CONCEPT

A Roadmap Towards Visible Light Mediated Electron Transfer Chemistry with Iridium(III) Complexes

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Abstract: Photo-induced electron transfer chemistry between molecules is a central theme in several fields including biology, physics and chemistry. Specifically, in photoredox catalysis, greater use has been made of iridium(III) complexes as they exhibit ground- and excited-state redox potentials that span a very large range. Unfortunately, most of these complexes suffer from limited visible light absorption properties. This concept article highlights recent developments in the synthesis of iridium(III) complexes with increased visible light absorption properties and their use as candidates for visible light driven redox catalysis. Fundamental tools are provided to enable the independent tuning of the HOMO and LUMO energy levels. Recent examples are given with the hope that this concept article will foster further developments of iridium(III)-based sensitizers for visible light driven reactivity.

Introduction

Since the early 2000s, iridium(III)-based compounds have emerged as promising candidates for applications in lighting devices,[1-4] life sciences[5-10] and photoredox chemistry.[11-24] In all these fields, the success of Ir(III) complexes relies on several key features, which include relatively long-lived excited-states and exceptional photo- and redox stability. However, it is the ability to accommodate up to three cyclometalated bonds (Ir-C) and the resulting impressive tunability of their optoelectronic properties that make Ir(III) complexes stand out. Such versatility is particularly striking in the series $[Ir(ppy)_x(bpy)_{3-x}]^{(3-x)+}$ (ppy = 2-phenylpyridine, bpy = 2,2'-bipyridine), where x varies between 0 and 3 (**Table 1**).[25] The number of Ir-C bonds has drastic effects on the frontier orbitals of the resulting complex due to the difference in σ-donation ability between Ir-C and Ir-N bonds.[26] One effect is the delocalization of the HOMO level onto the cyclometalated ligand framework. Consequently, this orbital is not exclusively confined to the metal center, as in ruthenium(II) tris-diimine complexes for example, and may be further stabilized/destabilized through strategic ligand modifications. In addition, a spatial separation of each frontier orbital enables independent tuning of either the HOMO or the LUMO.[27] This property has been exploited to adjust the HOMO-LUMO gap in order to achieve photoluminescence spanning a wide range of wavelengths.[28-32] Tuning this energy gap has allowed access to photocatalysts with interesting (photo)redox properties for electron transfer chemistry.[11-24, 33] Furthermore, the range of (photo)redox potentials available for Ir(III) complexes is far greater than for their Ru(II), Os(II) or Cu(I) counterparts (**Table 1** and **Figure 1**).[14, 15, 34] Nonetheless, a major drawback of Ir(III) complexes is their poor visible light harvesting capabilities, as prototypical complexes absorb mainly in the UV region, with limited absorption extending into the blue part of the spectrum (**Table 1**).

Several strategies have recently been developed to achieve robust visible light absorption for iridium(III) complexes. These approaches include modifications of the prototypical ppy (C-N) and bpy (N-N) ligands to tune the electronic energy levels. Other common approaches include extension of the π-conjugation across the ligands or linking them to additional chromophores with intense visible light absorption. This concept article provides an overview of these strategies and discusses their impact on the electrochemical properties of the resulting compounds. It is undeniably challenging to design Ir(III) complexes with increased visible light absorption, while maintaining redox properties competent for excited-state electron transfer with challenging substrates.

Table 1. Electrochemical and spectroscopic data for $[Ir(ppy)_x(bpy)_{3-x}]^{(3-x)+}$.

	$E_{1/2}$ ($Ir^{IV/III}$)[a]	$E_{1/2}$ ($L^{n/n-1}$)[a]	λ_{abs} / nm[b] (ε / $M^{-1}cm^{-1}$)	λ_{PL} / nm RT[c]	λ_{PL} / nm 77K[d]	Ref
fac-$[Ir(ppy)_3]$	+1.01	–1.95	375 (7200)[e]	517	494	25, 35, 36
$[Ir(ppy)_2(bpy)]^+$	+1.56	–1.16	410 (2800)	587	517	25, 37, 38
$[Ir(ppy)(bpy)_2]^{2+}$	+2.29	–0.96	390 (2800)	507	498	25, 37, 38
$[Ir(bpy)_3]^{3+}$	+2.34	–0.86	344 (3300)	452	441	25, 39, 40

[a] V *vs.* NHE in acetonitrile (adapted from the original work where necessary, $V_{NHE} = V_{SCE} + 0.24$ V, $V_{NHE} = V_{Fc+/0} + 0.64$ V)
[b] in MeOH at room temperature
[c] in acetonitrile at room temperature
[d] in 4:1 ethanol/methanol glass at 77 K
[e] in toluene at room temperature

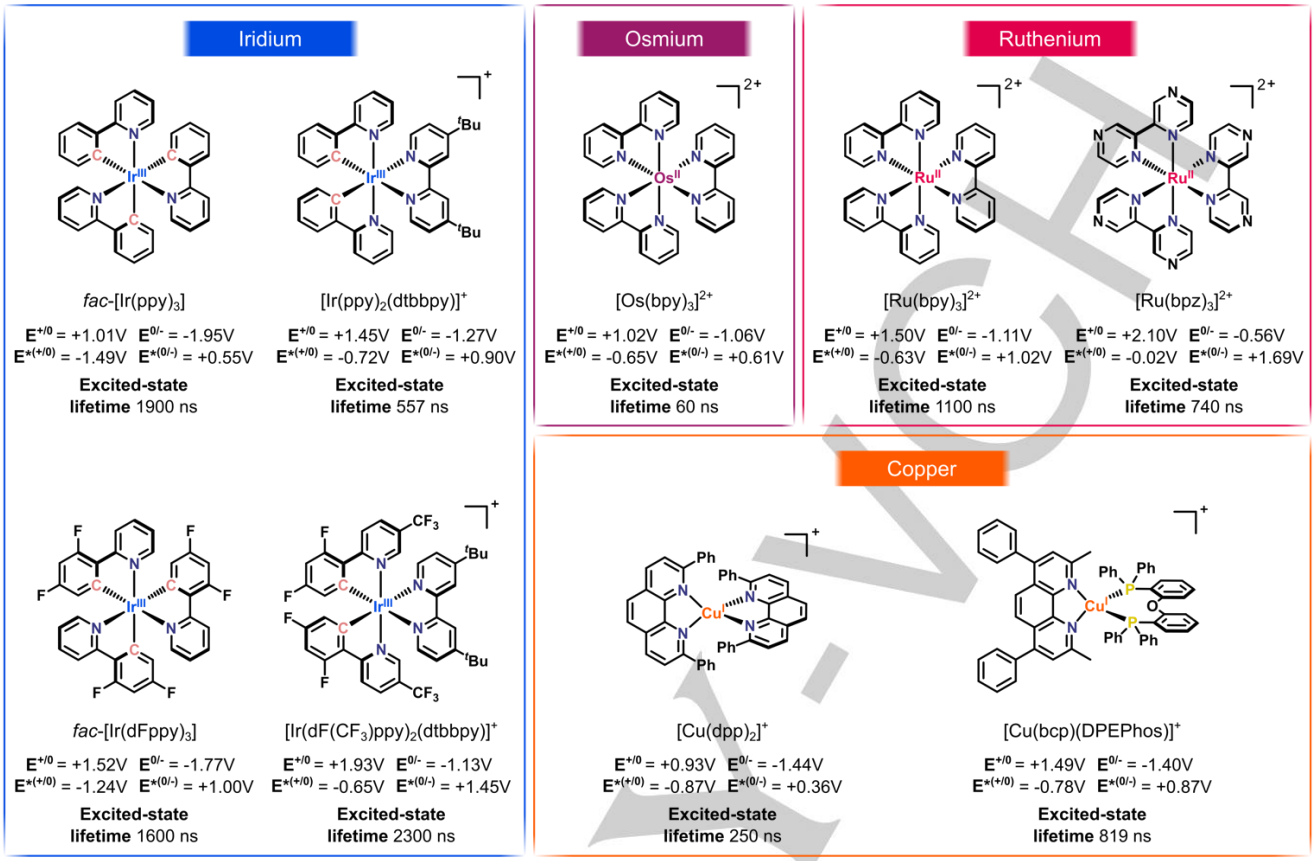

Figure 1. Typical photocatalysts based on iridium(III),[14, 15, 34, 41, 42] ruthenium(II),[43, 44] osmium(II)[45-47] and copper(I)[48, 49] for photoredox applications. Potentials are given *vs.* NHE in acetonitrile (adapted from the original work, $V_{NHE} = V_{SCE} + 0.24$ V, $V_{NHE} = V_{Fc^{+/0}} + 0.64$ V). Excited-state lifetimes (τ) are given under inert atmosphere in acetonitrile at room temperature.

As Ir-C bonds have such profound effects on the photophysical properties, complexes will be divided hereafter into different families according to the number of Ir-C bonds*; i.e.* no cyclometalated bonds (IrN_6), two cyclometalated bonds ((IrC_2N_4) or (IrC_2N_2LX) - LX being a monoanionic bidentate ligand), and finally three cyclometalated bonds (IrC_3N_3). Complexes with both bidentate and tridentate ligands will be thoroughly examined. Complexes with one cyclometalated bond (IrC_1N_5, IrC_1N_4Cl) will not be discussed here, as these are by so far scarce in the literature.[25, 50-52] First, the basic photochemistry of iridium complexes will be described, highlighting the main differences between the different families of complexes. Then, examples that showcase impressive visible light absorption will be presented, followed by examples that combine visible light absorption and desirable redox properties. Finally, a roadmap for the design of iridium(III) complexes that absorb visible light appreciably, while maintaining interesting photoredox properties for oxidative and reductive photochemistry, will be outlined.

Photochemistry of Iridium(III) Complexes

Electronic transitions and excited-state properties

UV-visible spectra of iridium(III) complexes typically involve a large number of different transitions (**Figure 2A**).[53, 54] While large molar absorption coefficients (~80000 $M^{-1}cm^{-1}$) are recorded in the UV region due to ligand-based π-π* transitions, charge transfer (CT) bands are usually present at wavelengths greater than 350 nm. Depending on the nature of the chelating ligands, these correspond to a mixture of metal-to-ligand (MLCT) and ligand-to-ligand (LLCT) transitions, which are usually characterized by slightly smaller molar absorption coefficients (5000-10000 $M^{-1}cm^{-1}$). Due to the large spin orbit coupling of the iridium center, small contributions from direct triplet excitation (<1000 $M^{-1}cm^{-1}$) may be observed in the visible range.[55] While the absorption bands are typically similar for the different families of complexes, they may vary in terms of energy, shape and molar absorption coefficients as an effect of the number of Ir-C bonds and the nature of the different chelating ligands.

Excitation of iridium(III) complexes results in relatively long-lived excited-states, with typical lifetimes (τ) that range from a few nanoseconds to several microseconds. Upon excitation, a Franck-Condon state is formed, which rapidly undergoes intersystem crossing (ISC) to a triplet excited-state.[56-62] The nature of this excited state is often invoked as a mixture of ligand-centered (^{3}LC) and metal-to-ligand charge transfer (^{3}MLCT) states.[27, 63, 64] The explanation for this mixed nature is the strong σ-donation ability of Ir-C bonds, which leads to a more electron rich metal core through delocalization of the HOMO onto the cyclometalated ligand framework. The subsequent destabilization

of the metal dπ orbitals promotes the mixing between different excited states when the number of Ir-C bonds increases (**Figure 2B**).

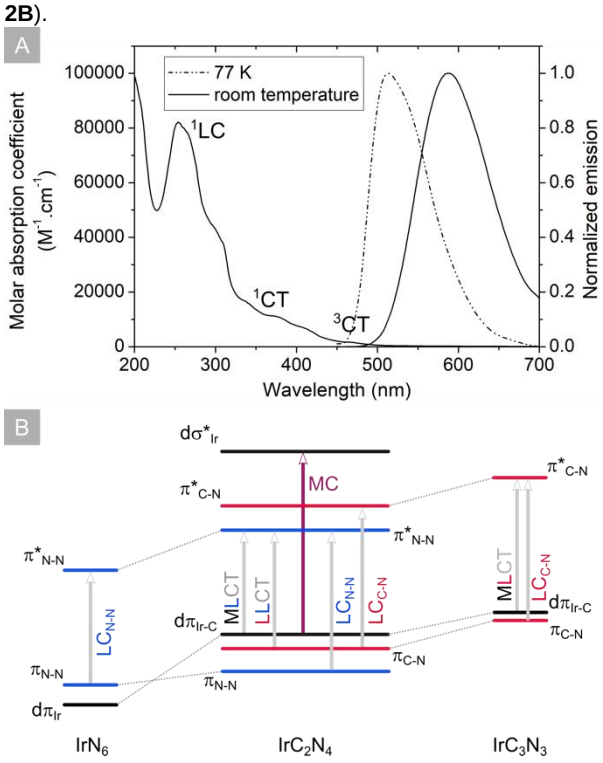

Figure 2. (A) UV-visible and photoluminescence spectra of $[Ir(ppy)_2(bpy)]^+$ in acetonitrile at room temperature (solid lines) and in 4:1 ethanol/methanol glass at 77 K (dashed line). (B) Influence of the number of Ir-C bonds on the electronic configuration and the lowest-energy transitions of Ir(III) complexes.

Although IrN_6 complexes are pure $^3LC_{N-N}$ emitters,[39] compounds with one, two or three C-N ligands usually possess mixed $^3LC_{C-N}/^3MLCT_{C-N}/^3MLCT_{N-N}/^3LC_{N-N/LX}$ excited states, their relative contribution varying with temperature and solvent.[27, 54, 63, 64] In addition, for heteroleptic IrC_2N_4 complexes, photoluminescence may also occur from ligand-to-ligand charge transfer (^{3}LLCT) states.[65, 66] Another major consequence of the difference in σ-donation ability between Ir-C and Ir-N bonds is the generally greater quantum yields and photostability of cyclometalated iridium(III) complexes, as compared to ruthenium(II) and osmium(II) tris-diimine sensitizers. The combination of a third-row transition metal and strong σ-donating ligands leads to a large ligand field splitting of the d-orbitals (Δ_0). The metal-based e_g (dσ*) subshell is thus driven well-above the ligand-based π* orbitals (**Figure 2B**), resulting in low-energy $^3LC/^3MLCT/^3LLCT$ excited states, free to emit without contributions from non-radiative decay of ^{3}MC states.[4, 27, 54] This effect is particularly strong when the complex contains at least two Ir-C bonds. Therefore, a vast majority of iridium(III)-based compounds developed so far for photochemical applications, are bis-cyclometalated and tris-cyclometalated complexes.

(Photo)electrochemical properties

The Ir-C bond influences the electrochemical properties of iridium(III) complexes in their ground- and excited-state by affecting the energy and the relative position of the frontier orbitals (**Figure 2B** and **Figure 3**). The excited-state oxidation and reduction potentials ($E_{1/2}(Ir^{*(n/n-1)})$) are determined using **equations 1** and **2**, where $E_{1/2}(Ir^{(n/n-1)})$ corresponds to the ground-state reduction potentials and $E_{0\text{-}0}$ corresponds to the free energy stored in the excited-state.[67] It should be noted that a more positive E^*_{red} ($E_{1/2}(Ir^{*(0/-)})$) implies a stronger photooxidant whereas a more negative E^*_{ox} ($E_{1/2}(Ir^{*(+/0)})$) implies a stronger photoreductant. $E_{0\text{-}0}$ energies are best determined from a Franck-Condon lineshape analysis of the photoluminescence at 77 K or from the intercept of the absorption and photoluminescence spectra, when possible.[68-71] Alternative methods to determine $E_{0\text{-}0}$ rely on i) a blue-edge tangent straight line fit, ii) an estimate via the absorption onset or iii) an estimate through the λmax of photoluminescence. The latter however, is an underestimation of $E_{0\text{-}0}$. These different methods to determine $E_{0\text{-}0}$ represent the main reason for disparate values in the literature.

$$E^*_{red} = E_{1/2}\left(Ir^{*(0/-)}\right) = E_{1/2}\left(L^{(n/n-1)}\right) + E_{0-0} \quad \text{Eq. 1}$$

$$E^*_{ox} = E_{1/2}\left(Ir^{*(+/0)}\right) = E_{1/2}\left(Ir^{(IV/III)}\right) - E_{0-0} \quad \text{Eq. 2}$$

For IrN_6 complexes (**Figure 3**), which have no Ir-C bonds, the electron density at the iridium metal center is relatively low, resulting in highly positive oxidation potentials.[40] Bipyridine-type ligands exhibit reduction potentials that are typically around –1V *vs.* NHE which, when combined with the relatively large $E_{0\text{-}0}$ of these iridium complexes, results in IrN_6 complexes that are potent excited-state oxidants (E^*_{red}), *i.e.* act as good electron acceptors in the excited-state.[35]

IrC_3N_3 complexes (**Figure 3**), which contain three cyclometalated bonds, exhibit increased electron density on the iridium core. Hence, IrC_3N_3 complexes have less positive metal-based oxidations than other Ir-C/N complexes. The result, as can be inferred from **equation 2**, is that these complexes behave as potent photo-reductants (E^*_{ox}).[35] Note that, due to chelation of three anionic ligands, IrC_3N_3 type complexes are neutral, hence limiting their solubility and practical use.

[Ir(C-N)$_2$LX] complexes (**Figure 3**), where LX is a monoanionic bidentate ligand, are neutral and photo-reducing. For these compounds, similarly to IrC_3N_3 complexes, the cyclometalated ligands usually dominates the optoelectronic properties, as typical acetylacetonate (acac) and picolinate (pic) ligands do not contribute substantially to either the HOMO or the LUMO levels.[72-75] However, changing for β-ketoiminate (acNac) or β-diketiminate (NacNac) ligands with more nitrogen donors further increases the photo-reducing power of such complexes.[76] This is a result of the stronger π-donor ability of these ligands, which destabilizes the HOMO orbital and leads to less positive oxidation potentials (**Figure 3**).

Finally, perhaps the most developed class of iridium(III) complexes for electron transfer chemistry is the cationic $[Ir(C\text{-}N)_2(N\text{-}N)]^+$ type complexes (**Figure 3**), which form the IrC_2N_4 family.[11-20, 33, 77, 78] These heteroleptic complexes encompass a much broader range of electrochemical behavior than the other classes. The electron-donating ability of the cyclometalated ligands results in mixing of the HOMO orbitals with those of the ligands, and hence an extension beyond the metal-based orbitals. The LUMO remains localized on the bipyridine ligand, and due to this spatial separation of the frontier orbitals, the HOMO and LUMO may be independently tuned through ligand modifications (**Figure 2B** and **Figure 3**).[27, 29] Consequently, this class of iridium complexes can be modified to become either more photo-oxidizing (E^*_{red}) or photo-reducing (E^*_{ox}). However, this property is not exclusive to IrC_2N_4 complexes. To some extent, independent control of the energy of each frontier orbital may be

achieved for most families of iridium(III) complexes. As will be discussed below, this constitutes a huge advantage for independent fine-tuning of the spectroscopic and electrochemical properties.

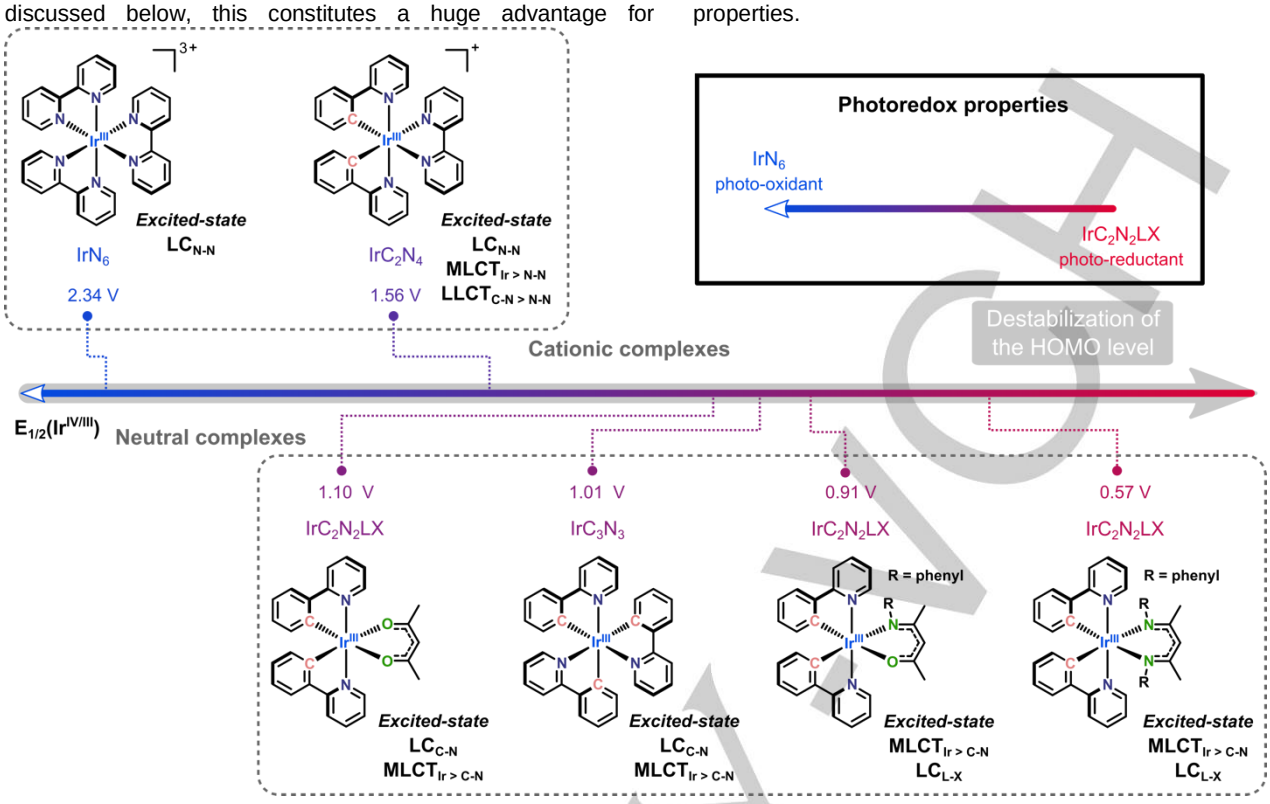

Figure 3. Representative families of Ir(III) complexes with typical bidentate ligands and their associated (photo)redox properties. Potentials are given *vs.* NHE in acetonitrile (adapted from the original work, $V_{NHE} = V_{SCE} + 0.24$ V, $V_{NHE} = V_{Fc^{+/0}} + 0.64$ V).

Approaches to increase visible light absorption

All families of iridium(III) complexes may be tuned to increase visible light absorption. Common strategies towards that goal are quite similar to the achievement of red-tuned photoluminescence and include i) addition of functional groups, ii) substitution of the archetypical ligands, iii) extended conjugation, and iv) chromophore coupling. Nevertheless, modifications of the complexes' electronic distribution also induce changes in their reduction potentials $E_{1/2}(Ir^{(n/n-1)})$, which ultimately impact the final light-induced applications. Here, for sake of clarity, the different approaches and their effects on the electronic configurations of the resulting complexes will be developed separately, but in reality, these are often combined. Finally, in the last section, the use of these approaches in each family of iridium(III) complexes to design compounds with highly desirable (photo)redox properties for electron transfer chemistry will be described.

Addition of functional groups

The most common strategy to tune the HOMO-LUMO gap and the related optoelectronic properties of Ir(III) complexes involves changes of the ligand scaffold through the addition of functional groups or chromophores. Substitution with electron-withdrawing (EW) groups stabilizes the involved orbitals, whereas modification of the ligands using electron-donating (ED) groups raises their energy. This approach has been comprehensively explored in the field of lighting devices in order to achieve blue to red photoluminescence.[28-32] In the same way, the HOMO-LUMO gap can be tuned to red-shift the light absorption via independent destabilization of the HOMO by ED groups and/or stabilization of the LUMO by EW groups. However, as reported for methoxy-[79] (**Ir1-2**) or cyano-substituted[80] (**Ir3**) IrC_2N_4 complexes (**Figure 4**), the impact on the absorption properties of the resulting complexes usually remains moderate when small functional groups are used (**Table 2**). By comparison, large electron-donor substituents, such as triphenylamine (TPA) (**Ir4**) (**Figure 4**), result in greater variations in the absorption profile (**Table 2**). This is a consequence of the increased contribution from intraligand charge transfer (ILCT) transitions, arising from the formation of an electron donor-acceptor pair on the modified ligand (**Figure 4**).[81]

Table 2. Electrochemical and spectroscopic data for $[Ir(ppy)_2(bpy)]^+$ and **Ir1-4**.

	$E_{1/2}$ ($Ir^{V/III}$)[a]	$E_{1/2}$ ($L^{n/n-1}$)[a]	λ_{abs} / nm[b] (ε / $M^{-1}cm^{-1}$)	λ_{PL} / nm[b]	Ref
$[Ir(ppy)_2(bpy)]^+$	+1.56	–1.16	412 (3600)	599	37, 38, 66
Ir1	+1.19	–1.16	425 (7000)	710	79
Ir2	+1.14	–1.28	425 (8000)	680	79
Ir3	+1.61	–0.56	530 (nr)[c]	750	80
Ir4	nr[c]	nr[c]	490 (53100)[d]	666[d]	81

[a] V *vs.* NHE in acetonitrile (adapted from the original work if necessary, $V_{NHE} = V_{SCE} + 0.24$ V, $V_{NHE} = V_{Fc^{+/0}} + 0.64$ V)

[b] in acetonitrile at room temperature
[c] not reported
[d] in CH_2Cl_2 at room temperature

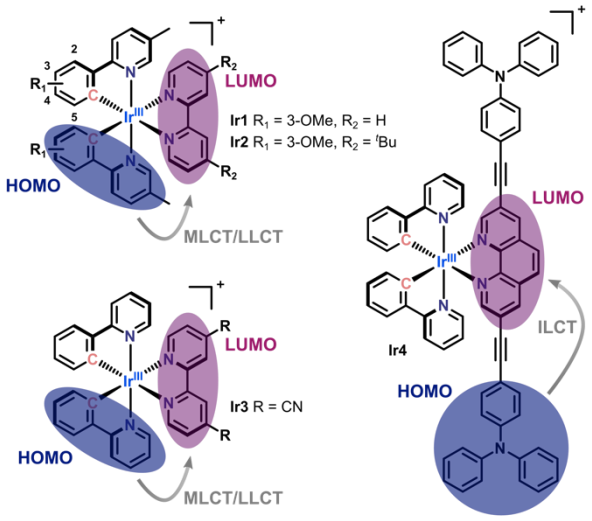

Figure 4. Methoxy-, cyano- and TPA-substituted IrC_2N_4 complexes and respective localization of their HOMO and LUMO orbitals.

Substitution of ligands

Another way to improve absorption properties consists in the direct substitution of the prototypical ligands. Most research has focused on replacing the 2-phenylpyridine (ppy) ligand, by altering the 6-membered phenyl and pyridine rings to 5-membered thiophene,[82-85] oxazole[86-89] or thiazole[90-93] rings (**Figure 5**). This methodology was successfully applied to each family of cyclometalated complexes (IrC_3N_3, IrC_2N_2LX, IrC_2N_4). Incorporation of an electron-rich atom with a higher polarizability, *i.e.* oxygen (oxazole) or sulfur (thiophene, thiazole), reduces the energy of the π-π* C-N centered transitions, thereby promoting its mixing with charge transfer transitions in the lowest-energy excited-state. For the resulting complexes, the main consequences are i) a red-shift of both absorption and photoluminescence spectra, ii) a photoluminescence spectrum with vibronic structure, iii) a longer excited-state lifetime, and iv) a larger molar absorption coefficient in the visible range. It is important to note that, in most cases, the stabilization of the LC_{C-N} is strengthened by the addition of a fused phenyl ring to form three corresponding ligands, *i.e.* 2-(benzo[*b*]-thiophen-2-yl)pyridine (btpy), 2-phenylbenzo[*d*]thiazole (pbt) and 2-phenylbenzo[*d*]oxazole (pbo) (**Figure 5**). According to the same approach, the cyclometalation of 1,8-naphthalenebenzimidazole (NBI) (**Figure 5**) has also been explored by several groups.[94-96] It was shown to improve the visible light absorption of the resulting cyclometalated complexes, again through the contribution from LC_{C-N} transitions to the lowest-energy excited-state. Finally, selone, thione and bis-arylaminoacenaphthene ligands (**Figure 5**) have occasionally been reported as other interesting ancillary ligands.[97-99] Compared to unsubstituted imidazole analogues, the introduction of thione of selone substituents was shown to redshift the absorption of the corresponding complex by roughly 30-40 nm with moderate molar absorption coefficients, i.e. 4600 $M^{-1}cm^{-1}$ and 2600 $M^{-1}cm^{-1}$ for the thione and selone substituents, respectively.

Increasing the conjugation

Another methodology to improve visible light absorption of iridium(III) complexes relies on the extension of the ligand conjugation. This approach may be applied in three different ways: i) addition of fused aromatic rings, ii) covalent bonds with polycyclic units, and iii) use of tridentate ligands (**Figure 6**).

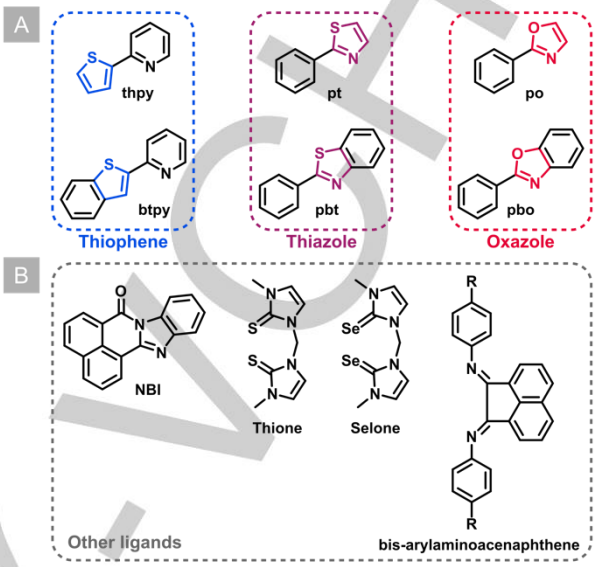

Figure 5. (A) Cyclometalated ligands with thiophene, thiazole and oxazole rings. (B) 1,8-naphthalenebenzimidazole (NBI), thione, selone and bis-arylaminoacenaphthene ligands.

- **Addition of fused aromatic rings**

The addition of fused aromatic rings has been extensively investigated in the literature, with the development of a wide variety of C-N[74, 100-109] and N-N ligands.[33, 110-112] Benzo-, naphtho-, quinoline-, quinoxaline- and other derivatives have been reported and are illustrated in **figure 6A**. For each type of ligand, the ground- and excited-state properties of the resulting complexes were rationalized as a function of the benzannulation site and the degree of π-conjugation. Concerning the cyclometalated (C-N) ligand,[74, 100-109] it was established that the expansion of the C-coordinated moiety raises the energy of the π_{C-N} and the $d\pi_{Ir-C}$ orbitals (**Figure 2B**), leading to a red-shift of the optical properties. The excited state remained mainly a charge transfer (CT) state, except with the largest ligands, where an increased contribution from LC_{C-N} transitions was concluded. Extending the conjugation of the N-coordinated moiety was shown to have a small impact on the HOMO energy, while inducing a red-shift of the absorbance and photoluminescence and strengthening the mixing between LC_{C-N} and CT transitions. This was due to the stabilization of the π^*_{C-N} orbital (**Figure 2B**), and resulted in i) a vibronically structured photoluminescence spectrum, ii) a long-lived excited-state, and iii) a larger molar absorption coefficient in the visible range. For the diimine (N-N) ligand,[33, 110-112] extended π-conjugation similarly led to a red-shift of the spectroscopic properties, here caused by the stabilization of π^*_{N-N} orbital (**Figure 2B**). In addition, when the degree of conjugation was high enough, the reduction of the π-π* gap promoted the mixing between LC_{N-N} and CT transitions, as indicated again by i) structured photoluminescence spectra, ii) longer excited-state lifetimes, and iii) larger molar absorption coefficients.

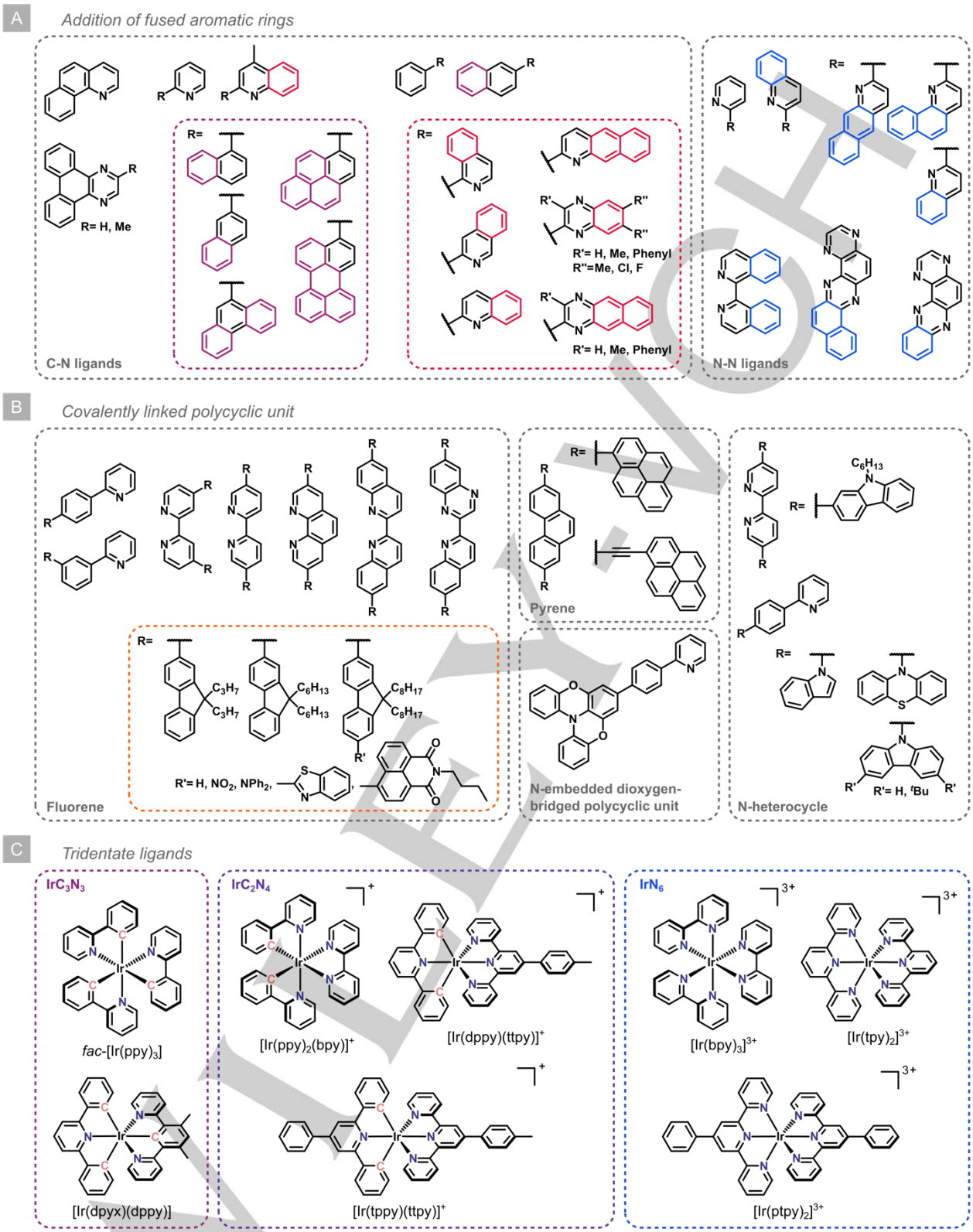

Figure 6. Approaches to extend ligand conjugation. (A) Examples of C-N and N-N ligands obtained through the addition of fused aromatic rings (B) Examples of ligands obtained through the covalent linking of polycyclic unit. (C) Examples of bis-tridentate Ir(III) complexes *vs.* tris-bidentate analogues

- **Covalently linked polycyclic units**

Covalently linked polycyclic units were also reported to improve conjugation. Most of the modifications reported concern the addition of fluorene derivatives (**Figure 6B**), mainly on cationic $[Ir(C\text{-}N)_2(N\text{-}N)]^+$ complexes.[113-120] Structural changes of both C-N and N-N ligands have been investigated, leading to completely different behaviors in each case. On the one hand, the introduction of a fluorene motif on the C-N ligand was shown to raise the energy of the $\pi_{C\text{-}N}$ and the $d\pi_{Ir\text{-}C}$ orbitals (**Figure 2B**), inducing a red-shift of the optical properties. This was a direct consequence of the electron-donor character of the fluorene substituent. However, for such C-N modified complexes, the visible part of the absorption spectrum remained dominated by mixed MLCT/LLCT transitions characterized by a small molar absorption coefficient. On the other hand, modifications of the diimine ligand with fluorene red-shifted the spectroscopic properties, but also strengthened the contribution from transitions with a high oscillator strength in the visible range. As previously discussed for TPA-modified ligands, these transitions were centered on the N-N ligand and ascribed to ILCT transitions between the electron-donor (fluorene) and acceptor (N-N) part of the diimine ligand. Based on the same approach, a high degree of ILCT in the excited state was also observed for IrC_2N_4 and IrN_6 complexes, where the N-N ligand was modified with pyrene linkers (**Figure 6B**).[81, 121, 122] Such a behavior was even highlighted for an IrC_3N_3 complex substituted with an N-embedded dioxygen-bridged polycyclic unit (**Figure 6B**).[123] Finally, several different N-heterocycle substituents (**Figure 6B**) were shown to have the same effect as fluorene substituents on the photophysical properties of IrC_2N_4 complexes, when they were covalently linked to ppy and bpy ligands.[124, 125]

- **Tridentate ligands**

The use of tridentate ligands represents the third way to expand conjugation around the Ir(III) center (**Figure 6C**). Bis-tridentate N^N^N complexes constitute the large majority of IrN_6 complexes while examples of cyclometalated bis-tridentate Ir(III) complexes remain scarce in the literature, mostly due to the harsh conditions required for their synthesis and the very poor associated yields.[126-129] Compared to their tris-bidentate analogues, bis-tridentate complexes offer some advantages because of their intrinsic axial symmetry, which is particularly desirable in supramolecular electron donor-acceptor assemblies, and results in the absence of helicoidal chirality of the Ir(III) center.[54, 130, 131] Finally, in terms of optical properties, their absorption spectrum is red-shifted and they display intense absorption bands, especially when the central ring of the tridentate ligands bears a phenyl moiety in *para* (*i.e.* 4') position (**Table 3**). This is the effect of the greater electronic delocalization of the excited state, associated with large tridentate ligands. It is important to specify that, due to the lower energy of their excited state and the related energy gap law, bis-tridentate complexes usually exhibit smaller photoluminescence quantum yields than their corresponding tris-bidentate analogues (**Table 3**).[132-135] However, as evidenced by experimental and theoretical studies, the nature of their excited-state is very similar, *i.e.* IrC_3N_3 (MLCT), IrC_2N_4 (MLCT/LLCT), IrN_6 (LC).[132-135]

Coupling with chromophores

Visible light absorption with large molar absorption coefficients is finally often achieved by using covalently linked organic chromophores. Such strategies have been developed using for example coumarin 6, bodipy,[136-138] naphthalimide[139-142] and perylenebisimide[143-145] derivatives (**Figure 7**). In most cases, the increased molar absorption coefficient is associated with chromophore-centered transitions. Hence, the main purpose of the iridium center is to promote efficient intersystem crossing *via* spin-orbit coupling, allowing the formation of a triplet excited chromophore, with a large quantum yield and long excited-state lifetime. However, due to the displacement of the excited-state onto the chromophore moiety, this strategy is often inadequate for achieving electron transfer chemistry, except when the chromophore itself directly acts as the cyclometalating ligand chelated on the iridium center. Indeed, in this particular case, electrochemical processes still involve the metal, which is important for reversibility.

Table 3. Spectroscopic data for various bis-tridentate Ir(III) complexes and their tris-bidentate analogues.

Family	Complex	λ_{abs} / nm[a] (ε / $M^{-1}cm^{-1}$)	λ_{PL} / nm[a]	Φ_{PL}[b]	τ / µs[b]	Ref
IrC_3N_3	*fac*-$[Ir(ppy)_3]$[c]	455 (2800)	510	0.40	1.9	41
	[Ir(dpyx)(dppy)]	481 (6820), 510 (7340)	585	0.21	3.9	146
IrC_2N_4	$[Ir(ppy)_2(bpy)]^+$	412 (3600)	599	0.035	0.3	37, 38, 66
	$[Ir(dppy)(ttpy)]^+$	445 (10230), 527 (6600)	678	0.033	2.1	129
	$[Ir(tppy)(ttpy)]^+$	436 (15400), 517 (9700)	684	0.027	1.6	134
IrN_6	$[Ir(bpy)_3]^{3+}$	344 (3300)	441	0.129	2.4	54
	$[Ir(tpy)_2]^{3+}$	352 (5800)	458	0.022	1.2	132
	$[Ir(ptpy)_2]^{3+}$	369 (20900)	494	0.32	2.5	147

[a] in acetonitrile at room temperature
[b] under argon atmosphere at room temperature
[c] absorption data in CH_2Cl_2, photoluminescence, quantum yield and excited-state lifetime in 2-methyltetrahydrofuran

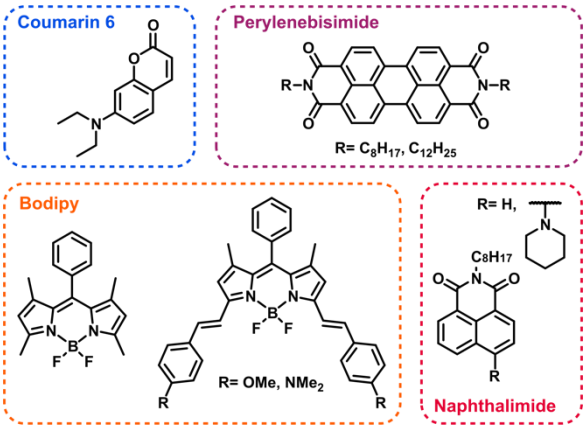

Figure 7. Typical chromophores covalently linked to iridium(III) complexes or directly chelated onto the Ir(III) center.

A roadmap for visible light mediated electron transfer chemistry

The development of iridium(III)-based compounds with appreciable visible light absorption relies on a combination of the different approaches that were previously described. However, while visible light absorption is a key property, the excited-state oxidation and reduction potentials are also determining factors, depending on the desired application. Here, we will discuss how the strategies examined in the previous sections can be applied to each family of complexes to provide compounds with great potencies as photo-oxidants and/or photo-reductants. Significant examples, spanning a wide range of excited-state potentials, will be presented hereafter and gathered in a recapitulative figure at the end of the manuscript.

IrN_6 complexes

IrN_6 complexes usually exhibit ligand-centered reductions at potentials around –1 V *vs.* NHE which, when combined to their relatively large $E_{0\text{-}0}$, result in potent photooxidizing complexes. Unfortunately, due to harsh synthetic conditions, they are rarely reported, and bis-tridentate derivatives constitute the large majority of IrN_6 complexes.

A heteroleptic complex (**Ir5**) (**Figure 8**) capable of selectively oxidizing DNA purines upon light excitation was reported by Jacques *et al.*.[148] Functionalization of the terpyridines in the 4' position by phenyl groups bearing OMe and COOH substituents induced a red-shift of the absorption spectrum compared to the reference complex $[Ir(tpy)_2]^{3+}$ (tpy = 2,2':6',2''-terpyridine) (**Table 4**). This was related to the increased electronic delocalization of the excited state. In spite of less energy stored in the excited state ($E_{0\text{-}0}$), this heteroleptic complex remained highly photo-oxidizing. The excited-state reduction potential, characterizing its ability to accept an electron upon light excitation, was estimated at 1.58V *vs.* NHE (**Table 4**), which was sufficient to oxidize purine DNA derivatives but not pyrimidine ones.

Table 4. Electrochemical and spectroscopic data for various IrN_6 complexes, *i.e.* $[Ir(bpy)_3]^{3+}$, $[Ir(tpy)_2]^{3+}$ and **Ir5-12**.

	$E_{1/2}(Ir^{IV/III})$[a]	$E_{1/2}(L^{n/n-1})$[a]	$E_{1/2}(Ir^{*(+/0)})$[b]	$E_{1/2}(Ir^{*(0/-)})$[b]	λ_{abs} / nm[c] (ε / $M^{-1}cm^{-1}$)	λ_{PL} / nm RT[c]	λ_{PL} / nm 77K[d]	$E_{0\text{-}0}$ / eV[e]	Ref
$[Ir(bpy)_3]^{3+}$	+2.34	–0.86	–0.41	+1.89	344 (3300)	452	441	2.75	25, 39, 40
$[Ir(tpy)_2]^{3+}$	>+2.6	–0.53	>-0.11	+2.18	352 (5800)	458	458	2.71	132
Ir5	>+2.4	–0.61	>+0.21	+1.58	382 (28100)	568	505[f]	2.19	148
Ir6	nr[g]	–0.52	/	+1.66	380 (27000)	570	510	2.18	149
Ir7	+2.4	–0.52	+0.20	+1.68	410 (46000)	566	514	2.20	130, 149
Ir8	>+2.4	–0.85	>–0.10	+1.65	448 (19700)	497	nr[g]	2.50	150
Ir9	>+2.4	–0.96	>–0.05	+1.49	459 (39500)	506	nr[g]	2.45	150
Ir10	nr[g]	nr[g]	/	/	504 (44800)	754	nr[g]	1.64	151
Ir11	nr[g]	nr[g]	/	/	493 (35100)	784	nr[g]	1.58	151
Ir12	+2.28[h]	+0.04[h]	+0.53	+1.79	444 (4100)	710	nr[g]	1.75	151

[a] V *vs.* NHE in acetonitrile (adapted from the original work if necessary, $V_{NHE} = V_{SCE} + 0.24$, $V_{NHE} = V_{Fc^{+/0}} + 0.64$)
[b] estimated from **equations 1-2**; $E^*_{ox} = E_{1/2}(Ir^{*(+/0)}) = E_{1/2}(Ir^{(IV/III)}) - E_{0\text{-}0}$, $E^*_{red} = E_{1/2}(Ir^{*(0/-)}) = E_{1/2}(L^{(n/n-1)}) + E_{0\text{-}0}$
[c] in acetonitrile at room temperature
[d] in butyronitrile glass at 77 K
[e] estimated from λ_{max} in acetonitrile at room temperature
[f] in 4:1 ethanol/methanol glass at 77 K
[g] not reported
[h] V *vs.* NHE in dimethylformamide (adapted from the original work, $V_{NHE} = V_{Fc^{+/0}} + 0.69$ V)

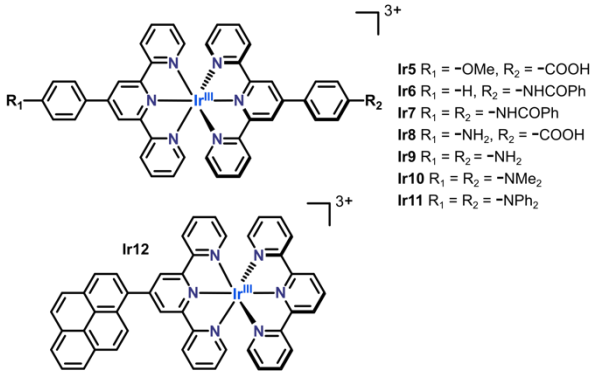

Figure 8. Selected examples of IrN_6 complexes with improved visible light absorption and interesting excited-state electrochemical properties.

Electrochemical and photophysical behaviors of other hetero- and homoleptic iridium(III) bis-terpyridine complexes have been reported. Substitutions in the 4' position of the terpyridine backbone influenced their excited-state properties. For example, Flamigni *et al.* highlighted a stronger ^{3}CT character for complexes bearing aryl-benzamide moieties (**Ir6-7**) (**Figure 8**).[149] Changes in their excited-state nature were reflected by absorption bands extending well beyond 400 nm and broad structureless photoluminescence profiles at room temperature (**Table 4**). As evidenced by electrochemical investigation, their (photo)electrochemical properties were however only slightly affected, as compared to the unsubstituted $[Ir(tpy)_2]^{3+}$ (**Table 4**). The disubstituted complex **Ir7** was also connected to a triphenylamine electron-donor and a naphthalene bisimide electron-acceptor to provide a triad characterized by a long-lived (120 µs) charge separated state at room temperature.[152]

More surprisingly, invariant excited-state redox properties (**Table 4**) were also recorded for complexes bearing strong electron-donor groups in the *para* (*i.e.* 4') position, *i.e.* amino,[150] dimethyl-amino,[151, 153] diphenyl-amino[151] and pyrene[151] (**Ir8-12**) (**Figure 8**). Indeed, in this case, the energy of the frontier orbitals was more dramatically modified. Introduction of electron-donor substituents raised the ground-state energy of the 4'-aryl substituent (π_{ph}) above that of the 2,2':6',2''-terpyridine backbone (π_{tpy}). Overall, the resulting complexes exhibited an intraligand charge transfer (ILCT) transition between π_{ph} and π_{tpy}* orbitals. This ILCT transition occurred around 450 nm with molar absorption coefficients ranging from 4100 to 44800 $M^{-1}cm^{-1}$ (**Table 4**). Ultimately, complexes **Ir8-12** behaved as potent photo-oxidizing complexes either because the free energy stored in the excited-state ($E_{0\text{-}0}$) remained surprisingly high (**Ir8-9**), or because the lower value of $E_{0\text{-}0}$ was offset by the easier reduction of the complex (**Ir12**).

IrC_3N_3 complexes

Charge-neutral tris-cyclometalated iridium(III) complexes, such as the prototypical *fac*-[Ir(ppy)$_3$], are potent photoreducing complexes, and have found broad applications in organic photocatalysis, in particular due to their spectacular ability to engage unactivated halide substrates in single electron transfer (SET) reactions.[154-157] However, IrC_3N_3 complexes have also been investigated for applications in other fields such as solar energy conversion, where improving their visible light absorption properties is desirable.

First examples are heteroleptic complexes (**Ir13-16**) reported by Yuan *et al.* in order to perform light-induced hydrogen evolution (**Figure 9**).[158] A combination of one thiazole- and two thiophene-based ligands, *i.e.* 2-phenylbenzo[*d*]thiazole (pbt) and 2-(thiophen-2-yl)pyridine (thpy), allowed access to compounds with interesting absorption properties (**Table 5**). As discussed previously, these changes are related to the incorporation of electron-rich sulfur atoms in the scaffold of both ligands. Theoretical calculations showed that the thiophene moieties (thpy ligands) increased the electron density on the iridium core, raising the HOMO energy, and simultaneously the greater electronic conjugation of the pbt ligand reduced the LUMO energy. Overall, this led to a smaller HOMO-LUMO gap, thereby red-shifting the optical properties for all complexes. The addition of CF_3 substituents enhanced this red-shift through stabilization of the LUMO level (**Ir14-15**). The valuable effect of one NMe_2 substituent on the absorption properties of **Ir16** probably stemmed from an increased donor-acceptor character of the pbt ligand, possibly involving contribution from an $ILCT_{pbt}$ transition at low-energy. Reported redox potentials agreed with the change in the HOMO and LUMO energy induced by the addition of sulfur-based ligands. The thpy ligand shifted the oxidation peak to a less positive value, whereas the reduction was made easier by the greater electronic conjugation of pbt (**Table 5**). All complexes were successful in achieving hydrogen photo-production. Quenching experiments and thermodynamic analyses showed that the iridium complex first photo-reduced a water reduction catalyst (WRC), before being regenerated by a sacrificial electron donor.

Other examples of interesting IrC_3N_3 complexes are **Ir17**[159] and **Ir18**[160] (**Figure 9**), which were recently used as light absorbers and electron donors in the field of organic photovoltaics. In **Ir17**, the azaperylene ligand afforded an extended conjugation due to its fused aromatic rings, leading to enhanced visible light absorption properties (**Table 5**), which even included weak (30 $M^{-1}cm^{-1}$) triplet absorption bands at 782 nm. The use of difluoro-phenylpyridine ligands lowered the HOMO energy level, as shown by the anodic shift of the oxidation potential to +1.25 V *vs.* NHE (**Table 5**).

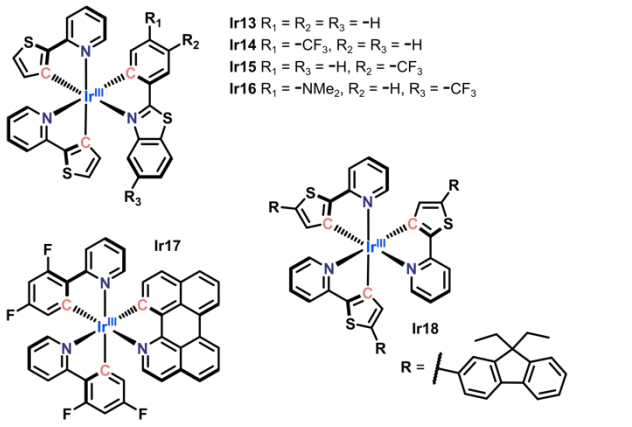

Figure 9. Examples of IrC_3N_3 complexes with improved visible light absorption for solar energy conversion.

Table 5. Electrochemical and spectroscopic data for various IrC_3N_3 complexes, i.e. *fac*-[Ir(ppy)$_3$] and **Ir13-18**.

	$E_{1/2}(Ir^{IV/III})$[a]	$E_{1/2}(L^{n/n-1})$[a]	$E_{1/2}(Ir^{*(+/0)})$[b]	$E_{1/2}(Ir^{*(0/-)})$[b]	λ_{abs} / nm[c] (ε / $M^{-1}cm^{-1}$)	λ_{PL} / nm RT[c]	λ_{PL} / nm 77K[d]	E_{0-0} / eV[e]	Ref
fac-[Ir(ppy)$_3$]	+1.01	–1.95	–1.38[f]	+0.34[f]	375 (7200)[g]	519	514	2.39	35, 36, 53
Ir13	+1.03	–1.66	–1.16	+0.53	389 (12500)	583	nr[h]	2.19[i]	158
Ir14	+1.12	–1.45	–0.97	+0.64	388 (7500)	611	nr[h]	2.09[i]	158
Ir15	+1.13	–1.51	–1.02	+0.62	385 (13000)	595	nr[h]	2.15[i]	158
Ir16	+0.94	–1.76	–1.34	+0.52	414 (30000)	555	nr[h]	2.28[i]	158
Ir17	+1.25[j]	–1.22[j]	–0.33	+0.36	540 (7000)	785	nr[h]	1.58	159
Ir18	+1.10[k]	–1.83[k]	–0.75	+0.02	480 (23000)	670	nr[h]	1.85	160

[a] V *vs.* NHE in dichloromethane
[b] estimated from **equations 1-2**; $E^*_{ox} = E_{1/2}(Ir^{*(+/0)}) = E_{1/2}(Ir^{(IV/III)}) - E_{0-0}$, $E^*_{red} = E_{1/2}(Ir^{*(0/-)}) = E_{1/2}(L^{(n/n-1)}) + E_{0-0}$
[c] in dichloromethane at room temperature
[d] in dichloromethane
[e] estimated from λ_{max} in dichloromethane at room temperature
[f] these values, recorded in dichloromethane, are different than the one reported in **Figure 1** (acetonitrile) and originate from a difference in the reported E_{0-0}
[g] in toluene
[h] not reported
[i] estimated from the high-side energy of the photoluminescence band at 10–20% of its maximum intensity
[j] V *vs.* NHE in dimethylformamide (adapted from the original work, $V_{NHE} = V_{Fc^{+/0}} + 0.69$ V)
[k] V *vs.* NHE in tetrahydrofuran (adapted from the original work, $V_{NHE} = V_{Fc^{+/0}} + 0.80$ V)

Solar cells were constructed with the architecture ITO/**Ir17**(5nm)/C_{60}(30nm)/PTCDI(10nm)/BCP(14nm)/Al. In this construction, the ITO electrode served as a hole acceptor, whereas C_{60} served as an electron acceptor. The N,N'-dihexyl-perylene-3,4,9,10-bis(carboxiimide) (PTCDI) improved electron injection between the C_{60} layer and the bathocuproine (BCP) exciton blocking layer. Noteworthy, this solar cell provided J_{SC} of 4.5 mA/cm^2, FF of 0.62 and V_{OC} of 0.99V which led to an overall efficiency of 2.8%. In **Ir18**, the combination of thiophene-pyridine cyclometalated ligands and fluorene substituents resulted in more intense visible light absorption, with molar absorption coefficients of 23000 $M^{-1}cm^{-1}$ at 480 nm. This complex was also investigated in bulk heterojunction solar cells with a ITO/PEDOT:PSS/**Ir18**/PCBM/Al architecture, where PCBM is a phenyl-C_{61}-butyric acid methyl ester electron acceptor and PEDOT:PSS is a conductive polymer mixture. Unfortunately, this type of solar cells only performed moderately, *i.e.* J_{SC} of 2.68 mA/cm^2, FF of 0.28 and V_{OC} of 0.66V which led to an overall efficiency of 0.51%.

IrC_2N_2LX complexes

Neutral, photo-reducing [Ir(C-N)$_2$(LX)] complexes usually exhibit very similar excited-state properties as tris-cyclometalated derivatives, due to the small contribution from typical LX ligands (*e.g.* acetylacetonate …) to either the HOMO or the LUMO level. Tuning of these excited-states has recently been achieved by Teets *et al.*, with the introduction of electron-rich β-ketoiminate (AcNac) and β-diketiminate (NacNac) LX ligands.[76] DFT calculations highlighted that, for these bis-cyclometalated complexes, previously depicted in **Figure 3**, the AcNac and the NacNac scaffolds significantly contributed to the HOMO energy. Electrochemical investigations provided further evidence of this effect, as shown by the shift of the $Ir^{IV/III}$ potential towards less positive values for AcNac and NacNac derivatives (**Table 6**). Interestingly, their photo-reducing character was consequently enhanced, providing compounds that were more potent photo-reductant than *fac*-[Ir(ppy)$_3$] (**Table 6**).

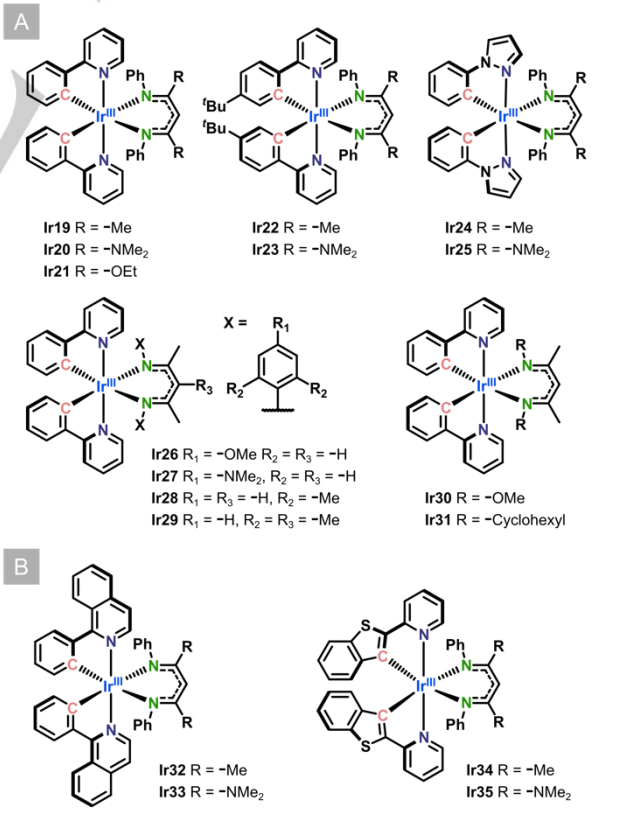

Figure 10. Examples of NacNac IrC_2N_2LX with interesting excited-state redox properties.

Table 6. Electrochemical and spectroscopic data for *fac*-[Ir(ppy)$_3$] and various IrC$_2$N$_2$LX complexes, *i.e.* [Ir(ppy)$_2$(acac)], [Ir(ppy)$_2$(AcNacMe)] and **Ir19-35**.

	$E_{1/2}(Ir^{IV/III})$[a]	$E_{1/2}(L^{n/n-1})$[a]	$E_{1/2}(Ir^{*(+/0)})$[b]	$E_{1/2}(Ir^{*(0/-)})$[b]	λ_{abs} / nm[c] (ε / $M^{-1}cm^{-1}$)	λ_{PL} / nm RT[d]	λ_{PL} / nm 77K[e]	E_{0-0} / eV[f]	Ref
fac-[Ir(ppy)$_3$]	+1.01	–1.95	–1.52	+0.49	375 (7200)[g]	508[h]	491[h]	2.53	35, 36, 161
[Ir(ppy)$_2$(acac)]	+1.10	nr[i]	–1.30	/[k]	460 (2000)[h]	516[h]	nr[i]	2.40[j]	76
[Ir(ppy)$_2$(AcNac^{Me})]	+0.91	–1.56	–1.55	+0.90	455 (2400)	564[c]	505	2.46	76
(**Ir19**) [Ir(ppy)$_2$(NacNac^{Me})]	+0.57	–1.56	–1.81	+0.82	460 (1800)	569[c]	522	2.38	76
(**Ir19**) [Ir(ppy)$_2$(NacNac^{Me})]	+0.57	–1.56	–1.81	+0.82	386 (13000)	595	522	2.38	162, 163
Ir20	+0.38	<–1.86	–1.84	<+0.36	393 (6100)	634	560	2.22	162, 163
Ir21	+0.67	<–1.86	–1.74	<+0.55	413 (6100)	571	515	2.41	162, 163
Ir22	+0.51	<–2.00	–1.84	<+0.35	386 (4200)	575	528	2.35	163
Ir23	+0.37	<–2.00	–1.85	<+0.22	391 (2300)	594	558	2.22	163
Ir24	+0.54	<–2.00	–1.79	<+0.33	308 (6700)	/[k]	533	2.33	163
Ir25	+0.39	<–2.00	–1.79	<+0.18	400 (5900)	637	570	2.18	163
Ir26	+0.53	<–2.00	–1.78	<+0.31	385 (2900)	576	536	2.31	163
Ir27	+0.41	<–2.00	–1.86	<+0.27	385 (3800)	/[k]	547	2.27	163
Ir28	+0.54	<–2.00	–1.70	<+0.24	391 (15000)	605	553	2.24	163
Ir29	+0.31	<–2.00	–1.79	<+0.10	421 (9500)	623[j]	592	2.10	163
Ir30	+0.49	<–2.00	–1.74	<+0.23	382 (4000)	632	557	2.23	163
Ir31	+0.25	<–2.00	–1.79	<+0.04	361 (10000)	661	607	2.04	163
Ir32	+0.58	–1.61	–1.31	+0.28	455 (8000)	714	658	1.89	164
Ir33	+0.47	–1.79	–1.39	+0.07	590 (10000)	707	666	1.86	165
Ir34	+0.71	–1.89	–1.37	+0.19	435 (6000)	605	596	2.08	164
Ir35	+0.45	–2.08	–1.57	–0.06	490 (3500)	633	614	2.02	165

[a] V *vs.* NHE in acetonitrile (adapted from the original work if necessary, $V_{NHE} = V_{SCE} + 0.24$ V, $V_{NHE} = V_{Fc^{+/0}} + 0.64$ V)
[b] estimated from **equations 1-2**; $E^*_{ox} = E_{1/2}(Ir^{*(+/0)}) = E_{1/2}(Ir^{(IV/III)}) - E_{0-0}$, $E^*_{red} = E_{1/2}(Ir^{*(0/-)}) = E_{1/2}(L^{(n/n-1)}) + E_{0-0}$
[c] in tetrahydrofuran at room temperature
[d] in acetonitrile at room temperature
[e] in toluene glass at 77 K
[f] estimated from λ_{max} at 77 K
[g] in toluene
[h] in 2-methyltetrahydrofuran at room temperature or glass at 77 K
[i] not reported
[j] estimated from λ_{max} in 2-methyltetrahydrofuran at room temperature
[k] not luminescent at room temperature
[l] in tetrahydrofuran

Based on this pioneering work, a library of NacNac derivatives (**Ir19-31**) (**Figure 10A**) were then investigated for excited-state electron transfer chemistry.[162, 163] Substitution of the NacNac backbone either in the 2, 3 or 4-position was shown to shift the oxidation peak to more or less positive values (**Table 6**). Addition of electron-donating NMe_2 substituents (**Ir20**, **23**, **25**) resulted in a 180-200 mV shift towards more negative values, whereas EtO substituents (**Ir21**) yielded a positive shift of 100 mV. In addition, the introduction of a methyl substituent on the central 3 position of the NacNac backbone (**Ir29**) induced a drastic 230 mV negative shift, as compared to the unsubstituted analogue. Influence of the basicity of the nitrogen atoms, and hence of substituents in the N and N' position of the NacNac ligand, was also highlighted (**Table 6**). Substitution of the phenyl moiety located on the N and N' position (**Ir26-29**) yielded changes in the $Ir^{IV/III}$ potential that were in accordance with Hammett parameters. This potential was also drastically shifted, up to a value of 0.25 V *vs.* NHE, when the phenyl moieties were replaced by more electron-rich, non-aromatic cyclohexyl substituents (**Ir31**). All the resulting complexes (**Ir19-31**) were more potent photo-reductants than *fac*-[Ir(ppy)$_3$], with 220-340 mV more negative excited-state redox potentials (**Table 6**). The photo-reducing character of several of these complexes was assessed, amongst others, in the presence of *p*-benzophenone (BP) ($E_{1/2}^{(BP/BP^{\bullet-})} = -2.04$ V NHE). Stern-Volmer analyses provided valuable kinetic information and showed that the quenching rate constant was larger for each complex as compared to *fac*-[Ir(ppy)$_3$]. As predicted by Marcus theory, this increase in electron transfer rate constants correlated well with the estimated larger driving forces. Photocatalytic

hydrodebromination of a challenging substrate, *i.e.* methyl 4-bromo-3-methyl benzoate, was then investigated.[163] Different complexes were outlined to perform as great photo-reductants, some of them rivalling with *fac*-[Ir(ppy)$_3$]. Although significant differences in performance were observed between the different photocatalysts, the authors were unable to determine whether these differences were due a variety of reaction rates or to stability issues with some complexes.

Concerning the absorption properties of **Ir19-31**, in spite of the changes recorded in their ground-state oxidation potentials, they all exhibited absorption around 400 nm (**Table 6**). Absorption at lower-energy was relatively moderate, with ε values smaller than 3200 $M^{-1}cm^{-1}$ at wavelength greater than 430 nm. Nevertheless, NacNac complexes (**Ir32-35**) bearing other cyclometalated ligands well-known to improve light absorption, *i.e.* 1-phenylisoquinoline (1-piq) and 2-(benzo[*b*]-thiophen-2-yl)pyridine (btpy), were also recently reported (**Figure 10B**).[164, 165] Unfortunately, the substitution of the C-N ligand led to a dramatic decrease of their photo-reducing power, due to the decreased free energy stored in the excited-state ($E_{0\text{-}0}$) (**Table 6**). This is probably the reason why these complexes with greater visible light absorption have not been investigated for photoredox catalysis.

IrC_2N_4 complexes

IrC_2N_4 (**Figure 11**) complexes probably represent the best studied class of iridium complexes due to the very wide range of accessible ground- and excited-state redox potentials. They have indeed been used for several applications that include, amongst others, CO_2 and H^+ reduction,[95, 100, 166, 167] halide oxidation,[33] dye-sensitized solar cells[168] and biosensing.[169]

In a recent study, IrC_2N_4 complexes bearing 4,4'-$(CH_2PO_3H_2)_2$-2,2'-bipyridine N-N ligands (**Ir36-39**) were anchored onto TiO_2 nanoparticles functionalized with a rhenium(I) complex competent for CO_2 reduction into CO.[166] The cyclometalated ligands were systematically varied to modify the oxidation and reduction potentials, as well as the absorption properties (**Table 7**). Less positive $Ir^{IV/III}$ potentials were recorded when electron-rich cyclometalating ligands such as piq and btp were used, whereas the ligand centered reductions remained almost unaltered across the series. This decreased energy gap in **Ir38** and **Ir39** led to appreciable absorption at 450 nm, reaching molar absorption coefficient values around 3000 and 6000 $M^{-1}cm^{-1}$ for **Ir38** and **Ir39**, respectively. All four complexes reported in that study were shown to undergo light-induced reactivity with a sacrificial 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) electron donor. The reduced complex was then able to inject an electron into the acceptor states of the TiO_2 nanoparticle, which acted as an electron relay to shuttle electron to the rhenium catalyst. In addition, immobilization on TiO_2 was shown to increase the stability of the iridium complexes under irradiation by decreasing the time spent in the mono-reduced state. The turn-over number (TON) using > 500 nm light could be increased from 213 to 734 by using additives such as TEOA.

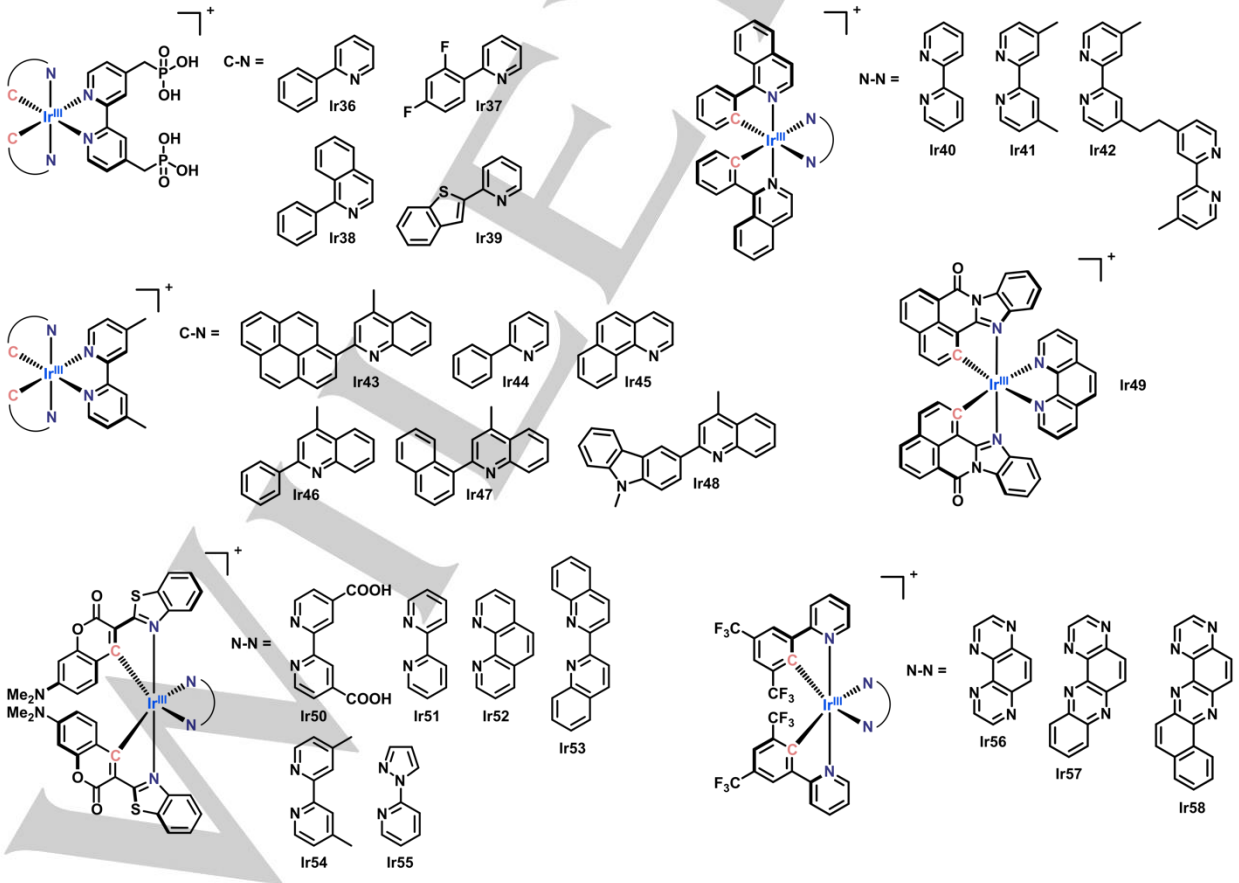

Figure 11. Examples of IrC_2N_4 complexes with interesting excited-state redox properties.

Table 7. Electrochemical and spectroscopic data for various IrC_2N_4 complexes.

	$E_{1/2}(Ir^{IV/III})$	$E_{1/2}(L^{n/n-1})$	$E_{1/2}(Ir^{*(+/0)})$[b]	$E_{1/2}(Ir^{*(0/-)})$[b]	λ_{abs} / nm (ε / $M^{-1}cm^{-1}$)	λ_{PL} / nm RT	λ_{PL} / nm 77K	$E_{0\text{-}0}$ / eV	Ref
Ir36	+1.81[a]	–1.07[a]	–0.93	+1.67	364 (5000)[c]	520[d]	452[e]	2.74	166
Ir37	+1.50[a]	–1.12[a]	–0.95	+1.33	469 (600)[c]	600[d]	506[e]	2.45	166
Ir38	+1.48[a]	–1.12[a]	–0.65	+1.01	445 (3000)[c]	595[d]	581[e]	2.13	166
Ir39	+1.25[a]	–1.13[a]	–0.88	+1.00	436 (6000)[c]	591[d]	582[e]	2.13	166
Ir40	+1.50[f]	–1.11[f]	–0.60	+0.99	442 (8100)[c]	595[g]	nr[h]	2.10	167
Ir41	+1.47[f]	–1.20[f]	–0.63	+0.90	444 (7800)[c]	595[g]	nr[h]	2.10	167
Ir42	+1.48[f]	–1.18[f]	–0.62	+0.92	444 (7400)[c]	594[g]	nr[h]	2.10	167
Ir43	+0.84[f]	–1.68[g]	–0.96	+0.12	444 (67000)[c]	700[g]	nr[h]	1.80	100, 170
Ir44	+1.58[i]	–1.13[i]	–0.87	+1.32	377 (5400)[k]	580[k]	nr[h]	2.45	100
Ir45	+1.51[j]	–1.07[i]	–0.92	+1.36	422 (6300)[k]	583[k]	nr[h]	2.43	100
Ir46	+1.57[i]	–1.15[i]	–0.77	+1.19	434 (5900)[k]	550[k]	nr[h]	2.34	100
Ir47	+1.53[i]	–1.13[i]	–0.55	+0.95	453 (7700)[k]	616[k]	nr[h]	2.08	100
Ir48	+1.24[j]	–1.15[i]	–1.03	+1.12	452 (11500)[k]	624[k]	nr[h]	2.27	100
Ir49	+1.74[a]	–0.92[a]	–0.31	+1.13	452 (11000)[l]	634[m]	nr[h]	2.05	95
Ir50	+1.32[a]	–0.64[a]	–0.93[j]	+1.61	480 (43800)[d]	nr[h]	nr[h]	2.25	168
Ir51	+1.32[a]	–0.98[a]	–0.83[j]	+1.17	483 (129000)[m]	589[m]	576	2.15	171
Ir52	+1.30[a]	–0.93[a]	–0.84[j]	+1.21	485 (126000)[m]	589[l]	579	2.14	171
Ir53	+1.37[a]	–0.54[a]	–0.56[j]	+1.39	480 (90000)[m]	N.D.[n]	644	1.93	171
Ir54	+1.33[a]	–1.06[a]	–0.82[j]	+1.09	478 (117000)[d]	587[d]	nr[h]	2.15	172
Ir55	+1.34[a]	–1.19[a]	–0.80[j]	+0.95	478 (122000)[d]	590[d]	nr[h]	2.14	172
Ir56	> 2.2	–0.41		+1.78	450 (500)	572	506	2.19	33
Ir57	> 2.2	–0.13		+1.77	450 (1400)	651	641	1.90	33
Ir58	> 2.2	–0.25		+1.76	450 (9800)	618	601	2.01	33

[a] V *vs.* NHE in acetonitrile (adapted from the original work, $V_{NHE} = V_{SCE} + 0.24$ V and $V_{NHE} = V_{Fc^{+/0}} + 0.64$ V)
[b] estimated from **equations 1-2**; $E^*_{ox} = E_{1/2}(Ir^{*(+/0)}) = E_{1/2}(Ir^{(IV/III)}) - E_{0\text{-}0}$, $E^*_{red} = E_{1/2}(Ir^{*(0/-)}) = E_{1/2}(L^{(n/n-1)}) + E_{0\text{-}0}$
[c] in dimethylformamide at room temperature
[d] in acetonitrile
[e] in 2-methyltetrahydrofuran
[f] V *vs.* NHE in acetonitrile (adapted from the original work, $V_{NHE} = V_{Ag+/Ag} + 0.55$ V)
[g] in dimethylacetamide
[h] not reported
[i] V *vs.* NHE in THF
[j] V *vs.* NHE in CH_2Cl_2 (adapted from the original work, $V_{NHE} = V_{Fc^{+/0}} + 0.60$)
[k] in dichloromethane
[l] in CH_3CN/H_2O 2:1
[m] in CH_2Cl_2/MeOH 9:1
[n] Not Detected

CO_2 reduction was also achieved using a combination of rhenium catalysts and iridium complexes (**Ir40-42**), either separate in solution or linked through a bridging ligand.[167] Cyclometalated piq ligands were used, which increased molar absorption coefficients at 444 nm to values between 7400 and 8100 $M^{-1}cm^{-1}$. Visible light excitation led to charge transfer from the Ir-C bond to the N-N type ligand. The metal-centered oxidation and first ligand-centered reduction remained almost identical in this series of iridium complexes. Excited-state electron transfer chemistry was then probed with 1-benzyl-1,4-dihydronicotinamide (BNAH) and BIH. The quenching rate constants were almost two orders of magnitude larger when BIH was used compared to BNAH. This increased excited-state quenching was also reflected in the CO_2 reduction catalysis. Furthermore, BIH can donate two electrons as well as one proton, which improved TON for CO_2 reduction to CO using > 500 nm irradiation. Similar systems were also developed using 2-(pyren-1-yl)-4-methylquinoline cyclometalated ligand (**Ir43**) which enhanced the molar absorption coefficient up to > 60000 $M^{-1}cm^{-1}$ at 450 nm. In that

specific example, a ruthenium catalyst was used instead of a rhenium one in order to favor CO_2 reduction to formate.[170]

Strategies to enhance visible light absorption by extending the conjugation of the cyclometalated ligands were also used in the field of hydrogen production (**Ir43-48**). The use of 4-methylquinoline coupled to pyrene (**Ir43**) or carbazole (**Ir48**) resulted in iridium complexes with molar absorption coefficients of 65500 $M^{-1}cm^{-1}$ and 11500 $M^{-1}cm^{-1}$ at 452 nm, respectively.[100] Unfortunately, amongst the 6 studied complexes, only 3 resulted in hydrogen production with TON that ranged from 400 to 1280. This result was explained by the inability of some iridium complexes to undergo excited-state electron transfer with the triethylamine sacrificial electron donor.

Very recently, the cyclometalation of 1,8-naphthalenebenzimidazole (NBI) was explored by Castellano *et al.* to produce **Ir49**.[94, 95] Direct chelation of NBI was reported to improve the visible light absorption and to push photoluminescence towards the red. As evidenced by TD-DFT calculations, this effect was attributed to an increased contribution of LC transitions to the lowest-energy excited state. In the absorption spectra, it resulted in large molar absorption coefficients, related to the higher oscillator strength of such transitions, as compared to classical MLCT/LLCT transitions. This led to a complex with molar absorption coefficient of 11000 $M^{-1}cm^{-1}$ at 452 nm. Electrochemical investigations on **Ir49** provided additional information on the effect of the NBI ligand.[95] The oxidation process was found to be located on the iridium center with strong contributions from the cyclometalated ligand. More surprisingly, the first and second reductions were also attributed to the two cyclometalated NBI ligands, showing that NBI dominated the optoelectronic properties of this complex. Contributions from the ancillary 1,10-phenanthroline ligand were thus reduced to a minimum, which is unusual for cationic IrC_2N_4 complexes. It was shown that hydrogen could be produced with a TON of 823 using 452±10 nm irradiation. The sequence of events leading to hydrogen production was investigated into great detail. Pulsed light excitation was followed by electron transfer from the N,N-dimethyl-*p*-toluidine sacrificial electron donor. The reduced complex could then activate the molecular $Co(dmgH)_2(py)Cl$ catalyst via subsequent electron transfer. The ^{3}LC excited-state nature promoted a large cage escape yield efficiency of 78% which allowed enhanced performance of H_2 photoproduction.

Cyclometalation of coumarin (C6) was also reported to drastically increase the visible light absorption properties of iridium complexes, with molar absorption coefficients around 480 nm that span 40000-150000 $M^{-1}cm^{-1}$ (**Ir50-55**). This allowed the development of iridium (III) complexes with uses in hydrogen photoproduction,[171, 172] DSSCs,[168] upconversion[139, 173, 174] or as biosensors,[169, 175-177] for example. **Ir50** was reported as a sensitizer for both *n*-type and *p*-type DSSCs. On TiO_2, currents of 1.71 mA cm^{-2} were measured, with an overall cell efficiency of 0.56%. This represents an overall low efficiency compared to champion ruthenium(II) photosensitizers.[178] On NiO, the photocurrent and the overall efficiency was drastically decreased to 0.45 mA cm^{-2} and 0.02%, respectively. Although this represents a modest efficiency, it was still a notable result for NiO electrodes and was made possible by the large molar absorption coefficient.

$Ir(C6)_2(LL)$, where LL is bpy (**Ir51**), phen (**Ir52**) or biq (**Ir53**) were investigated for hydrogen photoproduction using triethylamine as a sacrificial electron donor and $[Co(bpy)_3]Cl_2$ as a water-reduction catalyst. Irradiation was carried out at wavelengths greater than 440 nm which yielded TONs of 678, 701 and 114 for sensitizers **Ir51**, **Ir52** and **Ir53**, respectively. The lower TON observed with **Ir53** originated from endergonic reactivity between the reduced complex and the cobalt catalyst, as well as from the fast nonradiative decay of the excited state which competed with reductive quenching by TEA.

Ir54 and **Ir55** were also investigated for hydrogen production while incorporated into DPPC vesicle membranes. This allowed to expand photoproduction of hydrogen into pure aqueous solutions. In these systems, sodium ascorbate was used as a sacrificial electron donor and a Dubois-type nickel catalyst was used for hydrogen production. In the optimal conditions, a TON_{Ni} of 150 and 100 were obtained after 4h irradiation (λ>440 nm) of **Ir54** and **Ir55**, respectively.

Lastly, in tris-bidentate IrC_2N_4 complexes, extension of the conjugation of the N-N diimine ligand was investigated. Very recently, Bevernaegie *et. al.* reported three heteroleptic complexes of the IrC_2N_4 family, bearing ligands where the conjugation was systematically increased by the addition of fused phenyl rings (**Ir56-58**).[33] The ancillary ligands consisted of a ppy backbone modified with two CF_3 moieties on the phenyl ring. As a consequence, the Ir-C electron density was decreased, which in turn increased the photoxidizing character (**Table 7**). The N-N ligands were composed of a π-accepting 1,4,5,8-tetraazaphenanthrene (**Ir56**) backbone whose π-conjugation was increased by the addition of one (**Ir57**) or two (**Ir58**) phenyl rings. The introduction of additional phenyl rings led to a stabilization of the LUMO level, which in turn led to increased visible light absorption. Furthermore, fused phenyl rings also led to intraligand charge transfer (ILCT) bands between the phenyl electron rich part of the ligand, and the π-accepting TAP backbone. For **Ir58**, the absorption at 450 nm (9800 $M^{-1}cm^{-1}$) matched that of the prototypical $[Ru(bpy)_3]^{2+}$ complex. Interestingly, the independent tuning of the HOMO and LUMO levels resulted not only in iridium(III) complexes that appreciably absorbed visible light, but that were also potent photo-oxidants with excited-state reduction potentials, $E_{1/2}(Ir^{*(+/0)})$ of *ca.* 1.77 V *vs.* NHE. The three complexes were therefore investigated for visible-light induced electron transfer chemistry in acetonitrile and were shown to react with a variety of quenchers (organic and halides) whose oxidation potentials ranged from 0.7 to 1.50 V *vs.* NHE. In addition, Marcus analysis of the quenching rate constants allowed extrapolation of the one electron oxidation potentials $E_{1/2}(X^{\bullet/-})$ in acetonitrile for bromide and chloride as 1.35 ± 0.02 and 1.46 ± 0.05 V *vs.* NHE, respectively.

The last group of the IrC_2N_4 complexes to be discussed is the bis-tridentate cyclometalated Ir(III) complexes, with N^N^N and C^N^C ligands that were recently reported (**Figure 12**, **Table 8**).[135] The complexes were bearing a pyridine moiety that was either unsubstituted (**Ir59**), methylated (**Ir60**) or chelated onto a cobalt catalyst. All complexes displayed $E(Ir^{IV/III})$ redox processes at 1.36-1.41 V *vs.* NHE, highlighting that the HOMO level was not affected by methylation or chelation of the pendant pyridine. On the contrary, ligand-centered reductions were highly affected by methylation or chelation. Indeed, **Ir60** underwent a first reduction event –0.51 V *vs.* NHE followed by a second one at –0.94 V *vs.* NHE while **Ir59** exhibited a single ligand-centered reduction event at –0.96 V *vs.* NHE.

Table 8. Electrochemical and spectroscopic data for various bis-tridentate IrC_2N_4 complexes.

	$E_{1/2}(Ir^{IV/III})$[a]	$E_{1/2}(L^{n/n-1})$	$E_{1/2}(Ir^{*(+/0)})$[b]	$E_{1/2}(Ir^{*(0/-)})$[b]	λ_{abs} / nm (ε / $M^{-1}cm^{-1}$)[b]	λ_{PL} / nm RT[b]	λ_{PL} / nm 77K	$E_{0\text{-}0}$ / eV	Ref
Ir59	+1.36	–0.96	–0.48	+0.88	475 (9100), 514 (5500)	705	673	1.84	[135]
Ir60	+1.39	–0.51, –0.94	–0.33	+1.21	476 (9300), 540 (6700)	N.D	720	1.72	[135]
Ir61	+1.37	–1.06	–0.70	+1.01	477 (6330), 510 (5310)	679	XX	2.07	[179]
Ir62	+1.33	–1.06	–0.74	+1.01	483 (10400), 513 (9150)	685	XX	2.07	[179]
Ir63	+1.42	–1.13	–0.55	+0.84	482 (4410), 512 (3290)	654	XX	1.97	[179]
Ir64	+1.38	–1.15	–0.57	+0.80	459 (5600), 526 (2850)	653	XX	1.95	[179]

[a] V *vs.* NHE in CH_3CN (adapted from the original work, $V_{NHE} = V_{SCE} + 0.24$ V and $V_{NHE} = V_{Fc^{+/0}} + 0.64$ V)
[b] in CH_3CN

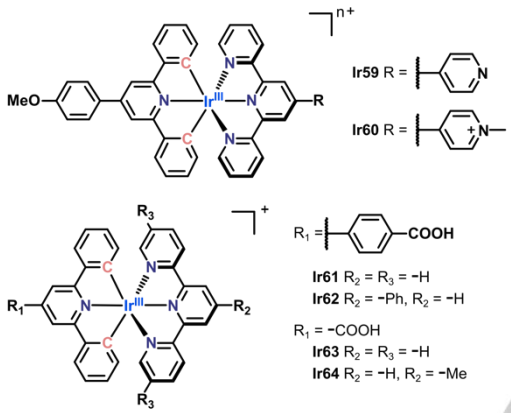

Figure 12. Examples of bis-tridentate IrC_2N_4 complexes.

All complexes exhibited absorption features in the UV region, attributed to ligand-centered transitions. Additional transitions were observed in the visible region with appreciable molar absorption coefficients. **Ir59** presented ground-state absorption features at 445 nm (9100 $M^{-1}cm^{-1}$) and 514 nm (5500 $M^{-1}cm^{-1}$) whereas these transitions were red-shifted by roughly 30 nm in **Ir60**, *i.e.* 476 nm (9300 $M^{-1}cm^{-1}$) and 540 nm (6700 $M^{-1}cm^{-1}$). Interestingly, when the dyad was irradiated with green LED centered at 525 nm in the presence of triethylamine, hydrogen production was observed with a TON of 113. When 452 nm light was used, a TON number of 225 over 35 hours was observed, that reached 440 after 66h.

Iridium bis-tridentate complexes have also been used as photosensitizers in dye-sensitized solar cells (DSSCs). Four bis-tridentate bis-cyclometalated complexes (**Ir61-64**) were anchored on nanocrystalline TiO_2.[179] The terpyridine ligand was functionalized with a carboxylic acid group that was either directly linked to the terpyridine backbone (**Ir63-64**) or separated by a phenyl spacer (**Ir61-62**). Three cyclometalated ligands were used, the unsubstituted diphenyl-pyridine (dpp) (**Ir61** and **Ir63**), the triphenyl-pyridine (tpp) (**Ir62**) or the di-tolyl-pyridine (dtp) (**Ir64**). Overall, these cyclometalating ligands did not significantly impact the HOMO energies, as all $Ir^{IV/III}$ redox processes fell within a 90 mV range. The UV-Vis absorption spectra were however strongly influenced by the triphenyl-pyridine ligand, bearing a phenyl moiety in *para* (*i.e.* 4') position of the pyridine ring. Indeed, compared to the other complexes, **Ir62** exhibited molar absorption coefficients that were 2-3 times large than the other complexes. DSSCs using **Ir64** performed the best under AM 1.5 (100 mW cm^{-2}) with an overall cell efficiency of 2.16%.

Conclusions

The development of iridium(III) complexes with increased visible light absorption, that still maintain interesting (photo)redox properties for electron transfer photochemistry, represents a challenging and highly rewarding endeavor. Indeed, these two properties are often intrinsically linked, and improving one of them usually impairs the other. Nonetheless, iridium(III) cyclometalated complexes represent a relatively unique opportunity as, to some extent, the HOMO and LUMO energy levels can be independently tuned. All of the strategies described herein showed distinct benefits and they can often be applied in concert with one another. Taking inspiration from the underlying principles that guide these electronic effects, a roadmap to impart traits to families of iridium complexes has been developed. By selectively opting for approaches that favor light absorption, particular electronic properties or a combination of both, an optimal iridium complex can be designed to fit specific needs. Appreciable visible light absorption features have been obtained for all families of iridium complexes (**Figure 13**). Hence, it is recommended to first select a family of iridium complexes for a desired application. For example, for applications where a strong photo-reductant is desired, IrC_3N_3 or IrC_2N_2LX complexes represent prime candidates, whose visible light absorption properties can be easily tuned. IrN_6 complexes are attractive candidates when strong photo-oxidants are required, but have, to date, remained underexplored. Finally, IrC_2N_4 complexes represent, thus far, the most utilized family, as these complexes can act both as photo-oxidants and photo-reductants (**Figure 13**) and robust strategies to tune their visible light absorption properties have been developed. Excited-state reactivity involves many challenges and opportunities, and it is hoped that the roadmap presented herein will allow for the design and development of new series of Ir(III) complexes with improved ground- and excited-state properties.

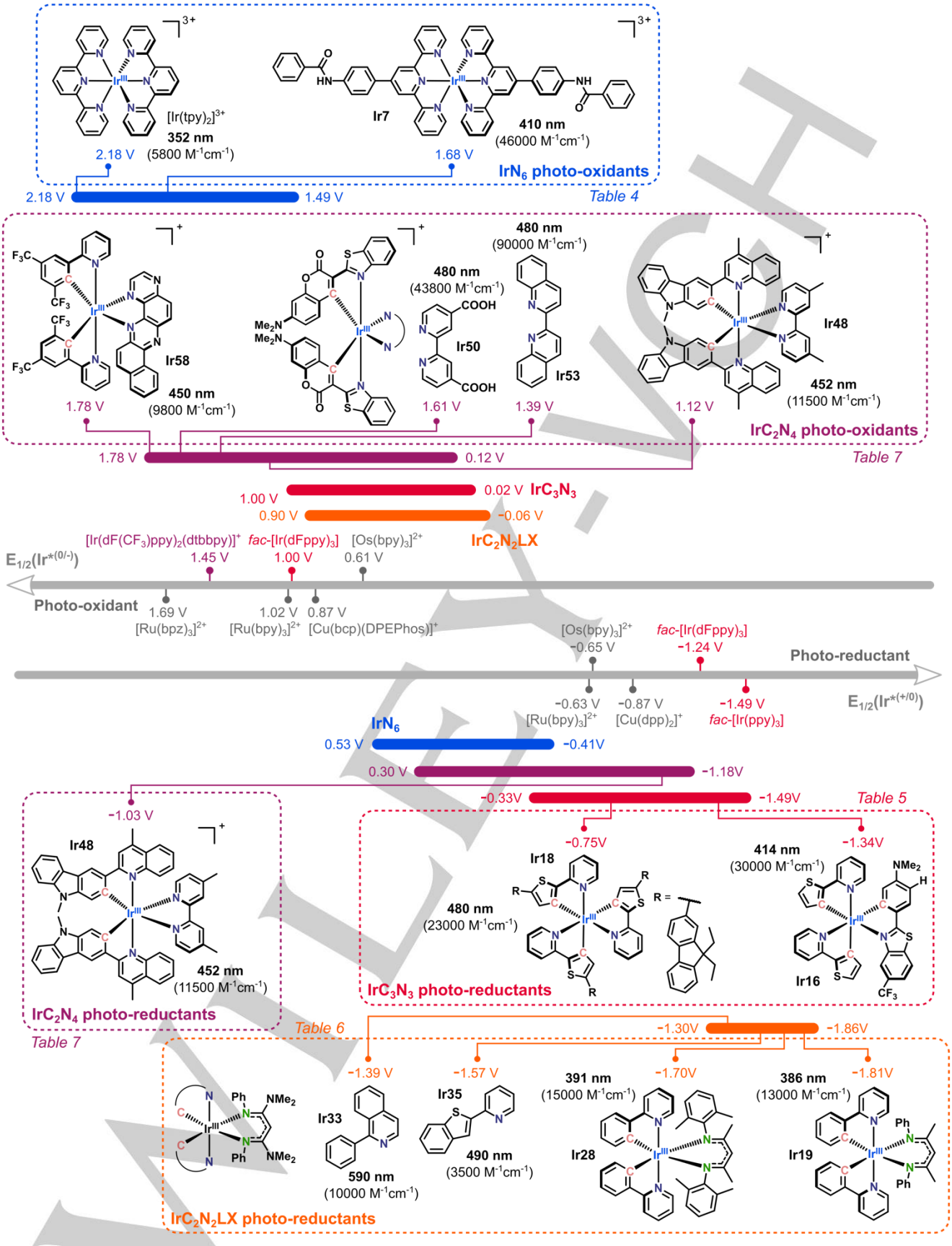

Figure 13. Excited-state oxidation and reduction potentials for selected iridium(III) complexes as well as prototypical ruthenium(II),[43, 44] osmium(II)[45-47] and copper(I)[48, 49] complexes. Potentials are given *vs.* NHE and referenced to the corresponding tables of this manuscript.

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Keywords: Photosensitizer • Visible light • Photoredox • Iridium • Cyclometalated

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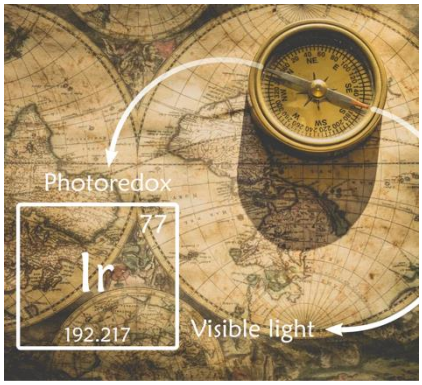

A roadmap towards the synthesis of iridium(III) complexes with increased visible light absorption and tailored ground- and excited-state redox properties is presented. Fundamental tools are provided to enable the independent tuning of the HOMO and LUMO energy levels. With these concepts in mind, iridium(III) complexes with excited-state redox properties that ranged from + 2.18 V to – 1.86 V *vs.* NHE were obtained.

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