Photophysical Integrity of the Iron(III) Scorpionate Framework in Iron(III)–NHC Complexes with Long-Lived $^{2}$LMCT Excited States

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ABSTRACT: Fe(III) complexes with N-heterocyclic carbene (NHC) ligands belong to the rare examples of Earth-abundant transition metal complexes with long-lived luminescent charge-transfer excited states that enable applications as photosensitizers for charge separation reactions. We report three new hexa-NHC complexes of this class: [Fe(brphtmeimb)$_2$]PF$_6$ (brphtmeimb $= \{(4$-bromophenyl)$_3$tris(3-methylimidazol-2-ylidene)borate$\}^{-}$, [Fe(meophtmeimb)$_2$]PF$_6$ (meophtmeimb $= \{(4$-methoxyphenyl)$_3$tris(3-methylimidazol-2-ylidene)borate$\}^{-}$, and [Fe(coohphtmeimb)$_2$]PF$_6$ (coohphtmeimb $= \{(4$-carboxyphenyl)$_3$tris(3-methylimidazol-2-ylidene)borate$\}^{-}$]. These were derived from the parent complex [Fe(phtmeimb)$_2$]PF$_6$ (phtmeimb $= \{phenyltris(3$-methylimidazol-2-ylidene)borate$\}^{-}$ by modification with electron-withdrawing and electron-donating substituents, respectively, at the 4-phenyl position of the ligand framework. All three Fe(III) hexa-NHC complexes were characterized by NMR spectroscopy, high-resolution mass spectroscopy, elemental analysis, single crystal X-ray diffraction analysis, electrochemistry, Mößbauer spectroscopy, electronic spectroscopy, magnetic susceptibility measurements, and quantum chemical calculations. Their ligand-to-metal charge-transfer ($^{2}$LMCT) excited states feature nanosecond lifetimes (1.6–1.7 ns) and sizable emission quantum yields (1.7–1.9%) through spin-allowed transition to the doublet ground state ($^{2}$GS), completely in line with the parent complex [Fe(phtmeimb)$_2$]PF$_6$ (2.0 ns and 2.1%). The integrity of the favorable excited state characteristics upon substitution of the ligand framework demonstrates the robustness of the scorpionate motif that tolerates modifications in the 4-phenyl position for applications such as the attachment in molecular or hybrid assemblies.

INTRODUCTION

The development of photosensitizers based on Earth-abundant, inexpensive, and nontoxic metals, with the goal of replacing the to-date widely used noble metals, has attracted a lot of interest in the field of coordination chemistry in recent years. Such research is motivated by the desire to use solar-energy conversion processes on a large scale. Until recently, the field of solar energy conversion based on coordination compounds has to a large degree focused on octahedral metal complexes of noble metals with low-spin 4d or 5d electronic configurations using different second and third row transition metals (TMs) including Ru(II), Re(I), Os(II), and Ir(III). The ligand field splitting in such transition metal complexes is inherently larger than that for the corresponding complexes containing first row TMs such as Cr, Mn, Fe, and Co. This shifts the metal-centered (MC) states to higher energies in the former case, which in turn results in slow deactivation of the photosensitive charge-transfer (CT) states. Together with the employment of π-accepting ligands such as 2,2-bipyridyl (bpy), in metal complexes involving 4d or 5d metal cations, this has led to the development of many metal complexes that have metal-to-ligand charge-transfer (MLCT) states lower than MC states in energy. This implies that, for the MLCT state, a state with demonstrated importance for photofunctional applications for metal complexes based on 4d and 5d metal cations, the deactivation of the excited state via the MC states is a concern only at elevated temperatures. Efficient intersystem crossing from 1MLCT states usually populates 3MLCT states that exhibit slow radiative and nonradiative relaxation to the ground state. Additionally, 4d and 5d metal complexes with π-accepting ligands display a relatively wide visible light absorption window and favorable
redox properties of the GS and the 3MLCT state. As a result, they are heavily featured in photophysical applications. In parallel, four-coordinate 5d complexes involving Pt(II) and Au(III) have also been investigated and successfully used in photophysical applications thanks to the strong ligand field connected to these third-row transition metals.

There have been some reports about photoactive Earth-abundant metal complexes, foremost from metal complexes containing TMs such as Cu(I), Cr(0), Mn(I/IV), and Co(III). The problem with first row transition metal complexes for photophysical applications in general is that the weak ligand field results in their MC states being relatively low in energy, providing a fast deactivation pathway and reducing the efficiency of the photofunctional MLCT states. For Fe(II) polypyridyl complexes, the most widely studied direct base metal analogues of the successful Ru-, Os- and Ir-polypyridyl photosensitizers, the MLCT states are deactivated on the 100 fs time scale to the low-lying MC states. McCusker and Heinze reported attempts to increase the MLCT excited state lifetime by employing ligands with increased bite angle and introducing π-accepting and/or push–pull moieties. Recently, McCusker reported a cage compound involving the Fe(II)(bpy)3 motif, exhibiting a 2.6 ps MLCT lifetime, the longest recorded to date for an iron polypyridine complex. However, the introduction of strongly σ-donating N-heterocyclic carbene (NHC) ligands in the field of photoactive iron complexes has significantly increased the excited state lifetime of Fe(II) MLCT states, reaching up to 528 ps. By increasing the ligand field strength, the MC states increase in energy, thus slowing down the deactivation of the MLCT state. The photophysical properties of Fe–NHC metal complexes have been further improved using different approaches. By employing the facial tridentate scorpionate pre-NHC ligand $\text{[phtmeimbH}_3\text{]}\text{(PF}_6\text{)}_2$ (where $\text{phtmeimbH}_3 = \{\text{hydridotris}(3\text{-methyl-1H-imidazol-3-i}m\text{-1-y}l)\text{borate}\}$), we synthesized the corresponding Fe(III) complex $\text{[Fe(phtmeimb)_2]}\text{PF}_6$ (where $\text{phtmeimb} = \{\text{phenyltris}(3\text{-methylimidazol-2-ylidene})\text{-borate}\}$). This complex showed an LMCT excited-state lifetime of 2 ns and an intense fluorescence with a 2.1% quantum yield, constituting the second example of room temperature photoluminescence from an iron complex. Further, the LMCT excited state was oxidatively and reductively quenched in bimolecular reactions using standard electron donors and acceptors, which was the first example of such quenching involving an iron charge-transfer state being demonstrated. Very recently, Therien synthesized an Fe–NHC–porphyrin conjugate that showed photoluminescence from a state with considerable MLCT contribution and Bauer found both MLCT and LMCT photoluminescence from photoexcited states of an Fe(III)–NHC-cyclometalated complex, as communicated in a preliminary report. In fact, there are only three examples of iron complexes with a nanosecond excited CT state lifetime outside the class of NHC complexes, namely, the Fe(II) complexes reported by Herbert involving strongly electron-donating amide ligands and the cyclometalated Fe(II) complex with a phenylphenanthroline framework reported by Berkfelf. Given the few examples of complexes with iron-based photoluminescence and/or long-lived iron-based CT states, it is clearly a challenging task to generate new iron-based complexes possessing photophysical properties that allow for efficient applications. However, there is an interest in modifying existing, promising iron NHC complexes, as described by the increase in reported Fe–NHC complexes from 2013 to date. Most new complexes are based on structural variations of the ligand framework of the first iron complex having a 3MLCT lifetime above 1 ps, the Fe–NHC complex $\text{[Fe(pbmi)}_3\text{]}\text{(PF}_6\text{)}_2$ (where pbmi = 1,1’-(pyridine-2,6-diyl)bis(3-methylimidazol-2-ylidene)). Here, we report the first series of modifications of $\text{[Fe(phtmeimb)_2]}\text{PF}_6$ with the purpose of finding possible structure–(photo)functional relationships based on the...
presence of electron-withdrawing and -donating substituents. To this end, the 4-position of the phenyl group present in the framework of the NHC scorpionate ligand \([\text{phtmeimbH}]^-\) was substituted with either bromo, carboxyl, or methoxy groups, respectively. The resulting Fe(III) complexes \([\text{Fe} \text{(brphtmeimb)}_2] \text{PF}_6\), \([\text{Fe} \text{(meophtmeimb)}_2] \text{PF}_6\), and \([\text{Fe} \text{(coohphtmeimb)}_2] \text{PF}_6\) are shown in Figure 1. The 4-phenyl position was chosen, as it constitutes an obvious point of further functionalization when considering possibilities for application, for instance, for immobilization of the \([\text{Fe} \text{(phtmeimb)}_2] \text{PF}_6\) framework on a surface, allowing for potential photofunctional applications based on the \([\text{Fe} \text{(phtmeimb)}_2]^{2+}\) chromophore attached to semiconductors, such as dye-sensitized solar cells and photocatalysts.

### RESULTS AND DISCUSSION

#### Synthesis and Spectroscopic Characterizations

The tridentate facial pre-NHC ligands \([\text{brphtmeimbH}]^-\) and \([\text{coohphtmeimbH}]^-\) were synthesized and characterized by spectroscopic methods. The synthesis and spectroscopic characterization of the Fe(III) complexes are shown in Scheme 1. The complexes were characterized by magnetization, EPR, and Mössbauer spectroscopy, as shown in Table 1.

**Table 1. Magnetization, EPR, and Mössbauer Results Used to Assign the Spin State of the Investigated Compounds**

| Complex                        | Magnetization | EPR           | Mössbauer (CS and QS), mm/s |
|--------------------------------|---------------|---------------|----------------------------|
| \([\text{Fe} \text{(phtmeimb)}_2]^{2+}\) | \(S = \frac{1}{2}\) \(g \approx 2.00\) | No Signal     | \((-0.090\) and \(1.539)\); low spin \(S = \frac{1}{2}\) |
| \([\text{Fe} \text{(brphtmeimb)}_2]^+\)    | \(S = \frac{1}{2}\) \(g \approx 2.00\) | No Signal     | \((-0.081\) and \(1.666); low spin \(S = \frac{1}{2}\) |
| \([\text{Fe} \text{(meophtmeimb)}_2]^+\)    | \(S = \frac{1}{2}\) \(g \approx 2.00\) | No Signal     | \((-0.089\) and \(1.620); low spin \(S = \frac{1}{2}\) |
| \([\text{Fe} \text{(coohphtmeimb)}_2]^+\)    | \(S = \frac{1}{2}\) \(g \approx 2.00\) | No Signal     | \((-0.056\) and \(1.595); low spin \(S = \frac{1}{2}\) |

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Figure 2. scXRD Molecular structures of \([\text{Fe} \text{(phtmeimb)}_2] \text{PF}_6\) (a), \([\text{Fe} \text{(brphtmeimb)}_2] \text{PF}_6\) (b), \([\text{Fe} \text{(meophtmeimb)}_2] \text{PF}_6\) (c), and \([\text{Fe} \text{(coohphtmeimb)}_2] \text{PF}_6\) (d). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms, counterions, and solvent molecules are omitted for clarity. Fe = orange; B = purple; N = blue; C = gray; Br = brown; O = red.

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Table 2. Steady State Photophysical Properties Including the Absorption Maximum (Abs max), Its Full Width at Half-Maximum (FWHM), the Peak Extinction Coefficient (ε), the Emission Maximum (Em max), Its FWHM, the Emission Quantum Yield (ϕ), and Finally the 0–0 Energy (E₀₀) of All Complexes Discussed in This Report

| Substituent                        | Abs max (nm/eV) | Abs fwhm (eV) | Ext coeff (M⁻¹ cm⁻¹) | Em max (nm/eV) | Em fwhm (eV) | ϕ (%) | E₀₀ (eV) |
|-----------------------------------|-----------------|---------------|----------------------|----------------|--------------|-------|---------|
| [Fe(phtmeimb)]PF₆               | 502/2.47        | 0.58          | 3000                 | 655/1.89       | 0.43         | 2.1   | 2.14    |
| [Fe(brphtmeimb)]PF₆             | 508/2.44        | 0.60          | 3500                 | 658/1.88       | 0.43         | 1.8   | 2.13    |
| [Fe(meophtmeimb)]PF₆            | 503/2.74        | 0.59          | 3600                 | 658/1.88       | 0.43         | 1.7   | 2.13    |
| [Fe(coohphtmeimb)]PF₆           | 505/2.46        | 0.58          | 3100                 | 661/1.88       | 0.43         | 1.9   | 2.14    |

*Defined as where the derivative of the spectrum with respect to wavelength is zero. bData from ref 23.
orbital degeneracy of the $t_{2g}$ orbitals expected for these close-to-octahedral structures will also make the electronic $g$-factor very sensitive to vibronic couplings. This can contribute to the minor differences observed in the susceptibilities but, more importantly, will also provide a mechanism for very system dependent broadening of EPR signals. For temperature-coded data, see Supporting Information section S5 and Figures S15–S17.

The EPR spectra of $[\text{Fe(brphtmeimb)}]_2\text{PF}_6$, $[\text{Fe(mephtmeimb)}]_2\text{PF}_6$, and $[\text{Fe(coohphtmeimb)}]_2\text{PF}_6$ do not show any EPR signal at X-band frequencies, in either perpendicular or parallel mode (for details, see Supporting Information Figure S18), areas of different Fe valencies are presented in a $QS$ vs $CS$ (at 80 K) diagram for other Fe-carbenes. The asymmetries of the Fe(III) doublet found at 80 K can furthermore be explained on the basis of magnetic relaxation effects and a negative sign of $QS$. The relaxation time of the magnetic moment (in fact, the Mößbauer effect detects the magnetic hyperfine field acting at the Fe nucleus) of the Fe(III) ion at 80 K is comparable to the observation time $\tau$ of the Mößbauer effect. The observation time $\tau$ corresponds to the mean lifetime of the nuclear excited level, in the case of $^{57}$Fe spectroscopy to $\sim 70$ ns. Magnetization, EPR, and Mößbauer results used to assign the spin state of the investigated compounds are summarized in Table 1.

**Steady State Spectroscopy.** The steady state absorption spectra of $[\text{Fe(brphtmeimb)}]_2\text{PF}_6$, $[\text{Fe(mephtmeimb)}]_2\text{PF}_6$, and $[\text{Fe(coohphtmeimb)}]_2\text{PF}_6$ are very similar to the parent complex $[\text{Fe(phtmeimb)}]_2\text{PF}_6$. In Supporting Information Figure S20, areas of different Fe valencies are presented in a $|QS|$ vs $CS$ (at 80 K) diagram for other Fe-carbenes. The asymmetries of the Fe(III) doublet found at 80 K can furthermore be explained on the basis of magnetic relaxation effects and a negative sign of $QS$. The relaxation time of the magnetic moment (in fact, the Mößbauer effect detects the magnetic hyperfine field acting at the Fe nucleus) of the Fe(III) ion at 80 K is comparable to the observation time $\tau$ of the Mößbauer effect. The observation time $\tau$ corresponds to the mean lifetime of the nuclear excited level, in the case of $^{57}$Fe spectroscopy to $\sim 70$ ns. Magnetization, EPR, and Mößbauer results used to assign the spin state of the investigated compounds are summarized in Table 1.
Table 3. Electrochemical and UV–vis Spectroscopic Data

| Complex                      | E/V                       | λmax/nm (ε/10⁴ M⁻¹ cm⁻¹) |
|------------------------------|---------------------------|---------------------------|
|                              | n = 0(Fe(II), MLCT)       | n = 1(Fe(III), LMCT)      | n = 2(Fe(IV), LMCT)      |
| [Fe(phtmeimb)]₂⁺            | -1.16                     | 348 (10.8)                | 715 (6.8)                |
| [Fe(bbrphtmeimb)]₂⁺         | -1.14                     | 352 (12.8)                | 715 (8.9)                |
| [Fe(moephtmeimb)]₂⁺         | -1.19                     | 363 (13.5)                | 716 (10.1)               |
| [Fe(coohphtmeimb)]₂⁺        | -1.13                     | 361 (13.9)                | 717 (8.1)                |

*In acetonitrile with 0.1 M N(α-buty)PF₆ vs Fc. *½Wave potential (CV). *Peak potential (DPV).
oxidation of [Fe(meophtmeimb)$_2$]PF$_6$ in combination with the marginal effects on the metal couples. Also, the MLCT bands of the Fe(II) complexes are rather similar in energy. This places the potentials for ligand reduction involved in the electronic excitation in all cases well below the lower limit of the potential window, while electrochemical reduction of [Fe(brphtmeimb)$_2$]$^{n+}$ can be observed already at $-2.3$ V.

These results support the notion that the observed electrochemical ligand oxidation and reduction processes are not involved in the spectroscopic transitions if they are essentially localized on the phenyl rings as one might anticipate in particular for ligand oxidation of [Fe(meophtmeimb)$_2$]$^{n+}$ and ligand reduction of [Fe(brphtmeimb)$_2$]$^{n-}$.

**Figure 6.** UV−vis spectroelectrochemistry of [Fe(brphtmeimb)$_2$]PF$_6$ (red line) in acetonitrile ($0.1 \text{ M N}(n\text{-butyl})_4\text{PF}_6$). Left: Reduction at $-1.44$ V generating [Fe(brphtmeimb)$_2$] (blue line). Right: Oxidation at $0.76$ V generating [Fe(brphtmeimb)$_2$]$^{2+}$ (blue line).

**Figure 7.** UV−vis spectroelectrochemistry of [Fe(meophtmeimb)$_2$]PF$_6$ (red line) in acetonitrile ($0.1 \text{ M N}(n\text{-butyl})_4\text{PF}_6$). Left: Reduction at $-1.44$ V generating [Fe(meophtmeimb)$_2$] (blue line). Right: Oxidation at $0.76$ V generating [Fe(meophtmeimb)$_2$]$^{2+}$ (blue line).

**Figure 8.** UV−vis spectroelectrochemistry of [Fe(coohphtmeimb)$_2$]PF$_6$ (red line) in acetonitrile ($0.1 \text{ M N}(n\text{-butyl})_4\text{PF}_6$). Left: Reduction at $-1.44$ V generating [Fe(coohphtmeimb)$_2$] (blue line). Right: Oxidation at $0.76$ V generating [Fe(coohphtmeimb)$_2$]$^{2+}$ (blue line).
Transient Absorption (TA) Spectroscopy. The transient absorption (TA) spectra of \([\text{Fe(phtmeimb)}_2]\text{PF}_6\), \([\text{Fe(brphtmeimb)}_2]\text{PF}_6\), \([\text{Fe(meophtmeimb)}_2]\text{PF}_6\), and \([\text{Fe(coohphtmeimb)}_2]\text{PF}_6\) in acetonitrile recorded 100 ps after excitation in the 2LMCT band at \(\sim 500\) nm are shown in Figure 9a. The TA spectra of all complexes share the same spectral features, and the selected time delay is representative for showing the fully developed spectra that later only decay. At 500 nm, the ground state bleach (GSB) region is overwhelmed by excited state absorption (ESA). The pronounced ESA below 450 nm is in line with the LMCT assignment and the corresponding absorption of the Fe(II) ground state (see Figures 6–8). Additional ESA with a peak around 580 nm and the broad absorption in the red and near-infrared region can be attributed to the NHC ligand radical with the superimposed stimulated emission signal peaking around 700 nm. The stimulated emission dynamics unambiguously reports on the evolution of the emissive excited state population. For \([\text{Fe(brphtmeilm)}_2]\text{PF}_6\), the selected kinetics at the before mentioned wavelengths are shown in Figure 9b; all kinetics follow the same exponential decay. The kinetics for the other complexes are shown in Supporting Information Figures S25 and S26.

### Table 4. Collected Photophysical Properties Including the Emission Quantum Yield (\(\phi\)), Excited State Lifetime (\(\tau\)), Radiative Decay Rate (\(k_r\)), and Non-Radiative Decay Rate (\(k_{nr}\)) of All Complexes Discussed in This Report

| Complex                              | \(\phi\) (%) | \(\tau\) (ns) | \(k_r(10^7 \text{ s}^{-1})\) | \(k_{nr}(10^8 \text{ s}^{-1})\) |
|---------------------------------------|--------------|---------------|------------------------------|-----------------------------|
| \([\text{Fe(phtmeimb)}_2]\text{PF}_6\) | 23           | 2.1           | 2.0                          | 1.1                         |
| \([\text{Fe(brphtmeimb)}_2]\text{PF}_6\) | 1.8          | 1.7           | 1.7                          | 1.1                         |
| \([\text{Fe(meophtmeimb)}_2]\text{PF}_6\) | 1.7          | 1.7           | 1.7                          | 1.0                         |
| \([\text{Fe(coohphtmeimb)}_2]\text{PF}_6\) | 1.9          | 1.6           | 1.6                          | 1.2                         |

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Figure 9. (a) Measured TA spectra at 100 ps of \([\text{Fe(phtmeimb)}_2]\text{PF}_6\), \([\text{Fe(brphtmeimb)}_2]\text{PF}_6\), \([\text{Fe(meophtmeimb)}_2]\text{PF}_6\), and \([\text{Fe(coohphtmeimb)}_2]\text{PF}_6\) in acetonitrile compared. The data has been chirp and background corrected and cut to remove excitation (\(\sim 500\) nm) scatter. (b) Kinetics at selected wavelengths of \([\text{Fe(brphtmeimb)}_2]\text{PF}_6\) also including the single exponential fit from global analysis (measured data is shown as symbols and the fit as solid lines). The kinetics for the other complexes are shown in Supporting Information Figures S25 and S26.
are thus very similar to the 2 ns previously reported for the parent complex [Fe(phtmeimb)₂]PF₆.¹³ Based on the quantum yield and the lifetime of the excited state, the substituents of [Fe(phtmeimb)₂]PF₆ have very minor effects on both radiative and nonradiative decay pathways (Table 4). (The nonradiative decay rate is increased from 5.0 × 10⁶ s⁻¹ for [Fe(phtmeimb)₂]PF₆ to ~6 × 10⁸ s⁻¹ for the substituted complexes.) Since the energetic positions of the MC states are very similar for all complexes (based on quantum chemical calculations, see Supporting Information section S11), the accelerated nonradiative decay of the substituted complexes could be due to faster internal conversion directly from the ²LMCT excited state to the ground state. The change in photophysical properties, however, is only minor, which means that introducing substituents to the [Fe(phtmeimb)₂]PF₆ framework still preserves strong photoluminescence from the ²LMCT state with an ~2 ns lifetime.

**Quantum Chemical Calculations.** Key points on the potential energy surfaces of [Fe(phtmeimb)₂]⁺⁺ as well as [Fe(brphtmeimb)₂]⁺⁺, [Fe(mephtmeimb)₂]⁺⁺, and [Fe(coohphtmeimb)₂]⁺⁺ congeners were calculated by using unrestricted density functional theory (DFT). For brevity and due to the close similarity between the different studied molecules, only the [Fe(brphtmeimb)₂]⁺⁺ energy profile has been plotted in Figure 10. The quantum chemical results reveal a doublet ground state (²GS) and quartet (⁴MC) and hextet states (⁶MC) stable under phenyl group functionalization following the same energy trend as previously reported for [Fe(phtmeimb)₂]⁺⁺.²³ The calculated spin density for the doublet ground state of all the investigated complexes is found to be mainly located on the metal and carbene lone pairs, as shown for [Fe(brphtmeimb)₂]⁺⁺ in Figure 10. Overall, the results from the quantum chemical calculations highlight the similarity of the electronic structure properties across the full series of complexes, including the lack of involvement of the phenyl-based moieties, which is consistent with the overall observed lack of electronic communication between the metal center and the side groups. The spin density on the metal in the relaxed quartet and hextet states indicates the same metal center nature of these states for the three iron carbene derivatives. All spin densities for [Fe(phtmeimb)₂]⁺⁺ and congeners are displayed in Supporting Information Table S8. The relaxed ground state geometries of the three iron complexes are in good agreement with the reported X-ray structures. The average iron–carbene distances are also reported in Supporting Information Tables S8–S12 for all complexes and suggest unremarkable structural changes due to addition to bromide, methoxy, or carboxylic groups in the 4-position of the phenyl.

**CONCLUSION**

In conclusion, for the triad [Fe(brphtmeimb)₂]PF₆, [Fe(mephtmeimb)₂]PF₆, and [Fe(coohphtmeimb)₂]PF₆ that are building on the parent compound [Fe(phtmeimb)₂]PF₆ containing the scorpionate ligand phtmeimb⁻, the substitution of the latter in the 4-phenyl position with either −Br, −OMe, or −COOH substituents did not result in any significant changes of the ground state properties such as geometry and magnetic properties, however adding three new iron complexes with ns lifetime and visible photoluminescence to the existing very small library of such complexes. Electrochemistry and quantum chemistry calculations indicate weak electronic communication between the phenyl moiety of the scorpionate ligand and the iron center, leading to only marginal electrochemical shifts between the complexes. The essentially identical charge-transfer absorption bands of the three complexes in their Fe(II), Fe(III), and Fe(IV) states, further suggest that the spectroscopically relevant ligand orbitals do not extend over the phenyl moieties. Importantly, the ²LMCT excited state of the substituted Fe(III) complexes not only retains the excited state energy but also shows only modestly reduced emission quantum yields and excited state lifetimes relative to the parent complex. This demonstrates that the favorable photophysical properties, characteristic of the parent complex, could be exploited in prospective photoactive assemblies with the 4-phenyl position as an attachment point. Our results reveal remarkably small effects of both electron-donating substituents on the ground and excited state properties, thereby demonstrating that the [Fe(phtmeimb)₂]PF₆ motif should tolerate a wide range of modification for the above purposes without loss of the favorable photofunctionalities.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02410. Synthesis, ¹H and ¹³C NMR spectra, HR-MS spectra, single crystal X-ray diffraction, magnetic susceptibility and magnetization measurements, Mößbauer spectroscopy, electron paramagnetic resonance measurements, steady state spectroscopy, steady state absorption, steady state emission, transient absorption spectroscopy,
TCSPC data, and quantum chemistry, including figures and tables (PDF)

Accession Codes
CCDC 2046060–2046062 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

REFERENCES

1. (a) Bozic-Weber, B.; Constable, E. C.; Housecroft, C. E. Light harvesting with Earth abundant d-block metals: Development of sensitizers in dye-sensitized solar cells (DSCs). Coord. Chem. Rev. 2013, 257, 3089–3106.

2. Balzani, V.; Credi, A.; Venturi, M. Photochemistry and photophysics of coordination compounds: An extended view. Coord. Chem. Rev. 1998, 171, 3–16.

3. Ford, P. C. From curiosity to applications. A personal perspective on inorganic photochemistry. Chem. Sci. 2016, 7, 2964–2986.

4. (a) Wengert, O. S. Photoactive Complexes with Earth-Abundant Metals. J. Am. Chem. Soc. 2018, 140 (42), 13522–13533. (b) Wengert, O. S. A bright future for photosensitizers. Nat. Chem. 2020, 12, 323–324. (c) Zhang, Y.; Schulz, M.; Wächtler, M.; Kernahl, M.; Dietzek, B. Cu(ii) vs. Ru(ii) photosensitizers: elucidation of electron transfer processes within a series of structurally related complexes containing an extended π-system. Coord. Chem. Rev. 2018, 356, 127–146.

5. (a) Wengert, O. S. Photoactive Complexes with Earth-Abundant Metals. J. Am. Chem. Soc. 2018, 140 (42), 13522–13533. (b) Wengert, O. S. A bright future for photosensitizers. Nat. Chem. 2020, 12, 323–324. (c) Zhang, Y.; Schulz, M.; Wächtler, M.; Kernahl, M.; Dietzek, B. Cu(ii) vs. Ru(ii) photosensitizers: elucidation of electron transfer processes within a series of structurally related complexes containing an extended π-system. Coord. Chem. Rev. 2018, 356, 127–146.

6. (d) Kauflord, S.; Rosemann, N. W.; Chábera, P.; Lindh, L.; Losada, L. B.; Uhlig, J.; Pascher, T.; Strand, D.; Wärnmark, K.; Yartsev, A.; Persson, P. Micr0second Photoluminescence and Photoreactivity of a Metal-Centered Excited State in a Hexacarbene–Co(III) Complex. J. Am. Chem. Soc. 2021, 143 (5), 1307–1312. (e) Hockin, B. M.; Li, C.; Robertson, N.; Zysman-Colman, E. Photoxidation catalysts based on earth-abundant metal complexes. Catal. Sci. Technol. 2019, 9, 889–915. (f) Cheung, K. P. S.; Sarkar, S.; Gevorgyan, V. Visible Light-Induced Transition Metal Catalysis. Chem. Rev. 2022, 122 (2), 1543–1625. (g) Wegeberg, C.; Häussinger, D.; Wenger, O. S. Pyrene–Decoration of a Chromium(0) Tris(disocyanide) Enhances Excited State Delocalization: A Strategy to Improve the Photoluminescence of 3d6Metal Complexes. J. Am. Chem. Soc. 2021, 143 (38), 15800–
(18) Reuter, T.; Kruse, A.; Schoch, R.; Lochbrunner, S.; Bauer, M.; Heinze, K. Higher MLCT lifetime of carbene iron(II) complexes by chelate ring expansion. Chem. Commun. 2021, 57, 7541–7544.

(19) Nair, S. S.; Bykowski, O. A.; Kupfer, S.; Wächter, M.; Winter, A.; Schubert, U. S.; Dietzek, B. Excitation Energy-Dependent Branching Dynamics Determines Photostability of Iron(II)–Mesionic Carbene Complexes. Inorg. Chem. 2021, 60 (12), 9157–9173.

(20) Becker, M.; Wyss, V.; Housecroft, C. E.; Contable, E. C. The influence of alkyl chains on the performance of DSCs employing iron(II) N-heterocyclic carbene sensitizers. Dalton Trans. 2021, 50, 16961–16969.

(21) Karpacheva, M.; Wyss, V.; Housecroft, C. E.; Contable, E. C. There is a Future for N-Heterocyclic Carbene Iron(II) Dyes in Dye-Sensitized Solar Cells: Improving Performance through Changes in the Electrolyte. Materials 2019, 12 (24), 4181.

(22) Forshaw, A. P.; Bontchev, R. P.; Smith, J. M. Oxidation of the Tris(carbene)borate Complex PhB(MeIm)2Mn(CO)3 to Mn2[PhB-(MeIm)]3(OTf). Inorg. Chem. 2007, 46 (10), 3792–3794.

(23) Kernbach, U.; Ramm, M.; Luger, P.; Fehlhammer, W. P. A Chelating Triscarbene Ligand and Its Hexacarbene Iron Complex. Angew. Chem., Int. Ed. Engl. 1996, 35, 310–312; Angew. Chem. 1996, 108, 333–335.

(24) Chábera, P.; Kjaer, K. S.; Kaul, N.; Prakash, O.; Chábera, P.; Rosemann, N. W.; Honarfar, A.; Gordivska, O.; Fredin, L. A.; Bergquist, K.; Hägström, L.; Ericsson, T.; Lindh, L.; Yartsev, A.; Styring, S.; Huang, P.; Uhlig, J.; Bendix, J.; Strand, D.; Sundström, V.; Persson, P.; Lomoth, R.; Wärnmark, K. Luminescence and reactivity of a charge-transfer excited iron complex with nanosecond lifetime. Science 2019, 363, 249–253.

(25) Chábera, P.; Kjaer, K. S.; Prakash, O.; Honarfar, A.; Liu, Y.; Fredin, L. A.; Harlang, T. C. B.; Lidin, S.; Uhlig, J.; Sundström, V.; Lomoth, R.; Persson, P.; Wärnmark, K. Fe6 Hexa N-Heterocyclic Carbene Complex with a S28 ps Metal-to-Ligand Charge-Transfer Excited-State Lifetime. J. Phys. Chem. Lett. 2018, 9 (3), 459–463.

(26) Jiang, T.; Bai, Y.; Zhang, P.; Han, Q.; Mitzi, D. B.; Therien, M. J. Electronic structure and photophysics of a supermolecular iron(III) complex with 100-ps ligand-to-metal charge transfer photoluminescence. Nature 2017, 543, 695–699.

(27) (a) Zimmer, P.; Müller, P.; Burkhardt, L.; Schepper, R.; Neuba, A.; Steube, J.; Dietrich, F.; Flörke, U.; Mangold, S.; Gerhards, M.; Bauer, M. N-Heterocyclic Carbene Complexes of Iron as Photosensitizers for Light-Induced Water Reduction. Eur. J. Inorg. Chem. 2017, 2017, 1504–1509. (b) Dierks, P.; Vukadinovic, Y.; Bauer, M. Photoactive iron complexes: more sustainable, but still a challenge. Inorg. Chem. Front. 2022, 9, 206–220.
1144−1150. (b) Larsen, C. B.; Braun, J. D.; Lozada, I. B.; Kunnus, K.; Biasin, E.; Kolodziej, C.; Burda, C.; Cordones, A. A.; Gaffney, K. J.; Herbert, D. E. Reduction of Electron Repulsion in Highly Covalent Fe-Amido Complexes Counteracts the Impact of a Weak Ligand Field on Excited-State Ordering. J. Am. Chem. Soc. 2021, 143 (49), 20645−20656.

(29) Leis, W.; Argüello Cordero, M. A.; Lochbrunner, S.; Schubert, H.; Berkefeld, A. A Photoreactive Iron(II) Complex Luminophore. J. Am. Chem. Soc. 2022, 144 (3), 1169−1173.

(30) O'Regan, B.; Gratzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. Nature 1991, 353, 737−740.

(31) Sharma, K.; Sharma, V.; Sahrama, S. S. Dye-Sensitized Solar Cells: fundamentals and Current Statues. Nanoscale Res. Lett. 2018, 13, 381.

(32) Wang, D.; Niu, F.; Mortelliti, M. J.; Sheridan, M. V.; Sherman, B. D.; Zhu, Y.; McBride, J. R.; Dempsey, J. L.; She, S.; Dares, C. J.; Li, F.; Meyer, T. J. A stable dye-sensitized photoelectrosynthesis cell mediated by a NiO overlayer for water oxidation. Proc. Natl. Acad. Sci. U.S.A. 2020, 117, 12564−12571.

(33) Ni, M.; Leung, M. K. H.; Leung, D. Y. C.; Sumathy, K. A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. Renewable and Sustainable Energy Reviews 2007, 11, 401−425.

(34) (a) Griffith, J. S. The Theory of Transition-Metal Ions; Cambridge Univ. Press: 1964; Chapter 12. (b) Duelund, L.; Tofflund, H. Electron paramagnetic resonance characteristics of some non-heme low-spin iron(III) complexes. Spectrochim. Acta, Part A 2000, 56, 331−340.

(35) Gutlich, P.; Bill, E.; Trautwein, A. Mössbauer Spectroscopy and Transition Metal Chemistry; Springer-Verlag: Berlin, Heidelberg, 2011.

(36) Müller, C.; Pascher, T.; Eriksson, A.; Chábera, P.; Uhlig, J. KiMoPack: A python Package for Kinetic Modeling of the Chemical Mechanism. J. Phys. Chem. J. Phys. Chem. A 2022, 126 (25), 4087−4099.

■ NOTE ADDED AFTER ASAP PUBLICATION

This Article was published ASAP on October 24, 2022 with production errors. Chemical names have been updated in the Abstract, and Scheme 1 and the Supporting Information file have been replaced. The corrected version was reposted on October 26, 2022.