ChemPubSoc Europe
DOI: 10.1002/ejic.201501467
EurJIC European Journal of Inorganic Chemistry
Communication

Photocatalysis

Hydrogen Photoevolution from a Green-Absorbing Iridium(III)–Cobalt(III) Dyad

Alexandre Jacques,[a] Olivier Schott,[b] Koen Robeyns,[a] Garry S. Hanan,*[b] and Benjamin Elias*[a]

Abstract: A bis-cyclometaling ligand afforded a novel Ir^{III}–Co^{III} dinuclear complex with vectorial electron transfer that evolved hydrogen gas upon yellow-light irradiation. The supramolecular photosystem provided increased stability during photocatalysis with respect to that of classic bidentate systems.

Introduction

The future of a sustainable energy supply relies on profound scientific and technological breakthroughs to provide efficient systems for the conversion and storage of renewable energy sources such as solar energy.[1] A photocatalytic hydrogen evolution reaction (HER) appears to be a promising solution to this issue.[2] Within a molecular approach, several components are usually required for an efficient HER: a catalyst, a photosensitizer (PS), a source of protons, and, in the case of half-reactions, a sacrificial electron donor. For several years, cobalt derivatives have drawn considerable attention as compounds that are more efficient and less expensive[3] than colloidal platinum[4] and palladium[5] catalysts. The catalyst and the PS may be added either as separate entities or as covalently linked dinuclear complexes prior to homogeneous catalysis. For instance, cobaloxime derivatives have been associated with transition-metal-based photosensitizers such as platinum,[6] ruthenium,[7] and rhenium[8] complexes. Recently, several Ru–Co dyads covalently connected to each other were developed and were shown to have higher photocatalytic activity than the independent units.[9] In addition, Ir–Co dyads[9b,10] were also designed to benefit from the superiority of Ir^{III} complexes in terms of photophysical and electrochemical tunability.[11] In these photosystems, the archetypical bidentate $[Ir(ppy)_2(bpy)]^+$ complexes (Figure 1, ppy = 2-phenylpyridine, bpy = 2,2′-bipyridine) were frequently used as photosensitizers in excess amounts to increase the turnover number (TON) of the catalytic cycle. To the best of our knowledge, supramolecular Ir–Co assemblies with terdentate ligands have not yet been described. A homoleptic $[Ir(phbpy)_2]^+$ complex (Figure 1, phbpy = 6-phenyl-2,2′-bipyridine) was used as a separate photosensitizer in a bimolecular reaction in association with a palladium colloidal catalyst and showed higher stability than their bidentate equivalents.[12] As opposed to $[Ir(ppy)_2(bpy)]^+$ in which the LUMO is bpy centered and the HOMO is located on the Ir/ppy fragment, $[Ir(phbpy)_2]^+$ has cyclometalating units on each of its two ligands (Figure 1), which hence dramatically affects the photophysics of the resulting complex, as described in other complexes of strongly donating ligands.[13] In this work, the iridium bis-terdentate [Ir(4′-Py-tpy)(4′-MeO-tppy)]$^+$ {Figure 1, 4′-Py-tpy = 4′-(4-pyridinyl)-2,2′;6′,2′′-terpyridine and 4′-MeO-tppy = 2,6-diphenyl-4-(4′-methoxyphenyl)pyridine} (termed hereafter [Ir-Py]$^+$) complex has two cyclometaling sites on the same terdentate ligand, which centers the LUMO on the N N N tridentate ligand. The absorption of [Ir-Py]$^+$ is redshifted relative to that of the *cis*-cyclometaling $[Ir(ppy)_2(bpy)]^+$ and $[Ir(phbpy)_2]^+$ complexes (Figure 1), and this allows a wider range of visible light to be harvested with significant absorptivity. In addition, the pendant pyridine moiety allows for easy covalent tethering of a cobaloxime onto the terpyridine ligand, which offers an efficient assembly for the directional electron transfer required for the HER.

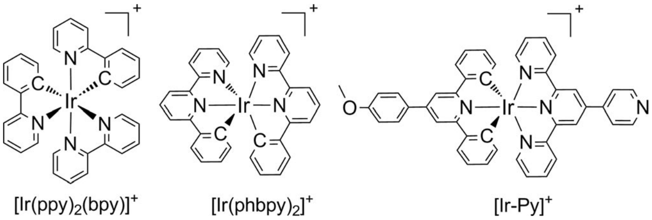

Figure 1. Structure of bis-cyclometalated Ir^{III} bidentate and tridentate complexes used for the HER.

Results and Discussion

The synthesis of the [Ir-Py-Co]$^+$ complex was achieved by replacing a chloro ligand from $[Co(dmgH)(dmgH_2)Cl_2]^+$ (for which dmgH and $dmgH_2$ are dimethylglyoxime and dimethylglyox-

---

[a] *Institute of Condensed Matter and Nanosciences, Molecules, Solids and Reactivity (IMCN/MOST), Université Catholique de Louvain,*
Place Louis Pasteur 1, 1348 Louvain-la-Neuve Belgium
E-mail: benjamin.elias@uclouvain.be
http://www.uclouvain.be/en-237299.html
[b] *Département de Chimie, Université de Montréal,*
2900 boul. Edouard-Montpetit, Montréal, Québec H3T 1J4 Canada
E-mail: garry.hanan@umontreal.ca

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201501467.

imate, respectively) by free pyridine of the previously described [Ir-Py]$^+$ complex.[14] Crystals suitable for X-ray crystal diffraction were obtained by slow diffusion of tetrahydrofuran into an acetonitrile solution of the [Ir-Py-Co]$^+$ complex at room temperature.

The solid-state structure (Figure 2) reveals that the cobalt complex coordinates to the pyridine ring, which is twisted by 32° with respect to the terpyridine ring. For the iridium moiety, distances and angles between atoms are in agreement with data described for a similar complex.[15] As a result, the Ir–C bonds [Ir1–C2 2.071(7) Å and Ir1–C14 2.117(10) Å] are longer than the peripheral Ir–N distances [Ir1–N32 2.022(5) Å and Ir1–N44 2.044(5) Å] owing to a strong mutual *trans* effect between both the C2 and C14 cyclometalated carbon atoms. The central Ir–N distances [Ir1–N8 1.988(15) Å and Ir1–N38 1.921(5) Å] are shorter than the peripheral Ir–C and Ir–N ones, which is in agreement with distances measured for previous similar structures.[15] The diphenylpyridine ring and the methoxyphenyl group are twisted by 35° with respect to one another. The six-coordinate cobalt(III) metal is chelated by two dmgH ligands, a chloride, and the bridging pyridine ring. The bond lengths and angles in [Ir-Py-Co]$^+$ [Co56–N53 1.967(5) Å] are in agreement with those measured for [Co(dmgH)$_2$PyCl],[16] [Co(dmgH)$_2$-(4-CNPy)Cl],[17] and [Co(dmgH)$_2$(4-MeO$_2$CPy)Cl][6a] (with Co–N$_{\text{pyridine}}$ distances = 1.959, 1.963, and 1.959 Å, respectively), which reveals that the structure of the dinuclear complex is not significantly different from that of the separate Ir$^{\text{III}}$ and Co$^{\text{III}}$ units. These data confirm the supramolecular structure of the dyad in the ground state.

The electrochemical data measured for [Ir-Py-Co]$^+$ in acetonitrile are gathered in Table 1. Values obtained for [Ir(ppy)$_2$(bpy)]$^+$, [Ir(phbpy)$_2$]$^+$, and [Ir-Py]$^+$ are also given for comparison purposes. For the dinuclear complex, a reversible one-electron oxidation wave was observed at +1.21 V that corresponds to the oxidation of the cyclometalated iridium fragment (Ir-C N C). This value is slightly more positive than that found for a similar [Ir-Py]$^+$ complex owing to the electron-withdrawing effect of the cobalt moiety.

Table 1. Electrochemical data of [Ir(ppy)$_2$(bpy)]$^+$, [Ir(phbpy)$_2$]$^+$, [Ir-Py]$^+$, and [Ir-Py-Co]$^+$ in acetonitrile.

Complex	E_{ox}[a] [V]	E_{red}[a] [V]
[Ir(ppy)$_2$(bpy)]$^+$	+1.29 (84)	−1.36 (66)
[Ir(phbpy)$_2$]$^+$	+1.31 (83)	−1.38 (66)
[Ir-Py]$^+$	+1.16 (70)	−1.16 (72)
[Ir-Py-Co]$^{+}$[b]	+1.21 (58)	−0.30 (ir); −0.93 (54); −1.08 (50)

[a] Potentials are given in V vs. Ag/AgCl. [b] Electrochemical data were measured with Bu$_4$NClO$_4$ 0.1 M at 100 mV s^{-1} with a complex concentration of 10^{-4} mol L^{-1}. For reversible waves, the difference between the anodic and cathodic peak potential [mV] is given in parentheses.

In the case of [Ir-Py-Co]$^+$, an irreversible one-electron reduction wave at −0.30 V corresponding to the reduction of Co$^{\text{III}}$ to Co$^{\text{II}}$ is observed. This value suggests that solvolysis of the Co$^{\text{III}}$–Cl bond occurs in solution similarly to that noticed for a Ru–Co complex.[9a] At a more negative potential, two reversible reduction waves centered at −0.93 and −1.08 V are found, which correspond to Co$^{\text{II/I}}$ reduction and reduction of the terpyridine moiety, respectively. These values are slightly less negative than those measured for the parent complexes [Co$^{\text{III}}$(dmgH)$_2$(py)Cl] (−0.98 V)[18] and [Ir-Py]$^+$ (−1.16 V) because the metal centers in the assembly are more electron-withdrawing than those in the separate complexes.

The spectroscopic data in acetonitrile are gathered in Table 2 and are shown in Figure 3. For [Ir-Py-Co]$^+$, on the basis of previous studies on cyclometalated Ir$^{\text{III}}$ complexes, the intense absorption bands between 282 and 325 nm are ascribed to ligand-centered (LC) transitions.[19] Absorption bands also appear in the visible region with two maxima at ca. 455 and 525 nm. These transitions correspond to metal/ligand-to-ligand charge transfer (MLLCT) from the cyclometalated iridium fragment (Ir-C N C) to the terpyridine ligand. The energies of the transitions in the visible region of this complex are redshifted relative to those of [Ir(ppy)$_2$(bpy)]$^+$ and [Ir(phbpy)$_2$]$^+$ because the LUMO energy of the 4′-Py-tpy ligand is much lower than that of bpy and phbpy.[11g] The lower energy absorption relative to that of [Ir-Py]$^+$ is due to the electron-withdrawing effect of

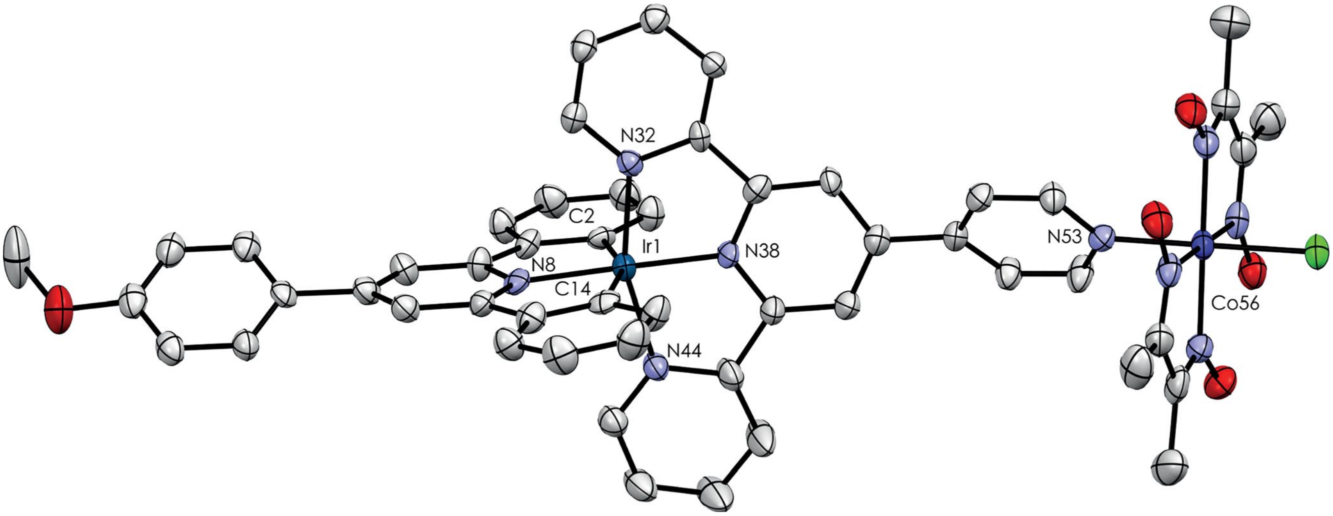

Figure 2. ORTEP representation of [Ir-Py-Co]$^+$ at the 50 % probability level. Hydrogen atoms, counterions, and co-crystallized solvent molecules are omitted for clarity.

Table 2. Spectroscopic data of $[Ir(ppy)_2(bpy)]^+$, $[Ir(phbpy)_2]^+$, [Ir-Py]$^+$, and [Ir-Py-Co]$^+$ in degassed acetonitrile at room temperature.

Complex	λ_{abs} [nm] (ε [$\times 10^2$ M^{-1} cm^{-1}])	$\lambda_{max\ em}$ [nm]	$\tau^{[a]}$ [µs]	$\Phi^{[b]}$ (Ar)	$k_r^{[c]}$ [$\times 10^3$ s^{-1}]
$[Ir(ppy)_2(bpy)]^+$	420 (29), 375 (60), 314 (169), 265 (425)	602	0.28	0.093	338.2
$[Ir(phbpy)_2]^+$	460 (12)	580	0.55	0.039	70.9
[Ir-Py]$^+$	514 (55), 445 (91), 324 (416), 283 (536)	705	1.05	0.006	6.1
[Ir-Py-Co]$^+$	527 (81), 457 (128), 326 (539), 282 (671)	–[d]	–[d]	–[d]	–[d]

[a] Excited state time. [b] Quantum yield was measured in air by using $[Ru(bpy)_3]^{2+}$ as a reference, $\Phi_{ref} = 0.028$ in CH_3CN,[20] $\lambda_{ex} = 450$ nm, 293 K. [c] Radiative rate constant determined under an atmosphere of argon at 293 K ($k_r = \Phi/\tau$). [d] Not emissive.

the cobalt(III) moiety, which stabilizes the LUMO of the 4′-Py-tpy.

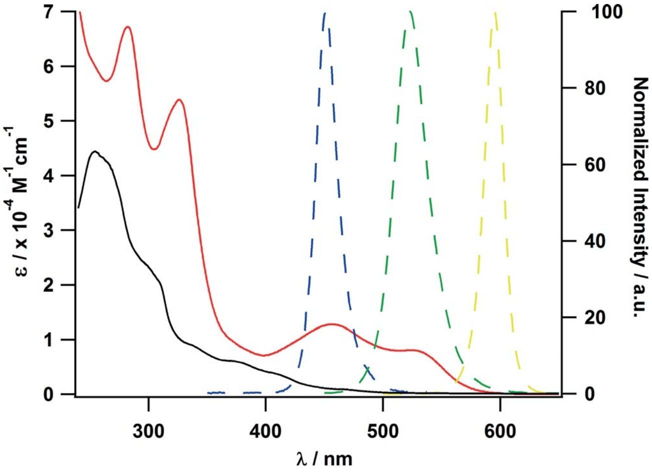

Figure 3. Absorption spectra (solid lines) of [Ir-Py-Co]$^+$ (red) and $[Ir(ppy)_2(bpy)]^+$ (black) in MeCN at 298 K under an atmosphere of argon as well as the emission spectra (dashed lines) of light-emitting diodes used as irradiation sources (blue, green, yellow).

The maximum emission wavelength of [Ir-Py]$^+$ is redshifted relative to that of $[Ir(ppy)_2(bpy)]^+$ and that of $[Ir(phbpy)_2]^+$ to 705 nm. The quantum yield dramatically decreases from 3.9 % for $[Ir(phbpy)_2]^+$ and 9.3 % for $[Ir(ppy)_2(bpy)]^+$ to 0.64 % for [Ir-Py]$^+$, whereas the excited state lifetime of [Ir-Py]$^+$ is double and triple (1.05 µs) that of the two other complexes. These observations are in agreement with the dramatic decrease in the radiative rate constant if the two cyclometalated carbon atoms are on the same ligand. Interestingly, [Ir-Py-Co]$^+$ is not emissive at room temperature. This luminescence quenching could be due to photoinduced electron transfer from the Ir^{III} center to the Co^{III} unit.

The spectroscopic and electrochemical data suggest that among other Ir^{III} derivatives, [Ir-Py-Co]$^+$ is the ideal candidate to evolve molecular hydrogen under irradiation. First, photoinduced electron transfer will be directed from the cyclometalated iridium fragment towards the terpyridine ligand, which is the LUMO of the ^{1}MLLCT excited state and is closer to the cobalt catalyst.[14] Furthermore, with extended absorption spectra up to 600 nm, [Ir-Py-Co]$^+$ should allow hydrogen photoproduction to occur at lower energy than the classic Ir^{III} complexes of phenylpyridine. To prove this effect, three light-emitting diodes (LEDs) with narrow wavelengths centered at 452, 525, and 595 nm were used for the HER. To compare the activity of [Ir-Py-Co]$^+$, a nonlinked $[Ir(ppy)_2(bpy)]^+$ system with $[Co(dmgH)_2PyCl]$ in the same molar concentration was analyzed in parallel experiments as a reference. All photoreactions were performed in acetonitrile with triethanolamine as the sacrificial electron donor and aqueous tetrafluoroboric acid as the proton source.

The photocatalytic HERs show no evidence for an induction time under blue and green irradiation for both systems, which suggests that the same molecular systems are involved in the photocatalytic reaction. Using blue light at 452 nm, the [Ir-Py-Co]$^+$ system reaches a TON of 225 over 35 h versus a TON of 22 for $[Ir(ppy)_2(bpy)]^+$/$[Co(dmgH)_2PyCl]$ over the same time, but the latter catalyst system is completely deactivated after the first 0.5 h (Figure 4). The photocatalytic performances of [Ir-Py-Co]$^+$ are comparable to those of the $[(ppy)_2Ir(L\text{-}pyr)Co(dmgBF_2)_2(OH_2)]^+$ device (TON = 210 after 15 h)[9b] and the tridentate dissociated system $[Ir(phbpy)_2]^+$/Pd $^{2+[12]}$ (TON = 137 after 5 h).

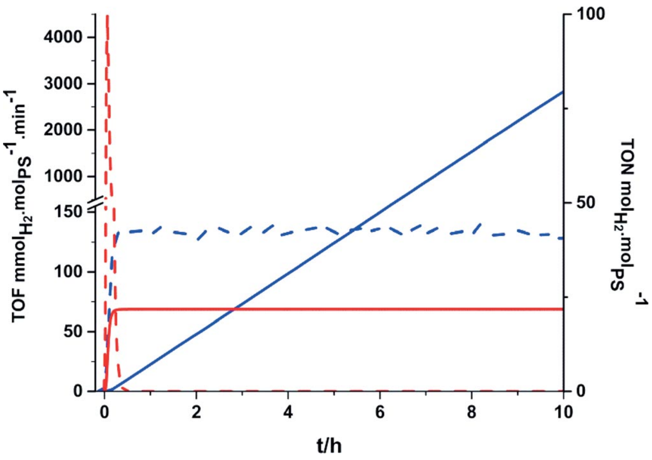

Figure 4. Hydrogen evolution of [Ir-Py-Co]$^+$ (blue) and $[Ir(ppy)_2(bpy)]^+$ with $[Co(dmgH)_2PyCl]$ (red). Solid line: TON, dashed line: TOF. Reaction conditions: 0.1 mM PS, 0.1 mM catalyst, 1 M triethanolamine, 0.1 M HBF_4. Solvent: acetonitrile, under an atmosphere of argon. Irradiation centered at 452 nm (see Figure 3).

The rate of activity for [Ir-Py-Co]$^+$ remains constant within 130 mmol$_{H_2}$ mol$_{PS}$$^{-1}$ min^{-1} during the first 15 h. Upon turning the lamp on, $[Ir(ppy)_2(bpy)]^+$ rapidly reaches its maximum activity at ca. 4500 mmol$_{H_2}$ mol$_{PS}$$^{-1}$ min^{-1} before a rapid decrease involving the decomposition of the photocatalytic system (Figure 4), albeit with a lower overall TON than [Ir-Py-Co]$^+$ (Table S5 in the Supporting Information). The rate of activity for [Ir-Py-Co]$^+$ is about one order of magnitude lower than that of the reference complex, and it lasts up to 66 h (TON = 440) if 4 equiv. of $dmgH_2$ is added to the reaction mixture,[8a] which is unusually long for Ir^{III} and Co^{III}/Co^{II} systems (see Table S5). Clearly, the use of an excess amount of the expensive $[Ir(ppy)_2(bpy)]^+$ photosensitizer is not optimal.

The green-light LED centered at 525 nm covers the tail of the $[Ir(ppy)_2(bpy)]^+$ absorption spectrum and overlays the $[Ir\text{-}Pyr\text{-}Co]^+$ band with appreciable molar absorptivity (see Figure 4 and Table 2). A molar absorptivity lower in the range of green light than in the range of blue light results in a concomitant decrease in hydrogen production; however, the tridentate system has more sustained hydrogen evolution: TON of 113 for $[Ir\text{-}Py\text{-}Co]^+$ and a TON of 12 for the reference system $[Ir(ppy)_2(bpy)]^+/[Co(dmgH)_2PyCl]$ (Figure 5). Concerning rate of activity, the overall decrease is remarkably different, as the reference system drops by over 4000 $mmol_{H_2}\ mol_{PS}^{-1}\ min^{-1}$ and $[Ir\text{-}Py\text{-}Co]^+$ decreases by only 30 $mmol_{H_2}\ mol_{PS}^{-1}\ min^{-1}$ and remains homogeneous. For the bidentate model system, however, the rate does not decay as rapidly as it does for blue light. Under yellow irradiation centered at 595 nm, $[Ir\text{-}Py\text{-}Co]^+$ starts a low production of hydrogen (TOF = 4 $mmol_{H_2}\ mol_{PS}^{-1}\ min^{-1}$) after 5 h, and no activity is detected for $[Ir(ppy)_2(bpy)]^+$ (Table S5). The $[Ir\text{-}Py\text{-}Co]^+$ system has low but sustainable activity from the start of the photoreaction until the end, which suggests that tridentate systems are much more stable with Ir^{III} than with Ru^{II}.[21] The low quantum yield of $[Ir\text{-}Py]^+$ could be related to the fact that this photoinduced electron-transfer rate is slower than that of $[Ir(ppy)_2(bpy)]^+$ (the low homogeneous activity of the Ir–Co assembly could also characterize directional electron transfer through the pyridylterpyridine to cobaloxime[19]). The pendant pyridine ring of $[Ir\text{-}Py]^+$ could act as an electron relay from the PS to the catalyst, as it links both entities[9d] and is the coordination site for cobaloxime. Coordination of cobaloxime to the PS appears to be a crucial factor for the efficiency and stability of the system.[9]

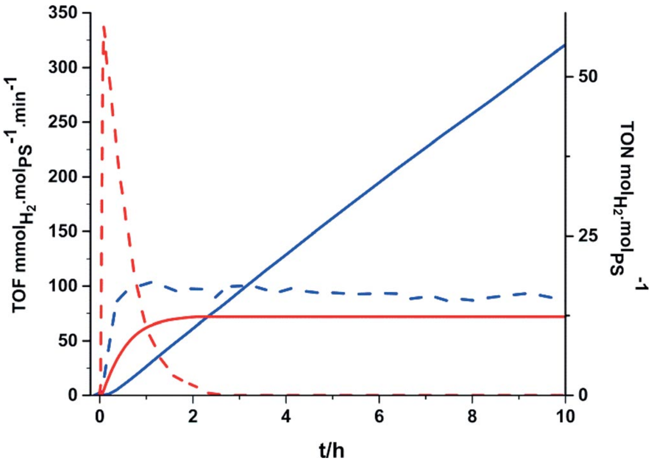

Figure 5. Hydrogen evolution of $[Ir\text{-}Py\text{-}Co]^+$ (blue) and $[Ir(ppy)_2(bpy)]^+$ with $[Co(dmgH)_2PyCl]$ (red). Solid line: TON, dashed line: TOF. Reaction conditions: 0.1 mM PS, 0.1 mM catalyst, 1 M triethanolamine, 0.1 M HBF_4. Solvent: acetonitrile, under an atmosphere of argon. Irradiation centered at 525 nm (Figure 3).

Conclusion

In summary, the new $[Ir\text{-}Py\text{-}Co]^+$ dyad presents much greater robustness than the bidentate equivalent for $[Ir(ppy)_2(bpy)]^+$ upon examining the HER at equivalent quantities of the Ir photosensitizer and the Co catalyst. The bis-cyclometalating ligand gives a HOMO with both metal and ligand nature that is relatively high in energy, while maintaining a low energy LUMO owing to the terpyridine ligand in the role of ancillary ligand of the Ir^{III} complex. This shift in ligand composition in comparison to phenylbipyridines allows greater control of the direction of the MLLCT transition towards the Co catalyst and also allows the HER to occur at lower energy than classic Ir^{III} compounds.

CCDC 1419882 (for $[Ir\text{-}Py\text{-}Co]^+$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

The authors gratefully acknowledge the Fonds National pour la Recherche Scientifique (F.R.S.-FNRS), Belgium, the Fonds pour la Formation à la Recherche dans l'Industrie et dans l'Agriculture (F.R.I.A.), Belgium, the Région Wallonne, Belgium, the Université Catholique de Louvain, Belgium, and the Prix Pierre et Colette Bauchau, Belgium for financial support. G. S. H. thanks the Natural Sciences and Engineering Research Council (NSERC), Canada and the Direction des Affaires Internationales de l'Université de Montréal, Canada for financial support. Prof. K. Van Hecke is thanked for allowing access to his diffractometer.

Keywords: Supramolecular chemistry · Photochemistry · Dihydrogen · Cobalt · Iridium

[1] R. F. Service, *Science* **2005**, *309*, 548–551.
[2] V. Balzani, A. Credi, M. Venturi, *ChemSusChem* **2008**, *1*, 26–58.
[3] V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem. Int. Ed.* **2011**, *50*, 7238–7266; *Angew. Chem.* **2011**, *123*, 7376–7405.
[4] a) K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159–244; b) C. K. Graetzel, M. Graetzel, *J. Am. Chem. Soc.* **1979**, *101*, 7741–7742; c) J. M. Lehn, J. P. Sauvage, *Nouv. J. Chim.* **1977**, *1*, 449–451.
[5] E. Amouyal, *Sol. Energy Mater. Sol. Cells* **1995**, *38*, 249–276.
[6] a) P. Jarosz, P. Du, J. Schneider, S.-H. Lee, D. McCamant, R. Eisenberg, *Inorg. Chem.* **2009**, *48*, 9653–9663; b) P. Du, K. Knowles, R. Eisenberg, *J. Am. Chem. Soc.* **2008**, *130*, 12576–12577.
[7] a) C. Creutz, H. A. Schwarz, N. Sutin, *J. Am. Chem. Soc.* **1984**, *106*, 3036–3037; b) J. M. Lehn, J. P. Sauvage, J. Simon, R. Ziessel, C. Piccinni-Leopardi, G. Germain, J. P. Declercq, M. Van Meerssche, *Nouv. J. Chim.* **1983**, *7*, 413–420; c) C. V. Krishnan, B. S. Brunschwig, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **1985**, *107*, 2005–2015.
[8] a) B. Probst, C. Kolano, P. Hamm, R. Alberto, *Inorg. Chem.* **2009**, *48*, 1836–1843; b) B. Probst, A. Rodenberg, M. Guttentag, P. Hamm, R. Alberto, *Inorg. Chem.* **2010**, *49*, 6453–6460; c) B. Probst, M. Guttentag, A. Rodenberg, P. Hamm, R. Alberto, *Inorg. Chem.* **2011**, *50*, 3404–3412; d) M. Guttentag, A. Rodenberg, R. Kopelent, B. Probst, C. Buchwalder, M. Brandstaetter, P. Hamm, R. Alberto, *Eur. J. Inorg. Chem.* **2012**, 59–64.
[9] a) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl, M. Fontecave, *Angew. Chem. Int. Ed.* **2008**, *47*, 564–567; *Angew. Chem.* **2008**, *120*, 574–577; b) A. Fihri, V. Artero, A. Pereira, M. Fontecave, *Dalton Trans.* **2008**, 5567–5569; c) C. Li, M. Wang, J. Pan, P. Zhang, R. Zhang, L. Sun, *J. Organomet. Chem.* **2009**, *694*, 2814–2819; d) E. Rousset, D. Chartrand, I. Ciofini, V. Marvaud, G. S. Hanan, *Chem. Commun.* **2015**, *51*, 9261–9264.
[10] S. Jasimuddin, T. Yamada, K. Fukuju, J. Otsuki, K. Sakai, *Chem. Commun.* **2010**, *46*, 8466–8468.
[11] a) M. Y. Wong, G. Xie, C. Tourbillon, M. Sandroni, D. B. Cordes, A. M. Z. Slawin, I. D. W. Samuel, E. Zysman-Colman, *Dalton Trans.* **2015**, *44*, 8419–8432; b) N. M. Shavaleev, G. Xie, S. Varghese, D. B. Cordes, A. M. Z. Slawin, C. Momblona, E. Orti, H. J. Bolink, I. D. W. Samuel, E. Zysman-Colman,

Inorg. Chem. **2015**, *54*, 5907–5914; c) K. Hasan, L. Donato, Y. Shen, J. D. Slinker, E. Zysman-Colman, *Dalton Trans.* **2014**, *43*, 13672–13682; d) B. F. DiSalle, S. Bernhard, *J. Am. Chem. Soc.* **2011**, *133*, 11819–11821; e) H. N. Kagalwala, E. Gottlieb, G. Li, T. Li, R. Jin, S. Bernhard, *Inorg. Chem.* **2013**, *52*, 9094–9101; f) I. N. Mills, H. N. Kagalwala, D. N. Chirdon, A. C. Brooks, S. Bernhard, *Polyhedron* **2014**, *82*, 104–108; g) D. N. Chirdon, W. J. Transue, H. N. Kagalwala, A. Kaur, A. B. Maurer, T. Pintauer, S. Bernhard, *Inorg. Chem.* **2014**, *53*, 1487–1499; h) S. Ladouceur, E. Zysman-Colman, *Eur. J. Inorg. Chem.* **2013**, 2985–3007.

[12] L. L. Tinker, S. Bernhard, *Inorg. Chem.* **2009**, *48*, 10507–10511.

[13] a) R. Lalrempuia, N. D. McDaniel, H. Mueller-Bunz, S. Bernhard, M. Albrecht, *Angew. Chem. Int. Ed.* **2010**, *49*, 9765–9768; *Angew. Chem.* **2010**, *122*, 9959–9962; b) A. K. Pal, G. S. Hanan, *Dalton Trans.* **2014**, *43*, 11811–11814; c) A. K. Pal, N. Zaccheroni, S. Campagna, G. S. Hanan, *Chem. Commun.* **2014**, *50*, 6846–6849; d) A. K. Pal, S. Serroni, N. Zaccheroni, S. Campagna, G. S. Hanan, *Chem. Sci.* **2014**, *5*, 4800–4811; e) A. K. Pal, G. S. Hanan, *Dalton Trans.* **2014**, *43*, 6567–6577; f) A. K. Pal, S. Nag, J. G. Ferreira, V. Brochery, G. La Ganga, A. Santoro, S. Serroni, S. Campagna, G. S. Hanan, *Inorg. Chem.* **2014**, *53*, 1679–1689; g) S. Nag, J. G. Ferreira, L. Chenneberg, P. D. Ducharme, G. S. Hanan, G. La Ganga, S. Serroni, S. Campagna, *Inorg. Chem.* **2011**, *50*, 7–9; h) A. K. Pal, P. D. Ducharme, G. S. Hanan, *Chem. Commun.* **2014**, *50*, 3303–3305; i) S. Ladouceur, D. Fortin, E. Zysman-Colman, *Inorg. Chem.* **2011**, *50*, 11514–11526; j) K. N. Swanick, S. Ladouceur, E. Zysman-Colman, Z. Ding, *RSC Adv.* **2013**, *3*, 19961–19964; k) V. L. Whittle, J. A. G. Williams, *Dalton Trans.* **2009**, 3929–3940; l) J. A. G. Williams, A. J. Wilkinson, V. L. Whittle, *Dalton Trans.* **2008**, 2081–2099.

[14] A. Jacques, T. Auvray, M. Cibian, G. S. Hanan, A. Kirsch-De Mesmaeker, B. Elias, *Inorg. Chem.* **2015**, submitted for publication.

[15] M. Polson, S. Fracasso, V. Bertolasi, M. Ravaglia, F. Scandola, *Inorg. Chem.* **2004**, *43*, 1950–1956.

[16] S. Geremia, R. Dreos, L. Randaccio, G. Tauzher, L. Antolini, *Inorg. Chim. Acta* **1994**, *216*, 125–129.

[17] C. Lopez, S. Alvarez, X. Solans, M. Font-Altaba, *Inorg. Chem.* **1986**, *25*, 2962–2969.

[18] M. Razavet, V. Artero, M. Fontecave, *Inorg. Chem.* **2005**, *44*, 4786–4795.

[19] M. Polson, M. Ravaglia, S. Fracasso, M. Garavelli, F. Scandola, *Inorg. Chem.* **2005**, *44*, 1282–1289.

[20] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277.

[21] K. L. Mulfort, D. M. Tiede, *J. Phys. Chem. B* **2010**, *114*, 14572–14581.

Received: December 21, 2015