

Picosecond MLCT Deactivation in Co(pppy)₃ via Jahn-Teller Distortion

*Justin T. Malme, Jenelle N. Weaver, Gregory S. Girolami, and Josh Vura-Weis**

Department of Chemistry, University of Illinois at Urbana-Champaign, Champaign 61801, United States

**email: vuraweis@illinois.edu*

Abstract

The excited-state dynamics of *fac*-Co(pppy)₃, where ppy = 2-[2-(pyridyl)phenyl], are measured with femtosecond UV-Vis transient absorption spectroscopy. The initial state is confirmed with spectroelectrochemistry to have significant metal-to-ligand charge transfer (MLCT) character, unlike other Co complexes that generally have ligand-to-metal charge transfer or ligand-field transitions in this energy range. Ground-state recovery occurs in 8.65 ps in dichloromethane. Density functional theory (DFT) calculations show that the MLCT state undergoes Jahn-Teller distortion and converts to a 5-coordinate ³MC state in which one Co-N bond is broken. The results highlights a potential pitfall of heteroleptic-bidentate ligands when designing strong-field ligands for transition metal chromophores.

An important scientific goal is to replace photoredox chromophores such as Ru(bpy)₃²⁺ and Ir(bpy)₃³⁺ with more earth-abundant alternatives based on 3d transition metals.^{1,2} Unfortunately, 3d transition metal complexes such as Fe(bpy)₃²⁺ generally have much shorter metal-to-ligand charge transfer (MLCT) excited-state lifetimes than their 4d or 5d analogs, owing to rapid deexcitation mediated by low-energy metal-centered (MC) states. Strategies to lengthen the excited-state lifetimes of Fe^{II} complexes, for example by ligand modifications that raise the relative energy of the MC excited states by leveraging strong σ -donation or the nephelauxetic effect, are promising but so far have met with limited success.³⁻

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Another strategy to raise the relative energy of the MC states is to change the metal but keep the ligands the same.¹ Switching from Fe^{II} to the isoelectronic d⁶ ion Co^{III} results in a stronger ligand field that should destabilize the MC excited states, but the higher oxidation state means that the metal may be more easily reduced than oxidized. As a result, photoexcitation of most Co^{III} complexes generates ligand-to-metal charge transfer (LMCT) excited states instead of the MLCT states that are common for Fe^{II} complexes. Sinha et al recently reported a Co^{III} complex with N-heterocyclic carbene ligands

(Co(L^{CNC})₂⁺) that has a strong absorption at 430 nm that generates an excited state with mixed MLCT/intraligand charge transfer character and a lifetime of 1.2 ns.¹³

In the current work,¹⁴ we present a study of the excited state dynamics of tris(2-[2-(pyridyl)phenyl]-cobalt(III), *fac*-Co(ppy)₃,¹⁵ which is the 3d congener of Ir(ppy)₃, a widely used photosensitizer and photocatalyst.^{16–19} Because the ppy ligand is a strong σ -donor, reduction of the cobalt center should be disfavored, and oxidation made more favorable. Consistent with this expectation, we report here that – unusually for Co^{III} complexes – photoexcitation of Co(ppy)₃ generates an MLCT excited state. The lifetime of this state is significantly shorter than both Ir(ppy)₃²⁰ and Co(L^{CNC})₂⁺ and we describe DFT studies to determine the reasons for the short lifetime.

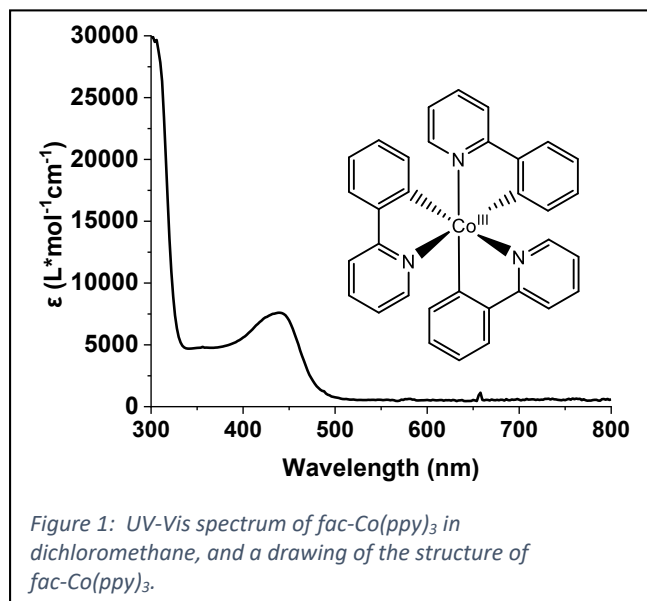


Figure 1: UV-Vis spectrum of *fac*-Co(ppy)₃ in dichloromethane, and a drawing of the structure of *fac*-Co(ppy)₃.

The UV-Vis spectrum of *fac*-Co(ppy)₃ (Figure 1) features one strong absorption band in the visible region at 438 nm ($\epsilon = 7600 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) that has previously been assigned as a MLCT transition¹⁵ (for comparison, LMCT bands for Co^{III} complexes are typically in the UV^{1,21,22}). Spectroelectrochemical measurements confirm the MLCT character of the excited state. It is known from cyclic voltammetry (CV) studies that oxidation of *fac*-Co(ppy)₃ occurs reversibly at the metal to give a Co^{IV} product, whereas reduction of *fac*-Co(ppy)₃ is ligand-based.¹⁵ We measured the UV-vis spectrum of *fac*-Co(ppy)₃ in DMF at 0.25 V vs. Ag/Ag⁺ (where the metal is oxidized) and -2.68 V vs. Ag/Ag⁺ (where the ligand is reduced). These spectra were combined according to the equation $\Delta A = (A_{\text{ox}} - A_{\text{red}}) - (2A_0)$ to give a simulated MLCT spectrum (Figure S2) that closely matches the transient spectrum (see below).

The preference of Co(ppy)₃ to form an MLCT excited state is due to the strong σ -donor and weak π -donor character of the ppy ligand.²¹ The strong σ -donation increases the energies of the metal-centered e_g^* orbitals; in fact, these orbitals must be higher energy than the ligand π^* orbitals, as shown by the finding that reduction of Co(ppy)₃ occurs at the ligand.

Femtosecond transient absorption studies show that excitation of dichloromethane solutions of *fac*-Co(ppy)₃ at 450 nm (see SI for procedure) causes ground state bleaching (GSB) of the MLCT band at 445

nm (Figure 2A). Two excited state absorption features can also be seen, one below 400 nm in the near

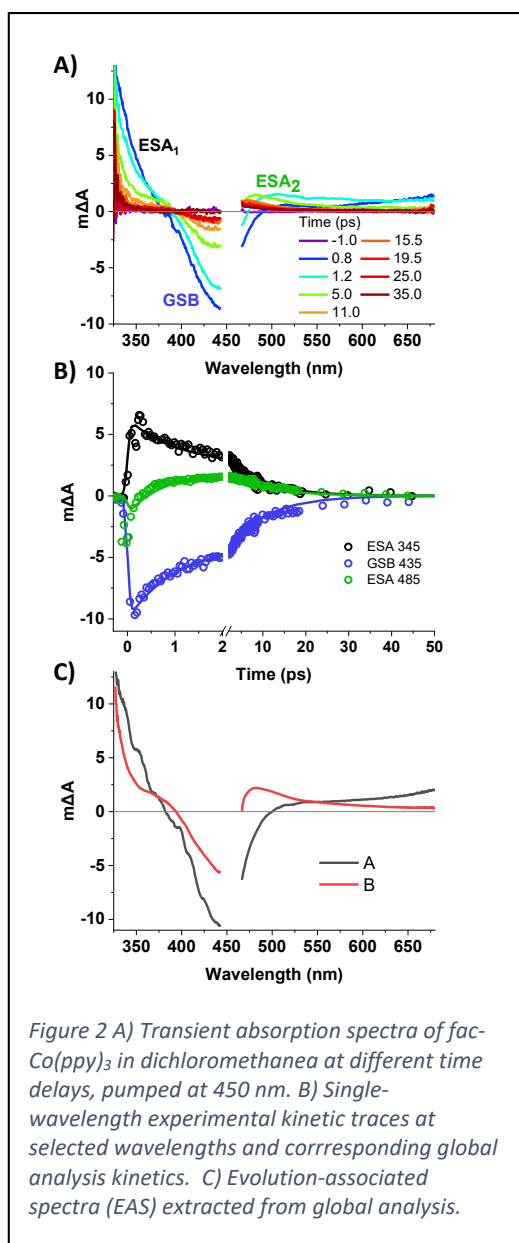


Figure 2 A) Transient absorption spectra of *fac*-Co(ppy)₃ in dichloromethane at different time delays, pumped at 450 nm. B) Single-wavelength experimental kinetic traces at selected wavelengths and corresponding global analysis kinetics. C) Evolution-associated spectra (EAS) extracted from global analysis.

UV (ESA₁) and one extending from 500 nm past the 700 nm limit of the probe window (ESA₂). Although ESA₁ and the GSB decay to zero with little apparent change in their shapes over their lifetimes, ESA₂ gradually blueshifts and sharpens, losing nearly all amplitude at wavelengths longer than ~600 nm.

Plots of the absorbance vs. time at several wavelengths (Figure 2B) show two general timescales, with one subpicosecond and one ~10 ps decay. The data set was therefore fit to a two-state

$A \xrightarrow{\tau_1} B \xrightarrow{\tau_2} GS$ sequential model convolved with a Gaussian instrument response function using the program Glotatan.²³

This analysis produces a set of evolution-associated spectra A and B (Figure 2C) and exponential time constants τ_1 and τ_2 (see Supporting Information for more details). State A has a wide GSB centered at 440 nm with a broad ESA from 500 nm into the near IR. Given the 120 fs instrument response function of the transient absorption instrument and the rapid (<100 fs) intersystem crossing in metal polypyridyl

complexes,²⁴ state A likely represents the ³MLCT state close to the Franck-Condon geometry. It decays into state B with a time constant of $\tau_1=0.80\pm0.01$ ps: simultaneously, the GSB narrows and the broad ESA blue shifts, loses almost all near IR amplitude, and eventually forms a much more distinct ESA

centered at 485 nm with a tail extending into the near IR. State B decays back to the ground state with a

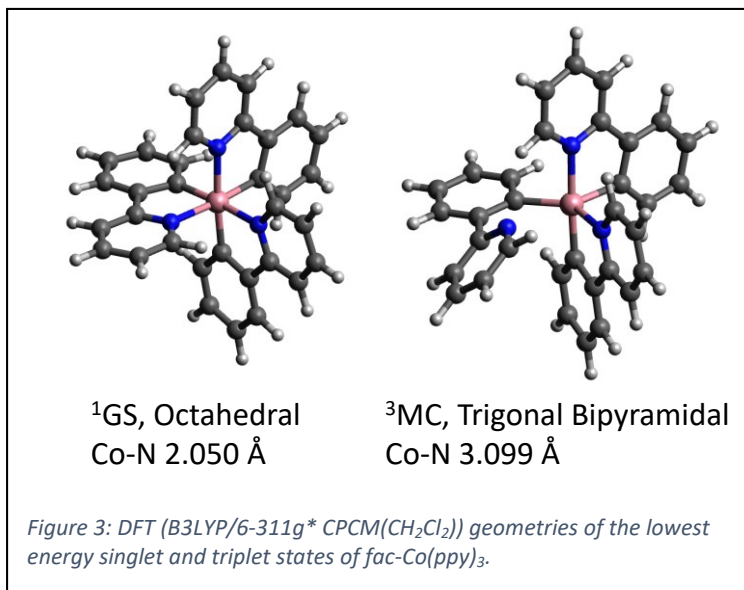
time constant of $\tau_2=8.65\pm0.03$ ps. The spectrum of state B resembles the spectroelectrochemically-simulated spectrum in Figure S2, and is therefore also assigned as having significant MLCT character.

To explore why Co(ppy)_3 has a relatively short excited state lifetime, and to confirm the MLCT character of its excited state, we performed both DFT geometry optimizations for the lowest energy singlet and lowest energy triplet states, and TDDFT calculations using the B3LYP^{25,26} functional, 6-311g* basis set, and CPCM(CH_2Cl_2) solvation model.²⁷⁻²⁹ All calculations were performed in the ORCA v5.0.3 software package.³⁰ To verify each optimized geometry was at a minimum, frequency calculations were

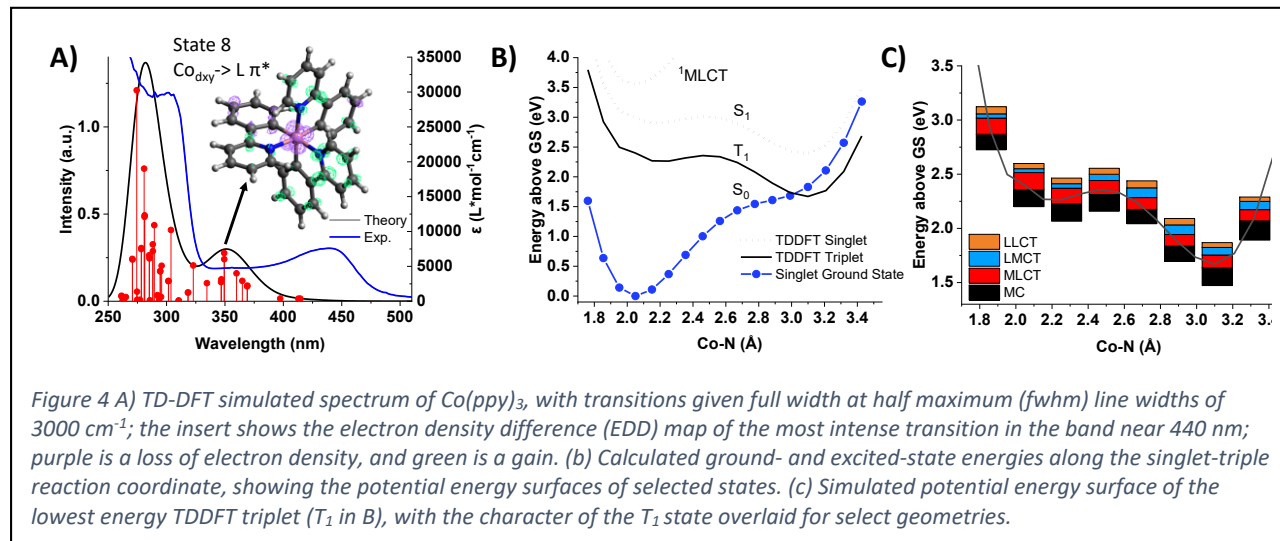
performed and checked for negative frequencies. In the singlet ground state, the Co^{III} ion has an octahedral coordination environment. In the lowest energy triplet state, which lies roughly 1.61 eV above the singlet ground state, the coordination environment is trigonal bipyramidal owing to rupture of one Co-N bond (Figure 3, also see SI).

A TD-DFT simulation made with the

program GaussSum³¹ of the UV-Vis absorption spectrum of Co(ppy)_3 (Figure 4A) resembles the shape of the observed spectrum, though the UV band is underestimated and visible band overestimated. This overestimation is approximately 0.7 eV, which is large but within expectation for the charge transfer band $3d^6$ transition metal complexes at this level of theory.³² The band near 350 nm, corresponding to the experimental spectrum's visible $^1\text{MLCT}$ band, is dominated by several transitions with Co(d) to $\text{L}(\pi^*)$



character, as demonstrated by the inset electron difference density (EDD) map, visualized using Avogadro.³³ A table of all major transitions under this band can be found in the SI (Table S1).²⁴



To simulate the excited-state potential energy surface, TDDFT calculations were performed for 17 intermediate geometries that interpolate between the optimized singlet and triplet geometries. The energy of the singlet ground state and three selected excited states are shown in Figure 4, representing a simplified version of a manifold of states that is shown in Figure S5. Individual TDDFT-calculated states were decomposed into ligand-to-ligand charge transfer (LLCT), ligand-to-metal charge transfer (LMCT), MLCT, and metal-centered (MC) character using the TheoDORÉ software package,³⁴ which achieves the decomposition through fragment-based analysis of the individual excitations contributing to a single TDDFT state. The lowest-lying triplet state is primarily of mixed MC/MLCT character, with the MLCT character decreasing from 40% to 29% as the potential energy surface is followed toward the ground state triplet geometry (Table S4). This mixed-character potential energy surface differs from those of prototypical Ir^{III} and Fe^{II} complexes. In the former there is a well-defined ^3MC electronic state higher in energy than the $^3\text{MLCT}$ state, whereas in the latter there are well-defined ^3MC and ^5MC states at significantly lower energy.

From these results, we propose the following deactivation mechanism for photo-excited Co(ppy)_3 : By analogy with other d^6 chromophores, the initially-formed $^1\text{MLCT}$ state undergoes intersystem crossing to a $^3\text{MLCT}$ state in tens of fs.²⁴ Over the next 0.80 ps (corresponding to t_1 in the global analysis), the $^3\text{MLCT}$ state relaxes through the dense manifold of electronic states to a triplet state with mixed $\text{Co(d)} \rightarrow \text{L}\pi^*$ and $\text{Co(d)} \rightarrow \text{Co(d}_{x^2-y^2})$ character. Vibrational relaxation of these states occurs on the same timescale. Occupation of the $\text{Co(d}_{x^2-y^2})$ orbital (which has strong metal-ligand σ -antibonding character) in the mixed

character state induces a Jahn-Teller distortion in which one pyridine donor group dissociates from the metal center, thus decreasing the coordination number from six- to five. Intersystem crossing back to the singlet ground state occurs in 8.65 ps (t_2 in the global analysis).

Photoexcitation of some other O_h d^6 complexes containing bidentate ligands is known to generate five-coordinate excited states: for example, D_{3h} 3T states were implicated in the room temperature nonradiative deactivation of emissive Ir^{III} complexes.³⁵ Such states were deactivating only when the energy of the D_{3h} triplet was lower than that of the O_h triplet and the ligand dissociation barrier was small. Indeed, this is the case for *fac*-Co(ppy)₃: the D_{3h} triplet is computed to be 0.6 eV lower than the O_h triplet, with a barrier of only 0.09 eV. This low barrier and large energy difference implies that the five-coordinate geometry is generated rapidly and irreversibly, resulting in the rapid deactivation of the excited state. Additionally, bidentate pyridylcarbene Fe^{II} complexes exhibit similar elongation of one metal-nitrogen coordinate in their lowest-energy 3T geometry, and as a result have similarly short excited state lifetimes.^{36–38} A Cr^0 scorpionate complex was also found to undergo dissociation of a single ligand in the 3MLCT state, followed by solvent coordination to the empty site.³⁹

Thus, the 3MC state of Co(ppy)₃ is short lived, as it is in $Fe(bpy)_3^{2+}$ but for different reasons. For Co(ppy)₃ this state ejects a ligand and becomes five-coordinate, whereas in $Fe(bpy)_3^{2+}$ and related complexes, the 3MC state undergoes cascading decay to a distorted but relatively long-lived 5MC state.^{40,41} In some other Fe^{II} complexes, the 3MC state is implicated in the direct nonradiative or otherwise fast decay of a desired excited state.³ More interestingly, the picosecond 3MC lifetimes of Co(ppy)₃ contrasts with the nanosecond and microsecond 3MC lifetimes seen for most other Co^{III} complexes, which are often sufficiently long to give rise to luminescence⁴² and to make Co(bpy)₃³⁺ an active photocatalyst.^{43,44} To determine why the 3MC states of Co(ppy)₃ and Co(bpy)₃³⁺ behave so differently, we computed the lowest-energy singlet and triplet geometries of Co(bpy)₃³⁺ (see Figure S9). Instead of ejecting a pyridine ligand and becoming five-coordinate, as seen for Co(ppy)₃, the lowest-energy triplet geometry of Co(bpy)₃³⁺ exhibits a Jahn-Teller distortion of a different symmetry (from D_3 to C_2) in which the six Co-N bonds lengthen but remain approximately the same length. We can attribute this difference to the unsymmetrical nature of the ppy ligand: the three phenyl rings are strong σ -donors that weaken the bonds to the *trans*-situated pyridine groups, thus facilitating dissociation of one of these groups. In addition, Eisenstein has shown that the triplet state of d_6 ML_5 complexes is Jahn-Teller active and that the presence of three strong σ -donating ligands favors the TBP geometry.⁴⁵

The combination of ultrafast transient absorption spectroscopy and TDDFT calculations in this work reveals that visible-light photoexcitation of Co(ppy)_3 initially forms a $^1\text{MLCT}$ state of Co^{IV} that evolves into a mixed $^3\text{MLCT}/^3\text{MC}$ excited state. The latter undergoes Jahn-Teller distortion to a five-coordinate D_{3h} geometry. This potential energy surface crosses the singlet ground-state surface, enabling rapid ground-state recovery. This behavior sharply contrasts with that of other Co^{III} complexes that have ^3MC excited states with lifetimes of up to several microseconds.^{42,44} This report shows that a strong ligand field alone is not sufficient to achieve long excited-state lifetimes: one must also consider constraining the energetically-accessible molecular distortions that enable crossing points in the potential energy surfaces. We recently reported an Fe^{II} chromophore with a macrocyclic tetradentate ligand that restricted such crossings, leading to a 1.25 ns lifetime at room temperature.⁴⁶ Balancing the ligand field around the entire coordination sphere may also lead to the disfavoring of the single metal-ligand bond lengthening demonstrated here. Finally, if heteroleptic ligands mixing strong and weak field elements are desired, care should be taken to follow strategies that do not put strong-donor ligands at positions allowing easy e_g^* population.^{47,48} Coordinating solvents could also be used to stabilize the five-coordinate species, extending the excited-state lifetime.³⁹ Such strategies, combined with the inherently larger ligand field of Co^{III} complexes, may lead to even longer lifetimes of potentially photoactive states. Nevertheless, examination of the photophysics of the 3d analog of fac-Ir(ppy)_3 is an important benchmarking step in the development of Co^{III} chromophores. Much like previous work on the analogous Fe(bpy)_3^{2+} , the sharply different photophysics of fac-Co(ppy)_3 reveal the weaknesses of replacing the metal with a more earth-abundant one, and the challenges that need to be overcome to realize high-performance 3d transition metal chromophores.

Supporting Information

Supporting Information: Experimental details and methods, ^1H NMR of the substance measured, additional global analysis, and additional computational data on the compound (PDF).

Author Information

Corresponding Author

* Josh Vura-Weis – Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States; <http://orcid.org/0000-0001-7734-3130>; Email: vuraweis@illinois.edu

Authors

Justin Malme – *Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States*

Jenelle N. Weaver – *Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States*

Gregory S. Girolami – *Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States; <http://orcid.org/0000-0002-7295-1775>*

Notes. The authors declare no competing financial interest.

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Synopsis. The uneven coordination environment of *fac*-Co(ppy)₃ results in excited state bond rupture, leading to a short excited state lifetime in spite of its high ligand field.

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