



# A study on Transition Metal Complexes of the First Row Luminescent

Uttam Mandal

Assistant Professor, Department of Physics, Bankura Sammilani College

Email: [uttammandal150@gmail.com](mailto:uttammandal150@gmail.com)

## Abstract:

A paradigm shift is taking place in inorganic photo-physics & photochemistry, where previously rare and precious elements predominated. New conceptual breakthroughs have shown that a wide range of components in different oxidation states can be used to produce emissive complexes, even though they have been known for some time. Complexes of V, Cr, Mn, Fe, Co, Ni, and Cu now exhibit electronic excited states to unexpected reactivity & photoluminescence characteristics. Also included in our Perspective are the main design strategies that led to the discovery of radically new types of 3d-metal-based luminophores as well as photosensitizers able to operate in solution at room temperature.

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## Introduction:

First-row transition metals may not be capable of mimicking platinum group metal coordination compounds in terms of their photophysical and electrochemical properties. For example, a 3d-metal has a much weaker ligand field than a 4d-metal or 5d-metal, because the 3d-orbitals have weakened spatial overlaps with relevant ligand orbitals than the 4d-orbitals (1). This is a major challenge for researchers. As a result, complexes to partially filled 3d-orbitals typically have a large number of metal-centred (MC) excited states that are close each other and to the electronic initial state. A cascade of non-radiative recombination relaxation processes can occur from one MC state to the next and back to the ground state in this scenario. In addition, the metal-ligand bonding situation differs greatly from the ground state in some MC states, for example, when d-electrons are encouraged from nonbonding to antibonding orbitals. A nuclear

coordinate such as, for example, the metal-ligand bond distance, can be used as a measure of how "distorted" the excited states of atoms are. To summarize, it is clear that low barriers to transitioning from one potential well to the next can result in rapid nonradiative relaxation.

Greater energy gaps between individual MC states and a large energy gap between both the lowest MC state as well as the electronic ground state are common in 4d- and 5d-metal complexes, due to the stronger ligand fields that are present (2). Nonradiative relaxation is becoming less efficient as the excitation energy is dissipated by an increasing number of vibrational quanta, allowing the lowest MC state to become luminescent & photochemically active. At lower energies, energetically high lying MC states allow for the introduction of fundamentally different excited states, for example ones where the electron density has been switched between the metallic and non-metallic components (3).



For many applications, the metal-to-ligand charge transfer (MLCT) & ligand-to-metal charge transfer (LMCT) described above are particularly appealing because it is the lowest excited state that typically governs the photophysical & photochemical properties (4). With respect to the ground state, these charge-transfer states have redox properties that allow them to participate in photo redox chemistry to organic substrates or to serve as semiconductor solar cell dyes. It is possible to transfer electron density from one ligand to another using ligand-to-ligand charge transfer (LLCT). So-called intraligand (IL) excitations, in which electron density redistribution typically occurs within the  $\pi$ -conjugation system of a single ligand, are fundamentally different from this process.

Due to strong spin-orbit coupling, many metal complexes facilitate rapid affect progress from singlet to lower-lying triplet excited

states. As a result, photoinduced transfer of electrons from triplet states can generate primary photoproducts that undergo less (unwanted) charge recombination and, as a result, lead to inherently greater quantum efficiencies of photoredox reactions than can be obtained from singlet states. They can also have improved kinetic reactivity due to their longer lifetimes. Compounds based on metals have a wide range of uses, including luminophores in organic light emitting diodes and light-emitting electrochemical cells (LEECs), photocatalysts in synthetic photochemistry & artificial photosynthesis, light harvesters in dye-sensitive solar cells and sensitizers for photochemical up conversion or for photodynamic therapy (5). Since cheap and abundant metals can be found, there are numerous reasons to look for photoactive complexes.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$d^0$	$d^0$	$d^2$	$d^3$	$d^3$	$d^5$	$d^6$	$d^8$	$d^{10}$	
+III	+IV	+III	+III	+IV	+III	+III	+II	+I	
			$d^6$	$d^6$					
			0	+I					

Figure 1: There have been significant advances in the understanding of luminescent complexes in recent years for red elements. A few examples of luminescent complexes have recently been discovered for these elements. Green: New elements in the landscape of particle emitters molecular complexes in room temperature solution. There are many ZnII complexes that emit luminescence, but they are typically ligand-centred. White: Elements whose room temperature solution emission is still a challenge and for which there have been no recent reports. There is a list of known examples of luminescent molecules in solution at room temperature, along with their spin states and corresponding oxidation states.

Copper(I) and chromium (III) complexes have long been known to emit in solution at room temperature, making them attractive candidates nearly 40 years ago (Figure-1)(6). Recent conceptual advances have been made with both metal ions, and complexes with exceptionally high luminescence quantum yields and long excited-state lifetimes have been described. However, recent studies have revived interest in elements like cobalt and nickel that had been neglected for a long time in molecular photo physics and photochemistry due to a few old reports on the emission of molecules complexed with these elements. Iron, the Earth's crust's most

abundant transition metal, has long been the subject of research, but two recent landmark studies have revealed new information that has the potential to transform the field. Despite their relative abundance, manganese and vanadium are relatively newcomers to the world of molecular complexes that exhibit luminescence in solution when kept at room temperature.

Molecular complexes containing first-row transition metals that glow in solution at room temperature are the focus of our Perspective. A compound emitting under these conditions typically has long enough excited-state lifetimes for diffusion-controlled



bimolecular reactions, making it suitable for photochemical applications that go far beyond simple lighting. These complexes are then referred to as "photoactive". There is a focus on complexes in which IL excitations play a dominant role (such as in many zinc (II) compounds), rather than complexes in which the metal directly influences photophysical and photochemical properties (7). When considering various 3d<sup>n</sup>-electron configurations, we divided our perspective into four main sections: one for each of the four main types of photoactive excited states (LLCT, MLCT, LMCT, and MC). We then give a brief forecast for the future of luminescent foundation metal complexes based on the theoretical insights gained from this survey.

#### **A total of 3d<sup>10</sup> (Cu<sup>I</sup>) complexes were emitted from LLCT emitters:**

3d<sup>10</sup> electron configuration has no low-energy MC states, so emissive excited states MLCT and LLCT can be installed relatively quickly in this configuration. A lot of attention has been paid to homoleptic bis(-diimine)copper(I) and heteroleptic variants that combine the -diimine with diphosphine ligands, but recent work showed that such four-coordinate tetrahedral Cu<sup>I</sup> MLCT luminophores were outperformed by two-coordinate linear Cu<sup>I</sup> LLCT emitters. It is possible to synthesize charge-neutral Cu<sup>I</sup> compounds in the solid state and also in solution at room temperature by combining unconventional N heterocyclic carbenes to N-bound amide ligands (8). The (anionic) amide ligands act as strong -electron donors, whereas the cyclic (alkyl)(amino)carbene (CAAC) binding affinities act as -acceptors, resulting in luminescence from an LLCT excited state. Traditional four-coordinate Cu<sup>I</sup> complexes have photoactive MLCT states that go through Jahn–Teller distortion and consequently increase nonradiative decay rates. This is a significant conceptual difference. Linear compound metals are still important because they mediate electronic coupling between donor and acceptor ligands and facilitate intersystem crossing (ISC) between the singlet and triplet states of the ligands through their d-orbitals. When the

donor and acceptor ligands are coplanar (as they are in the S<sub>0</sub> and T<sub>1</sub> states of well-designed complexes), the LLCT is strongly allowed in absorption and emission, which means that extinction coefficients are large (4000–6000 M<sup>-1</sup> cm<sup>-1</sup>) despite large donor–acceptor distances (about 3.7 Å) and high radiative decay rates (k<sub>r</sub>) (ca. 10<sup>5</sup>–10<sup>6</sup> s<sup>-1</sup>). Steric encumbrance on the carbene ligands slows down nonradiative relaxation in part by preventing undesirable bending (Renner–Teller) distortions. The Renner–Teller distortion can be minimized by the photoactive excited states' limited metal character.

linear Cu<sup>I</sup> complexes can be tuned in color by changing donor and acceptor ligands, for example by using cyclic monoamidocarbene (MAC\*) or cyclic diamidocarbene (DAC\*) with carbazates as donor and acceptor ligands, respectively. A common nonradiative deactivation pathway for traditional Cu<sup>I</sup> complexes is through the formation of exciplexes with solvent molecules, which is suppressed by the bulky 2,6-diphenyl (dipp) substituents on these carbenes' carbonyl groups (9). CAACs have a more extended -system and are more electrophilic than their alkyl counterparts (CAACs), resulting in a substantial red shift in the lowest-energy UV–vis absorption bands & providing access to deep red as well as near-infrared (NIR) luminophores. New compounds with abnormally low triplet energies & promising TADF properties can be found with high radiative rate constants & small singlet–triplet energy gaps.

#### **Mn<sup>I</sup> and Cr<sup>0</sup> Complexes & a 3d<sup>8</sup> (Ni<sup>II</sup>) Compound: MLCT Emitters:**

Ru<sup>II</sup>, Re<sup>I</sup>, Os<sup>II</sup>, and Ir<sup>III</sup> are some of the most commonly used MLCT emitters because of their 4d<sup>6</sup> & 5d<sup>6</sup> valence electron configurations. For a variety of reasons, including the high value and scarcity of the metals mentioned earlier, the prospect of acquiring analogous 3MLCT luminescence from 3d<sup>6</sup> complexes is appealing. No Fe<sup>II</sup> complexes emanating from an MLCT excited state under steady-state radiation at room temperature have been reported yet, despite



the fact that most efforts have been directed toward iron up until now (10). FeII's 3d-orbitals have a significantly weaker ligand field than RuII's 4d-orbitals, and in classical octahedral polypyridine complexes, the metal-centered 3T1g & 5T2g excited states are energetically below the lowest MLCT state in octahedral polypyridines. This means that when going from the MLCT to these MC states, relaxation takes place very quickly. Photoredox reactions can use the MC states, but they are not permissive. Longevity enhancement and elucidation of dark MLCT population & deactivation pathways have made significant progress in recent years. Since these compounds are not luminescent, they will not be discussed in any further detail.

The first luminescent MnI complexes were synthesized and characterized recently thanks to chelating isocyanide ligands. They are 3d6 MLCT emitters that are isoelectronic with FeII and Cr0, but the higher oxidation state of MnI complexes compared to Cr0 makes them more air-stable. They are first-row analogues of the well-known [Ru(bpy)3] and [Ru(tpy)2]+ compounds, and they glow with quantum yields of 0.03–0.05 percent in acetonitrile at room temperature. To counteract the detrimental effects of the 3T1g and 5T2g MC states, the  $\pi$ -acceptor isocyanide ligands create an extremely strong ligand field, which allows the blue MLCT emission to be competitive with nonradiative relaxation. However, due to the low quantum yields, it appears that molecular vibrations have been the primary relaxation pathway in this class of compounds up to this point. In contrast to the long-known MnI tricarbonyl diimines, that also undergo efficient CO ligand release (because of the high population growth of the above-mentioned dissociative MC states), these tris(diisocyanide) & bis(triisocyanide) manganese(I) compounds exhibit luminescence behavior, but no emission is associated with this process. For bimolecular electron transfer and (triplet–triplet) energy transfer reactions, the MLCT lifetimes of [Mn(Lbi)3]+ and [Mn(Ltri)2]+ are on the order of 1–2 ns in CH3CN at 20 °C (11). In this respect, manganese(I) isocyanide compounds

are similar to RuII polypyridines & cyclometalated IrIII complexes in terms of photoreactivity. Manganese's natural abundance in Earth's crust exceeds that of copper by a factor of 18, which is notable given the long-standing interest in copper by the photo physics & photochemistry community.

In the context of lamp (or at least light-initiated) cross coupling catalysis, the photophysics and photochemistry of molecular nickel(II) complexes have recently gained considerable attention, but this typically involves nonemissive NiII substances with energetically low-lying MC states which deactivate nonradiatively. Square-planar NiII compounds have recently been shown to emit a surprising amount of photoluminescence that appears to be caused by a fluorescent ligand. Several recent studies have focused on designing square-planar NiII complexes that can glow in the solid state at 298 K or in frozen glasses at 77 K, and have identified some key design principles. According to TD-DFT calculations, the carbazolylnickel(II) has a low-lying UV–vis absorption band that can be attributed to a mixed IL and MLCT excitation (located on the cyclometalating terdentate ligand). 77 K shows a lifetime of 0.11 s for weak luminescence, which suggests an emissive triplet state. Vibrational progressions of the ligand framework (ca. 1400 cm<sup>-1</sup>) in the 77 K emission spectrum point to a significant IL contribution (around 1400 cm<sup>-1</sup>). The use of terdentate ligands in strong fields appears to be a promising path to NiII complexes that exhibit MLCT luminescence, however. Tetrahedral Ni0 complexes, which have comparable physicochemical characteristics to four-coordinate Cu diimine complexes, have so far been the only way to achieve this, but these compounds are extremely sensitive to air pollution. The use of macrocyclic ligands in the photochemistry of NiII has been reported, but no emission has yet been observed.

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**For LMCT emission, we use the following complexes as LMCT emitters:**



Electron-rich ligands as well as electron-deficient metals are required in LMCT states with low energy levels. There are no nonradiative ways to deactivate the LMCT excited state in this case, so  $d0$  is the best valence electron configuration for accomplishing long-lived LMCT states. Because of this, group 3 and group 4 metals in the +III and +IV oxidation states are excellent candidates. It was discovered early on that the emissive excited state (LMCT) of  $[Cp^*2ScCl]$  in fluid room temperature solution had a luminescence lifetime of 2.0 ns and the p-Cl biden lone pair to the  $Sc^{3+}$  ion was responsible for this luminescence (12). Metallocenes based on TiIV with the general formula  $Cp_2TiX_2$  also exhibit LMCT luminescence, but only in the solid state at 77 K. Photoredox catalysis has recently become a focus for this class of compounds. At room temperature, a TiIV carbene complex was found to be non-emitting in solution, while its ZrIV&HfIV analogues did. ZrIV has been the focus of recent research, while TiIV has received scant attention. This suggests that room temp emission is more difficult to achieve with TiIV than with ZrIV.

In the solid state, the homoleptic  $[Mn(PhB(MeIm)_3)_2]^+$  complex  $M = MnIV$ , shows ruby-like red emission at room temperature, similar to many isoelectronic CrIII compounds, due to the electron-donating tris(carbene)borate ligand  $PhB(MeIm)_3$ , which stabilizes manganese in its +IV oxidation state (13). Despite the fact that several MC states of the  $d3$  valence electron configuration are lower in energy, this compound still shows green luminescence from an LMCT excited state (up to room temperature). It's possible that the high oscillator strength of the green emission spectra is due to a spin-allowed transition, which would imply a high radiative decay rate constant, making luminescence more competitive to nonradiative relaxation. With an emission lifetime of 50 ns at 85 K, the LMCT interpretation is also supported by the emission spectrum's vibrational fine structure, which shows advancements in the normal range of ligand breathing modes. As the first in a series of recent findings on unexpected LMCT emission levels from 3d-metal

complexes, this MnIV study focused on FeIII compounds, which will be discussed in more detail later.

### **Complexes of $3d^2$ (VIII), $3d^3$ (CrIII, MnIV), & $3d^6$ (CoIII) MC Emitters:**

To slow down nonradiative deactivation, spin-flip transitions typically lead to excited states that are only slightly distorted relative to the ground state because they don't affect the metal–ligand bonding situation significantly. The lowest excited states of octahedrally coordinated  $d2$  &  $d3$  complexes are expected to undergo such spin-flips in sufficiently strong ligand fields. At room temperature, some molecular CrIII complexes have been shown to emit luminescence from their spin-flip excited states; this has been known for a long time, but until recently only with low quantum yields.

Recently, there has been a resurgence in the study of luminescent CrIII complexes, thanks to the discovery of  $[Cr(ddpd)_2]$ . It has a larger bite angle than other tridentates, such as tpy, which means that it has a more powerful ligand field because of the better overlap between the metal 3d-orbitals and ligand orbitals. As a result, the energy gap between both the emissive  $2E_g$  as well as the higher-lying  $4T_2$  state is widened, resulting in a smaller thermal inhabitant of the latter state via reverse intersystem crossing and a restriction on nonradiative relaxation from this highly distorted excited state Deuteration of the ligands allowed for further optimizations, which resulted in a luminescence quantum yield of 30% and a 2E lifetime of 2.3 ms in solution at room temperature. The singlet oxygen awareness - raising capability of  $[Cr(ddpd)_2]^{3+}$  was utilised for photocatalysis, and both temperature and pressure sensing were possible. The majority of this work has been peer-reviewed.

### **Conclusions:**

RuII, OsII, ReI, IrIII, PtIII, and AuIII luminophores typically operate on the basis of MLCT transitions, which are commonly used in traditional luminophores. The photophysical behavior of copper in its +I oxidation state, with its  $d10$  subshell



completely filled, has been replicated nearly 40 years ago using copper. As a result of this early discovery, four-coordinate CuI-MLCT emitters have become a well-developed compound class in the field of valence electron configurations. Nonradiative easing via low-lying MC states is ultrafast in the open-shell 3d6 and 3d8 setups, making it difficult to install emissive excited states. FeII complexes have been the primary source of 3d6 MLCT emitters until recently, but despite progress made in enhancing their MLCT lifetimes and in recognizing their electronic structures, no FeII-based MLCT luminophores have yet been discovered. Isoelectronic Cr0 and MnI complexes recently discovered as 3d6 MLCT emitters show similar photophysical and chemical behavior to RuII polypyridines or cyclometalated IrIII complexes. The development of 3d8 MLCT luminophores using NiII has also made significant progress, but the breakthrough here has not yet been achieved in the sense that space MLCT emission has not yet been possible.

It was a paradigm shift when two-coordinate CuI complexes that are LLCT luminophores were discovered and MnIV and FeIII LMCT emitters were discovered. Reversal of the charge transport direction from MLCT to LLCT has a direct impact on potential uses in dye-sensitized solar cells; however, luminescence properties appear to be highly competitive with MLCT luminophores in terms of luminescence properties. Cu(I) MLCT luminophores have dominated research in the field of photophysics for a long time, but the new class of linear CuI LLCT emitters represents an important conceptual breakthrough in copper(I) photophysics. For increasing luminescence quantum yields, spin-allowed luminescence is present in the FeIII LMCT emitters that have been studied thus far. This makes radiative relaxation more viable with nonradiative processes on the basis of kinetics. Photoactive excited states may have a disadvantage for some applications because spin-allowed geminate charge coalescence is expected to hamper cage escape yields, which may limit the

effectiveness of these photosensitizer for photoinduced electron transfer.

In addition to the historically explored MLCT and MC transitions, recent developments beyond the first row of transition metals have opened up new perspectives on the types of emission that can be accessed. These include LMCT and LLCT. On the one hand, this includes elements such as Zr, Mo, and W, as well as f-elements (such as Ce) that are relatively abundant. While luminophores based on molecular structures of abundant main group elements are attracting increasing attention, they provide additional insights into how nonradiative loosening can be tamed. While this is happening, new developments in precious metal-based complexes (such as Ru, Rh, Re, Ir, or Pt) have advanced inorganic photophysics & photochemistry. Synthetic, spectroscopic and computational work appears to be crucial for the development of new designer luminophores, regardless of whether complexes of d-, f- or main group elements are considered.

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**Table 1: Full form of notation**

bpmp	2,6-bis(2-pyridinmethyl)pyridine
bpy	2,2'-bipyridine
btz	3,3'-dimethyl-1,1'-bis( <i>p</i> -tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene))
CAAC	cyclic (alkyl)(amino)carbene
Cp	cyclopentadienyl anion
Cp*	pentamethylcyclopentadienyl anion
CPL	circularly polarized luminescence
Cz	carbazolyl
DAC*	diamidocarbene
ddpd	<i>N,N'</i> -dimethyl- <i>N,N'</i> -dipyridine-2-ylpyridine-2,6-diamine)
dgpy	1,3-bis(3,4,7,8-tetrahydro-2 <i>H</i> -pyrimido[1,2- <i>a</i> ]pyrimidin-1(6 <i>H</i> )-yl)benzene
dgpz	3,5-bis(3,4,7,8-tetrahydro-2 <i>H</i> -pyrimido[1,2- <i>a</i> ]pyrimidin-1(6 <i>H</i> )-yl)pyridine
dipp	2,6-diisopropylphenyl
dpb	1,3-di(pyridine-2-yl)benzene
dqp	2,6-di(quinolin-8-yl)pyridine
dpc	3,6-di- <i>tert</i> -butyl-1,8-di(pyridine-2-yl)-carbazole
<sup>OMe</sup> dqp	2,6-di(quinolin-8-yl)-4-methoxy-pyridine
GS	ground state
HBulmP	1,1'-(1,3-phenylene)bis(3-butyl-1-imidazol-2-ylidene)
HImP	1,1'-(1,3-phenylene)bis(3-methyl-1-imidazol-2-ylidene)
HOMO	highest occupied molecular orbital
ISC	intersystem crossing
L <sup>bi</sup>	2,5-bis(3,5-di- <i>tert</i> -butyl-2-isocyanophenyl)thiophene
LLCT	ligand-to-ligand charge transfer
LMCT	ligand-to-metal charge transfer
L <sup>tBu</sup>	3,3'',5,5''-tetra- <i>tert</i> -butyl-2,2''-diisocyano-1,1':3',1''-terphenyl
L <sup>tri</sup>	5,5'-(2-isocyano-5-methyl-1,3-phenylene)bis(2-(3,5-di- <i>tert</i> -butyl-2-



	isocyanophenyl)thiophene)
LUMO	lowest unoccupied molecular orbital
MAC*	monoamido-aminocarbene
MC	metal-centered
MLCT	metal-to-ligand charge transfer
MMLCT	metal–metal-to-ligand charge transfer
OTf	triflate
PhB(MeIm) <sub>3</sub>	tris(3-methylimidazolin-2-ylidene)(phenyl)borate
phen	1,10-phenanthroline)
RISC	reverse intersystem crossing
TADF	thermally activated delayed fluorescence
TD-DFT	time-dependent density functional theory
tpe	1,1,1-tris(pyrid-2-yl)ethane)
tpy	2,2',6',2''-terpyridine; tren = tris(2-aminoethyl)amine

