Impact of Ligand Substitutions on Multielectron Redox Properties of Fe Complexes Supported by Nitrogenous Chelates

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Supporting Information

ABSTRACT: Redox flow batteries (RFBs) have recently been recognized as a potentially viable technology for scalable energy storage. To take full advantage of RFBs, one possible approach for achieving high energy densities is to maximize a number of redox events by utilizing charge carriers capable of multiple one-electron transfers within the electrochemical window of solvent. However, past efforts to develop more efficient electrolytes for nonaqueous RFBs have mostly been empirical. In this manuscript, we shed light on design principles by theoretically investigating the effects of systematically substituting pyridyl moieties with imine ligands within a series of Fe complexes with some experimental validation. We found that such replacement is an effective strategy for reducing the molecular weight-to-charge ratios of these complexes. Simultaneously, calculations suggest that the reduction potentials and ligand-based redox activity of such substituted N-heterocyclic Fe compounds might be maintained within their +4 → −1 charge states. Additionally, by theoretically examining the role of coordination geometry, vis-à-vis reducing the number of redox noninnocent ligands within the first coordination sphere, we have demonstrated that Fe complexes with one such ligand were also capable of supporting multielectron reduction events and exhibited reduction potentials similar to their parent analogs supported by two or three of the same multidentate ligands. However, some differences in redox nature within the lower (+2 → −1) charge states were also noticed. Specifically, complexes containing two bidentate ligands, or one tridentate ligand, exhibited ligand-based reductions, whereas compounds with one bidentate ligand exhibited metal-centered reductions. The current results pave the way toward the design of the next-generation of Fe complexes with lower molecular weights and greater stored energy for redox flow batteries.

1. INTRODUCTION

Due to the implementation of a rational design scheme, in which power density is decoupled from energy density, redox flow batteries (RFBs) have recently been recognized as a potentially viable technology for scalable energy storage and hence may facilitate better utilization of renewable energy into grid-scale systems.1–3 All-vanadium RFBs, which are based on one-electron redox couples (VIII/VIII and V/V couples), represent the most advanced non-hybrid RFBs that are being commercialized.4–5 Due to the high price of vanadium and the temperature limited, low solubility of electroactive species, replacement of vanadium by cheaper metals represents one of the logical options with respect to more economically competitive RFBs. Another avenue that can potentially reduce the cost of the RFB and improve the efficiency of commercial RFBs is via the utilization of multielectron charge carriers, capable of operating within multiple charge states and storing/releasing multiple electrons. For instance, zinc–bromine hybrid RFBs are attractive for commercialization6,7 since they offer one of the highest cell voltages, due to the release of two electrons per atom of zinc, thus exhibiting high energy densities. However, due to their hybrid configuration, in which all of the energy of one half-reaction is stored in the zinc anode, power and energy storage are not completely decoupled, hence, one of the electrodes cannot be scaled easily by adding/increasing tank size. Therefore, to take full advantage of RFBs, one viable approach for achieving high energy densities is to use charge carriers capable of multiple one-electron transfers within the electrochemical window (EW) of the chosen solvent. In this work, we use MeCN as a solvent of choice due to its low viscosity, relatively low price, and wide EW (5.75 V), which is greater than that of water (1.23 V), thus providing us with an opportunity to access more charge states.

It has previously been shown that mononuclear, N-heterocyclic Fe complexes are capable of multielectron transfer...
events in common organic solvents holding some promise to be employed in a wide range of areas, from energy storage\textsuperscript{8−13} to photovoltaic cells.\textsuperscript{14−21} The inherent stability of these complexes in low charge states has been attributed to the chelate effect, their strong π-acceptance qualities, as well as strong σ-donation by the N-heterocyclic ligand.\textsuperscript{14,22−28} Mössbauer spectroscopy and density functional theory (DFT) studies have revealed that the redox noninnocence of 2,2′-bipyridine (Bpy) and 2,2′:6′:2″-terpyridine (Tpy) ligands is responsible for three of the four reductions within [Fe(Bpy)\textsubscript{3}]\textsuperscript{+} and [Fe(Tpy)\textsubscript{2}]\textsuperscript{+} (n = +3, +2, +1, 0, −1) electron-transfer series, respectively.\textsuperscript{29} In principle, understanding the effects of metal−ligand bonds and the nature of ligand noninnocence upon the redox properties of mononuclear, N-heterocyclic Fe complexes across their multiple electron-transfer series, could potentially shed light on design principles that will facilitate the discovery of next-generation charge carriers for RFBs with higher energy densities. It is therefore critical to understand the effects that these redox-active moieties have on multielectron events and their redox potentials within Fe complexes as a function of the number and nature of coordinated ligands that they contain.\textsuperscript{10} It is worth noting that efforts to develop better electrolytes for nonaqueous RFBs have mostly been empirical, from both theoretical and experimental perspectives, with limited attempts toward the rational design of structural, electronic, and other RFB-relevant properties.\textsuperscript{30−32} Aqueous all-iron RFBs are described elsewhere.\textsuperscript{33}

In this paper, we systematically investigated a series of bidentate and tridentate Fe complexes (Figure 1) with the aim of identifying complexes that are stable across multiple charge states as well as maximizing the electrochemical potential-to-mass ratios of such species. Since the cost of the battery is dominated by the cost of the electrolyte in large nonaqueous systems, any increase to the total amount of charge it can store per unit of electrolyte will be beneficial. By lowering the mass,\textsuperscript{59} we increase the potential-to-mass ratio, thus such systems hold promise for RFBs with higher energy densities. In this regard, we have computationally, and in some cases, experimentally, explored the effects of substituting pyridyl ligands with low-molecular-weight (MW) imine groups, as well as varying the number of redox noninnocent ligands within the first coordination sphere of a series of Fe complexes. It is important to note that in this work, we consider only thermodynamic properties of such species that determine the capacity of the RFBs. In principle, kinetics (reactivity kinetics or transport kinetics) may also impact the performance, but not the capacity of the RFBs. We found that replacing pyridine fragments with imine groups is an effective way to reduce the MW of complexes, whereas simultaneously maintaining redox properties as well as the stability of these metal−ligand complexes. Additionally, by replacing pyridine moieties with redox-innocent solvent molecules, we have identified the minimum number of redox noninnocent ligands required for such systems to maintain similar redox performance as in the original unsubstituted complexes, thus unveiling some basic principles that can be used to design low-MW charge carriers while maintaining redox property. Specifically, it is found that at least three pyridyl rings, two pyridyl rings in combination with one imine moiety, or one pyridyl ring combined with two other supporting imine fragments are necessary to promote a ligand-based reduction event within 0 and −1 charge states, while also maintaining Fe in its lower oxidation states, i.e., Fe\textsuperscript{1+} or Fe\textsuperscript{1+/0}.

**Figure 1.** Fe complexes with N-heterocyclic ligands considered in this study, n = +4 → −1.
2. VALIDATION OF THE RESULTS: THEORY VS EXPERIMENT

2.1. Published Works for Fe(Bpy)_3 and Fe(Tpy)_2. To verify that our computationally obtained structures exhibit correct electronic states, we have compared Mulliken spin densities and multiplicities of Fe(Bpy)_3 and Fe(Tpy)_2 complexes with previous experimental and theoretical studies on these compounds, which used Mössbauer spectroscopy and DFT calculations to determine the oxidation states of Fe within the [Fe(Bpy)_3]^n+ and [Fe(Tpy)_2]^n+ (n = +3, +2, +1, 0, −1) series. Overall, we found excellent agreement for the oxidation states of Fe within both series, albeit with small differences in spin multiplicities and electron localization patterns among ligands. Specifically, our DFT results for the [Fe(Bpy)_3]^n+ (n = +4 → −1) series revealed a more delocalized picture of the spin densities, which is due to the fact that we used a generalized gradient approximation functional, Perdew–Burke–Ernzerhof (PBE), in comparison with a hybrid functional, B3LYP, that was previously used. According to the PBE calculations, Bpy ligands almost equally shared an electron upon each reduction step, whereas the B3LYP results showed a more localized picture with a subsequent reduction of each Bpy ligand. High-level wavefunction-based calculations on the [Fe(Bpy)_3]^+ complex are in accordance with our DFT calculations, confirming a singlet ground state. While the ground state for [Fe(Bpy)_3]^0 species remains uncertain based on the Mössbauer spectroscopy results, our calculations showed that the triplet state of [Fe(Bpy)_3]^0 is more stable than the singlet state by 4.8 kcal/mol, although the oxidation states of Fe in both triplet and singlet is the same, i.e., 2+. Akin to the experimental results, our calculations showed that the doublet and quartet states of the [Fe(Bpy)_3]^+ complex are energetically indistinguishable (0.05 kcal/mol in favor of the doublet state). It is noteworthy that in both states the metal center exhibits the 2+ oxidation state, and the 0 → −1 redox step is a ligand-based reduction. Given the degenerate energies of the doublet and quartet states as well as that other analogous bidentate ([Fe(α-ImPy)_3] and Fe(DIIm)_3) and tridentate ([Fe(α-ImPy)_2 Bpy] and Fe(DIP)_3) ligand containing complexes exhibit high-spin ground electronic configurations in the −1 charge state (Table S1), we use the quartet state of [Fe(Bpy)_3]^+ in future discussions. According to our PBE calculations, oxidation states of Fe for the [Fe(Tpy)_2]^n+ (n = 0 → −1) complexes coincide with the previously reported ones. The only difference is observed for [Fe(Tpy)_2]^1−, wherein quartet state is found to be 2.3 kcal/mol more stable than the doublet state, though in both cases the metal exhibits 2+ oxidation state. Similarly to the [Fe(Bpy)_3]^n+ (n = +4 → −1) series, PBE results did not reveal localized spin density on each Tpy ligand upon reduction from +1 → −1, rather that the Mulliken spin density is delocalized between both Tpy ligands. It is noteworthy that the nature of all reduction events from +4 → −1 (either ligand-based or metal-based) was found to be similar regardless of the choice of functional for [Fe(Bpy)_3]^n+ and [Fe(Tpy)_2]^n+. It is important to point out that an earlier systematic investigation of electronic structures of various complexes containing bipyrindine ligands with transition metals showed that PBE functional correctly predicted electronic states of the Fe bipyridine-containing complexes, matching the results obtained from multireference CASSCF and NEVPT2 methods.

2.2. Theoretical and Experimental UV–Vis Absorption Spectra of [Fe(α-ImPy)_3]^2+ in This Work. To further validate our theoretical calculations, we compare the UV–vis absorption spectrum of the [Fe(α-ImPy)_3]^2+ complex, which was experimentally synthesized and characterized in this study, with the corresponding computed absorption spectrum shown in Figure 2. The experimental spectrum exhibits three absorption bands at 203, 234–244, and 275–286 nm (see Figure S1 for the UV–vis spectra at various concentrations). The simulated UV–vis spectrum has similar absorption band shapes and shows great agreement with the experimental data, matching the bands positions and the splittings between the corresponding peaks within 15 nm, as shown in Table 1.

Table 1. Comparison of the Theoretical and Experimental UV–Vis Spectra of the [Fe(α-ImPy)_3]^2+ Complex

|                  | averaged absorption maxima (nm) | theor. | exp. |
|------------------|---------------------------------|--------|------|
|                  | averaged absorption maxima (nm) |        |      |
|                  | 1                               | 207.6  | 203  |
|                  | 2                               | 237.2  | 239  |
|                  | 3                               | 269.8  | 280  |
| splittings between the bands (nm) | theor. | exp. |
| 1 → 2            | 29.6                            | 36     |
| 2 → 3            | 32.6                            | 41     |
| 1 → 3            | 62.2                            | 77     |

The low energy band (3) of [Fe(α-ImPy)_3]^2+ is assigned to metal-to-ligand excitations, whereas the other two higher energy bands (1, 2) mostly correspond to ligand-to-ligand charge transfers.

3. RESULTS AND DISCUSSION

3.1. Reduction Potentials. We have computed the reduction potentials for all complexes illustrated in Figure 1 and compared them with available experimental data for the charge states of +4 → +3, +3 → +2, +2 → +1, +1 → 0, and 0
Relative to $F_{c0}/F_{c+}$ in MeCN in the full theoretical range (+4 pyridine ($\text{con}$) experimental values. This excellent agreement between free Bpy are all within 0.3 V of their corresponding studies.37

Experimental reduction potentials were measured relative to the saturated calomel electrode (SCE) reference electrode in MeCN solution. Addition of Fc as an internal standard was found to slightly decrease these values by $\sim$0.38 V was applied.37

$\alpha$-ImPy)3, Fe(Bpy)3, Fe(Tpy)2 complexes within the +3 charge states because there is less ligand stabilization. As a substitution may increase the reduction potentials of the high capacitors, but imines have inferior $\sigma$-donating properties, such as pyridyl (Bpy) and terpyridine (Tpy).24,52 massive ligands, such as bipyridine (Bpy) and tridentate coordination compounds, respectively.37

Free ligand theoretical (experimental) 0 reduction potentials: DiIm $\sim$2.58, $\alpha$-imino pyridine ($\alpha$-ImPy) $\sim$2.60, Bpy $\sim$2.60 ($\sim$2.5036), 2,6-diimino pyridine (DIP) $\sim$2.48, $\alpha$-ImBpy $\sim$2.51, and Tpy $\sim$2.39. In this work, the experimental reduction potentials of Fe($\alpha$-ImPy)$_3$ were measured relative to Ag reference electrodes (BASI) filled with 0.01 M AgNO$_3$ or AgBF$_4$/MeCN solution. Addition of Fe as an internal standard was found to slightly decrease these values by $\sim$0.08 V, in agreement with previous studies.37

$\alpha$-ImPy),42 2,6-diimino pyridines (DIPs),43 similar redox-active properties.40 The substitution of pyridyl Pyridyl Moieties with Imine Groups.

The redox properties of these compounds, as is presented below in the example of such substitutions by imine groups and MeCN molecules.

3.2. Impact on Redox Properties upon Substituting Pyridyl Moieties with Imine Groups. Imine group, which possesses lower MW compared to pyridyl group, exhibits similar redox-active properties.30 The substitution of pyridyl moieties with imine groups may reduce mass of the charge carriers and hence the cost of commercial systems, since the cost of any RFB system scales with its mass.41,59 It has been previously demonstrated that molecules bearing imine groups, such as $\alpha$-imino pyridines ($\alpha$-ImPy),42 2,6-diimino pyridines (DIPs),43–46 and closely related ligands,26,47–51 exhibit similar properties to those of N-heterocycles comprised of more massive ligands, such as bipyrindine (Bpy) and terpyridine (Tpy).24,52–58 Given that these ligands have similar $\pi$-acceptor capacities, but imines have inferior $\sigma$-donating properties, such substitution may increase the reduction potentials of the high charge states because there is less ligand stabilization. As a result, higher OV values (determined as the sum of all redox potentials within the entire electron-transfer series) can be expected, and hence, greater energy density for RFBs. Also, the introduction of imine groups may be used for further functionalization of the complexes at the imine nitrogen atom that could be used to potentially increase solubility. Thus, in addition to lowering MW, such substitution gives experimentalists another knob to balance MW with solubility. The overall energy density of the battery is also dependent on the solubility. Currently, a systematic study on this topic is

| Table 2. Theoretical Reduction Potentials (in Volts) of the Ligands$^a$ and Fe Coordination Compounds Illustrated in Figure 1 Relative to $F_{c0}/F_{c+}$ in MeCN in the Full Theoretical range (+4 $\rightarrow$ −1)$^a$ |
|-----|-----|-----|-----|-----|-----|-----|
| compound | +4 $\rightarrow$ +3 | +3 $\rightarrow$ +2 | +2 $\rightarrow$ +1 | +1 $\rightarrow$ 0 | 0 $\rightarrow$ −1 | OV | MW red. (%) |
| Fe(DiIm)$_3$ | 3.28 | 1.24 | −0.96 | −1.80 | −2.87 | 10.15 | −40 |
| Fe($\alpha$-ImPy)$_3$ | 2.62 | 0.88 | −1.30 | −1.97 | −2.39 | 9.16 | −20 |
| Fe(Bpy)$_3$ | 2.38 | 0.78 | −1.47 | −1.90 | −2.48 | 9.01 | 0 |
| Fe(DiIm)$_3$(MeCN)$_2$ | 3.22 | 1.29 | −1.12 | −2.06 | −3.12 | 10.81 | −40 |
| Fe($\alpha$-ImPy)$_3$(MeCN)$_2$ | 2.97 | 1.40 | −1.57 | −2.12 | −2.73 | 10.79 | −27 |
| Fe(Bpy)$_2$(MeCN)$_2$ | 2.57 | 0.99 | −1.53 | −2.04 | −2.80 | 9.93 | −14 |
| Fe(DiIm)(MeCN)$_3$ | 3.36 | 1.47 | −1.35 | −2.18 | −2.68 | 11.04 | −41 |
| Fe($\alpha$-ImPy)(MeCN)$_3$ | 2.76 | 1.10 | −1.37 | −2.10 | −2.89 | 10.22 | −35 |
| Fe(Bpy)(MeCN)$_3$ | 2.76 | 1.37 | −1.69 | −2.14 | −2.67 | 10.63 | −28 |
| Fe(DIP)$_2$ | 2.68 | 1.13 | −1.10 | −1.85 | −2.65 | 9.41 | −27 |
| Fe($\alpha$-ImBpy)$_2$ | 2.46 | 0.99 | −1.24 | −1.86 | −2.53 | 9.08 | −13 |
| Fe(Tpy)$_2$ | 2.29 | 0.89 | −1.36 | −1.88 | −2.40 | 8.82 | 0 |
| Fe(DIP)(MeCN)$_3$ | 2.85 | 1.29 | −1.26 | −1.61 | −3.00 | 10.01 | −34 |
| Fe($\alpha$-ImBpy)(MeCN)$_3$ | 2.71 | 1.19 | −1.34 | −1.67 | −2.87 | 9.78 | −27 |
| Fe(Tpy)(MeCN)$_3$ | 2.53 | 1.19 | −1.48 | −1.69 | −2.73 | 9.62 | −21 |

$^a$OV denotes the total output voltage, determined as the sum of all redox potentials within the entire electron-transfer series. Italicized values denote experimental reduction potentials. MW red. denotes the percentage reduction in MW relative to Fe(Bpy)$_3$ and Fe(Tpy)$_2$ for all bidentate and tridentate coordination compounds, respectively.37

As shown in Table 2 and Figure 3, the theoretical reduction potentials of Fe($\alpha$-ImPy)$_3$, Fe(Bpy)$_3$, Fe(Tpy)$_2$, and free Bpy are all within 0.3 V of their corresponding experimental values. This excellent agreement between experimental and theoretical redox potential lends us confidence to explore the impact of ligand substitutions on the redox properties of these compounds, as is presented below in the example of such substitutions by imine groups and MeCN molecules.

$\rightarrow$ −1. As shown in Table 2 and Figure 3, the theoretical reduction potentials of Fe($\alpha$-ImPy)$_3$, Fe(Bpy)$_3$, Fe(Tpy)$_2$, and free Bpy are all within 0.3 V of their corresponding experimental values. This excellent agreement between experimental and theoretical redox potential lends us confidence to explore the impact of ligand substitutions on the redox properties of these compounds, as is presented below in the example of such substitutions by imine groups and MeCN molecules.

![Figure 3. Theoretical vs experimental reduction potentials of Fe($\alpha$-ImPy)$_3$, Fe(Bpy)$_3$, Fe(Tpy)$_2$, complexes within the +3 $\rightarrow$ −1 charge states and that of free Bpy ligand.](image-url)
being undertaken, and the results will be reported in future works.

To address the effects of ligand substitutions on the redox properties of the complexes, we employed Mulliken spin density analysis for all MeCN-free Fe coordination compounds depicted in Figure 1. In this analysis, compounds are grouped together by the type of the ligand coordinated to the metal center, in which pyridyl ligands are sequentially substituted by imine fragments, as shown in Figure 4.

Beginning with the analysis of complexes supported by three bidentate ligands, the average Mulliken spin densities on the Fe center and the bidentate ligands within the Fe(Bpy)$_3$, Fe(α-ImPy)$_3$, and Fe(Dilm)$_3$ compounds can be viewed in Figure 4a (tabulated values are shown in Tables S2–S4). According to these data, the Fe center is reduced in the $+4 \rightarrow +2$ steps, whereas primarily ligands get reduced in the $+2 \rightarrow −1$ steps for all complexes. The $+2$ charge state corresponds to the closed-shell low-spin ground state of a Fe$^{2+}$ system, hence the net Mulliken spin density is equal to zero. Considering the trends across the series, one can deduce the nature of the redox event (metal or ligand based) as well as identify the oxidation state of the metal center. Since a pyridyl group is a better $\pi$-donor than an imine group, at the highest charge state of $+4$, the fully substituted Fe(Dilm)$_3$ complex exhibits a rare oxidation state of $+4$ on Fe, whereas Fe(Bpy)$_3$ and Fe(α-ImPy)$_3$ show an intermediate oxidation state of Fe$^{3+/4+}$. For all three complexes, the oxidation state of the Fe center coincides with their charge states at $+3$ and $+2$, respectively. In contrast, it takes on an intermediate oxidation state of Fe$^{2+/1+}$ within the lower charge states from $+2$ to $−1$.

Although the pyridyl and imine functional groups exhibit similar $\pi$-acceptance capacities, Bpy ligands in Fe(Bpy)$_3$ possess slightly more spin density than the α-ImPy and Dilm ligands in Fe(α-ImPy)$_3$ and Fe(Dilm)$_3$, in their lowest ($−1$) charge states (0.91, 0.83, 0.73 spin densities on each ligand). Overall, we observe that the number of the redox events is preserved upon the pyridyl-to-imine substitution, as is the qualitative redox performance. In addition, complete ligand substitution decreases the MW by 20 and 40% in Fe(α-ImPy)$_3$ and Fe(Dilm)$_3$, respectively (Table 2), thus lowering the molecular weight-to-charge ratios and increasing the likelihood of meeting cost targets for RFBs. It is noted that these considerations of the MW apply only for the charge carriers, without accounting for masses of the counter ions and the solvent, which are present in the whole RFB systems. More importantly, such substitution increases the OV values by as much as 1.14 V (from 9.01 V in Fe(Bpy)$_3$ to 9.16 V in Fe(α-ImPy)$_3$ and to 10.15 V in Fe(Dilm)$_3$). In principle, such imine-substituted complexes may harvest/release more energy and subsequently increase the energy density of RFBs. Although not all redox events reported in the full theoretical range ($+4 \rightarrow −1$) can exist within the EW of MeCN (−3.25 to 2.5 V) versus Fe$^*/$Fc under current experimental conditions as compared to the previously reported $−2.6$ to $2.9$ V window, Figure S3), they can potentially be observed in MeCN solutions doped with 0.1 M ionic liquids (ILs), which can widen the EW of solution, as previously suggested.

Specifically, it was previously shown that the introduction of the trifluorotris-(pentafluoroethyl)phosphate-based ILs as supporting electrolyte in MeCN solution can expand the oxidative window by up to 0.8 V, thus providing an opportunity to investigate compounds that are known to oxidize at high potentials. In principle, using low concentration of ILs may help experimentalists access higher oxidation states without appreciable increase of the overall MW for RFB. These theoretical insights are currently being systematically evaluated and will be part of the future work.

By further analyzing complexes containing tridentate ligands, i.e., Fe(Tpy)$_2$, Fe(α-ImBpy)$_2$, and Fe(DIP)$_2$, we found that the trends in their reduction behavior, spin delocalization, and OV values closely match those of their tris-bidentate ligand counterparts (Figure 4b and Tables S5–S7). Mulliken spin density analysis indicates that primarily metal-centered reduction events occur within the $+4 \rightarrow +2$ steps of the electron-transfer series, whereas the ligands get reduced in the $+2 \rightarrow −1$ steps. Similar to the series of complexes containing bidentate ligands, the Bpy ligands possess a greater amount of spin than the Dilm and α-ImPy ligands, though this difference is much smaller in magnitude for the complexes containing tridentate ligands because they each bear at least one pyridyl group. As a result, in the highest charge state of $+4$, Fe exhibits an intermediate oxidation state of $+3/+4$, even for the fully substituted Fe(DIP)$_2$. On the other hand, within the lower charge states ($+2 \rightarrow −1$), the oxidation state of Fe is still in between the $+2$ and $+1$ values. It is noteworthy that upon pyridyl group substitution by an imine moiety, the OV values increase from 8.82 V in Fe(Tpy)$_2$ to 9.08 V in Fe(α-ImBpy)$_2$ and further to 9.41 V in Fe(DIP)$_2$. At the same time, the MW...
decreases by 13% in Fe(α-ImBpy)2 and 27% in Fe(DIP)2 relative to that of Fe(Tpy)2.

Comparing complexes with bidentate and tridentate ligands, it is evident that the completely imine (for pyridyl group)-substituted complexes of the former set not only have lower MWs, but larger OV values (10.15 vs 9.41 V), while still preserving all redox events and performance within the +4 → −1 charge states. Overall, in considering all six complexes mentioned above, it was found that the average spin densities on the imine and pyridyl groups in their corresponding Fe complexes are very similar within each charge state. Hence, we believe that the imine for pyridyl group substitution is a potentially useful approach for the design of efficient charge carriers with lower MWs.

3.3. Impact of Number of Redox Noninnocent Ligands on Redox Properties. As described above in the example of the pyridyl-to-imine substitution, lowering the MW by substituting heavier redox noninnocent ligands with lighter counterparts is a potentially promising approach to reduce cost of RFBs, increase their solubility, and hence improve their performance.

Figure 5. Average Mulliken spin densities on Fe, the imine group, and the pyridine group. The subplots are organized by the number of noninnocent ligands for: (a) DiIm complexes, (b) α-ImPy complexes, (c) Bpy complexes, (d) DIP complexes, (e) α-ImBpy complexes, and (f) Tpy complexes.
efficiency. To further explore the effects of this substitution, we attempt to answer two questions: “is it possible to further reduce the MW of such complexes?” and “what is the smallest number of the redox noninnocent ligands that are needed to maintain the same redox performance as in the parent species?” To answer these questions, we substitute the redox noninnocent ligands in the complexes presented in Figure 1 by redox-innocent ligands, i.e., MeCN molecules, which could coordinate to the metal center to form similar octahedral complexes. Through this theoretical exercise, substitution of the ligands by MeCN may shed light on understanding the possibility of keeping the same redox performance (number and type of redox events) in complexes with a reduced number of redox noninnocent ligands as well as determine the minimum possible number of such ligands required for desirable redox properties. Hence, we theoretically explored the redox behavior of various MeCN-coordinated species for all charge states from +4 to −1 (Figure 5). We assessed the changes in their geometries as well as the redox properties across the whole electron-transfer series in relation to their parent complexes. Coordination of MeCN molecules to the Fe center has already been reported for a number of Fe-complex crystal structures containing pyridyl and imine moieties that resemble those considered in this study. For instance, (acetonitrile)-diaqua-(2,6-bis(4,4-dimethyl-4,5-dihydro-1,3-ox azol-2-yl)-imine)-iron(II)(bis(tetrafluoroborate)) and (acetonitrile)-diaqua-(N,N’-((pyridine-2,6-diyldieth-1-yl-1-ylidene)bis(2,6-diisopropylaniline))-iron(ii)bis(trifluoromethanesulfonate) hexacoordinate complexes contain one DIP-like tridentate ligand, one MeCN and two H2O molecules coordinated to the Fe metal. Similar DIP-like tetradentate ligand forms equatorial bonding with a Fe2+ center, which is coordinated to two MeCN molecules in axial positions. Other tetradentate complex contains two functionalized DiIm moieties in equatorial positions with one MeCN and one CO molecules coordinating axially to Fe. All these complexes serve as examples of Fe-containing complexes that can form coordination bonds with MeCN molecules. Hence, it illustrates the importance of understanding redox properties of MeCN-coordinated complexes, such as those considered in this study.

We first begin by addressing variations in the average Mulliken spin density on Fe, imine fragments, and pyridyl fragments within different charge states, as the number of the noninnocent ligands varies. One can see that the average Fe, imine, and pyridyl spin densities do not significantly vary with the number of the ligands within higher charge states, +4 → +2. In contrast, the average Mulliken spin densities on these fragments differ noticeably within the lower charge states, +2 → −1. Specifically, upon MeCN substitution, two different redox behaviors are noticed for complexes containing different numbers of ligands. Compounds (Figure 5a–c) supported by two bidentate ligands (i.e., one ligand is substituted by two MeCNs) show a substantial increase in the average spin density on each imine group and pyridyl ring, whereas the average spin density on the Fe center remains nearly constant (Tables S8–S10). That is especially pronounced for complexes containing one or more pyridyl ligand. This trend in spin density behavior indicates that the ligands are getting reduced as opposed to the metal center. The reverse observation is true for compounds with one bidentate ligand (i.e., two ligands are now substituted by four MeCNs), indicating that the Fe center is primarily reduced. On one hand, MeCN substitution to the second ligand results in lower π-acceptance capacities, requiring that the metal center accepts more electron density within the low charge states. On the other hand, a more electron-rich metal center also favors the displacement of MeCN molecules, as less electron donation is now required at the metal center. As a consequence, Fe(Bpy)(MeCN)α Fe(α-ImPy)(MeCN)α and Fe(DiIm)(MeCN)α complexes dissociate two MeCN molecules within their 0 and −1 charge states (Tables S11–S13) and adopt planar tetracoordinate geometries. Overall, ligand substitution by MeCN not only preserves all the redox events within the +4 → −1 charge states, but also increases the OV values for all three bidentate complexes by: 1.62 V from Fe(Bpy)3 to Fe(Bpy)(MeCN)4, 1.06 V from Fe(α-ImPy)3 to Fe(α-ImPy)(MeCN)4, and 0.89 V from Fe(DiIm)3 to Fe(DiIm)(MeCN)4. Concomitantly, the MW of these complexes decreases by 28, 35, and 41%, respectively. Comparing all six complexes wherein at least one bidentate ligand is substituted by MeCNs, i.e., Fe(Bpy)3(MeCN)2, Fe(α-ImPy)3(MeCN)2, Fe(DiIm)3(MeCN)2, Fe(Bpy)(MeCN)4, Fe(α-ImPy)(MeCN)4, and Fe(DiIm)(MeCN)4, it is evident that complexes with the same number of MeCNs exhibit larger OV values when they possess imine groups, thus also supporting the results obtained for the MeCN-free complexes upon pyridyl group substitution by imine fragments.

In a similar vein to the MeCN-free complexes, Bpy ligands possess a greater amount of spin than the DiIm and α-ImPy ligands across the electron-transfer series, and this difference gets progressively larger with an increasing number of MeCN molecules. This is particularly pronounced for the +4 charge state, in which the Fe centers of Fe(DiIm)(MeCN)α and Fe(α-ImPy)(MeCN)α possess a mixed valence +3/+4 oxidation state, whereas the Fe center of Fe(Bpy)(MeCN)4 is in a +3 oxidation state. As an exception, within the +2 → +1 charge states, the DiIm and α-ImPy ligands exhibit slightly better π-acceptor abilities than Bpy, resulting in ligand-based reduction within the Fe(DiIm)(MeCN)4 and Fe(α-ImPy)(MeCN)4 complexes, but Fe-based reduction in the Fe(Bpy)(MeCN)4 complex.

Ligand substitution within complexes supported by tridentate ligands does not drastically change their redox behavior. Akin to the MeCN-free parent complexes, compounds containing one tridentate ligand (i.e., one ligand substituted by three MeCNs) exhibit ligand-based reductions within the +2 → −1 charge states, whereas the spin densities on Fe centers stay almost the same (Figure 5d–f). At the same time, solvent-coordinated Fe(Tpy)(MeCN)α, Fe(α-ImPy)- (MeCN)3, and Fe(DIP)(MeCN)3 complexes have larger OV values and smaller MWs than their unsubstituted counterparts. Specifically, the former increase by 0.80, 0.70, and 0.60 V, whereas the latter decrease by 21, 27, and 34%, respectively. In comparing these three MeCN-substituted complexes, one can observe that the OV values increase with increasing number of imine groups, in accordance with the imine for pyridyl trend found for MeCN-free counterparts. In a similar manner to Fe(Bpy)(MeCN)4, Fe(α-ImPy)(MeCN)4, and Fe(DiIm)(MeCN)4 these tridentate complexes also dissociate “excess” electron-donor molecules of MeCN within the 0 and −1 charge states, but to a smaller extent, due to the stronger π-acceptor capacity of the tridentate ligands (only one MeCN is pushed out of the first coordination sphere, as shown in Tables S14–S16), resulting in five-coordinate complexes. The difference in the reduction schemes within the low charge states in
all of these complexes can be explained by the number and type of the \( \pi \)-acceptors (pyridyl or imine fragment) capable of accepting electrons within the low charge states. Obviously, complexes with three \( \text{Fe(Tpy)(MeCN)}_3 \), \( \text{Fe(\( \alpha \)-ImBpy)(MeCN)}_3 \), \( \text{Fe(DIP)(MeCN)}_3 \), or four \( \text{Fe(Bpy)}_2(\text{MeCN})_2 \), \( \text{Fe(\( \alpha \)-ImPy)}_2(\text{MeCN})_2 \), and \( \text{Fe(DiIm)}_2(\text{MeCN})_2 \) \( \pi \)-acceptors have stronger \( \pi \)-acceptance capabilities than complexes with two such fragments \( \text{Fe(Bpy)(MeCN)}_4 \), \( \text{Fe(\( \alpha \)-ImBpy)(MeCN)}_4 \), \( \text{Fe(DiIm)}(\text{MeCN})_4 \). It can thus be concluded that in most cases of MeCN-ligand substitution, either at least three pyridyl rings, two pyridyl rings and one imine moiety, or one pyridyl ring and two imine fragments are necessary for stabilization via ligand reduction within low charge states. Any other such ligand combination, wherein the number of \( \pi \)-acceptor fragments is less than three, would result in an Fe-based reduction event. Overall, considering all bidentate and tridentate MeCN-containing complexes, it was found that the \( \text{Fe(Bpy)}_2(\text{MeCN})_2 \), \( \text{Fe(\( \alpha \)-ImPy)}_2(\text{MeCN})_2 \), and \( \text{Fe(DiIm)}_2(\text{MeCN})_2 \) complexes maintain their geometries at each reduction event, hence holding potential to be used within the entire +4 \( \rightarrow \) −1 electron-transfer series. It is worth noting that the MeCN-substitution exercise is mainly to assess

Figure 6. Average Fe–N bond lengths of the imine group, pyridine group, and MeCN molecules. The subplots are organized by the number of noninnocent ligands for: (a) DiIm complexes, (b) \( \alpha \)-ImPy complexes, (c) Bpy complexes, (d) DIP complexes, (e) \( \alpha \)-ImBpy complexes, and (f) Tpy complexes.
the ability of these systems to function as the number of redox noninnocent ligands decreases, and it does not address the stability or concentration of a particular substituted species in the RFB scenarios. Instead, it helps us demonstrate that such complexes can maintain the redox behavior similar to their parent species, if they ever happen to be formed under certain experimental conditions.

Next, we assessed the effects of different numbers of redox noninnocent ligands on Fe–NIm, Fe–Npy, and Fe–NMeCN bond lengths as a function of charge state. These results are depicted in Figure 6. Overall, one can see that the Fe–N distances do not change significantly within the entire electron-transfer series for all bidentate and tridentate ligand-containing complexes considered in our study (maximum deviation equals to 0.15 Å). Due to the differences in σ-donating properties of imine and pyridyl groups, MeCN-free complexes exhibit somewhat larger changes in the Fe–Npy and Fe–Nim distances within their high charge states (+4 → +2), rather than within their lower (+2 → −1) charges states, i.e., 0.02–0.05 versus 0.01–0.02 Å. As expected, complexes with a larger number of imine moieties (Fe(Dilm)3 and Fe(DIP)3) exhibit larger deviations in the Fe–N distances within the high charge states as compared to their parent unsubstituted counterparts (Table S1). In contrast, complexes containing coordinated MeCNs exhibit greater changes in Fe–N distances within the whole series. Specifically, although the Fe–Npy and Fe–Nim distances vary in the range of 0.01–0.07 Å, the Fe–NMeCN distances exhibit greater deviations, i.e., 0.11–0.15 Å. In most of the cases, the deviations in the Fe–N distances become noticeably greater as the number of bound MeCN molecules is increased. However, the most pronounced changes in the Fe–NMeCN distances are observed within the 0 and −1 charge states due to the displacement of one or two MeCNs during the +1 → −1 reduction steps, as the bidentate and tridentate complexes with one redox noninnocent ligand adopt four- and five-coordinate geometries, respectively. In such cases, the Fe–NMeCN distances decrease by 0.08–0.14 Å to compensate. Except these few cases wherein MeCN molecules are displaced in low charge states, most complexes studied in this paper maintain their geometries, while exhibiting only small changes across the charge state series.

4. CONCLUSIONS

Herein, we have systematically investigated a series of redox noninnocent ligands to gain fundamental knowledge about low-MW Fe complexes, potentially capable of promoting multiple, one-electron redox events. Specifically, we have computationally investigated the role of coordination geometries and the nature of redox noninnocence upon substituting pyridyl groups with imine fragments and also by varying the number of the noninnocent ligands present within the first coordination sphere of the metal center. Our calculations show that pyridyl group substitution with an imine moiety is an effective way to lower the MW of charge carriers, while apparently maintaining the redox properties and metal–ligand bonding characteristics. This observation is confirmed by the experimental results of the Fe(α-ImPy)3 complex, which demonstrates an excellent agreement with theory for the four experimental reduction potentials within the +3 → −1 charge states. In a similar fashion to the parent pyridyl group containing complexes, calculations point to such imine containing derivatives primarily exhibiting metal-based reductions within high charge states (+4 → +2) and ligand-based reductions within lower charge states (+2 → −1). For all examined complexes, we found that although the imine and pyridyl groups exhibited similar redox noninnocent behavior within the low charge states, the Fe center was stabilized differently within the +4 charge state. Specifically, the pyridyl groups promoted either a +3 or an intermediate +3/+4 oxidation state of Fe, whereas the presence of imine groups stabilized the metal at the rare +4 state. This helped increase reduction potentials for the +4 → +3 step in the Fe complexes containing a larger number of imine groups. Overall, we found that for all MeCN-free complexes, pyridyl group substitution appreciably increases their OV values up to 1.14 and 0.59 V for bidentate and tridentate complexes, whereas reducing the molecular weight by 40 and 27%, respectively.

By examining the effect of redox-innocent ligand, MeCN, we observed that within high charge states (+4 → +2), Fe complexes with only one redox noninnocent ligand were also capable of multielectron reduction events, and these exhibited reduction potentials similar to their analogs supported by two or three redox noninnocent ligands, suggesting metal-based reduction. However, two different redox behaviors were noticed for complexes containing bidentate and tridentate ligands within lower charge states (+2 → −1). Specifically, Fe complexes supported by two redox noninnocent bidentate ligands, or one redox noninnocent tridentate ligand, exhibited ligand-based reductions, whereas corresponding compounds containing one bidentate ligand exhibited a metal-based reduction due to the significantly decreased number of π-acceptor groups. Additionally, our calculations show that for any Fe species wherein a pyridyl moiety is substituted by MeCN ligands, a combination of at least three pyridyl rings, two pyridyl rings with one imine, or one pyridyl ring with two imines is necessary for complex stabilization via ligand-based reduction within low charge states. It is also worth noting that among all MeCN-coordinated complexes only Fe-(Bpy)2(MeCN)2, Fe(α-ImPy)2(MeCN)2, and Fe-(Dilm)2(MeCN)2 complexes maintain structural integrity at each reduction step, thus holding potential to be used in RFBs within the entire +4 → −1 series. Other MeCN-substituted complexes may encounter structural stability issues in 0 and −1 charge states due to displacement of MeCNs, hence resulting in a decreased redox window, i.e., +4 → +1. Thus, our theoretical results have pointed to the possibility of maintaining similar redox properties within complexes with a decreased number of noninnocent ligands and identified the minimum number of such ligands needed to preserve the overall redox performance. We believe that these findings can potentially point toward the rationale design of new Fe-based complexes with lower MWs and larger OV values, which can be used to create more cost competitive RFBs with higher energy densities.

5. METHODS

5.1. Computational Details. The reduction potentials of all Fe complexes and free ligands were computed using the revised Born–Haber cycle, described elsewhere,62 in which all reduction steps are referenced to a calculated absolute half-cell potential of a ferrocene couple, i.e., Fe0 + A− → Fe+ + A−, as opposed to an experimental standard reference electrode, such as the standard hydrogen electrode or the saturated calomel electrode (SCE). All calculations were carried out with Gaussian 09 software package (version D.01).67 The PBE functional68,69 was utilized as it does not require the
applications of a correction term to the theoretical reduction potential, as suggested previously. In addition, recent studies have revealed that the PBE functional was less likely to show artificial charge separation in complexes with redox noninnocent ligands. The LANL2DZ effective core potential basis set was employed for Fe, the 6-311G(d) basis set was used for the C and N, and 6-31G was used for H atoms. Geometry optimizations of all compounds were performed in the gas phase, whereas single point energies in MeCN were obtained using a self-consistent reaction field approach based on the integral equation formalism of the polarized continuum model (PCM). Level of theory, implemented as the default PCM method in Gaussian 09. Frequency calculations were performed to ensure that the optimized geometries represented minima along the potential energy surface for each compound. All possible multiplicities were considered for the studied complexes within each charge state. The vertical transition energies to 50 excited states of [Fe(α-ImPy)]$^{2+}$ were computed using spin-unrestricted time-dependent-DFT with the LC-oPBE functional. Excited-state transitions were visualized using the absorption’s half-width at half-height of 0.10 eV. Natural transition orbital analysis was used to describe the nature of the charge transfer.

5.2. Experimental Details. 5.2.1. Synthesis Details of [Fe(α-ImPy)]$^{2+}$: [Fe(α-ImPy)]$^{2+}$ has been synthesized as ClO$_4^{-}$ and PF$_6^{-}$ complexes for kinetic measurements of isomerization and acid hydrolysis as well as for cyclic voltammetry. The pseudo-octahedral core has been found to adopt both mer and fac isomers (Figure S4) and to equilibrate these isomers in solution, with the mer isomer being the dominant species. As with the previously reported complexes, the trifluoromethanesulfonate (OTf$^-$) salt reported herein exhibits $^1$H NMR data consistent with low-spin Fe(II). MeCN (Aldrich, anhydrous grade) and diethyl ether (Aldrich, anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade) were stored over 4 Å molecular sieves in an anhydrous grade). Metal complexes were synthesized and stored in an Ar-filled glovebox. Pyridine-2-alddehyde was vacuum transferred immediately prior to use. Metal complexes were synthesized and stored in an Ar-filled glovebox. N(2-Pyrindinylmethylene)-methanamine (α-ImPy) was synthesized as has been reported in the literature. All other reagents were purchased commercially and used as-received. $^1$H NMR spectra (Figures S5–S7) were obtained on a Bruker AV400 spectrometer and referenced to either the residual solvent (MeCN-d$_3$; 1.94 ppm) or tetramethylsilane (0 ppm). UV–vis spectra were obtained on an Agilent 8453 spectrometer equipped with a Peltier temperature controller set to 25 ºC. Elemental analysis was performed at Atlantic Microlab (Norcross, GA).

5.2.1.1. ([α-ImPy])$_3$Fe([OTf]$^2_2$ α-ImPy (5.0 g, 42 mmol) was added to ca. 100 mL of MeCN in a 250 mL flask with stirring. To this solution, Fe([OTf]$^2_2$ (4.9 g, 14 mmol) was added, resulting in the immediate formation of a dark purple solution. This reaction mixture was left stirring overnight and then filtered through Celite. The filtrate was concentrated in vacuo, and the product was crystallized via diethyl ether. XRD analysis was performed within the Nova software package (version 2.1) on the second scan, raw data are shown in Figures S8–S13.

**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01921.

Experimental UV–vis spectrum of [Fe(α-ImPy)]$^{2+}$; theoretical UV–vis spectra of [Fe(α-ImPy)]$^{2+}$ and [Fe(α-ImPy)]$^{2+}$; theoretical reduction potentials; Mulliken spin density data; and Fe–N bond lengths of all studied complexes; relative free energies of bidentate and tridentate complexes within the −1 charge state; $^1$H NMR spectra of ([α-ImPy])$_3$Fe([OTf]$^2_2$ cyclic voltammetry data of [Fe(α-ImPy)]$^{2+}$ (PDF)

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Notes

The authors declare no competing financial interest.

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