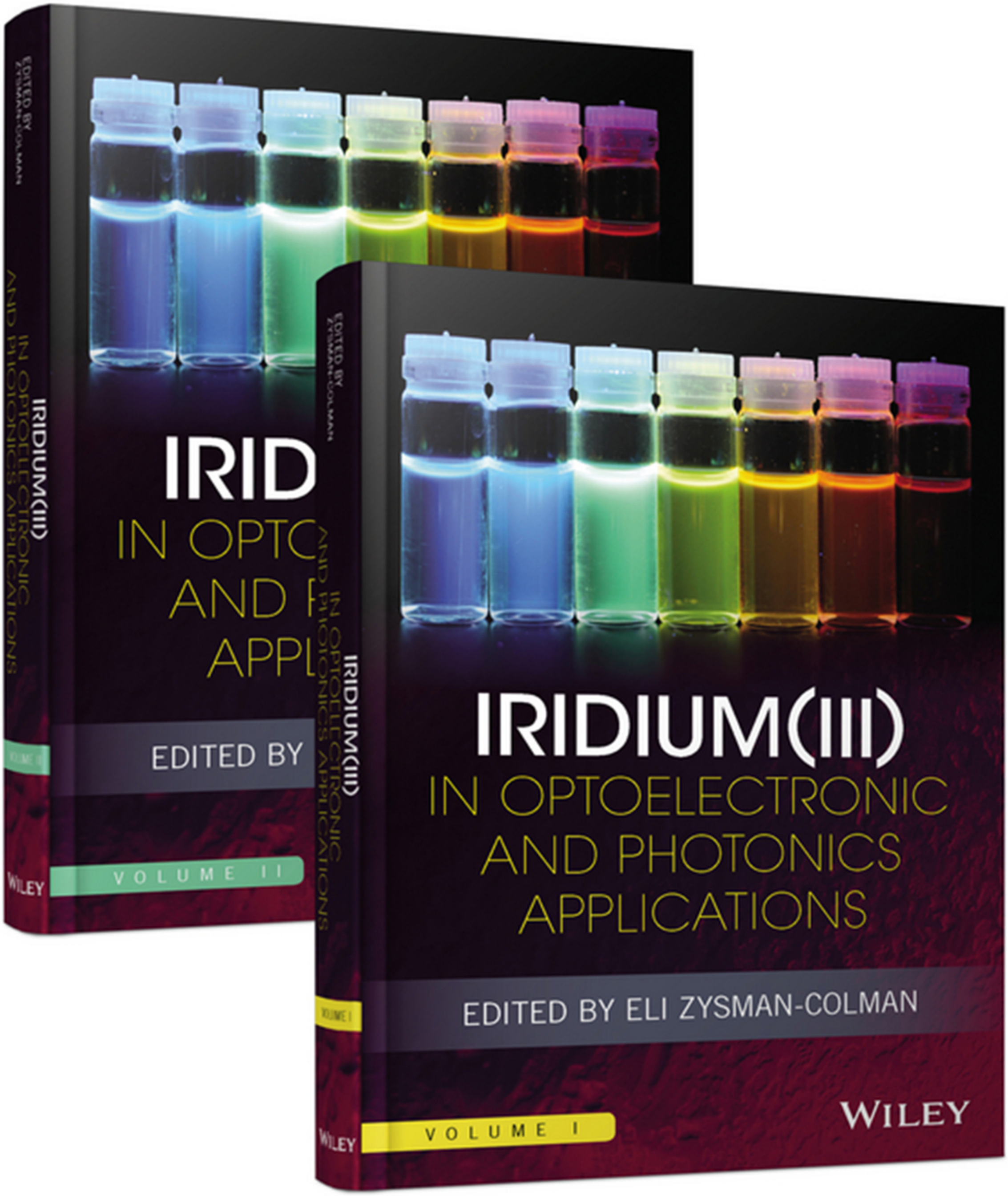
IRIDIUM(III)
IN OPTOELECTRONIC
AND PHOTONICS
APPLICATIONS
EDITED BY ELI ZYSMAN-COLMAN
VOLUME I
VOLUME II
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Iridium(III) in Optoelectronic and Photonics Applications

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Edited by

Eli Zysman-Colman
Organic Semiconductor Centre
EaStCHEM School of Chemistry
University of St Andrews
UK

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Dedicated to my parents Margo and Neil whose support
has been continuous and unwavering

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List of Contributors

Martin Albrecht
Department of Chemistry and Biochemistry
University of Bern
Switzerland

Etienne Baranoff
School of Chemistry
The University of Birmingham
UK

Stefan Bernhard
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA, USA

Felix N. Castellano
Department of Chemistry
North Carolina State University
Raleigh, NC, USA

Danielle N. Chirdon
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA, USA

Ilaria Corbucci
Department of Chemistry
Biology and Biotechnology and CIRCC
University of Perugia
Italy

Luisa De Cola
Institut de Science et d'Ingénierie
Supramoléculaires (ISIS)
Université de Strasbourg
France

Joseph C. Deaton
Department of Chemistry
North Carolina State University
Raleigh, NC, USA

Alberto Fernández-Gutiérrez
Department of Analytical Chemistry
Faculty of Science
University of Granada, Spain

J. F. Fernández-Sánchez
Department of Analytical Chemistry
Faculty of Science
University of Granada, Spain

Adam F. Henwood
Organic Semiconductor Centre
EaStCHEM School of Chemistry
University of St Andrews
UK

Conor F. Hogan
Department of Chemistry and Physics
La Trobe Institute for Molecular Science
La Trobe University
Melbourne, Victoria, Australia

Husain N. Kagalwala
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA, USA

Kenneth Kam-Wing Lo
Department of Biology and Chemistry
State Key Laboratory of Millimeter Waves
City University of Hong Kong
P.R. China

Karson Ka-Shun Tso
Department of Biology and Chemistry
State Key Laboratory of Millimeter Waves
City University of Hong Kong
P.R. China

Prashant Kumar
School of Chemistry
The University of Birmingham
UK

Sarah E. Laird
Department of Chemistry and Physics
La Trobe Institute for
Molecular Science
La Trobe University
Melbourne, Victoria, Australia

Wenbin Lin
Department of Chemistry
The University of Chicago
IL, USA

Elena Longhi
Institut de Science et d'Ingénierie
Supramoléculaires (ISIS)
Université de Strasbourg
France

Alceo Macchioni
Department of Chemistry
Biology and Biotechnology and CIRCC
University of Perugia
Italy

Marta Marín-Suárez
Department of Analytical Chemistry
Faculty of Science
University of Granada, Spain

Daniel Micheroni
Department of Chemistry
The University of Chicago
IL, USA

Timothy M. Monos
Department of Chemistry
University of Michigan
Ann Arbor, MI, USA

Teresa Ramón-Márquez
Department of Analytical Chemistry
Faculty of Science
University of Granada
Spain

Ulrich S. Schubert
Institute for Organic and Macromolecular
Chemistry (IOMC)
Jena Center for Soft Matter (JCSM)
Center for Energy and Environmental
Chemistry Jena (CEEC Jena)
Friedrich Schiller University Jena
Germany

Corey R. J. Stephenson
Department of Chemistry
University of Michigan
Ann Arbor, MI, USA

Yafei Wang
School of Chemistry
The University of Birmingham
UK
School of Materials Science and
Engineering
Changzhou University
China

J. A. Gareth Williams
Department of Chemistry
Durham University
UK

Andreas Winter
Institute for Organic and Macromolecular
Chemistry (IOMC)
Jena Center for Soft Matter (JCSM)
Center for Energy and Environmental
Chemistry Jena (CEEC Jena)
Friedrich Schiller University Jena
Germany

Eli Zysman-Colman
Organic Semiconductor Centre
EaStCHEM School of Chemistry
University of St Andrews
UK

Foreword

When I was an undergraduate student in the late 1980s, the quintessential photoactive coordination compound was $[Ru(bpy)_3]^{2+}$. I still remember the astonishment in learning the apparently unique combination of ground and excited state electronic properties of this complex and its derivatives. It looked sort of impossible to discover counterparts comparably good by browsing the periodic table and designing new chelating ligands. Of course, this proved incorrect. Indeed, the number of potential competitors of Ru(II) complexes in the area of photochemistry and its applications has increased, Ir(III) systems being a notable case.

In the late 1990s, iridium compounds were still a minor area of research. A quick bibliometric analysis shows that the number of papers published in the field at that time is basically background noise when compared to the skyrocketing trends of the last 15 years. In retrospect, this is not surprising; some physical properties of iridium and its scarcity on the Earth's crust did not make it a particularly sexy candidate to open new avenues in synthetic chemistry and advanced technological and biomedical applications.

The "iridium fever" is one of the most notable recent happenings in the domain of inorganic and organometallic chemistry. It has been driven by a relentless demand for efficient and sustainable solutions in the areas of photonics, analytical chemistry and catalysis. But it is not limited to applicative fields, because iridium compounds have also proven a remarkable playground to test and advance theoretical methods in complex systems. Despite this amazing success, books devoted to the chemistry of this element are rather limited or outdated. Surprisingly, a book covering optoelectronics and photonics of iridium materials was still missing.

This volume fills the gap. It encompasses discussions on consolidated aspects of iridium (photo)chemistry such as (i) design and synthesis (mono- and polynuclear complexes; soft, porous and polymeric materials); (ii) use in electroluminescent devices (OLEDs, LEECs); (iii) electrochemiluminescence, sensing, theranostics. Remarkably, it also presents developments in the area of photoredox catalysis and solar energy conversion, where iridium compounds can serve both as sensitizers and catalysts. These latter fields are still in their infancy.

Twenty years ago nobody anticipated the surge of iridium-based photoactive materials. Now we may foresee that the follow-up of this book will include applications that we do not envisage yet. Most probably, this will happen also because students and scholars will find these pages stimulating and inspiring.

Nicola Armaroli, ISOF-CNR
Bologna, January 2017

Preface

In the digital age, humanity has become reliant on myriad technologies, many of which depend on scarce elements. Of these, iridium is one of the most rare, about 40 times less abundant than gold. Most iridium is found in a thin layer of sediment, which coincides with the so-called K–Pg boundary that marks the Cretaceous–Paleogene extinction event where approximately 70% of plant and animal species, including the dinosaurs, were lost. The demise of the dinosaurs 65 million years ago to an iridium-rich asteroid and the discovery of this element in 1803 by British chemist Smithson Tennant have also now permitted some of the most promising optoelectronic materials to be developed. Iridium and its alloys and organometallic complexes have become very important across a wide range of applications – from ballpoint pen tips, to contacts in spark plugs, to catalysis. However, it is the desirable photophysical properties of iridium complexes that have made these compounds so attractive as components in optoelectronic applications.

This goal of this book is to provide the most comprehensive account of photoactive iridium complexes and their use across a wide variety of applications. The book will start with an overview of the synthesis of these complexes and discuss their photophysical properties. It will highlight not only mononuclear complexes but also the properties of multinuclear and polymeric iridium-based materials and the assembly of iridium complexes into larger supramolecular architectures such as MOFs and soft materials. Chapters devoted to the use of these iridium-based materials in diverse optoelectronic applications follow, including electroluminescent devices such as organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LEECs), electrochemiluminescence (ECL), bioimaging, sensing, light harvesting in the context of solar cell applications, in photoredox catalysis and as components for solar fuels.

The different contributions are written by leading experts in the field and are in a style that clearly explains the link between the structure of the iridium complex and its properties and use in optoelectronic applications. I am convinced that this book will become an important resource to both those in academia, including postgraduate students, and those in industry. I hope that these pages will stimulate further research to develop even more potent and attractive iridium-based materials.

I would like to take the opportunity to thank all of the contributors to this book for their efforts and for sharing my vision to develop a definitive resource for the synthesis, properties and applications of photoactive iridium complexes.

Eli Zysman-Colman
St Andrews, Fife, UK
2016

1

Archetypal Iridium(III) Compounds for Optoelectronic and Photonic Applications: Photophysical Properties and Synthetic Methods

Joseph C. Deaton and Felix N. Castellano

Department of Chemistry, North Carolina State University, Raleigh, NC, USA

1.1 Introduction

In the early years following the discovery and isolation of the element iridium, it was regarded as "not useful for anything" because of its apparent chemical inertness as a noble metal and the high temperatures required for forging iridium-based metal objects [1]. But steady advances in the fields of metallurgy, chemistry, physics, and materials science have culminated in numerous applications for the element. In particular, the succeeding chapters of this volume will each describe in detail an application utilizing the extraordinary photophysical properties and reversible electrochemistry of organometallic complexes of iridium. In this opening chapter, the photophysical properties and synthesis of the archetypal complexes suitable for these applications will be presented.

1.2 Iridium Complex Ion Dopants in Silver Halide Photographic Materials

Before proceeding with the review of their modern optoelectronic applications, it is worth noting that iridium complexes have already been in use for decades in a special type of optoelectronic product: silver halide photographic films and papers. The silver halide process is a unique optical process in a semiconductor because of a remarkable combination of solid state properties of the material [2, 3]. Well into the twentieth century, development of this technology proceeded in an empirical manner, mainly in industrial laboratories where trade secrets were more highly valued than scientific publications and sometimes even patents. Therefore the origin of the use of iridium complexes and their effects can be difficult to discern from the early literature and patents [4, 5 and references therein]. But in more recent literature, it has been shown

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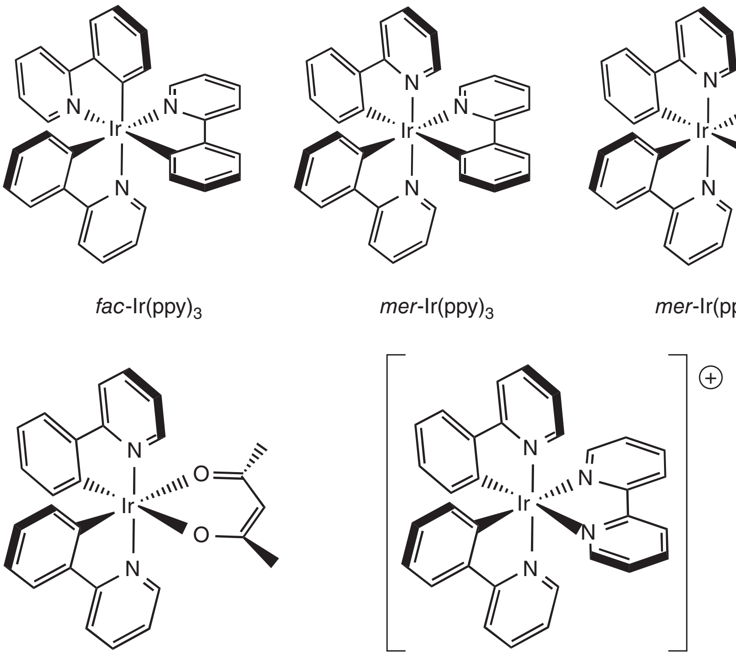
that iridium complexes such as $[IrCl_6]^{3-}$, $[IrBr_6]^{3-}$, and even molecules containing small organic ligands may be incorporated as impurity ion dopants into silver halide crystals or microcrystals where they function as traps for photoelectrons generated during light exposure, thus modulating the life cycle of the photoelectrons in the latent image forming process [6, 7]. In more recent patent disclosures, it was shown that an important effect of these dopants is to control what is known as reciprocity law failure for photographic exposures [8, 9]. Ideally, according to the reciprocity law, the image optical density formed after development of an exposed photographic film should be the same for the same value of total exposure, E, regardless of the combination of intensity, i, and exposure time, t, used to produce that exposure according to Equation 1.1:

$$E = it \tag{1.1}$$

In practice, photographic films and papers exhibit lower developed optical density for exposures made with relatively low intensity over longer time (low-intensity reciprocity failure) or for exposures made with high intensity over shorter time (high-intensity reciprocity failure) or both. Doping the silver halide microcrystals during precipitation with small concentrations of iridium complexes such as $[IrCl_6]^{3-}$ has been shown to reduce reciprocity law failure, although it cannot be totally eliminated for exposure extremes [8, 9]. The effect of the iridium dopant is not based on a photophysical property in the same sense as for the iridium complexes in applications described in succeeding chapters. Rather, the presence of the iridium dopant and its naturally accompanying charge compensation defect introduces a trap for electrons below the conduction band of the silver halide and thereby modulates the lifecycle of photoelectrons in the microcrystal. Dopants, such as the iridium complexes and a special class known as chemical sensitizers [2], do not affect how much light is absorbed by the silver halide, at least to a first approximation, but rather control how efficiently the light is used to form the latent image. Chemical sensitizers and dopants are therefore distinguished from organic sensitizing dyes, known as spectral sensitizers, which function through increasing light absorption and injecting the resultant photoelectrons into the silver halide conduction band [2], much like the Ru(II) dyes found in Grätzel-type dye sensitized solar cells.

1.3 Overview of the Photophysical Properties of C^N and C^C: Cyclometalated Ir(III) Complexes

Ir(III) complexes bearing C^N and C^C: cyclometalated ligands possess impressive photophysical properties that make these compounds highly desirable for the optoelectronic and photonic applications covered in this volume. Stereochemical illustrations of representative archetypal Ir(III) cyclometalates (Section 1.4) are presented in Scheme 1.1, and structural formulae for additional examples are shown in Scheme 1.2 in 2D. In these structures, the C^N and C^C: bidentate ligands are monoanionic, and the negative charge is donated by a C atom occupying one coordination site. In the case of the C^C: cyclometalates, the second coordination site is occupied by the neutral C-donor (designated C:) of the carbene moiety (Scheme 1.3). The :C^N and :C^C: types of carbene ligands are charge neutral and have been incorporated in heteroleptic complexes with



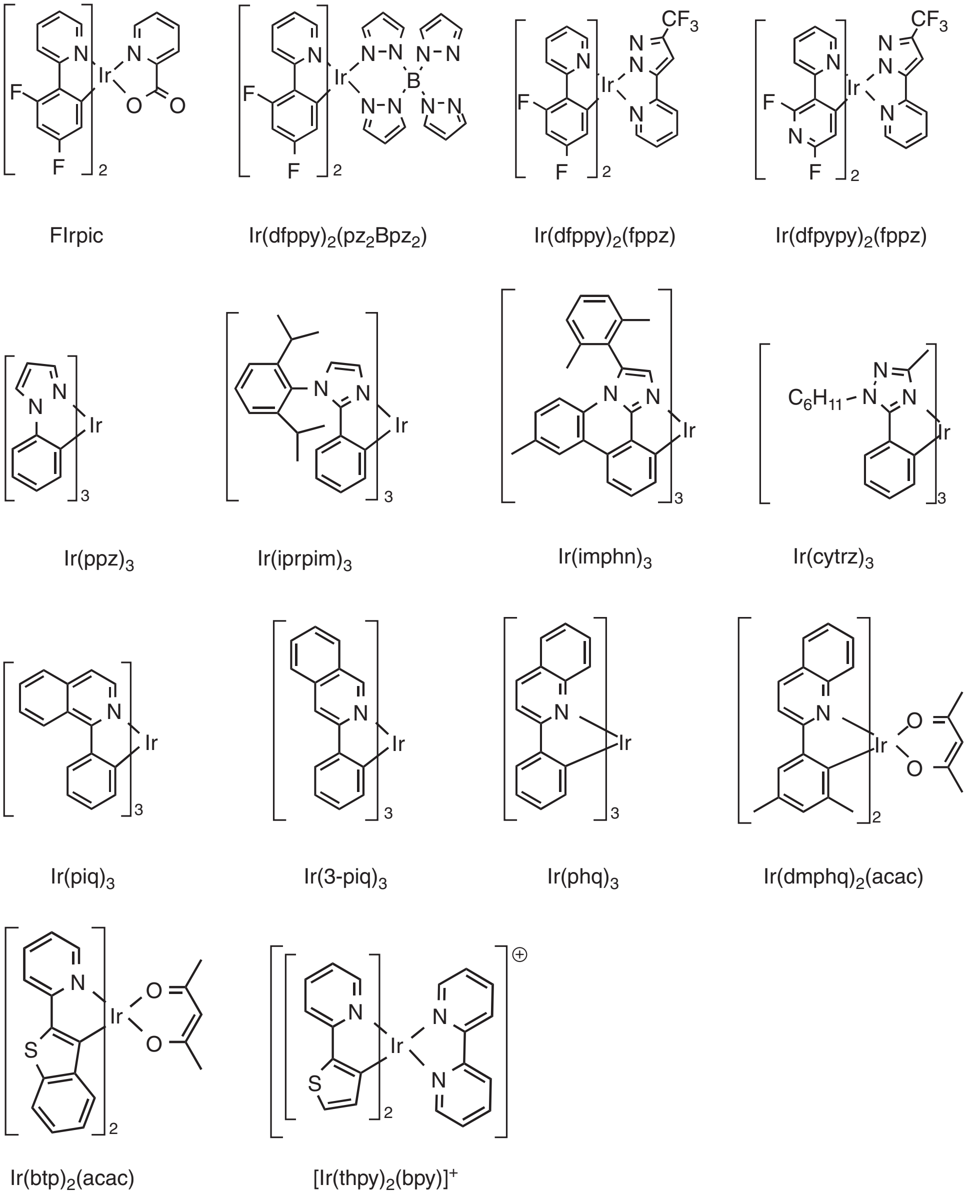
fac-Ir(ppy)$_3$ *mer*-Ir(ppy)$_3$ *mer*-Ir(ppy)$_3$(piq)

Ir(ppy)$_2$(acac) [Ir(ppy)$_2$(bpy)]$^+$

Scheme 1.1 Sterochemical diagrams of representative archetypal Ir(III) cyclometalates.

monoanionic C^N or C^C: ligands. Examples of Ir(III) cyclometalates with tridentate ligands are shown in Scheme 1.4. A list of abbreviations for ligands illustrated in the schemes and used in the text may be found at the end of the chapter. The Ir(III) complexes are generally obtained as racemic mixtures, and the structural diagrams in Schemes 1.1, 1.2, 1.3, and 1.4 are not meant to limit the representations to specific enantiomers. Because the properties of enantiomers differ only in optical activity, their properties will not be covered in succeeding sections, but the preparation and isolation of enantiomers and diastereomers will be covered in Section 1.9.

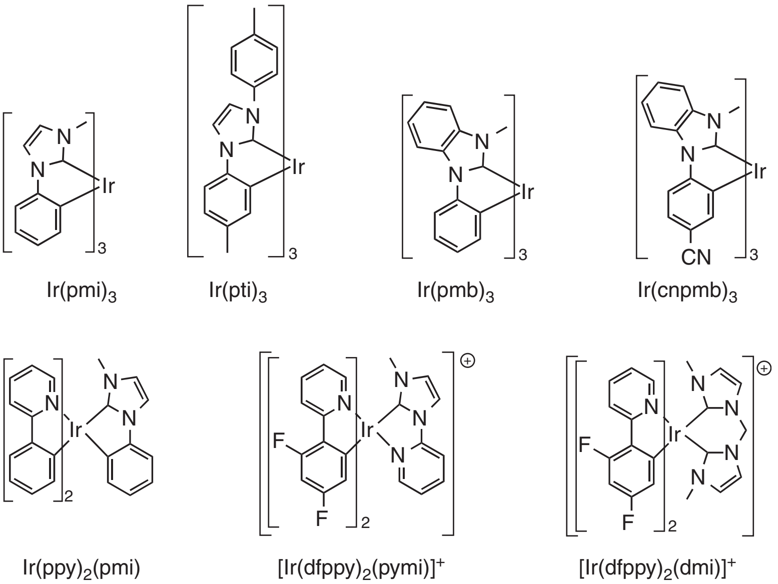
The proper nomenclature, for example, of the prototype compound is *fac*-tris(2-phenylpyridinato-N^C$^{2'}$)iridium(III) (*fac*-Ir(ppy)$_3$, Scheme 1.1). But often in the literature the prefix is omitted, and it is assumed that the facial isomer is being discussed because these are generally much more emissive than the meridional isomers (*mer*-Ir(ppy)$_3$, Scheme 1.1), at least in the case of the more common C^N cyclometalates (Section 1.4). The nomenclature is often further simplified to Ir(phenylpyridine)$_3$, for example, with the assumption that it is understood that the ortho-deprotonated form of the ligand (2′ carbon) is intended, not the neutral form. The C on the phenyl ring that is bonded to the pyridine ring is designated the 1′ position, and in numbering substituents on the phenyl ring, the point of metalation takes precedence as the 2′ position. Numbering positions of further substituents on the phenyl ring can therefore be different in the complex than in the free ligand and sometimes may be a point of confusion.



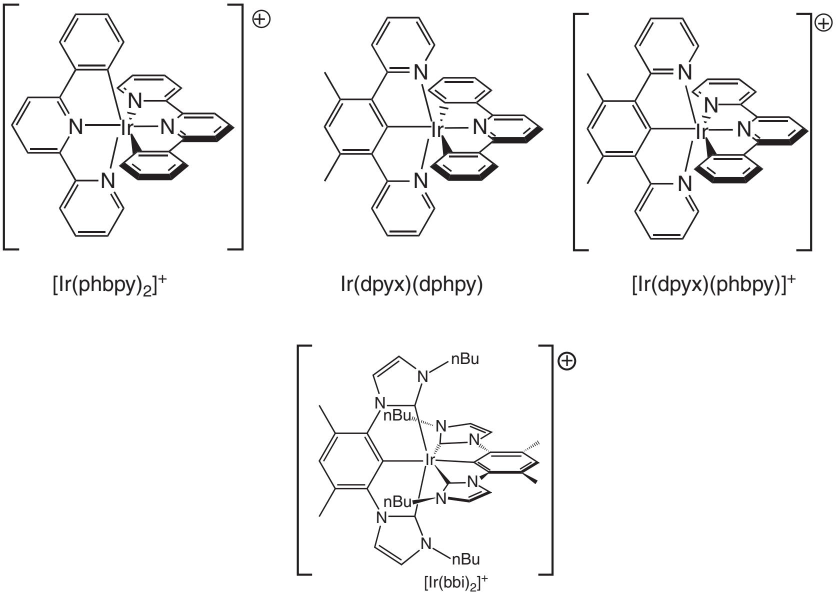
Scheme 1.2 Structural formulae of additional examples of Ir(III) cyclometalates.

Still other researchers designate the site of metalation as the 1′ C atom and number substituents accordingly.

The cyclometalated Ir(III) compounds are highly emissive because the lowest energy excited states are a mixture of metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) π–π^* states, not the non-radiative d–d states (Section 1.4). Schematic energy level diagrams of the frontier one-electron orbitals and the resultant zero-order



Scheme 1.3 Structural formulae of representative Ir(III) cyclometalates comprising carbene ligands.



Scheme 1.4 Sterochemical diagrams of representative Ir(III) cyclometalates comprising tridentate ligands.

many-electron states are shown in Figures 1.1 and 1.2, respectively. Note that the zero-order (i.e., prior to any mixing interactions) MLCT state is the lowest energy excited state within the singlet manifold, but as shown in Figure 1.2 often the LC is lowest within the triplet manifold because of greater electron-exchange interaction (Section 1.6).

In heteroleptic complexes wherein the HOMO comprises a mixture of Ir dπ orbitals and π orbitals of one ligand while the LUMO comprises a π^* orbital on another ligand such that the latter becomes the chromophoric ligand, the lowest triplet excited state may be described as a mixture of MLCT and ligand-to-ligand charge transfer (LLCT), sometimes referred to as metal–ligand-to-ligand charge transfer (MLLCT). This is commonly the case in cationic complexes of the type $[\mathrm{Ir(C^{\wedge}N)_2(N^{\wedge}N)}]^+$ where N^N is a diimine (Section 1.4) and is the chromophoric ligand. A less commonly encountered situation occurs when strong electron donor groups are substituents on the chromophoric ligand and an intra-ligand charge transfer (ILCT) occurs [10].

The photophysical properties of greatest practical value include rapid singlet-to-triplet intersystem crossing (ISC), high photoluminescence (PL) quantum yields, spectral tunability over the entire visible range through chemical structure variation, and fast phosphorescence decay rates generating bright triplet state PL. The zero-field splitting (ZFS) within the excited triplet state is an important property in characterizing the nature of this emissive state. In addition to meritorious photophysical properties, the reversible electrochemical properties of many of these compounds (Section 1.4) are necessary for robust stability in many applications, especially in optoelectronics.

The ISC rate, the radiative decay rate, the ZFS, and other spectroscopic features all depend upon the spin–orbit coupling (SOC) interaction between the lowest triplet and one or more singlet excited states, resulting in an admixture of some singlet character into the lowest triplet state (Section 1.7). The ZFS in the lowest triplet excited state may additionally depend upon SOC with a higher triplet state. Large SOC interactions are found in molecules comprising heavy atoms because the SOC constant generally increases with atomic number and is therefore quite large for Ir ($3909\,\mathrm{cm}^{-1}$) [11]. Note that this value is for zero-valent iridium, and in Ir(III) complexes the SOC constant would necessarily increase [12] and has been calculated to be $4430\,\mathrm{cm}^{-1}$ [13]. Even though the lowest triplet excited state may be dominantly LC in nature, it is evident that iridium orbitals must be involved through some admixture of MLCT character in order to produce the extraordinary photophysical properties in comparison with those of the free ligand (Section 1.7).

When some singlet character is mixed into triplet states, singlet excited states can rapidly intersystem cross to the triplet manifold with yields approaching unity and thermalize to the lowest triplet excited state. Thus, spin-allowed photon absorption that typically results in initial population of a Franck–Condon singlet excited state results in emission from the lowest triplet state when ISC is fast relative to the fluorescence emission rate from the singlet state. For this reason, such phosphorescent emitters can harvest both singlets and triplets formed in an “organic” light-emitting diode (OLED). According to the spin degeneracies, triplets comprise ¾ and singlets comprise ¼ of the excitons formed upon recombination of the electrochemically generated electrons and holes injected into an OLED. Consequently, the organometallic iridium cyclometalates are much more desirable as emitters for OLED applications (Chapter 6) than fluorescent emitters having equally high PL quantum yields because fluorescent dopants are limited to harvesting only singlet excitons. Thus, an OLED with a phosphorescent emitter can have an electroluminescence

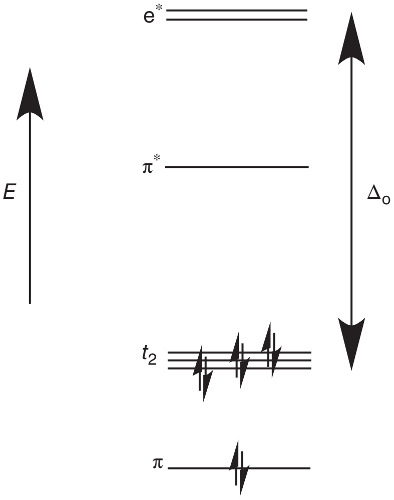


Figure 1.1 Energy level diagram for one-electron orbitals in d^6 MLCT–LC complexes.

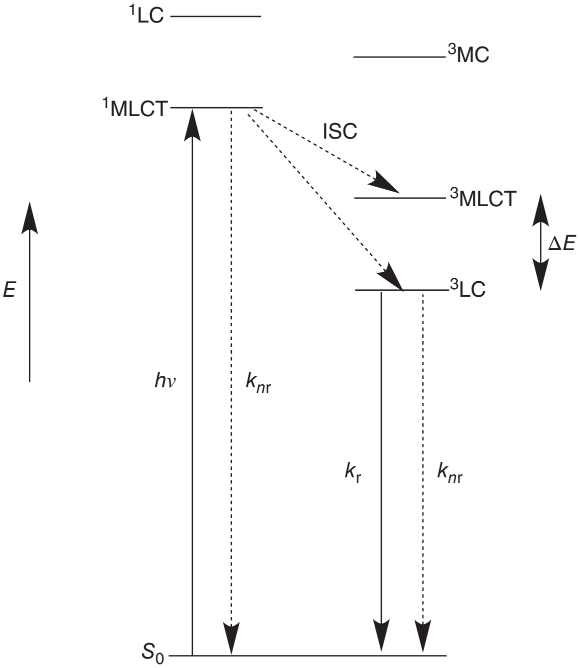


Figure 1.2 Jablonski diagram for the many-electron states in d^6 MLCT–LC complexes.

quantum yield (excluding optical out-coupling losses) approaching 100% of the phosphor's PL quantum yield, while the upper limit for an OLED comprising a fluorescent emitter is 25% of the fluorophore's PL quantum yield (ignoring additional singlets that may be formed through triplet–triplet annihilation [14]).

Determination of ISC rates requires ultrafast absorption or fluorescence techniques, often requiring deconvolution of the transient signal(s) from the instrument response function and has been reported for relatively few representative Ir(III) compounds to date [15–17]. The ISC rate for $Ir(ppy)_3$ was reported to be within 100 fs [16], and the ISC rate of $Ir(piq)_3$ was more distinctly determined to be 70 fs [17]. In view of calculations and experimental evidence (Section 1.7) that illustrate the excited states are highly mixed in terms of singlet and triplet character, some authors have even suggested that ISC is not a meaningful descriptor for the process of converting the initial Franck–Condon state to the lowest energy excited state and instead propose that this be viewed as a form of internal conversion (IC).

The PL quantum yield of the prototype *fac*-tris(2-phenylpyrdinato-$N^\wedge C^{2'}$-) iridium(III) ($Ir(ppy)_3$) in toluene ($\lambda_{max} = 516$ nm) was reported [18] to be 40% when it was first isolated. Subsequent determinations [19–21] revealed it to be much higher, up to 97% in 2-MeTHF [21] although it varies with solvent [22]. Quantum yields over 90% have also been reported for $Ir(ppy)_3$ diluted into polymers and organic semiconductor thin film host materials [19, 20, 23, 24]. This is an extraordinarily high quantum yield for a phosphorescent emitter, that is, one that emits via a formally spin-forbidden transition that gains intensity through SOC. The efficiencies achieved with Ir(III) cyclometalates in optimized OLEDs are indeed consistent with very high phosphorescence quantum yields and harvesting both singlet and triplet excitons [25].

In many reports of Ir(III) complexes, the phosphorescence quantum yields and observed decay times, τ_{obs}, in solution at room temperature are reported. The observed intensity decay rate, k_{obs}, is simply the reciprocal of the observed decay time constant (Equation 1.2). As implied by a single value of τ_{obs} or k_{obs}, the emission decay is normally a single exponential that obeys Equation 1.3 in solution samples where the environment is rapidly averaged. k_{obs} is obtained by fitting Equation 1.3 to the experimental PL intensity decay data. k_{obs} is simply the sum of radiative (k_r) and non-radiative (k_{nr}) decay rates (Equation 1.4). The PL quantum yield (Φ) is related to k_r and k_{nr} by Equation 1.5:

$$k_{obs} = \frac{1}{\tau_{obs}} \tag{1.2}$$

$$I(t) = I_0 \exp(-k_{obs}t) \tag{1.3}$$

$$k_{obs} = k_r + k_{nr} \tag{1.4}$$

$$\Phi = \frac{k_r}{k_{obs}} \tag{1.5}$$

Clearly, when the quantum yield is very high, k_{obs} is close to k_r. Reporting k_{obs} is most useful when quantum yields are also reported because then the values of k_r and k_{nr} can be separately obtained. The radiative rate constant k_r may be related to the strength of the SOC (Section 1.7), while k_{nr} depends additionally on other factors (Section 1.8).