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INORGANIC PHOTOCHEMISTRY

Something new under the sun

Robert J. Ortiz and David E. Herbert*

Department of Chemistry and the Manitoba Institute for Materials, University of Manitoba, 144
Dysart Road, Winnipeg, Manitoba, R3T 2N2, Canada; *david.herbert@umanitoba.ca
Twitter: @herbert_lab

Charge-transfer emission of any type is extremely rare for coordination complexes of iron. Now, an Fe(III) complex has been devised that shows two-colour luminescence arising from dual metal-to-ligand and ligand-to-metal charge-transfer emission.

While coordination complexes of transition metals can emit light from many different kinds of electronically excited states, 'metal-to-ligand charge-transfer' (MLCT) excited states represent some of the best studied and most widely applied[1]. To a first approximation, MLCT is characterized by redistribution of electron density from a metal-based orbital to a ligand-localized one, producing a transient hole (positive charge) at the metal and a ligand-centred radical anion. The opposite situation — relocation of electron density from a ligand-like orbital to a metal-based one — characterises ligand-to-metal charge transfer (LMCT). Despite decades of effort, only a tiny handful of iron coordination complexes have ever been reported to produce reasonably observable luminescence from MLCT[2] or LMCT[3] excited states. Writing in *Nature Chemistry*, Matthias Bauer and coworkers describe the first example of an iron coordination complex that exhibits 'dual emission' — that is, luminescence both from an excited state with LMCT character and from one with MLCT character[4].

To observe MLCT or LMCT-type emission, these excited states need to persist long enough before competing pathways lead to their deactivation, something which typically happens through 'dark' (non-emissive) metal-centered (MC) excited states. In addition to emission, should they survive long enough, charge-transfer (CT) excited states can also enhance the capability of a complex to act as an oxidant and/or reductant in bimolecular reactions. The spatial separation of charges in such excited states generates the chemical potential needed to drive photo-induced electron transfer (PET), which can be used to transform light into electrical or chemical energy.

Heavy metal sensitizers from the 2nd or 3rd row of the transition metal block — including ruthenium(II) *tris*(2,2'-bipyridine) $[Ru(bpy)_3]^{2+}$ and iridium(III) *tris*(2-phenylpyridine) ($Ir(ppy)_3$) — often display long-lived MLCT states, thanks to the strong ligand fields intrinsic to heavier metals that destabilize MC manifolds relative to MLCT ones, enabling strong emission and applications involving PET from photoredox catalysis[5] to dye-sensitized solar cells[6]. But with the environmental consequences of human activity including resource extraction becoming ever more immediate, finding ways to reproduce the useful light-harvesting properties of $[Ru(bpy)_3]^{2+}$ or $Ir(ppy)_3$ in complexes of more abundant materials — without compromising performance — is critical. In recent years, an increasingly detailed, collective understanding of how molecular structure can influence electronic excited states has rapidly expanded access to photoactive coordination complexes of 1st-row (3d) and other abundant transition metals[7]. Amongst the more sustainable elements in the d-block, photoactive iron complexes — incorporating the most widely used and least expensive metal — have long posed a tantalizing target.

Iron, however, has a problem. The lifetime of MLCT excited states in six-coordinate, pseudo-octahedral Fe(II) complexes are around a million times shorter than for isoelectronic Ru(II): while they form with roughly the same efficiency, the charge-separated states of Fe(II) do not tend to hang around long enough to allow for observable emission or bimolecular PET reactivity. Instead, these MLCT excited states rapidly convert into 'dark' MC excited states that conform to a rearrangement of electrons within the 1st-row metal's d orbitals. Lacking significant charge separation, these MC states typically do not behave in similarly profitable ways as CT ones.

The short CT excited-state lifetimes of coordination complexes of light transition metals originate in the attenuated overlap of metal 3d orbitals with those of the ligands, which weakens the corresponding metal-ligand bonding[8]. Incorporating increasingly strong σ-donating ligands — such as a doubly cyclometallated phenylphenanthroline scaffold[2] or *N*-heterocyclic carbenes (NHCs)[9] — to redress these weaker ligand fields can invert the energetic ordering of MLCT and MC manifolds and thereby extend the lifetime of the MLCT state in Fe(II) complexes. Electron-releasing, multidentate carbene ligands have also been used to create Fe(III) complexes with multi-nanosecond LMCT excited-state lifetimes — long enough to engage in PET[10] and luminesce at room temperature[11]. For such Fe(III) complexes, the emissive, long-lived CT state conserves the same spin multiplicity (^{2}LMCT) as the doublet ground state which contributes to the efficiency of the radiative process. To coax an iron complex into accessing emission from both MLCT and LMCT excited states — a rare feat, even for heavier transition metals — Bauer and colleagues introduce an inventive ligand design that combines cyclometallating phenyl rings and NHCs in a tridentate framework. This unique combination extends the lifetimes of what are best described as LMCT and MLCT excited states in an Fe(III) complex, leading to remarkable two-colour emission.

So why does it work? The exceptionally strongly donating scaffold shifts the $\mathrm{Fe^{II/III}}$ redox couple by nearly 1.5 V compared with analogous ligands bearing pyridines in place of the phenyl donors, explaining the stability of the ferric species to air and moisture. In addition, Bauer and coworkers observe a metal-centered oxidation close to the redox potential for the ferrocene/ferrocenium couple. The ability to both reduce and oxidize the metal helps facilitate formation of a lower energy LMCT excited state and a higher energy MLCT-type excited state. Vacant π-type orbitals on both the cyclometalling phenyl rings and the NHC ligands provide landing spots for the photoexcited electron in the MLCT excitation. The strongly donating ligand scaffold compensates for the weaker ligand field of iron, and the closest lying MC excited states appear to be too distorted to lead to overwhelming non-radiative relaxation. While the LMCT state has a shorter but still impressive 240 picosecond lifetime, the MLCT state lasts for a record 4.6 nanoseconds — long enough both for observable, spin-conserved luminescence and to engage in bimolecular oxidative/reductive quenching reactions.

Notwithstanding these ground-breaking findings, the quantum yields for the two emission processes are low (<1%) suggesting significant deactivation of both LMCT and MLCT excited states. Moreover, it's not obvious that commercial technologies involving the transduction of light energy into electricity or chemical potential will ultimately require a metal at all[12] and if they do, the identity of the metal is not necessarily the deciding contributor to manufacturing cost; ligands can be expensive to make, even at scale[13]. And emerging research is revealing that electron transfer, at least from iron(II) coordination complexes, does not always require excited states with CT character[14]. But science continues to imagine and invent potential applications for photoactive compounds that also exploit the presence of a many-electron metal centre[15]. Bauer and coworkers' thrilling report could very well prove to have cracked open the door for photoactive iron complexes — and it's through the cracks that the light first gets in.

Competing interests

The authors declare no competing interests.

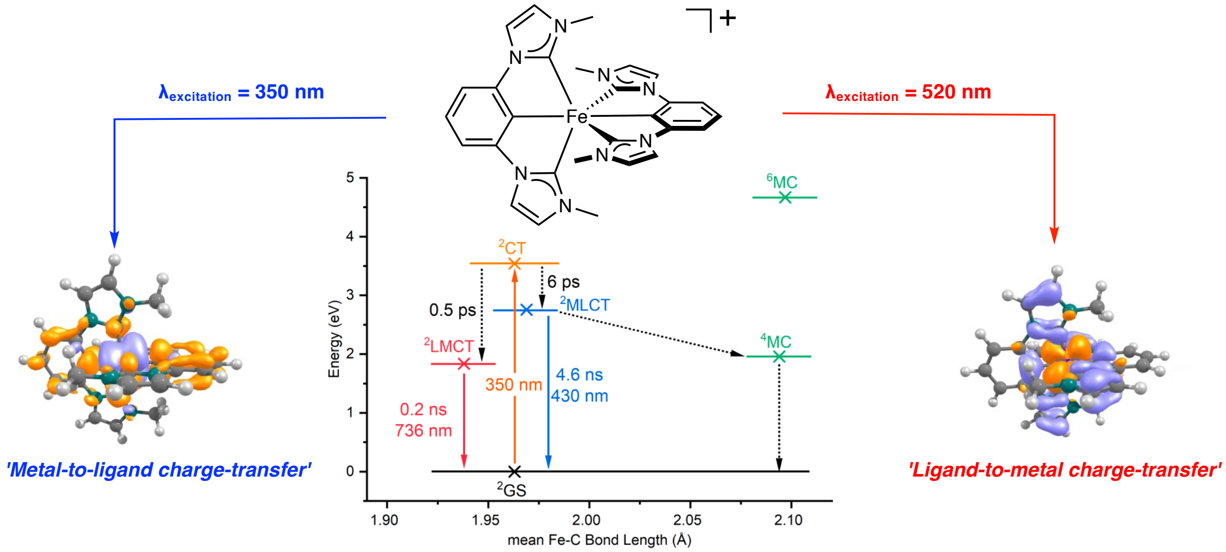

Figure 1: *The two emissive states of $[Fe(ImP)_2]^+$. Transition densities of the dominant MLCT (left) and LMCT (right) transitions are shown with the photogenerated 'hole' in purple and electron in orange (adapted from Figure 2c in ref.[2]) along with a summary of the emissive states and deactivation pathways (adapted from Figure 4a in ref.[2]).*

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