Supplemental Material for:

How Do Ring Size and π-Donating Thiolate Ligands Affect Redox-Active, α-Imino-N-heterocycle Ligand Activation?

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	Page
Experimental.	
General Methods	S5-S6
Synthesis of 2-benzylsulfanylmethyl-2-methyl-propane-1,3-(*tert*-Butyloxy carbonyl) diamine (**D**)	S6-S7
Synthesis of 2-thiomethyl-2-methyl-propane-1,3-(*tert*-Butyloxycarbonyl) diamine (**E**)	S7
Synthesis of 2-thiomethyl-2-methyl-propane-1,3-diamine dihydrochloride (**F**).	S8
Synthesis of 2-benzylsulfanylmethyl-2-methyl-propane-1,3-(tert-Butyloxycarbonyl) diamine (**G**)	S8-S9
Synthesis of 2-thiomethyl-2-methyl-propane-1,3-(tert-Butyloxycarbonyl)diamine (**H**)	S9
Synthesis of 2-thiomethyl-2-methyl-propane-1,3-diaminedihydrogenchloride (**I**)	S9-S10
Synthesis of $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(PF_6)_2$ (**1**).	S10-S11
Synthesis of $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**-BPh_4)	S11
Synthesis of $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(PF_6)_2$ (**2**).	S11
Synthesis of $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)_2$ (**2**-BPh_4).	S11-S12
Synthesis of $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2$•2MeCN (**3**).	S12
Synthesis of $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2$•2MeCN (**4**).	S12-S13
Synthesis of Thioether-ligated $[Fe^{II}(tame\text{-}(N_2S^{Bz}(^{Me}Im)_2(MeCN))]^+$ (**5**).	S13-S14
Computational Methods.	S14-S15
^{57}Fe Mössbauer Spectroscopy.	S15
Sulfur K-Edge X-Ray Absorption Spectroscopy.	S15-S16
X-ray Crystallographic Structure Determination.	S16-S18
Determining the Dimer-**3**/Monomer Equilibrium Constant	S19
Calculating the UV/vis Extinction Coefficients for Dimeric **3** and its Monomeric Derivative Using the Dimer/Monomer Equilibrium Dissociation Constant	S19-S22
Supplemental Figures and Schemes.	
Scheme S1. Synthetic Route to tame-N_2SH ligand **I**.	S6
Figure S1. Intraligand distances for **2** versus DFT calculated distances for neutral and mono-reduced (α-imino)quinoline ligands.	S23
Figure S2. Intraligand distances for **3** versus DFT calculated distances for neutral and mono-reduced (α-imino)imidazole ligands.	S24
Figure S3. ^1H NMR of **3** (in MeCN-d^3) in the presence (top) and absence (bottom) of $(Bu_4N)(N_3)$ showing that peaks in the paramagnetic region shift, consistent with azide binding to a paramagnetic species.	S24
Figure S4. LTQ ion trap mass spectrum of **3** in MeCN solution, versus theoretically calculated for a monocationic monomer. Isotopomers show that the majority of **3** converts to a monomer in solution.	S25
Figure S5. LTQ ion trap mass spectrum of **2** in MeCN solution, versus theoretically calculated for a dicationic dimer. Isotopomers show that **2** maintains its dimeric structure in solution.	S25
Figure S6. LTQ ion trap mass spectrum of **1** in MeCN solution, versus the theoretically calculated spectrum of a dicationic dimer. Isotopomers show that a portion of **1** maintains its dimeric structure in solution	S26
Figure S7. LTQ ion trap mass spectrum of **1** in MeCN solution, versus theoretically calculated for a monocationic monomer. Isotopomers show that a portion of **1** converts to a monomer in solution.	S26
Figure S8. Variable-temperature magnetic moment of **3** in MeCN-d^3 solution, as determined using the Evan's method.	S27

Figure S9. Reaction of **3** (0.045 mM) with O_2 in MeCN at 258 K. Scans taken at 1 min intervals. Inset shows pseudo-first order dependence.	S27
Figure S10. Cyclic voltammograms displaying the oxidation waves associated with complexes **1-3**, and the correlation of potentials with ring size.	S28
Figure S11. Cyclic voltammograms displaying the reduction waves associated with complexes **1-3**, and the correlation of potentials with ring size.	S28
Figure S12. Full range of normalized sulfur K-edge X-ray absorption spectra.	S29
Figure S13. Calculated sulfur K-edge X-ray absorption spectra, including representative transition difference densities for **1.** Regions of increased electron density (acceptors) are shown in purple, regions of decreased electron density (donors) are shown in teal.	S30
Figure S14. Calculated sulfur K-edge X-ray absorption spectra including representative transition difference densities for **2.** Regions of increased electron density (acceptors) are shown in purple, regions of decreased electron density (donors) are shown in teal. Transitions marked with a ✻ are shown in the manuscript Figure 10.	S31
Figure S15. Calculated sulfur K-edge X-ray absorption spectra, including representative transition difference densities for **3.** Regions of increased electron density (acceptors) are shown in purple, regions of decreased electron density (donors) are shown in teal.	S32
Figure S16. DFT calculated MO diagram for **1**.	S33
Figure S17. Zero-field Mössbauer spectrum of **1**.	S33
Figure S18. Electronic absorption spectrum of the Co(II) complex **4** in MeCN at 298 K.	S34
Figure S19. ^{1}H NMR spectrum of **5** in MeCN-d^3 at 298 K showing reproducibly observed peaks indicative of a paramagnetic species.	S34
Supplemental Tables	
Table S1. Sulfur K-edge XAS Pre-Edge Energies for **1-3**.	S35
Table S2. Selected DFT calculated bond distances (Å) for **1-3**.	S35
Table S3. Percent Sulfur Character in the Lowest Unoccupied (LUMO) and Highest Occupied Molecular Orbitals (HOMOs) of **1-3.**	S36
Table S4. Crystal Data for $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**).	S37
Table S5. Positional and Equivalent Isotropic Thermal Parameters for $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**).	S38-S39
Table S6 Bond Distances (Å) and Angles (deg) for $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**).	S40-S45
Table S7 Anisotropic Thermal Parameters for $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**).	S46-S47
Table S8 Hydrogen Atoms for $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**).	S48
Table S9. Crystal Data for $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)$•3MeCN •$Et_2O$ (**2**).	S49
Table S10. Positional and Equivalent Isotropic Thermal Parameters for $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)$•3MeCN •$Et_2O$ (**2**).	S50-S51
Table S11. Bond Distances (Å) and Angles (deg) for $[Fe^{II}(tame(N_2S(quino)_2)]_2(BPh_4)$•3MeCN •$Et_2O$ (**2**).	S52-S62
Table S12. Anisotropic Thermal Parameters for $[Fe^{II}(tame(N_2S(quino)_2)]_2(BPh_4)$ •3MeCN •Et_2O (**2**).	S63-S65
Table S13. Hydrogen Atoms for $[Fe^{II}(tame(N_2S(quino)_2)]_2(BPh_4)$•3MeCN •$Et_2O$ (**2**).	S66-S68
Table S14. Crystal Data for $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2$•2MeCN (**3**).	S69
Table S15. Positional and Equivalent Isotropic Thermal Parameters for $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2$•2MeCN (**3**).	S70-S71

Table S16. Bond Distances (Å) and Angles (deg) for $[Fe^{II}(tame(N_2S(^{Me}Im)_2)]_2(PF_6)_2$•2MeCN (**3**).	S72-S84
Table S17. Anisotropic Thermal Parameters for $[Fe^{II}(tame(N_2S(^{Me}Im)_2)]_2(PF_6)_2$ •2MeCN (**3**).	S85-S87
Table S18. Hydrogen Atoms for $[Fe^{II}(tame(N_2S(^{Me}Im)_2)]_2(PF_6)_2$•2MeCN (**3**).	S88-S89
Table S19. Crystal Data for $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2$• 2MeCN (**4**).	S90
Table S20. Positional and Equivalent Isotropic Thermal Parameters for $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2$• 2MeCN (**4**).	S91-S93
Table S21. Bond Distances (Å) and Angles (deg) for $[Co^{II}(tame(N_2S(^{Me}Im)_2)]_2(PF_6)_2$• 2MeCN (**4**).	S94-S104
Table S22. Anisotropic Thermal Parameters for $[Co^{II}(tame(N_2S(^{Me}Im)_2)]_2(PF_6)_2$ •2MeCN (**4**).	S105-S107
Table S23. Hydrogen Atoms for $[Co^{II}(tame(N_2S(^{Me}Im)_2)]_2(PF_6)_2$•2MeCN (**4**).	S108-S109
Table S24. Crystal Data for $[Fe^{II}(tame(N_2S^{Bz}(^{Me}Im)_2(MeCN))](PF_6)_2$•MeCN (**5**)	S110
Table S25. Positional and Equivalent Isotropic Thermal Parameters for $[Fe^{II}(tame(N_2S^{Bz}(^{Me}Im)_2(MeCN))](PF_6)_2$•MeCN (**5**)	S111-S112
Table S26. Bond Distances (Å) and Angles (deg) for $[Fe^{II}(tame(N_2S^{Bz}(^{Me}Im)_2(MeCN))](PF_6)_2$•MeCN (**5**)	S113-S120

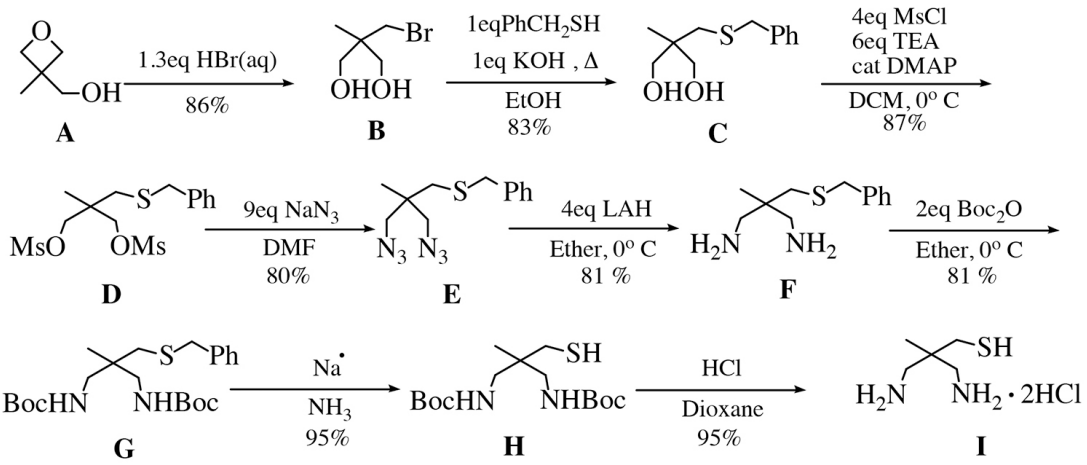
Experimental.

General Methods Sodium azide, 1-hydroxybenzotriazole (HOBt), dicyclohexylcarbodiimide, 3,3'-aminopropylamine, di-tert-butyl dicarbonate, 2-(tert-butoxycarbonylamino)isobutyric acid, iron(II) acetate, iron(II) chloride, and tetraphenyl phosphonium chloride were all purchased from TCI and used as received. DMSO-d_6 and $CDCl_3$ were purchased from Cambridge Isotope Labs and used as received. Ethanol was purchased from Decon and degassed prior to use. Diethyl ether was purchased from Fischer Scientific and purified using a solvent purification columns housed in a custom stainless steel cabinet and dispensed by a stainless steel Schlenk-line (GlassContour). All other solvents were purchased from Sigma Aldrich. MeOH, MeCN and CH_2Cl_2 were dried and distilled prior to use. A 48% aqueous solution of hydrobromic acid was purchased from Alfa-Aesar and used as received. Ammonia was obtained from Praxair while all other material was purchased and used as received from Sigma Aldrich.

^{1}H NMR spectra were obtained on a Bruker AV300, AV301, DRX499, or AV500. Chemical shifts are listed in parts per million and were reported relative the residual protio solvent. UV/Vis spectra were recorded on a Varian Cary 50 spectrophotometer equipped with a fiber optic cable connected to a "dip" ATR probe (C-technologies). A custom-built two neck solution sample holder equipped with a threaded glass connector was sized specifically to fit the "dip" probe. Mass spec data was collected on either a Bruker Esquire LC-Ion Trap Electrospray ionization mass specrometer (ESI-MS), or a LTQ ion trap mass spectrometer equipped with an HP 1100 capilary inlet. Cyclic voltammograms

were recorded in MeCN (0.1M $^{n}Bu_4N[PF_6]$ supporting electrolyte) on a PAR 263A potentiostat utilizing a classy carbon working electrode, platinum auxiliary electrode and an $Ag^{+}/AgNO_3$ reference electrode. X-ray crystallographic data was recorded on a Bruker APEX II single crystal X-ray diffractometer using Mo-radiation. Elemental analysis were preformed by Atlantic Microlab, Inc. Norcross, Ga.

All manipulations were performed using Schlenk techniques or under a N_2 atmosphere in a glovebox. The synthesis of 2-bromomethyl-2-methyl-propane-1,3-diol (**B**, Scheme S1), and 2-benzylsulfanyl methyl-2-methyl-propane-1,3-diol (**C**, Scheme S1) were carried out using a modified literature procedure.[1]



Scheme S1.

Synthesis of (3-methanesulfonyl-2-methanesulfonylmethyl-2-methyl-propylsulfanylmethyl)-benzene (D). Methanesulfonyl chloride (18.2 g, 159 mmol) was added dropwise to a CH_2Cl_2 (375 mL) solution containing **C** (Scheme S1) 9.0 g, 39.8 mmol),[1] triethylamine (24.1 g, 239 mmol) and a catalytic amount

of 4-dimethylaminopyridine (200-300 mg) at 0°C. The orange solution was monitored by TLC through the disappearance of the starting material. The reaction was then allowed to warm to room temperature. Water (300 mL) was added to the solution and extracted with CH_2Cl_2 (2 x 300 mL), the combined organics were washed with water and brine (2 x 100 mL each) prior to drying with sodium sulfate. Solvents were removed *in vacuo* and the orange oil was purified to an-off yellow oil by column chromatography (1:1 ethyl acetate:hexanes) in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5H), 4.07 (d, ^2J 9 Hz, 4H), 3.75 (s, 2H), 3.01 (s, 6H), 2.53 (s, 2H), 1.08 (s, 3H). ESI-MS: expected *m/z* for $C_{14}H_{22}O_6S_3$= 382.1 found *m/z*= 382.1.

Synthesis of (3-azido-2azidomethyl-2-methyl-propylsulfanylmethyl)-benzene (E). (3-methanesulfonyl-2-methanesulfonylmethyl-2-methyl-propylsulfanylmethyl)-benzene (**D**) (8.0 g, 21 mmol) was added to a solution of sodium azide (12.3 g, 189 mmol) in DMF (130 mL) and refluxed for 3 days. After cooling to room temperature, water (130 mL) was added and the organics were extracted with ethyl acetate (3x 200 mL). The combined organics were combined and washed water and brine (2 x 200 mL each) wherein the reaction mixture was dried with sodium sulfate. The solvent was removed *in vacuo* and the resulting yellow oil was purified by silica gel column chromatography (4:1 hexanes:ethyl acetate) to yield (**E**) as an off white oil in 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 5H), 3.74 (s, 2H), 3.29 (d, ^2J 9 Hz, 4H), 2.44 (s, 2H), 0.98 (s, 3H).

Synthesis of 2-benzylsulfanylmethyl-2-methyl-propane-1,3-diamine (F). (3-azido-2azidomethyl-2-methyl-propylsulfanylmethyl)-benzene (**E**, Scheme S1) (2.0 g, 7.2 mmol) was added drop wise to a stirred solution of lithium aluminum hydride (LAH) (1.1 g, 28.8 mmol) in ether (150 mL) at 0°C. Once the reaction was complete water was added slowly to quench the excess LIH. The reaction was then filtered through Celite and dried with sodium sulfate. The ether was removed *in vacuo* and the clear oil was placed in an aqueous solution (10 mL) and acidified to pH 2.0. The aqueous solution was washed with ether (3 x 20 mL) before being basified to pH 12.0. The product was then extracted ether (3 x 40 mL). The combined organics were dried with sodium sulfate and then removed *in vacuo* to yield (**F**) as a clear oil in 51% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 5H), 3.70 (s, 2H), 2.55 (S, 4H), 2.44 (s, 2H), 0.86 (s, 3H). ESI-MS: expected *m/z* for $C_{12}H_{20}N_2S$= 224.1, found *m/z*=225.1.

Synthesis of 2-benzylsulfanylmethyl-2-methyl-propane-1,3-(*tert*-Butyloxycarbonyl) diamine (G). 2-benzylsulfanylmethyl-2-methyl-propane-1,3-diamine (**F**) (4.7 g, 20 mmol) was dissolved in 50 ml of dichloromethane and cooled to 0°C. Di-*tert*-butyl dicarbonate (9.1 g, 40 mmol) was dissolved in 10 mL of dichlormethane and added dropwise to the solution of **F**. This solution was allowed to warm to room temperature overnight. The solution was washed 2x with brine (50 mL) and dried over Na_2SO_4. Volatiles were removed *in vacuo* to afford **G** as a white solid in 95% yield (8.1 g) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5H), 5.03 (bs, 2H), 3.69 (s, 2H), 3.048 (*dd*, ^{3}J 7.5 Hz, ^{2}J 14.7 Hz, 2H), 2.80

(*dd*, ^{3}J 6.3 Hz, ^{2}J 14.9 Hz 2H), 2.35 (s, 2H), 1.44 (s, 18H), 0.86 (s, 3H). ESI-MS: expected *m/z* for $C_{22}H_{36}N_2O_4S$= 424.1, found *m/z*=425.1

Synthesis of 2-thiomethyl-2-methyl-propane-1,3-(*tert*-Butyloxycarbonyl) diamine (H). To a stirred solution of liquid ammonia (50 mL) cooled to -78°C, was added sodium metal (200 mg). 2.9 g (6.8 mmol) of **G** (Scheme S1) was added in 0.3g amounts. Additional sodium was periodically added in small proportions to maintain the deep blue color. The completion of the reaction was assumed once the solution maintained its deep blue color for more than 1 h. Ammonium chloride was added until the solution changed from blue to yellow, thus quenching the sodium. The liquid ammonia was evaporated under a stream of N_2. A 50 mL, 0.025M K_2HPO_4 and 0.025M NaH_2PO_4 aqueous solution was then added and the reaction was acidified with 37% HCl until the reaction reached a pH of 2. The organic product was extracted with dichloromethane (4 x 75 mL). The organics were then dried with Na_2SO_4 and the volatiles were removed to afford **H** as a foul smelling oil in 93% yield (2.1 g) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.26 (bs, 2H), 3.00 (*m*, 4H), 2.41 (d, ^{3}J 9 Hz 2H), 1.66 (t, ^{3}J 9 Hz 1H), 1.46 (s, 18H) 0.89 (s, 3H). ESI-MS: expected *m/z* for $C_{15}H_{30}N_2O_4S$= 334.1, found *m/z*=335.1

Synthesis of 2-thiomethyl-2-methyl-propane-1,3-diamine dihydrogenchloride (I). 5 mL of 4M HCl in dioxane was added to Boc-protected **H** (2.1g, 6.4 mmol) in 2mL of methanol. Gas evolution was observed and the solution was allowed to stir overnight. The volatiles were removed *in vacuo* to afford **I**, tame-N_2S•2HCl, as a white solid in 95% yield (1.2 g) ^{1}H NMR (300 MHz,

d_6-DMSO) δ 8.12 (bs, 5H, NH_2), 2.91 (bs, 4H), 2.65 (s, 2H), 1.02 (s, 3H). ESI-MS: expected *m/z* for $C_5H_{16}Cl_2N_2S$= 207.1, found *m/z*=135.1 (expected minus 2 HCl)

Synthesis of $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(PF_6)_2$ (1). 2-thiomethyl-2-methyl-propane-1,3-diamine dihydrogenchloride (**I**) (0.2 g, 1mmol) was added to a vial containing a stirred solution of sodium methoxide (0.156g, 3mmol) in 10 mL of methanol. 2-pyridinecarboxaldehyde (0.21 g, 2mmol) was then added and the stirred suspension was cooled to -40° C. In a separate vial iron (II) chloride dissolved in 5 mL of methanol and cooled to -40° C. The iron solution was then slowly added to the organic solution. Immediately, the solution became a deep turquoise color. This was stirred for 1h at which time sodium hexafluorophosphate (0.168 g, 1 mmol) was added. This solution was stirred overnight at which time a dark solid precipitated was observed. The methanol was removed *in vacuo*, and the resulting solid was dissolved in acetonitrile, and filtered through celite. The deep turquoise solution was concentrated to a minimal volume (~2 mL) upon which ether was layered to isolate a deep blue solid in 70% yield (360 mg). Electronic absorption spectrum: λ_{max} (nm) (ε ($M^{-1}cm^{-1}$): (MeCN): 420 (6,150), 580 (9,100), and 650 (11,800)). ^{1}H NMR (300 MHz, d_3-MeCN) δ 9.3 (s, 1H), 9.00 (s, 1H), 8.97 (s, 1H) 8.15, (m, 3H), 7.75 (t ^3J 7.5 Hz, 1H), 7.45 (m, 2H), 7.09 (t ^3J 7 Hz, 1H), 4.14 (d ^2J 12.7 Hz, 1H) 3.77 (m, 3H), 1.04 (s, 3H), 0.90 (d, ^2J 13.3 Hz 1H), 0.31 (d ^2J 13.4 Hz, 1H); ^{13}C NMR (500 MHz, MeCN-d_3) δ 169.2 (s, 2C), 168.5 (s, 2C), 160.2 (s, 2C), 158.9 (s, 2C), 154.4 (s, 2C), 153.3 (s, 2C), 136.9 (s, 2C), 136.1 (s, 2C) 128.8 (s, 2C), 128.1 (s, 2C),

125.4 (s, 2C), 125.2 (s, 2C), 69.0 (s, 2C), 67.0 (s, 2C), 43.4 (s, 2C), 26.6 (s, 2C), 24.8 (s, 2C) ESI-MS: expected *m/z* for $[C_{34}H_{38}N_8S_2Fe_2]^{2+}$= 367.1, found *m/z*=367.1 Elemental Analysis for $C_{34}H_{38}F_{12}N_8P_2S_2Fe_2$ Calculated: C, 39.86; H, 3.74; N, 10.94. Found C, 39.28; H, 3.73; N; 10.80.

Synthesis of $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$: The tetraphenylborate salt of **1** was prepared using the method described above for the PF_6^- salt, except the 1 mmol of $NaPF_6$ was replaced with 1 mmol of $NaBPh_4$. Crystals with were grown by layering MeOH onto a MeCN solution. ESI-MS: expected *m/z* for $[C_{34}H_{38}N_8S_2Fe_2]^{2+}$= 367.1, found *m/z*=367.1. Electronic absorption spectrum: λ_{max} (nm) (ε ($M^{-1}cm^{-1}$): (MeCN): 420 (6,150), 580 (9,100), and 650 (11,800)).

Synthesis of $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(PF_6)_2$ (2). Complex **2** was synthesized using a procedure analogous to that of **1**. A deep blue solid was isolated by layering ether onto a concentrated solution of **2** in DCM in 67% yield. λ_{max} (nm) (ε ($M^{-1}cm^{-1}$): (MeCN): 420 (6,240), 607 (14,830), and 719 (19,500)). ^{1}H NMR (300 MHz, MeCN-d_3) δ 9.81 (s, 2H), 8.30 (d ^2J 8.5 Hz, 2H), 8.06 (d ^2J 8.4 Hz, 2H), 7.90 (d ^2J 7.8 Hz, 2H), 7.58 (t ^3J 7.4 Hz, 2H), 7.47 (t ^3J 7.7hz, 2H), 6.50 (d ^2J 8.3 Hz, 2H), 4.77 (d ^2J 15.1 Hz, 2H) 3.87 (d ^2J 15.1 Hz, 3H), 0.67 (s, 3H), 0.00 (s, 2H) ESI-MS: expected *m/z* for $[C_{50}H_{46}N_8S_2Fe_2]^{2+}$ = 467.1, found *m/z* = 467.1. Elemental Analysis for $C_{50}H_{46}F_{12}N_8P_2S_2Fe_2CH_2Cl_2$ Calculated: C, 46.77; H, 3.69; N, 8.56. Found C, 46.85; H, 3.73; N; 8.11.

Synthesis of $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)_2$ (2-BPh_4). The tetraphenylborate salt of **2** was prepared using the method described above for the PF_6^- salt, except the 1 mmol of $NaPF_6$ was replaced with 1 mmol of $NaBPh_4$.

Crystals were grown via slow vapor diffusion of Et_2O into a MeCN solution. Electronic absorption spectrum: λ_{max} (nm) (ε ($M^{-1}cm^{-1}$): (MeCN): 420 (6,240), 607 (14,830), and 719 (19,500)). ESI-MS: expected *m/z* for $[C_{50}H_{46}N_8S_2Fe_2]^{2+}$= 467.1, found *m/z*=467.1.

Synthesis of $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2))]_2(PF_6)_2$•2MeCN (3). Complex **2** was synthesized using the same procedure used to prepare **1,** except 1-methyl-2-imidazolecarboxaldehyde was used in place of 2-pyridinecarboxaldehyde. A royal blue solid was obtained in 85% yield from layering of ether onto a concentrated volume of acetonitrile. Crystals were isolated via slow diffusion of ether into a concentrated solution of acetonitrile. Electronic absorption spectrum dimeric **3**: λ_{max} (ε ($M^{-1}cm^{-1}$): (MeCN): 619(12,400); (MeOH) 595(4,600) nm. Electronic absorption spectrum monomeric **3**: λ_{max} (ε ($M^{-1}cm^{-1}$): (MeCN): 619 (6,100) nm. Magnetic moment (solution MeCN-d_3 298 K)= 2.89 μ_B. ESI-MS: expected *m/z* for $[C_{30}H_{43}N_{12}S_2Fe_2]^{2+}$= 373.5, found *m/z*=373.1 Elemental Analysis for $C_{30}H_{42}F_{12}N_{12}P_2S_2Fe_2CH_3CN$ Calculated: C, 35.67; H, 4.21; N, 16.90. Found C, 35.57; H, 4.14; N; 16.74.

Synthesis of $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2))]_2(PF_6)_2$•2MeCN (4). The tripodal thiolate bis-amine ligand **I** (Scheme S1, 0.2 g, 1 mmol) was added to a vial containing a stirred solution of sodium methoxide (0.156 g, 3 mmol) in 10ml of methanol. 1-methyl-2-imidizolecarboxaldehyde (0.21 g, 2 mmol) was then added and the stirred suspension was cooled to -40° C. In a separate vial cobalt (II) chloride was dissolved in 5 mL of MeOH and cooled to -40° C. The cobalt

solution was then slowly added to the organic solution. This was stirred for 1h, at which time sodium hexafluorophosphate (0.168 g, 1 mmol) was added. This solution was stirred overnight at which time an orange precipitate was observed. The MeOH was removed *in vacuo* and the solid was dissolved in MeCN, and filtered through celite. The MeCN was removed to a minimal volume and layered with Et_2O to isolated a red powder in 93% yield (265 mg). A slow layered diffusion of Et_2O into MeCN afforded X-ray quality crystals of **4**. λ_{max} (nm) (ε ($M^{-1}cm^{-1}$)): (MeCN): 385(2100), 512 sh (654). Magnetic moment (solution, MeCN-d_3, 298K)= 3.98 μ_B/Co. ESI-MS: expected *m/z* for $[C_{30}H_{43}N_{12}S_2Co_2]^{2+}$= 376.1, found *m/z* = 376.2. Elemental Analysis for $C_{30}H_{43}F_{12}N_{12}P_2S_2Co_2$ Calculated: C, 34.56; H, 4.06; N, 16.12. Found: C, 34.41; H, 4.04; N; 15.95.

Synthesis of $[Fe^{II}$(tame-(N_2S^{Bz}(^{Me}Im)$_2$(MeCN))$]^+$ (**5**)**.** 2-benzylsulfanylmethyl-2-methyl-propane-1,3-diamine (**6**) (0.1 g, 0.44 mmol) was added to a vial and dissolved in 8 mL of MeOH. 1-methyl-2-imidizolecarboxaldehyde (0.1 g, 0.88 mmol) was then added and the solution was cooled to -40° C. In a separate vial iron (II) chloride (0.055 g, 0.44 mmol) was dissolved in 3 ml of MeOH and cooled to -40° C. The iron solution was then slowly added to the organic solution. Immediately, the solution became red. This was stirred for 1h at which time sodium hexafluorophosphate (0.148 g, 0.88 mmol) was added. The MeOH was removed *in vacuo* and the resulting solid was dissolved in MeCN and filtered through celite. The red solution was concentrated to a minimal volume (2 mL) upon which Et_2O was layered to isolate a deep red solid in 45% yield (150 mg). λ_{max} (nm) (ε ($M^{-1}cm^{-1}$): (MeCN): 512(2850). Magnetic moment (solution, MeCN-

d_3, 298K)= 5.04μ_B. Elemental Analysis for $C_{24}H_{31}F_{12}N_7P_2SFe$ Calculated: C, 36.24; H, 3.93; N, 12.33. Found: C, 35.74; H, 3.97; N; 12.41.

Computational Methods. All calculations were performed using the ORCA quantum chemistry package developed by Neese and coworkers.[2] All calculations employed the def2-TZVP(-f) basis set and the def2-TZVP/J auxiliary basis set for Coulomb fitting, the atom-pairwise dispersion correction of Grimme (D3BJ),[3,4] and tight convergence criteria were required for the SCF solutions. All calculations used the Grid5 (GridX5) integration grid size, the zeroth-order regular approximation (ZORA),[5] and the conductor-like screening model (COSMO) with acetonitrile as a solvent.[6] Geometries were optimized for all complexes using the BP86 functional with the resolution of the identity (RI) approximation,[7,8] and initiated from crystallographic coordinates when available. The calculation was converged to tight optimization criteria. Selected calculations employed the broken-symmetry formalism to model coupled paramagnetic sites. For the calculation of ^{57}Fe Mössbauer parameters, the specialized core properties basis set (CP-PPP) with an integration grid of 7 was selected for Fe. The quadrupole splitting parameters were obtained from the output of the calculation, and the calculated isomer shifts were determined using the calibration study of Römelt et al.[9] Time-dependent DFT (TD-DFT) calculations utilized the same parameters but with the CAM-B3LYP[10] range-separated hybrid density functional and the RI chain-of-spheres (RIJCOSX) approximation.[11,12] Calculation of the electronic absorption and sulfur K-edge X-ray absorption spectra were performed by selecting all available donors and

acceptors or by localizing the donor space to the 1s orbitals of sulfur, respectively.[13] A Gaussian broadening of 3200 cm^{-1} (respectively 0.5 eV) full width at half max was applied to the discrete transition moments. Molecular orbital isosurfaces and transition difference densities were visualized using UCSF Chimera.[14]

^{57}Fe Mössbauer Spectroscopy. Mössbauer spectra were recorded in transmission mode with a constant-acceleration Wissel Mössbauer spectrometer, with a ^{57}Co source in a Rh matrix and a Janis closed-cycle He cryostat operating at 80 K. Samples were anaerobically prepared by grinding crystalline solid into a powder using a mortar and pestle. The powder was then sealed in a shallow Teflon cup. Isomer shifts are reported in mm/s and referenced to iron metal at room temperature. Quadrupole splittings are also reported in mm/s. Experimental data were simulated and fit using the Mfit program.[15]

Sulfur K-Edge X-Ray Absorption Spectroscopy. All the compounds used for S K-edge X-ray Absorption Spectroscopy (XAS) measurements were powders diluted in BN, within a 1:1 ratio. The powders were finely ground using a mortar and pestle, attached to an aluminum plate with double-sided carbon tape and covered with a 5 μm thick polypropylene foil. Sulfur K-Edge XAS experiments were performed at undulator beam line ID26 at the European Synchrotron Radiation Facility (ESRF), Grenoble France. ESRF is a 6 GeV storage ring, providing 200 mA electron beam current in a decay mode. A flat double crystal Si(111) monochromator was employed to select the energy of the incoming X-ray photons, giving and intrinsic resolution $\Delta E/E$ of about 10^{-4}. The X-

rays beam size was 250 μm (H) x 50 μm (V). The XAS measurements were performed in total fluorescence (TFY) mode, using a Si PIN diode to collect the fluorescent X-ray photons. In order to minimalize the scattering contribution to the obtained signal, the sample was positioned at the angle of ~45°degrees to the incident photon beam. The measurements were done at room temperature in a vacuum environment of about 10^{-6} mbar.[16] Two consecutive scans were obtained and averaged for each compound in order to obtain reasonable signal-to-noise ratios. The acquisition time for each of the XAS scans, collected in the range 2450-2550 eV range, was 60 seconds. No sign of radiation induced damage was observed over the acquisition time. The energy of the incident photons was calibrated using the spectrum of elemental sulfur, setting the energy of the first edge feature to 2472 eV.[17] Data were background corrected and normalized using the Athena package,[18] by fitting a second-order polynomial to the pre- and post-edge regions and setting the edge jump to unity. The full range of the normalized spectra is shown in Figure S12.

X-ray Crystallographic Structure Determination. A dark green prism of **$[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (1-BPh_4)**, measuring 0.34 x 0.22 x 0.22 mm^3 was mounted on a glass capillary needle with oil and frozen at -143 °C under a stream of cold nitrogen. Data was collected on a Nonius Kappa CCD X-ray diffractometer, with Mo-radiation. The crystal-to-detector distance was 30 mm and exposure time was 30 seconds per degree for all sets. The scan width was 1.5°. The data collection was 95% complete to 23.26° in ϑ. A total of 9273 reflections were collected covering the indices, h = -26 to 22, k = -23 to 23, l = -27 to 27. Of these, 5042 were symmetry in dependent, and the R_{int} = 0.1378

indicated that the data was of less than average quality (0.07). Indexing and unit cell refinement indicated an orthorhombic P lattice in the space group P_{bcn} (No. 60).

A lustrous green prism of $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)\bullet 2MeCN\bullet Et_2O$ (**2-BPh$_4$**), measuring 0.20 x 0.15 x 0.13 mm^3 was mounted on a loop with oil. Data was collected at -173 °C on a Bruker APEX II single crystal X-ray diffractometer with Mo-radiation. The crystal-to-detector distance was 40 mm and exposure time was 10 seconds per frame for all sets. The scan width was 0.5°. Data collection was 100% complete to 25° in ϑ. A total of 128992 reflections were collected covering the indices, h = -18 to 18, k = -18 to 18, l = -19 to 19. 11639 reflections were symmetry independent and the R_{int} = 0.0287 indicated that the data was of better than average quality (0.07). Indexing and unit cell refinement indicated a triclinic lattice. The space group was found to be $P\bar{1}$ (No. 2).

A blue crystal of $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2\bullet 2MeCN$ (**3**), measuring 0.10 x 0.05 x 0.05 mm^3, was mounted on a loop with oil. Data was collected at -173 °C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 40 mm and exposure time was 30 seconds per frame for all sets. The scan width was 0.5°. Data collection was 99.9% complete to 25° in ϑ. A total of 50076 reflections were collected covering the indices, h = -19 to 19, k = -20 to 20, l = -21 to 20. 14435 reflections were symmetry independent and the R_{int} = 0.0608 indicated that the data was of slightly better than average quality (0.07). Indexing and unit cell refinement indicated a triclinic lattice. The space group was found to be $P\bar{1}$ (No. 2).

A red crystal of $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**4**), measuring 0.15 x 0.05 x 0.05 mm^3 was mounted on a loop with oil. Data was collected at -173°C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 40 mm and exposure time was 5 seconds per frame for all sets. The scan width was 0.5°. Data collection was 99.9% complete to 25° in ϑ. A total of 107396 reflections were collected covering the indices, h = -15 to 15, k = -18 to 18, l = -25 to 25. 15125 reflections were symmetry independent and the R_{int} = 0.0643 indicated that the data was of better than average quality (0.07). Indexing and unit cell refinement indicated a triclinic lattice. The space group was found to be $P\bar{1}$ (No. 2).

A purple block of $[Fe^{II}(tame\text{-}(N_2S^{Bz}(^{Me}Im)_2(MeCN))](PF_6)_2 \bullet MeCN$ (**5**), measuring 0.08 x 0.03 x 0.03 mm^3 was mounted on a loop with oil. Data was collected at -173 °C on a Bruker APEX II single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 40 mm and exposure time was 30 seconds per frame for all sets. The scan width was 0.5°. Data collection was 99.2% complete to 25° in ϑ. A total of 21050 reflections were collected covering the indices, h = -13 to 13, k = -15 to 15, l = -15 to 15. 6841 reflections were symmetry independent and the R_{int} = 0.0820 indicated that the data was of average quality. Indexing and unit cell refinement indicated a triclinic lattice. The space group was found to be $P\bar{1}$ (No. 2).

Determining the Dimer-3/Monomer Equilibrium Constant K_{eq}(298 K). The ambient temperature equilibrium constant for the $Fe^{II}Fe^{II}$-**3** dimer (D) to Fe^{II} monomer (M) interconversion (eqns (1) and (2)) was calculated using solution Evan's method magnetic data, as described below. At 298 K, μ_{eff} for **3** was determined to be 2.9 μ_B in MeCN. This increases to μ_{eff} = 3.7 μ_B at 330 K, presumably reflecting a shift in the equilibrium towards a

$$K_{eq} = \frac{[M]^2}{[D]} \quad (1)$$

$$D \rightleftarrows 2M \quad (2)$$

paramagnetic monomer (M). In the solid state, the structure of **3** was shown to be diamagnetic (S= 0) by low T Mossbauer spectroscopy (at 80 K), and dimeric by X-ray crystallography (at 100 K). A magnetic moment of 3.7 μ_B suggests that the monomer is high-spin S= 2, as opposed to intermediate-spin S= 1, since the latter would have a maximum spin-only μ_{eff} of 2.83, and μ_B and 3.7 μ_B exceeds that number. Athough one can not rule out the possibility that dimeric **3** possesses a thermally accessible higher spin-state, the observation of both a dimer and monomer in high resolution mass spectral data provides evidence for an equilibrium. The increased reactivity of **3** towards small molecules, relative to **1** and **2**, would also be consistent with the formation of a monomer in solution. One can calculate the fraction of paramagnetic monomer species at 298 K under the conditions used for the Evan 's method measurements (5.02 μmol of Fe in 550 μL of MeCN-d^3) using the ratio μ_{eff}^2(expt)/μ_{eff}^2(theoretical). If 100% of the solution consisted of an S= 2 monomer, then μ_{eff}(theoretical) would be 4.9 μ_B. A magnetic moment of 2.9 μ_B at 298 K would thus indicate that 35% of the iron is a paramagnetic monomer (1.76 μmol) in solution, and 65% a diamagnetic dimer (3.26 μmol of Fe, or 1.63 μmol of dimer). The effective magnetic moment squared (μ_{eff}^2) was used for this calculation because the measureable macroscopic quantity χ_p is dependent on μ_{eff}^2. One can then use this information to calculate the dimer/monomer equilibrium constant at 298 K: $K_{eq}^{298\ K} = (3.20\times10^{-3})^2/(2.96\times10^{-3}) = 3.46\times10^{-3}$ M.

Calculating the UV/vis Extinction Coefficients of Dimeric-3 and its Monomeric Derivative Using the Dimer/Monomer Equilibrium Constant K_{eq}. Assuming that both dimeric **3** and its monomeric derivative contribute to the absorbance at λ_{max} = 619 nm, we can use Beer's law (eqn (3), pathlength ℓ= 1 cm) and the equilibrium concentrations of dimer and monomer to

$$A^{619} = \epsilon_M[M]_{eq} + \varepsilon_D[D]_{eq} \quad (3)$$

determine the extinction coefficients for these two species. Equilibrium monomer and dimer concentrations, $[M]_{eq}$ and $[D]_{eq}$, were determined using two simultaneous equations, eqn (1) and eqn (4). The first of these, eqn (4), relates the initial total Fe concentration to the monomer and dimer concentrations at equilibrium, and the second involves the equilibrium expression of eqn (1). Extinction coefficients for solutions consisting of mixtures of dimeric **3** and its monomeric

$$[Fe]_{tot} = [Fe]_{init} = [M]_{eq} + 2[D]_{eq} \quad (4)$$

derivative were determined at two different total concentrations of Fe ($[Fe]_{init}$= 0.120 mM, and 0.240 mM). Rearranging eqn (4), we can solve for $[D]_{eq}$ in terms of $[M]_{eq}$ and $[Fe]_{init}$ (eqn (5)), and then plug this into the equilibrium expression of eqn (1) to afford eqn (6). Solving the

$$[D]_{eq} = \frac{([Fe]_{init} - [M]_{eq})}{2} \quad (5)$$

$$K_{eq} = \frac{2[M]_{eq}{}^2}{([Fe]_{init} - [M]_{eq})} = 0.00346 \quad (6)$$

quadratic equation (eqns (7) – (10)), we obtain $[M]_{eq}$= 0.113 m<u>M</u> when $[Fe]_{init}$ = 0.120 m<u>M</u>, and $[M]_{eq}$= 0.213 m<u>M</u> when $[Fe]_{init}$ = 0.240 m<u>M</u>. Plugging these values for $[M]_{eq}$ into eqn (5) gives $[D]_{eq}$= 0.00357 m<u>M,</u> and $[D]_{eq}$= 0.0134 m<u>M</u>, respectively, indicating that the equilibrium mixtures consist mainly of paramagnetic monomer, M.

$$[M]_{eq}{}^2 + 0.00173[M]_{eq} - 0.00173(1.20\times10^{-4}\ M) = 0 \quad (7)$$

$$[M_{eq}] = \frac{-0.00173 \pm \sqrt{(0.00173)^2 + 4(2.08\times10^{-7})}}{2} \quad (8)$$

$$[M]_{eq}{}^2 + 0.00173[M]_{eq} - 0.00173(2.40\times10^{-4}\ M) = 0 \quad (9)$$

$$[M_{eq}] = \frac{-0.00173 \pm \sqrt{(0.00173)^2 + 4(4.15\times10^{-7})}}{2} \quad (10)$$

The measured absorbance at λ_{max} = 619 nm was determined to be A^{619}= 0.73 when $[Fe]_{init}$ = 0.120 m<u>M</u>, and A^{619}= 1.45 when $[Fe]_{init}$ = 0.240 m<u>M</u>. The two equations (11) and (12) can then be used to solve for the two unknown extinction coefficients, $\boldsymbol{\varepsilon_M}$ and $\boldsymbol{\varepsilon_D}$. Rearranging eqn (11)

$$0.73 = 1.13\times10^{-4}\epsilon_M + 3.57\times10^{-6}\varepsilon_D \quad (11)$$

$$1.45 = 2.13\times10^{-4}\epsilon_M + 1.34\times10^{-5}\varepsilon_D \quad (12)$$

provides us with an expression for $\boldsymbol{\varepsilon_D}$, eqn (13), in terms of $\boldsymbol{\varepsilon_M}$, which can then be inserted into eqn (12) in order to solve for $\boldsymbol{\varepsilon_M}$ (eqns (14) – (17)). If we then insert this value for $\boldsymbol{\varepsilon_M}$

$$\varepsilon_D = \frac{0.73 - 1.13\times10^{-4}\epsilon_M}{3.57\times10^{-6}} \quad (13)$$

$$1.45 = 2.13\times10^{-4}\epsilon_M + 1.34\times10^{-5}\ \frac{(0.73 - 1.13\times10^{-4}\epsilon_M)}{3.57\times10^{-6}} \quad (14)$$

$$1.45 = 2.13\times10^{-4}\epsilon_M + 2.74 - 4.24\times10^{-4}\epsilon_M \quad (15)$$

$$1.29 = 2.11\times10^{-4}\epsilon_M \quad (16)$$

$$\epsilon_M = 6110\ M^{-1}cm^{-1} \quad (17)$$

into eqn (12), we can solve eqns (18)-(20) for the extinction coefficient for dimer-**3**.

$$1.45 = 2.13\times10^{-4}(6110\ M^{-1}cm^{-1}) + 1.34\times10^{-5}\varepsilon_D \quad (18)$$

$$0.148 = 1.34\times10^{-5}\varepsilon_D \quad (19)$$

$$\varepsilon_D = 11{,}030\ M^{-1}cm^{-1} \quad (20)$$

Similarly, we can rearrange eqn (12) to obtain an expression for $\boldsymbol{\varepsilon_D}$, eqn (21), in terms of $\boldsymbol{\varepsilon_M}$, which can then be inserted into eqn (11) in order to solve for $\boldsymbol{\varepsilon_M}$ (eqns (22) – (25)). If

$$\varepsilon_D = \frac{1.45 - 2.13\times10^{-4}\epsilon_M}{1.34\times10^{-5}} \quad (21)$$

$$0.73 = 1.13\times10^{-4}\epsilon_M + 3.57\times10^{-6}\ \frac{(1.45 - 2.13\times10^{-4}\epsilon_M)}{1.34\times10^{-5}} \quad (22)$$

$$0.73 = 1.13\times10^{-4}\epsilon_M + 0.386 - 5.67\times10^{-5}\epsilon_M \quad (23)$$

$$0.344 = 5.63\times10^{-5}\epsilon_M \quad (24)$$

$$\epsilon_M = 6110\ M^{-1}cm^{-1} \quad (25)$$

we then insert this value for $\boldsymbol{\varepsilon_M}$ into eqn (11), we can solve eqns (26)-(28) for the extinction coefficient for dimer-**3.**

$$0.73 = 1.13\times10^{-4}(6110\ M^{-1}cm^{-1}) + 3.57\times10^{-6}\varepsilon_D \quad (26)$$

$$0.0396 = 3.57\times10^{-6}\varepsilon_D \quad (27)$$

$$\varepsilon_D = 11{,}080\ M^{-1}cm^{-1} \quad (28)$$

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Supplemental Figures.

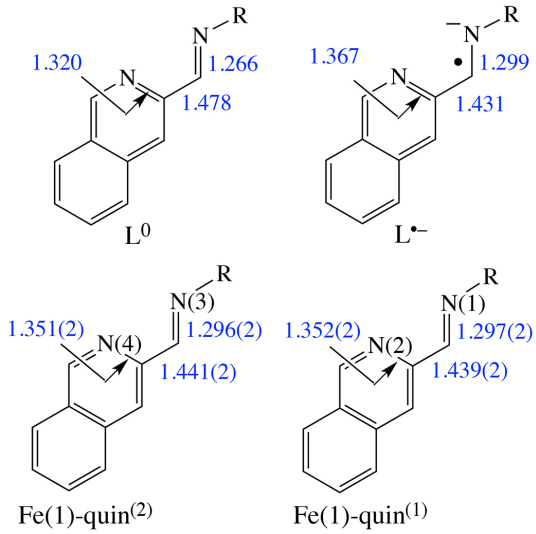


Figure S1. Intraligand distances for **2** versus DFT calculated distances for neutral and mono-reduced (α-imino)quinoline ligands.

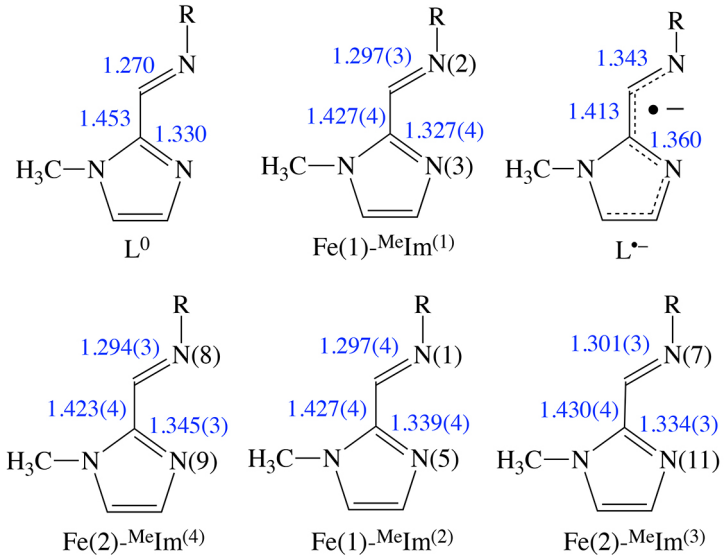


Figure S2. Intraligand distances for **3** versus DFT calculated distances for neutral and mono-reduced (α-imino)imidazole ligands.

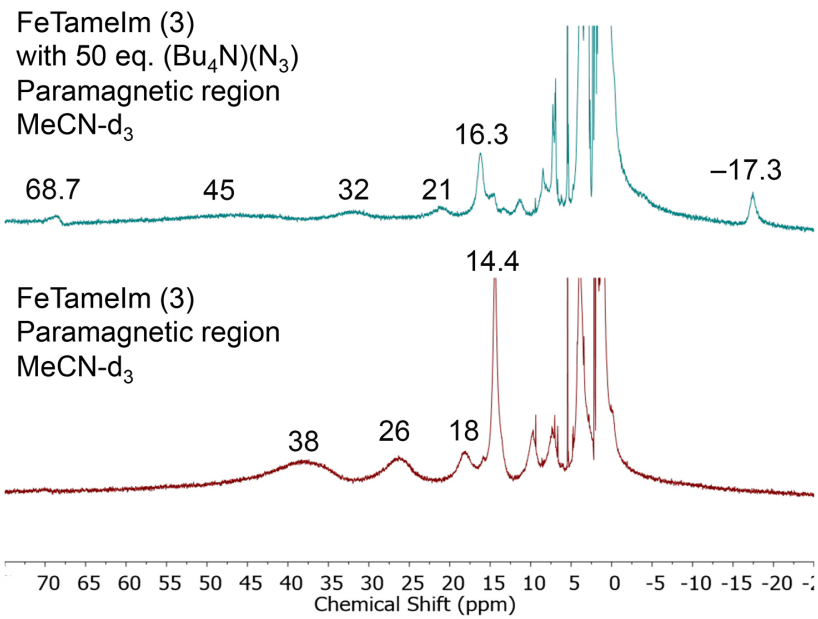


Figure S3. ^{1}H NMR of **3** (in MeCN-d^{3}) in the presence (top) and absence (bottom) of $(Bu_4N)(N_3)$ showing that peaks in the paramagnetic region shift, consistent with azide binding to a paramagnetic species.

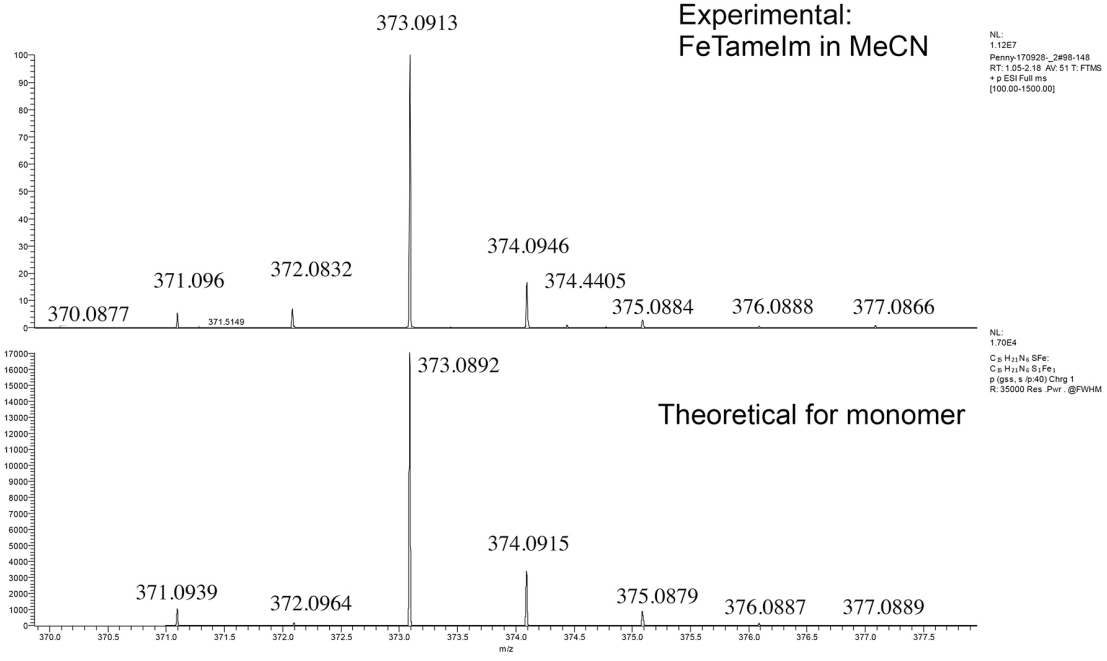


Figure S4. LTQ ion trap mass spectrum of **3** in MeCN solution, versus theoretically calculated for a monocationic monomer. Isotopomers show that the majority of **3** converts to a monomer in solution.

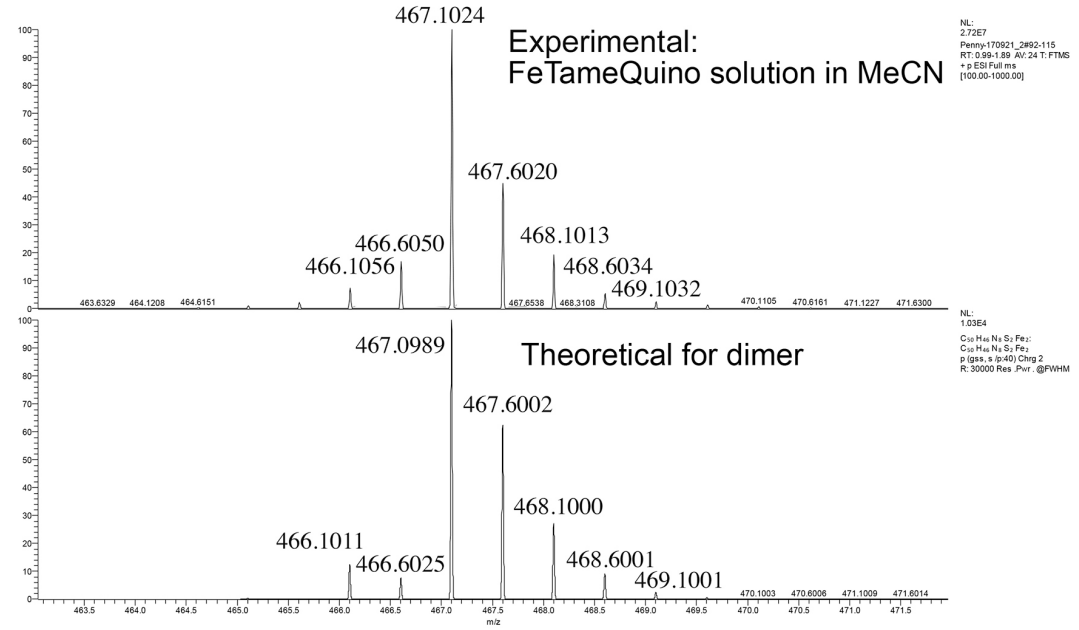


Figure S5. LTQ ion trap mass spectrum of **2** in MeCN solution, versus theoretically calculated for a dicationic dimer. Isotopomers show that **2** maintains its dimeric structure in solution.

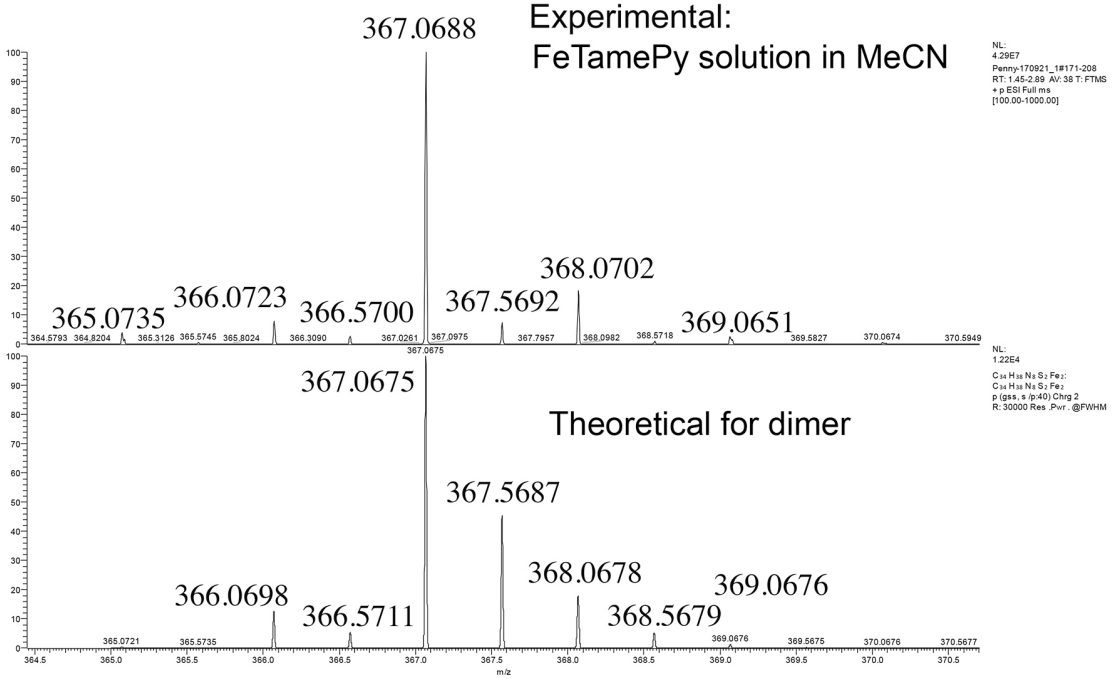


Figure S6. LTQ ion trap mass spectrum of **1** in MeCN solution, versus the theoretically calculated spectrum of a dicationic dimer. Isotopomers show that a portion of **1** maintains its dimeric structure in solution.

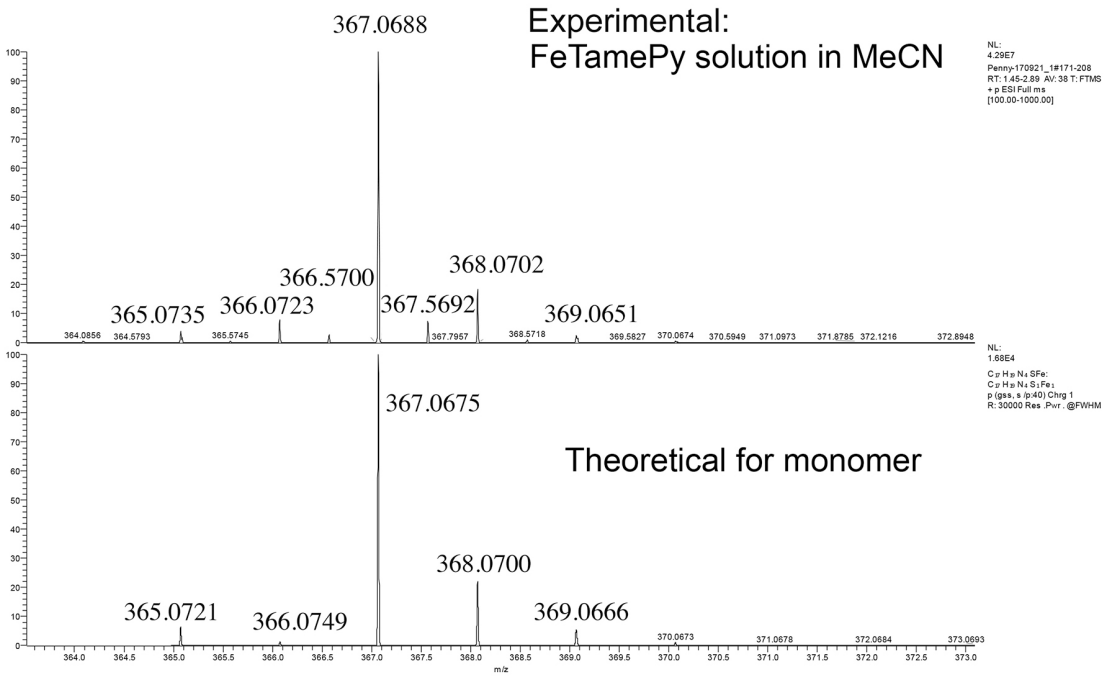


Figure S7. LTQ ion trap mass spectrum of **1** in MeCN solution, versus theoretically calculated for a monocationic monomer. Isotopomers show that a portion of **1** converts to a monomer in solution.

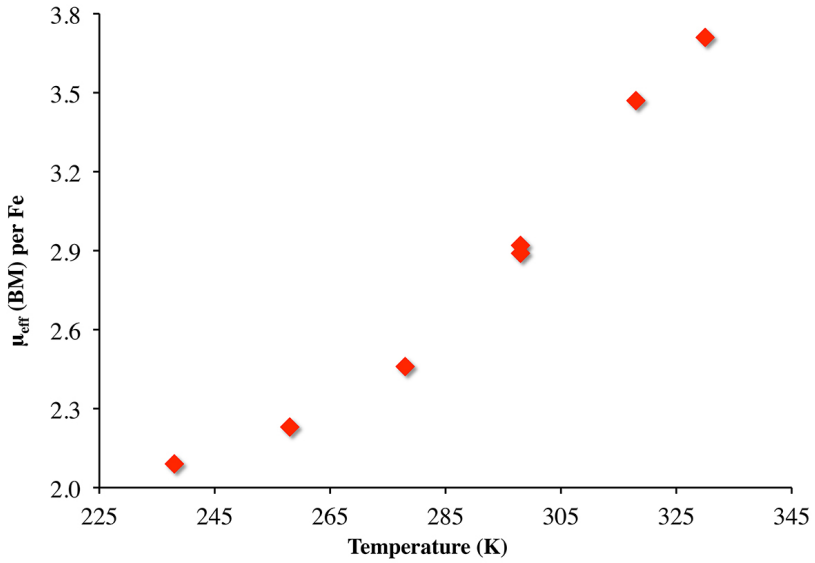


Figure S8. Variable-temperature magnetic moment of **3** in MeCN-d^3 solution, as determined using the Evan's method.

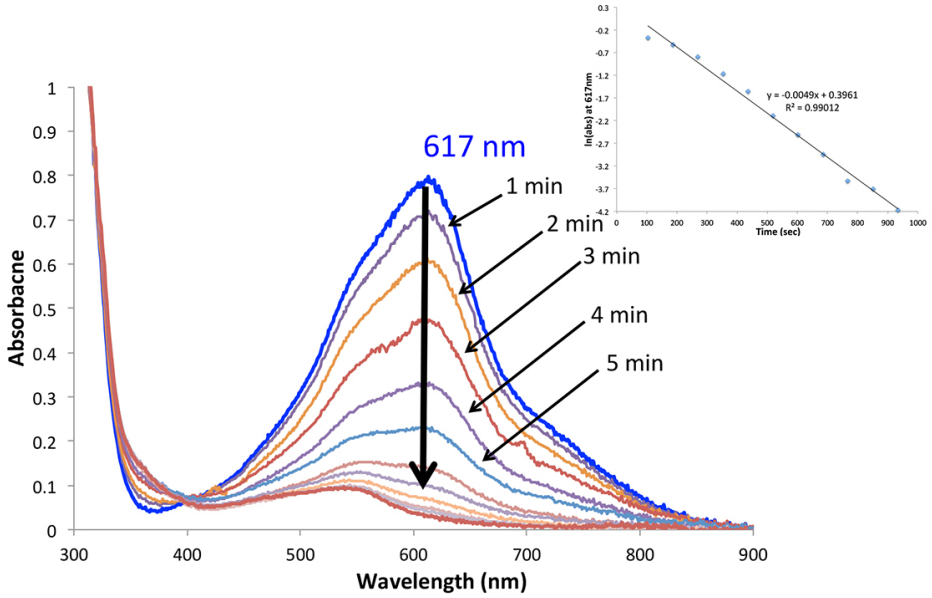


Figure S9. Reaction of **3** (0.045 mM) with O_2 in MeCN at 258 K. Scans taken at 1 min intervals. Inset shows pseudo-first order dependence.

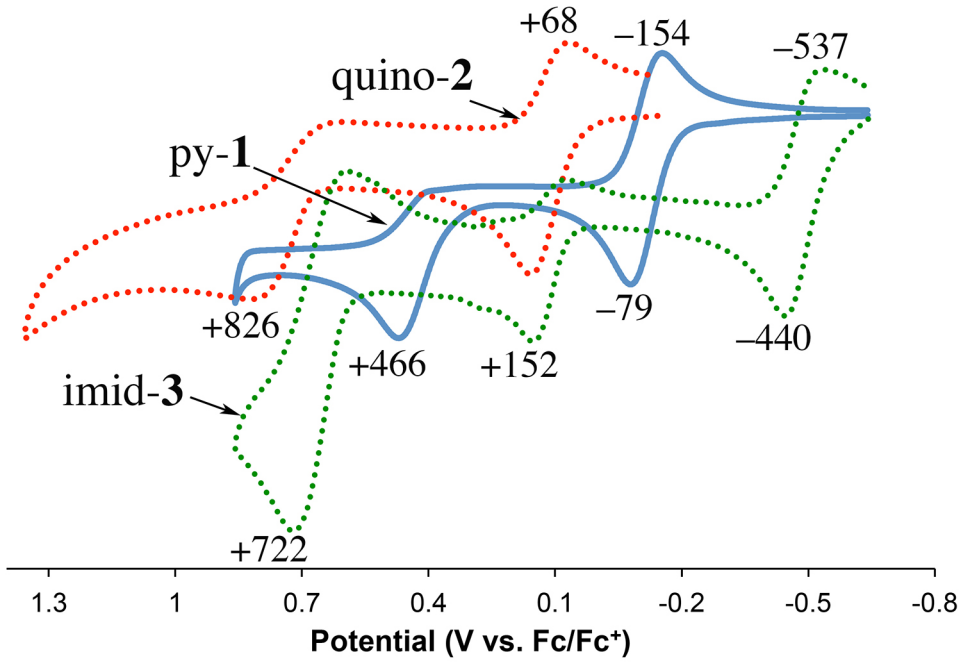


Figure S10. Cyclic voltammograms displaying the oxidation waves associated with complexes **1-3**, and the correlation of potentials with ring size.

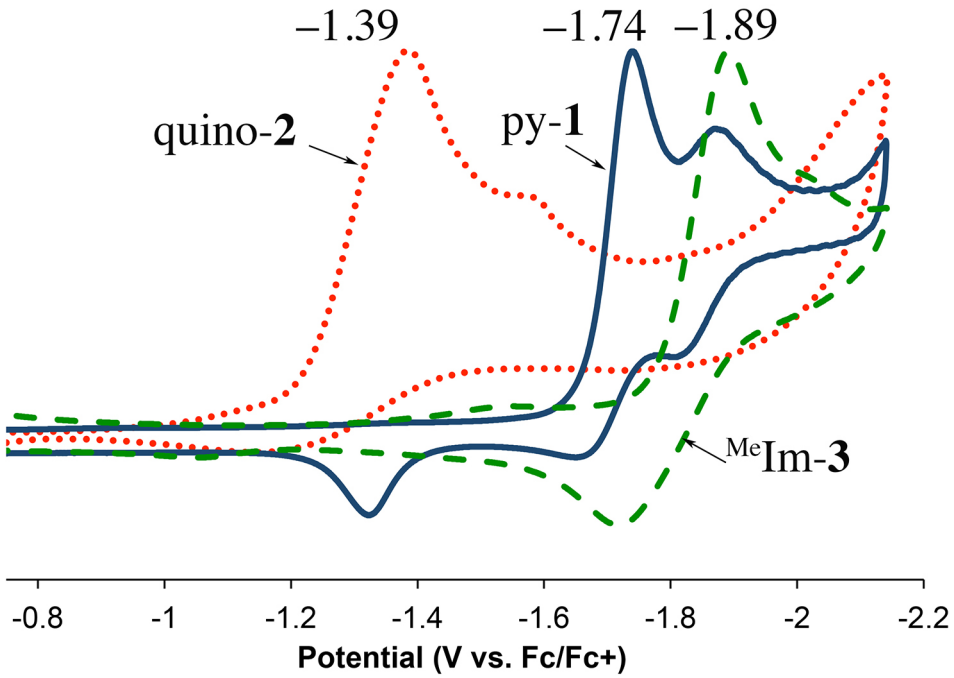


Figure S11. Cyclic voltammograms displaying the reduction waves associated with complexes **1-3**, and the correlation of potentials with ring size.

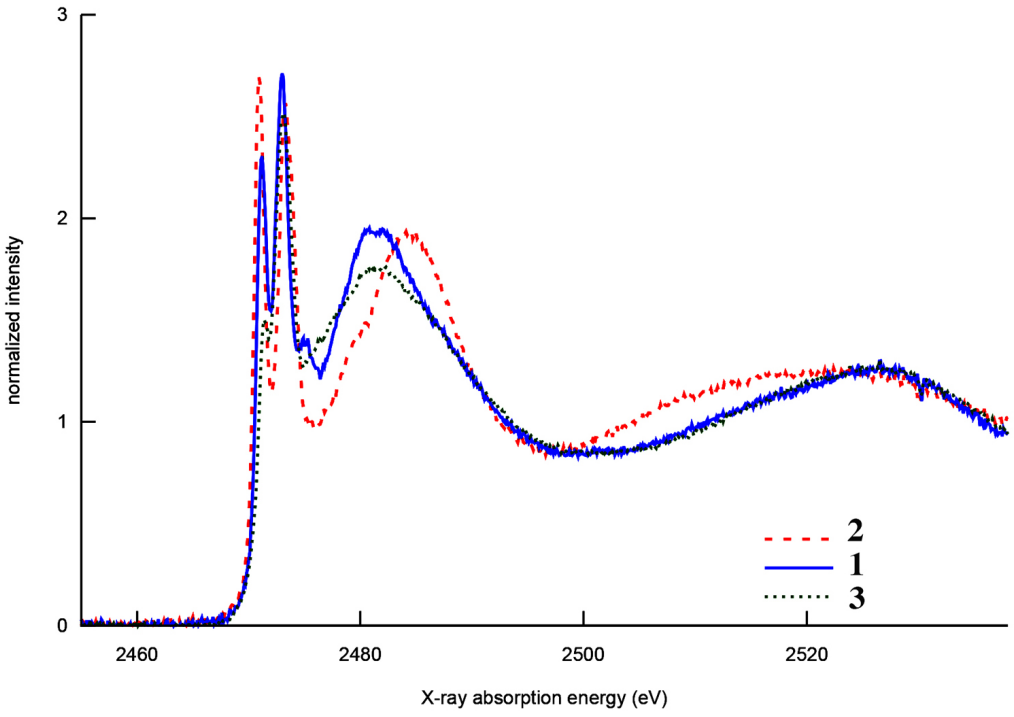


Figure S12. Full range of the normalized sulfur K-edge X-ray absorption spectra.

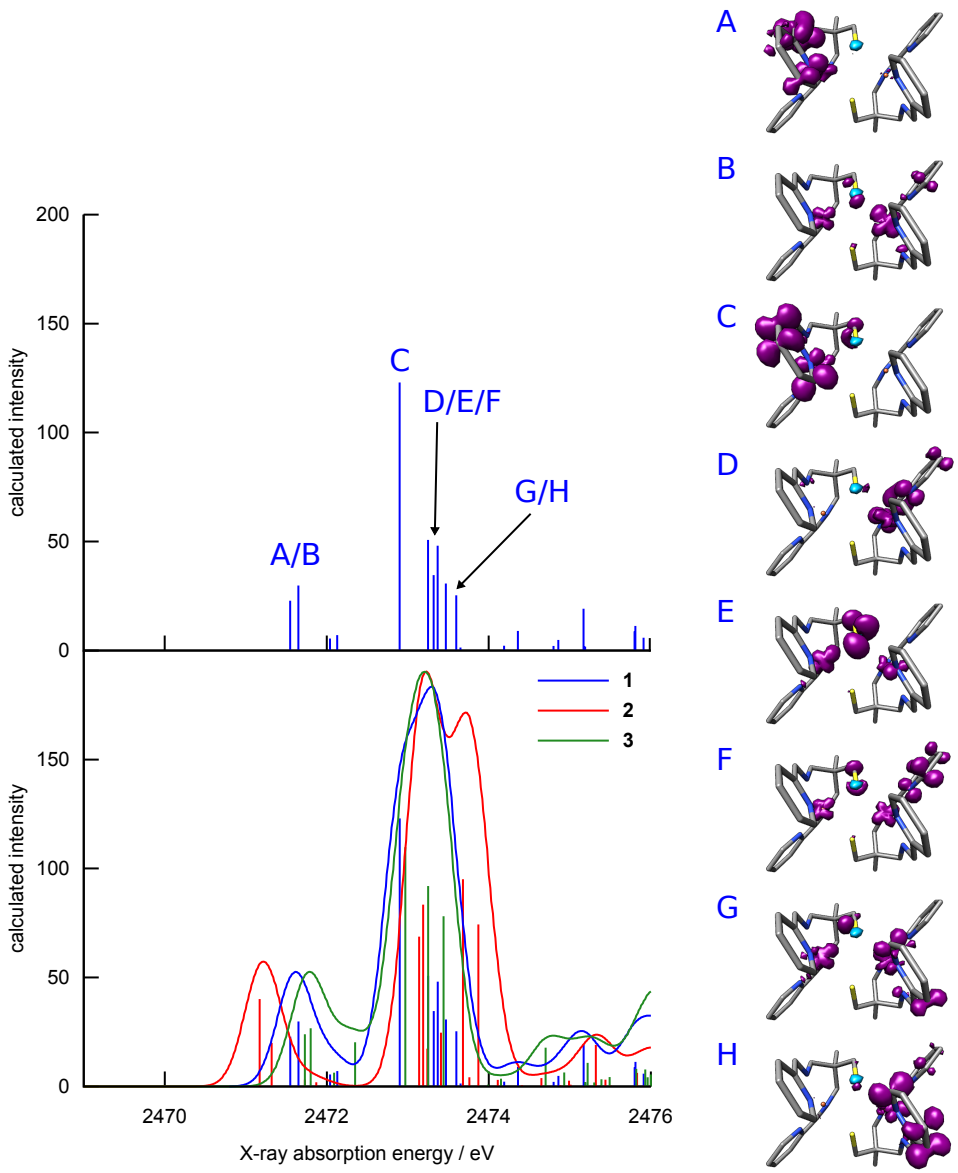


Figure S13. Calculated sulfur K-edge X-ray absorption spectra, including representative transition difference densities for **1.** Regions of increased electron density (acceptors) are shown in purple, regions of decreased electron density (donors) are shown in teal.

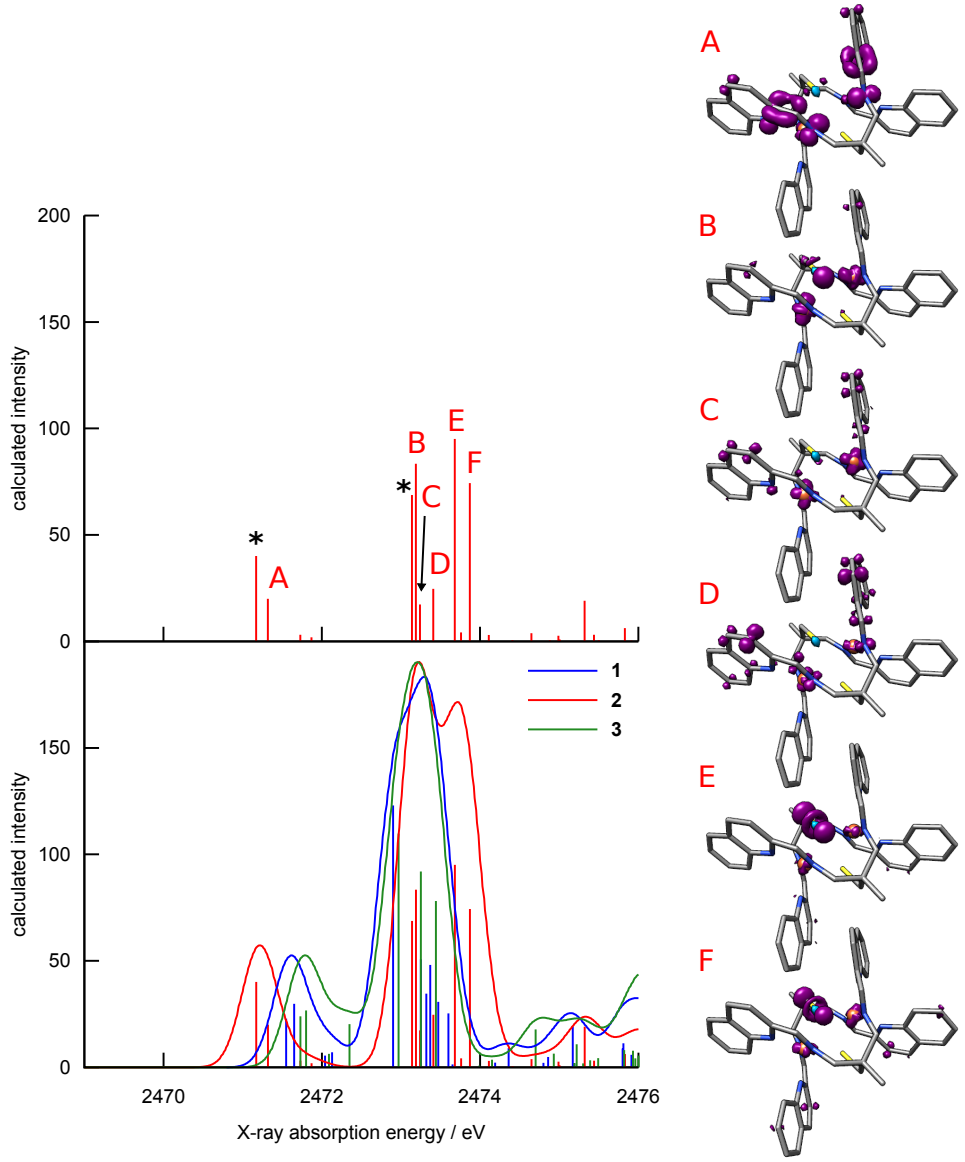


Figure S14. Calculated sulfur K-edge X-ray absorption spectra including representative transition difference densities for **2.** Regions of increased electron density (acceptors) are shown in purple, regions of decreased electron density (donors) are shown in teal. Transitions marked with a ✻ are shown in the manuscript Figure 10.

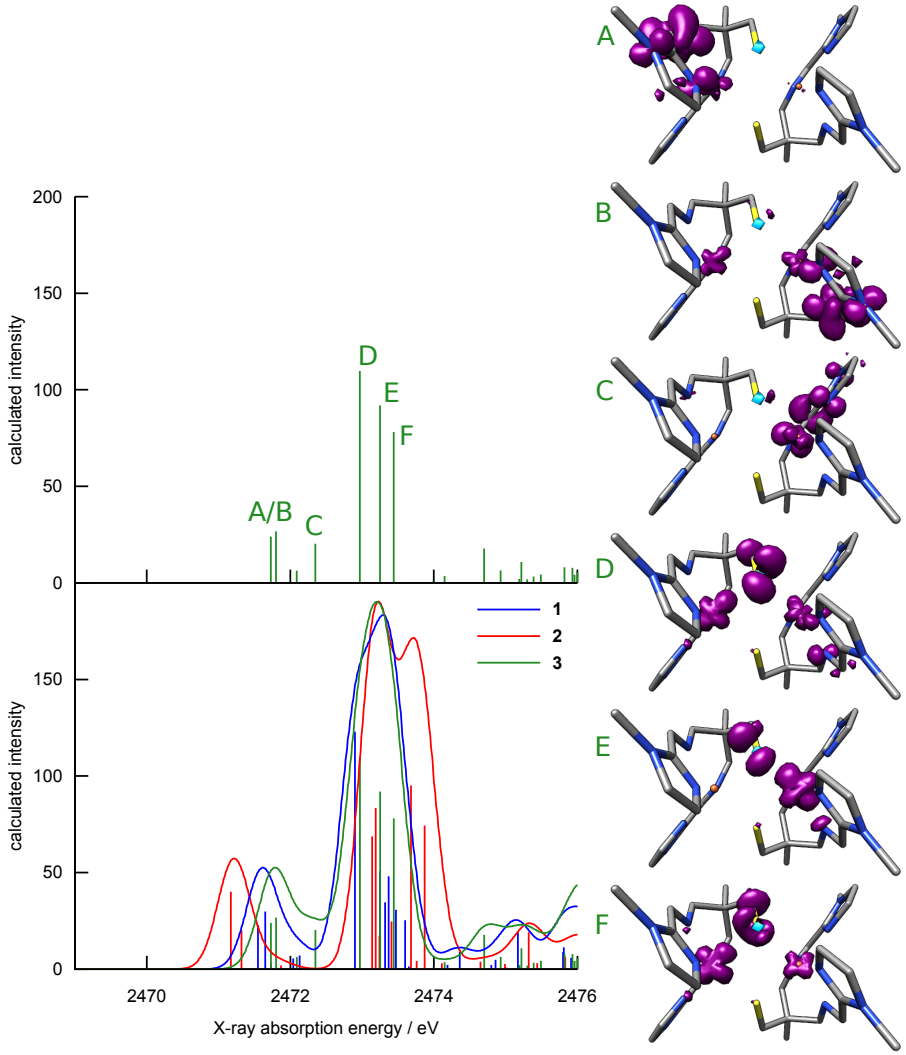


Figure S15. Calculated sulfur K-edge X-ray absorption spectra, including representative transition difference densities for **3.** Regions of increased electron density (acceptors) are shown in purple, regions of decreased electron density (donors) are shown in teal.

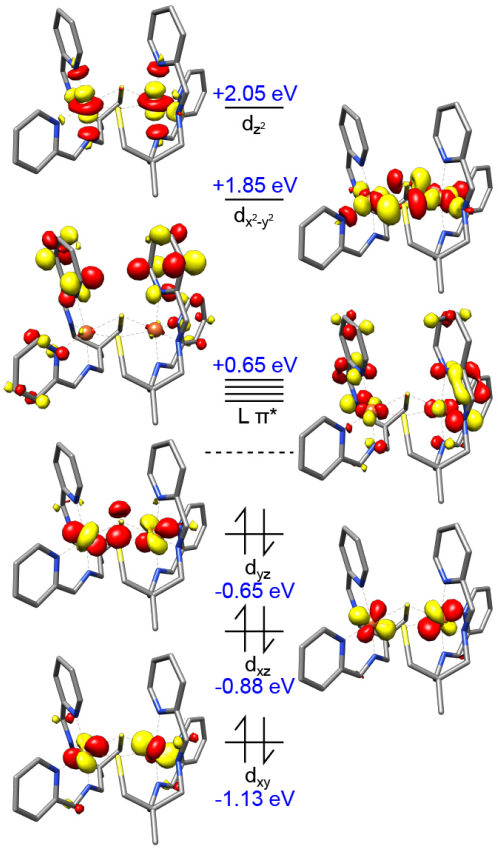


Figure S16. DFT calculated MO diagram for **1**.

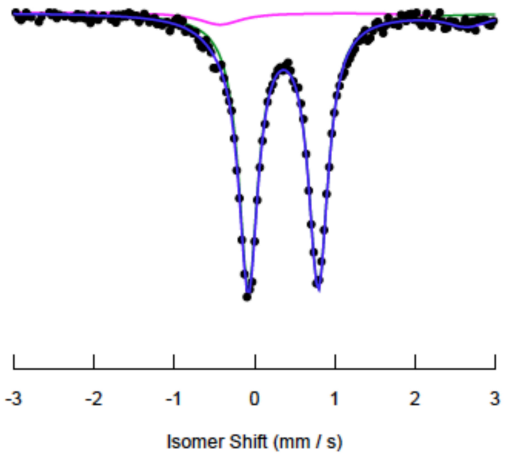


Figure S17. Zero-field Mössbauer spectrum of **1**.

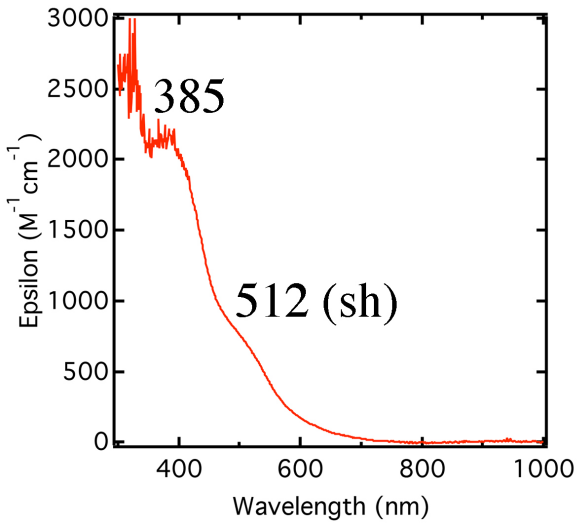


Figure S18. Electronic absorption spectrum of the Co(II) complex **4** in MeCN at 298 K.

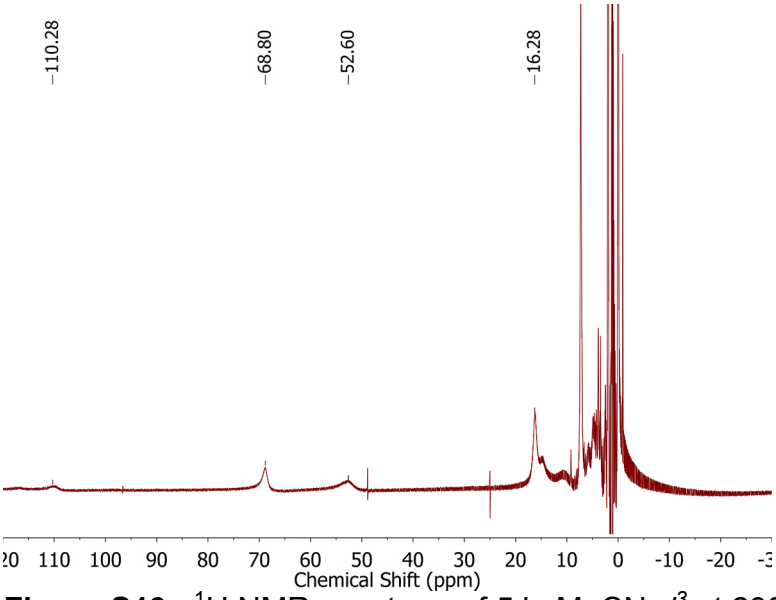


Figure S19. ^{1}H NMR spectrum of **5** in MeCN-d^3 at 298 K showing reproducibly observed peaks indicative of a paramagnetic species.

Table S1. Sulfur K-edge XAS Pre-Edge Energies for **1-3**.

	Pre-Edge Peak #1 (eV)	Pre-Edge Peak #2 (eV)
1	2471.2	2473.0
2	2470.9	2473.3
3	2471.4	2473.1

Table S2. Selected DFT calculated bond distances (Å) for **1-3**.

	1	2	3 Fe(1)*	3 Fe(2)
Fe-S(1)	2.270	2.243	2.323	2.320
Fe-S(2)	2.283	2.243	2.322	2.328
Fe-N(1)^{imine}	1.900	1.925	1.949	1.956
Fe-N(2)^{imine}	1.890	1.927	1.954	1.960
Fe(1)-N(3)^{NHet}	1.957	1.937	1.982	1.980
Fe(1)-N(4)^{NHet}	1.962	1.936	1.990	1.982
Fe-N(7)^{imine}	N/A	N/A	1.949	1.956
Fe-N(8)^{imine}	N/A	N/A	1.954	1.960
Intra-Ligand				
N^{im}(1)-C^{im}	1.310	1.313	1.293	1.293
C^{im}-C^{ipso}	1.432	1.439	1.426	1.428
N^{im}(2)-C^{im}	1.306	1.313	1.290	1.290
C^{im}-C^{ipso}	1.434	1.439	1.429	1.430

*Note: For **1** and **2**, the two halves of the dimer are related by a crystallographic inversion center, whereas the space group of **3** is less symmetric.

Table S3. Percent Sulfur Character in the Lowest Unoccupied (LUMO) and Highest Occupied Molecular Orbitals (HOMOs) of **1**-**3.**

Compound	Orbital	% Fe	% S	% Lπ*
Fe(II) Pyr (**1**)	d_{yz}	65.8	1.1	23.1
	d_{xz}	78.1	1.7	10.5
	d_{xv}	71.6	7.9	11.0
	Lπ*	12.9	1.8	65.3
	d_{x2-y2}	51.1	20.2	18.6
	d_{z2}	60.8	6.0	21.0
Fe(II) Quino (**2**)	d_{yz}	56.0	6.9	27.8
	d_{xz}	70.1	2.5	17.8
	d_{xv}	78.6	3.2	10.1
	Lπ*	15.3	2.3	62.0
	d_{x2-v2}	46.5	17.8	22.7
	d_{z2}	55.6	6.9	24.8
Fe(II) Imid (**3**)	d_{yz}	70.4	1.25	18.1
	d_{xz}	81.9	1.2	8.6
	d_{xy}	75.25	6.3	10.0
	Lπ*	12.2	1.4	66.6
	d_{x2-v2}	58.5	21.1	12.4
	d_{z2}	65.6	5.6	18.7

Table S4. Crystal data and structure refinement for $[Fe^{II}(tame(N_2S(py)_2)]_2(BPh_4)_2$ (**1**).

Identification code	rmt-i-147
Empirical formula	C82 H78 B2 Fe2 N8 S2
Formula weight	1372.99
Temperature	130(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbcn (No. 60)
Unit cell dimensions	a= 19.7560(6) A alpha = 90 deg. b= 18.2950(7) A beta = 90 deg. c= 20.3950(8) A gamma = 90 deg.
Volume	7371.5(5) A^3
Z, Calculated density	8, 1.237 mg/m^3
Absorption coefficient	0.500 mm^-1
F(000)	2880
Crystal size	0.34 x 0.22 x 0.22 mm
Theta range for data collection	2.99 to 23.26 deg.
Limiting indices	-26≤h≤22, -23≤k≤23, -27≤l≤27
Reflections collected / unique	9273 / 5042 [R(int) = 0.1378]
Completeness to theta = 23.26	95.0 %
Absorption correction	HKL-2000
Max. and min. transmission	0.8980 and 0.8485
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5042 / 0 / 433
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0582, wR2 = 0.1168
R indices (all data)	R1 = 0.1267, wR2 = 0.1405
Largest diff. peak and hole	0.898 and -0.368 e.A^-3

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	4256(1)	2816(1)	2070(1)	27(1)
S(1)	5383(1)	2990(1)	1874(1)	30(1)
N(1)	4248(2)	1776(2)	2002(2)	34(1)
N(2)	4215(2)	2833(3)	1132(2)	40(1)
N(3)	4115(2)	3888(2)	1944(2)	35(1)
N(4)	3321(2)	2622(2)	2379(2)	32(1)
C(1)	2863(2)	3105(3)	2605(2)	34(1)
C(2)	2239(3)	2897(3)	2838(2)	42(1)
C(3)	2077(3)	2167(4)	2870(3)	47(2)
C(4)	2541(3)	1672(3)	2649(3)	44(2)
C(5)	3166(3)	1898(3)	2409(2)	32(1)
C(6)	3687(3)	1451(3)	2151(3)	37(1)
C(7)	4774(3)	1361(3)	1649(3)	43(2)
C(8)	4435(3)	2192(3)	744(3)	45(2)
C(9)	5607(3)	2321(3)	1266(3)	41(2)
C(10)	5022(3)	1783(3)	1057(3)	40(1)
C(11)	5314(3)	1254(4)	562(3)	61(2)
C(12)	4164(2)	3473(4)	861(3)	42(2)
C(13)	4089(2)	4069(3)	1294(3)	40(2)
C(14)	4020(3)	4807(4)	1104(4)	63(2)
C(15)	3999(3)	5334(5)	1553(5)	81(3)
C(16)	4029(3)	5154(3)	2217(4)	61(2)
C(17)	4077(3)	4416(3)	2391(3)	46(2)
C(18)	2970(2)	4692(3)	4588(2)	32(1)
C(19)	3579(3)	4372(3)	4415(3)	48(2)
C(20)	4140(3)	4781(4)	4194(3)	60(2)
C(21)	4092(3)	5512(4)	4138(3)	61(2)
C(22)	3503(3)	5859(3)	4296(2)	49(2)
C(23)	2953(3)	5446(3)	4521(2)	43(2)
C(24)	1917(3)	4710(3)	5417(2)	31(1)
C(25)	2288(3)	4882(3)	5983(2)	38(1)
C(26)	2001(3)	5295(3)	6497(3)	46(2)
C(27)	1350(3)	5530(3)	6455(3)	47(2)
C(28)	972(3)	5368(3)	5913(3)	40(1)
C(29)	1258(3)	4953(3)	5404(3)	33(1)
C(30)	1752(2)	4180(3)	4207(2)	30(1)
C(31)	1700(3)	4684(3)	3711(2)	49(2)
C(32)	1197(4)	4656(4)	3231(3)	67(2)
C(33)	728(3)	4131(5)	3245(3)	69(2)
C(34)	751(3)	3584(5)	3730(3)	73(2)
C(35)	1270(3)	3630(4)	4197(2)	49(2)
C(36)	2486(2)	3416(3)	5059(2)	31(1)
C(37)	2442(3)	3147(3)	5693(3)	43(2)
C(38)	2603(3)	2434(3)	5863(3)	52(2)
C(39)	2806(3)	1935(3)	5403(3)	48(2)
C(40)	2872(3)	2185(3)	4752(2)	39(1)

C(41)	2705(2)	2880(3)	4599(2)	33(1)
B(1)	2284(3)	4241(3)	4823(3)	31(1)

Table S6. Bond lengths [A] and angles [deg] for [Fe^{II}(tame-$(N_2S(py)_2)$]$_2$(BPh_4)$_2$ (**1**) .

Fe(1)-N(1)	1.908(4)
Fe(1)-N(2)	1.916(4)
Fe(1)-N(4)	1.984(4)
Fe(1)-N(3)	1.997(4)
Fe(1)-S(1)	2.2838(13)
Fe(1)-S(1')	2.2896(14)
S(1)-C(9)	1.797(5)
S(1)-Fe(1')	2.2897(14)
N(1)-C(6)	1.294(6)
N(1)-C(7)	1.475(6)
N(2)-C(12)	1.300(7)
N(2)-C(8)	1.479(7)
N(3)-C(17)	1.330(7)
N(3)-C(13)	1.367(6)
N(4)-C(1)	1.346(6)
N(4)-C(5)	1.360(6)
C(1)-C(2)	1.376(7)
C(1)-H(1)	0.9302
C(2)-C(3)	1.376(8)
C(2)-H(2)	0.9301
C(3)-C(4)	1.364(8)
C(3)-H(3)	0.9302
C(4)-C(5)	1.392(7)
C(4)-H(4)	0.9301
C(5)-C(6)	1.417(7)
C(6)-H(6)	0.9296
C(7)-C(10)	1.515(8)
C(7)-H(7A)	0.9693
C(7)-H(7B)	0.9703
C(8)-C(10)	1.522(8)
C(8)-H(8A)	0.9698
C(8)-H(8B)	0.9702
C(9)-C(10)	1.578(7)
C(9)-H(9A)	0.9701
C(9)-H(9B)	0.9699
C(10)-C(11)	1.513(7)
C(11)-H(11A)	0.9598
C(11)-H(11B)	0.9599
C(11)-H(11C)	0.9599
C(12)-C(13)	1.411(8)
C(12)-H(12)	0.9299
C(13)-C(14)	1.411(9)
C(14)-C(15)	1.330(10)
C(14)-H(14)	0.9302
C(15)-C(16)	1.396(10)
C(15)-H(15)	0.9301
C(16)-C(17)	1.399(8)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9297
C(18)-C(19)	1.382(7)
C(18)-C(23)	1.386(7)

C(18)-B(1)	1.658(8)
C(19)-C(20)	1.412(8)
C(19)-H(19)	0.9300
C(20)-C(21)	1.346(9)
C(20)-H(20)	0.9301
C(21)-C(22)	1.363(9)
C(21)-H(21)	0.9302
C(22)-C(23)	1.401(8)
C(22)-H(22)	0.9294
C(23)-H(23)	0.9301
C(24)-C(29)	1.377(7)
C(24)-C(25)	1.402(7)
C(24)-B(1)	1.653(7)
C(25)-C(26)	1.412(8)
C(25)-H(25)	0.9303
C(26)-C(27)	1.358(8)
C(26)-H(26)	0.9298
C(27)-C(28)	1.366(8)
C(27)-H(27)	0.9298
C(28)-C(29)	1.404(7)
C(28)-H(28)	0.9301
C(29)-H(29)	0.9302
C(30)-C(31)	1.374(7)
C(30)-C(35)	1.385(8)
C(30)-B(1)	1.642(7)
C(31)-C(32)	1.395(9)
C(31)-H(31)	0.9300
C(32)-C(33)	1.334(10)
C(32)-H(32)	0.9299
C(33)-C(34)	1.408(10)
C(33)-H(33)	0.9300
C(34)-C(35)	1.402(8)
C(34)-H(34)	0.9302
C(35)-H(35)	0.9300
C(36)-C(37)	1.387(7)
C(36)-C(41)	1.425(7)
C(36)-B(1)	1.633(8)
C(37)-C(38)	1.388(8)
C(37)-H(37)	0.9302
C(38)-C(39)	1.370(8)
C(38)-H(38)	0.9303
C(39)-C(40)	1.409(7)
C(39)-H(39)	0.9301
C(40)-C(41)	1.351(7)
C(40)-H(40)	0.9301
C(41)-H(41)	0.9297

N(1)-Fe(1)-N(2)	86.7(2)
N(1)-Fe(1)-N(4)	80.61(17)
N(2)-Fe(1)-N(4)	106.30(16)
N(1)-Fe(1)-N(3)	165.63(17)
N(2)-Fe(1)-N(3)	81.4(2)
N(4)-Fe(1)-N(3)	95.01(17)
N(1)-Fe(1)-S(1)	97.66(13)
N(2)-Fe(1)-S(1)	82.20(12)

N(4)-Fe(1)-S(1)	171.13(12)
N(3)-Fe(1)-S(1)	88.69(12)
N(1)-Fe(1)-S(1')	102.07(13)
N(2)-Fe(1)-S(1')	161.83(13)
N(4)-Fe(1)-S(1')	90.95(12)
N(3)-Fe(1)-S(1')	91.63(13)
S(1)-Fe(1)-S(1')	80.87(5)
C(9)-S(1)-Fe(1)	105.50(17)
C(9)-S(1)-Fe(1')	118.5(2)
Fe(1)-S(1)-Fe(1')	96.91(5)
C(6)-N(1)-C(7)	118.8(4)
C(6)-N(1)-Fe(1)	116.6(3)
C(7)-N(1)-Fe(1)	122.9(3)
C(12)-N(2)-C(8)	120.6(5)
C(12)-N(2)-Fe(1)	116.2(4)
C(8)-N(2)-Fe(1)	120.7(4)
C(17)-N(3)-C(13)	119.1(5)
C(17)-N(3)-Fe(1)	129.3(4)
C(13)-N(3)-Fe(1)	111.5(4)
C(1)-N(4)-C(5)	118.2(4)
C(1)-N(4)-Fe(1)	128.1(4)
C(5)-N(4)-Fe(1)	113.5(3)
N(4)-C(1)-C(2)	122.6(5)
N(4)-C(1)-H(1)	118.9
C(2)-C(1)-H(1)	118.5
C(1)-C(2)-C(3)	119.6(5)
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.4
C(4)-C(3)-C(2)	118.2(5)
C(4)-C(3)-H(3)	121.0
C(2)-C(3)-H(3)	120.7
C(3)-C(4)-C(5)	121.0(5)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.1
N(4)-C(5)-C(4)	120.4(5)
N(4)-C(5)-C(6)	112.4(4)
C(4)-C(5)-C(6)	127.2(5)
N(1)-C(6)-C(5)	116.4(5)
N(1)-C(6)-H(6)	121.6
C(5)-C(6)-H(6)	122.0
N(1)-C(7)-C(10)	110.7(5)
N(1)-C(7)-H(7A)	108.7
C(10)-C(7)-H(7A)	108.7
N(1)-C(7)-H(7B)	110.6
C(10)-C(7)-H(7B)	109.7
H(7A)-C(7)-H(7B)	108.2
N(2)-C(8)-C(10)	112.9(4)
N(2)-C(8)-H(8A)	108.4
C(10)-C(8)-H(8A)	108.9
N(2)-C(8)-H(8B)	109.4
C(10)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9
C(10)-C(9)-S(1)	115.5(3)
C(10)-C(9)-H(9A)	108.9
S(1)-C(9)-H(9A)	109.0

C(10)-C(9)-H(9B)	107.3
S(1)-C(9)-H(9B)	108.4
H(9A)-C(9)-H(9B)	107.4
C(11)-C(10)-C(7)	109.2(5)
C(11)-C(10)-C(8)	109.0(5)
C(7)-C(10)-C(8)	109.8(4)
C(11)-C(10)-C(9)	107.5(4)
C(7)-C(10)-C(9)	109.8(4)
C(8)-C(10)-C(9)	111.4(5)
C(10)-C(11)-H(11A)	109.6
C(10)-C(11)-H(11B)	109.0
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.8
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.4
N(2)-C(12)-C(13)	116.0(5)
N(2)-C(12)-H(12)	121.6
C(13)-C(12)-H(12)	122.4
N(3)-C(13)-C(12)	114.7(5)
N(3)-C(13)-C(14)	120.1(6)
C(12)-C(13)-C(14)	125.2(6)
C(15)-C(14)-C(13)	120.5(7)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	119.4
C(14)-C(15)-C(16)	119.7(7)
C(14)-C(15)-H(15)	120.3
C(16)-C(15)-H(15)	120.0
C(15)-C(16)-C(17)	118.4(7)
C(15)-C(16)-H(16)	121.4
C(17)-C(16)-H(16)	120.1
N(3)-C(17)-C(16)	122.1(6)
N(3)-C(17)-H(17)	119.1
C(16)-C(17)-H(17)	118.8
C(19)-C(18)-C(23)	114.6(5)
C(19)-C(18)-B(1)	125.0(5)
C(23)-C(18)-B(1)	120.3(5)
C(18)-C(19)-C(20)	122.8(6)
C(18)-C(19)-H(19)	118.8
C(20)-C(19)-H(19)	118.5
C(21)-C(20)-C(19)	119.8(6)
C(21)-C(20)-H(20)	120.5
C(19)-C(20)-H(20)	119.7
C(20)-C(21)-C(22)	120.2(6)
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.8
C(21)-C(22)-C(23)	119.2(6)
C(21)-C(22)-H(22)	120.8
C(23)-C(22)-H(22)	120.0
C(18)-C(23)-C(22)	123.3(6)
C(18)-C(23)-H(23)	118.4
C(22)-C(23)-H(23)	118.3
C(29)-C(24)-C(25)	116.0(5)
C(29)-C(24)-B(1)	124.6(4)
C(25)-C(24)-B(1)	119.4(4)
C(24)-C(25)-C(26)	121.4(5)

C(24)-C(25)-H(25)	119.3
C(26)-C(25)-H(25)	119.4
C(27)-C(26)-C(25)	120.2(5)
C(27)-C(26)-H(26)	120.6
C(25)-C(26)-H(26)	119.2
C(26)-C(27)-C(28)	120.0(5)
C(26)-C(27)-H(27)	120.1
C(28)-C(27)-H(27)	119.9
C(27)-C(28)-C(29)	119.6(5)
C(27)-C(28)-H(28)	120.6
C(29)-C(28)-H(28)	119.8
C(24)-C(29)-C(28)	122.8(5)
C(24)-C(29)-H(29)	118.7
C(28)-C(29)-H(29)	118.5
C(31)-C(30)-C(35)	115.1(5)
C(31)-C(30)-B(1)	124.5(5)
C(35)-C(30)-B(1)	120.1(5)
C(30)-C(31)-C(32)	123.1(6)
C(30)-C(31)-H(31)	118.9
C(32)-C(31)-H(31)	118.1
C(33)-C(32)-C(31)	120.4(7)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.9
C(32)-C(33)-C(34)	120.2(6)
C(32)-C(33)-H(33)	120.4
C(34)-C(33)-H(33)	119.4
C(35)-C(34)-C(33)	117.3(7)
C(35)-C(34)-H(34)	121.2
C(33)-C(34)-H(34)	121.5
C(30)-C(35)-C(34)	123.8(6)
C(30)-C(35)-H(35)	119.0
C(34)-C(35)-H(35)	117.2
C(37)-C(36)-C(41)	113.0(5)
C(37)-C(36)-B(1)	126.0(4)
C(41)-C(36)-B(1)	121.0(4)
C(36)-C(37)-C(38)	123.5(5)
C(36)-C(37)-H(37)	118.1
C(38)-C(37)-H(37)	118.4
C(39)-C(38)-C(37)	121.5(5)
C(39)-C(38)-H(38)	118.9
C(37)-C(38)-H(38)	119.5
C(38)-C(39)-C(40)	117.2(5)
C(38)-C(39)-H(39)	121.6
C(40)-C(39)-H(39)	121.2
C(41)-C(40)-C(39)	120.0(5)
C(41)-C(40)-H(40)	120.2
C(39)-C(40)-H(40)	119.8
C(40)-C(41)-C(36)	124.7(5)
C(40)-C(41)-H(41)	117.8
C(36)-C(41)-H(41)	117.5
C(36)-B(1)-C(30)	108.6(4)
C(36)-B(1)-C(24)	111.7(4)
C(30)-B(1)-C(24)	108.4(4)
C(36)-B(1)-C(18)	110.2(4)
C(30)-B(1)-C(18)	109.7(4)

C(24)-B(1)-C(18)	108.1(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

Table S7. Anisotropic displacement parameters (A^2 x 10^3) for [Fe^{II}(tame-$(N_2S(py)_2)$]$_2$(BPh_4)$_2$ (**1**). The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	29(1)	29(1)	24(1)	0(1)	0(1)	-2(1)
S(1)	28(1)	36(1)	24(1)	1(1)	-2(1)	-6(1)
N(1)	31(2)	38(2)	34(2)	-5(2)	-2(2)	3(2)
N(2)	19(2)	72(3)	28(2)	-3(3)	-5(2)	-10(2)
N(3)	29(2)	33(3)	43(3)	10(2)	-11(2)	-6(2)
N(4)	34(2)	33(3)	28(2)	-4(2)	0(2)	0(2)
C(1)	33(3)	42(3)	26(3)	-4(3)	-6(2)	5(3)
C(2)	38(3)	61(4)	27(3)	-7(3)	-2(2)	6(3)
C(3)	33(3)	69(4)	39(3)	2(3)	11(3)	-4(3)
C(4)	41(3)	45(4)	45(3)	8(3)	3(3)	-13(3)
C(5)	29(3)	38(3)	28(3)	4(2)	-3(2)	-5(3)
C(6)	30(3)	28(3)	53(4)	1(3)	-1(3)	-7(3)
C(7)	43(3)	35(3)	50(4)	-21(3)	4(3)	-1(3)
C(8)	32(3)	71(4)	34(3)	-21(3)	3(2)	-7(3)
C(9)	30(3)	59(4)	35(3)	-5(3)	7(2)	-1(3)
C(10)	29(3)	54(4)	38(3)	-26(3)	1(3)	-11(3)
C(11)	41(4)	77(5)	65(4)	-33(4)	4(3)	-8(3)
C(12)	28(3)	67(4)	31(3)	23(3)	-4(3)	9(3)
C(13)	24(3)	51(4)	44(4)	26(3)	-7(2)	1(3)
C(14)	39(4)	63(5)	87(5)	37(5)	2(4)	-1(3)
C(15)	45(4)	52(5)	147(9)	49(6)	-20(5)	-2(4)
C(16)	42(4)	35(4)	107(6)	1(4)	-26(4)	6(3)
C(17)	43(3)	37(4)	59(4)	-2(3)	-14(3)	0(3)
C(18)	29(3)	36(3)	30(3)	-6(2)	5(2)	0(2)
C(19)	40(3)	45(4)	60(4)	-18(3)	13(3)	-8(3)
C(20)	51(4)	63(5)	66(4)	-23(4)	29(3)	-14(3)
C(21)	57(4)	72(5)	54(4)	-28(4)	30(3)	-28(4)
C(22)	67(4)	49(4)	32(3)	-1(3)	6(3)	-19(3)
C(23)	51(4)	43(4)	37(3)	3(3)	7(3)	-7(3)
C(24)	36(3)	32(3)	23(3)	7(2)	3(2)	-7(2)
C(25)	38(3)	46(4)	31(3)	-3(3)	8(3)	-7(3)
C(26)	69(4)	39(4)	30(3)	-1(3)	2(3)	-14(3)
C(27)	74(5)	30(3)	36(4)	3(3)	20(3)	-3(3)
C(28)	48(3)	34(3)	37(3)	9(3)	12(3)	3(3)
C(29)	40(3)	29(3)	30(3)	8(2)	5(2)	6(3)
C(30)	25(3)	42(3)	24(3)	-4(3)	2(2)	13(3)
C(31)	84(5)	40(4)	24(3)	0(3)	-15(3)	15(3)
C(32)	91(6)	65(5)	45(4)	-7(4)	-19(4)	28(4)
C(33)	45(4)	133(7)	30(4)	-22(4)	-13(3)	28(5)
C(34)	27(3)	161(8)	31(4)	-10(4)	6(3)	-19(4)
C(35)	32(3)	92(5)	23(3)	1(3)	1(3)	-3(3)
C(36)	26(3)	39(3)	27(3)	1(3)	2(2)	-1(2)
C(37)	56(4)	44(4)	30(3)	5(3)	6(3)	20(3)
C(38)	70(4)	54(4)	32(3)	7(3)	16(3)	27(3)
C(39)	61(4)	41(4)	43(4)	18(3)	10(3)	16(3)

C(40)	41(3)	46(4)	31(3)	−3(3)	9(2)	−2(3)
C(41)	38(3)	33(3)	27(3)	6(3)	5(2)	7(3)
B(1)	28(3)	38(4)	26(3)	−2(3)	4(3)	8(3)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $[Fe^{II}(tame\text{-}(N_2S(py)_2)]_2(BPh_4)_2$ (**1**).

	x	y	z	U(eq)
H(1)	2969	3600	2598	40
H(2)	1932	3249	2980	50
H(3)	1658	2016	3027	57
H(4)	2444	1175	2667	52
H(6)	3630	952	2090	44
H(7A)	4582	902	1502	51
H(7B)	5152	1253	1937	51
H(8A)	4572	2360	313	54
H(8B)	4056	1860	688	54
H(9A)	5775	2571	879	50
H(9B)	5975	2025	1437	50
H(11A)	4956	967	374	73
H(11B)	5630	937	779	73
H(11C)	5542	1519	221	73
H(12)	4169	3531	408	51
H(14)	3998	4923	661	76
H(15)	3960	5820	1426	98
H(16)	4014	5512	2541	74
H(17)	4090	4293	2833	55
H(19)	3623	3868	4452	58
H(20)	4542	4542	4091	72
H(21)	4457	5780	3981	73
H(22)	3467	6364	4264	59
H(23)	2556	5690	4629	52
H(25)	2733	4720	6019	46
H(26)	2262	5404	6863	55
H(27)	1162	5802	6794	56
H(28)	525	5526	5881	47
H(29)	994	4851	5038	39
H(31)	2011	5065	3693	59
H(32)	1188	5005	2899	80
H(33)	386	4120	2931	83
H(34)	434	3209	3742	88
H(35)	1284	3270	4518	59
H(37)	2293	3462	6021	52
H(38)	2565	2286	6298	62
H(39)	2911	1456	5516	58
H(40)	3023	1866	4427	47
H(41)	2737	3021	4162	39

Table S9. Crystal data and structure refinement for $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)\bullet 3MeCN \bullet Et_2O$ **(2)**.

Identification code	bkl_7_040_0m	
Empirical formula	$C_{110}H_{106.6}B_2Fe_2N_{12.7}O_{0.6}S_2$	
Formula weight	1814.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.5249(16) Å	a= 71.249(5)°.
	b = 13.6085(16) Å	b= 66.021(5)°.
	c = 14.5700(16) Å	g = 78.500(6)°.
Volume	2312.8(5) Å^3	
Z	1	
Density (calculated)	1.303 Mg/m^3	
Absorption coefficient	0.418 mm^{-1}	
F(000)	955	
Crystal size	0.20 x 0.15 x 0.13 mm^3	
Theta range for data collection	1.82 to 28.51°.	
Index ranges	-18<=h<=18, -18<=k<=18, -19<=l<=19	
Reflections collected	128992	
Independent reflections	11639 [R(int) = 0.0287]	
Completeness to theta = 25.00°	100.0 %	
Max. and min. transmission	0.9477 and 0.9211	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11639 / 18 / 619	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0811	
R indices (all data)	R1 = 0.0363, wR2 = 0.0855	
Largest diff. peak and hole	0.401 and -0.524 e.Å^{-3}	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)\bullet 3MeCN \bullet Et_2O$ **(2)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1385(1)	7850(1)	4339(1)	18(1)
C(2)	658(1)	7515(1)	5487(1)	18(1)
C(3)	759(1)	6317(1)	5766(1)	23(1)
C(4)	531(1)	12116(1)	4323(1)	19(1)
C(5)	2354(1)	10278(1)	2419(1)	19(1)
C(6)	2339(1)	9302(1)	3197(1)	18(1)
C(7)	-1055(1)	12216(1)	3785(1)	18(1)
C(8)	-1844(1)	10799(1)	3832(1)	18(1)
C(9)	-1696(1)	9824(1)	3583(1)	17(1)
C(10)	-2562(1)	9372(1)	3607(1)	20(1)
C(11)	-2340(1)	8495(1)	3277(1)	21(1)
C(12)	-1247(1)	8110(1)	2844(1)	19(1)
C(13)	-964(1)	7265(1)	2401(1)	25(1)
C(14)	99(1)	6963(1)	1913(1)	28(1)
C(15)	927(1)	7503(1)	1837(1)	25(1)
C(16)	686(1)	8307(1)	2284(1)	21(1)
C(17)	-407(1)	8618(1)	2817(1)	17(1)
C(18)	3332(1)	10697(1)	1671(1)	23(1)
C(19)	3293(1)	11542(1)	871(1)	24(1)
C(20)	2279(1)	11951(1)	779(1)	22(1)
C(21)	2194(1)	12781(1)	-77(1)	27(1)
C(22)	1212(1)	13123(1)	-176(1)	28(1)
C(23)	274(1)	12630(1)	561(1)	25(1)
C(24)	322(1)	11835(1)	1409(1)	21(1)
C(25)	1319(1)	11492(1)	1553(1)	19(1)
C(26)	7627(1)	3964(1)	2196(1)	35(1)
C(27)	7580(1)	4870(1)	2449(1)	31(1)
C(28)	6643(1)	5547(1)	2594(1)	25(1)
C(29)	5712(1)	5341(1)	2507(1)	22(1)
C(30)	4476(1)	6703(1)	1502(1)	22(1)
C(31)	4869(1)	6237(1)	680(1)	30(1)
C(32)	4691(1)	6695(1)	-252(1)	36(1)
C(33)	4121(1)	7652(1)	-412(1)	34(1)
C(34)	3890(1)	7672(1)	1311(1)	29(1)
C(35)	3718(1)	8143(1)	380(1)	34(1)
C(36)	6714(1)	3710(1)	2137(1)	36(1)
C(37)	4644(1)	7019(1)	3177(1)	20(1)
C(38)	4240(1)	6878(1)	4259(1)	22(1)

C(39)	4308(1)	7610(1)	4713(1)	25(1)
C(40)	4767(1)	8537(1)	4094(1)	26(1)
C(41)	5191(1)	8704(1)	3019(1)	25(1)
C(42)	5142(1)	7953(1)	2579(1)	22(1)
C(43)	3569(1)	5428(1)	3395(1)	21(1)
C(44)	2623(1)	5518(1)	3191(1)	25(1)
C(45)	1754(1)	4909(1)	3851(1)	29(1)
C(46)	1799(1)	4194(1)	4757(1)	29(1)
C(47)	2724(1)	4079(1)	4986(1)	28(1)
C(48)	3593(1)	4673(1)	4312(1)	25(1)
B(2)	5777(1)	4385(1)	2302(1)	30(1)
N(1)	1390(1)	8963(1)	3783(1)	16(1)
N(2)	1363(1)	10686(1)	2402(1)	17(1)
N(3)	-988(1)	11120(1)	3800(1)	16(1)
N(4)	-650(1)	9434(1)	3261(1)	16(1)
N(5)	553(2)	4471(2)	1556(2)	65(1)
C(49)	1437(3)	4616(3)	1214(3)	49(1)
C(50)	2581(3)	4822(3)	765(3)	64(1)
N(5B)	1141(11)	4005(9)	1899(9)	49(1)
C(49B)	1754(13)	4569(13)	1282(17)	49(1)
C(50B)	2507(15)	5326(11)	524(13)	49(1)
N(5C)	1818(8)	3749(7)	1995(6)	49(1)
C(49C)	2011(12)	4418(9)	1263(10)	49(1)
C(50C)	2247(11)	5229(9)	303(8)	49(1)
N(7)	1748(4)	8814(3)	-1163(3)	48(1)
C(53)	1636(7)	9491(7)	-827(9)	48(1)
C(54)	1501(5)	10344(4)	-387(4)	48(1)
C(55)	-2012(5)	9685(4)	651(4)	41(1)
C(56)	-1057(4)	10189(4)	516(4)	41(1)
O(1)	-107(2)	9657(3)	-69(3)	41(1)
C(57)	876(4)	10064(4)	-268(4)	41(1)
C(58)	1789(6)	9435(7)	-887(9)	41(1)
N(6)	-5332(1)	8762(1)	6515(2)	51(1)
C(51)	-4549(1)	8313(1)	6575(1)	32(1)
C(52)	-3549(1)	7744(1)	6653(2)	40(1)
B(1)	4605(1)	6135(1)	2640(1)	20(1)
S(1)	867(1)	10727(1)	4594(1)	14(1)
Fe(1)	209(1)	10042(1)	3743(1)	14(1)

Table S11. Bond lengths [Å] and angles [°] for $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)\bullet 3MeCN \bullet Et_2O$ **(2)**.

Fe(1)-N(1)	1.9489(10)
Fe(1)-N(3)	1.9964(10)
Fe(1)-N(2)	1.9491(10)
Fe(1)-N(4)	1.9868(10)
Fe(1)-S(1)	2.2734(3)
Fe(1')-S(1)	2.2789(4)
Fe(1)-S(1')	2.2789(4)
C(1)-N(1)	1.4697(15)
C(1)-C(2)	1.5241(17)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(4')	1.5231(16)
C(2)-C(7')	1.5305(16)
C(2)-C(3)	1.5395(17)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(2')	1.5232(16)
C(4)-S(1)	1.8051(13)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-N(2)	1.3520(16)
C(5)-C(18)	1.4115(17)
C(5)-C(6)	1.4394(18)
C(6)-N(1)	1.2967(15)
C(6)-H(6)	0.9500
C(7)-N(3)	1.4699(15)
C(7)-C(2')	1.5305(16)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(3)	1.2963(15)
C(8)-C(9)	1.4407(17)
C(8)-H(8)	0.9500
C(9)-N(4)	1.3511(15)
C(9)-C(10)	1.4104(16)
C(10)-C(11)	1.3623(18)
C(10)-H(10)	0.9500
C(11)-C(12)	1.4151(18)
C(11)-H(11)	0.9500
C(12)-C(13)	1.4105(18)
C(12)-C(17)	1.4237(16)
C(13)-C(14)	1.365(2)
C(13)-H(13)	0.9500

C(14)-C(15)	1.4080(19)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3688(18)
C(15)-H(15)	0.9500
C(16)-C(17)	1.4133(17)
C(16)-H(16)	0.9500
C(17)-N(4)	1.3792(15)
C(18)-C(19)	1.360(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.4163(19)
C(19)-H(19)	0.9500
C(20)-C(21)	1.4150(19)
C(20)-C(25)	1.4247(17)
C(21)-C(22)	1.366(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.408(2)
C(22)-H(22)	0.9500
C(23)-C(24)	1.3712(18)
C(23)-H(23)	0.9500
C(24)-C(25)	1.4124(17)
C(24)-H(24)	0.9500
C(25)-N(2)	1.3776(16)
C(26)-C(27)	1.379(2)
C(26)-C(36)	1.389(2)
C(26)-H(26)	0.9500
C(27)-C(28)	1.3933(19)
C(27)-H(27)	0.9500
C(28)-C(29)	1.4044(18)
C(28)-H(28)	0.9500
C(29)-B(2)	1.405(2)
C(29)-B(1)	1.6435(19)
C(30)-C(31)	1.3979(19)
C(30)-C(34)	1.404(2)
C(30)-B(1)	1.6540(19)
C(31)-C(32)	1.397(2)
C(31)-H(31)	0.9500
C(32)-C(33)	1.377(3)
C(32)-H(32)	0.9500
C(33)-C(35)	1.383(2)
C(33)-H(33)	0.9500
C(34)-C(35)	1.394(2)
C(34)-H(34)	0.9500
C(35)-H(35)	0.9500
C(36)-B(2)	1.392(2)
C(36)-H(36)	0.9500
C(37)-C(38)	1.4024(18)

C(37)-C(42)	1.4072(18)
C(37)-B(1)	1.6507(19)
C(38)-C(39)	1.3953(18)
C(38)-H(38)	0.9500
C(39)-C(40)	1.384(2)
C(39)-H(39)	0.9500
C(40)-C(41)	1.388(2)
C(40)-H(40)	0.9500
C(41)-C(42)	1.3941(19)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(43)-C(44)	1.4017(18)
C(43)-C(48)	1.4068(19)
C(43)-B(1)	1.6441(19)
C(44)-C(45)	1.3963(19)
C(44)-H(44)	0.9500
C(45)-C(46)	1.381(2)
C(45)-H(45)	0.9500
C(46)-C(47)	1.388(2)
C(46)-H(46)	0.9500
C(47)-C(48)	1.3892(19)
C(47)-H(47)	0.9500
C(48)-H(48)	0.9500
B(2)-H(2)	0.9500
N(5)-C(49)	1.123(4)
C(49)-C(50)	1.461(4)
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
N(5B)-C(49B)	1.135(2)
C(49B)-C(50B)	1.446(2)
C(50B)-H(50D)	0.9800
C(50B)-H(50E)	0.9800
C(50B)-H(50F)	0.9800
N(5C)-C(49C)	1.132(11)
C(49C)-C(50C)	1.435(12)
C(50C)-H(50G)	0.9800
C(50C)-H(50H)	0.9800
C(50C)-H(50I)	0.9800
N(7)-C(53)	1.134(2)
N(7)-H(58B)	0.8729
N(7)-H(58C)	1.0151
C(53)-C(54)	1.445(2)
C(53)-H(58A)	1.1222
C(53)-H(58B)	1.0002
C(53)-H(58C)	1.0468

C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(54)-H(57A)	1.0826
C(54)-H(57B)	1.0804
C(54)-H(58A)	1.5863
C(55)-C(58)#2	1.462(8)
C(55)-C(57)#2	1.475(8)
C(55)-C(56)	1.496(6)
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-C(57)#2	0.532(6)
C(56)-C(58)#2	1.037(9)
C(56)-O(1)	1.427(4)
C(56)-O(1)#2	1.468(7)
C(56)-H(56A)	0.9900
C(56)-H(56B)	0.9900
O(1)-C(57)#2	1.008(6)
O(1)-O(1)#2	1.127(7)
O(1)-C(57)	1.427(4)
O(1)-C(56)#2	1.468(7)
C(57)-C(56)#2	0.532(6)
C(57)-O(1)#2	1.008(6)
C(57)-C(55)#2	1.475(8)
C(57)-C(58)	1.496(6)
C(57)-H(57A)	0.9900
C(57)-H(57B)	0.9900
C(58)-C(56)#2	1.037(9)
C(58)-C(55)#2	1.462(8)
C(58)-H(58A)	0.9800
C(58)-H(58B)	0.9800
C(58)-H(58C)	0.9800
N(6)-C(51)	1.134(2)
C(51)-C(52)	1.446(2)
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800

N(1)-C(1)-C(2)	119.10(10)
N(1)-C(1)-H(1A)	107.5
C(2)-C(1)-H(1A)	107.5
N(1)-C(1)-H(1B)	107.5
C(2)-C(1)-H(1B)	107.5
H(1A)-C(1)-H(1B)	107.0
C(4)#1-C(2)-C(1)	112.48(10)

C(4)#1-C(2)-C(7)#1	112.10(10)
C(1)-C(2)-C(7)#1	113.80(10)
C(4)#1-C(2)-C(3)	107.92(10)
C(1)-C(2)-C(3)	104.60(10)
C(7)#1-C(2)-C(3)	105.20(10)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)#1-C(4)-S(1)	116.63(8)
C(2)#1-C(4)-H(4A)	108.1
S(1)-C(4)-H(4A)	108.1
C(2)#1-C(4)-H(4B)	108.1
S(1)-C(4)-H(4B)	108.1
H(4A)-C(4)-H(4B)	107.3
N(2)-C(5)-C(18)	123.54(12)
N(2)-C(5)-C(6)	113.93(10)
C(18)-C(5)-C(6)	122.14(11)
N(1)-C(6)-C(5)	116.00(11)
N(1)-C(6)-H(6)	122.0
C(5)-C(6)-H(6)	122.0
N(3)-C(7)-C(2)#1	118.99(10)
N(3)-C(7)-H(7A)	107.6
C(2)#1-C(7)-H(7A)	107.6
N(3)-C(7)-H(7B)	107.6
C(2)#1-C(7)-H(7B)	107.6
H(7A)-C(7)-H(7B)	107.0
N(3)-C(8)-C(9)	116.22(11)
N(3)-C(8)-H(8)	121.9
C(9)-C(8)-H(8)	121.9
N(4)-C(9)-C(10)	123.99(11)
N(4)-C(9)-C(8)	113.54(10)
C(10)-C(9)-C(8)	122.33(11)
C(11)-C(10)-C(9)	118.73(11)
C(11)-C(10)-H(10)	120.6
C(9)-C(10)-H(10)	120.6
C(10)-C(11)-C(12)	119.34(11)
C(10)-C(11)-H(11)	120.3
C(12)-C(11)-H(11)	120.3
C(13)-C(12)-C(11)	121.75(11)
C(13)-C(12)-C(17)	119.10(12)
C(11)-C(12)-C(17)	119.09(11)
C(14)-C(13)-C(12)	120.64(12)
C(14)-C(13)-H(13)	119.7

C(12)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	120.12(13)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	120.93(12)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(15)-C(16)-C(17)	120.04(12)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
N(4)-C(17)-C(16)	120.02(11)
N(4)-C(17)-C(12)	120.90(11)
C(16)-C(17)-C(12)	119.03(11)
C(19)-C(18)-C(5)	119.10(12)
C(19)-C(18)-H(18)	120.4
C(5)-C(18)-H(18)	120.4
C(18)-C(19)-C(20)	119.36(12)
C(18)-C(19)-H(19)	120.3
C(20)-C(19)-H(19)	120.3
C(21)-C(20)-C(19)	122.01(12)
C(21)-C(20)-C(25)	118.95(12)
C(19)-C(20)-C(25)	119.01(12)
C(22)-C(21)-C(20)	120.77(12)
C(22)-C(21)-H(21)	119.6
C(20)-C(21)-H(21)	119.6
C(21)-C(22)-C(23)	120.14(13)
C(21)-C(22)-H(22)	119.9
C(23)-C(22)-H(22)	119.9
C(24)-C(23)-C(22)	120.67(13)
C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7
C(23)-C(24)-C(25)	120.42(12)
C(23)-C(24)-H(24)	119.8
C(25)-C(24)-H(24)	119.8
N(2)-C(25)-C(24)	120.07(11)
N(2)-C(25)-C(20)	120.93(11)
C(24)-C(25)-C(20)	118.91(12)
C(27)-C(26)-C(36)	119.22(14)
C(27)-C(26)-H(26)	120.4
C(36)-C(26)-H(26)	120.4
C(26)-C(27)-C(28)	120.33(14)
C(26)-C(27)-H(27)	119.8
C(28)-C(27)-H(27)	119.8
C(27)-C(28)-C(29)	122.47(14)
C(27)-C(28)-H(28)	118.8
C(29)-C(28)-H(28)	118.8

C(28)-C(29)-B(2)	115.25(12)
C(28)-C(29)-B(1)	123.92(12)
B(2)-C(29)-B(1)	120.82(12)
C(31)-C(30)-C(34)	114.38(13)
C(31)-C(30)-B(1)	123.44(12)
C(34)-C(30)-B(1)	122.04(11)
C(32)-C(31)-C(30)	122.87(15)
C(32)-C(31)-H(31)	118.6
C(30)-C(31)-H(31)	118.6
C(33)-C(32)-C(31)	120.89(14)
C(33)-C(32)-H(32)	119.6
C(31)-C(32)-H(32)	119.6
C(32)-C(33)-C(35)	118.24(14)
C(32)-C(33)-H(33)	120.9
C(35)-C(33)-H(33)	120.9
C(35)-C(34)-C(30)	123.31(14)
C(35)-C(34)-H(34)	118.3
C(30)-C(34)-H(34)	118.3
C(33)-C(35)-C(34)	120.31(15)
C(33)-C(35)-H(35)	119.8
C(34)-C(35)-H(35)	119.8
C(26)-C(36)-B(2)	119.79(15)
C(26)-C(36)-H(36)	120.1
B(2)-C(36)-H(36)	120.1
C(38)-C(37)-C(42)	114.77(12)
C(38)-C(37)-B(1)	123.02(11)
C(42)-C(37)-B(1)	122.12(11)
C(39)-C(38)-C(37)	122.97(12)
C(39)-C(38)-H(38)	118.5
C(37)-C(38)-H(38)	118.5
C(40)-C(39)-C(38)	120.36(13)
C(40)-C(39)-H(39)	119.8
C(38)-C(39)-H(39)	119.8
C(39)-C(40)-C(41)	118.63(13)
C(39)-C(40)-H(40)	120.7
C(41)-C(40)-H(40)	120.7
C(40)-C(41)-C(42)	120.26(13)
C(40)-C(41)-H(41)	119.9
C(42)-C(41)-H(41)	119.9
C(41)-C(42)-C(37)	122.92(13)
C(41)-C(42)-H(42)	118.5
C(37)-C(42)-H(42)	118.5
C(44)-C(43)-C(48)	115.50(12)
C(44)-C(43)-B(1)	124.07(12)
C(48)-C(43)-B(1)	120.44(11)
C(45)-C(44)-C(43)	122.73(13)

C(45)-C(44)-H(44)	118.6
C(43)-C(44)-H(44)	118.6
C(46)-C(45)-C(44)	119.96(14)
C(46)-C(45)-H(45)	120.0
C(44)-C(45)-H(45)	120.0
C(45)-C(46)-C(47)	119.08(13)
C(45)-C(46)-H(46)	120.5
C(47)-C(46)-H(46)	120.5
C(46)-C(47)-C(48)	120.47(14)
C(46)-C(47)-H(47)	119.8
C(48)-C(47)-H(47)	119.8
C(47)-C(48)-C(43)	122.23(13)
C(47)-C(48)-H(48)	118.9
C(43)-C(48)-H(48)	118.9
C(36)-B(2)-C(29)	122.82(14)
C(36)-B(2)-H(2)	118.6
C(29)-B(2)-H(2)	118.6
C(6)-N(1)-C(1)	115.75(10)
C(6)-N(1)-Fe(1)	112.83(8)
C(1)-N(1)-Fe(1)	131.41(8)
C(5)-N(2)-C(25)	117.66(10)
C(5)-N(2)-Fe(1)	110.07(8)
C(25)-N(2)-Fe(1)	132.01(8)
C(8)-N(3)-C(7)	116.46(10)
C(8)-N(3)-Fe(1)	112.85(8)
C(7)-N(3)-Fe(1)	130.66(8)
C(9)-N(4)-C(17)	117.23(10)
C(9)-N(4)-Fe(1)	110.12(8)
C(17)-N(4)-Fe(1)	131.87(8)
N(5)-C(49)-C(50)	179.1(4)
N(5B)-C(49B)-C(50B)	177(2)
C(49B)-C(50B)-H(50D)	109.5
C(49B)-C(50B)-H(50E)	109.5
H(50D)-C(50B)-H(50E)	109.5
C(49B)-C(50B)-H(50F)	109.5
H(50D)-C(50B)-H(50F)	109.5
H(50E)-C(50B)-H(50F)	109.5
N(5C)-C(49C)-C(50C)	176.6(16)
C(53)-N(7)-H(58B)	58.0
C(53)-N(7)-H(58C)	58.0
H(58B)-N(7)-H(58C)	115.7
N(7)-C(53)-C(54)	179.1(12)
N(7)-C(53)-H(58A)	104.5
C(54)-C(53)-H(58A)	75.1
N(7)-C(53)-H(58B)	47.8
C(54)-C(53)-H(58B)	133.0

H(58A)-C(53)-H(58B)	97.7
N(7)-C(53)-H(58C)	55.3
C(54)-C(53)-H(58C)	123.9
H(58A)-C(53)-H(58C)	95.0
H(58B)-C(53)-H(58C)	102.8
C(53)-C(54)-H(57A)	98.6
H(54A)-C(54)-H(57A)	30.5
H(54B)-C(54)-H(57A)	87.6
H(54C)-C(54)-H(57A)	138.9
C(53)-C(54)-H(57B)	97.0
H(54A)-C(54)-H(57B)	121.2
H(54B)-C(54)-H(57B)	14.0
H(54C)-C(54)-H(57B)	109.2
H(57A)-C(54)-H(57B)	96.0
C(53)-C(54)-H(58A)	43.1
H(54A)-C(54)-H(58A)	113.6
H(54B)-C(54)-H(58A)	134.9
H(54C)-C(54)-H(58A)	67.9
H(57A)-C(54)-H(58A)	125.1
H(57B)-C(54)-H(58A)	121.2
C(58)#2-C(55)-C(57)#2	61.2(3)
C(58)#2-C(55)-C(56)	41.0(3)
C(57)#2-C(55)-C(56)	20.6(3)
C(58)#2-C(55)-H(55A)	68.8
C(57)#2-C(55)-H(55A)	130.0
C(56)-C(55)-H(55A)	109.7
C(58)#2-C(55)-H(55B)	126.0
C(57)#2-C(55)-H(55B)	101.3
C(56)-C(55)-H(55B)	109.3
H(55A)-C(55)-H(55B)	109.5
C(58)#2-C(55)-H(55C)	122.1
C(57)#2-C(55)-H(55C)	95.5
C(56)-C(55)-H(55C)	109.3
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(57)#2-C(56)-C(58)#2	142.9(11)
C(57)#2-C(56)-O(1)	30.8(7)
C(58)#2-C(56)-O(1)	173.4(7)
C(57)#2-C(56)-O(1)#2	75.1(7)
C(58)#2-C(56)-O(1)#2	138.9(5)
O(1)-C(56)-O(1)#2	45.8(3)
C(57)#2-C(56)-C(55)	77.5(8)
C(58)#2-C(56)-C(55)	67.7(6)
O(1)-C(56)-C(55)	107.1(3)
O(1)#2-C(56)-C(55)	152.6(4)
C(57)#2-C(56)-H(56A)	114.1

C(58)#2-C(56)-H(56A)	68.9
O(1)-C(56)-H(56A)	110.4
O(1)#2-C(56)-H(56A)	81.8
C(55)-C(56)-H(56A)	110.2
C(57)#2-C(56)-H(56B)	130.5
C(58)#2-C(56)-H(56B)	75.7
O(1)-C(56)-H(56B)	110.4
O(1)#2-C(56)-H(56B)	87.6
C(55)-C(56)-H(56B)	110.2
H(56A)-C(56)-H(56B)	108.6
C(57)#2-O(1)-O(1)#2	83.7(4)
C(57)#2-O(1)-C(57)	128.3(4)
O(1)#2-O(1)-C(57)	44.6(3)
C(57)#2-O(1)-C(56)	15.7(4)
O(1)#2-O(1)-C(56)	69.0(4)
C(57)-O(1)-C(56)	113.4(4)
C(57)#2-O(1)-C(56)#2	148.3(5)
O(1)#2-O(1)-C(56)#2	65.2(3)
C(57)-O(1)-C(56)#2	21.1(3)
C(56)-O(1)-C(56)#2	134.2(3)
C(56)#2-C(57)-O(1)#2	133.5(10)
C(56)#2-C(57)-O(1)	83.8(8)
O(1)#2-C(57)-O(1)	51.7(4)
C(56)#2-C(57)-C(55)#2	81.9(7)
O(1)#2-C(57)-C(55)#2	141.8(5)
O(1)-C(57)-C(55)#2	165.7(4)
C(56)#2-C(57)-C(58)	24.7(7)
O(1)#2-C(57)-C(58)	158.1(5)
O(1)-C(57)-C(58)	107.0(3)
C(55)#2-C(57)-C(58)	58.9(4)
C(56)#2-C(57)-H(57A)	128.3
O(1)#2-C(57)-H(57A)	85.3
O(1)-C(57)-H(57A)	110.4
C(55)#2-C(57)-H(57A)	79.1
C(58)-C(57)-H(57A)	110.3
C(56)#2-C(57)-H(57B)	112.1
O(1)#2-C(57)-H(57B)	77.5
O(1)-C(57)-H(57B)	110.4
C(55)#2-C(57)-H(57B)	74.9
C(58)-C(57)-H(57B)	110.1
H(57A)-C(57)-H(57B)	108.6
C(56)#2-C(58)-C(55)#2	71.3(4)
C(56)#2-C(58)-C(57)	12.4(4)
C(55)#2-C(58)-C(57)	59.8(4)
C(56)#2-C(58)-H(58A)	120.9
C(55)#2-C(58)-H(58A)	49.9

C(57)-C(58)-H(58A)	109.8
C(56)#2-C(58)-H(58B)	99.2
C(55)#2-C(58)-H(58B)	125.9
C(57)-C(58)-H(58B)	109.4
H(58A)-C(58)-H(58B)	109.5
C(56)#2-C(58)-H(58C)	107.6
C(55)#2-C(58)-H(58C)	124.3
C(57)-C(58)-H(58C)	109.2
H(58A)-C(58)-H(58C)	109.5
H(58B)-C(58)-H(58C)	109.5
N(6)-C(51)-C(52)	179.82(18)
C(51)-C(52)-H(52A)	109.5
C(51)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(51)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(29)-B(1)-C(43)	107.20(11)
C(29)-B(1)-C(37)	109.31(10)
C(43)-B(1)-C(37)	110.60(10)
C(29)-B(1)-C(30)	111.02(10)
C(43)-B(1)-C(30)	108.31(10)
C(37)-B(1)-C(30)	110.35(11)
C(4)-S(1)-Fe(1)	109.68(4)
C(4)-S(1)-Fe(1')	108.94(4)
Fe(1)-S(1)-Fe(1')	98.137(15)
N(1)-Fe(1)-N(3)	176.07(4)
N(1)-Fe(1)-N(4)	101.50(4)
N(3)-Fe(1)-N(4)	81.02(4)
N(1)-Fe(1)-N(2)	80.81(4)
N(3)-Fe(1)-N(2)	101.70(4)
N(4)-Fe(1)-N(2)	102.06(4)
N(1)-Fe(1)-S(1)	84.58(3)
N(3)-Fe(1)-S(1)	92.41(3)
N(4)-Fe(1)-S(1)	167.98(3)
N(2)-Fe(1)-S(1)	89.09(3)
N(1)-Fe(1)-S(1')	92.30(3)
N(3)-Fe(1)-S(1')	84.76(3)
N(4)-Fe(1)-S(1')	87.49(3)
N(2)-Fe(1)-S(1')	169.14(3)
S(1)-Fe(1)-S(1')	81.863(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1 #2 -x,-y+2,-z

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Fe^{II}(tame(N_2S(quino)_2)]_2(BPh_4)\bullet 3MeCN \bullet Et_2O$ **(2)**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	18(1)	19(1)	18(1)	-7(1)	-7(1)	0(1)
C(2)	17(1)	18(1)	18(1)	-5(1)	-7(1)	-2(1)
C(3)	24(1)	18(1)	28(1)	-5(1)	-11(1)	-2(1)
C(4)	17(1)	17(1)	23(1)	-4(1)	-7(1)	-3(1)
C(5)	15(1)	25(1)	17(1)	-8(1)	-4(1)	-4(1)
C(6)	14(1)	25(1)	19(1)	-9(1)	-6(1)	-1(1)
C(7)	18(1)	19(1)	17(1)	-4(1)	-8(1)	-1(1)
C(8)	14(1)	23(1)	16(1)	-5(1)	-7(1)	0(1)
C(9)	15(1)	23(1)	15(1)	-4(1)	-7(1)	-2(1)
C(10)	14(1)	26(1)	22(1)	-5(1)	-8(1)	-3(1)
C(11)	19(1)	26(1)	23(1)	-4(1)	-10(1)	-6(1)
C(12)	20(1)	24(1)	17(1)	-5(1)	-9(1)	-4(1)
C(13)	25(1)	29(1)	27(1)	-11(1)	-12(1)	-6(1)
C(14)	30(1)	34(1)	30(1)	-18(1)	-12(1)	-1(1)
C(15)	21(1)	36(1)	22(1)	-15(1)	-8(1)	1(1)
C(16)	18(1)	30(1)	16(1)	-8(1)	-7(1)	-3(1)
C(17)	18(1)	23(1)	13(1)	-4(1)	-7(1)	-3(1)
C(18)	15(1)	32(1)	21(1)	-9(1)	-3(1)	-5(1)
C(19)	19(1)	33(1)	19(1)	-8(1)	-1(1)	-10(1)
C(20)	22(1)	27(1)	15(1)	-6(1)	-3(1)	-8(1)
C(21)	30(1)	31(1)	16(1)	-3(1)	-4(1)	-11(1)
C(22)	37(1)	30(1)	16(1)	0(1)	-10(1)	-7(1)
C(23)	27(1)	31(1)	18(1)	-5(1)	-10(1)	-3(1)
C(24)	20(1)	27(1)	15(1)	-6(1)	-6(1)	-4(1)
C(25)	20(1)	24(1)	13(1)	-6(1)	-4(1)	-5(1)
C(26)	30(1)	43(1)	21(1)	-5(1)	-7(1)	13(1)
C(27)	21(1)	40(1)	22(1)	1(1)	-8(1)	0(1)
C(28)	21(1)	30(1)	19(1)	-1(1)	-7(1)	-3(1)
C(29)	20(1)	28(1)	16(1)	-6(1)	-4(1)	-2(1)
C(30)	16(1)	31(1)	19(1)	-6(1)	-4(1)	-8(1)

C(31)	39(1)	29(1)	23(1)	-7(1)	-9(1)	-11(1)
C(32)	50(1)	41(1)	22(1)	-9(1)	-11(1)	-18(1)
C(33)	31(1)	51(1)	21(1)	-1(1)	-12(1)	-17(1)
C(34)	19(1)	44(1)	22(1)	-10(1)	-7(1)	2(1)
C(35)	22(1)	50(1)	26(1)	-5(1)	-10(1)	1(1)
C(36)	42(1)	36(1)	31(1)	-16(1)	-13(1)	11(1)
C(37)	14(1)	24(1)	22(1)	-7(1)	-7(1)	-1(1)
C(38)	18(1)	26(1)	23(1)	-8(1)	-7(1)	-2(1)
C(39)	19(1)	35(1)	25(1)	-14(1)	-9(1)	0(1)
C(40)	18(1)	31(1)	37(1)	-17(1)	-12(1)	1(1)
C(41)	17(1)	25(1)	36(1)	-8(1)	-10(1)	-3(1)
C(42)	16(1)	27(1)	23(1)	-7(1)	-6(1)	-1(1)
C(43)	20(1)	24(1)	20(1)	-9(1)	-4(1)	-4(1)
C(44)	22(1)	32(1)	21(1)	-9(1)	-5(1)	-7(1)
C(45)	23(1)	37(1)	31(1)	-15(1)	-5(1)	-10(1)
C(46)	29(1)	26(1)	30(1)	-13(1)	1(1)	-12(1)
C(47)	34(1)	22(1)	25(1)	-7(1)	-5(1)	-6(1)
C(48)	25(1)	24(1)	25(1)	-7(1)	-7(1)	-3(1)
B(2)	29(1)	34(1)	29(1)	-14(1)	-10(1)	2(1)
N(1)	15(1)	20(1)	14(1)	-7(1)	-6(1)	-2(1)
N(2)	15(1)	23(1)	14(1)	-6(1)	-4(1)	-4(1)
N(3)	15(1)	20(1)	13(1)	-4(1)	-5(1)	-2(1)
N(4)	14(1)	22(1)	14(1)	-4(1)	-6(1)	-2(1)
N(5)	48(2)	70(2)	68(2)	-48(2)	16(1)	-18(1)
C(49)	54(2)	41(1)	38(1)	-21(1)	8(1)	-13(1)
C(50)	46(2)	74(2)	66(2)	-33(2)	-1(2)	-12(2)
N(5B)	54(2)	41(1)	38(1)	-21(1)	8(1)	-13(1)
C(49B)	54(2)	41(1)	38(1)	-21(1)	8(1)	-13(1)
C(50B)	54(2)	41(1)	38(1)	-21(1)	8(1)	-13(1)
N(5C)	54(2)	41(1)	38(1)	-21(1)	8(1)	-13(1)
C(49C)	54(2)	41(1)	38(1)	-21(1)	8(1)	-13(1)
C(50C)	54(2)	41(1)	38(1)	-21(1)	8(1)	-13(1)
N(7)	50(2)	56(2)	36(2)	-8(1)	-19(1)	-5(2)
C(53)	50(2)	56(2)	36(2)	-8(1)	-19(1)	-5(2)
C(54)	50(2)	56(2)	36(2)	-8(1)	-19(1)	-5(2)
C(55)	59(2)	36(1)	31(1)	-4(1)	-23(1)	-7(1)

C(56)	59(2)	36(1)	31(1)	-4(1)	-23(1)	-7(1)
O(1)	59(2)	36(1)	31(1)	-4(1)	-23(1)	-7(1)
C(57)	59(2)	36(1)	31(1)	-4(1)	-23(1)	-7(1)
C(58)	59(2)	36(1)	31(1)	-4(1)	-23(1)	-7(1)
N(6)	54(1)	40(1)	66(1)	-16(1)	-31(1)	9(1)
C(51)	39(1)	28(1)	32(1)	-11(1)	-12(1)	-3(1)
C(52)	31(1)	44(1)	46(1)	-20(1)	-12(1)	1(1)
B(1)	17(1)	25(1)	18(1)	-7(1)	-5(1)	-4(1)
S(1)	12(1)	18(1)	14(1)	-4(1)	-4(1)	-3(1)
Fe(1)	11(1)	19(1)	12(1)	-4(1)	-4(1)	-2(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Fe^{II}(tame\text{-}(N_2S(quino)_2)]_2(BPh_4)\bullet 3MeCN \bullet Et_2O$ **(2)**.

	x	y	z	U(eq)
H(1A)	2139	7590	4282	22
H(1B)	1180	7486	3960	22
H(3A)	328	6039	6506	35
H(3B)	1522	6060	5628	35
H(3C)	492	6089	5341	35
H(4A)	761	12384	4756	23
H(4B)	965	12435	3584	23
H(6)	2985	8929	3276	22
H(7A)	-1824	12490	3943	22
H(7B)	-640	12602	3063	22
H(8)	-2531	11185	4009	21
H(10)	-3285	9672	3850	24
H(11)	-2913	8145	3335	26
H(13)	-1519	6902	2443	30
H(14)	280	6387	1624	34
H(15)	1664	7306	1469	30
H(16)	1254	8656	2237	25
H(18)	4009	10392	1725	27
H(19)	3939	11856	379	29
H(21)	2826	13105	-588	32
H(22)	1163	13693	-743	34
H(23)	-400	12851	470	30
H(24)	-319	11514	1903	25
H(26)	8277	3518	2064	42
H(27)	8189	5033	2524	37
H(28)	6634	6172	2757	30
H(31)	5274	5580	759	36
H(32)	4967	6341	-783	43
H(33)	4007	7967	-1048	41
H(34)	3595	8024	1843	35
H(35)	3322	8804	289	41

H(36)	6728	3078	1985	44
H(38)	3905	6256	4702	26
H(39)	4039	7471	5450	30
H(40)	4791	9049	4398	32
H(41)	5515	9333	2581	30
H(42)	5458	8077	1842	27
H(44)	2571	6013	2578	30
H(45)	1133	4986	3677	35
H(46)	1205	3787	5216	35
H(47)	2762	3591	5607	34
H(48)	4225	4567	4476	30
H(2)	5154	4191	2275	36
H(50A)	2801	5114	9	96
H(50B)	3022	4171	917	96
H(50C)	2686	5320	1070	96
H(50D)	3185	5184	655	73
H(50E)	2189	6026	584	73
H(50F)	2659	5281	-179	73
H(50G)	1574	5512	179	73
H(50H)	2755	4944	-273	73
H(50I)	2574	5784	349	73
H(54A)	1356	10072	361	71
H(54B)	889	10826	-493	71
H(54C)	2165	10712	-732	71
H(55A)	-2685	10038	1037	61
H(55B)	-1965	8951	1038	61
H(55C)	-2008	9732	-36	61
H(56A)	-1101	10935	139	49
H(56B)	-1042	10134	1204	49
H(57A)	951	10009	395	49
H(57B)	882	10806	-669	49
H(58A)	2480	9719	-1082	61
H(58B)	1678	9459	-1518	61
H(58C)	1803	8712	-464	61
H(52A)	-2940	8174	6193	60
H(52B)	-3436	7102	6443	60

H(52C)	-3592	7570	7374	60

Table S14. Crystal data and structure refinement for $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**3**).

Identification code	bkl_7_97_0ma	
Empirical formula	C70 H99 F24 Fe4 N29 P4 S4	
Formula weight	2278.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.9227(10) Å	α= 97.318(6)°.
	b = 14.5427(19) Å	β= 116.683(4)°.
	c = 15.0078(11) Å	γ = 112.025(6)°.
Volume	2351.0(4) Å^3	
Z	1	
Density (calculated)	1.609 mg/m^3	
Absorption coefficient	0.868 mm^{-1}	
F(000)	1166	
Crystal size	0.10 x 0.05 x 0.05 mm^3	
Theta range for data collection	2.10 to 30.73°.	
Index ranges	-19<=h<=19, -20<=k<=20, -21<=l<=20	
Reflections collected	50076	
Independent reflections	14435 [R(int) = 0.0608]	
Completeness to theta = 25.00°	99.9 %	
Max. and min. transmission	0.9579 and 0.9182	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14435 / 12 / 661	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1081	
R indices (all data)	R1 = 0.0976, wR2 = 0.1270	
Largest diff. peak and hole	1.293 and -0.870 e.Å^{-3}	

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**3**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4358(3)	4921(2)	2548(2)	28(1)
C(2)	3539(3)	4860(2)	2984(2)	21(1)
C(3)	3620(3)	4122(2)	3626(2)	19(1)
C(4)	2220(3)	4400(2)	2036(2)	22(1)
C(5)	4017(3)	6006(2)	3677(2)	22(1)
C(6)	4146(3)	6617(2)	5310(2)	21(1)
C(7)	3507(3)	6376(2)	5845(2)	21(1)
C(8)	1955(3)	5440(2)	5944(2)	25(1)
C(9)	2890(3)	6133(2)	6946(2)	27(1)
C(10)	5072(3)	7557(3)	7781(2)	32(1)
C(11)	638(3)	4834(2)	1687(2)	22(1)
C(12)	173(3)	5302(2)	2171(2)	22(1)
C(13)	216(3)	6084(2)	3531(2)	25(1)
C(14)	-666(3)	6102(2)	2646(3)	29(1)
C(15)	-1470(3)	5448(3)	665(2)	35(1)
C(16)	-2756(3)	1403(2)	444(2)	27(1)
C(17)	-1527(2)	1798(2)	1495(2)	20(1)
C(18)	-1253(2)	2817(2)	2249(2)	22(1)
C(19)	-527(2)	2021(2)	1238(2)	19(1)
C(20)	-1658(2)	914(2)	1968(2)	21(1)
C(21)	-829(2)	1044(2)	3781(2)	18(1)
C(22)	252(2)	1569(2)	4828(2)	17(1)
C(23)	2183(3)	2673(2)	6002(2)	20(1)
C(24)	1691(3)	2171(2)	6523(2)	22(1)
C(25)	-442(3)	786(2)	5958(2)	26(1)
C(26)	925(2)	1410(2)	1754(2)	18(1)
C(27)	1762(2)	1232(2)	2610(2)	16(1)
C(28)	2718(2)	1297(2)	4241(2)	18(1)
C(29)	3013(2)	754(2)	3688(2)	20(1)
C(30)	2315(3)	90(2)	1743(2)	27(1)
N(1)	1466(2)	4645(2)	2357(2)	19(1)
N(2)	3457(2)	6036(2)	4303(2)	20(1)
N(3)	2351(2)	5592(2)	5262(2)	20(1)
N(5)	3875(2)	6721(2)	6887(2)	24(1)
N(4)	742(2)	5577(2)	3233(2)	20(1)
N(6)	-699(2)	5601(2)	1783(2)	27(1)
N(7)	514(2)	1969(2)	2063(2)	16(1)
N(8)	-612(2)	1276(2)	3063(2)	17(1)

N(9)	1282(2)	2293(2)	4935(2)	16(1)
N(11)	472(2)	1476(2)	5775(2)	20(1)
N(10)	1928(2)	1589(2)	3560(2)	15(1)
N(12)	2412(2)	714(2)	2654(2)	19(1)
N(13)	3680(7)	6615(7)	-513(6)	62(1)
C(31)	4403(9)	7155(8)	371(6)	62(1)
C(32)	5201(8)	7863(7)	1460(6)	62(1)
N(13B)	3968(7)	6531(6)	-415(6)	62(1)
C(31B)	4623(9)	7309(7)	320(7)	62(1)
C(32B)	5553(8)	8264(6)	1229(7)	62(1)
N(14)	8308(4)	3098(3)	8961(3)	64(1)
C(33)	7944(3)	2648(3)	8091(3)	39(1)
C(34)	7519(4)	2106(3)	7015(3)	46(1)
N(15)	5984(11)	5741(9)	1429(10)	114(3)
C(35)	5302(18)	5359(14)	532(14)	114(3)
C(36)	4590(17)	4904(14)	-606(13)	114(3)
F(1)	3659(2)	9167(2)	7127(2)	53(1)
F(2)	5315(2)	10510(2)	7351(2)	48(1)
F(3)	4387(2)	10074(2)	5582(2)	63(1)
F(4)	2719(2)	8720(2)	5344(2)	60(1)
F(5)	4598(2)	8853(2)	6311(2)	40(1)
F(6)	3431(2)	10371(2)	6378(2)	33(1)
F(7)	2769(4)	3069(3)	10131(4)	46(1)
F(8)	476(4)	784(3)	8532(4)	48(1)
F(9)	1146(5)	2427(4)	8460(3)	38(1)
F(10)	2102(5)	1414(4)	10209(4)	52(2)
F(11)	851(5)	2158(4)	9779(4)	40(1)
F(12)	2392(5)	1702(4)	8890(4)	44(1)
F(13)	477(5)	2012(4)	8641(4)	57(1)
F(14)	2719(4)	1581(3)	9918(3)	50(1)
F(15)	1988(5)	2592(3)	10373(3)	54(1)
F(16)	1239(5)	1029(4)	8219(3)	52(1)
F(17)	2442(5)	2768(3)	9125(4)	61(1)
F(18)	765(4)	838(3)	9462(3)	47(1)
P(1)	4009(1)	9605(1)	6340(1)	25(1)
P(2)	1615(1)	1863(1)	9320(1)	30(1)
S(1)	2776(1)	3961(1)	4294(1)	17(1)
S(2)	200(1)	3454(1)	3546(1)	18(1)
Fe(1)	1818(1)	4950(1)	3783(1)	17(1)
Fe(2)	1018(1)	2357(1)	3545(1)	14(1)

Table S16. Bond lengths [Å] and angles [°] for $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**3**)

Fe(1)-N(1)	1.917(2)
Fe(1)-N(2)	1.923(2)
Fe(1)-N(3)	1.955(2)
Fe(1)-N(4)	1.966(2)
Fe(2)-N(7)	1.933(2)
Fe(2)-N(8)	1.925(2)
Fe(2)-N(9)	1.970(2)
Fe(2)-N(10)	1.973(2)
C(1)-C(2)	1.532(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(4)	1.528(4)
C(2)-C(3)	1.533(4)
C(2)-C(5)	1.552(4)
C(3)-S(1)	1.831(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-N(1)	1.467(4)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-N(2)	1.471(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-N(2)	1.297(3)
C(6)-C(7)	1.427(4)
C(6)-H(6)	0.9500
C(7)-N(3)	1.327(4)
C(7)-N(5)	1.359(4)
C(8)-C(9)	1.358(4)
C(8)-N(3)	1.367(4)
C(8)-H(8)	0.9500
C(9)-N(5)	1.368(4)

C(9)-H(9)	0.9500
C(10)-N(5)	1.454(4)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-N(1)	1.297(4)
C(11)-C(12)	1.427(4)
C(11)-H(11)	0.9500
C(12)-N(4)	1.339(4)
C(12)-N(6)	1.353(4)
C(13)-C(14)	1.356(4)
C(13)-N(4)	1.377(4)
C(13)-H(13)	0.9500
C(14)-N(6)	1.375(4)
C(14)-H(14)	0.9500
C(15)-N(6)	1.457(4)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.534(4)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(19)	1.537(4)
C(17)-C(20)	1.538(4)
C(17)-C(18)	1.545(4)
C(18)-S(2)	1.826(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-N(7)	1.461(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-N(8)	1.467(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-N(8)	1.294(3)

C(21)-C(22)	1.423(4)
C(21)-H(21)	0.9500
C(22)-N(9)	1.345(3)
C(22)-N(11)	1.350(3)
C(23)-C(24)	1.365(4)
C(23)-N(9)	1.376(3)
C(23)-H(23)	0.9500
C(24)-N(11)	1.369(4)
C(24)-H(24)	0.9500
C(25)-N(11)	1.458(3)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-N(7)	1.301(3)
C(26)-C(27)	1.430(4)
C(26)-H(26)	0.9500
C(27)-N(10)	1.334(3)
C(27)-N(12)	1.364(3)
C(28)-C(29)	1.366(4)
C(28)-N(10)	1.374(3)
C(28)-H(28)	0.9500
C(29)-N(12)	1.374(3)
C(29)-H(29)	0.9500
C(30)-N(12)	1.461(3)
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
N(13)-C(31)	1.155(4)
C(31)-C(32)	1.431(4)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
N(13B)-C(31B)	1.155(4)
C(31B)-C(32B)	1.431(4)
C(32B)-H(32D)	0.9800
C(32B)-H(32E)	0.9800

C(32B)-H(32F)	0.9800
N(14)-C(33)	1.154(4)
C(33)-C(34)	1.431(4)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
N(15)-C(35)	1.134(15)
N(15)-C(36)#1	1.14(2)
C(35)-C(36)#1	0.47(3)
C(35)-C(36)	1.428(12)
C(35)-C(35)#1	1.44(4)
C(36)-C(35)#1	0.47(3)
C(36)-N(15)#1	1.14(2)
C(36)-C(36)#1	1.57(3)
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
F(1)-P(1)	1.586(2)
F(2)-P(1)	1.600(2)
F(3)-P(1)	1.581(2)
F(4)-P(1)	1.575(2)
F(5)-P(1)	1.601(2)
F(6)-P(1)	1.6093(19)
F(7)-P(2)	1.651(4)
F(8)-P(2)	1.534(4)
F(9)-P(2)	1.637(4)
F(10)-P(2)	1.551(4)
F(11)-P(2)	1.648(4)
F(12)-P(2)	1.555(4)
F(13)-P(2)	1.569(4)
F(14)-P(2)	1.632(4)
F(15)-P(2)	1.522(4)
F(16)-P(2)	1.647(4)
F(17)-P(2)	1.552(4)
F(18)-P(2)	1.627(4)
S(1)-Fe(1)	2.2883(8)

S(1)-Fe(2)	2.2965(8)
S(2)-Fe(2)	2.2825(8)
S(2)-Fe(1)	2.3109(8)

C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(4)-C(2)-C(1)	108.0(2)
C(4)-C(2)-C(3)	110.4(2)
C(1)-C(2)-C(3)	107.4(2)
C(4)-C(2)-C(5)	110.5(2)
C(1)-C(2)-C(5)	107.6(2)
C(3)-C(2)-C(5)	112.7(2)
C(2)-C(3)-S(1)	116.35(19)
C(2)-C(3)-H(3A)	108.2
S(1)-C(3)-H(3A)	108.2
C(2)-C(3)-H(3B)	108.2
S(1)-C(3)-H(3B)	108.2
H(3A)-C(3)-H(3B)	107.4
N(1)-C(4)-C(2)	111.4(2)
N(1)-C(4)-H(4A)	109.4
C(2)-C(4)-H(4A)	109.4
N(1)-C(4)-H(4B)	109.4
C(2)-C(4)-H(4B)	109.4
H(4A)-C(4)-H(4B)	108.0
N(2)-C(5)-C(2)	112.8(2)
N(2)-C(5)-H(5A)	109.0
C(2)-C(5)-H(5A)	109.0
N(2)-C(5)-H(5B)	109.0
C(2)-C(5)-H(5B)	109.0
H(5A)-C(5)-H(5B)	107.8
N(2)-C(6)-C(7)	112.6(3)
N(2)-C(6)-H(6)	123.7

C(7)-C(6)-H(6)	123.7
N(3)-C(7)-N(4)	110.3(2)
N(3)-C(7)-C(6)	116.5(2)
N(4)-C(7)-C(6)	132.8(3)
C(9)-C(8)-N(3)	108.9(3)
C(9)-C(8)-H(8)	125.6
N(3)-C(8)-H(8)	125.6
C(8)-C(9)-N(4)	107.2(3)
C(8)-C(9)-H(9)	126.4
N(5)-C(9)-H(9)	126.4
N(5)-C(10)-H(10A)	109.5
N(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
N(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-C(12)	112.5(2)
N(1)-C(11)-H(11)	123.8
C(12)-C(11)-H(11)	123.8
N(4)-C(12)-N(6)	110.8(2)
N(4)-C(12)-C(11)	116.2(3)
N(6)-C(12)-C(11)	132.8(3)
C(14)-C(13)-N(4)	108.8(3)
C(14)-C(13)-H(13)	125.6
N(4)-C(13)-H(13)	125.6
C(13)-C(14)-N(6)	107.6(3)
C(13)-C(14)-H(14)	126.2
N(6)-C(14)-H(14)	126.2
N(6)-C(15)-H(15A)	109.5
N(6)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(6)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-H(16A)	109.5
C(17)-C(16)-H(16B)	109.5

H(16A)-C(16)-H(16B)	109.5
C(17)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(16)-C(17)-C(19)	108.0(2)
C(16)-C(17)-C(20)	107.8(2)
C(19)-C(17)-C(20)	110.3(2)
C(16)-C(17)-C(18)	108.1(2)
C(19)-C(17)-C(18)	111.2(2)
C(20)-C(17)-C(18)	111.3(2)
C(17)-C(18)-S(2)	115.81(19)
C(17)-C(18)-H(18A)	108.3
S(2)-C(18)-H(18A)	108.3
C(17)-C(18)-H(18B)	108.3
S(2)-C(18)-H(18B)	108.3
H(18A)-C(18)-H(18B)	107.4
N(7)-C(19)-C(17)	110.9(2)
N(7)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19A)	109.5
N(7)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	108.0
N(8)-C(20)-C(17)	112.2(2)
N(8)-C(20)-H(20A)	109.2
C(17)-C(20)-H(20A)	109.2
N(8)-C(20)-H(20B)	109.2
C(17)-C(20)-H(20B)	109.2
H(20A)-C(20)-H(20B)	107.9
N(8)-C(21)-C(22)	112.5(2)
N(8)-C(21)-H(21)	123.7
C(22)-C(21)-H(21)	123.7
N(9)-C(22)-N(10)	110.9(2)
N(9)-C(22)-C(21)	116.8(2)
N(11)-C(22)-C(21)	132.3(2)
C(24)-C(23)-N(9)	109.3(2)
C(24)-C(23)-H(23)	125.4

N(9)-C(23)-H(23)	125.4
C(23)-C(24)-N(11)	107.0(2)
C(23)-C(24)-H(24)	126.5
N(11)-C(24)-H(24)	126.5
N(11)-C(25)-H(25A)	109.5
N(11)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
N(11)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(7)-C(26)-C(27)	112.8(2)
N(7)-C(26)-H(26)	123.6
C(27)-C(26)-H(26)	123.6
N(10)-C(27)-N(12)	111.0(2)
N(10)-C(27)-C(26)	116.2(2)
N(12)-C(27)-C(26)	132.6(2)
C(29)-C(28)-N(10)	108.9(2)
C(29)-C(28)-H(28)	125.5
N(10)-C(28)-H(28)	125.5
C(28)-C(29)-N(12)	107.5(2)
C(28)-C(29)-H(29)	126.3
N(12)-C(29)-H(29)	126.3
N(12)-C(30)-H(30A)	109.5
N(12)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
N(12)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(11)-N(1)-C(4)	117.9(2)
C(11)-N(1)-Fe(1)	117.39(19)
C(4)-N(1)-Fe(1)	123.77(18)
C(6)-N(2)-C(5)	120.0(2)
C(6)-N(2)-Fe(1)	117.13(19)
C(5)-N(2)-Fe(1)	120.51(17)
C(7)-N(3)-C(8)	106.8(2)
C(7)-N(3)-Fe(1)	112.57(18)

C(8)-N(3)-Fe(1)	140.3(2)
C(7)-N(5)-C(9)	106.8(2)
C(7)-N(5)-C(10)	127.7(3)
C(9)-N(5)-C(10)	125.4(3)
C(12)-N(4)-C(13)	106.1(2)
C(12)-N(4)-Fe(1)	111.38(18)
C(13)-N(4)-Fe(1)	141.6(2)
C(12)-N(6)-C(14)	106.6(2)
C(12)-N(6)-C(15)	125.3(3)
C(14)-N(6)-C(15)	128.1(3)
C(26)-N(7)-C(19)	117.6(2)
C(26)-N(7)-Fe(2)	117.41(18)
C(19)-N(7)-Fe(2)	122.94(17)
C(21)-N(8)-C(20)	118.8(2)
C(21)-N(8)-Fe(2)	117.63(18)
C(20)-N(8)-Fe(2)	121.84(17)
C(22)-N(9)-C(23)	105.6(2)
C(22)-N(9)-Fe(2)	111.63(17)
C(23)-N(9)-Fe(2)	142.50(19)
C(22)-N(11)-C(24)	107.2(2)
C(22)-N(11)-C(25)	125.7(2)
C(24)-N(11)-C(25)	127.1(2)
C(27)-N(10)-C(28)	106.3(2)
C(27)-N(10)-Fe(2)	112.76(17)
C(28)-N(10)-Fe(2)	140.96(18)
C(27)-N(12)-C(29)	106.3(2)
C(27)-N(12)-C(30)	126.2(2)
C(29)-N(12)-C(30)	126.8(2)
N(13)-C(31)-C(32)	173.5(11)
N(13B)-C(31B)-C(32B)	173.1(11)
N(14)-C(33)-C(34)	178.7(4)
C(35)-N(15)-C(36)#1	23.8(16)
C(36)#1-C(35)-N(15)	79(4)
C(36)#1-C(35)-C(36)	99(4)
N(15)-C(35)-C(36)	172.0(17)
C(36)#1-C(35)-C(35)#1	80(4)

N(15)-C(35)-C(35)#1	157(3)
C(36)-C(35)-C(35)#1	18.8(13)
C(35)#1-C(36)-N(15)#1	77(4)
C(35)#1-C(36)-C(35)	81(4)
N(15)#1-C(36)-C(35)	157.6(16)
C(35)#1-C(36)-C(36)#1	64(4)
N(15)#1-C(36)-C(36)#1	141(2)
C(35)-C(36)-C(36)#1	17.2(12)
C(35)#1-C(36)-H(36A)	71.5
N(15)#1-C(36)-H(36A)	71.1
C(35)-C(36)-H(36A)	109.2
C(36)#1-C(36)-H(36A)	101.8
C(35)#1-C(36)-H(36B)	167.5
N(15)#1-C(36)-H(36B)	90.9
C(35)-C(36)-H(36B)	109.3
C(36)#1-C(36)-H(36B)	126.3
H(36A)-C(36)-H(36B)	109.5
C(35)#1-C(36)-H(36C)	59.6
N(15)#1-C(36)-H(36C)	52.1
C(35)-C(36)-H(36C)	109.9
C(36)#1-C(36)-H(36C)	99.1
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
F(4)-P(1)-F(3)	90.72(15)
F(4)-P(1)-F(1)	90.82(15)
F(3)-P(1)-F(1)	178.35(17)
F(4)-P(1)-F(2)	179.60(13)
F(3)-P(1)-F(2)	89.27(14)
F(1)-P(1)-F(2)	89.18(14)
F(4)-P(1)-F(5)	90.92(12)
F(3)-P(1)-F(5)	89.60(12)
F(1)-P(1)-F(5)	90.95(11)
F(2)-P(1)-F(5)	89.48(11)
F(4)-P(1)-F(6)	89.66(11)
F(3)-P(1)-F(6)	90.31(12)
F(1)-P(1)-F(6)	89.13(11)

F(2)-P(1)-F(6)	89.94(11)
F(5)-P(1)-F(6)	179.42(13)
F(15)-P(2)-F(8)	131.4(3)
F(15)-P(2)-F(10)	70.6(3)
F(8)-P(2)-F(10)	93.4(3)
F(15)-P(2)-F(17)	93.9(2)
F(8)-P(2)-F(17)	130.4(3)
F(10)-P(2)-F(17)	124.7(3)
F(15)-P(2)-F(12)	131.7(3)
F(8)-P(2)-F(12)	93.3(3)
F(10)-P(2)-F(12)	92.8(3)
F(17)-P(2)-F(12)	58.2(2)
F(15)-P(2)-F(13)	93.8(3)
F(8)-P(2)-F(13)	69.6(2)
F(10)-P(2)-F(13)	140.6(3)
F(17)-P(2)-F(13)	91.3(3)
F(12)-P(2)-F(13)	122.4(3)
F(15)-P(2)-F(18)	90.8(2)
F(8)-P(2)-F(18)	46.4(2)
F(10)-P(2)-F(18)	54.7(2)
F(17)-P(2)-F(18)	174.6(2)
F(12)-P(2)-F(18)	116.5(2)
F(13)-P(2)-F(18)	91.0(3)
F(15)-P(2)-F(14)	92.1(3)
F(8)-P(2)-F(14)	104.4(2)
F(10)-P(2)-F(14)	40.1(2)
F(17)-P(2)-F(14)	90.9(3)
F(12)-P(2)-F(14)	54.3(2)
F(13)-P(2)-F(14)	173.5(2)
F(18)-P(2)-F(14)	86.3(2)
F(15)-P(2)-F(9)	104.8(2)
F(8)-P(2)-F(9)	90.5(3)
F(10)-P(2)-F(9)	175.3(3)
F(17)-P(2)-F(9)	53.7(2)
F(12)-P(2)-F(9)	89.7(2)
F(13)-P(2)-F(9)	39.1(2)

F(18)-P(2)-F(9)	127.3(3)
F(14)-P(2)-F(9)	141.1(3)
F(15)-P(2)-F(16)	176.5(2)
F(8)-P(2)-F(16)	48.0(2)
F(10)-P(2)-F(16)	106.0(3)
F(17)-P(2)-F(16)	88.1(3)
F(12)-P(2)-F(16)	47.5(2)
F(13)-P(2)-F(16)	89.0(2)
F(18)-P(2)-F(16)	87.1(2)
F(14)-P(2)-F(16)	85.0(2)
F(9)-P(2)-F(16)	78.7(2)
F(15)-P(2)-F(11)	45.9(2)
F(8)-P(2)-F(11)	91.0(3)
F(10)-P(2)-F(11)	90.9(3)
F(17)-P(2)-F(11)	115.9(2)
F(12)-P(2)-F(11)	174.2(2)
F(13)-P(2)-F(11)	55.7(2)
F(18)-P(2)-F(11)	69.3(2)
F(14)-P(2)-F(11)	128.2(2)
F(9)-P(2)-F(11)	86.3(2)
F(16)-P(2)-F(11)	135.4(3)
F(15)-P(2)-F(7)	47.5(2)
F(8)-P(2)-F(7)	175.3(3)
F(10)-P(2)-F(7)	90.3(3)
F(17)-P(2)-F(7)	48.6(2)
F(12)-P(2)-F(7)	89.4(3)
F(13)-P(2)-F(7)	105.7(2)
F(18)-P(2)-F(7)	135.1(2)
F(14)-P(2)-F(7)	80.3(2)
F(9)-P(2)-F(7)	85.7(2)
F(16)-P(2)-F(7)	133.5(3)
F(11)-P(2)-F(7)	86.0(3)
C(3)-S(1)-Fe(1)	103.34(9)
C(3)-S(1)-Fe(2)	115.74(9)
Fe(1)-S(1)-Fe(2)	96.70(3)
C(18)-S(2)-Fe(2)	104.45(9)

C(18)-S(2)-Fe(1)	117.64(10)
Fe(2)-S(2)-Fe(1)	96.46(3)
N(1)-Fe(1)-N(2)	89.65(10)
N(1)-Fe(1)-N(3)	167.11(10)
N(2)-Fe(1)-N(3)	81.01(10)
N(1)-Fe(1)-N(4)	80.89(10)
N(2)-Fe(1)-N(4)	106.40(10)
N(3)-Fe(1)-N(4)	93.19(10)
N(1)-Fe(1)-S(1)	97.84(7)
N(2)-Fe(1)-S(1)	82.89(7)
N(3)-Fe(1)-S(1)	89.84(7)
N(4)-Fe(1)-S(1)	170.58(7)
N(1)-Fe(1)-S(2)	100.43(7)
N(2)-Fe(1)-S(2)	161.71(7)
N(3)-Fe(1)-S(2)	90.99(7)
N(4)-Fe(1)-S(2)	90.36(7)
S(1)-Fe(1)-S(2)	80.65(3)
N(8)-Fe(2)-N(7)	86.88(9)
N(8)-Fe(2)-N(9)	80.99(9)
N(7)-Fe(2)-N(9)	163.06(9)
N(8)-Fe(2)-N(10)	105.35(9)
N(7)-Fe(2)-N(10)	80.60(9)
N(9)-Fe(2)-N(10)	91.20(9)
N(8)-Fe(2)-S(2)	82.90(7)
N(7)-Fe(2)-S(2)	97.94(7)
N(9)-Fe(2)-S(2)	92.29(7)
N(10)-Fe(2)-S(2)	171.47(7)
N(8)-Fe(2)-S(1)	162.91(7)
N(7)-Fe(2)-S(1)	101.19(7)
N(9)-Fe(2)-S(1)	93.70(7)
N(10)-Fe(2)-S(1)	90.92(7)
S(2)-Fe(2)-S(1)	81.09(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table S17. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for [Fe^{II}(tame-($N_2S(^{Me}Im)_2$)]$_2$(PF_6)$_2$•2MeCN (**3**). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(2)	26(2)	28(2)	4(1)	19(1)	4(1)
C(2)	21(1)	18(1)	20(1)	2(1)	13(1)	5(1)
C(3)	18(1)	17(1)	20(1)	2(1)	12(1)	5(1)
C(4)	24(2)	22(1)	18(1)	4(1)	13(1)	7(1)
C(5)	23(2)	17(1)	22(1)	3(1)	15(1)	4(1)
C(6)	20(1)	14(1)	22(1)	2(1)	12(1)	4(1)
C(7)	26(2)	17(1)	19(1)	3(1)	12(1)	10(1)
C(8)	27(2)	27(2)	26(2)	8(1)	19(1)	12(1)
C(9)	34(2)	32(2)	24(2)	9(1)	20(1)	18(2)
C(10)	33(2)	32(2)	18(1)	-1(1)	10(1)	14(2)
C(11)	26(2)	17(1)	18(1)	4(1)	11(1)	9(1)
C(12)	24(2)	17(1)	21(1)	6(1)	11(1)	9(1)
C(13)	29(2)	21(1)	27(2)	6(1)	18(1)	12(1)
C(14)	30(2)	27(2)	33(2)	9(1)	17(2)	17(1)
C(15)	38(2)	37(2)	26(2)	9(1)	10(2)	24(2)
C(16)	18(1)	29(2)	23(2)	6(1)	5(1)	9(1)
C(17)	14(1)	20(1)	20(1)	6(1)	7(1)	7(1)
C(18)	15(1)	23(1)	21(1)	4(1)	7(1)	9(1)
C(19)	16(1)	18(1)	15(1)	4(1)	5(1)	8(1)
C(20)	14(1)	19(1)	19(1)	3(1)	6(1)	3(1)
C(21)	15(1)	17(1)	20(1)	5(1)	10(1)	6(1)
C(22)	17(1)	16(1)	20(1)	6(1)	13(1)	8(1)
C(23)	15(1)	20(1)	17(1)	3(1)	8(1)	4(1)
C(24)	21(1)	24(1)	17(1)	5(1)	10(1)	9(1)
C(25)	25(2)	26(2)	29(2)	13(1)	19(1)	9(1)
C(26)	17(1)	17(1)	15(1)	4(1)	8(1)	5(1)
C(27)	14(1)	15(1)	18(1)	3(1)	9(1)	6(1)
C(28)	15(1)	18(1)	18(1)	6(1)	8(1)	5(1)
C(29)	16(1)	18(1)	20(1)	4(1)	8(1)	7(1)
C(30)	26(2)	29(2)	25(2)	1(1)	14(1)	15(1)

N(1)	20(1)	15(1)	18(1)	2(1)	11(1)	5(1)
N(2)	23(1)	13(1)	19(1)	2(1)	13(1)	4(1)
N(3)	22(1)	17(1)	20(1)	4(1)	12(1)	8(1)
N(5)	27(1)	22(1)	19(1)	2(1)	12(1)	11(1)
N(4)	21(1)	16(1)	22(1)	5(1)	13(1)	7(1)
N(6)	30(1)	25(1)	26(1)	9(1)	12(1)	16(1)
N(7)	14(1)	15(1)	16(1)	4(1)	7(1)	5(1)
N(8)	15(1)	14(1)	17(1)	4(1)	7(1)	6(1)
N(9)	14(1)	14(1)	16(1)	3(1)	9(1)	5(1)
N(11)	19(1)	21(1)	21(1)	7(1)	13(1)	7(1)
N(10)	14(1)	14(1)	16(1)	4(1)	9(1)	4(1)
N(12)	18(1)	19(1)	18(1)	4(1)	10(1)	9(1)
N(14)	91(3)	32(2)	56(2)	12(2)	48(2)	9(2)
C(33)	46(2)	21(2)	50(2)	12(2)	32(2)	10(2)
C(34)	61(3)	25(2)	48(2)	7(2)	37(2)	10(2)
F(1)	65(2)	77(2)	73(2)	54(1)	58(1)	52(1)
F(2)	23(1)	49(1)	48(1)	1(1)	7(1)	15(1)
F(3)	73(2)	112(2)	65(2)	65(2)	57(2)	64(2)
F(4)	29(1)	53(1)	55(1)	-16(1)	3(1)	16(1)
F(5)	35(1)	43(1)	50(1)	12(1)	24(1)	25(1)
F(6)	26(1)	35(1)	40(1)	13(1)	16(1)	18(1)
F(7)	34(3)	30(2)	34(3)	-2(2)	6(2)	0(2)
F(8)	42(3)	20(2)	56(3)	6(2)	18(3)	4(2)
F(9)	58(3)	40(3)	30(2)	21(2)	28(2)	29(3)
F(10)	60(4)	71(4)	50(3)	46(3)	32(3)	43(3)
F(11)	47(3)	48(3)	45(3)	21(2)	34(3)	29(3)
F(12)	60(3)	45(3)	62(3)	29(3)	50(3)	33(3)
F(13)	67(3)	51(3)	58(3)	18(2)	28(3)	42(3)
F(14)	47(3)	51(3)	29(2)	5(2)	6(2)	24(2)
F(15)	75(4)	29(2)	43(2)	-7(2)	38(3)	9(2)
F(16)	85(4)	56(3)	25(2)	16(2)	23(2)	50(3)
F(17)	79(4)	45(3)	81(4)	30(3)	61(3)	27(3)
F(18)	51(3)	21(2)	37(2)	3(2)	18(2)	-2(2)
P(1)	20(1)	32(1)	24(1)	9(1)	13(1)	13(1)
P(2)	37(1)	26(1)	25(1)	9(1)	17(1)	13(1)
S(1)	14(1)	15(1)	16(1)	2(1)	8(1)	4(1)

S(2)	17(1)	16(1)	20(1)	4(1)	11(1)	7(1)
Fe(1)	18(1)	14(1)	17(1)	3(1)	10(1)	5(1)
Fe(2)	12(1)	13(1)	14(1)	3(1)	7(1)	4(1)

Table S18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $[Fe^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**3**).

	x	y	z	U(eq)
H(1A)	3996	4231	2010	42
H(1B)	5180	5105	3133	42
H(1C)	4423	5465	2221	42
H(3A)	4499	4395	4174	23
H(3B)	3313	3412	3137	23
H(4A)	2231	4697	1480	26
H(4B)	1849	3620	1724	26
H(5A)	4922	6352	4171	27
H(5B)	3838	6418	3207	27
H(6)	4983	7144	5654	25
H(8)	1157	4933	5748	30
H(9)	2864	6197	7572	33
H(10A)	5699	7647	7614	47
H(10B)	5275	7364	8419	47
H(10C)	5048	8224	7913	47
H(11)	372	4679	955	26
H(13)	435	6374	4241	30
H(14)	-1169	6405	2627	35
H(15A)	-989	5976	475	52
H(15B)	-2178	5532	554	52
H(15C)	-1762	4733	215	52
H(16A)	-3005	705	-9	40
H(16B)	-2661	1907	74	40
H(16C)	-3387	1344	597	40
H(18A)	-1932	2641	2371	26
H(18B)	-1255	3337	1883	26
H(19A)	-880	1492	540	22
H(19B)	-239	2734	1186	22
H(20A)	-2427	660	1965	25
H(20B)	-1725	308	1513	25

H(21)	-1622	574	3626	22
H(23)	3016	3201	6325	24
H(24)	2114	2282	7263	27
H(25A)	-746	1194	6216	39
H(25B)	-64	501	6493	39
H(25C)	-1130	198	5288	39
H(26)	692	1148	1035	21
H(28)	3011	1449	4978	22
H(29)	3537	457	3967	24
H(30A)	1564	-601	1381	40
H(30B)	3034	-17	1994	40
H(30C)	2282	469	1244	40
H(32A)	4934	7534	1896	93
H(32B)	5168	8528	1510	93
H(32C)	6046	8012	1720	93
H(32D)	6357	8448	1329	93
H(32E)	5570	8155	1866	93
H(32F)	5369	8842	1114	93
H(34A)	7570	2611	6641	69
H(34B)	6662	1542	6650	69
H(34C)	8033	1795	7016	69
H(36A)	5120	4908	-852	172
H(36B)	4211	5315	-894	172
H(36C)	3964	4186	-839	172

Table S19. Crystal data and structure refinement for $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**4**).

Identification code	bkl7_139_0m	
Empirical formula	C36 H51 Co2 F12 N15 P2 S2	
Formula weight	1165.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.9597(3) Å	α= 93.948(2)°.
	b = 13.0171(4) Å	β= 102.099(2)°.
	c = 17.9975(5) Å	γ = 95.177(2)°.
Volume	2490.14(12) $Å^3$	
Z	2	
Density (calculated)	1.555 mg/m^3	
Absorption coefficient	0.905 mm^{-1}	
F(000)	1192	
Crystal size	0.15 x 0.05 x 0.05 mm^3	
Theta range for data collection	2.01 to 30.68°.	
Index ranges	-15≤h≤15, -18≤k≤18, -25≤l≤25	
Reflections collected	107396	
Independent reflections	15125 [R(int) = 0.0643]	
Completeness to theta = 25.00°	99.9 %	
Max. and min. transmission	0.9562 and 0.8763	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15125 / 0 / 631	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0752	
R indices (all data)	R1 = 0.0657, wR2 = 0.0863	
Largest diff. peak and hole	0.673 and -0.507 $e.Å^{-3}$	

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**4**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2063(2)	1473(2)	4155(1)	19(1)
C(2)	2886(2)	641(1)	3953(1)	18(1)
C(3)	2431(2)	-367(2)	4260(1)	24(1)
C(4)	4275(2)	917(2)	4352(1)	20(1)
C(5)	5479(2)	2538(2)	4765(1)	18(1)
C(6)	5804(2)	3585(1)	4595(1)	17(1)
C(7)	5706(2)	4937(1)	3963(1)	18(1)
C(8)	6460(2)	5236(2)	4669(1)	20(1)
C(9)	7209(2)	4316(2)	5844(1)	25(1)
C(10)	2728(2)	413(2)	3088(1)	19(1)
C(11)	4217(2)	780(1)	2344(1)	18(1)
C(12)	5094(2)	1544(2)	2128(1)	18(1)
C(13)	6135(2)	3025(2)	2142(1)	22(1)
C(14)	6453(2)	2377(2)	1598(1)	24(1)
C(15)	5758(2)	512(2)	1086(1)	30(1)
C(16)	2962(2)	3894(2)	1392(1)	20(1)
C(17)	1952(2)	3162(2)	828(1)	19(1)
C(18)	2308(2)	3140(2)	46(1)	27(1)
C(19)	1919(2)	2038(2)	1048(1)	19(1)
C(20)	374(2)	1017(1)	1490(1)	18(1)
C(21)	-416(2)	930(2)	2036(1)	19(1)
C(22)	-1239(2)	1403(2)	2970(1)	24(1)
C(23)	-1742(2)	408(2)	2720(1)	26(1)
C(24)	-1446(2)	-897(2)	1675(1)	34(1)
C(25)	651(2)	3556(2)	725(1)	20(1)
C(26)	-416(2)	4453(2)	1538(1)	20(1)
C(27)	-691(2)	4589(2)	2291(1)	20(1)
C(28)	-591(2)	4346(2)	3470(1)	26(1)
C(29)	-1383(2)	5085(2)	3292(1)	29(1)
C(30)	-2183(2)	5954(2)	2099(1)	37(1)

C(31)	2225(2)	6592(2)	2146(2)	40(1)
C(32)	1318(2)	7101(2)	2462(1)	37(1)
C(33)	9447(2)	7876(3)	4293(2)	53(1)
C(34)	10537(2)	7580(2)	4800(2)	38(1)
C(35)	5267(2)	3519(2)	-889(1)	36(1)
C(36)	6010(2)	3969(2)	-158(1)	35(1)
N(1)	4761(1)	1957(1)	4218(1)	17(1)
N(2)	5297(1)	3907(1)	3924(1)	17(1)
N(3)	6517(1)	4374(1)	5063(1)	19(1)
N(4)	3545(1)	1140(1)	2778(1)	17(1)
N(5)	5284(1)	2501(1)	2473(1)	18(1)
N(6)	5787(2)	1440(1)	1596(1)	21(1)
N(7)	1152(1)	1839(1)	1604(1)	17(1)
N(8)	-413(1)	1724(1)	2542(1)	19(1)
N(9)	-1220(2)	115(1)	2121(1)	23(1)
N(10)	253(1)	3726(1)	1441(1)	18(1)
N(11)	-160(2)	4037(1)	2841(1)	20(1)
N(12)	-1443(2)	5233(1)	2541(1)	25(1)
N(13)	598(3)	7495(2)	2713(2)	65(1)
N(14)	11403(3)	7360(2)	5195(1)	54(1)
N(15)	6587(3)	4336(2)	413(1)	53(1)
F(1)	3773(2)	853(1)	6365(1)	48(1)
F(2)	4680(2)	1473(1)	7581(1)	51(1)
F(3)	4651(1)	3109(1)	7240(1)	30(1)
F(4)	2859(1)	2018(1)	6999(1)	37(1)
F(5)	5567(1)	1939(1)	6606(1)	37(1)
F(6)	3741(1)	2496(1)	6029(1)	34(1)
F(7)	1810(2)	7550(1)	625(1)	61(1)
F(8)	3527(1)	8588(1)	533(1)	52(1)
F(9)	2348(2)	9880(1)	262(1)	61(1)
F(10)	2287(2)	9111(2)	1327(1)	84(1)
F(11)	1823(1)	8345(1)	-430(1)	36(1)
F(12)	614(1)	8858(1)	356(1)	47(1)
P(1)	4211(1)	1980(1)	6802(1)	24(1)
P(2)	2070(1)	8724(1)	453(1)	29(1)
S(1)	2206(1)	2724(1)	3756(1)	16(1)

S(2)	2909(1)	3943(1)	2402(1)	17(1)
Co(1)	4029(1)	2730(1)	3220(1)	15(1)
Co(2)	990(1)	2967(1)	2477(1)	15(1)

Table S21. Bond lengths [Å] and angles [°] for $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet 2MeCN$ (**4**).

C(1)-C(2)	1.543(3)
C(1)-S(1)	1.8308(19)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(10)	1.535(3)
C(2)-C(4)	1.539(3)
C(2)-C(3)	1.539(3)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-N(1)	1.464(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-N(1)	1.275(2)
C(5)-C(6)	1.447(3)
C(5)-H(5)	0.9500
C(6)-N(4)	1.332(2)
C(6)-N(5)	1.354(2)
C(7)-N(4)	1.366(2)
C(7)-C(8)	1.372(3)
C(7)-H(7)	0.9500
C(8)-N(5)	1.368(3)
C(8)-H(8)	0.9500
C(9)-N(5)	1.460(2)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-N(2)	1.462(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-N(2)	1.274(2)
C(11)-C(12)	1.449(3)
C(11)-H(11)	0.9500
C(12)-N(3)	1.331(2)

C(12)-N(6)	1.349(2)
C(13)-N(3)	1.365(2)
C(13)-C(14)	1.369(3)
C(13)-H(13)	0.9500
C(14)-N(6)	1.363(3)
C(14)-H(14)	0.9500
C(15)-N(6)	1.461(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.540(3)
C(16)-S(2)	1.8268(19)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.536(3)
C(17)-C(25)	1.538(3)
C(17)-C(19)	1.541(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-N(7)	1.458(2)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-N(7)	1.283(2)
C(20)-C(21)	1.442(3)
C(20)-H(20)	0.9500
C(21)-N(10)	1.329(2)
C(21)-N(9)	1.355(2)
C(22)-N(10)	1.361(2)
C(22)-C(23)	1.367(3)
C(22)-H(22)	0.9500
C(23)-N(11)	1.370(3)
C(23)-H(23)	0.9500
C(24)-N(11)	1.467(3)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800

C(24)-H(24C)	0.9800
C(25)-N(8)	1.455(2)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-N(8)	1.272(2)
C(26)-C(27)	1.451(3)
C(26)-H(26)	0.9500
C(27)-N(9)	1.329(3)
C(27)-N(12)	1.347(2)
C(28)-C(29)	1.362(3)
C(28)-N(9)	1.364(2)
C(28)-H(28)	0.9500
C(29)-N(12)	1.369(3)
C(29)-H(29)	0.9500
C(30)-N(12)	1.463(3)
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-C(32)	1.435(4)
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-N(13)	1.131(3)
C(33)-C(34)	1.443(4)
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-N(14)	1.132(3)
C(35)-C(36)	1.448(3)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-N(15)	1.135(3)
N(1)-Co(1)	2.1620(16)
N(4)-Co(1)	2.1205(15)
N(2)-Co(1)	2.1446(15)

N(3)-Co(1)	2.1410(16)
N(7)-Co(2)	2.1225(16)
N(10)-Co(2)	2.1556(15)
N(8)-Co(2)	2.2078(16)
N(9)-Co(2)	2.1205(16)
F(1)-P(1)	1.5993(14)
F(2)-P(1)	1.5981(15)
F(3)-P(1)	1.6018(13)
F(4)-P(1)	1.5983(14)
F(5)-P(1)	1.6022(14)
F(6)-P(1)	1.5947(14)
F(7)-P(2)	1.5928(17)
F(8)-P(2)	1.5992(15)
F(9)-P(2)	1.5844(17)
F(10)-P(2)	1.5802(17)
F(11)-P(2)	1.5911(14)
F(12)-P(2)	1.5960(15)
S(1)-Co(1)	2.3930(5)
S(1)-Co(2)	2.4616(5)
S(2)-Co(2)	2.3912(5)
S(2)-Co(1)	2.4653(5)

C(2)-C(1)-S(1)	118.39(13)
C(2)-C(1)-H(1A)	107.7
S(1)-C(1)-H(1A)	107.7
C(2)-C(1)-H(1B)	107.7
S(1)-C(1)-H(1B)	107.7
H(1A)-C(1)-H(1B)	107.1
C(10)-C(2)-C(4)	111.47(15)
C(10)-C(2)-C(3)	106.98(15)
C(4)-C(2)-C(3)	106.85(15)
C(10)-C(2)-C(1)	112.24(15)
C(4)-C(2)-C(1)	111.92(15)
C(3)-C(2)-C(1)	107.01(15)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5

H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
N(1)-C(4)-C(2)	112.33(15)
N(1)-C(4)-H(4A)	109.1
C(2)-C(4)-H(4A)	109.1
N(1)-C(4)-H(4B)	109.1
C(2)-C(4)-H(4B)	109.1
H(4A)-C(4)-H(4B)	107.9
N(1)-C(5)-C(6)	115.32(17)
N(1)-C(5)-H(5)	122.3
C(6)-C(5)-H(5)	122.3
N(4)-C(6)-N(5)	110.88(17)
N(4)-C(6)-C(5)	120.40(16)
N(5)-C(6)-C(5)	128.49(17)
N(4)-C(7)-C(8)	109.13(17)
N(4)-C(7)-H(7)	125.4
C(8)-C(7)-H(7)	125.4
N(5)-C(8)-C(7)	106.68(16)
N(5)-C(8)-H(8)	126.7
C(7)-C(8)-H(8)	126.7
N(5)-C(9)-H(9A)	109.5
N(5)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(5)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(2)-C(10)-C(2)	111.79(14)
N(2)-C(10)-H(10A)	109.3
C(2)-C(10)-H(10A)	109.3
N(2)-C(10)-H(10B)	109.3
C(2)-C(10)-H(10B)	109.3
H(10A)-C(10)-H(10B)	107.9
N(2)-C(11)-C(12)	114.91(17)
N(2)-C(11)-H(11)	122.5

C(12)-C(11)-H(11)	122.5
N(3)-C(12)-N(6)	111.44(16)
N(3)-C(12)-C(11)	119.66(16)
N(6)-C(12)-C(11)	128.90(17)
N(3)-C(13)-C(14)	109.63(17)
N(3)-C(13)-H(13)	125.2
C(14)-C(13)-H(13)	125.2
N(6)-C(14)-C(13)	106.50(17)
N(6)-C(14)-H(14)	126.7
C(13)-C(14)-H(14)	126.7
N(6)-C(15)-H(15A)	109.5
N(6)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(6)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-S(2)	117.69(13)
C(17)-C(16)-H(16A)	107.9
S(2)-C(16)-H(16A)	107.9
C(17)-C(16)-H(16B)	107.9
S(2)-C(16)-H(16B)	107.9
H(16A)-C(16)-H(16B)	107.2
C(18)-C(17)-C(25)	106.96(16)
C(18)-C(17)-C(16)	107.67(15)
C(25)-C(17)-C(16)	111.89(16)
C(18)-C(17)-C(19)	106.25(15)
C(25)-C(17)-C(19)	111.65(15)
C(16)-C(17)-C(19)	112.05(15)
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(7)-C(19)-C(17)	113.04(15)
N(7)-C(19)-H(19A)	109.0

C(17)-C(19)-H(19A)	109.0
N(7)-C(19)-H(19B)	109.0
C(17)-C(19)-H(19B)	109.0
H(19A)-C(19)-H(19B)	107.8
N(7)-C(20)-C(21)	114.79(17)
N(7)-C(20)-H(20)	122.6
C(21)-C(20)-H(20)	122.6
N(10)-C(21)-N(9)	111.29(17)
N(10)-C(21)-C(20)	119.97(16)
N(11)-C(21)-C(20)	128.74(17)
N(10)-C(22)-C(23)	109.65(18)
N(10)-C(22)-H(22)	125.2
C(23)-C(22)-H(22)	125.2
C(22)-C(23)-N(11)	106.58(17)
C(22)-C(23)-H(23)	126.7
N(11)-C(23)-H(23)	126.7
N(11)-C(24)-H(24A)	109.5
N(11)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
N(11)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(8)-C(25)-C(17)	112.96(15)
N(8)-C(25)-H(25A)	109.0
C(17)-C(25)-H(25A)	109.0
N(8)-C(25)-H(25B)	109.0
C(17)-C(25)-H(25B)	109.0
H(25A)-C(25)-H(25B)	107.8
N(8)-C(26)-C(27)	115.31(18)
N(8)-C(26)-H(26)	122.3
C(27)-C(26)-H(26)	122.3
N(9)-C(27)-N(12)	111.35(17)
N(9)-C(27)-C(26)	120.03(17)
N(12)-C(27)-C(26)	128.62(18)
C(29)-C(28)-N(9)	109.32(19)
C(29)-C(28)-H(28)	125.3

N(9)-C(28)-H(28)	125.3
C(28)-C(29)-N(12)	106.85(18)
C(28)-C(29)-H(29)	126.6
N(12)-C(29)-H(29)	126.6
N(12)-C(30)-H(30A)	109.5
N(12)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
N(12)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(32)-C(31)-H(31A)	109.5
C(32)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(32)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
N(13)-C(32)-C(31)	179.5(3)
C(34)-C(33)-H(33A)	109.5
C(34)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(34)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
N(14)-C(34)-C(33)	179.0(3)
C(36)-C(35)-H(35A)	109.5
C(36)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(36)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
N(15)-C(36)-C(35)	179.0(3)
C(5)-N(1)-C(4)	119.70(16)
C(5)-N(1)-Co(1)	115.09(13)
C(4)-N(1)-Co(1)	123.81(11)
C(6)-N(4)-C(7)	106.26(15)
C(6)-N(4)-Co(1)	111.73(12)

C(7)-N(4)-Co(1)	141.63(13)
C(6)-N(5)-C(8)	107.05(15)
C(6)-N(5)-C(9)	126.51(17)
C(8)-N(5)-C(9)	126.45(16)
C(11)-N(2)-C(10)	118.62(16)
C(11)-N(2)-Co(1)	116.38(12)
C(10)-N(2)-Co(1)	123.23(12)
C(12)-N(3)-C(13)	105.46(16)
C(12)-N(3)-Co(1)	111.83(12)
C(13)-N(3)-Co(1)	142.08(13)
C(12)-N(6)-C(14)	106.98(16)
C(12)-N(6)-C(15)	125.85(17)
C(14)-N(6)-C(15)	127.07(17)
C(20)-N(7)-C(19)	118.82(16)
C(20)-N(7)-Co(2)	116.96(13)
C(19)-N(7)-Co(2)	123.14(12)
C(21)-N(10)-C(22)	105.87(16)
C(21)-N(10)-Co(2)	111.27(12)
C(22)-N(10)-Co(2)	142.45(13)
C(21)-N(11)-C(23)	106.60(16)
C(21)-N(11)-C(24)	126.43(18)
C(23)-N(11)-C(24)	126.93(17)
C(26)-N(8)-C(25)	120.28(17)
C(26)-N(8)-Co(2)	115.07(13)
C(25)-N(8)-Co(2)	123.85(12)
C(27)-N(9)-C(28)	105.85(17)
C(27)-N(9)-Co(2)	113.38(12)
C(28)-N(9)-Co(2)	140.73(15)
C(27)-N(12)-C(29)	106.63(18)
C(27)-N(12)-C(30)	127.00(19)
C(29)-N(12)-C(30)	126.37(18)
F(6)-P(1)-F(2)	179.50(8)
F(6)-P(1)-F(4)	90.25(8)
F(2)-P(1)-F(4)	89.53(8)
F(6)-P(1)-F(1)	90.25(8)
F(2)-P(1)-F(1)	90.20(9)

F(4)-P(1)-F(1)	90.09(8)
F(6)-P(1)-F(3)	89.83(7)
F(2)-P(1)-F(3)	89.73(8)
F(4)-P(1)-F(3)	89.93(7)
F(1)-P(1)-F(3)	179.93(12)
F(6)-P(1)-F(5)	89.95(7)
F(2)-P(1)-F(5)	90.28(8)
F(4)-P(1)-F(5)	179.78(9)
F(1)-P(1)-F(5)	89.81(8)
F(3)-P(1)-F(5)	90.17(7)
F(10)-P(2)-F(9)	89.82(12)
F(10)-P(2)-F(11)	178.72(11)
F(9)-P(2)-F(11)	89.83(9)
F(10)-P(2)-F(7)	91.59(11)
F(9)-P(2)-F(7)	178.29(11)
F(11)-P(2)-F(7)	88.78(9)
F(10)-P(2)-F(12)	89.41(9)
F(9)-P(2)-F(12)	90.75(9)
F(11)-P(2)-F(12)	89.37(7)
F(7)-P(2)-F(12)	90.23(9)
F(10)-P(2)-F(8)	91.62(10)
F(9)-P(2)-F(8)	88.97(9)
F(11)-P(2)-F(8)	89.61(8)
F(7)-P(2)-F(8)	90.03(9)
F(12)-P(2)-F(8)	178.94(9)
C(1)-S(1)-Co(1)	105.46(6)
C(1)-S(1)-Co(2)	120.65(6)
Co(1)-S(1)-Co(2)	87.862(17)
C(16)-S(2)-Co(2)	106.73(6)
C(16)-S(2)-Co(1)	119.67(7)
Co(2)-S(2)-Co(1)	87.818(17)
N(2)-Co(1)-N(5)	92.60(6)
N(2)-Co(1)-N(4)	150.23(6)
N(5)-Co(1)-N(4)	76.48(6)
N(2)-Co(1)-N(1)	77.05(6)
N(5)-Co(1)-N(1)	105.20(6)

N(4)-Co(1)-N(1)	79.25(6)
N(2)-Co(1)-S(1)	103.02(4)
N(5)-Co(1)-S(1)	163.69(4)
N(4)-Co(1)-S(1)	91.71(4)
N(1)-Co(1)-S(1)	83.16(4)
N(2)-Co(1)-S(2)	94.49(5)
N(5)-Co(1)-S(2)	92.32(5)
N(4)-Co(1)-S(2)	113.30(4)
N(1)-Co(1)-S(2)	160.73(4)
S(1)-Co(1)-S(2)	81.940(17)
N(11)-Co(2)-N(7)	145.55(6)
N(11)-Co(2)-N(8)	89.07(6)
N(7)-Co(2)-N(8)	76.53(6)
N(11)-Co(2)-N(10)	75.89(6)
N(7)-Co(2)-N(10)	78.48(6)
N(8)-Co(2)-N(10)	106.50(6)
N(11)-Co(2)-S(2)	106.72(5)
N(7)-Co(2)-S(2)	92.23(4)
N(8)-Co(2)-S(2)	163.51(5)
N(10)-Co(2)-S(2)	82.52(4)
N(11)-Co(2)-S(1)	96.58(5)
N(7)-Co(2)-S(1)	114.69(4)
N(8)-Co(2)-S(1)	91.63(4)
N(10)-Co(2)-S(1)	160.04(4)
S(2)-Co(2)-S(1)	82.052(17)

Symmetry transformations used to generate equivalent atoms:

Table S22. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for [Co^{II}(tame-($N_2S(^{Me}Im)_2$)]$_2$(PF_6)$_2$• 2MeCN (**4**). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(1)	19(1)	19(1)	6(1)	6(1)	2(1)
C(2)	19(1)	16(1)	19(1)	5(1)	4(1)	0(1)
C(3)	27(1)	19(1)	26(1)	8(1)	5(1)	-1(1)
C(4)	22(1)	15(1)	21(1)	5(1)	2(1)	2(1)
C(5)	17(1)	20(1)	17(1)	2(1)	2(1)	4(1)
C(6)	15(1)	18(1)	17(1)	-1(1)	3(1)	2(1)
C(7)	19(1)	15(1)	20(1)	1(1)	4(1)	-1(1)
C(8)	20(1)	16(1)	23(1)	-2(1)	6(1)	-1(1)
C(9)	24(1)	27(1)	19(1)	-3(1)	-1(1)	1(1)
C(10)	20(1)	15(1)	21(1)	2(1)	4(1)	-1(1)
C(11)	19(1)	14(1)	20(1)	-1(1)	0(1)	2(1)
C(12)	16(1)	18(1)	18(1)	0(1)	2(1)	3(1)
C(13)	20(1)	20(1)	27(1)	2(1)	6(1)	-2(1)
C(14)	19(1)	26(1)	27(1)	2(1)	9(1)	0(1)
C(15)	31(1)	28(1)	31(1)	-8(1)	12(1)	2(1)
C(16)	22(1)	20(1)	18(1)	5(1)	4(1)	0(1)
C(17)	21(1)	20(1)	15(1)	2(1)	5(1)	1(1)
C(18)	32(1)	30(1)	20(1)	3(1)	10(1)	2(1)
C(19)	21(1)	19(1)	19(1)	0(1)	7(1)	3(1)
C(20)	21(1)	14(1)	19(1)	1(1)	1(1)	2(1)
C(21)	18(1)	16(1)	22(1)	2(1)	1(1)	-2(1)
C(22)	22(1)	26(1)	22(1)	3(1)	7(1)	0(1)
C(23)	25(1)	26(1)	28(1)	6(1)	7(1)	-3(1)
C(24)	39(1)	18(1)	42(1)	-3(1)	10(1)	-6(1)
C(25)	24(1)	21(1)	16(1)	3(1)	2(1)	3(1)
C(26)	18(1)	18(1)	23(1)	3(1)	0(1)	3(1)
C(27)	17(1)	17(1)	25(1)	-1(1)	4(1)	1(1)
C(28)	26(1)	28(1)	24(1)	-3(1)	11(1)	-2(1)
C(29)	23(1)	30(1)	34(1)	-8(1)	11(1)	1(1)
C(30)	32(1)	31(1)	44(1)	-6(1)	-1(1)	19(1)

C(31)	42(1)	30(1)	44(1)	5(1)	1(1)	9(1)
C(32)	34(1)	37(1)	38(1)	6(1)	4(1)	-1(1)
C(33)	33(1)	81(2)	46(2)	-6(2)	14(1)	5(1)
C(34)	40(1)	40(2)	38(1)	-4(1)	22(1)	-2(1)
C(35)	31(1)	41(1)	35(1)	2(1)	6(1)	5(1)
C(36)	44(1)	27(1)	35(1)	7(1)	9(1)	2(1)
N(1)	15(1)	17(1)	19(1)	2(1)	2(1)	2(1)
N(4)	18(1)	14(1)	17(1)	-1(1)	4(1)	0(1)
N(5)	17(1)	21(1)	17(1)	-4(1)	2(1)	-1(1)
N(2)	17(1)	16(1)	16(1)	1(1)	1(1)	0(1)
N(3)	18(1)	17(1)	20(1)	2(1)	4(1)	2(1)
N(6)	19(1)	22(1)	21(1)	-1(1)	6(1)	2(1)
N(7)	18(1)	16(1)	18(1)	3(1)	3(1)	3(1)
N(10)	19(1)	18(1)	19(1)	2(1)	3(1)	1(1)
N(11)	25(1)	17(1)	26(1)	2(1)	5(1)	-3(1)
N(8)	18(1)	18(1)	17(1)	0(1)	2(1)	0(1)
N(9)	22(1)	18(1)	21(1)	-1(1)	6(1)	1(1)
N(12)	19(1)	22(1)	31(1)	-5(1)	3(1)	5(1)
N(13)	51(2)	85(2)	63(2)	0(2)	22(1)	10(1)
N(14)	62(2)	57(2)	49(1)	10(1)	22(1)	18(1)
N(15)	79(2)	33(1)	41(1)	7(1)	-1(1)	-2(1)
F(1)	69(1)	23(1)	59(1)	-10(1)	38(1)	-5(1)
F(2)	83(1)	45(1)	38(1)	24(1)	27(1)	34(1)
F(3)	33(1)	25(1)	30(1)	-2(1)	6(1)	3(1)
F(4)	37(1)	30(1)	48(1)	-2(1)	26(1)	-1(1)
F(5)	33(1)	47(1)	37(1)	3(1)	15(1)	13(1)
F(6)	34(1)	39(1)	26(1)	8(1)	3(1)	0(1)
F(7)	62(1)	52(1)	60(1)	29(1)	-9(1)	-14(1)
F(8)	26(1)	46(1)	76(1)	0(1)	-9(1)	5(1)
F(9)	54(1)	21(1)	114(2)	-2(1)	32(1)	4(1)
F(10)	67(1)	132(2)	34(1)	-34(1)	-2(1)	-30(1)
F(11)	32(1)	48(1)	30(1)	0(1)	10(1)	7(1)
F(12)	28(1)	65(1)	45(1)	-22(1)	13(1)	0(1)
P(1)	33(1)	19(1)	25(1)	4(1)	14(1)	5(1)
P(2)	26(1)	30(1)	27(1)	-3(1)	2(1)	-3(1)
S(1)	18(1)	15(1)	16(1)	1(1)	3(1)	1(1)

S(2)	18(1)	16(1)	16(1)	2(1)	2(1)	0(1)
Co(1)	16(1)	13(1)	15(1)	0(1)	2(1)	0(1)
Co(2)	16(1)	14(1)	15(1)	0(1)	3(1)	1(1)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $[Co^{II}(tame\text{-}(N_2S(^{Me}Im)_2)]_2(PF_6)_2 \bullet$ 2MeCN (**4**).

	x	y	z	U(eq)
H(1A)	2247	1607	4717	23
H(1B)	1175	1175	3993	23
H(3A)	1579	-615	3976	36
H(3B)	2430	-233	4802	36
H(3C)	2995	-893	4197	36
H(4A)	4368	872	4907	23
H(4B)	4780	405	4162	23
H(5)	5780	2300	5250	22
H(7)	5500	5376	3565	21
H(8)	6864	5910	4849	24
H(9A)	6691	3894	6116	37
H(9B)	7414	5016	6105	37
H(9C)	7985	4001	5834	37
H(10A)	2925	-301	2976	23
H(10B)	1843	456	2834	23
H(11)	4148	66	2175	22
H(13)	6457	3732	2270	27
H(14)	7025	2547	1284	28
H(15A)	5746	-100	1373	45
H(15B)	6506	560	866	45
H(15C)	5004	453	675	45
H(16A)	2909	4604	1231	24
H(16B)	3794	3695	1342	24
H(18A)	1622	2762	-341	40
H(18B)	3071	2794	68	40
H(18C)	2460	3850	-88	40
H(19A)	1586	1561	582	23
H(19B)	2787	1888	1261	23
H(20)	322	505	1079	22
H(22)	-1437	1809	3379	28

H(23)	-2336	1	2922	32
H(24A)	-1678	-800	1130	50
H(24B)	-2129	-1320	1821	50
H(24C)	-681	-1248	1776	50
H(25A)	670	4214	481	24
H(25B)	27	3045	379	24
H(26)	-716	4877	1145	24
H(28)	-372	4088	3956	31
H(29)	-1812	5430	3626	35
H(30A)	-1649	6596	2088	55
H(30B)	-2881	6109	2336	55
H(30C)	-2515	5640	1576	55
H(31A)	2396	5962	2400	59
H(31B)	3004	7057	2222	59
H(31C)	1896	6408	1598	59
H(33A)	9385	8615	4400	79
H(33B)	8692	7472	4370	79
H(33C)	9524	7740	3763	79
H(35A)	4383	3403	-858	54
H(35B)	5562	2856	-1023	54
H(35C)	5352	3991	-1280	54

Table S24. Crystal data and structure refinement for Thioether-Ligated [Fe^{II}(tame-(N_2S^{Bz}(^{Me}Im)$_2$(MeCN))](PF_6)$_2$•MeCN (**5**)

Identification code	bkl7_152_0m	
Empirical formula	C26 H34 F12 Fe N8 P2 S	
Formula weight	836.46	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.2287(11) Å	α= 88.369(5)°.
	b = 12.2948(13) Å	β= 74.465(5)°.
	c = 12.7375(14) Å	γ = 84.959(5)°.
Volume	1687.7(3) Å^3	
Z	2	
Density (calculated)	1.646 mg/m^3	
Absorption coefficient	0.704 mm^{-1}	
F(000)	852	
Crystal size	0.08 x 0.03 x 0.03 mm^3	
Theta range for data collection	2.16 to 26.47°.	
Index ranges	-13<=h<=14, -15<=k<=15, -15<=l<=15	
Reflections collected	21050	
Independent reflections	6841 [R(int) = 0.0820]	
Completeness to theta = 25.00°	99.2 %	
Max. and min. transmission	0.9792 and 0.9459	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6841 / 0 / 456	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1207	
R indices (all data)	R1 = 0.1222, wR2 = 0.1446	
Largest diff. peak and hole	0.822 and -0.556 e.Å^{-3}	

Table S25. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Thioether-Ligated [Fe^{II}(tame-(N_2S^{Bz}(^{Me}Im)$_2$(MeCN))](PF_6)$_2$•MeCN (**5**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5849(4)	6262(4)	8632(3)	18(1)
C(2)	5006(4)	8226(4)	7761(4)	23(1)
C(3)	5756(4)	9147(4)	7170(4)	18(1)
C(4)	5091(5)	10235(4)	7671(4)	27(1)
C(5)	5817(4)	9164(3)	5954(4)	18(1)
C(6)	5674(4)	7724(4)	4797(4)	17(1)
C(7)	6041(4)	6604(4)	4505(3)	17(1)
C(8)	7010(4)	5033(4)	4587(4)	16(1)
C(9)	6319(4)	4964(4)	3864(4)	20(1)
C(10)	4837(4)	6260(4)	3162(4)	20(1)
C(11)	7090(4)	9070(4)	7321(4)	23(1)
C(12)	8540(4)	7607(4)	7511(4)	18(1)
C(13)	9006(4)	6502(4)	7208(4)	17(1)
C(14)	9111(4)	4993(4)	6351(3)	16(1)
C(15)	9960(4)	4869(4)	6946(4)	19(1)
C(16)	10646(4)	6066(4)	8205(4)	24(1)
C(17)	4663(4)	6358(4)	9522(3)	16(1)
C(18)	3668(4)	5780(4)	9484(4)	17(1)
C(19)	2546(4)	5914(4)	10281(4)	19(1)
C(20)	2421(4)	6624(4)	11126(4)	23(1)
C(21)	3396(5)	7198(4)	11188(4)	26(1)
C(22)	4530(4)	7069(4)	10386(4)	21(1)
C(23)	9332(5)	7966(4)	4158(4)	23(1)
C(24)	10177(4)	8521(4)	3290(4)	25(1)
C(25)	8449(7)	614(5)	9790(6)	58(2)
C(26)	8551(6)	1128(5)	10743(5)	49(2)
N(1)	6183(3)	8074(3)	5496(3)	15(1)
N(3)	6841(3)	6063(3)	4985(3)	16(1)
N(5)	5704(3)	5955(3)	3821(3)	16(1)

N(2)	7734(3)	7994(3)	7017(3)	16(1)
N(3)	8505(3)	6008(3)	6523(3)	15(1)
N(6)	9882(3)	5823(3)	7495(3)	16(1)
N(7)	8668(3)	7526(3)	4815(3)	18(1)
N(8)	8413(7)	188(5)	9001(6)	87(2)
F(1)	493(3)	3320(3)	9068(3)	48(1)
F(2)	1284(4)	1569(3)	8838(3)	66(1)
F(3)	2428(3)	3857(2)	8689(3)	50(1)
F(4)	3205(3)	2122(3)	8488(3)	46(1)
F(5)	1890(3)	2813(3)	7523(2)	46(1)
F(6)	1816(3)	2651(4)	10030(3)	70(1)
F(7)	8947(3)	1642(3)	3063(2)	39(1)
F(8)	8658(3)	2641(2)	4596(3)	36(1)
F(9)	7044(3)	2469(2)	3877(3)	39(1)
F(10)	7372(3)	633(2)	3923(2)	33(1)
F(11)	7095(3)	1621(2)	5463(2)	34(1)
F(12)	8981(3)	804(2)	4646(3)	38(1)
P(1)	1852(1)	2699(1)	8791(1)	23(1)
P(2)	8027(1)	1637(1)	4256(1)	25(1)
S(1)	5580(1)	6815(1)	7354(1)	15(1)
Fe(1)	7328(1)	7037(1)	5999(1)	13(1)

Table S26. Bond lengths [Å] and angles [°] for Thioether-Ligated [Fe^{II}(tame-(N_2S^{Bz}(^{Me}Im)$_2$(MeCN))](PF_6)$_2$•MeCN (**5**).

C(1)-C(17)	1.498(6)
C(1)-S(1)	1.835(4)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.528(6)
C(2)-S(1)	1.836(4)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(5)	1.531(6)
C(3)-C(4)	1.540(6)
C(3)-C(11)	1.555(6)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-N(1)	1.458(5)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-N(1)	1.281(5)
C(6)-C(7)	1.432(6)
C(6)-H(6)	0.9500
C(7)-N(3)	1.337(5)
C(7)-N(5)	1.345(5)
C(8)-N(3)	1.357(5)
C(8)-C(9)	1.361(6)
C(8)-H(8)	0.9500
C(9)-N(5)	1.354(6)
C(9)-H(9)	0.9500
C(10)-N(5)	1.466(5)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-N(2)	1.461(5)
C(11)-H(11A)	0.9900

C(11)-H(11B)	0.9900
C(12)-N(2)	1.287(5)
C(12)-C(13)	1.436(6)
C(12)-H(12)	0.9500
C(13)-N(4)	1.341(5)
C(13)-N(6)	1.352(5)
C(14)-N(4)	1.362(5)
C(14)-C(15)	1.364(6)
C(14)-H(14)	0.9500
C(15)-N(6)	1.368(6)
C(15)-H(15)	0.9500
C(16)-N(6)	1.456(5)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.388(6)
C(17)-C(22)	1.394(6)
C(18)-C(19)	1.391(6)
C(18)-H(18)	0.9500
C(19)-C(20)	1.375(6)
C(19)-H(19)	0.9500
C(20)-C(21)	1.374(6)
C(20)-H(20)	0.9500
C(21)-C(22)	1.402(7)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-N(7)	1.121(6)
C(23)-C(24)	1.449(7)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-N(8)	1.158(8)
C(25)-C(26)	1.420(9)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800

N(1)-Fe(1)	1.948(4)
N(3)-Fe(1)	1.996(4)
N(2)-Fe(1)	1.941(4)
N(4)-Fe(1)	1.981(4)
N(7)-Fe(1)	1.947(4)
F(1)-P(1)	1.600(3)
F(2)-P(1)	1.572(3)
F(3)-P(1)	1.603(3)
F(4)-P(1)	1.572(3)
F(5)-P(1)	1.608(3)
F(6)-P(1)	1.566(3)
F(7)-P(2)	1.591(3)
F(8)-P(2)	1.601(3)
F(9)-P(2)	1.599(3)
F(10)-P(2)	1.613(3)
F(11)-P(2)	1.613(3)
F(12)-P(2)	1.583(3)
S(1)-Fe(1)	2.2715(13)

C(17)-C(1)-S(1)	110.0(3)
C(17)-C(1)-H(1A)	109.7
S(1)-C(1)-H(1A)	109.7
C(17)-C(1)-H(1B)	109.7
S(1)-C(1)-H(1B)	109.7
H(1A)-C(1)-H(1B)	108.2
C(3)-C(2)-S(1)	118.1(3)
C(3)-C(2)-H(2A)	107.8
S(1)-C(2)-H(2A)	107.8
C(3)-C(2)-H(2B)	107.8
S(1)-C(2)-H(2B)	107.8
H(2A)-C(2)-H(2B)	107.1
C(2)-C(3)-C(5)	111.1(4)
C(2)-C(3)-C(4)	107.7(4)
C(5)-C(3)-C(4)	108.3(4)
C(2)-C(3)-C(11)	112.3(4)
C(5)-C(3)-C(11)	109.8(4)

C(4)-C(3)-C(11)	107.4(4)
C(3)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(3)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
N(1)-C(5)-C(3)	110.3(3)
N(1)-C(5)-H(5A)	109.6
C(3)-C(5)-H(5A)	109.6
N(1)-C(5)-H(5B)	109.6
C(3)-C(5)-H(5B)	109.6
H(5A)-C(5)-H(5B)	108.1
N(1)-C(6)-C(7)	113.7(4)
N(1)-C(6)-H(6)	123.1
C(7)-C(6)-H(6)	123.1
N(3)-C(7)-N(5)	111.2(4)
N(3)-C(7)-C(6)	117.6(4)
N(5)-C(7)-C(6)	131.2(4)
N(3)-C(8)-C(9)	109.1(4)
N(3)-C(8)-H(8)	125.4
C(9)-C(8)-H(8)	125.4
N(5)-C(9)-C(8)	107.5(4)
N(5)-C(9)-H(9)	126.2
C(8)-C(9)-H(9)	126.2
N(5)-C(10)-H(10A)	109.5
N(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
N(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(2)-C(11)-C(3)	111.4(3)
N(2)-C(11)-H(11A)	109.4
C(3)-C(11)-H(11A)	109.4
N(2)-C(11)-H(11B)	109.4
C(3)-C(11)-H(11B)	109.4

H(11A)-C(11)-H(11B)	108.0
N(2)-C(12)-C(13)	113.0(4)
N(2)-C(12)-H(12)	123.5
C(13)-C(12)-H(12)	123.5
N(4)-C(13)-N(6)	110.9(4)
N(4)-C(13)-C(12)	117.3(4)
N(6)-C(13)-C(12)	131.9(4)
N(4)-C(14)-C(15)	109.3(4)
N(4)-C(14)-H(14)	125.4
C(15)-C(14)-H(14)	125.4
C(14)-C(15)-N(6)	107.2(4)
C(14)-C(15)-H(15)	126.4
N(6)-C(15)-H(15)	126.4
N(6)-C(16)-H(16A)	109.5
N(6)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
N(6)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	118.9(4)
C(18)-C(17)-C(1)	121.1(4)
C(22)-C(17)-C(1)	120.0(4)
C(17)-C(18)-C(19)	121.1(4)
C(17)-C(18)-H(18)	119.5
C(19)-C(18)-H(18)	119.5
C(20)-C(19)-C(18)	119.6(4)
C(20)-C(19)-H(19)	120.2
C(18)-C(19)-H(19)	120.2
C(21)-C(20)-C(19)	120.5(4)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(20)-C(21)-C(22)	120.3(4)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8
C(17)-C(22)-C(21)	119.7(4)
C(17)-C(22)-H(22)	120.2

C(21)-C(22)-H(22)	120.2
N(7)-C(23)-C(24)	178.6(5)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(8)-C(25)-C(26)	177.5(9)
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(6)-N(1)-C(5)	120.4(4)
C(6)-N(1)-Fe(1)	116.7(3)
C(5)-N(1)-Fe(1)	122.6(3)
C(7)-N(3)-C(8)	105.6(4)
C(7)-N(3)-Fe(1)	110.7(3)
C(8)-N(3)-Fe(1)	143.7(3)
C(7)-N(5)-C(9)	106.6(4)
C(7)-N(5)-C(10)	126.7(4)
C(9)-N(5)-C(10)	126.8(4)
C(12)-N(2)-C(11)	119.1(4)
C(12)-N(2)-Fe(1)	117.1(3)
C(11)-N(2)-Fe(1)	123.5(3)
C(13)-N(4)-C(14)	106.0(4)
C(13)-N(4)-Fe(1)	111.1(3)
C(14)-N(4)-Fe(1)	142.4(3)
C(13)-N(6)-C(15)	106.7(4)
C(13)-N(6)-C(16)	127.3(4)
C(15)-N(6)-C(16)	126.0(4)
C(23)-N(7)-Fe(1)	168.8(4)
F(6)-P(1)-F(2)	92.8(2)
F(6)-P(1)-F(4)	90.46(19)

F(2)-P(1)-F(4)	91.1(2)
F(6)-P(1)-F(1)	90.87(19)
F(2)-P(1)-F(1)	90.5(2)
F(4)-P(1)-F(1)	177.9(2)
F(6)-P(1)-F(3)	89.7(2)
F(2)-P(1)-F(3)	177.4(2)
F(4)-P(1)-F(3)	89.13(18)
F(1)-P(1)-F(3)	89.26(19)
F(6)-P(1)-F(5)	177.2(2)
F(2)-P(1)-F(5)	89.8(2)
F(4)-P(1)-F(5)	90.56(18)
F(1)-P(1)-F(5)	88.04(18)
F(3)-P(1)-F(5)	87.69(19)
F(12)-P(2)-F(7)	90.05(17)
F(12)-P(2)-F(9)	178.95(19)
F(7)-P(2)-F(9)	90.87(17)
F(12)-P(2)-F(8)	90.33(16)
F(7)-P(2)-F(8)	90.64(17)
F(9)-P(2)-F(8)	90.19(16)
F(12)-P(2)-F(11)	89.72(17)
F(7)-P(2)-F(11)	179.51(17)
F(9)-P(2)-F(11)	89.36(17)
F(8)-P(2)-F(11)	89.79(16)
F(12)-P(2)-F(10)	90.23(16)
F(7)-P(2)-F(10)	90.02(16)
F(9)-P(2)-F(10)	89.25(16)
F(8)-P(2)-F(10)	179.13(18)
F(11)-P(2)-F(10)	89.55(16)
C(1)-S(1)-C(2)	100.5(2)
C(1)-S(1)-Fe(1)	114.82(15)
C(2)-S(1)-Fe(1)	102.66(16)
N(2)-Fe(1)-N(7)	91.13(15)
N(2)-Fe(1)-N(1)	97.57(15)
N(7)-Fe(1)-N(1)	88.59(15)
N(2)-Fe(1)-N(4)	81.30(15)
N(7)-Fe(1)-N(4)	91.13(15)

N(1)-Fe(1)-N(4)	178.83(15)
N(2)-Fe(1)-N(3)	177.72(15)
N(7)-Fe(1)-N(3)	90.76(15)
N(1)-Fe(1)-N(3)	81.22(15)
N(5)-Fe(1)-N(3)	99.93(15)
N(2)-Fe(1)-S(1)	84.99(11)
N(7)-Fe(1)-S(1)	168.29(11)
N(1)-Fe(1)-S(1)	80.99(11)
N(4)-Fe(1)-S(1)	99.18(11)
N(3)-Fe(1)-S(1)	92.90(11)

Symmetry transformations used to generate equivalent atoms:

Table S27. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Thioether-Ligated $[Fe^{II}(tame\text{-}(N_2S^{Bz}(^{Me}Im)_2(MeCN))](PF_6)_2 \bullet MeCN$ (**5**). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	17(2)	19(3)	18(2)	4(2)	-8(2)	1(2)
C(2)	24(3)	16(3)	25(3)	2(2)	-3(2)	5(2)
C(3)	21(3)	11(2)	22(3)	-2(2)	-5(2)	3(2)
C(4)	39(3)	16(3)	27(3)	-4(2)	-12(2)	3(2)
C(5)	25(3)	11(2)	20(2)	3(2)	-11(2)	1(2)
C(6)	16(2)	21(3)	16(2)	7(2)	-5(2)	-1(2)
C(7)	18(2)	21(3)	13(2)	3(2)	-5(2)	-3(2)
C(8)	14(2)	16(2)	19(2)	1(2)	-3(2)	-4(2)
C(9)	21(3)	19(3)	17(2)	0(2)	0(2)	-4(2)
C(10)	25(3)	20(3)	19(2)	0(2)	-10(2)	-1(2)
C(11)	30(3)	14(3)	28(3)	-8(2)	-15(2)	2(2)
C(12)	14(2)	26(3)	15(2)	-3(2)	-3(2)	-3(2)
C(13)	11(2)	24(3)	15(2)	6(2)	-1(2)	-2(2)
C(14)	21(3)	15(2)	12(2)	3(2)	-4(2)	-3(2)
C(15)	20(3)	17(3)	20(2)	7(2)	-4(2)	-2(2)
C(16)	22(3)	32(3)	20(3)	0(2)	-13(2)	1(2)
C(17)	14(2)	20(3)	14(2)	5(2)	-4(2)	2(2)
C(18)	20(3)	15(2)	17(2)	-1(2)	-8(2)	-3(2)
C(19)	19(3)	19(3)	22(3)	8(2)	-9(2)	-9(2)
C(20)	14(3)	29(3)	20(3)	1(2)	1(2)	5(2)
C(21)	32(3)	30(3)	17(3)	-1(2)	-7(2)	-2(2)
C(22)	25(3)	20(3)	20(3)	-3(2)	-7(2)	-3(2)
C(23)	24(3)	24(3)	21(3)	-4(2)	-7(2)	-1(2)
C(24)	27(3)	27(3)	18(3)	-2(2)	3(2)	-6(2)
C(25)	92(6)	32(4)	67(5)	12(3)	-51(5)	-14(4)
C(26)	49(4)	52(4)	45(4)	-5(3)	-12(3)	-5(3)
N(1)	16(2)	14(2)	15(2)	4(2)	-4(2)	-7(2)
N(3)	14(2)	17(2)	14(2)	3(2)	-1(2)	-2(2)
N(5)	16(2)	16(2)	16(2)	3(2)	-5(2)	-7(2)
N(2)	13(2)	12(2)	22(2)	4(2)	-6(2)	-2(2)

N(4)	13(2)	19(2)	12(2)	2(2)	-2(2)	-1(2)
N(6)	14(2)	21(2)	11(2)	5(2)	-3(2)	-1(2)
N(7)	16(2)	17(2)	20(2)	0(2)	-6(2)	1(2)
N(8)	145(7)	62(4)	85(5)	11(4)	-76(5)	-42(4)
F(1)	20(2)	74(3)	48(2)	11(2)	-10(2)	5(2)
F(2)	77(3)	43(2)	93(3)	27(2)	-43(2)	-34(2)
F(3)	45(2)	30(2)	79(3)	-9(2)	-21(2)	-8(2)
F(4)	29(2)	41(2)	65(2)	-13(2)	-11(2)	12(2)
F(5)	52(2)	56(2)	28(2)	2(2)	-10(2)	-3(2)
F(6)	63(3)	119(4)	27(2)	1(2)	-18(2)	18(2)
F(7)	30(2)	46(2)	37(2)	2(2)	0(1)	-10(2)
F(8)	31(2)	24(2)	55(2)	-4(1)	-13(2)	-7(1)
F(9)	29(2)	36(2)	55(2)	14(2)	-20(2)	-2(1)
F(10)	37(2)	30(2)	36(2)	5(1)	-12(2)	-18(1)
F(11)	32(2)	35(2)	31(2)	2(1)	-3(1)	-6(1)
F(12)	39(2)	29(2)	49(2)	-6(1)	-19(2)	13(1)
P(1)	19(1)	26(1)	24(1)	-1(1)	-5(1)	-3(1)
P(2)	22(1)	21(1)	32(1)	3(1)	-7(1)	-3(1)
S(1)	16(1)	14(1)	14(1)	2(1)	-4(1)	-1(1)
Fe(1)	14(1)	13(1)	13(1)	2(1)	-4(1)	-2(1)

Table S28. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Thioether-Ligated [Fe^{II}(tame-(N_2S^{Bz}(^{Me}Im)$_2$(MeCN))](PF_6)$_2$•MeCN (**5**).

	x	y	z	U(eq)
H(1A)	6170	5485	8532	21
H(1B)	6477	6667	8834	21
H(2A)	4157	8354	7669	27
H(2B)	4937	8289	8549	27
H(4A)	4241	10305	7595	40
H(4B)	5539	10842	7292	40
H(4C)	5068	10249	8445	40
H(5A)	4996	9425	5854	22
H(5B)	6425	9674	5567	22
H(6)	5107	8167	4499	21
H(8)	7527	4452	4781	20
H(9)	6276	4335	3464	24
H(10A)	4190	6801	3555	31
H(10B)	4456	5611	3023	31
H(10C)	5286	6572	2467	31
H(11A)	7566	9635	6866	28
H(11B)	7045	9215	8092	28
H(12)	8801	8010	8023	22
H(14)	8965	4456	5888	19
H(15)	10503	4238	6973	23
H(16A)	11300	6519	7811	35
H(16B)	11023	5383	8435	35
H(16C)	10129	6460	8848	35
H(18)	3755	5284	8905	20
H(19)	1870	5517	10243	23
H(20)	1655	6719	11671	27
H(21)	3302	7684	11777	31
H(22)	5203	7465	10432	26
H(24A)	11033	8306	3308	38
H(24B)	10007	9312	3390	38

H(24C)	10064	8320	2587	38
H(26A)	8229	670	11380	73
H(26B)	8069	1840	10829	73
H(26C)	9423	1231	10676	73

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