



**Luminescent complexes made from chelating isocyanide  
ligands and earth-abundant metals**

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## Luminescent complexes made from chelating isocyanide ligands and earth-abundant metals

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In this invited frontier article, recently discovered  $d^6$  and  $d^{10}$  complexes with long-lived metal-to-ligand charge transfer (MLCT) excited states are highlighted. Chelating diisocyanide ligands give access to emissive Mo(0) and Cr(0) complexes with  $d^6$  electron configuration exhibiting photophysical properties similar to those of Ru(II) polypyridines or cyclometalated Ir(III) complexes. With Ni(0), these ligands yield luminescent tetrahedral  $d^{10}$  complexes similar to isoelectronic Cu(I) bis(diimine) compounds.

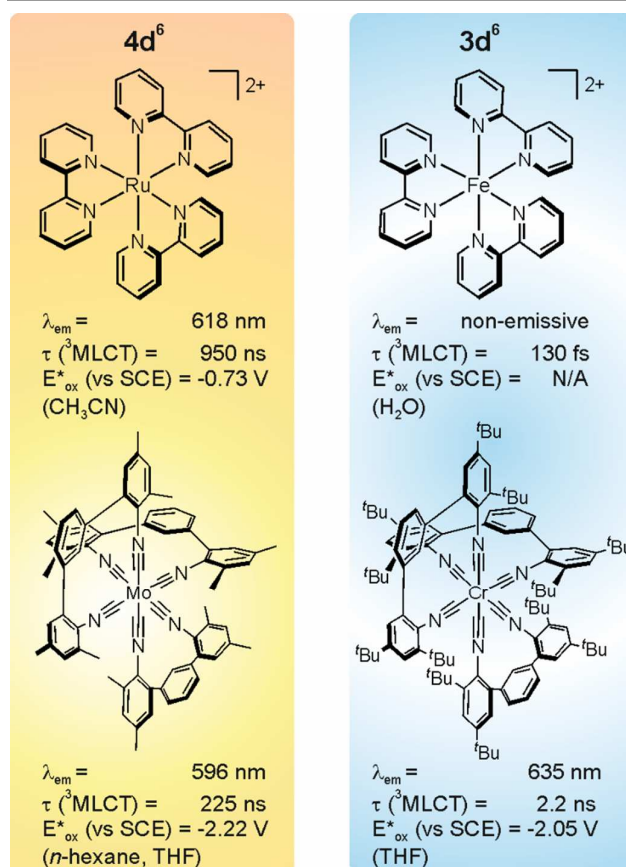
### Introduction

Metal complexes with either  $4d^6$  or  $5d^6$  electron configuration and suitable ligands have long been known to exhibit favorable electronic structures that give rise to rich photophysics and photochemistry. The most prominent members of this family are arguably Ru(II) polypyridines (with Ru(2,2'-bipyridine)<sub>3</sub><sup>2+</sup> as a prototype) and cyclometalated Ir(III) complexes.<sup>1</sup> Applications of such complexes include for example lighting devices,<sup>1b</sup> solar cells,<sup>2</sup> photoredox catalysis,<sup>3</sup> and sensors. The low-spin  $d^6$  electron configuration as well as energetically low-lying empty ligand orbitals are crucially important for <sup>3</sup>MLCT excited states with lifetimes on the order of ~100 ns and associated luminescence phenomena. There is a long-standing interest in replacing the precious metals Ru(II) and Ir(III) by more earth abundant elements, but this is not a straightforward endeavor. Fe(II) complexes, for example, typically exhibit very short-lived MLCT excited states (~130 fs – 37 ps), due to the presence of low-lying d-d excited states in the comparatively weak ligand field of the  $3d^6$  configuration.<sup>4</sup>

### Discussion

Building on a few papers published more than 40 years ago,<sup>5</sup> and inspired by recent reports on W(0) complexes with monodentate isocyanide ligands,<sup>6</sup> we synthesized and explored a new family of Cr(0) and Mo(0) complexes with chelating diisocyanide ligands.<sup>7</sup> Isocyanide groups are needed to stabilize the low oxidation states of these metals,<sup>8</sup> and a *meta*-terphenyl backbone was suitable for accessing a relatively rigid bidentate chelator. (With few exceptions,<sup>9</sup> earlier studies of chelating diisocyanides had focused on more

flexible and other types of ligand backbones).<sup>10</sup> Homoleptic Cr(0) and Mo(0) tris(diisocyanide) complexes are readily obtained with our ligands, and they are luminescent in fluid solution at room temperature (Figure 1).<sup>7</sup>



**Figure 1.** Molecular structures of  $d^6$  metal complexes along with some key photophysical and electrochemical properties. ( $\lambda_{em}$  = emission band maximum;  $\tau$ (<sup>3</sup>MLCT) = <sup>3</sup>MLCT lifetime in de-aerated solvents at room temperature;  $E^*_{ox}$  = oxidation potential in the emissive <sup>3</sup>MLCT state).

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The Mo(0) complex emits  $^3\text{MLCT}$  luminescence with a band maximum ( $\lambda_{\text{em}}$ ) at 596 nm and a lifetime ( $\tau(^3\text{MLCT})$ ) of 225 ns in de-aerated *n*-hexane at room temperature.<sup>11b</sup> For comparison,  $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$  emits at 618 nm with a lifetime of 950 ns in de-aerated  $\text{CH}_3\text{CN}$ . Like in the isoelectronic Ru(II) species, the first oxidation process of our Mo(0) complex is metal-based, but it occurs at much lower potential given the higher electron density at Mo(0) compared to Ru(II). The oxidation potential in the long-lived  $^3\text{MLCT}$  excited state ( $E_{\text{ox}}^*$ ) is -2.22 V vs. SCE, compared to -0.73 V vs. SCE for  $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ , and thus our complex is a considerably stronger excited-state reductant than  $\text{Ir}(2\text{-phenylpyridine})_3$  ( $E_{\text{ox}}^* = -1.7$  V vs. SCE), which is widely used for photoredox catalysis.<sup>12</sup> We demonstrated that our Mo(0) complex is a competent photoredox catalyst for certain organic transformations that are inaccessible with  $^3\text{MLCT}$ -excited  $\text{Ir}(2\text{-phenylpyridine})_3$  due to lack of similarly strong reducing ability.<sup>7, 11b</sup>

Since Fe(II) complexes are usually non-luminescent, the observation of photoluminescence from an isoelectronic  $3d^6$  complex, such as the Cr(0) tris(diisocyanide) complex in Figure 1, is remarkable.<sup>11a</sup> The current record  $^3\text{MLCT}$  lifetime for Fe(II) complexes is 37 ps on  $\text{Al}_2\text{O}_3$  nanofilms,<sup>13</sup> whereas in  $\text{Fe}(2,2'\text{-bipyridine})_3^{2+}$  the MLCT excited state relaxes to lower lying d-d states within  $\sim 130$  fs.<sup>4</sup> Against these reference points, the 2.2 ns  $^3\text{MLCT}$  lifetime observed for our Cr(0) complex in de-aerated THF at room temperature compares very favorably and encourages further investigations of related  $3d^6$  complexes.<sup>14</sup> We demonstrated that the Cr(0) complex can be used as a sensitizer for triplet-triplet annihilation upconversion, but given the 2.2 ns  $^3\text{MLCT}$  lifetime comparatively high annihilator concentrations were of course required.<sup>7, 11a</sup>

complexes, exhibiting an emission band maximum at 441 nm and a  $^3\text{MLCT}$  lifetime of 250 ns in de-aerated  $\text{CH}_3\text{CN}$  (Figure 2, left).<sup>15</sup> The phenyl-substituents in *ortho*-position to the ligating N atoms help impede planarization of the tetrahedral complex in the MLCT excited state,<sup>17</sup> thereby leading to higher luminescence quantum yields and longer  $^3\text{MLCT}$  lifetimes. We adapted this design strategy to diisocyanide ligands that can chelate to Ni(0), leading us to a ligand backbone comprised of five aryls and two isocyanide groups (Figure 2, right).<sup>18</sup> The resulting homoleptic Ni(0) complex emits at 511 nm, but only in frozen 2-methyl-THF solution at 77 K. Further improvements will be necessary to obtain Ni(0) isocyanide complexes that luminesce in fluid solution at room temperature, but this certainly is a very realistic goal.

## Conclusions

In summary, chelating diisocyanide ligands provide access to photoactive metal complexes based on Cr(0), Mo(0), and Ni(0). The Cr(0) and Mo(0) systems seem particularly relevant because they are essentially analogues of  $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$  made from earth-abundant elements. The fact that the Cr(0) complex luminesces while isoelectronic Fe(II) complexes commonly relax nonradiatively would appear to be of fundamental importance, given the very large number of prior studies on the photophysics of Fe(II) compounds. It remains to be seen what practical implications these new findings have, but the initial studies highlighted herein suggest that this new class of  $d^6$  MLCT luminophores and photosensitizers has considerable potential.<sup>19</sup>

There have been a series of highly interesting other recent developments in the area of photoactive metal complexes based on earth-abundant elements. This includes for example the synthesis and investigation of Zr(IV) and Fe(III) complexes exhibiting photoactive LMCT excited states,<sup>20</sup> the discovery of new Cr(III) polypyridines and usage of such complexes in various photophysical and photochemical contexts,<sup>21</sup> or the successful use of Cu(I) complexes in a broad variety of photoredox-catalyzed reactions.<sup>22</sup> At the same time, work on photoactive Fe(II) complexes continues to get significant attention.<sup>23</sup> All these efforts and findings demonstrate that coordination chemistry, in combination with inorganic photophysics and photochemistry,<sup>24</sup> continues to make important contributions to chemistry at large.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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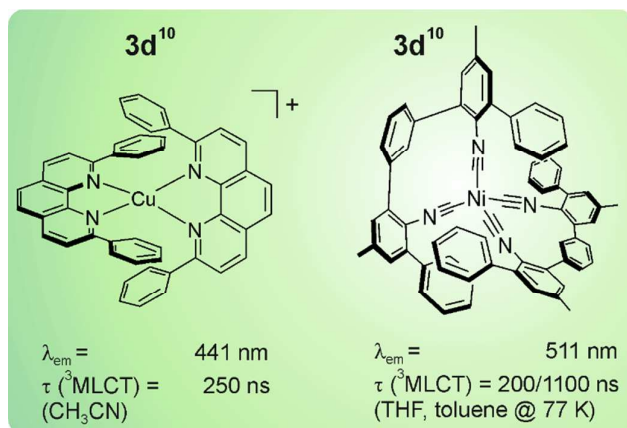


Figure 2. Molecular structures along with some key photophysical and electrochemical properties of two  $d^6$  metal complexes.<sup>15, 18</sup>

Aside from the abovementioned  $d^6$  species,  $d^{10}$  complexes represent an important family of  $^3\text{MLCT}$  emitters. Key focus until now has been on Cu(I) complexes,<sup>15</sup> initially on homoleptic bis(diimines) and later on heteroleptic variants with diimine and diphosphine ligands.<sup>16</sup>  $\text{Cu}(\text{dpp})_2^+$  (dpp = 2,9-diphenyl-1,10-phenanthroline) is the prototype of this class of

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Table of contents graphic and text

Cr	←	Fe	Co	Ni	←	Cu
Mo	←	Ru	Rh	Pd		Ag
W		Re	Os	Ir		Pt
						Au

Cr(0), Mo(0), and Ni(0) complexes with diisocyanide ligands have recently been discovered as isoelectronic analogues of well-known Fe(II), Ru(II), and Cu(I) complexes.