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Altering the Coordination of Iron Porphyrins by Ionic Liquid Nanodomains in Mixed Solvent Systems

Abderrahman Atifi Marquette University

Michael D. Ryan Marquette University, michael.ryan@marquette.edu

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Contents

Altering the Coordination of Iron Porphyrins by Ionic Liquid Nanodomains in Mixed Solvent Systems

Abderrahman Atifi

Marquette University, Milwaukee, WI Michael D. Ryan Marquette University, Milwaukee, WI

Abstract

The solvent environment around iron porphyrin complexes was examined using mixed molecular/RTIL (room temperature ionic liquid) solutions. The formation of nanodomains in these solutions provides different solvation environments for substrates that could have significant impact on their chemical reactivity. Iron porphyrins (Fe(P)), whose properties are sensitive to solvent and ligation changes, were used to probe the molecular/RTIL environment. The addition of RTILs to molecular solvents shifted the redox potentials to more positive values. When there was no ligation change upon reduction, the shift in the *E*° values were correlated to the Gutmann acceptor number, as was observed for other porphyrins with similar charge changes. As %RTIL approached 100 %, there was insufficient THF to maintain coordination and the E° values were much more dependent upon the %RTIL. In the case of Fe^{III}(P)(Cl), the shifts in the *E*° values were driven by the release of the chloride ion and its strong attraction to the ionic liquid environment. The spectroscopic properties and distribution of the Fe^{II} and Fe^I species into the RTIL nanodomains were monitored with visible spectroelectrochemistry, ¹⁹F NMR and EPR spectroscopy. This investigation shows that coordination and charge delocalization (metal versus ligand) in the metalloporphyrins redox products can be altered by the RTIL fraction in the solvent system, allowing an easy tuning of their chemical reactivity.

Introduction

Room temperature ionic liquids (RTILs) have been shown to be efficient catalysts for the activation of small molecules such as CO2. Their ionic structure can bypass the single electron reduced intermediate, which is often energetically unfavorable. On the other hand, RTILs are expensive and have high viscosities which may limit their application. To minimize these effects, they are often mixed with

molecular solvents. It will be the aim of this work to probe the relationship between bulk properties of the molecular solvent/RTIL mixtures with the physical properties of the solutes (such as visible spectra and redox potentials) as the ratio of molecular solvent to RTIL changes. While there have been many reports on the relationship between the solute's physical properties and the bulk properties of RTIL[s1](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0001) and relating them to molecular solvents, there have been fewer studies on mixed molecular solvent/RTIL mixtures.² Changes in these molecular properties can give a unique insight into the interaction between solutes and mixed molecular solvent/RTIL solutions. $2c$

Metal catalysts such as metalloporphyrins are often able to activate small molecules such as $CO₂$, $O₂$, NH₃, and N₂. For example, Savéant et al.³ showed that it was feasible to convert CO₂ to CO with low valent iron porphyrins. Significantly larger efficiencies were obtained using proton sources as part of the catalyst.⁴ Metals other than iron have also been used as a $CO₂$ -reduction catalyst.⁵ Alternatively, RTILs can be used to lower the energy for the electron transfer by ion pairing with the charged species that are formed. This approach was used by Rosen et al., $\frac{6}{5}$ along with a proton source and a silver electrode to greatly reduce the overpotential for the $CO₂$ to CO conversion. Both approaches were combined by Choi et al.⁷ In their work, an iron porphyrin/RTIL co-catalyst and a proton donor were used to increase the $CO₂$ to CO reduction efficiency. In order to develop the best catalyst, the influence of all these factors need to be understood. Although most of the focus has been on $CO₂$ activation, RTILs have used in the activation of other small molecules. The reduction of N_2 to ammonia occurred much more efficiently at an RTIL-coated working electrode. 8 The addition of RTILs has also been found to increase the efficiency of the oxygen reduction reaction (ORR), $\frac{9}{2}$ as well as the oxidation of ammonia to dinitrogen.¹⁰ An understanding of the interactions between the RTIL and the $CO₂$ -reducing catalyst can have a significant impact on the reduction product. Lau et al.¹¹ examined the role of an imidazolium based RTIL on the reduction of $CO₂$ at a silver electrode. The role of the RTIL is involved not only in the efficiency of CO₂ reduction, but also with the identity of the ultimate product.¹² Sun et al.¹³ examined the role of RTILs in switching the reduction product from oxalate to CO. The reduction of $CO₂$ in molecular solvents has been studied extensively using voltammetry, 14 or by DFT methods.^{5b} When RTILs are mixed with molecular solvents, the ions are only homogeneously dispersed at low concentrations.¹⁵ At higher concentrations, nanodomains of RTILs are formed, 16 with initially islands of RTIL in a molecular solvent matrix (solvent-rich mixture) to eventually molecular solvent islands in a RTIL matrix (RTIL-rich mixture). Substrates can partition between these two nanodomains (molecular solvent/RTIL), and, in these nanodomains, sense an environment that differs from the bulk parameters. The extent of this partitioning can have a significant effect on the redox potentials, especially for dianions (e.g., DNB^{2−}, DNB=dinitrobenzene)^{2d, [17](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0017)} or monoanions that interact strongly with the RTIL (NiOEPone⁻, OEPone=octaethylporphinone).^{2e} For example, the two one-electron waves of dinitrobenzene can collapse into a single two-electron wave in an ionic liquid.^{2d, [17](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0017)} Nikitina et al.¹⁸ showed significant shifts in the *E*° values, especially for dianionic species. In addition, planar species are more likely to partition in the RTIL nanodomain than spherical substrates. $2f$ The solution structure of redox catalysts in the presence of RTILs has a significant effect on their redox potential and their ability to interact with substrates. It has been shown that this interaction can extend beyond the stabilization of the anionic species, and can lead to changes in the electronic structure of the species.^{2e} For example in Ni(OEPone)⁻, the infrared band for the carbonyl band was significantly downshifted in the presence of the RTIL, and the visible spectrum of this species showed significant differences in the Soret band as compared to the spectrum in molecular solvents. The Ni(OEPone)⁻ spectrum in RTILs was most similar to a Ni^{II} porphyrin

radical anion as opposed to a Ni^I species in molecular solvents. The changes in the infrared and visible spectra were attributed to the strong interactions between the porphyrin anion and the RTIL.

In the examples above, the changes that we observed in the presence of the RTIL were mainly the effect of solvation due to ion pairing or nanodomains. Changes in the molecular structure due to coordination changes were not studied. Iron porphyrins, a common redox catalyst, can form complexes with a coordination number of 4–6 in solution, as well as changes in the spin state and oxidation state. Therefore, the presence of RTILs in mixed molecular solvent/RTIL solution can change the redox behavior of the iron catalyst by changing ligation solvation or spin-state of the complex. Changes in coordination have a significant effect on the catalytic properties of these complexes, especially in regards to substrate bonding. In this report, we will examine the effect of RTILs in mixed solutions on the redox properties, coordination number and electronic state of iron porphyrins in order to understand the interaction between the solute and the molecular solvent/RTIL system.

Results and Discussion

Cyclic Voltammetry of Fe(FP)(ClO4)/Cl in pure solvents

The effect of RTILs on iron porphyrin redox properties was first examined using cyclic voltammetry. In order to maximize the solubility of the ferric porphyrin in the RTIL solution, the tetra(pentafluorophenyl)porphyrin (FP) ligand was used in this work. In addition, the presence of fluorine atoms on the phenyl groups significantly lowered the redox potential of each step, and had the added advantage that ¹⁹F NMR could be exploited to investigate the effect of RTILs on the different redox states of the iron porphyrin. Ferric porphyrin can be reduced in three one electron redox processes as shown below (omitting ligand/solvent coordination [Eq. [1-3\]](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-disp-0001%20#chem201701540-disp-0002%20#chem201701540-disp-0003):

 $Fe^{III}(FP)^+e^- \rightarrow Fe^{II}(FP)$ (1) $Fe^{II}(FP) + e^- \rightarrow Fe^{I}(FP)^-$ (2) $Fe^{1}(FP)^{-} + e^{-} \rightarrow Fe^{0}(FP)^{2-}$ (3)

In THF, the perchlorate ligand in Fe(FP)(ClO₄) was displaced by the THF solvent to form the bis-THF complex.^{[1](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0001)9} The three reduction waves in THF are shown in Figure 1 (red trace). In order to minimize the changes in the potential as the solvent system was changed, all potentials (Table S1) were referenced versus decamethylferrocene (DmFc).²⁰ In AmNTf₂ (ethyldimethylpropylammonium bis(trifluoromethylsulfonyl)imide), only two reversible waves were observed. Both waves were shifted to more positive potentials (Figure [1,](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0001) blue trace), with the second wave being shifted more strongly than the first. As expected from the increased viscosity of AmNTf₂ versus THF, the current was significantly lower in AmNTf₂, but was consistent with the Stokes–Einstein equation. The third wave, which was observed in THF, was not observed in AmNTf₂ due to the narrowing of the solvent window. This was not an intrinsic property of A mNTf₂ as a wider window was observed for other substrates. The failure to observed this wave was probably due to the reaction of Fe(P)^{2−} with tetraalkylammonium ions.²¹ The shift in the E° ₁ between THF and AmNTf₂ was 167 mV, while the E° ₂ potential shifted by 322 mV, nearly twice as much. In both solvents, the first and second redox processes were nearly reversible. Including solvent coordination, the first wave in THF for Fe(FP)(ClO₄) can be written as Eq. [4:](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-disp-0004)

 $Fe^{III}(FP)(THF)_{2}^{+} + e^{-} \rightleftarrows Fe^{II}(FP)(THF)_{2}$ (4)

Figure 1 Cyclic voltammetry of 0.6 mM Fe(FP)(ClO₄) in THF (red trace) and in AmNTf₂ (blue trace, current multiplied by a factor of 3). Scan rate: 100 mV s-1. Potential referenced vs. decamethylferrocene (DmFc).

Previous work has shown that the ferrous complex is also a bis-THF complex.²² In AmNTf₂, the coordination of the ferric complex is unclear as perchlorate and NTf₂⁻ are both conjugate bases of superacids with similar pK_a values for their conjugate acids.²³ Based on the pK_a values in dichloroethane, perchlorate is a weaker base than NTf₂⁻ though the latter species might not bind as well due to steric reasons. On the other hand, the large concentration difference between CIO₄⁻ and NTf₂⁻ would favor coordination by the latter. The reversibility of the both reductions in AmNTf₂, though, are consistent with the absence of coordination changes upon reduction. The solvent coordination of the ferrous species will be examined in more detail using spectroscopic methods. The shift in the *E*°1 and *E*°2 values in changing the solvent from THF to AmNTf₂ was larger than was observed for Ni(OEP)^{+/0} (101 mV) and Ni(OEP)^{0/−1} (234 mV) where the charge changes are the same as for the first and second reductions of Fe(FP)(ClO4). The cyclic voltammetric results indicate a very strong stabilization of the reduced species by the RTIL.

In Figure [2,](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0002) the cyclic voltammetry in THF of Fe(FP)Cl (green trace) is compared to the voltammetry of Fe(FP)(ClO₄) (red trace). The first reduction of Fe(FP)(Cl) in THF was shifted to more negative potentials as compared to Fe(FP)(ClO4) (261 mV). This large shift was due to chloride ligation of the Fe(FP)(Cl) species. The first wave can be written as $[Eq. 5]$ $[Eq. 5]$:

 $Fe(FP)(Cl) + e^- + 2THF \rightarrow Fe(FP)(THF)_2 + Cl^{-}(5)$

Figure 2 Cyclic voltammetry of 0.6 mM Fe(FP)(ClO₄)/Cl in THF and AmNTf₂ at 100 mV s^{−1}. Fe(FP)(ClO₄) in THF: red trace; Fe(FP)Cl in THF: green trace; Fe(FP)Cl in AmNTf₂: blue trace (current multiplied by 2.5). Potential referenced vs. decamethylferrocene (DmFc).

The peak potentials for the second wave in THF for $Fe(FP)(ClO₄)$ and $Fe(FP)(Cl)$ occurred at nearly the same potential (-1.016 V), indicating that the same redox process occurred in THF (Reaction 2). This result also confirmed the loss of Cl[−] from the complex upon the ferric reduction. Otherwise, the second wave would have been shifted to a potential negative of the Fe(FP)(ClO₄) complex.

The cyclic voltammetry of Fe(FP)(Cl) in AmNTf_{[2](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0002)} is shown in Figure 2 (blue trace). The first wave was shifted positive of the wave in THF (382 mV). This was a considerably larger shift that was observed for Fe(FP)(ClO₄) (167 mV). The second wave was not shifted as much and was not reversible. In this case the Δ*E*^p value will be used instead of the Δ*E*° value. The difference in peak potentials between the second wave in THF and in AmNTf₂ was 156 mV. More importantly, the second peak potential of Fe(FP)(Cl) in AmNTf₂ was 262 mV negative of the wave for Fe(FP)(ClO₄), in that same solvent. This indicates that the redox couple for Fe(FP)(Cl) was different from that of Fe(FP)(ClO₄) in AmNTf₂. This will be investigated more later, but, at this point, the evidence indicates that the ferrous complex remained coordinated to chloride on the voltammetric timescale $[Eq. 6-8]$ $[Eq. 6-8]$.

 $Fe^{III}(FP)(Cl) + e^- \rightleftharpoons Fe^{II}(FP)(Cl^-)$ (6)

As a result, the second wave involved both the reduction of iron and the loss of chloride, leading to an irreversible wave (EC mechanism).

 $Fe^{II}(FP)(Cl)^{-} + e^{-} \rightleftarrows Fe(FP)(Cl)^{2-}$ (7)

 $Fe(FP)(Cl)^{2-} \rightleftarrows Fe(FP)^{-} + Cl(8)$

For the second reduction, there is no net change in the charge of the metal complex so its solvation in the RTIL should be similar. From an energetics point of view, the solvation of Cl[−] by the RTIL could be responsible for the positive shift in the redox potential. Spectroscopic studies that will be discussed later will investigated the coordination structure of the reduction products.

Visible spectroelectrochemistry of Fe(FP)(ClO4)/Cl in pure solvents

The visible spectroelectrochemistry of Fe(FP)(ClO₄) in THF is shown in Supporting Information Figure S1 (red trace). The results are summarized in Table [1.](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-tbl-0001) The spectra of Fe(FP)⁺, Fe(FP), and Fe(FP)⁻ are similar to their tetraphenylporphyrin (TPP) analogues, with small blue shifts in the Soret band for the FP

complexes. In THF, the Soret band for Fe(FP)[−] was more bleached than the Fe(TPP)[−] complex[.24a,](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0024a)[24c](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0024c) The spectroelectrochemistry of Fe(FP)(ClO₄) in AmNTf₂ is shown in Figure [3.](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0003) The spectrum of the ferric complex in AmNTf₂ was quite similar to the complex in THF, with only a slight blueshift in the Soret band (THF: 394 nm; AmNTf2: 392 nm). The ferric complex in THF has been identified as a bis-THF adduct. As NTf₂⁻ has a basicity very similar to ClO₄⁻, the large concentration difference would favor NTf₂⁻ coordination. The Soret band for the ferrous complex (first reduction product) in $AmNT₂$ (410 nm) was blue-shifted from the band in THF (420 nm), but otherwise the spectra appeared to be similar. The ferrous complex in THF is known to be a bis-THF complex, as was the ferric complex. The visible spectra of 4-, 5- and 6-coordinate ferrous porphyrins complexes are well known. A 4-coordinate complex such as Fe(TPP) in benzene or dichloromethane has a split Soret band with peaks at 420 and 455 nm.²⁵ For 5coordinate anions complexes such as halide complexes of Fe(TPP), the Soret band is redshifted (440 nm).²⁶ While one might expect such a spectrum for Fe(FP) in AmNTf₂, NTf₂⁻ is a very weak ligand, and the charge is quite diffuse. Formally, the negative charge is on the nitrogen atom (NTf₂⁻: F₃C-SO₂-N-SO₂- CF_3^-). This atom can ion pair with the solvent cation, leaving the relatively neutral SO₂ group to interact with the iron atom. A bis-coordination is possible with this structure. As a result, the interaction of the SO₂ group with the iron atom is more like a weak solvation interaction, rather than a covalent ironanion bond. The coordination of the ferric/ferrous complexes with NTf₂⁻ will be examined later by ¹⁹F NMR.

Figure 3 Visible spectroelectrochemistry of 0.5 mm Fe(FP)(ClO₄) in AmNTf₂. A) First reduction at −0.60 V vs. Ag/AgNO₃. Red: 0 s; Green: 10, 45, 90, 110, 130 s; Blue: Fe(FP)⁻. B) Second reduction at -1.20 V vs. Ag/AgNO₃. Blue: 0 s; Green: 10, 20, 30, 50 s; Red: 200 s.

The second reduction of Fe(FP)(ClO₄) in AmNTf₂ (Figure $\underline{3}$ $\underline{3}$ $\underline{3}$ B) yielded a spectrum that was considerably different from the spectrum in THF (Figure S1B). The Soret band for Fe'(FP)⁻ was almost completely bleached in THF, but a strong Soret band was observed in AmNTf₂, with an absorbance maximum at 434 nm. The stronger Soret band may indicate less delocalization of the Fe' electron density to the porphyrin ring in $AmNTf₂$.

In the spectroelectrochemical reduction of Fe(FP)(Cl) in THF (Figure S2), the same ferrous complex was formed as was observed with Fe(FP)(ClO₄), indicating that the first reduction product was a bis-THF ferrous porphyrin. Similarly, the products of the second and third reduction of Fe(FP)(Cl) was the same as were observed with Fe(FP)(ClO₄) (Figure S2).

The spectra in AmNTf₂ were considerably more complex than were observed for the perchlorate complex because of the ability of Cl[−] to coordinate with Fe^{II}. At higher concentrations of the ferric porphyrin, the reduction of Fe(FP)Cl in AmNTf₂ gave clear isosbestic points over the entire reduction, but yielded a spectrum significantly different from that observed in THF. The ferrous spectrum was consistent with a Fe(FP)Cl[−] complex with a Soret band at 435 nm (Figure [4](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0004) A), considerably shifted from the 410 nm Soret band for the perchlorate complex. If the spectroelectrochemistry was carried out at lower concentrations of ferric porphyrin, significant dissociation of Fe(FP)(Cl)[−] occurred, and the band at 414 nm was observed, similar to the Fe^{II}(FP) spectrum in AmNTf₂ generated from Fe(FP)(ClO₄). This confirms the tentative assignment of the initial products in Reaction 6. While Fe(FP)(Cl)[−] is the initial ferrous complex, a slow dissociation of Cl[−] does occur (Figure [4](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0004) B), forming the Fe["](FP) complex which

was very similar to the ferrous complex in THF. While the slow dissociation is quite important for spectroscopic studies, the voltammetric results will reflect a chloride coordinated ferrous complex.

Figure 4 Visible spectroelectrochemistry of 0.5 mm Fe(FP)(Cl) in AmNTf2. A) First reduction. *E*applied=−0.60 V vs. Ag/AgNO3. Red: 0 s; Green: 50, 500, 1000, 1500, 2500 s; Blue: 4000 s. B) First reduction. *E*_{applied}=−0.60 V vs. Ag/AgNO₃. Blue: 4000 s; Green: 5957 s, 7960 s; Red: 9262 s. C) Second Reduction. *E*applied=−1.40 V vs. Ag/AgNO3. Red: 63 s; Green: 313, 463, 713, 1214 s. Blue: 3467 s. All times are measured from the beginning of the potential step.

When the potential was stepped to the second wave (Figure 4 C), the spectrum in AmNTf₂ was consistent with the Fe(FP)[−] complex formed from Fe(FP)(ClO4). This indicated that the same spectral species was formed in AmNTf₂, whether one started with Fe(FP)(Cl) or Fe(FP)(ClO₄). While the transition from Fe(FP) to Fe(FP)[−] in AmNTf₂ is clear in this experiment, a comparison of the blue traces in Figure [4](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0004) A (Fe(FP)(Cl)⁻) and in Figure [4](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0004) C (Fe(FP)⁻) show the spectra are quite similar (Figure S3). The Soret bands differ by about 2 nm (Fe(FP)⁻: 433 nm; Fe(FP)(Cl)⁻: 435 nm), and the Q-band for Fe(FP)⁻ was 557 nm, while it was 566 nm for Fe(FP)(Cl)⁻. If the scan rate was increased or the step time was decreased, the conversion of Fe(FP)(Cl)[−] to Fe(FP) will not occur, and the spectral changes upon reduction were not as large as was observed in Figure [4.](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0004) Further spectroscopic studies using NMR and EPR will provide additional confirmation that the species are indeed different, but the results from Figure [4](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0004) clearly show that the conversion from Fe(FP) to Fe(FP)[−] will only occur at a more negative potential.

In the reverse scan, at −0.60 V vs. Ag/AgNO₃, the band for Fe^{II}(FP) appeared first, and then followed by the formation of some Fe"(FP)(Cl)[−] species, though the chloride complex is still a minor species. Further oxidation at +0.40 V ultimately led to the formation of Fe(FP)(Cl) (Figure S4).

Cyclic voltammetry of Fe(FP)(ClO4)/Cl in mixed RTIL/molecular solvents

The voltammetric and spectroscopic studies in THF and AmNTf₂ have shown significant differences for the iron complexes between the molecular and RTIL environment. Previous work has shown the formation of nanodomains in mixed solvent which will preferentially solvate solutes in the mixture. $2e,27$ $2e,27$ In order to investigate the effect of these nanodomains on substrates, the voltammetry of Fe(FP)(Cl)/(ClO4) was investigated in mixed solvent solutions. In Figure [5](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0005) A (red symbols), the variation in the *E*°1 values vs. DmFc for Fe(FP)(ClO4) as a function of log(%RTIL) is shown. For most of the mixture ratios, the E° ₁ values for Fe(FP)(ClO₄) were linearly dependent upon the log(%RTIL) until the solution became nearly pure AmNTf₂. At 100 % AmNTf₂, there was a significant discontinuity.

Figure 5 Variation of the *E*° values in THF/AmNTf₂ mixtures as a function of the %RTIL. A) *E*[°]₁ for Fe(FP)(ClO4)/(Cl) and *E*° for the oxidation of Ni(OEP). B) *E*°2 for Fe(FP)(ClO4)/(Cl) and *E*° for the reduction of Ni(OEP). Compound: Fe(FP)(ClO₄) (λ), left axis; Fe(FP)(Cl) (λ), left axis; Ni(OEP) (λ), right axis.

In THF, the first redox process is given by Reaction 4. This involved the transformation from a cation to a neutral species. For comparison, the variation in the *E*° values for Ni(OEP) oxidation is also shown in Figure [5](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0005) A (black symbols). As can be seen, the slope of these two curves are quite similar until the solutions approach 100 % RTIL. At this point, there is significant curvature in the Fe(FP)⁺/Fe(FP) process, but not in the Ni(OEP)⁺/Ni(OEP) reduction. Plotting the same data versus the Gutmann acceptor number (AN) (Figure S5A), the transition towards 100 % RTIL is more pronounced. In this plot, a modest curvature is seen for Ni(OEP) while a more pronounced trend is seen for Fe(FP)⁺. Clearly, the loss of THF coordination affected the Fe(FP)⁺/Fe(FP) potential more than the Ni(OEP)⁺/Ni(OEP) potential. The variation in Fe(FP)(Cl)/Fe(FP) redox potential as a function of the Gutmann AN is also plotted in Figure S5 (green symbols). In this case, the redox process is given by Reaction 5. The porphyrin species is

uncharged in both the ferric and ferrous states but the net change is from neutral to negative one. RTILs generally affect the 0/-1 transition more than the +1/0 transition, and this was the case here. The steep slope for the *E*° value for Fe(FP)(Cl) versus %RTIL and Gutman AN is consistent with the stronger solvation of anions. Figure [5](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0005) B shows the slope of the *E*° for Ni(OEP)/Ni(OEP)[−] as a function of log(%RTIL), which is comparable to the variation of the *E°* for Fe(FP)(Cl)/Fe(FP) in Figure [5](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0005) A. Because the charge on the ferric and ferrous porphyrins are the same (neutral), the solvation of these species should be similar in AmNTf₂, but the Cl[−] would be strongly solvated in the RTIL nanodomain. The strong solvation of this ion drives the *E*° to more positive potentials, rather than the solvation of the porphyrin species in the RTIL nanodomain (as was observed for Ni(OEPone)).^{2e} The strong nonlinearity for the *E*° values for Fe(FP)⁺/Fe(FP) occurred as the ligand THF for the ferric and ferrous species were replaced with NTf₂⁻. This behavior was unusual compared to other redox species that have been previously examined. Previous work with Ni(OEP), 2e C₆₀^{[2f](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0002f)} and dinitrobenzene^{2d} showed that there was significant linearity over the entire log(%RTIL) range. This would indicate a significant change in the solvation environment when the mixtures reflect primarily the RTIL nanodomain.

For the second reduction, the *E*° values for the Fe(FP)(ClO4) and Fe(FP)(Cl) complexes were strongly dependent upon the %RTIL (Figure [5](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0005) B). For both species, the charge transition was from 0 to −1. There was little difference between the chloro- and perchlorate-complexes of Fe(FP) as the %RTIL changed. The slopes were similar to the Ni(OEP)^{0/−} redox process (Figure [5](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0005) B). The non-linearity of the *E*[°]₂ values started at a much lower %RTIL (about 70 %), with significantly larger stabilization of the reduced species. This change in slope was not observed for the Ni(OEP)^{0/−} reduction at higher %RTIL. Clearly, as the %RTIL increased, the solvation/coordination environment changed significantly.

As was discussed in the previous section, the voltammetry of Fe(FP)(Cl) had an anomaly that the second reduction was less reversible in AmNTf₂ than in THF. Interestingly, when a small amount of THF was added, the reversibility of the Fe^{II}(FP)/Fe(FP)⁻ wave improved considerably (Figure S6). The shape of the wave was consistent with the dissociation of chloride from the Fe(FP)(Cl)[−] complex, rather than a quasireversible electron transfer or uncompensated resistance (the first wave in the voltammogram reflects uncompensated resistance). These results are consistent with Reactions 7–8.

Visible spectroelectrochemistry of Fe(FP)(ClO4)/Cl in mixed RTIL/molecular solvents The visible spectroelectrochemistry of Fe(FP)(ClO₄) has shown that Fe^{lI}(FP) and Fe(FP)[−] have distinctive spectra in the THF and A mNT f_2 environment especially in the Soret region. In order to interpret the voltammetric data in mixed solvents, the visible spectroelectrochemistry of Fe(FP)(ClO4) was undertaken. This is the simpler complex to interpret because the ferric and ferrous species are solvent coordinated in THF. From the features of the visible spectrum it should be possible to interpret the solvent environment around the iron species in mixed THF/RTIL solutions.

The first reduction of Fe(FP)(ClO₄) in 50 % THF/AmNTf₂ is shown in Figure 6 A. The spectra are qualitatively similar to the reduction in THF. The Soret band shifted from 392 to 418 nm upon reduction. A close examination of Figure [6](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0006) A, though, shows a smaller Soret band at about 410 nm which is the *λ*max for Fe^{II}(FP) in AmNTf₂. Figure [6](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0006) B shows the visible spectra for Fe^{II}(FP) in 50 % THF/AmNTf₂, THF and AmNTf₂. It is clear that the ferrous species has partitioned between the two nanodomains. While the Fe["](FP) band for the THF nanodomain dominates, the Fe["](FP) Soret band in AmNTf₂ is weaker so an overall analysis shows that Fe^{II}(FP) roughly equally distributed between the THF and RTIL nanodomains.

The stronger solvation by the AmNTf₂ nanodomain would shift the E° ₁ values positively as the %AmNTf₂ is increased.

Figure 6 Visible spectroelectrochemistry of 0.5 mm Fe(FP)(ClO₄) in THF/50 %AmNTf₂. A) First reduction. Red: +0.20 V; Green: −0.02, −0.06, −0.10, −0.14, −0.20, −0.28 V. Blue: −0.32 V. B) Black trace: Fe^{II}(FP) in 50 % THF/AmNTf₂; red trace: Fe^{II}(FP) in THF; blue trace: Fe^{II}(F) in AmNTf₂. C) Second reduction. Blue: −0.32 V; Green: −0.72, −0.82, −0.88, −0.94, −0.98 V; Black: −1.00 V. All potentials vs. Ag/AgNO3.

The second reduction of Fe(FP)(ClO₄) is shown in Figure [6](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0006) C, the Soret band shifted from 418 to 428 nm upon the second reduction to form Fe(FP)⁻. The shape and position of this band for Fe(FP)⁻ was consistent with an RTIL nanodomain. Unfortunately, because Fe(FP)[−] in THF is mostly transparent in that spectral region, it is difficult to calculate the percent Fe(FP)⁻ in the RTIL. A reasonable estimate can be made by comparing the ferric band in the starting spectra with the Fe(FP)⁻ spectrum. In AmNTf₂, the two bands have nearly the same molar absorptivity, but in the mixed solution, the Fe(FP)[−] is 80 % of the ferric absorbance. This would indicate an enhanced solubility of Fe(FP)[−] in the RTIL nanodomain. The lack of good isosbectic points in the second reduction is consistent with the presence of some Fe(FP)[−] in the THF nanodomain.

The spectroelectrochemistry of Fe(FP)(Cl) in mixed solvents was more complex. The reduction of Fe(FP)(Cl) yields Fe(FP) in THF and Fe(FP)(Cl)⁻ (initially) in AmNTf₂. As was shown in Figure [4](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0004) B, the Fe(FP)(Cl)[−] in AmNTf₂ slowly converted to Fe(FP) with a Soret band at 410 nm. In mixtures of THF/AmNTf₂, additional reactions are possible. Figure [7](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0007) shows the visible spectra of Fe(FP)(Cl)⁻ in different mixtures. With no THF present, the Soret band for Fe(FP)(Cl)[−] at 435 nm is formed, which slowly converted to Fe(FP) (410 nm). In the presence of small amounts of THF (2 %), a new band at 418 nm appeared with a decrease in the 435 nm band. Eventually at 20 % THF, the Fe(FP)(Cl)[−] band is gone

with the 418 nm band being the most prominent. The band at 418 nm is indicative of the Fe(FP)(THF)₂ complex. The broadness of the band, though, indicates that there is significant partitioning between the THF and AmNTf₂ nanodomains. These results show a sharp transition in the coordination of the ferrous species with small amounts of THF. These spectral results are consistent with the strong curvature of the *E*° values versus %AmNTf₂ as the mixtures approach 100 %.

Figure 7 UV/Visible spectra of Fe(FP)(Cl)[−] in mixed AmNTf2/THF solutions. 100 % AmNTf2 (black), 98 % AmNTf2 (red), 93 % AmNTf² (green), 50 % AmNTf² (blue).

 19 F NMR of iron porphyrins in THF, AmNTf₂ and mixed solvent solutions

The ¹⁹F NMR chemical shifts for the various iron porphyrin complexes in THF and AmNTf₂ are shown in Table [2.](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-tbl-0002) The values of the ferric and ferrous complexes in THF are consistent with previous reports, where available.^{28, [29](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0029)} One of the characteristics of the spectra is the splitting of the o- and m-resonances due to the asymmetry of the 5-coordinate complexes. The chemical shifts indicate that Fe(FP)(THF)₂⁺ is the primary species of the Fe(FP)(ClO₄) in THF. Interestingly, no splitting was observed for Fe^{III}(FP)(ClO₄) in AmNTf₂ which would indicate that the perchlorate ligand is displaced in the RTIL. The lack of splitting is consistent with a bis-NTf₂⁻ complex, proposed earlier in this paper. Splitting of the *o*- and *m*resonances was observed for Fe(FP)(Cl) in THF and AmNTf₂ (only m- and p-resonances were observed in $AmNT₂$). Only minor shifts in the ferric species were observed when the RTIL solvent was replaced by THF, with maximum shifts of 1–2 ppm. This was consistent with the visible spectra.

Compound	Solvent	o-Resonance	p-Resonance	m-Resonance	Reference
H_2FP	CD ₂ Cl ₂	-137.1	-152.7	-162.1	[28a]
$Fe^{III}(FP)(ClO4)$	THF	-134.7	-152.7	-161.7	this work
	AmNTf ₂	-132.8	-151.3	-161.0	this work
Fe ^{II} (FP)Cl	CD ₂ Cl ₂	$-102.0, -105.1$	-148.5	$-152.1, -157.0$	[28a]
	$[D_6]$ acetone	$-105.8, -107.7$	-150.2	$-153.9, -156.0$	[28b]
	THF	$-118.1, -119.5$	-153.1	$-158.2, -160.5$	this work
	$[D_3]CH_3CN$	$-107.7, -108.8$	-150.9	$-154.7, -156.7$	this work
	AmNTf ₂		-149.0	$-154.3, -156.5$	this work
Fe ^{II} (FP)(THF) ₂	$[D_8]THF$	-140.4	-157.7	-165.3	[28a]
	THF	-141.8	-159.3	-167.1	this work
Fe ^H (FP)	$[D_8]$ toluene	-135.5	-152.2	-161.4	[28a]
	AmNT f_2	-129.9	-153.2	-160.6	this work
			$(-152.8)^{[a]}$	$(-160.1)^{[a]}$	
Fe"(FP)Cl-	$[D_8]$ toluene	$-131.0, -132.2$	-157.9	$-165.1, -166.0$	[28a]
	[D ₃] acetonitrile	$-126.0, -127.7$	-154.2	-160.3	[28c]
	$[D_8]THF$	-142.5	-163.4	-174.1	[28c]
$Fe(FP)$ -	THF	-141.5	$-162.1(-162.3)$	$-172.9(-173.0)$	this work
		(-141.5)			
	AmNTf ₂	-137.0	-153.2	-160.6	this work

Table 2.¹⁹F NMR spectra of iron porphyrin complexes

[a] Obtained by the reduction of Fe(FP)(Cl).

For the ferrous species, $Fe(FP)(ClO₄)$ and $Fe(FP)(Cl)$ formed the same $Fe^{II}(FP)(THF)₂$ complex in THF (Table [2\)](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-tbl-0002). No splitting in the o - or *m*-resonances were observed. While this does not prove that a Fe^{II}(FP)(THF)₂ complex was formed, the chemical shifts were different from the Fe(FP)(Cl)[−] complex in THF, made by the addition of a chloride salt. These results are consistent with the visible spectra, which were the same for both complexes. Larger shifts were observed though for $Fe^{II}(FP)$ when the solvent was changed from THF to AmNTf₂. The *o*-resonances decreased by about 11 ppm, while the *p*- and *m*-resonances decreased by 5–6 ppm. This also reflects changes in the visible spectra between the THF and AmNT f_2 environment. In addition, the Fe^{II}(FP) spectra was the same in AmNT f_2 whether one started with the chloride or perchlorate complex. This was consistent with the slow dissociation of Cl[−] from the Fe["](FP)(Cl)[−] complex.

As with the ferrous complex, the Fe(FP)[−] complex was identical whether one started with the Cl[−] or ClO₄[−] complex. In THF, the *o*-resonance was quite similar to the ferrous complex, while the *p*-resonances increased by 4 ppm and the *m*-resonances by 11 ppm. In AmNTf₂, the chemical shifts of the *p*- and *m*resonances decreased from their values in THF. In addition, in AmNTf2, the *p*- and *m*-resonances for Fe(FP)⁻ and Fe^{II}(FP) are similar but the *o*-resonances differed.

In order to understand the solvation changes in mixed solvents, the 19 F NMR spectra for Fe(FP) complexes as a function of %AmNTf₂ were obtained. For the ferric complexes, the chemical shifts were small and the major effect of AmNTf₂ was a broadening due to the increase in viscosity. The ferrous porphyrins showed significant shifts when the solvent was changed. The *meta*-fluorine shifted from −167.1 to −161.8 ppm when the solvent was changed from THF to AmNTf2. There were similar shifts for the *para*-fluorine. The ¹⁹F NMR spectra of THF/AmNTf₂ mixtures are shown in Figure [8](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0008) A. At lower concentrations of AmNTf₂ (less than 60–70 %), single ¹⁹F NMR resonances were observed due to exchange between the AmNTf₂/THF nanodomains. This was different from the visible spectra where separate species were observed, due to the difference in the time domains for visible versus NMR spectroscopy. At higher concentrations of $AMNT₂$, discrete resonances for the two nanodomains were observed. Figure [9](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0009) shows the deconvolution of Fe^{II}(FP) in 80 % AmNTf₂. The green shaded areas were identified as Fe["](FP) in the AmNTf₂ nanodomain. The *meta*-resonances at -162.1/-163.1 ppm corresponded well with the −160.6 ppm value in pure AmNTf₂, with *para*-resonances at −155.3 ppm (−153.2 ppm in pure AmNTf2) and *ortho*‐resonances at −127.4 and −130.9 ppm, the average of which is close to the resonance in pure AmNTf2 (−129.9 ppm). The split resonances may be due to the slow rotation of the phenyl groups in the highly viscous RTIL. The blue shaded resonances (−138.9, −155.8 and -164.2 ppm) corresponded well with Fe["](FP)(THF)₂ (-141.8 , -153.2 and -167.1 ppm). A minor red component was consistent with some residual ferric complex.

Figure 8 ¹⁹F NMR of Fe^{II}(FP) (A) and Fe(FP)⁻ (B) in mixed THF/AmNTf₂ solutions. (v/v)% AmNTf₂ are given in the figures.

Figure 9 19F NMR spectrum of Fe(FP) in 80 % AmNTf2/THF. Green peaks: Fe(FP) in AmNTf2; Blue peaks: Fe(FP) in THF; Red peak: residual Fe(FP)(Cl).

The variation in the ¹⁹F chemical shift of Fe(FP)⁻ as a function of %RTIL is shown in Figure [8](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0008) B. Significant solvation within the RTIL nanodomain could be observed at low concentrations of AmNTf₂. This is to be expected as anions are better solvated within the RTIL than neutral species. Below 50 % AmNTf₂, single resonances were observed for each fluorine indicating fast exchange between the two nanodomains. At 50 % AmNTf2, the resonances became broader, and resonances for the two domains began to appear. For example, the *meta*‐resonances (−172.8 ppm in THF) shifted gradually to lower values up to 20 % AmNTf₂, a much weaker signal was seen in 50 % AmNTf₂ and the *meta*-resonance in AmNTf₂ (about −163 ppm) was the dominant species. The ¹⁹F NMR spectra are consistent with significant solvation of the Fe(FP)[−] species in the RTIL‐nanodomain around 50 % RTIL. This also corresponded to the beginning of the non-linearity in the *E*°2 values versus %RTIL (or Gutmann AN). Dissolution in the RTIL appears to be correlated with the change in iron solvation from THF to NTf₂⁻, as the %THF declined. This will be further investigated using EPR.

EPR spectra of Fe(FP)[−] in THF and AmNTf2

Samples of Fe(FP)[−] were synthetized using borohydride reduction (which was also used for NMR analysis), and studied using EPR spectroscopy. The EPR spectra of Fe(FP)⁻ in THF and AmNTf₂ are shown in Figure [10.](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0010) The EPR spectrum of Fe(FP)[−] in THF (red trace) was consistent with the previous work of Srivatsa et al.³⁰ for Fe(TPP)⁻ in DMF, with g-values of 2.29 and 1.93 (2.28 and 1.93 for Fe(TPP)⁻). The Fe(FP)⁻ complex has been characterized as a Fe^I complex with the unpaired electron in the d₂₂ orbital. The g_⊥ is quite sensitive to the axial coordination of the iron, with the g_⊥ decreasing in the presence of stronger ligands (e.g., pyridine).³⁰ When the solvent was changed to AmNTf₂, the g_{\perp} value increased significantly to 2.65 (Figure [10,](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-fig-0010) blue trace). This change reflects the loss of THF coordination, leaving an Fe' species either uncoordinated or weakly coordinated with NTf₂⁻. Donohoe et al.³¹ speculated that the changes in the EPR in the presence of pyridine were due to the replacement of the solvent (DMF) with pyridine. This work is consistent with the observation that there is significant interaction between THF and Fe^I, at least at low temperatures.

Figure 10 EPR spectra for Fe(FP)⁻ in THF (red) and in AmNTf₂ (blue).

Solvation of iron porphyrins in mixed solvents and its effect on redox potentials The effect of ionic liquids on the redox potentials is a combination of coordination changes and solvation of the iron complexes. The shifts in the *E*°1 as a function of the Gutmann AN in the linear region (18 mV/AN) was similar to the Ni(OEP) oxidation (22 mV/AN), where the change in charge upon reduction was the same. The variation in *E*°1 for Fe(FP)(Cl) was considerably larger (93 mV/AN) as compared to $Ni(OEP)$ reduction (53 mV/AN). The large difference between Fe(FP)(ClO₄) and Fe(FP)(Cl) is quite intriguing in that the porphyrin products are identical (Fe^{II}(FP)(THF)₂) and the interaction between the cation (Fe^{III}(FP)(THF)₂⁺) or the neutral (Fe(FP)(Cl)) and an RTIL is minimal. The driving force for the shift in the *E*°1 values for Fe(FP)(Cl), as the %RTIL is increased, is probably due to solvation of the Cl[−] in the RTIL nanodomain. As a small anion, it should interact strongly with the RTIL.

As the %RTIL approaches 100 %, the ¹⁹F NMR provides evidence for coordination changes as the source of the non-linearity in the *E*°1 values as a function of log(%RTIL)/Gutmann AN. Even when the %RTIL was relatively high (80–90 %), coordination between the ferrous porphyrin and THF remained. The significant shifts in the E° ₁ value versus %RTIL only occurred near 100 % RTIL, where coordination between the Fe^{II} porphyrin and THF was lost.

Generally, the visible spectra of reduction products in molecular solvents and RTILs are characterized by shifts in the absorbance maxima due to solvation effects. Overall the spectra in RTILs are similar to the spectra in molecular solvent. Examples of this are Fe^{II}(FP) in this work, and Ni(OEP)^{- ee} The exceptions to this observation though are quite enlightening. While the RTIL anions are generally very weak bases, they are still capable of displacing Cl[−] from ferrous complexes.

The visible spectroelectrochemistry showed that $Fe^{II}(TP)$ in AmNTf₂ is coordinated, probably with the NTf₂⁻ anion. The ¹⁹F NMR showed that the phenyl fluorine resonance were split as the %RTIL approached 100 %. At 100 % RTIL, single resonances were observed due to NTf₂⁻ coordination. The transfer between the THF and RTIL nanodomain can be written as $[Eq. 9]$ $[Eq. 9]$:

 $Fe^{II}(FP)(THF)_2 + 2NTf_2^- \rightleftarrows Fe^{II}(NTf_2)_2^{2-} + 2THF$ (9)

where Fe^{II}(FP)(THF)₂ is in the THF nanodomain and Fe^{II}(FP)(NTf₂)₂²⁻ is in the RTIL nanodomain. At low %THF, this reaction would be expected to be slow. The charge on the product ferrous complex is probably minimized by strong ion pairing with the RTIL.

The spectral features of ferrous porphyrins are consistent with a six coordinate complex in AmNTf₂, even though coordination occurs with the NTf₂⁻ anion. This is possible due to the strong ion pairing of the RTIL to the anion. The displacement of anions such as Cl[−] from the ferrous complex is slow, and is not seen on the voltammetric timescale. Entropy was probably the driving force for this reaction. As a result, the net stoichiometric reaction in voltammetry was a one-electron reduction of Fe(FP)(Cl) to Fe(FP)(Cl)[−] while, in spectroelectrochemistry or NMR spectroscopy, Fe(FP) was formed.

For the second reduction, the E° for the Fe(FP)(Cl) and Fe(FP)(ClO₄) as a function of Gutmann AN are nearly the same (56 and 55 mV/AN, respectively), using the initial linear region. This was quite similar to the Ni(OEP)0/−1 redox process (53 mV/AN). As with the first reduction, the non-linear region of the *E*° versus Gutmann AN correlated with the broadening and splitting of the ¹⁹F NMR spectra. This was also probably due to coordination changes during the transfer of Fe(FP)[−] to the RTIL phase with loss of THF, which occurs at a lower %RTIL for the Fe^I porphyrin. The EPR showed a much weaker solvent interaction of Fe(FP)[−] with the RTIL, and was consistent with the loss of THF. A reaction similar to Reaction 9 can be written for Fe(FP)[−][Eq. <u>[10\]](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-disp-0010)</u>:

 $Fe(FP)(THF)^{-} \rightleftarrows FE(FP)^{-} + THF$ (10)

in which Fe(FP)(THF)[−] is in the THF nanodomain and Fe(FP)[−] is in the RTIL nanodomain.

The most significant coordination changes between the molecular solvent and the RTIL complex is the Fe(FP)[−] complex. In THF, the visible spectrum for Fe(FP)[−] was considerably bleached due to delocalization of the *d*₂₂ electron to the porphyrin ring. On the other hand, Fe(FP)[−] in AmNTf₂ showed a metal centered reduction of Fe(FP) with a strong Soret band, quite similar to Fe(TPP)⁻,^{[24c](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0024c)} as well as Fe(FP)(Cl)[−] in AmNTf2. The mostly metal centered reduction is probably favored by the weaker interaction between the solvent anion (NTf₂⁻) and the negatively charged Fe(FP)⁻. Such a formulation was also consistent with the EPR spectrum where the shift in the *g*-value was related to a greater electron density on the *d*_{z2}-orbital. The opposite effect was observed for Ni(OEPone)⁻, where the mostly metal centered reduction of Ni(OEPone)⁻ in THF was switched to significant ring delocalization in AmNTf₂, as shown by the significant downshift in the ring carbonyl band.^{2e}

Conclusion

This work shows that the solvent coordination of iron porphyrins in the presence of RTILs has a strong effect on the redox and spectroscopic properties. Previous work on mixed RTIL/molecular solvent solutions has shown a smooth transition in the redox potential as the solution was changed from pure molecular solvent to pure RTIL solutions. Iron porphyrins do not follow that behavior, with significant changes in the redox and visible spectra as the molecular solvent coordination is lost. Ni(OEP) shows only modest changes in the *E*° versus %RTIL/Gutmann AN as the mixture approach pure RTIL. Similar behavior was observed for fullerides and dinitrobenzene. In the case of iron porphyrins, coordination with the molecular solvent (THF) maintains itself, even in RTIL-rich mixtures. Surprisingly, significant changes in the redox and visible spectra have been observed as the solvent system approaches neat RTIL. This behavior is more pronounced for the more negatively charged species, due to higher

partitioning within the RTIL nanodomains and the loss of solvent coordination. Therefore, while the linear relationship between the *E*° values and the Gutmann AN is a good measure of solvation changes, the non‐linearity near 100 % is reflective of coordination changes at the metal site.

Changes in the electronic structure of the reduced product (metal vs. porphyrin reduction) should be reflected in the catalytic properties of the metal center. In addition to the positive shift in the redox potential by RTILs, the current work indicates that Fe^I porphyrins in an RTIL environment would be more nucleophilic, making them better catalysts for reactions that are initiated by nucleophilic attack. This finding is consistent with the recent work of Choi et al.,^{7} where the iron porphyrin/RTIL system increased the rate and selectivity of CO₂ activation at very low over-potentials. In their work, the addition of an RTIL caused the overpotential for $CO₂$ reduction to be lowered by 670 mV, and a four-fold increase in the turnover frequency. Ongoing efforts in our laboratory are being extended towards studies on the effects of the RTIL nanodomains on the chemical reactivity of iron porphyrin redox systems.

Experimental Section

Chemicals

Ethyldimethylpropylammonium bis(trifluoromethylsulfonyl)imide (AmNTf₂), tetrabutylammonium borohydride (TBABH4, 98 %), silver perchlorate (AgClO4), iron tetrakis(pentafluorophenyl)porphyrin chloride (FeF20TPPCl, 98 %), tetrabutylammonium perchlorate (TBAP) and anhydrous tetrahydrofuran (THF, 98.9 %) were purchased from Sigma‐Aldrich Chemical Co. Decamethylferrocene (DmFc) (99%) was purchased from VWR. Anhydrous tetrahydrofuran (THF) was refluxed in the presence of sodium and benzophenone under nitrogen until the solution turned a persistent dark blue. Water was removed from the RTIL by passing N_2 over the solvent heated at 70–90 °C. The amount of water in the RTIL was measured by monitoring the stripping peak on a gold electrode due to water. 2d, [32](https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201701540#chem201701540-bib-0032) Substantial reduction in the water concentration was obtained as evidenced by the complete disappearance of the water stripping peak.

Fe(TF₂₀PP)(ClO₄) (Fe(FP)ClO₄)) was prepared by exchanging the chloride ligand in Fe(TF₂₀PP)Cl by using the procedure of Ogoshi et al.³³ Reduction of Fe(TF₂₀PP)(ClO₄) was carried out by adding one equivalent of TBABH₄ in THF, and removing the solvent. Addition of 1.5 mole equivalent of TBABH₄ to the ferrous solution led to the low valent Fe'(FP)⁻.

Instrumentation

Cyclic voltammetry was carried out at a platinum electrode $(1.6 \text{ mm or } 10 \mu)$, and a platinum wire was used as auxiliary electrode. Potentials were measured relative to the $Ag/AgNO₃$ (in CH₃CN) reference electrode. The measurements were carried out using a Model 600D Series Electrochemical Analyzer/Workstation (CHI Version 12.06). A low-volume thin layer quartz cell, which was purchased from BAS Instruments, was used for UV/Visible spectroelectrochemical experiments. A platinum mesh was used as working electrode, a platinum wire was used as auxiliary electrode. Potentials were measured relative to the Ag/AgNO₃ (in CH₃CN) reference electrode. UV/visible spectra were recorded on a HP8452A diode array spectrophotometer. All solutions were prepared and filled into the voltammetric or spectroelectrochemical cells in the glovebox under an argon environment. Proton and fluorine NMR measurements were performed using a Varian 400 MHz FT spectrometer. EPR measurements were performed at liquid nitrogen temperatures, using a Bruker ELEXSYS E600 equipped with an ER4415DM

cavity resonating at 9.63 GHz, an Oxford Instruments ITC503 temperature controller and ESR-900 He flow cryostat.

Procedures

For electrochemical experiments, all solutions were prepared and filled into cells in the glovebox under an argon environment. Tetrabutylammonium perchlorate was used as electrolyte in molecular solvent experiments. UV/Visible spectroelectrochemical experiments were carried out by either scanning or stepping the potentials at the corresponding waves. For mixture of molecular solvents/RTILs, a total volume of 0.3–0.5 mL for voltammetry, 0.2–0.5 mL NMR and 0.1–0.2 mL for spectroelectrochemistry were prepared using micropipette. The Gutmann acceptor numbers were calculated using an NMR procedure developed by Schmeisser et al. $\frac{34}{2}$ and further described by Atifi and Ryan.^{2e} The best fit empirical equation in Table S1 was generated using the curve fitter algorithm in MATLAB. Deconvolution of the ¹⁹F NMR spectra was carried out using GRAM/32 AI software (ThermoGalactic).

Conflict of interest

The authors declare no conflict of interest.

Supporting Information

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