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A Fe$^{II}$ Hexa N-Heterocyclic Carbene Complex with a 528 ps Metal-to-Ligand Charge-Transfer Excited-State Lifetime

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**ABSTRACT:** The iron carbene complex $[\text{Fe}^{\text{II}}(\text{btz})_3](\text{PF}_6)_2$ (where btz = 3,3'-dimethyl-1,1'-bis(p-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene)) has been synthesized, isolated and characterized as a low-spin ferrous complex. It exhibits strong metal-to-ligand charge transfer (MLCT) absorption bands throughout the visible spectrum, and excitation of these bands gives rise to a $^3$MLCT state with a 528 ps excited state lifetime in CH$_3$CN solution that is more than one order of magnitude longer compared to the MLCT lifetime of any previously reported Fe$^{\text{II}}$ complex. The low potential of the $[\text{Fe}(\text{btz})_3]^{3+}/[\text{Fe}(\text{btz})_3]^{2+}$ redox couple makes the $^3$MLCT state of $[\text{Fe}^{\text{II}}(\text{btz})_3]^{2+}$ a potent photoreductant that can be generated by light absorption throughout the visible spectrum. Taken together with our recent results on the $[\text{Fe}^{\text{III}}(\text{btz})_3]^{3+}$ form of this complex, these results show that the Fe$^{\text{II}}$ and Fe$^{\text{III}}$ oxidation states of the same Fe(btz)$_3$ complex feature long lived MLCT and LMCT states, respectively, demonstrating the versatility of iron N-heterocyclic carbene complexes as promising light-harvesters for a broad range of oxidizing and reducing conditions.

**TOC GRAPHICS**

Fe$^{\text{II}}$ hexa NHC carbene

$\tau(^3\text{MLCT}) = 528$ ps
KEYWORDS: iron(II), N-heterocyclic carbene, long-lived excited state, broad absorption, light harvesting, solar energy conversion

Transition metal complexes with long-lived charge transfer (CT) states\(^1\) are attractive light-harvesters, for solar-to-chemical, as well as solar-to-electricity\(^2,3\) energy conversion.\(^4\) The development of Earth-abundant metal complexes to replace rare and expensive elements, such as Ru, for photophysical and photochemical applications has been a longstanding effort.\(^5\) Iron is an obvious candidate, but traditional Fe\(^{II}\) polypyridyl complexes suffer from ultrafast deactivation of the \(^3\)MLCT excited states via high-spin (triplet and quintet) metal centered (\(^3/5\)MC) states, an effect of smaller ligand field splitting compared to corresponding complexes of its heavier metal congener Ru.\(^6,7,8,9,10,11,12,13,14,15\) Among other approaches\(^16,17,18,19\), recent progress on iron complexes has been spearheaded by the introduction of Fe\(^{II}\) light-harvesting complexes with strongly electron \(\sigma\)-donating N-heterocyclic carbene (NHC) ligands\(^20,21,22\), that has yielded \(^3\)MLCT excited state lifetimes up to a few tens of ps.\(^23,24\) Recently obtained \(^3\)MLCT excited state lifetimes for Fe\(^{II}\) complexes in solution (26 ps\(^25\)) and attached to an Al\(_2\)O\(_3\) surface (37 ps\(^26\)) are the longest \(^3\)MLCT excited state lifetimes reported to this date for any Fe\(^{II}\) complex.\(^23\)

Recently, we completely saturated the octahedral Fe center with six NHC-moieties in a homoleptic trisbidentate complex, Fe(btz)\(_3\).\(^27\) The strongly electron donating NHC ligand set favors the facile oxidation of the iron center in the synthetic procedure,\(^23\) yielding the Fe\(^{III}\) complex [Fe(btz)\(_3\)](PF\(_6\))\(_3\). This Fe\(^{III}\) hexa NHC complex was found to have the longest charge transfer excited-state lifetime involving an iron center hitherto reported of 100 ps, and is the first iron complex to exhibit room temperature photoluminescence involving the iron center.\(^27\)
Interestingly, the photophysics of this complex involves ligand-to-metal charge transfer (LMCT) excitations from a low-spin Fe$^{\text{III}}$ ground state to a $^2$LMCT excited state of the complex.

![Diagram](Image)

**Figure 1.** ChemDraw (left) and X-ray diffraction structure (right) of Fe(btz)$_3^{2+}$ with Fe in red, N in blue and C in grey. Hydrogen atoms and counter-ions are omitted for clarity.

Here we present results for the Fe$^{\text{II}}$ analogue, [Fe(btz)$_3$](PF$_6$)$_2$, of the Fe$^{\text{III}}$ complex [Fe(btz)$_3$](PF$_6$)$_3$, including the isolation and crystallization of the Fe$^{\text{II}}$ complex (**Figure 1**) as well as an investigation of its excited state dynamics by time-resolved spectroscopy, beyond the previously reported spectroelectrochemical characterization of in situ generated [Fe(btz)$_3$]$^{2+}$.27 We can now for the first time compare the properties of $^2$LMCT and $^3$MLCT excited states of the same iron complex in its Fe$^{\text{II}}$ and Fe$^{\text{III}}$ oxidation state, respectively.

The homoleptic iron-*tris*-btz complex [Fe(btz)$_3$](PF$_6$)$_2$ was obtained by diothionite reduction of [Fe(btz)$_3$](PF$_6$)$_3$ in deaerated CH$_3$CN.27 After removing the solvent and recrystallization, a dark-brown product was now isolated and fully characterized as the [PF$_6$]$^{-}$ salt of the homoleptic complex [Fe(btz)$_3$]$^{2+}$ by $^1$H, $^{13}$C,$^1$H nuclear magnetic resonance (NMR) spectroscopy in deaerated CD$_3$CN, elemental (CHN) analysis, and high resolution mass spectrometry (see SI).
[Fe(btz)₃](PF₆)₂ is completely stable in the solid state and in deaerated CH₃CN solution but is swiftly oxidized to the corresponding Fe³⁺ complex if the solution contains air.

X-ray quality crystals were obtained from the corresponding BPh₄⁻ complex (see SI). X-ray diffraction analysis of [Fe(btz)₃](BPh₄)₂ reveals that the structure of the Fe²⁺ complex is remarkably similar to that of the Fe³⁺ species; the carbene carbon atoms that form the first coordination shell around Fe²⁺ form a flattened octahedron where the Fe²⁺-C bonds are all in the range 1.91-2.01 Å (1.94 – 1.98 Å for the Fe³⁺ complex) and the bite angle C-Fe²⁺-C within the individual ligands range between 77.4° and 78.4° (79.0° – 79.3° for the Fe³⁺ complex).

**Figure 2.** Comparison of calculated excitations of [Fe(btz)₃]²⁺ using B3LYP*/6-311G(d,p)/CH₃CN (black vertical lines) and measured absorption spectrum (red) of [Fe(btz)₃]²⁺ in deaerated CH₃CN. UV part detailed in the inset.
The electronic absorption spectrum of [Fe(btz)$_3$]$^{2+}$ dissolved in deaerated CH$_3$CN is shown in Figure 2. Any contamination with the Fe$^{III}$ complex could be excluded by comparison to spectra obtained in situ through electrochemical or chemical (see SI) reduction of [Fe(btz)$_3$]$^{3+}$ (Reference 27).

**Figure 3.** Summary of the quantum chemically calculated energetics of [Fe(btz)$_3$]$^{2+}$ as obtained from B3LYP*/6-311G(d,p)/CH$_3$CN calculations, with parabolic energy surfaces sketched qualitatively as visual guides for discussion purposes (centre), together with absorption properties (left) as well as redox properties in deaerated CH$_3$CN (right) summarized schematically.

As recently reported, both [Fe(btz)$_3$]$^{3+}$ and [Fe(btz)$_3$]$^{2+}$ in CH$_3$CN exhibit strong absorption bands in the UV (**Figure 2, inset**), attributed to $\pi_{\text{btz}} - \pi^*_{\text{btz}}$ transitions ($\lambda_{\pi-\pi^*} = 304$ nm, 4 eV), while the lowest-lying visible absorption bands can be assigned to $d_{\text{Fe}} - \pi^*_{\text{btz}}$ MLCT and $\pi_{\text{btz}} - d_{\text{Fe}}$ LMCT transitions in the Fe$^{II}$ and Fe$^{III}$ oxidation states, respectively. The energy of the $\pi_{\text{btz}} - \pi^*_{\text{btz}}$
transition (4 eV) matches well with the sum of the $\pi_{btz} - d_{Fe}$ LMCT ($\lambda_{LMCT} = 540$ nm, 2.3 eV) and $d_{Fe} - \pi^{*}_{btz}$ MLCT energies ($\lambda_{MLCT} = 730$ nm, 1.7 eV) and are in reasonable agreement with the electrochemically determined potentials of the Fe(III/II) couple ($E_{1/2} = −0.58$ V versus Fc$^{+/0}$), the first ligand reduction ($E_{pc} = −2.38$ V versus Fc$^{+/0}$), and the first ligand oxidation process ($E_{pa} = 1.16$ V versus Fc$^{+/0}$).27 Further evidence for the assignment is provided by time-dependent density functional theory (TD-DFT) calculations. The calculated transitions are shown as black vertical lines in the absorption spectrum presented in Figure 2. The calculations readily characterize the 730 nm and 450 nm absorption bands as MLCT transitions from metal d-orbitals to the lowest and to higher lying btz $\pi^*$ orbitals, respectively (see SI).

To gain further insight into the electronic properties of $[\text{Fe(btz)}_3]^{2+}$, we have also calculated key excited state energies (details in SI). Figure 3 schematically shows the calculated energy minima of excited states relevant to the excited state cascade of $[\text{Fe(btz)}_3]^{2+}$, along a reaction coordinate defined by the average Fe-ligand distance. This allows comparisons to be made e.g. with the related $[(\text{bpy})\text{Fe(btz)}_2]^{2+}$ complex that we also recently investigated computationally (details in SI). For $[\text{Fe(btz)}_3]^{2+}$, a relaxed $^3\text{MLCT}$ state was identified with a calculated minimum energy ~1 eV above the ground state and geometry close to the ground state, suggesting that a $^3\text{MLCT}$ state should be experimentally observable. The calculations show that the relative energetics of the relevant excited states of $[\text{Fe(btz)}_3]^{2+}$ is not very different from $[(\text{bpy})\text{Fe(btz)}_2]^{2+}$. However, the optimized minimum of the $^3\text{MC}$ state of $[\text{Fe(btz)}_3]^{2+}$ is significantly more distorted along the Fe-ligand bond-length reaction coordinate compared to $[(\text{bpy})\text{Fe(btz)}_2]^{2+}$. This indicates that the hexa NHC environment provides an unusually strong ligand field for this Fe$^{II}$ complex, in accordance with the recent findings for $[\text{Fe}^{III}(\text{btz})_3]^{3+}$.21 All together, the computational predictions thus suggest the possibility to observe a comparatively long-lived $^3\text{MLCT}$ state for
[Fe(btz)$_3$]$^{2+}$ in relation to the growing series of Fe$^{II}$ NHC complexes with $^3$MLCT lifetimes on the 10’s of ps timescale. Additionally, the computational results of [Fe(btz)$_3$]$^{2+}$ suggest that the $^5$MC state is not energetically accessible for the deactivation cascade, so that this will not be a traditional spin-crossover (SCO) complex.

**FIGURE 4** (a) Visible to near-infrared femtosecond transient absorption spectra of [Fe(btz)$_3$](PF$_6$)$_2$ in deaerated CH$_3$CN at selected time points from 200 fs to 1 ns. Inverted absorption spectrum of [Fe(btz)$_3$] (PF$_6$)$_2$ in deaerated CH$_3$CN is shown as dashed black line. (b) Kinetics of [Fe(btz)$_3$](PF$_6$)$_2$ in deaerated CH$_3$CN at selected wavelengths (solid lines) and
corresponding fits (dashed lines) from global analysis, note that the time axis changes from
linear to logarithmic at 30 ps. (c) Species associated spectra SAS1 and SAS2 of [Fe(btz)$_3$](PF$_6$)$_2$
in deaerated CH$_3$CN obtained from global analysis to give the spectral components that describe
the temporal evolution of the TA spectrum (see text for details). Samples were excited with
800 nm pump pulses (max $5.5 \times 10^{14}$ photons cm$^{-2}$ pulse$^{-1}$).

The excited-state dynamics following excitation of the MLCT bands were investigated using
transient absorption (TA) spectroscopy. The transient absorption (TA) spectra recorded at
selected time delays following excitation at 800 nm are presented together with the inverted
ground state absorption spectrum in Figure 4a. The TA spectrum is well described by the ground
state bleach (GSB) overlaid with a strong excited state absorption (ESA) feature below ~425 nm
and a weaker ESA above ~450 nm. This weaker ESA reduces the GSB in the wavelength region
~450-750 nm, such that the measured TA spectrum exhibits a weaker bleach than just inversion
of the ground state absorption spectrum would suggest. Above ~900 nm, where there is very
little ground state absorption the TA spectrum is dominated by ESA. The transient spectra
undergo small spectral shifts on the few picosecond timescale, but are otherwise described by a
simultaneous decay of all transient features. Thus, the kinetics of the TA spectrum is fitted well
by a bi-exponential at all wavelengths as illustrated in Figure 4b, returning lifetimes of $3.6 \pm
0.4$ ps and $528 \pm 34$ ps. Since the short-lived exponential lifetime is not associated with any
ground state recovery (see SI, Figure S14), we can assume a sequential exponential model for
the excited state cascade. With this excited state model, global analysis (GA) of the TA yields
the two species associated spectra (SAS1 and SAS2) shown in Figure 4c. The characteristic
lifetimes of the two SAS are the same, $3.6$ ps and $528$ ps, as identified from the kinetic fits and
capture the complete decay of the transient signal.
At the instance of excitation, the transient spectrum is described by SAS1, which evolves with a 3.6 ps characteristic time constant into a transient spectrum described by SAS2, whose decay back to the ground state occurs with the 528 ps time constant. The interconversion of SAS1 to SAS2 results in a loss of the ESA centered at 420 nm, and the enhanced ESA contributions in the >550 nm region, leaving the red/NIR part of the ESA unchanged. Thus, the 3.6 ps spectral dynamics accounts for a decrease of ESA below 425 nm, and a blue-shift of the centroid of the observable part of that feature. Meanwhile the broad >550 nm ESA feature increases in intensity with the centroid also shifting somewhat towards the blue side of the spectrum. The 3.6 ps spectral dynamics captured by the SAS1→SAS2 transition is consistent with either initial vibrational cooling or excited state electronic transitions into lower-lying excited states, followed by a complete ground state recovery with a 528 ps lifetime. Based on previous results, we expect the initially excited \(^1\)MLCT state to undergo intersystem crossing into a \(^3\)MLCT state on the 20 fs time scale, giving rise to no significant changes in the TA spectrum, measured with the current time resolution of \(~100\) fs.

The 528 ps ground state recovery is the longest observed excited state lifetime for any iron carbene light-harvesting complex. From the broader perspective of iron complexes, an excited state lifetime of several hundred ps falls in an interesting intermediate time regime that could either be a, for iron, record long lived \(^3\)MLCT state, or a lower lying metal-centered state of either triplet (\(^3\)MC) or quintet (\(^5\)MC) multiplicity (reached through an electronic transition from the \(^3\)MLCT state). These possibilities have all been discussed in recent literature, and are therefore elaborated below.

The 528 ps species, associated with SAS2, has pronounced ESA features, both a strong feature in the blue, and a broad, weaker feature to the red of the GSB. Such ESA features are typically
associated with MLCT states, both in Fe$^{II}$ and Ru$^{II}$ centered systems.20,23,28,31,32 and is also consistent with a calculated manifold of $^3$MLCT states according to TD-DFT (see SI). The 3.6 ps spectral dynamics captured by SAS1 comprising a lowering and blue-shift of the <425 nm ESA feature, and an increase and blue-shift of the >550 nm ESA feature, is extremely similar to the 3.4 ps spectral dynamics of $[(bpy)Fe(CN)_4]^{2-}$ (bpy = 2,2'-bipyridyl) in CH$_3$CN, which was unambiguously assigned to vibrational cooling and solvation of a $^3$MLCT state by a combination of TA and transient x-ray spectroscopy28,30 (See SI). The observed spectral dynamics therefore fits very well with an assignment where the 528 ps lifetime species is a $^3$MLCT state, and the 3.6 ps dynamics is a combination of vibrational cooling and solvation within this state.

The $^5$MC state is energetically inaccessible according to the quantum chemistry (QC) calculations, and for all previously reported Fe$^{II}$-centered systems investigated by TA, SCO into a $^5$MC state is accompanied by a complete loss of all significant ESA features occurring on the few hundred femtosecond time scale20,29. Therefore, the observation that the excited state with a 528 ps lifetime has significant ESA features as evidenced by the 10 ps TA spectrum and SAS2 (Figure 4), combined with the observation that all spectral dynamics happen with a 3.6 ps characteristic lifetime, strongly suggests that the 528 ps component is very unlikely to correspond to decay of the $^5$MC state.

We finally consider the alternative assignment of the 528 ps state as a triplet metal centered ($^3$MC) state that would be energetically plausible judging from the QC calculations. The experimental investigation of the role of $^3$MC states in the deactivation of photoexcited iron complexes has emerged as a topic of significant current interest,16,17 including emerging capabilities to make definite spin assignments using ultrafast X-ray spectroscopic techniques.29,30 In Fe-centered systems, such $^3$MC states are typically spectroscopically elusive.
few- or sub-picosecond lifetime intermediate states in either light-induced spin-crossover, or ground state recovery. For Ru-centered systems however, excited \(^3\)MC states have recently been identified with TA, and have been shown to result in a complete decay of the ESA features in the blue part of the visible spectrum (< 450 nm). In \([\text{Fe(btz)}_3]^{2+}\) the <425 nm ESA feature is present from the instance of excitation, remaining throughout the excited state lifetime and is not present in the absorption spectrum of the oxidized ([Fe(btz)_3]\(^{3+}\)) species. There is also no indication of suitable TD-DFT calculated excited triplet states at the relaxed \(^3\)MC geometry to match the broad experimental >550 nm ESA feature (see SI). We therefore consider a long-lived \(^3\)MC state to be an unlikely candidate for the 528 ps excited state. It can furthermore be noted that the 528 ps component can only be associated with the \(^3\)MC state if the deactivation from the \(^3\)MLCT state is completed in 3.6 ps or faster. Such a short lifetime of the \(^3\)MLCT state would go against the available information for the expanding series of iron carbene complexes with \(^3\)MLCT lifetimes in the 10’s of ps range, in light of the strong σ-donation for the hexa NHC motif in the present complex. This conclusion is further supported by the calculated state energies and inferred potential energy surfaces shown in Figure 3. The calculated strong driving force of \(\sim 0.8\) eV for the \(^3\)MC→GS transition, also suggests that the lifetime of the \(^3\)MC state should not be significantly longer than the few-ps upper bound reported for both \([\text{Fe(bpy)(btz)}_2]^{2+}\) and \([\text{(bpy)Fe(CN)}_4]^{2-}\).

For the recently reported \([\text{Fe(btz)}_3]^{3+}\) (Reference 27), fluorescence could be detected as a result of the allowed LMCT→GS transition (τ = 100 ps, Φ = 3.5·10\(^{-4}\) in deaerated CH\(_3\)CN, at RT) and was an efficient marker of the state energy. For \([\text{Fe(btz)}_3]^{2+}\), the \(^3\)MLCT→GS is a spin forbidden transition, reducing the rate of photoluminescence by around two orders of magnitude and putting the expected quantum yield at around 10\(^{-5}\) close to that of e.g. \([\text{Ru(tpy)}_2]^{2+}\) (where tpy =
2,2’:6’,2”-terpyridine).\textsuperscript{33} This is below our detection threshold of around $10^{-4}$ for emission in the near IR. Therefore, attempts to measure emission from the $^3$MLCT state were unsuccessful. Nevertheless, all available results from experiments and calculations show that only the assignment of the 528 ps lifetime to the decay of the $^3$MLCT state is consistent with knowledge accumulated for many Fe-complexes of NHC-type.

In summary, with [Fe(btz)$_3$]$^{2+}$ we have achieved a more than tenfold longer $^3$MLCT lifetime (528 ps) than any previously reported (26 ps) for an iron complex in solution.\textsuperscript{25} Together with the 100 ps $^2$LMCT lifetime of its Fe$^{III}$ oxidation state\textsuperscript{27} the Fe(btz)$_3$ hexa-NHC motif hence represents an unprecedented example of long-lived charge transfer states with lifetimes in the 100’s of ps range in both the Fe$^{II}$ and Fe$^{III}$ oxidation state of the same complex. While the excited state energy of the $^3$MLCT state is rather low, about 1 eV, the low potential of the [Fe(btz)$_3$]$^{3+}$/[Fe(btz)$_3$]$^{2+}$ redox couple at -0.58 V vs. Fe$^{+}/0$ (Ref 27) nevertheless renders it a strong photoelectrode (E\textsubscript{o}(3+/2+*) ≈ -1.6 V vs. Fe$^{+}/0$; the excited $^3$MLCT state is ~1 eV over the ground state, vide supra) that can be generated by absorption of low energy photons up to the far red end of the visible spectrum. At the same time the $^2$LMCT state of the Fe$^{III}$ oxidation state is a very strong oxidant (E\textsubscript{o}(3+/2+*) ≈ 1.5 V vs. Fe$^{+}/0$; the $^2$MLCT exited state energy is 2.1 eV\textsuperscript{27}). Together, these findings demonstrate the remarkable ability of the NHC ligands to block the rapid deactivation of CT excited states via MC scavenger states in both Fe$^{II}$ and Fe$^{III}$ complexes resulting in greatly increased lifetimes of both $^3$MLCT and $^2$LMCT states, which may lead to applications as photosensitizers with very versatile excited state redox properties.

ASSOCIATED CONTENT

Supporting Information.
The Supporting Information is available free of charge on the ACS Publications website. Synthesis, x-ray diffraction, TA experiments and analysis and computational chemistry, including Figures S1-S19, Tables S1-S6 (PDF); X-ray crystallographic data for [Fe(btz)₃](PF₆)₂ (CIF)

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