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Investigation of Solvation and Solvent Coordination Effects in Iron Porphyrin Nitrosyls by Infrared Spectroelectrochemistry and DFT Calculations

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ABSTRACT:

The visible and infrared spectroelectrochemistry of Fe(OEPone)(NO) (H₂OEPone = octaethylporphyrone) were examined in methylene chloride and THF. The visible spectrum of Fe(OEPone)(NO) were similar in both solvents. Unlike other ferrous porphyrin nitrosyls, a six-coordinate complex was formed with THF as a ligand. This led to two nitrosyl bands in the infrared spectrum. The absorbance of these bands depended on the concentration of THF in the solution. Solvation and coordination effects on the carbonyl and nitrosyl bands were observed for both the

nitrosyl and reduced nitrosyl complexes. DFT calculations were carried out to interpret the spectral changes.

KEYWORDS:

solvent coordination, iron porphyrin nitrosyl, infrared spectroelectrochemistry, DFT

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INTRODUCTION

Changes in the coordination geometry of iron-porphyrin complexes can have a significant impact on their properties and reactivities. Iron porphyrin dioxygen and carbon monoxide complexes are typically six coordinate if ligands are present [1]. Ferrous nitrosyl porphyrins though are generally five-coordinate, even in the presence of ligands. Ligation of nitrosyl complexes generally weakens both the nitrosyl and the bond of the *trans*-ligand [2], often leading to dissociation of the NO and the formation of a bis-ligated complex [3-7]. In ferrous guanylate cyclase (sGC), the formation of a nitrosyl complex leads to the loss of histidine ligation and the formation of a 5-coordinate nitrosyl complex [8,9].

Yoshimura et al. [10] examined the effect of solvation on the nitrosyl bond of the Fe(PPDME)(NO) complex (PPDME = protoporphyrin-dimethyl ester). The energy of the band varied over a narrow range for a variety of solvents between 1658 and 1684 cm^{-1} , with the most significant shift only being observed for the strongest coordinating solvents such as acetonitrile (1658 cm^{-1}) and DMSO (1660 cm^{-1}). Only a small shift was observed between CCl_4 (1684 cm^{-1}) [11] and THF (1673 cm^{-1}). The shifts in the nitrosyl band in the solvents studied were ascribed to solvation rather than coordination effects. Amines such as pyridine did yield bands for the five- and six-coordinate complexes. Nitrosyl bands for the six-coordinate amine complexes were observed between 1618 and 1643 cm^{-1} [10]. Linear relationships were observed between the pK_a of the base and the ν_{NO} stretching frequencies, but different linear relationships were observed for imidazoles, pyridines and aliphatic amines. The largest shifts were observed for imidazole, with smaller shifts for pyridines, then aliphatic amines. The shifts varied from 30 cm^{-1} for 3-chloropyridine ($\text{pK}_a = 2.84$) to 47 cm^{-1} for 4-methylimidazole ($\text{pK}_a = 7.52$) and 4-dimethylaminopyridine ($\text{pK}_a = 9.70$).

The visible spectra of iron porphyrin nitrosyl complexes in the presence of nitrogenase bases were studied by Yoshimura and Ozaki [6]. Wyllie et al. [12] examined the crystal structures of five- and six-coordinate iron(II) porphyrin nitrosyls. Six-coordinate Fe(TPP)(NO) complexes with 1-methylimidazole or 4-methylpiperidine led to a lengthening and weakening the Fe-N bond *trans* to the NO [3,12-14]. In the six-coordinate complex, the spin density (0.8) was mostly localized on the NO group while there was a lower spin density (0.5) for the five-coordinate complex [3]. The formation constants, K , for pyridines and amines with iron porphyrin nitrosyls were determined using voltammetry by Choi and Ryan [4] and Liu et al. [15]. The K values were found to be generally small. The formation constants for Fe(OEPone)(NO) and Fe(OEPdione)(NO) (OEPdione = 2,4-octaethylporphinedione) with pyridines were larger than Fe(OEP)(NO)/pyridine complexes.

The infrared spectroelectrochemistry of Fe(P)(NO) complexes where P = porphyrins or porphyrinones has been examined in our laboratory, mostly in THF [16]. Upon further study, it was found that

Fe(OEPone)(NO) (H₂OEPone = octaethylporphinone, Figure 1) was more complex than reported with evidence of solvent (THF) coordination, that was not observed for Fe(OEP)(NO).

RESULTS AND DISCUSSION

Infrared Spectroscopy of Fe(OEPone)(NO). The infrared spectrum of Fe(OEPone)(NO) in methylene chloride was typical of other metalloporphyrin nitrosyls (Figure 2). The ν_{NO} bands in methylene chloride and KBr were identical (Table 1). Similar results were also observed for Fe(OEP)(NO). The downshift for ¹⁵NO substitution for ^{na}NO (na = normal abundance) in methylene chloride was also consistent with metalloporphyrin nitrosyls. The infrared spectrum for Fe(OEPone)(NO) in THF though was significantly different. The ν_{NO} band at 1680 cm⁻¹ was still observed in THF, but a new band was also seen at 1658 cm⁻¹ (Figure 2). These bands have been previously observed, but the lower energy band was not attributed to be a nitrosyl vibration [16] because isotopic substitution was not done. In this work, it was found that both bands were sensitive to ¹⁵NO substitution. The lower energy nitrosyl band in THF was consistent with a six-coordinate iron porphyrin nitrosyl complex. For nitrogen-ligands, two nitrosyl bands were observed in the infrared spectra of Fe(PPDME)(NO) in the presence of nitrogen ligands, the first was due to the 5-coordinate ferrous nitrosyl complex and the second (with a downshift of 33 cm⁻¹) was due to the 6-coordinate complex. Ligation *trans*- to the nitrosyl ligand in iron porphyrin complexes is generally weak. For example, the equilibrium constant for the ligation of pyridine with Fe(OEP)(NO) is about 0.3, which increased to 4.8 for Fe(OEPone)(NO) [15].

Repeating the experiment with Fe(OEP)(NO), only a single isotopically sensitive ¹⁵NO band was observed in methylene chloride and THF. In addition, there was no significant difference in the ν_{NO} band between KBr pellets and THF. The infrared bands for ν_{CO} and ν_{NO} are summarized in Table 1. In addition to the downshift of the nitrosyl band, the ν_{CO} was upshifted by 5 cm⁻¹ in THF as compared to methylene chloride. On the other hand, the ν_{NO} was the same in methylene chloride and the five-coordinate complex in THF (1681 cm⁻¹) (Table 1).

The appearance of the 1658 cm⁻¹ band was found to be a function of the %THF in methylene chloride (Figure S1). The band could be clearly observed at 60% THF or more, and the height of the band, relative to the 1680 cm⁻¹ band increased as the %THF increased. A rough estimate of the percent 6-coordinate complex that was present was estimated by using the absorbance of the ν_{CO} band as a reference and assuming that the molar absorptivity of the ν_{CO} band of the 5- and 6- coordinate is the same. With these rough assumptions, 22% of the iron nitrosyl species was 6-coordinate in 60% THF, increasing to 46% in pure THF. This would yield a K for the formation of the 6-coordinate THF complex to be 0.07±0.02.

Spectroelectrochemical Reduction of Fe(OEPone)(NO) in methylene chloride and THF. The visible spectroelectrochemistry of Fe(OEPone)(NO) in methylene chloride is shown in Figure S2. The Soret band shifted from 406 to 410 nm, and decreased slightly in absorbance. In the longer wavelength region, the 625 nm band disappeared and two new bands at 532 and 612 nm appeared. Similar results were observed for the reduction of Fe(OEPone)(NO) in THF (Figure S3), with the Soret band shifting from 410 to 415 nm, and the Q-band for the nitrosyl complex was 618 nm, and for the reduced nitrosyl complex the bands were 535 and 607 nm.

The infrared spectroelectrochemical difference spectra of Fe(OEPone)(NO) in methylene chloride is shown in Figure 3. The general features show the reduction of the carbonyl band at 1710 cm⁻¹ and the nitrosyl band at 1681 cm⁻¹. The reduced nitrosyl band at 1440 cm⁻¹ increased as the reduction proceeded. The carbonyl band was considerably downshifted by the reduction, as can be seen by the

positive ν_{A} band at 1662 cm^{-1} . The insert in Figure 3 shows the absorbance spectra for $\text{Fe}(\text{OEPone})(\text{NO})$ and $\text{Fe}(\text{OEPone})(\text{NO})^-$ between 1750 and 1600 cm^{-1} . The band at 1669 cm^{-1} for ν_{CO} can be seen (the overlap with the nitrosyl band caused a shift in the difference spectrum). This downshift was comparable to the ν_{CO} band shift that was observed for the formation of $\text{Fe}(\text{OEPone})^-$ in THF (1671 cm^{-1}) [16]. The infrared spectroelectrochemistry of $\text{Fe}(\text{OEPone})(^{15}\text{NO})$ was carried out (Figure S4). The nitrosyl band was downshifted to 1647 cm^{-1} and the reduced nitrosyl band to 1410 cm^{-1} . These shifts were consistent with the isotopic substitution. As expected, the carbonyl bands for the nitrosyl and the reduced nitrosyl complexes were unchanged from the normal abundance spectra.

The infrared spectroelectrochemistry of $\text{Fe}(\text{OEPone})(\text{NO})$ in THF is shown in Figure 4. Both Fe-NO bands decreased as the reduction proceeded but only one ν_{NO} (1440 cm^{-1}) was observed for the reduced nitrosyl product, which was a value typical of other reduced ferrous porphyrin nitrosyls [16], and $\text{Fe}(\text{OEPone})(\text{NO})$ in methylene chloride. The downshift of the ν_{CO} band is significantly smaller (1715 to 1702 cm^{-1}) than the shift observed earlier in methylene chloride. The results were confirmed for $\text{Fe}(\text{OEPone})(^{15}\text{NO})$ (Figure S5) where the nitrosyl and the reduced nitrosyl bands were both downshifted as expected, and the carbonyl bands were at the same position as for the normal abundance spectra. The small shift in the ν_{CO} band as compared to methylene chloride was probably due to solvation rather than coordination effects. This will be investigated in the next section. Voltammetric data showed no evidence for 6-coordinate complexes for the reduced nitrosyl complex, consistent with the fact that stronger ligands showed no evidence of coordination [4,15].

DFT Calculations. DFT calculations were carried out on the 5- and 6-coordinate $\text{Fe}(\text{OEPone})(\text{NO})$ complexes and their reduction product. In general, the localized functionals such as m06L and bp86 predicted stronger Fe-THF interactions than m06 and mpwvwn. In fact, mpwvwn predicted no bond between iron and THF. For the other functionals, the Fe-O(THF) bond lengths from 2.489 \AA (bp86) to 2.569 \AA (m06) were calculated. These bond lengths were somewhat longer than the experimental Fe-O(THF) bond length in $\text{Fe}(\text{TPP})(\text{THF})_2$ of 2.351 \AA [17]. The calculated O-Fe-N bond angle in $\text{Fe}(\text{OEPone})(\text{THF})(\text{NO})$ was found to be 173° , with the deviation due to the known tilt of the Fe-NO group. The DFT calculations were consistent with a weak complexation of THF to the iron-nitrosyl complex.

The calculated ν_{NO} and ν_{CO} bands for $\text{Fe}(\text{OEPone})(\text{NO})$ complexes are shown in Table 1. The m06 functional predicted the longest Fe-O(THF) bond, and also predicted that THF coordination would not affect the ν_{NO} and ν_{CO} bands. As would be expected, a shorter Fe-O(THF) bond led to a greater downshift in the ν_{NO} band, dropping by 8 cm^{-1} for m06L to 18 cm^{-1} for bp86. These compare with the observed downshift of 23 cm^{-1} . The absolute values of the ν_{NO} and ν_{CO} energies followed trends which we have seen earlier. The bp86 functional predicts reasonably well the experimental values without a scale factor, but its energies are systematically low [18]. The m06 and m06L generally need a scale factor of 0.94 and 0.96, respectively, for these complexes. In this work, the bp86 predicted a small upshift in the ν_{CO} band upon forming the THF complex (as was observed), while the m06 functional showed no shift and the m06L functional predicted a downshift.

As was discussed earlier [3], the SOMO for $\text{Fe}(\text{OEPone})(\text{NO})(\text{THF})$ is mostly localized on the Fe-NO moiety (Figure S6). By contrast, there was significant delocalization of the electron density in the five coordinate complex (Figure S6). Similar results were observed by Praneeth et al. [3] for $\text{Fe}(\text{P})(\text{NO})$ complexes with nitrogen ligands.

DFT calculations of Fe(OEPone)(NO)(THF)- showed a much weaker interaction between the Fe atom and THF than was observed for the nitrosyl complex. The Fe-O(THF) bond length increased from 2.530 Å to 2.657 Å (m06L), with an O-Fe-N bond angle of 176°. As discussed earlier, stronger ligands such as pyridine showed no evidence for coordination with the reduced nitrosyl complex. Thus, both DFT calculations and experimental evidence showed that the reduced iron nitrosyl species was 5-coordinate. The most significant difference in the infrared spectra between Fe(OEPone)(NO)- in THF and methylene chloride is the carbonyl band. Only a small downshift was observed for ν_{CO} in THF solution (1715 to 1702 cm^{-1} , or 13 cm^{-1} downshift), while the ν_{CO} in methylene chloride decreased from 1710 to 1669 cm^{-1} (41 cm^{-1} downshift). The origin of this shift is not due to coordination differences, but rather due to solvation. Evidence for this can be seen in comparing the HOMO for Fe(OEPone)(NO)- with and without solvation (Figure 5). Figure 5A shows the HOMO for THFsolvated Fe(OEPone)(NO)-. The electron density was mostly on the Fe-NO moiety, with essentially no electron density on the carbonyl group. By contrast, Figure 5B (for the unsolvated complex) showed an increased electron density on the carbonyl group, in an anti-bonding π^* -orbital, weakening the C-O bond, consistent with a larger downshift in the poorly solvating methylene chloride. This has been observed before for Ni(OEPone)- where interactions between a strongly associated cation and the carbonyl group [19] downshifted the ν_{CO} band by increasing the electron density on the carbonyl group, and hence, the π^* -orbital. The observed differences in the ν_{CO} between the two solvents can be best attributed to solvation rather than iron coordination effects.

EXPERIMENTAL

Materials and Reagents. Tetrahydrofuran (THF) and methylene chloride (CH_2Cl_2) were purchased from Sigma-Aldrich Chemical Co. THF- d_8 and methylene chloride- d_2 were purchased from Cambridge Isotope Laboratories. The deuteriated solvents were used for infrared spectroelectrochemical experiments. Octaethylporphyrone was purchased from Frontier Scientific, and iron was inserted and the nitrosyl complex synthesized by literature procedures [20,21].

Equipment and Procedures. The FTIR spectroelectrochemical cell was described previously [16]. The infrared spectra were obtained using 64 scans and 2 cm^{-1} resolution, recorded with a Thermo Nicolet-FTIR spectrophotometer (Model 670 Nexus) with a MCT detector. The visible spectroelectrochemical experiments have been previously described [22]. The UV/Visible spectra were recorded on a HP 8452A diode array spectrophotometer. All solutions were prepared in the glove box under dinitrogen. For UV/Visible spectra, a slow cyclic scan of the potential was used. For the FTIR, potentials were chosen to be sufficiently negative to insure complete electrolysis.

Computational Methods. Electronic structure calculations were carried out with the Gaussian 09 suite of programs [23] using the procedures previously described [22], or, as noted, by the Gaussian 16 suite of program [24]. Infrared frequencies were corrected with scale factors of 0.94 for m06, 0.96 for m06L and 1.0 for mpwvwn and bp86.

CONCLUSIONS

Solvents can affect spectral and redox properties of a complex by either solvation or coordination effects. Ferrous porphyrin nitrosyl complexes are often 5-coordinate, and 6-coordinate complexes are prone to the loss of NO and the formation of bis-ligand complexes. While Fe(OEP)(NO) shows no evidence of coordination with THF, the porphyrone analogue was able to form a 6-coordinate complex with THF. In this work, the combination of infrared spectroelectrochemistry and DFT calculations made it possible to identify changes that were primarily due to coordination or solvation. Solvent

coordination by THF to the ferrous nitrosyl complex was the source of the significant downshift in the ν_{NO} band for Fe(OEPone)(NO). For Fe(OEPone)(NO)-, solvation was the source of the observed changes in the carbonyl band, with little evidence for the formation of a six-coordinate complex. This was consistent with previous studies where the reduced iron-nitrosyl complex was a much weaker Lewis acid. On the other hand, the solvation of the reduced Fenitrosyl moiety by THF drew electron density away from the π^* -orbital between C and O, causing the ν_{CO} to downshift significantly less than was observed in a non-coordinating solvent such as methylene chloride.

References

1. Linder DP, Silvernail NJ, Barabanschikov A, Zhao J, Alp EE, Sturhahn W, Sage JT, Scheidt WR and Rodgers KR. *J. Am. Chem. Soc.* 2014; **136**: 9818-9821.
2. Komatsu T, Matsukawa Y and Tsuchida E. *Chem. Lett.* 2000: 1060-1061.
3. Praneeth VKK, Näther C, Peters G and Lehnert N. *Inorg. Chem.* 2006; **45**: 2795-2811.
4. Choi I-K and Ryan MD. *Inorg. Chim. Acta* 1988; **153**: 25-30.
5. Lançon D and Kadish KM. *J. Am. Chem. Soc.* 1983; **105**: 5610-5617.
6. Yoshimura T and Ozaki T. *Arch. Biochem. Biophys.* 1984; **229**: 126-135.
7. Bohle DS and Hung CH. *J. Am. Chem. Soc.* 1995; **117**: 9584-9585.
8. Stone JR and Marletta MA. *Biochemistry* 1994; **33**: 5636-5640.
9. Hunt AP and Lehnert N. *Acc. Chem. Res.* 2015; **48**: 2117-2125.
10. Yoshimura T. *Arch. Biochem. Biophys.* 1983; **220**: 167-178.
11. Yoshimura T. *Bull. Chem. Soc. Jpn.* 1978; **51**: 1237-1238.
12. Wyllie GRA, Schulz CE and Scheidt WR. *Inorg. Chem.* 2003; **42**: 5722-5734.
13. Scheidt WR and Piciulo PL. *J. Am. Chem. Soc.* 1976; **98**: 1913-1919.
14. Scheidt WR, Brinegar AC, Ferro EB and Kirner JF. *J. Am. Chem. Soc.* 1977; **99**: 7315-7322.
15. Liu YM, DeSilva C and Ryan MD. *Inorg. Chim. Acta* 1997; **258**: 247-255.
16. Wei Z and Ryan MD. *Inorg. Chem.* 2010; **49**: 6948-6954.
17. Reed CA, Mashiko T, Scheidt WR, Spartialian K and Lang G. *J. Am. Chem. Soc.* 1980; **102**: 2302-2306.
18. Tutunea F, Atifi A and Ryan MD. *J. Electroanal. Chem.* 2015; **744**: 17-24.
19. Atifi A and Ryan MD. *Anal. Chem.* 2015; **87**: 12245-12253.
20. Stolzenberg AM, Strauss SH and Holm RH. *J. Am. Chem. Soc.* 1981; **103**: 4763-4778.
21. Choi I-K, Liu YM, Wei Z and Ryan MD. *Inorg. Chem.* 1997; **36**: 3113-3118.
22. Rahman MH and Ryan MD. *Eur. J. Inorg. Chem.* 2018: 1762-1765.
23. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone B, Mennucci B, Petersson GA, Natatsuji H, Caricota M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Jr., Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J and Fox DJ; Gaussian, Inc.: Wallingford,CT, 2009.
24. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li X, Caricato M, Marenich AV, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, Ortiz JV, Izmaylov AF, Sonnenberg JL, Williams, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski VG, Gao J, Rega N,

Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery Jr. JA, Peralta JE, Ogliaro F, Bearpark MJ, Heyd JJ, Brothers EN, Kudin KN, Staroverov VN, Keith TA, Kobayashi R, Normand J, Raghavachari K, Rendell AP, Burant JC, Iyengar SS, Tomasi J, Cossi M, Millam JM, Klene M, Adamo C, Cammi R, Ochterski JW, Martin RL, Morokuma K, Farkas O, Foresman JB and Fox DJ: Wallingford, CT, 2016.

Figure 1. Structure of octaethylporphirone.

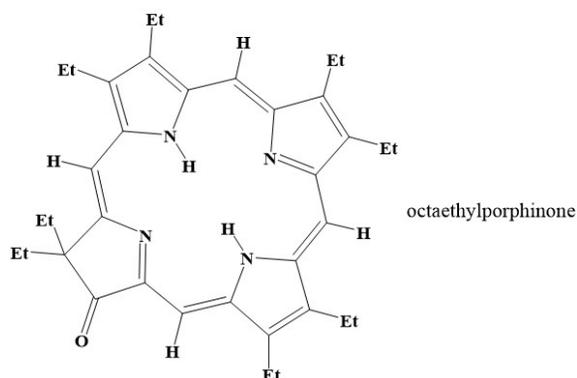


Figure 2. Infrared spectra of Fe(OEPone)(NO) in methylene chloride and THF. Fe(OEPone)(naNO): CH₂Cl₂ (red), THF (black); Fe(OEPone)(¹⁵NO): CH₂Cl₂ (blue), THF (green).

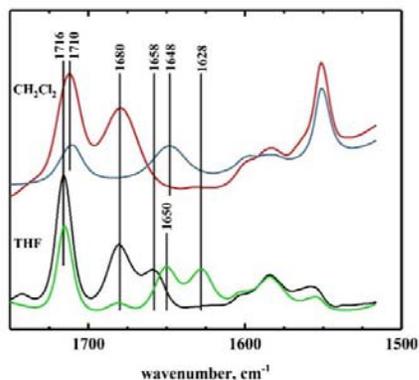


Figure 3. Difference infrared spectroelectrochemical spectra of Fe(OEPone)(NO) in CD₂Cl₂. Red spectra: initial difference spectrum; green: intermediate spectra; blue: final spectrum. Insert: Absorbance spectrum of Fe(OEPone)(NO) (red); spectrum of Fe(OEPone)(NO)- (blue).

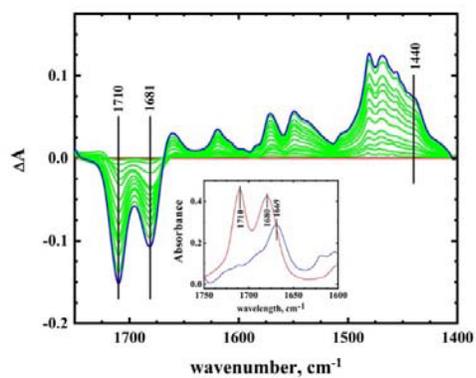


Figure 4. Difference infrared spectroelectrochemical spectra of Fe(OEPone)(NO) in THF. Red spectra: initial difference spectrum; green: intermediate spectra; blue: final spectrum.

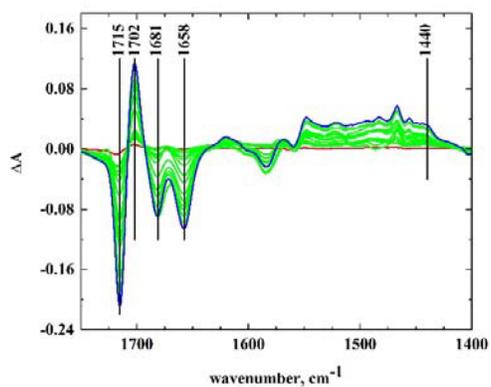


Figure 5. HOMO orbitals for Fe(OEPone)(NO)- with THF solvation (A) and without solvation (B). Functional: m06. Gaussian 16.

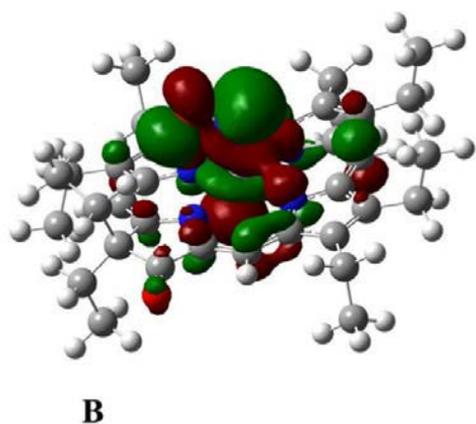
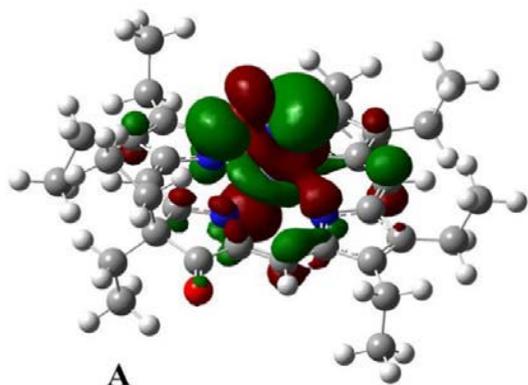
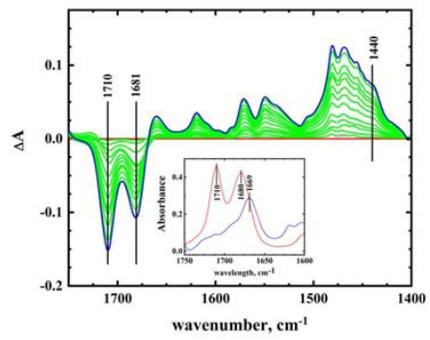


Table 1. Experimental and calculated infrared bands for CO and NO vibrations

Compound		Solvent	ν_{CO} , cm^{-1}	ν_{NO} , cm^{-1}
Fe(Oxepine)(NO)	Experimental	CH ₂ Cl ₂	1710	1681
	Experimental	THF	1715	1681
	Experimental	Kabir	1715	1681
	DFT/m06	---	1720	1683
	DFT/m06L	---	1718	1702
	DFT/bp86	---	1701	1690
Fe(OEPone)(THF)(NO)	Experimental	THF	1715	1658
	DFT/m06	---	1721	1683
	DFT/m06L	---	1713	1694
	DFT/bp86	---	1698	1672
Fe(OEPone)(NO) ⁻	Experimental	CH ₂ Cl ₂	1669	1440
	Experimental	THF	1702	1440
	DFT/m06	---	1679	1538

Graphical Abstract



Investigation of Solvation and Solvent Coordination Effects in Iron Porphyrin Nitrosyls by Infrared Spectroelectrochemistry and DFT Calculations

Md. Hafizur Rahman and Michael D. Ryan*

Figure S1. Infrared spectra of Fe(OEPone)(NO) in mixtures of THF and CH₂Cl₂. %THF: 0% THF (black); 60% THF (green); 80% THF (blue); 100% THF (purple).

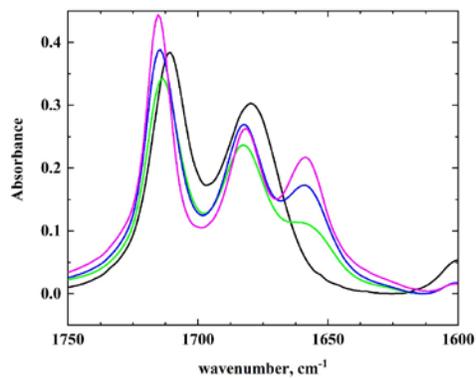


Figure S2. Visible spectroelectrochemistry of Fe(OEPone)(NO) in methylene chloride with 0.10 M TBAP. Potentials: -800 mV (black) and -1396 mV (red); intermediate spectra (green; -1176 mV, -1216 mV, -1256 mV, -1316 mV). Potentials vs Ag/AgNO₃.

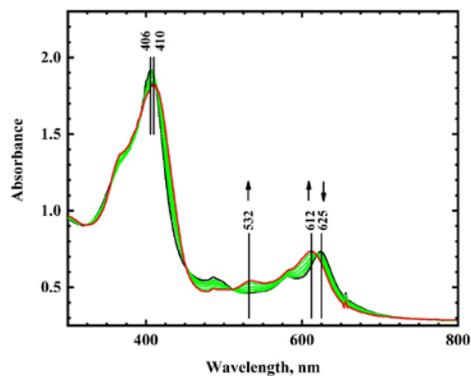


Figure S3. Visible spectroelectrochemistry of Fe(OEPone)(NO) in THF with 0.10 M TBAP. Potentials: -800 mV (black) and -1396 mV (red); intermediate spectra (green) -996 mV, -1116 mV, -1196 mV, -1276 mV. Potentials vs Ag/AgNO₃.

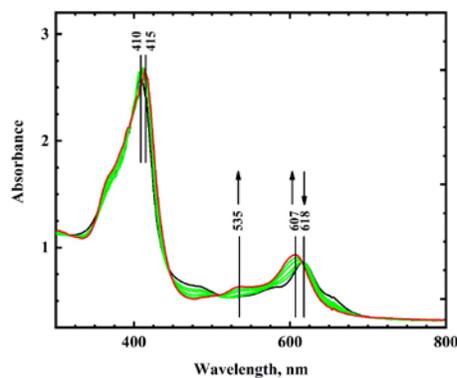


Figure S4. Infrared spectroelectrochemistry of Fe(OEPone)(¹⁵NO) in CH₂Cl₂-d₂. Initial spectrum (red): after 37 s; Intermediate spectra (green): after 74, 107, 140, 169, 237, 401, 596, 759 and 879 s; Final spectrum (blue): after 1018 s. Insert: Absorbance spectra in THF of Fe(OEPone)(¹⁵NO) (blue) and Fe(OEPone)(¹⁵NO)⁻ (red).

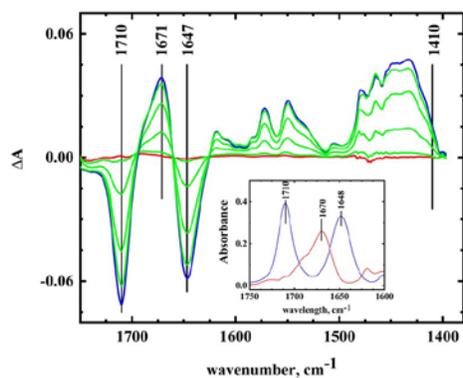


Figure S5. Infrared spectroelectrochemistry of Fe(OEPone)(¹⁵NO) in THF-d₈. Initial spectrum (red): after 37 s; Intermediate spectra (green): after 74, 107, 140, 169, 237, 401, 596, 759 and 879 s; Final spectrum (blue): after 1018 s.

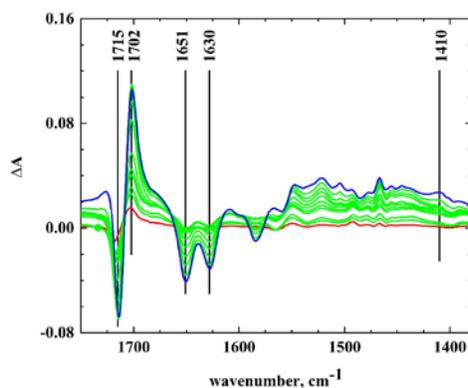


Figure S6. SOMO for Fe(OEPone)(NO)(THF) and Fe(OEPone)(NO) (m06l functional).

