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Phase and Redox Shifted Four Iron / Four Sulfur Clusters; Fluorous Analogs of Metalloenzyme Cofactors†

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Abstract. Reactions of (1) $[Q]_2[Fe_4S_4(SC(CH_3)_3)_4]$ and the fluorous thiols $HS(CH_2)_nR_{f8}$ (n = 2, 3; R_{f8} = $(CF_2)_7CF_3$)), or (2) $[Na]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$ (n = 2, 3) and $[PhCH_2P((CH_2)_3R_{f6})_3][Br]$ or [PPN][Cl] (PPN = $Ph_3P{\cdots}N{\cdots}PPh_3$), give the title compounds $[Q]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$, comprised of a fluorous dianion and in some cases fluorous cations, with (1) Q/n = Ph_4P/2 (**4**, 67%), Ph_4P/3 (**5**, 67%), Me_4N/3 (69%), and $Ph_3P(CH_2)_2R_{f6}$/2 (73%) or (2) $PhCH_2P((CH_2)_3R_{f6})_3$/2 (**14**, 39%), $PhCH_2P((CH_2)_3R_{f6})_3$/3 (**15**, 63%), and PPN/2 (36%). The educt $[Ph_3P(CH_2)_2R_{f6}]_2[Fe_4S_4(SC(CH_3)_3)_4]$ is in turn prepared from $FeCl_3$, $HSC(CH_3)_3/CH_3ONa$, and $[Ph_3P(CH_2)_2R_{f6}][I]$, and the educts $[Na]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$ from $[Na]_2[Fe_4S_4(SC(CH_3)_3)_4]$ and $HS(CH_2)_nR_{f8}$. The SCH_2 ^1H and ^{13}C NMR signals of these paramagnetic salts appear 8.7-10.3 and 32.3-34.9 ppm downfield from those of the corresponding thiols, but the chemical shifts of other signals are nearly normal. The UV-visible spectra show bands similar to those of non-fluorous analogs (290-298 nm and 406-415 nm; ε = 25700 and 19200 $M^{-1}cm^{-1}$ for **5**). The singly fluorous salts are soluble in organic solvents of moderate polarity, but not in fluorous solvents. The doubly fluorous salts **14**, **15** are soluble in all fluorous solvents assayed, with partition coefficients of >99.65:<0.35 ($CF_3C_6F_{11}$/toluene) and 93.2-93.1:6.9-6.8 (FC-72/THF). Cyclic voltammograms carried out using a platinum working microelectrode show that **4** is 0.08 V thermodynamically easier to reduce than **5**.

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Introduction

Iron/sulfur clusters are pervasive throughout biology,[1] and approximately cubic Fe_4S_4 systems featuring four iron bound thiolate ligands constitute one of the most prominent classes.[2] During the sixties and seventies, syntheses of model compounds of the formula $\underline{n}Q^+$ $[Fe_4S_4(SR)_4]^{n-}$ were developed, with Q^+ typically an alkali metal, ammonium, or phosphonium cation.[2a,3-5] Their "electron reservoir" properties were studied in detail; species could be generated in five redox states, with n = 0 (4Fe(III)), 1 (3Fe(III)/1Fe(II)), 2 (2Fe(III)/2Fe(II)), 3 (1Fe(III)/3Fe(II)), and 4 (4Fe(II)).[6] Spectroscopic features were carefully compared with those of related iron-sulfur proteins,[7] and a number of complexes were tested as components of functional models for various metalloenzymes.[8]

More recently, analogs in which the thiolates have been replaced by cyanide or "modern" N-heterocyclic carbene ligands, $\underline{n}Q^+$ $[Fe_4S_4(CN)_4]^{n-}$ or $[Fe_4S_4(NHC)_4]^{n-}$, have been reported.[9,10] Consistent with the markedly different electronic properties of these ligands, the redox potentials shift dramatically, allowing the first isolations of "all ferrous" (4Fe(II)) clusters. This proved of special interest in view of evidence supporting an all ferrous iron/sulfur assembly in one of the two nitrogenaese proteins from *Azotobacter vinelandii*.[11]

Horváth, Rábai, our group, and many others have demonstrated that by introducing appropriate numbers of perfluoroalkyl groups ($(CF_2)_{n-1}CF_3 = R_{fn}$) of sufficient lengths, a variety of neutral molecules can be rendered soluble in nonpolar fluorous liquid phases, such as perfluorohexanes (FC-72).[12] We have also shown that many ionic compounds,[13] such as organic ammonium and phosphonium salts, as well as salts of inorganic polycations,[14] can similarly be rendered soluble in fluorous phases.[15,16] As such, it was natural to speculate whether the right combination of fluorous thiolate substituents and fluorous cations might render salts of the type $\underline{n}Q^+$ $[Fe_4S_4(SR)_4]^{n-}$ soluble in fluorous media. In addition to this "phase shift", the thiolate based R_{fn} moieties should also shift redox potentials, rendering reductions to ferrous rich states thermodynamically more favorable.

This line of investigation could have practical aspects. Although "nothing sticks to Teflon", small nonpolar molecules retain appreciable solubilities in fluorous solvents.[15] Such fluids possess very low "cavitation energies",[17] creating space for small nonpolar guests but offering little in the way of enthalpically favorable interactions. For this reason, various perfluorinated media have been studied as oxygen carriers or blood substitutes, and even commercialized for this purpose.[18] In this context, the central role of iron/sulfur clusters in nitrogen fixation is well established.[19] The reactants nitrogen and hydrogen have, as with oxygen, appreciable solubilities in fluorous solvents, as tabulated below.[20,21] Hence, this represents a tantalizing but to our knowledge overlooked environment for nitrogen fixation. Furthermore, since the reduction products hydrazine and ammonia are highly polar, they should have very low solubilities in fluorous solvents and readily phase separate.

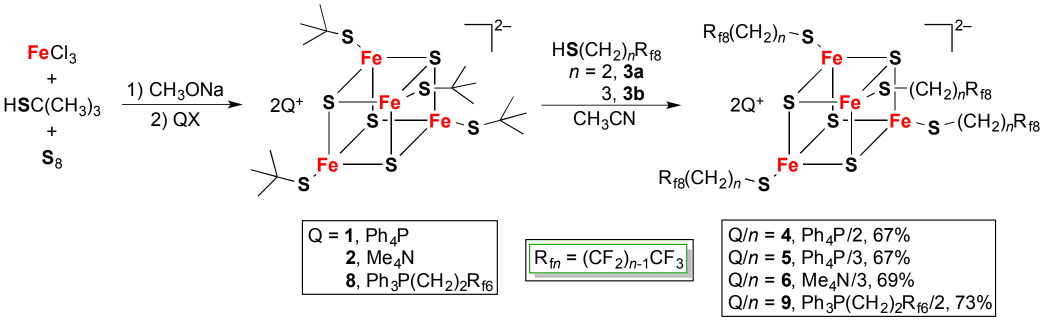
Accordingly, in this paper we report convenient syntheses of the paramagnetic 2Fe(III)/ 2Fe(II) iron/sulfur cluster salts $[Q]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$, which feature a fluorous dianion and cations that exhibit a range of fluorophilicities: non-fluorous, "light fluorous", and "heavy fluorous".[22] Their spectroscopic and phase properties are investigated, and redox characteristics analyzed, thus providing a solid baseline for future applications of these unique complexes.

Results

1. Syntheses of Fluorous Iron/Sulfur Clusters. The *t*-butylthiolate substituted iron/sulfur cluster salts $[Ph_4P]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**1**) and $[Me_4N]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**2**) were prepared by literature procedures as depicted in Scheme 1.[3] These compounds have been shown to react with slight excesses of thiols (HSR) to give substitution products of the formula $[Q]_2[Fe_4S_4(SR)_4]$.[4,5] Accordingly, the fluorous aliphatic thiols $HS(CH_2)_nR_{f8}$ (**3a**, $n = 2$; **3b**, $n = 3$), which feature two and three "methylene spacer" segments, were synthesized as previously described.[23]

As shown in Scheme 1, a CH_3CN solution of the phosphonium salt **1** was treated with the "two spacer" thiol **3a** (6.25 equiv). Workup gave the target cluster $[Ph_4P]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (**4**) as a dark brown solid in 67% yield. A similar reaction with the "three spacer" thiol **3b** (5.0 equiv) gave the homolog $[Ph_4P]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (**5**) in 67% yield. When the ammonium salt **2** and **3b** were similarly reacted, $[Me_4N]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (**6**) was isolated in 69%

yield. The characterization of these complexes is described below.

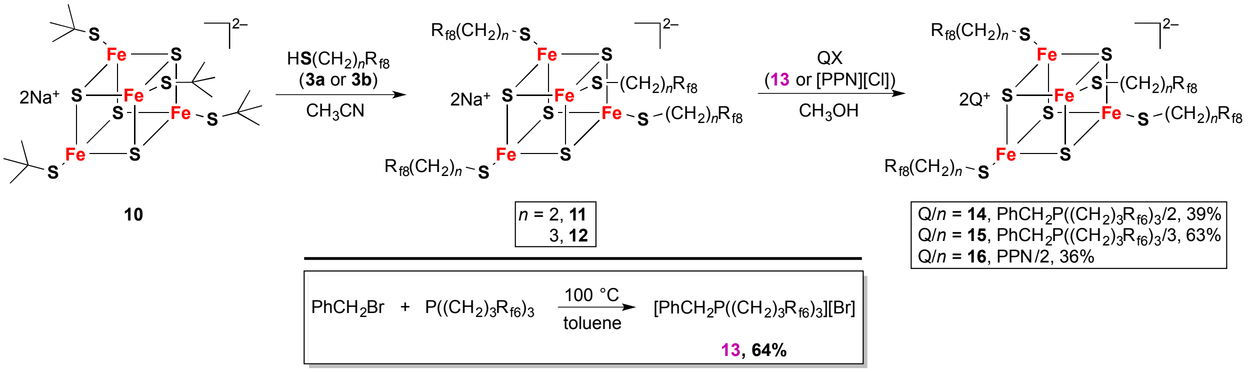


Scheme 1. Syntheses of fluorous iron/sulfur clusters by thiolate ligand exchange.

Salts with both fluorous anions and cations were sought. Efforts began with a sequence similar to that used to prepare **1** and **2** (Scheme 1). Thus, an anhydrous CH_3OH solution of CH_3-ONa and $HSC(CH_3)_3$ (ca. 4 equiv each; the latter also serves as a reductant) was treated with anhydrous $FeCl_3$ (1.0 equiv) and then elemental sulfur (1.0 equiv). After a filtration step (to give a solution of a disodium salt described below), the previously reported "light fluorous" phosphonium salt $[Ph_3P(CH_2)_2R_{f6}][I]$ (**7**;[24] 0.75 equiv or a 1.5 fold excess) was added. Workup gave crude $[Ph_3P(CH_2)_2R_{f6}]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**8**) as a black solid in ca. 25% yield. The NMR spectrum indicated a purity of ca. 90%, which despite extensive attempts could not be improved. However, this sufficed for subsequent chemistry.

Next, a CH_3CN solution of **8** was treated with the "two spacer" thiol $HS(CH_2)_2R_{f8}$ (**3a**, 6.0 equiv). Workup as above gave the target doubly fluorous salt $[Ph_3P(CH_2)_2R_{f6}]_2[Fe_4S_4(S$-$(CH_2)_2R_{f8})_4]$ (**9**) as a dark brown solid in 73% yield. This sample was pure by NMR, although the carbon microanalysis was slightly high (31.69% vs. 31.02% calcd).

Approaches to doubly fluorous systems involving cation metatheses were then investigated. First, an anhydrous CH_3OH solution of CH_3ONa, $HSC(CH_3)_3$ (ca. 4 equiv each), $FeCl_3$ (1.0 equiv), and elemental sulfur (1.0 equiv) were combined as in Scheme 1. An intermediate workup gave the crude *t*-butylthiolate substituted disodium salt $[Na]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**10**) as a black solid. Others have similarly generated this species and exchanged the thiolate ligands in situ.[3] Thus, as shown in Scheme 2, the fluorous thiols **3a**,**b** (ca. 4 equiv) were added, and workups gave the new disodium salts $[Na]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$ (**11**, n = 2, 81%; **12**, n = 3, 50%). The former could only be obtained in crude form, but the latter was pure by NMR. Complex **11** could also be prepared in comparable yield and purity in a single step from $FeCl_3$, a CH_3OH solution of CH_3ONa, elemental sulfur, and **3a** in place of $HSC(CH_3)_3$.



Scheme 2. Syntheses of fluorous iron/sulfur clusters by cation exchange.

Next, a "heavy fluorous" phosphonium salt was sought. Thus, as depicted in Scheme 2 (bottom), the known "heavy fluorous" phosphine $P((CH_2)_3R_{f6})_3$[25] and benzyl bromide were reacted in toluene at 100 °C. Workup gave the new salt $[PhCH_2P((CH_2)_3R_{f6})_3][Br]$ (**13**) as a colorless sticky but analytically pure liquid in 64% yield. The fluorous disodium salts **11** and **12** were then combined with **13** (2.0 equiv) in MeOH. Workups gave the dark brown doubly fluorous salts $[PhCH_2P((CH_2)_3R_{f6})_3]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (**14**) and $[PhCH_2P((CH_2)_3R_{f6})_3]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (**15**) in 39% and 63% yields, respectively. The lower yield of the former can be attributed to the lower purity of the precursor **11**.

Extensive attempts were made to grow single crystals of the preceding salts. However, in only one case was a crystal obtained that diffracted. The perfluoroalkyl chains were hopelessly disordered, although refinement unambiguously located the $(FeS)_4S_4$ core and two Ph_4P^+ cations. In another effort to obtain a crystalline sample, crude **11** and [PPN][Cl][26] (PPN = $Ph_3P\cdots N\cdots PPh_3$) were combined in degassed MeOH. Workup gave the salt $[PPN]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (**16**) as dark brown plates in 36% yield. However, crystallization again failed.

2. Properties of Fluorous Iron/Sulfur Clusters. The fluorous iron/sulfur clusters **4-6**, **9** and **14-16** were characterized by a variety of techniques, but due to their lower purities, the synthetic intermediates **8** and **11** were not further examined. The doubly fluorous salts (**14**, **15**) gave satisfactory microanalyses. However, the carbon values of other salts were slightly off (0.67-0.70% for **4** and **9**), and in two cases the sulfur values similarly deviated (**12**, **16**).

As summarized in Table 1, solubilities were qualitatively surveyed. All of the singly fluorous salts (**4-6**, **16**) were soluble in organic solvents of moderate polarity, but not in fluorous solvents. Those with non-fluorous phosphonium cations (**4**, **5**, **16**) exhibited some solubility in less polar solvents such as Et_2O, benzene, and toluene, but the tetraethylammonium salt (**6**) did not. In contrast, the two doubly fluorous salts with "heavy fluorous" cations (**14**, **15**) were soluble in all of the fluorous solvents assayed, and much less soluble in common organic solvents with the exception of THF. Complex **9**, with a "light fluorous" cation, was insoluble in fluorous solvents and quite variable with respect to organic solvents.

(insert Table 1 here)

Fluorous/organic partition coefficients for **14** and **15** were probed by UV-visible spectroscopy as described in the experimental section. Neither **14** nor **15** showed a detectable level of solubility in toluene. Hence, it was only possible to set a boundary value of >99.65:<0.35 for the $CF_3C_6F_{11}$/toluene partition coefficients (the most frequently assayed solvent combination in the literature).[16] However, due to the greater solubilities of **14** and **15** in THF, FC-72/THF partition coefficients could be measured. As is not surprising given that **14** and **15** differ by only four methylene groups, they were identical within experimental error (93.2:6.8 and 93.1:6.9).

With all complexes, a full set of ^{1}H and ^{13}C NMR signals could be observed, and representative spectra are provided in the supporting information. Consistent with much literature precedent,[4h,5b,6d,e,7c] the $FeSC\underline{\mathbf{H}}_2$ ^{1}H signals were shifted markedly downfield to δ 12.9-11.4 ppm (CD_2Cl_2, acetone-d_6, or THF-d_8), as opposed to δ 2.61-2.75 ppm ($CDCl_3$) for the $HSC\underline{\mathbf{H}}_2$ signals of the free thiols.[23] In contrast, the $FeSCH_2C\underline{\mathbf{H}}_2R_{f8}$ signals of the "two methylene spacer" complexes **4** and **16** appeared at δ 2.29-2.46 ppm, essentially identical to the free thiol $HSCH_2$-$C\underline{\mathbf{H}}_2R_{f8}$ signal (δ 2.4 ppm).[23b] The $FeSCH_2C\underline{\mathbf{H}}_2$ signals were not resolved or unambiguously assignable in the other compounds, in part because many couplings exhibited by the free thiols could no longer be observed. However, their chemical shifts could be bounded within a slightly expanded range.

All ^{13}C NMR spectra were recorded with both ^{1}H and ^{19}F decoupling, simplifying analyses. The R_{f8} segments exhibited chemical shifts very close to those of related diamagnetic compounds, with values ranging from δ 125.7 to 108.4 ppm in accord with previous compilations.[27] The $FeS\underline{\mathbf{C}}H_2$ ^{13}C signals in complexes with $FeS(CH_2)_2R_{f8}$ linkages appeared at δ 75.7-71.8 ppm, and those in complexes with $FeS(CH_2)_3R_{f8}$ linkages appeared at δ 58.7-56.1 ppm. These assignments, which represent downfield shifts of δ 32.3-34.9 ppm from the free thiols,[23] are based upon similar shifts described for non-fluorous analogs earlier.[28] The ^{19}F NMR spectra showed normal chemical shift patterns for the CF_2 and CF_3 groups.[27]

Given the solubility data in Table 1, it was not possible to measure UV-visible spectra in a single solvent. Complex **4** showed two absorptions (CH_3CN) at 294 and 406 nm (ε = 22200 and 16000 $M^{-1}cm^{-1}$), with the latter appearing as a peak on the broader former band as it tailed into the visible. These bands ranged from 290 to 298 nm and 406 to 415 nm with **5, 6**, **9** and **14-16** (CH_3CN or THF), and representative spectra are provided in the supporting information. For comparison, the UV-visible spectrum of *t*-butylthiolate substituted $[n\text{-}Bu_4N]_2[Fe_4S_4(SC(CH_3)_3)_4]$ is slightly red shifted, with bands in DMF at 303 and 417 nm (ε = 21800 and 16700 $M^{-1}cm^{-1}$).[6a,b,7b] In contrast, in fluorous solvents, **14** and **15** exhibited a single absorption (FC-72: **14**, 415 nm, ε = 11700 $M^{-1}cm^{-1}$; **15**, 422 nm, ε = 16900 $M^{-1}cm^{-1}$).

A final question concerns the degree to which the redox properties of these iron/sulfur clusters are influenced by the electron withdrawing R_{f8} groups. It has been established that ca. six methylene spacers are needed for "complete" insulation.[29] Thus, cyclic voltammograms were sought. However, when DMF and CH_3CN solutions of **4-6** or **9** were treated with the supporting electrolyte $[n\text{-}Bu_4N][PF_6]$ (0.1 M in DMF or CH_3CN), dark precipitates formed, together with yellow supernatants. Analogous behavior was not observed with the *t*-butylthiolate substituted analog $[Ph_4P]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**1**), which has an extensively studied electrochemistry. Thus, this behavior was tentatively attributed to an irreversible condensation to an insoluble bulk Fe_xS_y system. Such cluster aggregation processes have been documented previously.[30]

A variety of other electrolytes were screened, including several with very poorly nucleophilic tetraarylborate anions (Ar = C_6F_5, 3,5-$C_6H_3(CF_3)_2$) but always with the same outcome. However, when cyclic voltammograms are recorded using microelectrodes, electrolyte concentrations can be greatly reduced.[31] Thus, as depicted in Figure 1, when a 10 µM platinum working microelectrode was employed, DMF solutions of **4** and **5** (5.0×10^{-4} M) charged with much lower electrolyte concentrations (3.0×10^{-3} M [n-Bu_4N][$B(C_6F_5)_4$]) exhibited well behaved, chemically reversible reductions.[32] As would be expected, **4**, with a two methylene spacer, proved thermodynamically easier to reduce than **5**, with a three methylene spacer ($E_{1/2}$ –2.32 vs. –2.40 V vs. ferrocene/ferrocenium). No oxidations were observed in anodic scans out to –0.08 V.

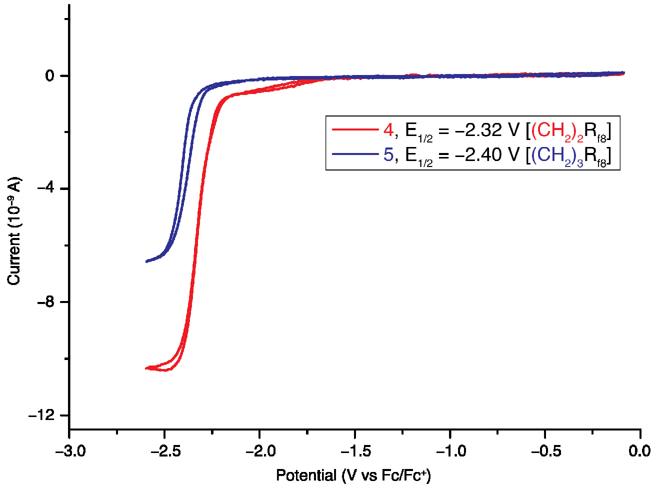


Figure 1. Cyclic voltammograms of **4** and **5** in DMF (5.0×10^{-4} M) containing [n-Bu_4N][$B(C_6F_5)_4$] supporting electrolyte (3.0×10^{-3} M) using a platinum working microelectrode (10 µM diameter) and recorded at ambient temperature and 100 mV/sec.

Discussion

Schemes 1 and 2 establish the ready availability of fluorous iron/sulfur clusters of the formula $[Q]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$. Compounds in which only the dianion is fluorous preferentially dissolve in organic solvents, whereas those that also incorporate "heavy fluorous" cations become fluorophilic. Despite the very low polarity of fluorous solvents, increasing numbers of ionic compounds are being realized that exhibit appreciable solubility.[13d] Some have proven to be catalysts for reactions in fluorous phases.[13b-d]

One motivation for the present study has been the possibility of carrying out nitrogen fixation in a fluorous phase. Most nitrogenaeses are comprised of an iron protein containing Fe_4S_4 clusters and an iron/molybdenum protein featuring a structurally more complex cluster.[1,11] One attraction of fluorous phases is their high solubilities for the diatomic gases oxygen, nitrogen, and hydrogen,[20,21] the basis for which is noted above. There are several commonly employed measures of solubility, three of which are provided in Table 2. The most important are the mol fraction of a gas in a saturated solution (the data compiled in most reference books), and the molarity (the important quantity for rate expressions). With respect to the latter, the solubility of hydrogen in fluorous solvents is approximately twice that in THF, and the solubility of nitrogen is approximately 2.5 times that in THF. The solubility increase with oxygen is intermediate. When solubilities in mol fractions are compared, the differences are much greater, due (as worked through elsewhere)[15] to the higher molecular weights of fluorous solvents vs. THF.

(insert Table 2 here)

Of course, achieving abiological nitrogen fixation will require more than just iron/sulfur clusters, so much more fundamental work remains to be done. Nonetheless, the high polarity of the product ammonia should promote phase separation from the fluorous medium, facilitating catalyst separation and recovery. If the reaction pathways involve polar intermediates, such as hydrazine, these also may phase separate, leading to unconventional product distributions.

However, given the experimental difficulties with cyclic voltammograms noted above, the title claim of "redox shifted" iron/sulfur clusters remains only partially quantified. Regardless, this is a certainty from well established inductive effects.[29] Iron/sulfur clusters with fluorous thiolates will be electron deficient and therefore thermodynamically easier to reduce. This is reflected by less negative $E_{1/2}$ value of **4** (–2.32 V) versus **5** (–2.40 V), indicating a more facile reduction, consistent with the decreased methylene spacer length.

The title compounds can be compared to the phenylthiolate and pentafluorophenylthiolate substituted clusters $[Q]_2[Fe_4S_4(SC_6H_5)_4]$[6a] and $[Q]_2[Fe_4S_4(SC_6F_5)_4]$[3a] (Q = Et_4N and *n*-Bu_4N, respectively). Both of these undergo reversible one electron reductions, with the pentafluorophenylthiolate substituted complex proving 0.25 V easier to reduce ($\Delta E_{1/2}$, DMF).[6a] It should be emphasized in passing that molecules with pentafluorophenyl groups are *not* fluorous,[22] as the polarizability of the π cloud commonly leads to significant solubilities in organic solvents. However, both the phenylthiolate and pentafluorophenylthiolate substituted complexes could likely be rendered fluorous by appending sufficient numbers of R_{fn} aryl substituents.

One obvious extension of this study would be to iron/sulfur clusters with CH_2R_{fn} and SR_{fn} substituents (one or zero methylene spacers). Thiols of the formula $HSCH_2R_{fn}$ are easily accessed with n = 1-3,[33] and higher homologs (n = 8)[34] have been reported. However, to our knowledge spacerless fluorous thiols HSR_{fn} are not yet available in preparatively useful quantities. Complexes in either of these series would be expected to be slightly more fluorophilic, and much more redox shifted (easier to reduce).

In summary, this study has established the ready availability of fluorous iron/sulfur clusters of the formula $[Q]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$, where Q is a (1) non-fluorous phosphonium or ammonium cation, (2) a "light fluorous" phosphonium cation, or (3) a "heavy fluorous" phosphonium salt. In general, the spectroscopic properties are very similar to those of the non-fluorous analogs. However, the phase and redox properties are significantly affected, both of which have the potential to open up new applications for these unusual analogs of metalloenzyme cofactors.

Experimental Section

General. All reactions and workups were conducted under N_2 atmospheres. Solvents were purified as follows: hexane, toluene, THF, Et_2O, and CH_2Cl_2 were dried and degassed using a Glass Contour Solvent System; acetone, DMSO, DMF, EtOAc, $CHCl_3$, and benzene were distilled from CaH_2 or 4 Å molecular sieves (beads) under N_2 atmospheres; CH_3CN was distilled from CaH_2 and CH_3OH from sodium under N_2 atmospheres; FC-72 (perfluorohexane), $CF_3C_6F_{11}$ (perfluoromethylcyclohexane), FC-70 ($(C_5F_{11})_3N$), and FC-75 (perfluoro-2-butyltetrahydrofuran) were degassed and dried over 4 Å molecular sieves (beads) under N_2 atmospheres; C_6F_6 was used as received; $CDCl_3$, CD_3CN, CD_2Cl_2, acetone-d_6, and THF-d_8 were dried over 4 Å molecular sieves (beads) and used in a glove box. The thiols $HS(CH_2)_nR_{f8}$ (**3**, n = **a**, 2; **b**, 3)[23] and clusters $[Ph_4P]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**1**)[3] and $[Me_4N]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**2**)[3] were synthesized according to literature procedures. Other chemicals were used as received from common commercial sources; the $FeCl_3$ and CH_3ONa were stored and used in a glove box.

^1H, $^{13}C\{^1H,^{19}F\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectra were recorded on 300 or 500 MHz spectrometers in sealed tubes at ambient probe temperatures and referenced as follows (δ, ppm): ^1H, residual internal $CHCl_3$ (7.26), CHD_2CN (1.94), $CHDCl_2$ (5.33), acetone-d_5 (2.05), or THF-d_6 (3.58); ^{13}C, internal $CDCl_3$ (77.3), CD_3CN (118.7), CD_2Cl_2 (54.0), acetone-d_6 (29.9), or THF-d_8 (25.4); ^{19}F, external trifluoromethylbenzene (–63.3); ^{31}P, external aqueous 85% phosphoric acid (0.0). UV-visible spectra were recorded using a Shimadzu UV spectrometer (UV-1800) with capped cuvettes. Microanalyses were conducted by Atlantic Microlab.

Crude $[Ph_3P(CH_2)_2R_{f6}]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (8). In a procedure similar to those reported for **1** and **2**,[3] a Schlenk flask was charged with CH_3ONa (1.62 g, 30.0 mmol) and CH_3OH (30 mL), and $HSC(CH_3)_3$ (3.4 mL, 30.2 mmol) was added by syringe with stirring. After 5 min, a solution of anhydrous $FeCl_3$ (1.21 g, 7.47 mmol) in CH_3OH (20 mL) was added. After 5 min, sulfur (0.240 g, 7.50 mmol) was added. After 16 h, the mixture was filtered. A Schlenk flask was charged with $[Ph_3P(CH_2)_2R_{f6}][I]$ (**7**,[24] 4.18 g, 5.68 mmol) and the filtrate with stirring. After 2 h, the mixture was concentrated to dryness. The sticky solid was dissolved in THF (20 mL), and Et_2O (120 mL) was added. The mixture was stored at –35 °C. After 24 h, the sample was filtered. The black solid was extracted with CH_3CN, and the extracts were filtered. The solvent was removed by oil pump vacuum, and the sticky black solid was extracted with THF. The extract was filtered and the solvent was removed by oil pump vacuum. The black solid was washed with Et_2O and dried by oil pump vacuum to give crude **8** (0.921 g, 0.48 mmol, 25%). Although the sample is impure by NMR, this does not affect preparative use.

$[Q]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$ (general procedure). A Schlenk flask was charged with **1**, **2**, or **8** (0.138 g, 0.086 g, or 0.200 g; 0.100 mmol) and CH_3CN (10 mL). Then **3a** (0.300 g, 0.625 mmol) or **3b** (0.250 g, 0.506 mmol) was added with stirring. After 12 h, the solvent was slowly removed by oil pump vacuum. The black solid was washed with Et_2O/hexane (33:67 v/v; samples are pure by NMR at this stage) and recrystallized from CH_3CN/Et_2O or THF/hexane to give a dark brown solid (**4**, 0.199 g, 0.067 mmol, 67%; **5**, 0.201 g, 0.067 mmol, 67%; **6**, 0.170 g, 0.069 mmol, 69%; **9**, 0.256 g, 0.073 mmol, 73%).

$[Ph_4P]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (**4**): Anal. Cacld. for $C_{88}H_{56}F_{68}Fe_4P_2S_8$: C, 35.86; H, 1.92; S, 8.70. Found: C, 35.16; H, 1.78; S, 8.36. MS (*m*/*z*, negative ESI): 1133.79, $[Fe_4S_4(S(CH_2)_2R_{f8})_4]^{2-}$, 100% (calc for 1132.8/1133.3/1133.8/1334.3/1134.8: 23:13:100:58:50; found: 26:13:100:27:20).

NMR (*δ*, CD_2Cl_2): ^1H (300 MHz) 11.6 (br s, 8H, $4SC\underline{H}_2$), 7.83 (s, 8H, 8*p*-$C_6\underline{H}_5$), 7.68 and 7.55 (s and d, J_{HP} = 7.8 Hz, 2 × 16H, 8*o,m*-$C_6\underline{H}_5$), 2.29 (br s, 8H, $4C\underline{H}_2R_{f8}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz) 136.3 (s, C_{Ar}), 135.3 (d, J_{CP} = 10.3 Hz, C_{Ar}), 131.5 (d, J_{CP} = 13.0 Hz, C_{Ar}), 123.9 (s, C_F), 117.8 (d, J_{CP} = 89.8 Hz, *i*-C_{Ar}), 117.1 (s, C_F), 112.6 (s, C_F), 111.5 (s, C_F), 110.9 (s, C_F), 110.8 (s, C_F), 110.2 (s, C_F), 108.4 (s, C_F), 71.8 (s, SCH_2), 31.6 (s, CH_2R_{f8}); ^{19}F (282 MHz) –81.3 (t, J_{FF} = 10.1 Hz, 12F, $4CF_3$), –112.0 (s, 8F, $4CF_2$), –121.7 (s, 8F, $4CF_2$), –122.3 (m, 16F, $8CF_2$), –122.6 (s, 8F, $4CF_2$), –123.1 (s, 8F, $4CF_2$), –126.5 (m, 8F, $4CF_2$); $^{31}P\{^1H\}$ (200 MHz) 25.2 (s). UV-visible (nm, 6.11×10^{-5} M in CH_3CN (ε, $M^{-1}cm^{-1}$)): 294 (22200), 406 (16000).

$[Ph_4P]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (**5**): Anal. Cacld. for $C_{92}H_{64}F_{68}Fe_4P_2S_8$: C, 36.79; H, 2.15; S, 8.54. Found: C, 35.62; H, 2.15; S, 8.57.[35]

NMR (*δ*, CD_2Cl_2): ^1H (500 MHz) 12.3 (br s, 8H, $4SC\underline{H}_2$), 7.92 (s, 8H, 8*p*-$C_6\underline{H}_5$), 7.77 and 7.62 (s and d, J_{HP} = 9.3 Hz, 2 × 16H, 8*o,m*-$C_6\underline{H}_5$), 2.71 and 2.52 (2 br s, 2 × 8H, $4C\underline{H}_2C\underline{H}_2R_{f8}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz) 136.5 (s, C_{Ar}), 135.4 (d, J_{CP} = 10.3 Hz, C_{Ar}), 131.7 (d, J_{CP} = 12.1 Hz, C_{Ar}), 120.6 (s, C_F), 117.8 (d, J_{CP} = 89.3 Hz, *i*-C_{Ar}), 117.1 (s, C_F), 111.4 (s, C_F), 111.3 (s, C_F), 110.9 (s, C_F), 110.8 (s, C_F), 110.2 (s, C_F), 108.4 (s, C_F), 56.1 (s, SCH_2), 36.2 and 29.8 (2 s, $CH_2CH_2R_{f8}$); ^{19}F (470 MHz) –79.4 (t, J_{FF} = 10.1 Hz, 12F, $4CF_3$), –110.8 (s, 8F, $4CF_2$), –119.9 (s, 8F, $4CF_2$), –120.3 (s, 16F, $8CF_2$), –121.1 (s, 16F, $8CF_2$), –124.6 (m, 8F, $4CF_2$); $^{31}P\{^1H\}$ (200 MHz) 25.2 (s). UV-visible (nm, 7.50×10^{-5} M in CH_3CN (ε, $M^{-1}cm^{-1}$)): 297 (25700), 410 (19200).

$[Me_4N]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (**6**): Anal. Cacld. for $C_{52}H_{48}F_{68}Fe_4N_2S_8$: C, 25.26; H, 1.96; N, 1.13; S, 10.37. Found: C, 23.71; H, 1.99; N, 1.30; S, 9.78.[35]

NMR (δ, acetone-d_6): ^{1}H (300 MHz) 12.3 (br s, 8H, $4SC\underline{H}_2$), 3.45 (s, 24H, $2(C\underline{H}_3)_4N$), 2.85 and 2.66 (2 br s, 2 × 8H, $4C\underline{H}_2C\underline{H}_2R_{f8}$); $^{13}C\{^1H,^{19}F\}$ (CD_3CN, 125 MHz) 120.7 (s, C_F), 118.8 (s, C_F), 111.5 (s, C_F), 111.4 (s, C_F), 110.9 (s, C_F), 110.8 (s, C_F), 110.2 (s, C_F), 108.4 (s, C_F), 57.5 and 55.8 (2 s, SCH_2 and CH_3), 35.9 and 29.0 (2 s, $CH_2CH_2R_{f8}$); ^{19}F (282 MHz) –81.7 (t, J_{FF} = 10.3 Hz, 12F, $4CF_3$), –112.5 (m, 8F, $4CF_2$), –121.9 (s, 8F, $4CF_2$), –122.4 (s, 16F, $8CF_2$), –123.0 (s, 8F, $4CF_2$), –123.3 (s, 8F, $4CF_2$), –126.8 (m, 8F, $4CF_2$). UV-visible (nm, 8.09×10^{-5} M in CH_3CN (ε, $M^{-1}cm^{-1}$)): 298 (30800), 408 (22500).

$[Ph_3P(CH_2)_2R_{f6}]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (**9**): Anal. Cacld. for $C_{92}H_{54}F_{94}Fe_4P_2S_8$: C, 31.69; H, 1.56; S, 7.36. Found: C, 31.02; H, 1.55; S, 7.08.

NMR (δ, THF-d_8): ^{1}H (500 MHz) 11.6 (br s, 8H, $4SC\underline{H}_2$), 7.89-7.82 (m, 30H, $6C_6\underline{H}_5$), 3.84 (br s, 4H, $2PC\underline{H}_2$), 2.70-2.48 (m, 12H, $2C\underline{H}_2R_{f6}$ and $4C\underline{H}_2R_{f8}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz)[36a] 136.6 (s, C_{Ar}), 136.2 (d, J_{CP} = 10.2 Hz, C_{Ar}), 132.5 (d, J_{CP} = 12.6 Hz, C_{Ar}), 124.0 (s, C_F), 118.2 (s, C_F), 118.1 (s, C_F), 118.0 (d, J_{CP} = 87.0 Hz, *i*-C_{Ar}), 117.5 (s, C_F), 113.0 (s, C_F), 112.0 (s, C_F), 111.3 (s, C_F), 111.2 (s, C_F), 111.1 (s, C_F), 110.6 (s, C_F), 110.5 (s, C_F), 108.8 (s, C_F), 73.0 (s, SCH_2), 31.3 (s, CH_2), 27.0 (s, CH_2), 19.9 (d, J_{CP} = 56.7 Hz, CH_2); ^{19}F (470 MHz) –81.9 to –82.0 (m, 18F, $6CF_3$), –112.2 (s, 8F, $4CF_2$), –112.6 (s, 4F, $2CF_2$), –122.0 (s, 8F, $4CF_2$), –122.4 to –122.7 (m, 32F, $16CF_2$), –123.5 (s, 12F, $6CF_2$), –127.0 (s, 12F, $6CF_2$); $^{31}P\{^1H\}$ (200 MHz) 25.4 (s). UV-visible (nm, 9.56×10^{-5} M in CH_3CN (ε, $M^{-1}cm^{-1}$)): 295 (26300), 406 (17900).

$[Na]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$. A (general procedure). A Schlenk flask was charged with CH_3ONa (3.24 g, 60.0 mmol) and CH_3OH (60 mL), and $HSC(CH_3)_3$ (6.7 mL, 59.6 mmol) was added by syringe with stirring. After 5 min, a solution of anhydrous $FeCl_3$ (2.43 g, 15.0 mmol) in CH_3OH (40 mL) was added. After 5 min, sulfur (0.480 g, 15.0 mmol) was added. After 16 h, the mixture was filtered. The solvent was removed from the filtrate by oil pump vacuum to give a black solid, which was washed with hexane/Et_2O (80:20, v/v) and dried by oil pump vacuum to give crude $[Na]_2[Fe_4S_4(SC(CH_3)_3)_4]$ (**10**; 3.21 g, ca. 4.26 mmol). Another Schlenk flask was charged with **10** (0.380 g, ca. 0.504 mmol, or 0.190 g, ca. 0.252 mmol) and CH_3CN (50 mL or 25 mL), and **3a** (0.981 g, 2.04 mmol) or **3b** (0.494 g, 1.00 mmol) was added by syringe with stirring.

The mixture was kept at 50 °C for 4 h and filtered. The filtrate was concentrated to dryness. The residue was washed with hexane and dried by oil pump vacuum to give crude $[Na]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (**11**; 0.816 g, 0.353 mmol, 81% based on $FeCl_3$) or analytically pure $[Na]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (**12**; 0.254 g, 0.107 mmol, 50% based on $FeCl_3$) as black solids. **B**. (alternative procedure for **11**). A Schlenk flask was charged with CH_3ONa (0.81 g, 15.0 mmol) and CH_3OH (30 mL), and **3a** (7.20 g, 15.0 mmol) was added by syringe with stirring. After 5 min, a solution of anhydrous $FeCl_3$ (0.61 g, 3.75 mmol) in CH_3OH (15 mL) was added. After 5 min, sulfur (0.120 g, 3.75 mmol) was added. After 16 h, the mixture was filtered. The solvent was removed from the filtrate by oil pump vacuum. The residue was washed with hexane/Et_2O (75:25 v/v) and dried by oil pump vacuum to give crude **11** as a black solid (1.65 g, 0.713 mmol, 76%). The ^{19}F NMR spectra for both preparations of **11** showed impurities not evident in the ^1H NMR spectrum, but these are removed in subsequent cation metathesis steps.

$[Na]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (**12**): Anal. Cacld. for $C_{44}H_{24}F_{68}Fe_4Na_2S_8$: C, 22.29; H, 1.02; S, 10.82. Found: C, 21.92; H, 1.29; S, 9.71.[35]

NMR (*δ*, THF-d_8): ^1H (500 MHz) 12.2 (br s, 8H, $4SC\underline{H}_2$), 2.90 and 2.66 (2 br s, 2 × 8H, $4C\underline{H}_2C\underline{H}_2R_{f8}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz) 122.5 (s, C_F), 119.0 (s, C_F), 113.4 (s, C_F), 113.3 (s, C_F), 112.8 (s, C_F), 112.7 (s, C_F), 112.1 (s, C_F), 110.3 (s, C_F), 58.7 (s, SCH_2), 38.0 and 31.0 (2 s, $CH_2CH_2R_{f8}$); ^{19}F (470 MHz) –80.1 (s, 12F, $4CF_3$), –111.0 (s, 8F, $4CF_2$), –120.2 (s, 8F, $4CF_2$), –120.7 (m, 16F, $8CF_2$), –121.4 (s, 8F, $4CF_2$), –121.5 (s, 8F, $4CF_2$), –125.1 (s, 8F, $4CF_2$).

$[PhCH_2P((CH_2)_3R_{f6})_3][Br]$ (**13**): A closed Schlenk flask was charged with $P((CH_2)_3R_{f6})_3$ (0.277 g, 0.248 mmol),[25] benzyl bromide (0.051 g, 0.298 mmol), and toluene (4 mL). The mixture was kept at 100 °C for 2 d with stirring and cooled to room temperature. The upper layer was decanted. The lower layer was shaken with hexane and allowed to stand. The upper layer was decanted. Then C_6F_6 was added to give a homogeneous solution. Then hexane was added (ca. 10 fold volumetric excess), and after 2 d the upper layer was decanted and the lower layer dried by oil pump vacuum to give **13** (0.205 g, 0.159 mmol, 64%) as a colorless sticky liquid. Anal. Cacld. for $C_{34}H_{25}BrF_{39}P$: C, 31.77; H, 1.96. Found: C, 31.56; H, 1.96.

NMR (δ, $CDCl_3$): ^1H (500 MHz) 7.42 (m, 5H, $C_6\underline{H}_5$), 4.36 (d, J_{HP} = 14.9 Hz, 2H, Ph-$C\underline{H}_2P$), 2.79 (m, 6H, $3PC\underline{H}_2CH_2CH_2R_{f6}$), 2.29 (m, 6H, $3PCH_2CH_2C\underline{H}_2R_{f6}$), 1.85 (m, 6H, 3P-$CH_2C\underline{H}_2CH_2R_{f6}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz) 130.1 (s, C_{Ar}), 129.7 (d, J_{CP} = 4.2 Hz, C_{Ar}), 129.4 (s, C_{Ar}), 126.8 (d, J_{CP} = 8.3 Hz, C_{Ar}), 117.8 (s, C_F), 117.1 (s, C_F), 110.9 (s, C_F), 110.7 (s, C_F), 110.1 (s, C_F), 108.4 (s, C_F), 31.2 (d, J_{CP} = 16.7 Hz, CH_2), 26.9 (s, CH_2), 18.6 (d, J_{CP} = 48.0 Hz, CH_2), 13.7 (s, CH_2); ^{19}F (470 MHz) –80.9 (t, J_{FF} = 9.5 Hz, 9F, $3CF_3$), –113.9 (m, 6F, $3CF_2$), –121.9 (s, 6F, $3CF_2$), –122.9 (s, 6F, $3CF_2$), –123.4 (s, 6F, $3CF_2$), –126.2 (m, 6F, $3CF_2$); $^{31}P\{^1H\}$ (200 MHz) 28.9 (s).

$[PhCH_2P((CH_2)_3R_{f6})_3]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$ (general procedure). A Schlenk flask was charged with **11** (0.145 g, 0.066 mmol) or **12** (0.095 g, 0.040 mmol) and then **13** (0.171 g, 0.133 mmol or 0.102 g, 0.079 mmol), and CH_3OH (20 mL) with stirring. After 0.5 h, the supernatant was removed by syringe. The solid was extracted with THF. The extracts were concentrated to dryness and the crude product was crystallized from THF/hexane (20:80, v/v) at –35 °C and dried by oil pump vacuum to give **14** (0.119 g, 0.025 mmol, 39%) or **15** (0.120 g, 0.025 mmol, 63%) as a dark brown solid.

$[PhCH_2P((CH_2)_3R_{f6})_3]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (14): Anal. Cacld. for $C_{108}H_{66}F_{146}Fe_4$-P_2S_8: C, 27.72; H, 1.42; S, 5.48. Found: C, 27.52; H, 1.48; S, 5.21.

NMR (δ, THF-d_8): ^1H (500 MHz) 12.4 (br s, 8H, $4SC\underline{H}_2$), 7.32 (br s, 10H, $2C_6\underline{H}_5$), 3.75 (br s, 4H, $2C_6H_5C\underline{H}_2P$), 2.31 (m, 32H, $6PC\underline{H}_2CH_2CH_2R_{f6}$, $6PCH_2CH_2C\underline{H}_2R_{f6}$ and $4C\underline{H}_2R_{f8}$), 1.93 (br s, 12H, $6PCH_2C\underline{H}_2CH_2R_{f6}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz)[36b] 133.5 (s, C_{Ar}), 131.6 (s, C_{Ar}), 130.6 (s, C_{Ar}), 129.9 (d, J_{CP} = 4.2 Hz, C_{Ar}), 125.2 (s, C_F), 120.7 (s, C_F), 119.1 (s, C_F), 119.0 (s, C_F), 114.4 (s, C_F), 113.5 (s, C_F), 113.0 (s, C_F), 112.8 (s, C_F), 112.7 (s, C_F), 112.1 (s, C_F), 110.4 (s, C_F), 110.3 (s, C_F), 73.7 (s, SCH_2), 37.4 (s, CH_2), 31.5 (s, CH_2), 31.1 (s, CH_2), 17.8 (s, CH_2); ^{19}F (470 MHz) –82.1 (s, 30F, $10CF_3$), –112.3 (s, 8F, $4CF_2$), –113.8 (s, 12F, $6CF_2$), –122.3 (s, 20F, $10CF_2$), –122.7 to –122.8 (m, 24F, $12CF_2$), –123.2 (s, 12F, $6CF_2$), –123.6 (s, 20F, $10CF_2$), –127.0 (s, 20F, $10CF_2$); $^{31}P\{^1H\}$ (200 MHz) 35.0 (s). UV-visible (nm (ε, $M^{-1}cm^{-1}$)): 5.56×10^{-5} M in THF, 292 (23700), 410 (17800); 7.78×10^{-5} M in FC-72, 415 (11700).

$[PhCH_2P((CH_2)_3R_{f6})_3]_2[Fe_4S_4(S(CH_2)_3R_{f8})_4]$ (15): Anal. Cacld. for $C_{112}H_{74}F_{146}Fe_4P_2S_8$: C, 28.41; H, 1.58; S, 5.42. Found: C, 28.57; H, 1.56; S, 5.22.

NMR (*δ*, THF-d_8): ^1H (500 MHz) 12.9 (br s, 8H, $4SC\underline{H}_2$), 7.42-7.34 (m, 10H, $2C_6\underline{H}_5$), 3.83 (br s, 4H, $2C_6H_5C\underline{H}_2P$), 2.90 and 2.65 (2 br s, 2 × 8H, $4C\underline{H}_2C\underline{H}_2R_{f8}$), 2.41 (br s, 24H, $6PC\underline{H}_2CH_2CH_2R_{f6}$ and $6PCH_2CH_2C\underline{H}_2R_{f6}$), 2.02 (br s, 12H, $6PCH_2C\underline{H}_2CH_2R_{f6}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz)[36c] 132.0 (s, C_{Ar}), 129.7 (s, C_{Ar}), 128.7 (s, C_{Ar}), 128.0 (d, J_{CP} = 8.1 Hz, C_{Ar}), 120.5 (s, C_F), 118.9 (s, C_F), 117.2 (s, C_F), 117.1 (s, C_F), 111.4 (s, C_F), 111.4 (s, C_F), 111.1 (s, C_F), 110.9 (s, C_F), 110.9 (s, C_F), 110.8 (s, C_F), 110.3 (s, C_F), 108.5 (s, C_F), 108.4 (s, C_F), 36.2 (s, CH_2), 35.7 (s, CH_2), 16.2 (s, CH_2); ^{19}F (470 MHz) –80.1 to –80.2 (m, 30F, $10CF_3$), –111.3 (s, 8F, $4CF_2$), –112.0 (s, 12F, $6CF_2$), –120.4 (m, 20F, $10CF_2$), –120.8 (s, 20F, $10CF_2$), –121.3 (s, 12F, $6CF_2$), –121.7 (s, 24F, $12CF_2$), –125.1 (s, 20F, $10CF_2$); $^{31}P\{^1H\}$ (200 MHz) 35.3 (s). UV-visible (nm (ε, $M^{-1}cm^{-1}$)): 7.18 × 10^{-5} M in THF, 290 (27800), 415 (21900); 9.88 × 10^{-5} M in FC-72, 422 (16900).

$[PPN]_2[Fe_4S_4(S(CH_2)_2R_{f8})_4]$ (16). A Schlenk flask was charged with **11** (0.218 g, 0.094 mmol), [PPN][Cl][26] (PPN = $Ph_3P\cdots N\cdots PPh_3$; 0.120 g, 0.209 mmol), and CH_3OH (10 mL) with stirring. After 2 h, the mixture was cooled to 0 °C and concentrated to ca. 1 mL. A solid formed, and the supernatant was removed by syringe. The solid was extracted with THF (8 mL). The solvent was removed from the extract by oil pump vacuum. The solid was washed with Et_2O/hexane (17:83, v/v) and crystallized from THF/hexane (20:80 v/v) at –35 °C and dried by oil pump vacuum to give **16** (0.112 g, 0.034 mmol, 36%) as dark brown plates. Anal. Cacld. for $C_{112}H_{76}F_{68}Fe_4N_2P_4S_8$: C, 40.21; H, 2.29; N, 0.84; S, 7.67. Found: C, 39.75; H, 2.27; N, 0.89; S, 6.90.[35]

NMR (*δ*, THF-d_8): ^1H (500 MHz) 11.4 (br s, 8H, $4SC\underline{H}_2$), 7.58-7.48 (m, 60H, $12C_6\underline{H}_5$), 2.46 (br s, 8H, $4C\underline{H}_2R_{f8}$); $^{13}C\{^1H,^{19}F\}$ (125 MHz) 136.6 (s, C_{Ar}), 135.3 (t, J_{CP} = 4.6 Hz, C_{Ar}), 132.6 (t, J_{CP} = 5.6 Hz, C_{Ar}), 129.9 (d, J_{CP} = 107.9 Hz, C_{Ar}), 125.7 (s, C_F), 119.0 (s, C_F), 114.6 (s, C_F), 113.6 (s, C_F), 112.9 (s, C_F), 112.7 (s, C_F), 112.1 (s, C_F), 110.3 (s, C_F), 75.7 (s, SCH_2), 33.1 (s, CH_2R_{f8}); ^{19}F (470 MHz) –80.0 (t, J_{FF} = 10.2 Hz, 12F, $4CF_3$), –110.1 (s, 8F, $4CF_2$), –120.0 (s, 8F, $4CF_2$), –120.7 (s, 24F, $12CF_2$), –121.6 (s, 8F, $4CF_2$), –125.1 (m, 8F, $4CF_2$);

$^{31}P\{^1H\}$ (200 MHz) 21.5 (s). UV-visible (nm, 9.97×10^{-5} M in CH_3CN (ε, $M^{-1}cm^{-1}$)): 406 (10900).

Partition Coefficients. **A**. A volumetric flask (25 mL) was charged with **15** (0.0140 g, 0.00296 mmol) and $CF_3C_6F_{11}$ (25 mL), capped, and vigorously shaken. Then 5.0 mL was transferred to a vial and toluene (5.0 mL) was added. The mixture was thoroughly shaken and allowed to stand. The two phases were separated and analyzed by UV-visible spectroscopy under an inert atmosphere. The A values associated with the 413 bands were 2.0731 ($CF_3C_6F_{11}$) and 0.0073 (toluene, an upper bound). Given the biased ratio (>99.65:<0.35), no correction for ε values was applied. An analogous protocol with **14** gave the same limiting ratio (>99.65:<0.35). **B**. A volumetric flask (25 mL) was charged with **15** (0.0117 g, 0.00247 mmol) and FC-72 (25 mL), capped, and vigorously shaken. Then 5.0 mL was transferred to a UV-visible cell, and the 420 nm band gave an A value of 1.6668. Another 5.0 mL aliquot was shaken with THF (5.0 mL). The sample was allowed to stand. The two phases were separated, and the fluorous phase exhibited a 420 nm band with an A value of 1.5523. This gave a FC-72/THF partition coefficient of 93.1:6.9. An analogous protocol with **14** gave a similar ratio (93.2:6.8).

Cyclic Voltammetry. Electrochemical studies were preformed utilizing a Metrohm Eco Chemie Autolab PGSTAT30 potentiostat/galvanostat with a FRA2-module for electrochemical impedance studies and a bipotentiostat module. The General Purpose Electrochemical Software (GPES) supplied by the potentiostat manufacturer was utilized to record and process the data. All manipulations and studies were performed in a dry box under a nitrogen atmosphere. The DMF was dried using an Innovative Technology, Pure Solv solvent purifier with a double purifying column and thoroughly degassed by a nitrogen sparge prior to use. Experiments were performed using a three electrode cell fitted with a Pt working microelectrode (10 µM diameter, CH Instruments, Inc., CHI107), a Pt wire counter electrode, a $Ag/AgNO_3$ reference electrode (Ag wire dipped in a 0.010 M $AgNO_3$ solution prepared in a 0.10 M [*n*-Bu_4N][PF_6] solution in acetonitrile), a scan rate of 100 mV/sec, and DMF solutions that were 5.0×10^{-4} M in analyte and 3.0×10^{-3} M in [*n*-Bu_4N][$B(C_6F_5)_4$] supporting electrolyte (synthesized by a literature procedure)[37].

Potentials were referenced to an external ferrocene/ferrocenium reference redox couple ($E°$ = 0.0919 V vs Ag/$AgNO_3$).

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Notes and references

(1) Iron Sulfur Clusters in Chemistry and Biology, T. Rouault, Ed.; De Gruyter, Berlin, 2014.

(2) (a) Rao, P. V; Holm, R. H. *Chem. Rev.* **2004**, *104*, 527-559. (b) Lee, S. C.; Lo, W.; Holm, R. H. *Chem. Rev.* **2014**, *114*, 3579-3600.

(3) (a) Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *97*, 3523-3532. (b) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1093-1094. (c) Christou, G.; Garner, C. D.; Balasubramaniam, A.; Ridge, B.; Rydo, H. N. *Inorg. Syn.* **1982**, 33-37.

(4) (a) Que, Jr. L.; Bobrik, M. A.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4168-4178. (b) Dukes, G. R.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 528-533. (c) Job, R. C.; Bruice, T. C. *Proc. Nat. Acad. Sci. USA* **1975**, *72*, 2478-2482. (d) Johnson, R. W.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5338-5344. (e) Weigel, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 4184-4191. (f) Klein Gebbink, R. J. M.; Klink, S. I.; Feiters, M. C.; Nolte, R. J. M. *Eur. J. Inorg. Chem.* **2000**, 2087-2099. (g) Ueda, M.; Mochida, T. *Inorg. Chim. Acta.* **2003**, *353*, 306-309. (h) Lo, W.; Huang, S.; Zheng, S.-L.; Holm, R. H. *Inorg. Chem.* **2011**, *50*, 11082-11090.

(5) (a) Sharma, A. K.; Kim, N.; Cameron, C. S.; Lyndon, M.; Gorman, C. B. *Inorg. Chem.* **2010**, *49*, 5072-5078. (b) Lo, W.; Scott, T. A.; Zhang, P.; Ling, C. -C.; Holm, R. H. *J. Inorg. Biochem.* **2011**, *105*, 497-508.

(6) (a) DePamphilis, B. V.; Averill, B. A.; Herskovitz, T.; Que, Jr. L.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4159-4167. (b) Cambray, J.; Lane, R. W.; Wedd, A. G.; Johnson, R. W.; Holm, R. H. *Inorg. Chem.* **1977**, *16*, 2565-2571. (c) Okuno, Y.; Uoto, K.; Yonemitsu, O.; Tomohiro, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1018-1020. (d) Lenormand, A.; Iveson, P.; Jordanov, J. *Inorg. Chim. Acta.* **1996**, *251*, 119-123. (e) Zhou, C.; Raebiger, J. W.; Segal, B. M.; Holm, R. H. *Inorg. Chim. Acta.* **2000**, *300-302*, 892-902. (f) van der Geer, E. P. L.; Li, Q.; van Koten, G.; Klein Gebbink, R. J. M.; Hessen, B. *Inorg. Chim. Acta.* **2008**, *361*, 1811-1818.

(7) (a) Lane, R. W.; Wedd, A. G.; Gillum, W. O.; Laskowski, E. J.; Holm, R. H.; Frankel, R. B.; Papaefthymiou, G. C. *J. Am. Chem. Soc.* **1977**, *99*, 2350-2352. (b) Hill, C. L.; Renaud, J.; Holm, R. H.; Mortenson, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 2549-2557. (c) Reynolds, J. G.; Laskowski, E. J.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5315-5322. (d) Laskowski, E. J.; Frankel, R. B.; Gillum, W. O.; Papaefthymiou, G. C.; Renaud, J.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5322-5337. (e) Reynolds, J. G.; Coyle, C. L.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4350-4355.

(8) (a) van Tamelen, E. E.; Gladysz, J. A.; Miller, J. S. *J. Am. Chem. Soc.* **1973**, *95*, 1347-1348. (b) van Tamelen, E. E.; Gladysz, J. A.; Brûlet, C. R. *J. Am. Chem. Soc.* **1974**, *96*, 3020-3021. (c) Karlin, K. D. *Science* **1993**, *261*, 701-708. (d) Fontecilla-Camps, J. C.; Amara, P.; Cavazza, C.; Nicolet, Y.; Volbeda, A. *Nature*, **2009**, *460*, 814-822.

(9) (a) Scott, T. A.; Zhou, H. -C. *Angew. Chem.* **2004**, *116*, 5746-5749; *Angew. Chem. Int. Ed.* **2004**, *43*, 5628-5631. (b) Scott, T. A.; Berlinguette, C. P.; Holm, R. H.; Zhou, H.-C. *Proc. Nat. Acad. Sci.* **2005**, *102*, 9741-9744.

(10) Deng, L.; Holm, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 9878-9886.

(11) Münck, E.; Bominaar, E. L. *Science* **2008**, *321*, 1452-1453.

(12) *Handbook of Fluorous Chemistry*, Gladysz, J. A.; Curran, D. P.; Horváth, I. T. Eds.; Wiley/VCH, Weinheim, **2004**.

(13) (a) Emnet, C.; Weber, K. M.; Vidal, J. A.; Consorti, C. S.; Stuart, A. M.; Gladysz, J. A. *Adv. Synth. Catal.* **2006**, *348*, 1625-1634. (b) Consorti, C. S.; Jurisch, M.; Gladysz, J. A. *Org.*

Lett. **2007**, *9*, 2309-2312. (c) Mandal, D.; Jurisch, M.; Consorti, C. S.; Gladysz, J. A. *Chem. Asian J.* **2008**, *3*, 1772-1782. (d) Mandal, D.; Gladysz, J. A. *Tetrahedron* **2010**, *66*, 1070-1077, and literature from other groups cited therein.

(14) Ghosh, S. K.; Ojeda, A. S.; Guerrero-Leal, J.; Bhuvanesh, N.; Gladysz, J. A. *Inorg. Chem.* **2013**, *52*, 9369-9378.

(15) "Fluorous Solvents and Related Media", Gladysz, J. A.; Emnet, C. in *Handbook of Fluorous Chemistry*, Gladysz, J. A.; Curran, D. P.; Horváth, I. T. Eds.; Wiley/VCH, Weinheim, **2004**, Chapter 3.

(16) "Partition Coefficients involving Fluorous Solvents", Gladysz, J. A.; Emnet, C.; Rábai, J. in *Handbook of Fluorous Chemistry*, Gladysz, J. A.; Curran, D. P.; Horváth, I. T. Eds.; Wiley/VCH, Weinheim, 2004, Chapter 6.

(17) (a) Nelson, J. K.; Hashad, I. F. M. *J. Phys. D: Appl. Phys.* **1976**, *9*, 203-210. (b) Christenson, H. K.; Claesson, P. M. *Science* **1988**, *239*, 390-392.

(18) (a) Remy, B.; Deby-Dupont, G.; Lamy, M. *Brit. Med. Bull.* **1999**, *55*, 277-298. (b) Spahn, D. R. *Critical Care* **1999**, *3*, R93-R97.

(19) (a) *Nitrogen Fixation*, Postgate, J. R., 3rd Ed.; Cambridge, UK, **1998**. (b) MacLeod, K. C.; Holland, P. L. *Nature Chem.* **2013**, *5*, 559-565.

(20) (a) *IUPAC Solubility Data Series*, Battino, R. Ed.; Pergamon: New York, **1981**, Volume 7, pp. 320 and 321. (b) *IUPAC Solubility Data Series*, Young, C. L., Ed.; Pergamon: New York, **1981**, Volume 5/6, p. 243. (c) Patrick, C. R. *Preparation, Properties, and Industrial Applications of Organofluorine Compounds*, Banks, R. E., Ed.; Ellis Horwood: New York, **1982**, p. 53.

(21) Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data.* **1984**, *13*, 563-600.

(22) "Fluorous Chemistry: Scope and Definition", Horváth, I. T.; Curran, D. P.; Gladysz, J. A. in *Handbook of Fluorous Chemistry*, Gladysz, J. A.; Curran, D. P.; Horváth, I. T. Eds.; Wiley/VCH, Weinheim, **2004**, Chapter 1.

(23) (a) Szonyi, F.; Cambon, A. *J. Fluorine Chem.* **1989**, *42*, 59-68. (b) Naud, C.; Calas, P.; Blancou, A.; Commeyras, A. *J. Fluorine Chem.* **2000**, *104*, 173-183. (c) Rocaboy, C.; Gladysz, J. A. *New J. Chem.* **2003**, *27*, 39-49.

(24) Rocaboy, C.; Rutherford, D.; Bennett, B. L.; Gladysz, J. A. *J. Phys. Org. Chem.* **2000**, *13*, 596-603.

(25) (a) Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. A., *J. Org. Chem.* **1998**, *63*, 6302-6308. (b) Vlád, G.; Richter, F.; Horváth, I. *Org. Lett.* **2004**, *6*, 4559-4561. (c) The exact route employed to this compound can be found in Jurish, M. doctoral dissertation, University Erlangen-Nürnberg, 2008. See also Emnet, C.; Gladysz, J. A. *Synthesis* **2005**, 1012-1018.

(26) Kukushkin, V. Y.; Moiseev, A. I. *Inorg. Chim. Acta.* **1990**, *176*, 79-81.

(27) (a) Dolbier, W. R. *Guide to Fluorine NMR for Organic Chemists*, Wiley, Hoboken, New Jersey, **2009**, p 196. (b) Gladysz, J. A.; Jurisch, M. *Topics in Current Chemistry* **2012**, *308*, 1-24.

(28) Crozet, M.; Chaussade, M.; Bardet, M.; Emsley, L.; Lamotte, B.; Mouesca, J. -M. *J. Phys. Chem. A* **2000**, *104*, 9990-10000.

(29) Jiao, H.; Le Stang, S.; Soós, T.; Meier, R.; Kowski, K.; Rademacher, P.; Jafarpour, L.; Hamard, J.-B.; Nolan, S. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 1516-1523.

(30) Goh, C.; Segal, B. M.; Huang, J.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 11844-11853.

(31) *Microelectrodes: Theory and Applications*, Montenegro, I.; Queirós, M. A.; Daschbach, J. L. Eds.; Sprinter, **1991**.

(32) A reviewer has noted that the shape of the CV traces in Figure 1 (sigmoidal) differs from those often depicted in the literature (with cathodic and anodic peaks). This is a simple consequence of using microelectrodes as opposed to conventional electrodes; it is connected to edge effects (radial diffusion) that dominate over linear diffusion with very small electrodes: Bond, A. M. *Analyst*, **1994**, *110*, R1-R21.

(33) (a) Harris, Jr. J. F.; Sheppard, W. A. *J. Org. Chem.* **1961**, *26*, 354-358. (b) Freter, R.;

Pohl, E. R.; Wilson, J. M.; Hupe, D. J. *J. Org. Chem.* **1979**, *44*, 1771-1774. (c) Hupe, D. J.; Pohl, E. R. *Israel J. Chem.* **1985**, *26*, 395-399.

(34) Privitera, N.; Naon, R.; Riess, J. G. *Int. J. Pharm.* **1994**, *104*, 41-48.

(35) These data do not indicate an analytical pure sample, but are provided nonetheless to illustrate the best fit obtained to date.

(36) Several carbon signals were not observed: (a) two CF_2 signals; (b) one CH_2 and two CF_2 signals, (c) four CH_2 and one CF_2 signals.

(37) Türp, D.; Wagner, J; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 4962-4965; *Angew. Chem.* **2011**, *123*, 5064-5067.

List of Captions

Scheme 1. Syntheses of fluorous iron/sulfur clusters by thiolate ligand exchange.

Scheme 2. Syntheses of fluorous iron/sulfur clusters by cation exchange.

Figure 1. Cyclic voltammograms of **4** and **5** in DMF (5.0×10^{-4} M) containing [n-Bu_4N][$B(C_6F_5)_4$] supporting electrolyte (3.0×10^{-3} M) using a platinum working microelectrode (10 µM diameter) and recorded at ambient temperature and 100 mV/sec.

Table 1. Qualitative solubility data for the fluorous iron/sulfur clusters (room temperature).[a]

Table 2. Solubilities of oxygen, hydrogen, and nitrogen in fluorous solvents and THF.[a]

TEXT for TABLE OF CONTENTS GRAPHIC

The title compounds, $[Q]_2[Fe_4S_4(S(CH_2)_nR_{f8})_4]$, feature dianions with four fluorous thiolate ligands and cations that are non-fluorous, "light fluorous", or "heavy fluorous"; fluorous/organic partition coefficients can reach >93:<7.

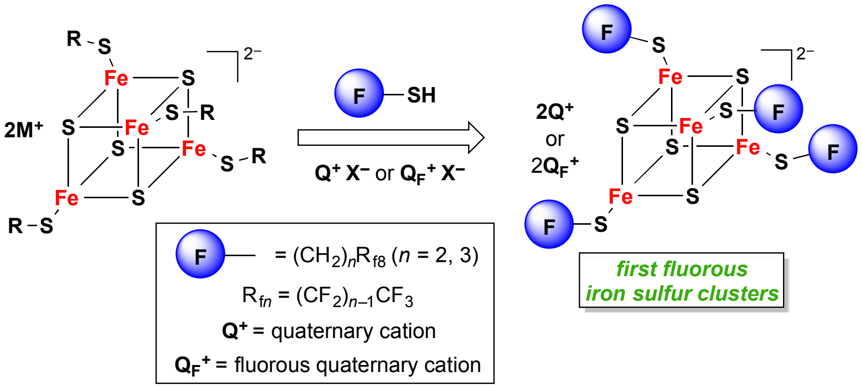

Table 1. Qualitative solubility data for the fluorous iron/sulfur clusters (room temperature).[a]

Solvent	Complex						
	4	**5**	**6**	**9**	**14**	**15**	**16**
CH_3OH	soluble	soluble	soluble	soluble	insoluble	insoluble	soluble
acetone	highly soluble	highly soluble	highly soluble	highly soluble	slightly soluble	slightly soluble	highly soluble
CH_3CN	highly soluble	highly soluble	highly soluble	highly soluble	slightly soluble	slightly soluble	highly soluble
DMSO	soluble	soluble	soluble	slightly soluble	insoluble	insoluble	soluble
DMF	soluble	soluble	soluble	soluble	slightly soluble	slightly soluble	soluble
EtOAc	soluble	soluble	slightly soluble	slightly soluble	slightly soluble	slightly soluble	slightly soluble
$CHCl_3$	soluble	soluble	insoluble	soluble	insoluble	insoluble	soluble
CH_2Cl_2	highly soluble	highly soluble	slightly soluble	soluble	insoluble	insoluble	highly soluble
Et_2O	soluble	soluble	insoluble	insoluble	slightly soluble	slightly soluble	soluble
THF	soluble	soluble	soluble	soluble	soluble	soluble	highly soluble
C_6H_6	slightly soluble	slightly soluble	insoluble	insoluble	insoluble	insoluble	soluble
toluene	slightly soluble	slightly soluble	insoluble	insoluble	insoluble	insoluble	soluble
hexane	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
FC-70[b]	insoluble	insoluble	insoluble	insoluble	soluble	soluble	insoluble
FC-72[c]	insoluble	insoluble	insoluble	insoluble	soluble	soluble	insoluble
$CF_3C_6F_{11}$[d]	insoluble	insoluble	insoluble	insoluble	soluble	soluble	insoluble
FC-75[e]	insoluble	insoluble	insoluble	insoluble	soluble	soluble	insoluble

[a] N_2 atmosphere; [b] $(C_5F_{11})_3N$; [c] perfluorohexanes; [d] perfluoro(methylcyclohexane); [e] perfluoro(2-butyltetrahydrofuran).

Table 2. Solubilities of oxygen, hydrogen, and nitrogen in fluorous solvents and THF.[a]

Solubility	$CF_3C_6F_{11}$ [b]	C_7F_{16} [c]	THF [d]
O_2 (mol fraction)	0.00456 [e,f]	0.00555 [e,f]	0.000816 [e]
O_2 (mol ratio)	0.00458 [g]	0.00558	0.000817
O_2 (mol/L)	**0.0234**	**0.0251**	**0.0101** [g]
H_2 (mol fraction)	0.0012 [h]	0.0014007 [i]	0.000274 [i]
H_2 (mol ratio)	0.0012 [g]	0.0014027	0.000274
H_2 (mol/L)	**0.0061**	**0.0063071**	**0.00338** [g]
N_2 (mol fraction)	0.00331 [j]	0.00390 [j]	0.000521 [j]
N_2 (mol ratio)	0.00332	0.00392	0.000521
N_2 (mol/L)	**0.0169**	**0.0176**	**0.00643**

[a] Data were, unless noted, obtained at T = 298.15 K with a partial pressure (O_2, H_2, or N_2) P = 101.325 KPa.

[b] perfluoromethylcyclohexane; 1.787 g/mL at 298.15 K.

[c] perfluoroheptane; 1.745 g/mL at 298.15 K.

[d] THF = tetrahydrofuran; 0.889 g/mL at 298.15 K.

[e] *IUPAC Solubility Data Series*, Battino, R., Ed.; Pergamon: New York, **1981**, Volume 7.

[f] For this determination, the total pressure is 101.325 KPa.

[g] There is a slight error in this value in an earlier version of this table: "Fluorous Solvents and Related Media", Gladysz, J. A.; Emnet, C. in *Handbook of Fluorous Chemistry*, Gladysz, J. A.; Curran, D. P.; Horváth, I. T. Eds.; Wiley/VCH, Weinheim, **2004**, p. 17.

[h] Patrick, C. R. In *Preparation, Properties, and Industrial Applications of Organofluorine Compounds*, Banks, R. E., Ed.; Ellis Horwood: New York, **1982**, p. 53

[i] *IUPAC Solubility Data Series*, Young, C. L., Ed.; Pergamon: New York, **1981**, Volume 5/6.

[j] Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data*, **1984**, *13*, 563-600.