</sub> series	L1 = bpy	L2 = bpy	L3 = CN <sup>-</sup> , CN <sup>-</sup> (9); CCH <sup>-</sup> , CCH <sup>-</sup> (10); CPh <sup>-</sup> , CPh <sup>-</sup> (11); bridged-bisCC <sup>2-</sup> (12); bridged-biscarbene (13)
FeN <sub>2</sub> P <sub>2</sub> C <sub>2</sub> series	L1 = bpy	L2 = dmpe	L3 = CN <sup>-</sup> , CN <sup>-</sup> (14); CCH <sup>-</sup> , CCH <sup>-</sup> (15); CPh <sup>-</sup> , CPh <sup>-</sup> (16); bridged-bisCC <sup>2-</sup> (17); bridged-biscarbene (18)
	L1 = bpy	L2 = dppe	L3 = CCH <sup>-</sup> , CCH <sup>-</sup> (19)
	L1 = bpy	L2 = dppf	L3 = CCH <sup>-</sup> , CCH <sup>-</sup> (20); bridged-bisCC <sup>2-</sup> (21)

Figure 1 displays the resulting Jablonski diagram for all the studied complexes. Data for  $\text{Fe}(\text{tpy})_2^{2+}$  was taken from ref 13. Complexes showing a low-lying MC state will be gradually cleared from the discussion. This is the case for those in the  $\text{FeN}_5\text{C}$  and  $\text{FeN}_3\text{P}_2\text{C}$  series, which all show an unfavorable low-lying  $^3\text{MC}$  state. This characteristic can be directly related to the possibility to elongate two *trans* Fe-N bonds via the population of a pseudo  $d_{2z}$ -type  $d\sigma^*$  orbital.

Figure 1. Comparative Jablonski diagram for complexes **1-21** displaying the lowest singlet, triplet and quintet states.



Within each series, the N-heterocyclic carbene complexes systematically present the largest HOMO-LUMO gap and the smallest gap between the LUMO and the first  $d\sigma^*$  orbital (Supporting Information). This results in a lowest triplet state of MC nature, including for complexes **13** and **18**.

In the  $\text{FeN}_2\text{P}_2\text{C}_2$  series, the complexes with the next worse donors (**14** with cyanide, **19-20** with  $\text{PAR}_2$ ) display  $^3\text{MLCT}$  states with a higher energetic content ( $>1$  eV), due to the least destabilization of the HOMO through moderate donor effects. This is also seen in the cyanide complex **9** ( $\text{FeN}_4\text{C}_2$  series), resulting in a lowest triplet state of MC nature, which is fully consistent with Sutin's<sup>20</sup> and Ferrere's<sup>21-23</sup> spectroscopic studies on *cis*- $\text{Fe}(\text{bpy})_2(\text{CN})_2$ .

The replacement of two Fe-N bonds by two Fe-P bonds always leads to the destabilization of the  $^5\text{MC}$  state (compare, for instance, **1/5** or **9/14**). This is attributed to the fact that  $^5\text{MC}$  equilibrium geometries show elongated Fe-P bonds, but elongating a stronger Fe-P bond (with a  $\sim 0.8$  mdyne/Å force constant) is more unfavorable than elongating a Fe-N ( $\sim 0.5$ ) or a Fe-carbene ( $\sim 0.6$ ) bond. Covalent bonds between Fe and an anionic carbon atom are the strongest of all ( $\sim 1.5$ ) and show little elongation ( $<10\%$ ), even in  $^5\text{MC}$  states (Supporting Information). The tendency to elongate more easily Fe-N vs. Fe-P bonds is also clear in the  $^3\text{MC}$  geometries of the  $\text{FeN}_3\text{P}_2\text{C}$  series, which all involve stretched Fe-N bonds.

When the  $\sigma$ -donating properties of the bis(phosphine) ligand are diminished by replacing  $\text{PR}_2$  with  $\text{PAR}_2$ , the  $^5\text{MC}$  state is either degenerate with (**19**) or more stable than (**20-21**) the  $^3\text{MLCT}$  state. Therefore the strongly electron-donating bis(dimethylphosphino)ethane proves to be an essential contributor to the sought properties.

Finally, the CCPh derivatives were envisaged for synthetic reasons, to check that the presence of the phenyl substituent did not perturb the excited state distribution. Indeed, complexes **10/11** and **15/16** compare very well.

It is worth noting the diversity of <sup>5</sup>MC geometries (Supporting Information). Some remain classical, hexacoordinated species, with extended bond lengths and similar angles with respect to the ground state geometries (**1-6**, **8**, **13**, **18**). In the FeN<sub>4</sub>C<sub>2</sub> series, significant angular distortions appear in the <sup>5</sup>MC states of **9-11** and **14** (the C-Fe-C angle opens from *ca.* 90 to 114±2°). The <sup>5</sup>MC state of the bridged bis(acetylide) complex **12** is special in that the constraints imposed by the bridge induce the bis(acetylide) to bend towards one bpy. On the other hand, several <sup>5</sup>MC states appear highly distorted pentacoordinated species with strongly modified angles that tend to open the way to solvent attack : **7**, **15-17**, **19**. Using the constrained dppf bis(phosphine) ligand remarkably prevents angular distortions in the <sup>5</sup>MC states of **20-21**.

To summarize, the best complexes proposed in this study are thus **10-12** and **14-17**, all displaying a lowest excited state of <sup>3</sup>MLCT nature, in the 0.6-1.2 eV energy range. The examined complexes would thus be emissive in the infrared region. They would also be effective as chromophores and as photoinduced electron donors.

By giving access to the excited state distribution, thus by allowing us to anticipate the photophysical properties, DFT permits, with a limited cost, to design new complexes and to foresee if they are worth being synthesized. In this respect, computational chemistry should gradually take its place in the early stages of research projects. Obviously many other constraints (synthesis, solubility, stability etc) subsequently come into play, which makes the art of chemistry so rich and valuable.

**Supporting Information.** Computational details, selected distances, views of the <sup>5</sup>MC geometries, eigenvalues of relevant molecular orbitals, cartesian coordinates.

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### ACKNOWLEDGMENT

This work was performed using HPC resources from CALMIP (Grant 2015-[p1112]).

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## TOC graphic

The development of iron(II) complexes with photophysical properties (luminescence, electron transfer) is currently a major challenge. This contribution examines the computational design of more than 20 new complexes. Seven of them display a lowest excited state of  $^3\text{MLCT}$  nature, and should therefore be of great interest to the inorganic photophysics community.

