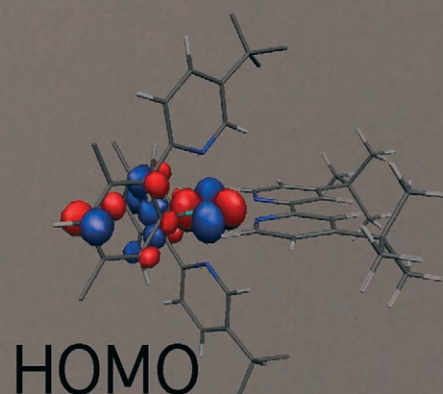
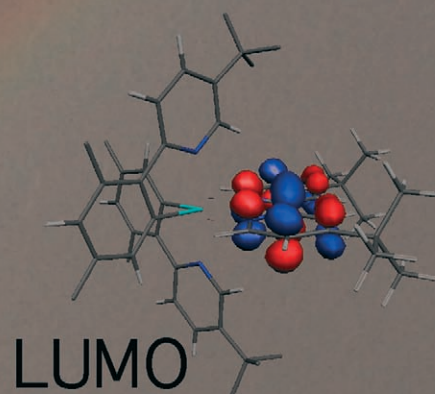


26 Fe 55.85 44	27 Co 58.93 45	28 Ni 58.69 46
44 Ru 101.07 76	45 Rh 102.91 77	46 Pd 106.4 78
76 Os 190.2	77 Ir 192.2	78 Pt 195.08

Designing cyclometalated Ir^{III} complexes with attractive photophysical and photochemical properties: Controlling the electronic structure through deliberate synthetic modifications.



Synthetically Tailored Excited States: Phosphorescent, Cyclometalated Iridium(III) Complexes and Their Applications

Michael S. Lowry and Stefan Bernhard*^[a]

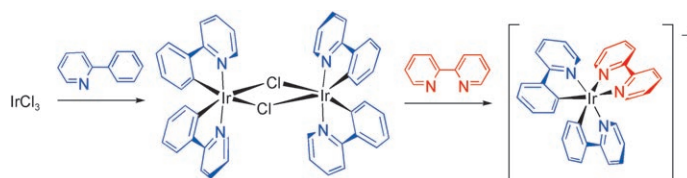
Abstract: Phosphorescent iridium(III) complexes are being widely explored for their utility in diverse photo-physical applications. The performance of these materials in such roles depends heavily on their excited-state properties, which can be tuned through ligand and substituent effects. This concept article focuses on methods for synthetically tailoring the properties of bis-cyclometalated iridium(III) materials, and explores the factors governing the nature of their lowest excited state.

Keywords: iridium • luminescence • OLEDs • photo-chemistry • structure–property relationships

Introduction

Luminescent transition-metal complexes are appealing for their utility in diverse applications.^[1–5] The effectiveness of a complex in a specific role is determined by its excited-state properties and can be manipulated through synthetic modifications. Early work in this field focused predominantly on tris-diimine ruthenium(II) complexes (e.g., [Ru(bpy)₃]²⁺), but these materials offered limited color tuning capability due to thermal population of a nonemissive metal-centered (³MC) state.^[6] Iridium(III) complexes, on the other hand, enable broader tuning possibilities due to their increased ligand-field stabilization energy (LFSE) and, as a consequence, less thermally accessible ³MC states. Splitting of the d orbitals can be further enhanced with strong-field ligands and, as a result, bis-cyclometalated iridium(III) complexes have displaced ruthenium(II) compounds at the forefront of many photochemical and photophysical investigations.^[7–12]

In particular, the reversible electrochemistry, synthetic versatility, and robust nature of iridium(III) complexes render them appealing materials for a multitude of applications. Bis-cyclometalated iridium(III) complexes can be prepared according to the two-step synthesis presented in Scheme 1, in which the net charge of the mononuclear com-



Scheme 1. Synthesis of a heteroleptic, bis-cyclometalated iridium(III) complex. A dichloro-bridged diiridium dimer involving a cyclometalating ligand (e.g., 2-phenylpyridine, ppy, blue) is isolated and subsequently cleaved using an ancillary ligand (e.g., 2,2'-bipyridine, bpy, red) to yield mononuclear iridium(III) complexes (e.g., [Ir(ppy)₂(bpy)]⁺).

plex can be determined by the nature of the ancillary ligand (Figure 1).^[11–14] By independently modifying the cyclometalating and ancillary ligands, it is possible to endow a complex with specific photophysical and electrochemical traits and to tune its ability to perform in areas such as organic light-emitting diodes (OLEDs),^[13–15] luminescence-based sensors,^[3,16,17] and photocatalysis.^[18]

Nature of the Excited State

The two principle transitions that are observed in the long-lived excited state of iridium(III) complexes are: 1) metal-to-ligand charge transfer (MLCT) in which an electron is promoted from a metal d orbital to a vacant π^* orbital on one of the ligands, and 2) ligand-centered (LC) transitions in which an electron is promoted between π orbitals on one of the coordinated ligands.^[6,7] Strong spin-orbit coupling from the iridium(III) center facilitates intersystem crossing to energetically similar triplet states and enables the formation of an emissive, mixed (triplet) excited state [T₁; Eq (1)]

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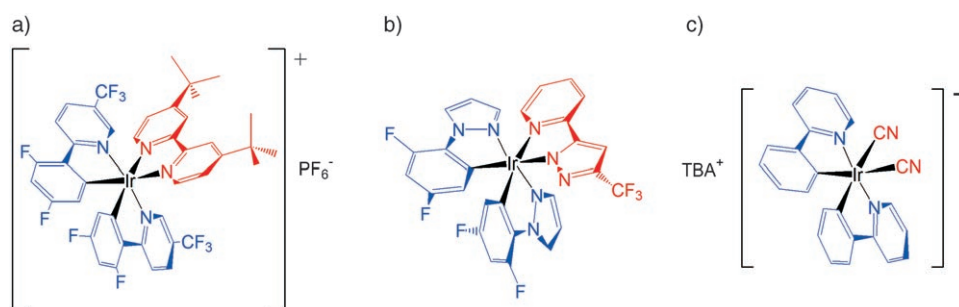


Figure 1. Bis-cyclometalated (shown in blue) iridium(III) luminophores. The net charge of the complex is determined by the ancillary ligand(s) (shown in red): a) cationic $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})]^+\text{PF}_6^-$ (dFCF_3ppy = 5-trifluoromethyl-2-(2',4'-difluorophenyl)-pyridine; dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine), b) neutral $[\text{Ir}(\text{dFpz})_2(\text{CF}_3\text{ppz})]$ (dFpz = 1-(2',4'-difluorophenyl)-pyrazole; CF_3ppz = 2-(5-trifluoromethylpyrazol-3-yl)-pyridine), and c) anionic $[\text{TBA}]^+[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ (TBA^+ = tetrabutylammonium, CN^- = cyanide).

in which the coefficients a and b refer to the contributions of the $^3\text{MLCT}$ and ^3LC states, respectively.^[6,7,19] An excited-state manifold ($a \approx b$) is presented in Figure 2.

$$\Psi_{T_1} = a\Psi_{\text{MLCT}} + b\Psi_{\text{LC}} \quad (1)$$

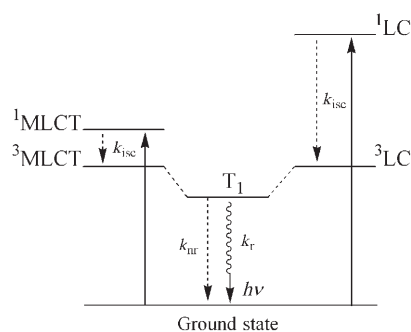


Figure 2. The energetic closeness and degree of overlap between $^3\text{MLCT}$ and ^3LC states results in the formation of a mixed lowest excited state (T_1). The excited molecule relaxes to the ground state through radiative (k_r) and nonradiative (k_{nr}) pathways.

Tremendous efforts have been made to understand the nature of the excited state as well as the structural factors by which it is controlled. A combination of excited-state lifetime measurements,^[9] time-resolved luminescence spectroscopy,^[8,20,21] and computational investigations^[22,23] have provided significant insight into the nature of the excited state in bis-cyclometalated iridium(III) complexes. For example, Hay accurately described the HOMO and HOMO-1 as metal and cyclometalating ligand (π) orbitals and the LUMO and LUMO+1 as vacant (π^*) ligand orbitals in $[\text{Ir}(\text{ppy})_2(\text{bza})]$ (in which ppy = 2-phenylpyridine, bza = 1-phenyl-1,3-butanedione) by using time-dependent density-functional theory (TD-DFT).^[23] Similar results have been attained with other neutral and ionic iridium(III) complexes.^[11,14,22,23] Thus, it appears feasible for the excited state of bis-cyclometalated iridium(III) complexes to contain mixed MLCT-LC character (Figure 3). It is worth noting that these calculations correspond to the absolute energy of

the associated orbitals (i.e., singlet transition energies for which the ^1LC state is significantly larger than the $^1\text{MLCT}$ state) and that singlet-triplet stabilization energies must be considered before further predictions can be made about the energy of the emissive state.^[7,11]

Tuning Strategies

Excited-state mixing occurs when sufficient overlap is present between the ^3LC and

$^3\text{MLCT}$ states.^[24] Thus, it is possible to control the energy of the lowest excited state by deliberately adjusting the energy of metal and ligand orbitals, which can be achieved through substituent effects^[25,26] or by changing the ligand parent structure entirely (e.g., ppy vs. 1-phenylpyrazole, ppz).^[14,27] Structural control is facilitated by the multistep synthesis

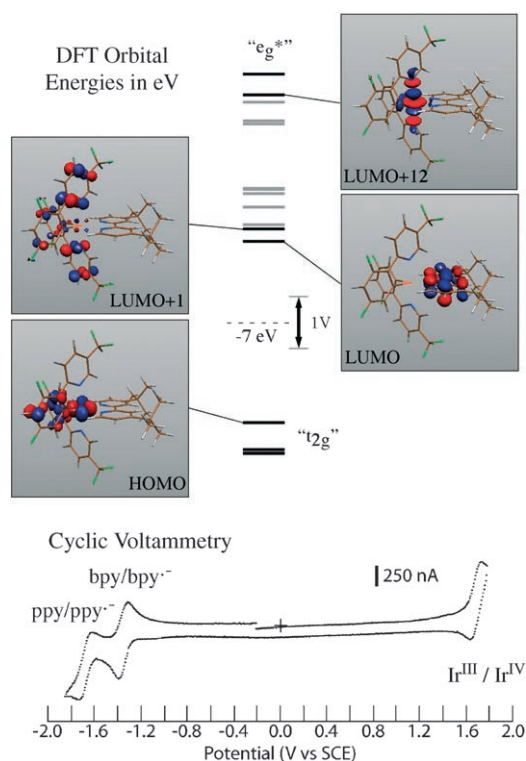


Figure 3. Molecular orbital diagram for $[\text{Ir}(\text{dFCF}_3\text{ppy})_2(\text{dtbbpy})]^+$ (Figure 1a) obtained from DFT calculations. The HOMO is composed primarily of metal d orbitals with some contributions from ligand (ppy-based, phenyl) orbitals, while the LUMO and LUMO+1 are localized on separate ligands (bpy- and ppy-based, respectively). Ligand-field splitting is evident between the HOMO (" t_{2g} ") and LUMO+1 (" e_g^* "). The calculated orbital energies are corroborated by experimental evidence (cyclic voltammetry).

shown in Scheme 1 in which different ligands are independently added to the coordination sphere.

When both classes of ligands provide orbitals that participate in the excited-state transitions, the cyclometalating ligand tends to be associated with the ^3LC transition and the ancillary ligand with the $^3\text{MLCT}$ transition.^[23,24] In such cases, the excited state can be tuned directly through ligand modifications, because each ligand is linked to a different transition. By monitoring the effect of various ligand permutations within the coordination sphere, it is possible to gain insight into the factors that govern the photophysical and electrochemical behavior of heteroleptic iridium(III) complexes, and to tailor materials with specific excited-state properties.^[11,28]

In some excited complexes, interligand electron transfer (ILET) from the cyclometalating ligand to the ancillary ligand is possible. The net properties of these materials can be controlled almost exclusively by the ancillary ligand. For instance, Park's group observed emission across the visible spectrum by changing the structure of the ancillary ligand in a series of complexes that underwent ILET prior to emission.^[29] Campagna's group further demonstrated that if the structure of the ancillary ligand is modified such that some of its π density overlaps the plane of chelation for the cyclometalating ligand, another charge transfer transition (sigma-bond-to-ligand charge transfer, SBLCT^[30]) is feasible.^[31] As a result, electron density can be transferred from a carbon-metal σ bond to the ancillary ligand, and site-specific tuning can be achieved.

When only the cyclometalating ligand contributes π^* orbitals at an appropriate energy for the excited-state transitions, both transitions tend to be associated with the cyclometalating ligand. Meanwhile the ancillary ligand (e.g., 2,4-pentanedione, *acac*) plays a more passive role in determining the nature of the excited state; influencing the energy of the metal orbitals by inductive communication through σ bonds.^[32] Thus, even a "nonparticipating" ancillary ligand can be used to adjust the energy of the MLCT state as well as the degree of mixing between the states.

One of the most effective methods for tuning the energy of the lowest excited state involves changing the degree of conjugation in the structure of the participating (cyclometalating and/or ancillary) ligands.^[11,27,28] As the coordination sphere becomes more diffuse, the corresponding orbitals are stabilized. It follows, then, that the excited-state transitions can be tuned by altering the size of the ligands and also by localizing electron density in discrete regions of the molecule or by partially destroying ligand aromaticity. For example, bulky pendant groups can be used to distort a ligand from planarity, which will destabilize its π orbitals, and, as a result, increase the size of the associated $^3\text{MLCT}$ or ^3LC transition. A critical drawback of this approach is that enhanced internal strain may promote nonradiative decay, whereby higher excited-state energy is attained at the expense of other important properties (e.g., luminous intensity and excited-state lifetime).^[33–35] Alternatively, recent investigations of iridium(III) complexes involving terdentate cyclo-

metalating ligands (e.g., 2,6-diphenyl-pyridine^[36,37] and 1,3-bis-(1-methyl-benzimidazol-2-yl)benzene^[38]) have shown that low-energy emission can be readily achieved in complexes containing ligands with extended π systems.^[36–38]

Another promising method for tuning (and fine-tuning) the excited-state properties of iridium(III) complexes involves deliberate functionalization of the ligands through the use of substituent groups. By modifying the symmetry and inductive influence of a ligand with different substituents, it is possible to control metal–ligand bonding as well as ligand orbital energies and, thus, to control the nature of the lowest excited state. Tremendous color versatility has been achieved with iridium(III) luminophores in this manner (Figure 4), and a broad range of excited-state lifetimes (from nanoseconds to several microseconds) as well as phosphorescent yields (approaching 100%) have been reported.^[11,14]

In particular, electronic effects have been considered due to their profound influence on orbital energies as well as the relative ease with which electron-withdrawing (e.g., -F, -CF₃) and electron-donating (e.g., -C(CH₃)₃, -OCH₃) groups can be incorporated into the ligand structure. Electron-withdrawing substituents tend to stabilize the HOMO by removing electron density from the metal, whereas donating groups have an inverse effect.^[11,14,39,40] This relationship is convoluted by the fact that withdrawing groups may also lower the energy of the LUMO (i.e., increasing the electron affinity of the parent ligand).^[14] Fortunately, the cyclometalating and ancillary ligands can be separately substituted with electron-withdrawing and -donating groups in heteroleptic complexes, which enables deliberate control over the excited state.

The position of these substituents with respect to the coordinating carbon of a cyclometalating ligand will strongly influence the LFSE of the resulting complex.^[41] For example, electron-withdrawing groups *meta* to the site of coordination (and donating groups *ortho* or *para* to this position) increase the field strength of the ligand and concomitantly enhance d-orbital splitting. Interestingly, opposing spectroscopic trends have been observed for fluoro (-F) and trifluoromethyl (-CF₃) substituents at the same position of a cyclometalating ring despite their similar electronic effects.^[40] This difference has been attributed to the mesomeric and inductive ability of the fluorine atom as opposed to the purely inductive ability of the trifluoromethyl group. Thus, it is important to consider the total impact of a substituent group when designing ligand systems for excited-state tuning.

Due to the high number of ligand and substituent variables that influence the nature of the excited state in heteroleptic iridium(III) complexes, their electrochemical and photophysical properties are not always easy to predict a priori. To this end, our group has developed a set of combinatorial procedures—involving parallel synthesis and high-throughput screening—to examine the effect of multiple structural (and site-dependent) variables in tandem.^[11] As our understanding of structure–property relationships improves, we

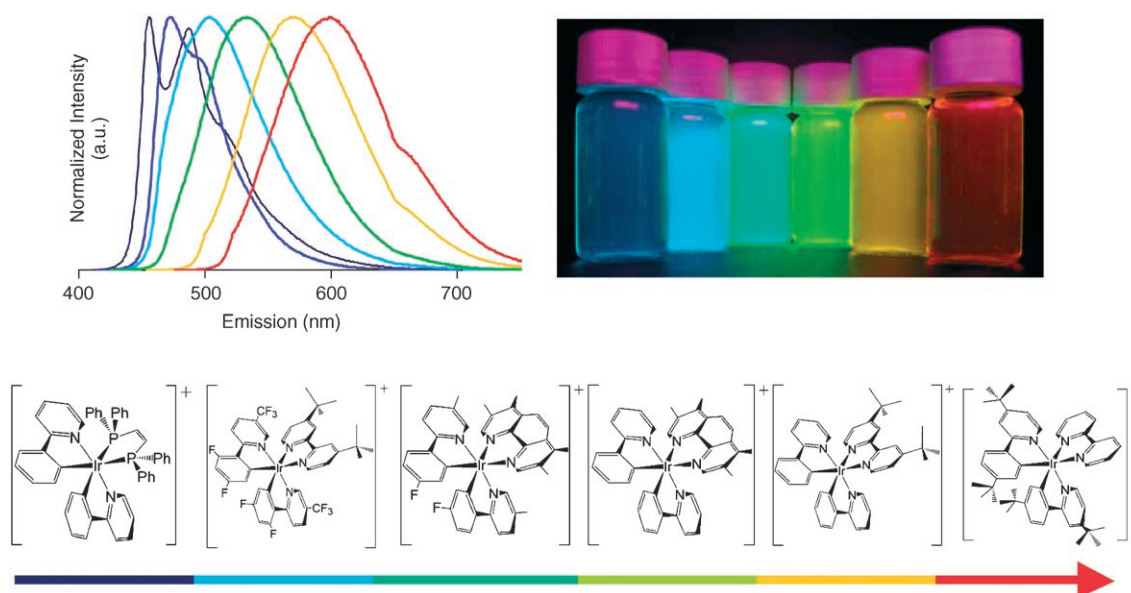


Figure 4. Color versatility expressed by a series of six cationic iridium(III) luminophores. Their structures are listed in order of increasing emission wavelength (blue to red). The evolution of ^3LC (vibrationally structured, high-energy bands) and $^3\text{MLCT}$ character (structureless, low-energy bands) in the luminescence spectra are indicative of a mixed excited state.

have found that DFT calculations provide an excellent method for modeling orbital configurations and extrapolating the energy of the lowest excited state.^[11,14] These techniques in conjunction with the other strategies presented herein have facilitated and expedited the design of useful materials for various optoelectronic,^[4,39] analytical,^[3,16] and photocatalytic applications.^[18] Four areas in which the highly tunable nature of iridium(III) complexes have improved the performance of inorganic materials are discussed below.

OLED applications

Transition-metal-based, organic light-emitting diodes (OLEDs) are considered viable candidates for flat-panel displays due to their color versatility, low operation voltages, and phosphorescent efficiency.^[42,43] The first complex-based OLED was assembled by Tang and VanSlyke in 1987 containing an Alq_3 chromophore ($q=8$ -hydroxyquinoline) that emits green light (550 nm) from a singlet excited state.^[44] Considerable attention has since been placed on altering device characteristics through strategic modifications to the chromophore. In particular, complexes containing a heavy transition metal center, such as iridium(III),^[45] ruthenium(II),^[46] or osmium(II)^[47] are targeted for electroluminescence studies because of the increased theoretical limit for emission efficiency from triplet emitting complexes (nearly 100%) over singlet emitters ($\leq 25\%$).^[48]

OLEDs that are constructed with *neutral* complexes typically consist of the luminescent chromophore embedded in an organic matrix (e.g., 4,4'-*N,N'*-dicarbazolylbiphenyl, CBP), sandwiched between multiple layers of charge transport materials (e.g., 2,9-dimethyl-4,7-diphenyl-1,10-phenan-

throline, BCP and 4,4'-bis-[*N*-(naphthyl-*N*-phenylamino)bi-phenyl, α -NPD, respectively), and capped with a low work-function cathode (e.g., LiF/Al) and a transparent anode (e.g., indium–tin oxide, ITO; Figure 5a).^[49] By systematically

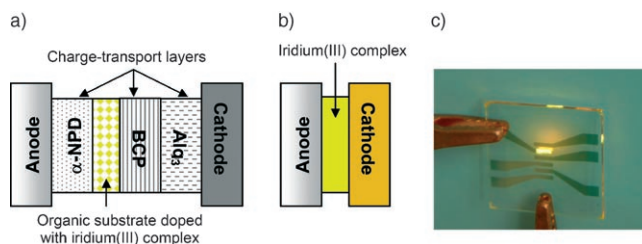


Figure 5. a) A multilayer device ensemble involving an organic material (e.g., CBP) doped with a neutral or anionic iridium(III) chromophore. This matrix is sandwiched between hole- (e.g., α -NPD) and electron-injecting (e.g., Alq_3 , $q=8$ -hydroxyquinoline) layers as well as a hole blocking layer (e.g., BCP) and capped with a low work-function cathode (e.g., LiF/Al) and a transparent anode (e.g., ITO). b) Single-layer device geometry in which a cationic iridium(III) chromophore is spin-coated on an ITO substrate and capped with a gold electrode. c) Electroluminescence from $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ in a single-layer, air-stable device (560 nm).

adjusting the nature of the excited state in the chromophore, Thompson and Forrest have observed emission across the visible spectrum.^[15,28] Similarly, Holmes and Friend fine-tuned electroluminescence in the green-to-blue regime through synthetic modifications to the chromophore and, more importantly, improved the operational lifetime of the devices through the use of more stable (i.e., less labile) ancillary ligands.^[50] Neutral iridium(III) complexes have spurred tremendous interest (beyond the scope of this manu-

script) over the course past ten years and a concise review of the advances in this field is overdue.

Recently, *cationic* iridium(III) complexes have emerged in OLED applications due to their ability to electroluminescence from a single-layer of neat complex sandwiched directly between two air-stable electrodes, such as ITO and gold (Figure 5b, c).^[45] This simple device geometry is made feasible by the presence of mobile counterions that redistribute in the presence of an applied potential and facilitate charge injection at the electrodes. Additionally, charge-transport occurs through a hopping mechanism, which enables low turn-on voltages (<3 V) and device operation from an alternating current (AC) power source.^[4] The discovery of novel cationic luminophores has been catalyzed by the development of an exhaustive library of prospective materials using the combinatorial procedures that were developed in our group.^[11] Recently, we reported yellow (560 nm),^[45] green (531 nm)^[51,52] and blue-green (497 nm)^[14] electroluminescence from complexes containing a ppy-bpy backbone. By adjusting the size (and, thus, energy) of the aromatic ligands, Thompson's group achieved red electroluminescence (635 nm) and also observed a slight hypsochromic shift (492 nm) over these pioneering complexes.^[27] Nevertheless, efforts to optimize cationic systems in OLED applications and to achieve pure blue electroluminescence (450 nm) are ongoing.

OLED fabrication has also been successful with *anionic* complexes of the form $[\text{Ir}(\text{ppy})_2\text{X}_2]^{-1}$ ($\text{X} = \text{CN}^{-}, \text{NCO}^{-}$), in which device assemblies resemble the multilayer ensembles utilized for neutral chromophores.^[13] In such cases, the pseudo-halogen (X) influences the energy of the metal d orbitals by adjusting the LFSE and, thus, provides a viable platform for color tuning. As such, yellow (556 nm; $\text{X} = \text{CN}^{-}$) and blue-green (500 nm; $\text{X} = \text{NCO}^{-}$) emission have been observed.^[13] Notably, device stability and efficiency also improved in systems with large LFSE (in which the ^3MC state is no longer accessible), but pursuit of pure blue electroluminescence persists.

Oxygen Sensor Applications

The long-lived triplet excited state of luminescent iridium(III) complexes enables efficient energy transfer with the triplet ground state of molecular oxygen, resulting in luminescence quenching and the formation of singlet oxygen.^[53] Consequently, iridium(III) luminophores can be utilized as oxygen probes in various medicinal, chemical, and environmental sensors.^[16,54] Oxygen concentration is quantified according to sudden changes in the luminescent properties of the complex and, thus, materials with high quantum yield and long excited-state lifetime (i.e., several microseconds) are highly desirable for facile, sensitive detection. Mixed-ligand iridium(III) complexes are particularly intriguing due to their broadly tunable excited-state properties, durability, and high chemical stability in the presence of singlet oxygen.^[16] A significant setback to the implementation of

solid-state iridium(III)-based sensors has been the occurrence of self-quenching between neighboring molecules. One potential solution involves separating luminescent dyes by embedding them in oxygen permeable polymer matrices, but the sensitivity of such systems is limited by low loading concentrations in order to prevent dye aggregation.^[16] Efforts to improve the loading concentration have included covalently binding the luminophores to the polymeric host^[55] as well as adjusting the charge and size of the dye molecules,^[56] but investigations in this field are ongoing.

Bioanalytical Applications

The rich electrochemical and photophysical characteristics of iridium(III) complexes also render them strong candidates for bioanalytical applications. The intense emission and long excited-state lifetimes of the iridium(III) complexes enable sensitive, time-resolved detection and their large Stokes shift helps minimize self-quenching between dispersed materials.^[57] More importantly, luminescent iridium(III) complexes can be used to label biomaterials due their ability to either covalently (e.g., aldehyde-amine cross-linking)^[58] or noncovalently (e.g., DNA intercalation)^[59] bind biological substrates. Bound complexes typically express different luminescent properties than their free analogs due to changes in the rigidity and hydrophobicity of the surrounding environment.^[59] Thus, luminescent labels provide a facile method for monitoring bioconjugation reactions and quantifying the binding affinity between different substrates.^[3,60] A comprehensive review of the role of iridium(III) and other transition-metal complexes in bioanalytical applications as well as methods for improving their luminescent properties was reported by Lo and co-workers in 2005.^[3]

Photocatalytic Water Splitting

The challenge of converting solar radiation to conveniently usable forms of energy has been considered by many researchers. One promising solution involves harnessing solar energy through a photocatalytic cycle to split water into hydrogen and oxygen.^[5,61,62] This process can be conceptualized as two half-reactions in which water is oxidized to molecular oxygen and reduced to molecular hydrogen. In particular, the high gravimetric energy density and clean combustion products of hydrogen render it a highly viable source of fuel and, as such, significant attention has been placed on hydrogen production. Typical photoreduction schemes employ a transition-metal photosensitizer in conjunction with an electron relay to collect and store radiant energy and convert protons into molecular hydrogen.^[5,61]

Heteroleptic iridium(III) complexes are appealing photosensitizers due to their highly tunable properties, and, in fact, we recently reported an iridium(III) photosensitizer that exhibits tremendous improvements in hydrogen produc-

tion over the previous state-of-the-art literature standard, $[\text{Ru}(\text{dmphen})_3]^{2+}$ ($\text{dmphen} = 4,7\text{-dimethyl-1,10-phenanthroline}$).^[14] This increase in hydrogen production has been traced to the improved reducing strength (i.e., ability to pass an electron to the electron relay) of iridium(III) complexes over ruthenium(II) complexes. An overview of the ground and excited-state redox properties of these materials were reported in a recent publication.^[14]

Other highly promising iridium(III) complexes have also been targeted by using a high-throughput technology that was developed in our laboratory, whereby multiple photosensitizers were simultaneously screened under variable reaction conditions. A custom-built parallel photoreactor—consisting of a series of ultra-bright light emitting diodes (500 mW \pm 10% at 465 nm) connected to a multiwell sample holder mounted on an orbital shaker—was employed along with a Ni/Pd thin film commercial hydrogen sensor (Figure 6).^[18] This methodology has helped us pinpoint structural and photophysical traits that are conducive to hydrogen production and also provided insight into the interplay between the photosensitizer and electron relay in the catalytic loop, yet considerable strides still need to be made before a sustainable “hydrogen economy” can be developed.

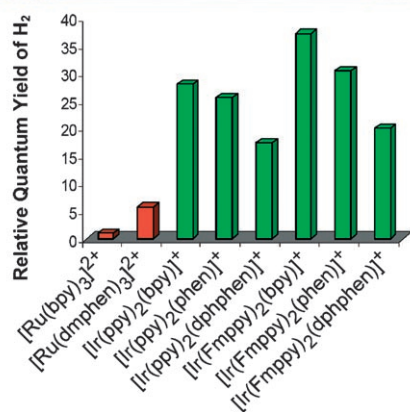
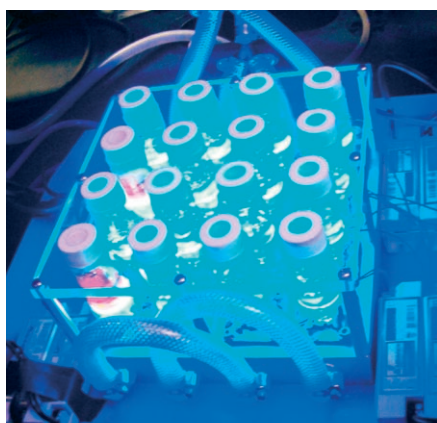


Figure 6. A water-cooled parallel photoreactor with ultrabright LEDs for studying photocatalytic reactions. Iridium(III) complexes (green) that exhibit a tremendous increase in hydrogen production over ruthenium(II) standards (orange) have been identified using this high-throughput technique (Fmppy = 5-methyl-2-(4'-fluorophenyl)-pyridine; phen = 1,10-phenanthroline; dphphen = 4,7-diphenyl-1,10-phenanthroline).

Conclusions and Prospects

The nature and energy of the excited state in mixed-ligand iridium(III) complexes can be manipulated by deliberate chemical synthesis. Synthetic control is facilitated by the dependence of the excited state on the orbital configurations within a molecule as well as the relative ease by which different parent ligand structures can be coordinated to the metal center. Consequently, heteroleptic iridium(III) complexes can be tailored to express specific luminescent properties or to serve a specific functional role (e.g., cross-linking) and iridium(III)-based materials are being explored for a plethora of applications. The improved performance of iridium(III) complexes over alternate transition metal centers as well as the straightforward manner in which their properties can be tuned has positioned heteroleptic iridium(III) complexes at the forefront of modern photochemistry and we can expect that they will remain there throughout the foreseeable future.

Acknowledgements

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- [1] M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, D. J. Robbins, *J. Chem. Soc. Perkin Trans. 2* **1984**, 1293–1301.
- [2] B. Higgins, B. A. DeGraff, J. N. Demas, *Inorg. Chem.* **2005**, *44*, 6662–6669.
- [3] K. K.-W. Lo, W.-K. Hui, C.-K. Chung, K. H.-K. Tsang, D. C.-M. Ng, N. Zhu, K.-K. Cheung, *Coord. Chem. Rev.* **2005**, *249*, 1434–1450.
- [4] J. Slinker, D. Bernards, P. L. Houston, H. D. Abruña, S. Bernhard, G. G. Malliaras, *Chem. Commun.* **2003**, 2392–2399.
- [5] M. Kirch, J. M. Lehn, J. P. Sauvage, *Helv. Chim. Acta* **1979**, *62*, 1345–1384.
- [6] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, New York, NY, **1992**.
- [7] N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, **1978**.
- [8] M. G. Colombo, A. Hauser, H. U. Güdel, *Inorg. Chem.* **1993**, *32*, 3088–3092.
- [9] K. A. King, R. J. Watts, *J. Am. Chem. Soc.* **1987**, *109*, 1589–1590.
- [10] D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum Press, New York, NY, **1994**.
- [11] M. S. Lowry, W. R. Hudson, R. A. Pascal, Jr., S. Bernhard, *J. Am. Chem. Soc.* **2004**, *126*, 14129–14135.
- [12] C.-H. Yang, S.-W. Li, Y. Chi, Y.-M. Cheng, Y.-S. Yeh, P.-T. Chou, G.-H. Lee, C.-H. Wang, C.-F. Shu, *Inorg. Chem.* **2005**, *44*, 7770–7780.
- [13] Md. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, M. Graetzel, *J. Am. Chem. Soc.* **2003**, *125*, 8790–8797.
- [14] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, Jr., G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712–5719.
- [15] C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *79*, 2082–2084.

- [16] M. C. DeRosa, D. J. Hodgson, G. D. Enright, B. Dawson, C. E. B. Evans, R. J. Crutchley, *J. Am. Chem. Soc.* **2004**, *126*, 7619–7626.
- [17] M.-L. Ho, F.-M. Hwang, P.-N. Chen, Y.-H. Hu, Y.-M. Cheng, K.-S. Chen, G.-H. Lee, Y. Chi, P.-T. Chou, *Org. Biomol. Chem.* **2006**, *4*, 98–103.
- [18] J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510.
- [19] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979.
- [20] A. P. Wilde, K. A. King, R. J. Watts, *J. Phys. Chem.* **1991**, *95*, 629–634.
- [21] R. J. Watts, *J. Am. Chem. Soc.* **1974**, *96*, 6186–6187.
- [22] T. H. Kwon, H. S. Cho, M. K. Kim, J. W. Kim, J. J. Kim, K. H. Lee, S. J. Park, I. S. Shin, H. Kim, D. M. Shin, Y. K. Chung, J. I. Hong, *Organometallics* **2005**, *24*, 1578–1585.
- [23] P. J. Hay, *J. Phys. Chem. A* **2002**, *106*, 1634–1641.
- [24] M. G. Colombo, A. Hauser, H. U. Güdel, *Top. Curr. Chem.* **1994**, *171*, 143–171.
- [25] R. J. Watts, J. Van Houten, *J. Am. Chem. Soc.* **1974**, *96*, 4334–4335.
- [26] K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson, R. J. Watts, *Inorg. Chem.* **1991**, *30*, 1685–1687.
- [27] A. B. Tamayo, S. Garon, T. Sajoto, P. I. Djurovich, I. M. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 8723–8732.
- [28] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304–4312.
- [29] Y. You, S. Y. Park, *J. Am. Chem. Soc.* **2005**, *127*, 12438–12439.
- [30] P. Didier, I. Ortman, A. Kirsch-De Mesmaeker, R. J. Watts, *Inorg. Chem.* **1993**, *32*, 5239–5245.
- [31] F. Neve, M. La Deda, A. Crispini, A. Bellusci, F. Puntoriero, S. Campagna, *Organometallics* **2004**, *23*, 5856–5863.
- [32] J. Li, P. I. Djurovich, B. D. Alleyne, M. Yousufuddin, N. N. Ho, J. C. Thomas, J. C. Peters, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 1713–1727.
- [33] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697–2705.
- [34] A. Juris, V. Balzani, P. Belsler, A. von Zelewsky, *Helv. Chim. Acta* **1981**, *64*, 2175–2182.
- [35] M. S. Lowry, S. Bernhard, Princeton University, Princeton, NJ, unpublished results, **2005**.
- [36] A. J. Wilkinson, A. E. Goeta, C. E. Foster, J. A. G. Williams, *Inorg. Chem.* **2004**, *43*, 6513–6515.
- [37] M. Polson, S. Fracasso, V. Bertolasi, M. Ravaglia, F. Scandola, *Inorg. Chem.* **2004**, *43*, 1950–1956.
- [38] T. Yutaka, S. Obara, S. Ogawa, K. Nozaki, N. Ikeda, T. Ohno, Y. Ishii, K. Sakai, M.-a. Haga, *Inorg. Chem.* **2005**, *44*, 4737–4746.
- [39] I. R. Laskar, T.-M. Chen, *Chem. Mater.* **2004**, *16*, 111–117.
- [40] P. Coppo, E. A. Plummer, L. De Cola, *Chem. Commun.* **2004**, 1774–1775.
- [41] T. Tsuzuki, N. Shirasawa, T. Suzuki, S. Tokito, *Adv. Mater.* **2003**, *15*, 1455–1458.
- [42] E. Holder, B. M. W. Langeveld, U. S. Schubert, *Adv. Mater.* **2005**, *17*, 1109–1121.
- [43] S. Forrest, P. Burrows, M. Thompson, *IEEE Spectrum* **2000**, *37*, 29–34.
- [44] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913–915.
- [45] J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G. G. Malliaras, *J. Am. Chem. Soc.* **2004**, *126*, 2763–2767.
- [46] H. Rudmann, S. Shimada, M. F. Rubner, *J. Am. Chem. Soc.* **2002**, *124*, 4918–4921.
- [47] S. Bernhard, X. Gao, G. G. Malliaras, H. D. Abruña, *Adv. Mater.* **2002**, *14*, 433–436.
- [48] C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* **2001**, *90*, 5048–5051.
- [49] I. R. Laskar, S.-F. Hsu, T.-M. Chen, *Polyhedron* **2005**, *24*, 189–200.
- [50] C. S. K. Mak, A. Hayer, S. I. Pascu, S. E. Watkins, A. B. Holmes, A. Köhler, R. H. Friend, *Chem. Commun.* **2005**, 4708–4710.
- [51] J. D. Slinker, C. Y. Koh, G. G. Malliaras, M. S. Lowry, S. Bernhard, *Appl. Phys. Lett.* **2005**, *86*, 173506–173508.
- [52] S. T. Parker, J. D. Slinker, M. S. Lowry, M. P. Cox, S. Bernhard, G. G. Malliaras, *Chem. Mater.* **2005**, *17*, 3187–3190.
- [53] M. C. DeRosa, P. J. Mosher, C. E. B. Evans, R. J. Crutchley, *Macromol. Symp.* **2003**, *196*, 235–248.
- [54] Y. Amao, Y. Ishikawa, I. Okura, *Anal. Chim. Acta* **2001**, *445*, 177–182.
- [55] M. C. DeRosa, P. J. Mosher, G. P. A. Yap, K.-S. Focsaneanu, R. J. Crutchley, C. E. B. Evans, *Inorg. Chem.* **2003**, *42*, 4864–4872.
- [56] G. Di Marco, M. Lanza, A. Mamo, I. Stefio, C. Di Pietro, G. Romeo, S. Campagna, *Anal. Chem.* **1998**, *70*, 5019–5023.
- [57] K. K.-W. Lo, D. C.-M. Ng, C.-K. Chung, *Organometallics* **2001**, *20*, 4999–5001.
- [58] K. K.-W. Lo, C.-K. Chung, N. Zhu, *Chem. Eur. J.* **2003**, *9*, 475–483.
- [59] K. K.-W. Lo, C.-K. Chung, N. Zhu, *Chem. Eur. J.* **2006**, *12*, 1500–1512.
- [60] K. K.-W. Lo, C.-K. Chung, T. K.-M. Lee, L.-H. Lui, K. H.-K. Tsang, N. Zhu, *Inorg. Chem.* **2003**, *42*, 6886–6897.
- [61] K. Kalyanasundaram, J. Kiwi, M. Grätzel, *Helv. Chim. Acta* **1978**, *61*, 2720–2730.
- [62] C. V. Krishnan, B. S. Brunschwig, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **1985**, *107*, 2005–2015.

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