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Luminescent chromium(0) and manganese(i) complexes

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In this Frontier article, recently discovered chromium(0) and manganese(i) complexes emitting from metal-to-ligand charge transfer (MLCT) excited states are highlighted. Chelating isocyanide ligands give access to this new class of $3d^6$ emitters with MLCT lifetimes in (or close to) the nanosecond regime in solution at room temperature. Although the so far achievable luminescence quantum yields in these open-shell complexes are yet comparatively low, the photophysical properties of the new chromium(0) and manganese(i) isocyanides are reminiscent of those of well-known ruthenium(II) polypyridines. Our findings provide insight into how undesired nonradiative MLCT deactivation in $3d^6$ complexes can be counteracted, and they seem therefore relevant for the further development of new luminescent first-row transition metal complexes based on iron(II) and cobalt(III) in addition to chromium(0) and manganese(i).

Introduction

Transition metal complexes of precious $4d^6$ and $5d^6$ ions such as ruthenium(II) and iridium(III) have extensively been explored in the fields of inorganic photophysics and photochemistry due to their favorable electronic structures leading to long-lived and emissive MLCT excited states with attractive redox properties. Consequently, these complexes have been widely used as luminophores, sensitizers, photoredox catalysts, and dyes in solar cells.^{1–7} The use of more earth-abundant metal elements is, however, an obvious goal to secure cheaper and more sustainable technologies. With their d^6 valence electron configuration, cobalt(III), iron(II), manganese(i) and chromium(0) are in principle isoelectronic and earth-abundant possible alternatives to ruthenium(II) and iridium(III). The challenge with the use of first-row transition metals with an open-shell configuration is their weak ligand fields (compare Fig. 1a and b), which result in energetically low-lying metal-centered (MC) excited states that can typically enable fast nonradiative deactivation of the MLCT excited state back to the electronic ground state (compare Fig. 1c and d).^{8–10} In $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) the ³MLCT lifetime is for instance on the order of 500 ns, but in $[\text{Fe}(\text{bpy})_3]^{2+}$ it is only *ca.* 50–100 fs.^{11,12} Recent work on new types of iron(II) compounds has led to MLCT lifetimes up to a few nanoseconds, but no MLCT photoluminescence was detectable.^{13–16}

Discussion

Inspired by early studies of group 6 metal complexes with monodentate isocyanide ligands^{17,18} and recent reports of luminescent tungsten(0) complexes with other types of monodentate isocyanides,^{22–24} our group discovered that chelating isocyanide ligands facilitate access to luminescent chromium(0) and manganese(i) complexes (Fig. 2).^{19–21} The collective σ -donating and π -accepting properties of the isocyanide ligands²⁵ cause a strong ligand field, in which the above-mentioned MC states are energetically less accessible than in typical iron(II) polypyridines,²⁶ thereby allowing for emission from the lowest MLCT excited state. The chelating nature of our di- and trisocyanides imparts robustness, and possibly contributes to reducing the efficiency of (undesired) non-radiative excited-state relaxation processes as a consequence of enhanced rigidity.²⁷ Owing to improved ligand design, we have now been able to make the important step from luminescent molybdenum(0)^{27–29} and tungsten(0)^{17,18,22–24,67} complexes to emissive compounds of the first-row of transition metals.^{19–21,30}

The chelating bidentate ligand L^H (Fig. 2) provided access to the complex $[\text{Cr}(L^H)_3]$, which was our first example of a $3d^6$ complex emitting in solution at room temperature (Table 1 and Fig. 3a black).¹⁹ Prior to that, MLCT emission from $3d^6$ complexes under such conditions had been largely unknown, though an early study already reported on photoluminescence from $[\text{Cr}(\text{CO})_4(\text{bpy})]$, but this was a rather curious case of a presumed dual emission.^{31,32} Group 6 metal carbonyls typically undergo photo-dissociation of CO ligands,^{33,34} and against this background chelating isocyanides seem advantageous to avoid photo-degradation due to loss of ligands. The ³MLCT

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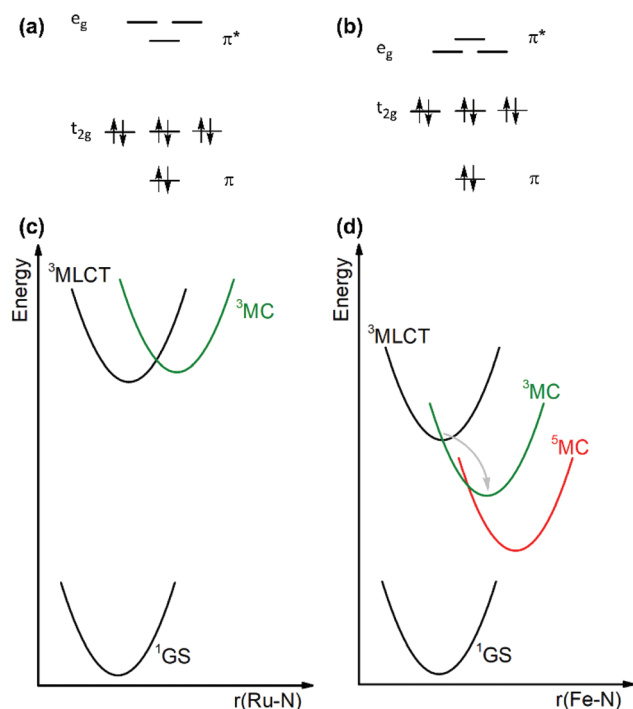


Fig. 1 Schematic representation of the low-spin d^6 electron configuration in O_h point symmetry, including ligand-based π/π^* orbitals in addition to metal-based t_{2g} and e_g orbitals in either a strong (a) or weak (b) ligand field as encountered for example in $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$, respectively. Simplified potential well diagrams with the key electronic states of (c) $[\text{Ru}(\text{bpy})_3]^{2+}$ and (d) $[\text{Fe}(\text{bpy})_3]^{2+}$. ^1GS denotes the electronic ground state. The horizontal axes in (c) and (d) are nuclear coordinates, along which the complexes distort upon electronic excitation. Here, this has been oversimplified to the metal–ligand bond distances.

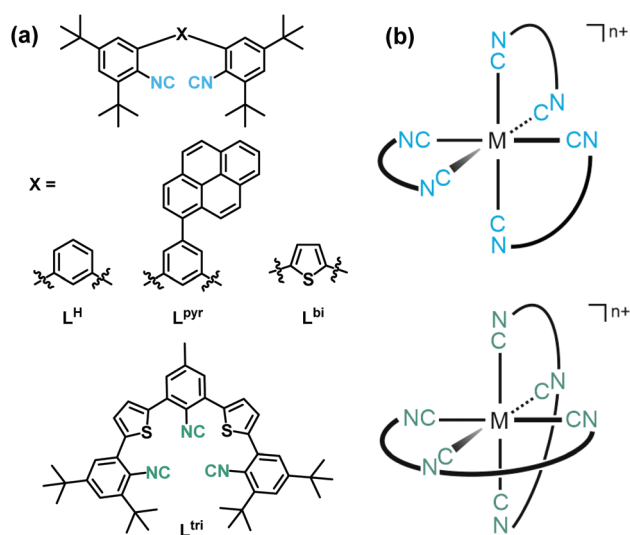


Fig. 2 (a) Molecular structures of the chelating diisocyanide ligands L^H , L^{Pyr} , L^{bi} and the trisocyanide ligand L^{tri} . (b) Generic structures of homoleptic tris(diisocyanide) (up) and bis(triisocyanide) (down) complexes. $M = \text{Cr}^0$, $n = 0$; $M = \text{Mn}^I$, $n = 1$.

excited state lifetime of $[\text{Cr}(\text{L}^H)_3]$ is 2.2 ns in deaerated THF, which is long enough for $[\text{Cr}(\text{L}^H)_3]$ to engage as photosensitizer in a triplet–triplet annihilation upconversion process with anthracene.¹⁹

The luminescence quantum yield of $[\text{Cr}(\text{L}^H)_3]$ is, however, barely above the detection limit (10^{-5}), making further improvement of the ligand and complex design highly desirable. We have previously shown that modifications of the diisocyanide ligand backbone allow for adjustment of the photophysical properties of isoelectronic molybdenum(0) tris(diisocyanide) complexes,^{27–29} hence we reasoned that an improved ligand design could potentially enhance the photophysical properties of chromium(0) MLCT emitters.

Extension of the π -system of the α -diimine ligands of ruthenium(II) complexes has previously been identified as a useful strategy to improve the photophysical properties of $4d^6$ MLCT luminophores.^{35–38} This change in ligand design can have one of two advantageous effects. First, it can lead to a more delocalized MLCT excited state relative to complexes bearing ligands without extended π -system. Second, it can cause an electronic structure in which a ligand-centered (LC) excited state localized on the extended π -system becomes important for the overall photophysics. The first scenario is commonly referred to as the *delocalization effect*,^{35,36,39–45} and the latter is often referred to as the *triplet reservoir effect*.^{37,38,46–48} Which one of these two effects dominates is largely dependent on whether there is substantial electronic coupling between the metal core and the extended π -system, or whether these two parts are electronically decoupled from one another. For the triplet reservoir effect, it is furthermore necessary that the emissive $^3\text{MLCT}$ excited state and the ^3LC state are energetically close to each other, such that the typically very long-lived ^3LC (dark) state over time can feed the more rapidly decaying luminescent $^3\text{MLCT}$ excited state, hereby elongating the excited state lifetime of the d^6 emitter. It seemed interesting to explore whether these concepts known from previous $4d^6$ complexes are also applicable to $3d^6$ congeners, and for that purpose we targeted the attachment of an extended π -system at the periphery of the L^H ligand, and the subsequent coordination of the resulting new ligand to chromium(0). The energy of the emissive $^3\text{MLCT}$ excited state of $[\text{Cr}(\text{L}^H)_3]$ was estimated to 2.05 eV, which is close to the triplet energy of pyrene (2.10 eV),^{19,49} suggesting that pyrenyl substituents at L^H might result in one of the two abovementioned effects.

Indeed, the luminescent compound $[\text{Cr}(\text{L}^{Pyr})_3]$ (Fig. 1) has substantially improved photophysical properties relative to the $[\text{Cr}(\text{L}^H)_3]$ parent complex without anchored pyrene moieties (Table 1).²⁰ Its (average) $^3\text{MLCT}$ lifetime of 6.10 ns in deaerated cyclooctane at 20 °C is, to the best of our knowledge, the longest $^3\text{MLCT}$ lifetime reported to date for any $3d^6$ complex under comparable conditions. Recent record $^3\text{MLCT}$ lifetimes (of dark, non-emissive states) for isoelectronic Fe^{II} complexes are 528 ps and 2.6 ns.^{13,14} Remarkably, the luminescence quantum yield (ϕ) of 9×10^{-4} for $[\text{Cr}(\text{L}^{Pyr})_3]$ is 90 times greater than that of $[\text{Cr}(\text{L}^H)_3]$, and this is despite a redshift of the emission by 1100 cm^{-1} for $[\text{Cr}(\text{L}^{Pyr})_3]$ relative to $[\text{Cr}(\text{L}^H)_3]$ (Fig. 3a). Typically, luminescence decays of MLCT emitters



Table 1 Overview of some photophysical parameters of luminescent chromium(0) and manganese(i) complexes in deaerated solutions at room temperature

Complex	Solvent	λ_{abs} [nm]	λ_{em} [nm]	λ_{em}^a at 77 K [nm]	τ_1, τ_2, τ_3 [ns]	τ_{avg} [ns]	ϕ [%]	Ref
$[\text{Cr}(\text{L}^{\text{H}})_3]$	THF	475	630	645	2.2 (100%)	2.2	0.001	19
$[\text{Cr}(\text{L}^{\text{PyT}})_3]$	Cyclooctane	475	682	692	4.05 ns (48%), 8.00 ns (52%)	6.10	0.09	20
$[\text{Mn}(\text{L}^{\text{bi}})_3]^+$	CH_3CN	385	485	480; 620	0.374 ns (79.2%), 1.84 ns (19.3%), 5.85 ns (1.5%)	0.74	0.05	21
$[\text{Mn}(\text{L}^{\text{tri}})_2]^+$	CH_3CN	395	525	480; 600	0.635 ns (56.4%), 2.07 ns (33.6%), 6.74 ns (10.0%)	1.73	0.03	21

^aData obtained in 2-methyl-THF. λ_{abs} : ¹MLCT absorption band maxima, λ_{em} : emission band maxima, τ_{1-3} : luminescence lifetime decay components, τ_{avg} : weighted average luminescence lifetime.

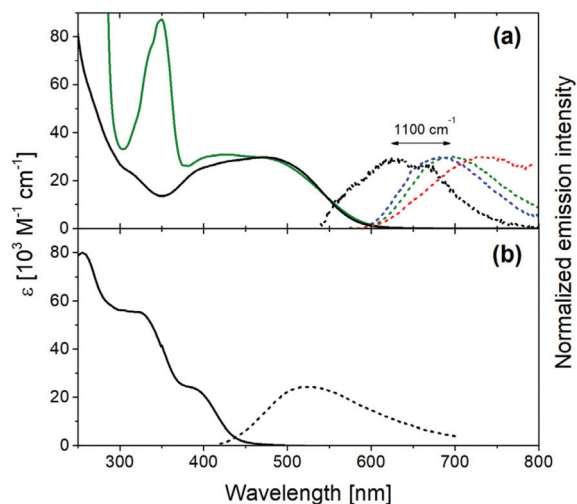


Fig. 3 (a) UV-Vis absorption spectra (solid) of $[\text{Cr}(\text{L}^{\text{H}})_3]$ in deaerated THF (black) and $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ in deaerated cyclooctane (green) as well as emission spectra (dashed) of $[\text{Cr}(\text{L}^{\text{H}})_3]$ in deaerated THF (black) and $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ in deaerated solutions of *n*-hexane (blue), cyclooctane (green) and toluene (red). $[\text{Cr}(\text{L}^{\text{H}})_3]$ and $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ were excited at 532 nm and 473 nm, respectively. (b) UV-Vis absorption spectrum (solid) and emission spectrum (dashed) of $[\text{Mn}(\text{L}^{\text{tri}})_2]^+$ in deaerated acetonitrile. Excitation occurred at 410 nm. All data sets were obtained at 20 °C.

follow the so-called *energy gap law*, according to which a lower excited-state energy enables more rapid nonradiative emission.⁵⁰ Against this background, the much enhanced photoluminescence properties of the pyrene-decorated Cr^0 complex are all the more remarkable. The photophysics of $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ are dominated by the delocalization effect, which is reflected in noticeable electronic coupling between the chromium(0) core and the pyrenyl in the excited ³MLCT state. Specifically, redshifted emission maxima of $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ relative to $[\text{Cr}(\text{L}^{\text{H}})_3]$ and a strong emission solvatochromic effect are detected for $[\text{Cr}(\text{L}^{\text{PyT}})_3]$, which was not observed for $[\text{Cr}(\text{L}^{\text{H}})_3]$. The emission band maximum for $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ shifts from 675 nm in *n*-hexane to 740 nm in toluene (Fig. 3a), whereas in $[\text{Cr}(\text{L}^{\text{H}})_3]$ the emission band maximum only shifts by 5 nm between these two solvents. Such a strong emission solvatochromism suggests that the change in dipole moment between the ground state and the emissive ³MLCT state is larger in $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ than in $[\text{Cr}(\text{L}^{\text{H}})_3]$. This in turn is compatible with the view that the

excited electron in the emissive ³MLCT state of $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ is delocalized over a larger portion of the ligand π -system (diisocyanide *m*-terphenyl backbone and attached pyrene unit) than in the ³MLCT state of $[\text{Cr}(\text{L}^{\text{H}})_3]$ (in which only the diisocyanide *m*-terphenyl backbone but no pyrene is present). As a consequence, the photoactive MLCT excited state in $[\text{Cr}(\text{L}^{\text{PyT}})_3]$, likely becomes less distorted than in $[\text{Cr}(\text{L}^{\text{H}})_3]$, which leads to a smaller overlap between vibrational wavefunctions of the ground and excited state potential energy surfaces.^{39,42} This effect can be expected to decrease non-radiative excited-state decay rates and likely contributes substantially to the improved photophysical properties of $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ relative to $[\text{Cr}(\text{L}^{\text{H}})_3]$, though other (yet unidentified effects) could play important roles as well.

The MLCT luminescence lifetimes and quantum yields for $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ exhibit an unusual bell-shaped dependence on solvent polarity indicative of two counteracting effects governing the MLCT deactivation,²⁰ a behavior that is not typically seen for precious metal-based 4d⁶ and 5d⁶ MLCT lumino-phores. Polar solvents stabilize the emissive ³MLCT state of $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ and thereby decrease the energy gap to the electronic ground state, which accelerates non-radiative relaxation. Conversely, apolar solvents raise the ³MLCT energy but presumably decrease the barrier for thermal deactivation *via* nearby higher lying MC excited states.^{51,52} The sweet spot with optimal luminescence lifetime and quantum yield of $[\text{Cr}(\text{L}^{\text{PyT}})_3]$ is reached in cyclooctane.

Complexation of manganese(i) to the chelating bidentate isocyanide ligand L^{bi} and the tridentate isocyanide L^{tri} (Fig. 2a) resulted in the first examples of MLCT-luminescent manganese complexes in solution at room temperature.²¹ Previously, only a molecular complex of manganese(iv) with luminescence properties has been reported, however, this compound was reported to emit primarily in the solid state and not from an MLCT state.⁵³ Both $[\text{Mn}(\text{L}^{\text{bi}})_3]^+$ and $[\text{Mn}(\text{L}^{\text{tri}})_2]^+$ (Fig. 3b) have a broad unstructured emission band around 500 nm, and the luminescence lifetimes approach the nanosecond regime in deaerated acetonitrile at room temperature (Table 1). The photoactive excited states have dominant MLCT character, as demonstrated by a combination of UV-Vis transient absorption and spectro-electrochemical studies. These MLCT states participate in electron transfer processes, as shown by a laser experiment, in which methyl viologen was reduced transiently from its initial dication to the radical



monoanion form. Furthermore, the photoactive MLCT excited states of $[\text{Mn}(\text{L}^{\text{bi}})_3]^+$ and $[\text{Mn}(\text{L}^{\text{tri}})_2]^+$ engage in bimolecular triplet-triplet energy transfer reactions with polyaromatic hydrocarbons possessing triplet energies below 2.3 eV. For instance, in an UV-Vis transient absorption experiment performed in the presence of excess pyrene, the hydrocarbon triplet excited state was readily detectable following selective excitation of the Mn^{I} complexes. This experiment confirms that the energy-donating excited state has triplet spin multiplicity. Certain aspects of the Mn^{I} isocyanide photophysics have remained yet somewhat unclear, for example the role of a ligand-centered $^3\pi-\pi^*$ excited state, which will require further studies to comprehend in detail.

The manganese(I) isocyanide complexes are air stable, and their oxidation to the +II oxidation state is reversible. This opens perspectives for possible applications in photocatalysis, in which the $^3\text{MLCT}$ -excited manganese(I) complexes could act as electron donors to various substrates. After photo-oxidation, the initial +I oxidation state of manganese can likely be regenerated with common sacrificial reagents such as tertiary amines, because the reduction of Mn^{II} to Mn^{I} is comparatively easy to accomplish in this class of compounds.^{17,54} In the case of chromium, the analogous d^5 to d^6 reduction of Cr^{I} to Cr^0 is more difficult to achieve, mainly because of the lower (cationic) charge of Cr^{I} compared to Mn^{II} .⁵⁵ Consequently, substantially stronger sacrificial electron donors than the commonly used tertiary amines would likely be required in photo-redox reactions based on chromium(0) catalysts.

Conclusions

Our recent progress on luminescent chromium(0) and manganese(I) complexes demonstrates that with sophisticated ligand design, it is possible to obtain d^6 emitters based on earth-abundant elements, which are essentially analogues of the extensively explored $[\text{Ru}(\text{bpy})_3]^{2+}$ and its numerous $4d^6$ and $5d^6$ congeners. These luminescent $3d^6$ complexes have a rich photoreactivity, which include photoinduced electron transfer as well as triplet energy transfer, and furthermore they are amenable to photochemical (triplet-triplet annihilation) upconversion.

Deactivation of the lowest MLCT state of isoelectronic iron (II) complexes often occurs on a very rapid time-scale due to low-lying MC excited states. In analogy, we found that low-lying excited MC states play an important role in the deactivation of the MLCT states in our isoelectronic chromium(0) and manganese(I) complexes. Even subtle changes in solvent polarity can significantly influence the radiative and non-radiative decay rates, which highlights some of the challenges associated with the comparatively weak ligand fields encountered in first-row transition metal complexes relative to those of the second or the third row of d-metals (compare Fig. 1a and b). The issue of low-lying MC states (Fig. 1d) is a key difference between the $3d^6$ compounds considered here and the well-known class of emissive Cu^{I} complexes, which have a

completely filled $3d^{10}$ subshell.^{56,57} This makes it much more difficult to establish long-lived and luminescent MLCT excited states in the open-shell compounds, whilst recent studies of linear copper(I) complexes have reported outstanding luminescence properties.^{58–60} Similarly, newly designed Cr^{III} (d^3) complexes feature remarkable luminescence quantum yields and excited state lifetimes,^{61–63} but those are complexes emitting from so-called spin-flip (MC) states, which are very little distorted relative to the electronic ground state, and as such are not directly comparable to the MLCT excited states of d^6 compounds. Another strategy to develop d^6 emitters is to install luminescent MC states rather than MLCT states. This was recently accomplished for a Co^{III} complex with the use of a scorpionate carbene ligand.⁶⁴ The same ligand has also proven useful in making an iron(III) (d^5) complex emit from a ligand-to-metal charge transfer (LMCT) excited state, applicable to photocatalytic reactions.^{65,66,68} Thus, each d-electron configuration has its own photophysical characteristics, and further research in all directions seems highly desirable in the interest of broadening our understanding of photoactive excited states in first-row transition metal complexes.

Author contributions

The manuscript was written through contributions of all authors.

Conflicts of interest

There are no conflicts to declare.

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