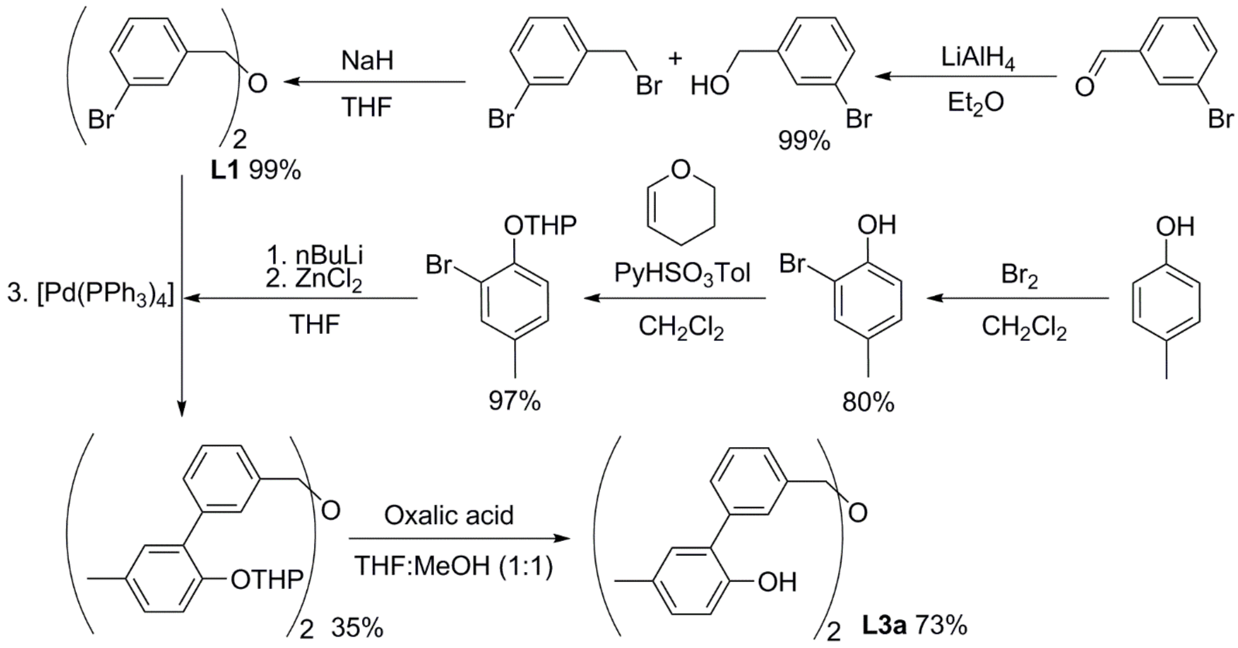
Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

^{19}F NMR Study of Ligand Dynamics in Carboxylate-Bridged Diiron(II) Complexes Supported by a Macrocyclic Ligand

Mikael A. Minier and Stephen J. Lippard*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
E-mail: lippard@mit.edu

Table of Contents Page(s)



Scheme S1: Original synthesis of H_2PIM.

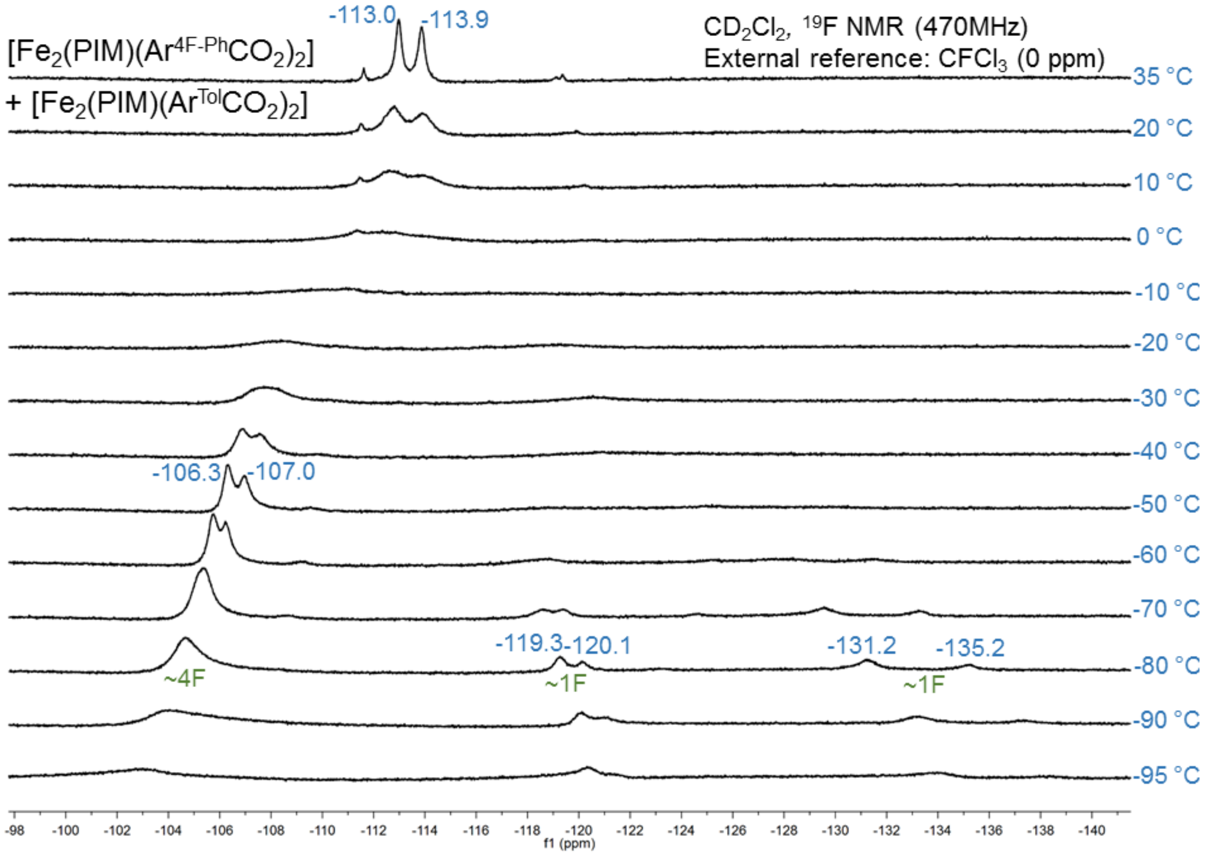


Figure S1: VT ^{19}F-NMR (470 MHz) of a mixture of **2** and **10** in CD_2Cl_2. Minor impurities are observed at higher temperatures.

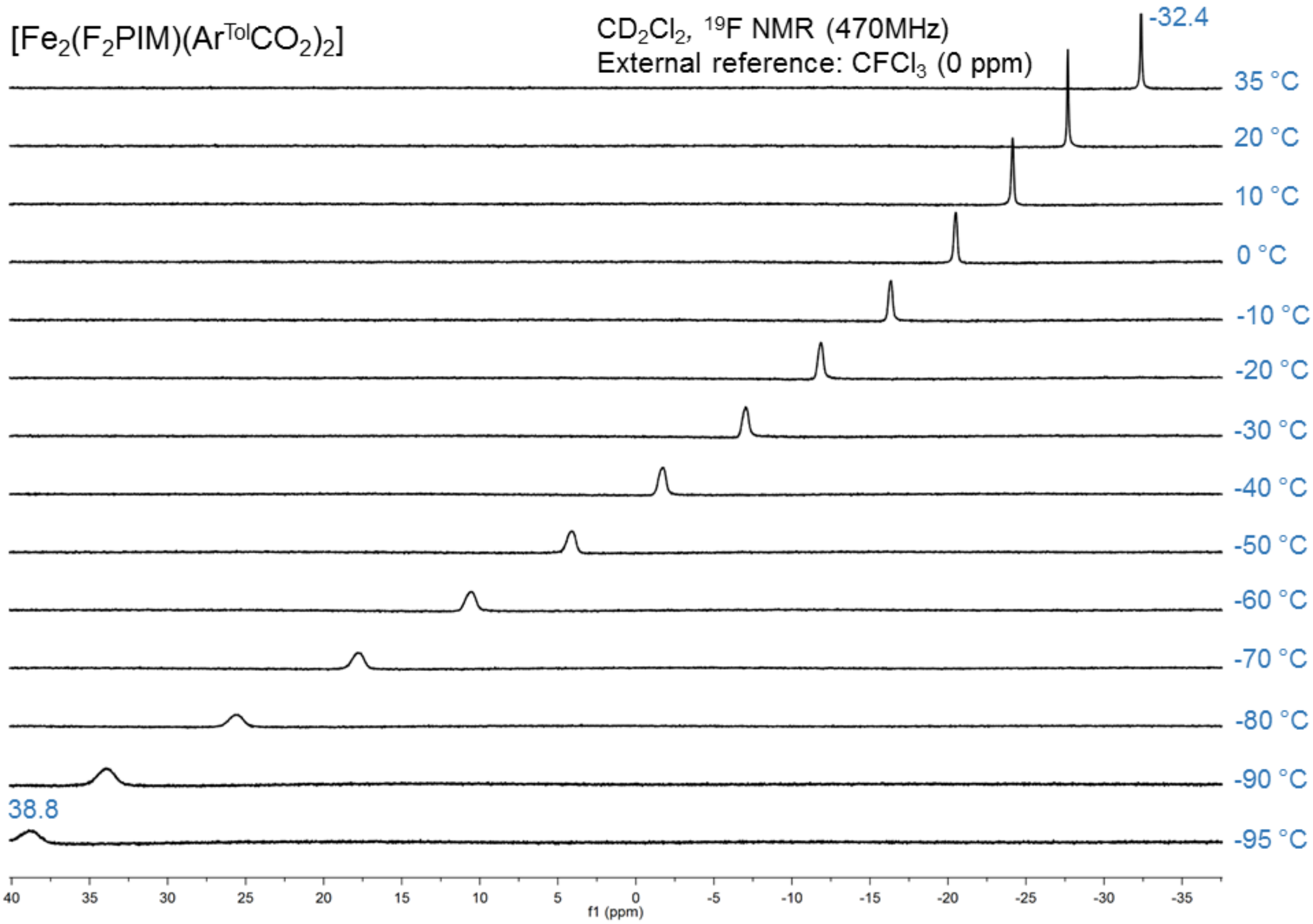


Figure S2: VT ^{19}F-NMR (470 MHz) of **11** in CD$_2$Cl$_2$.

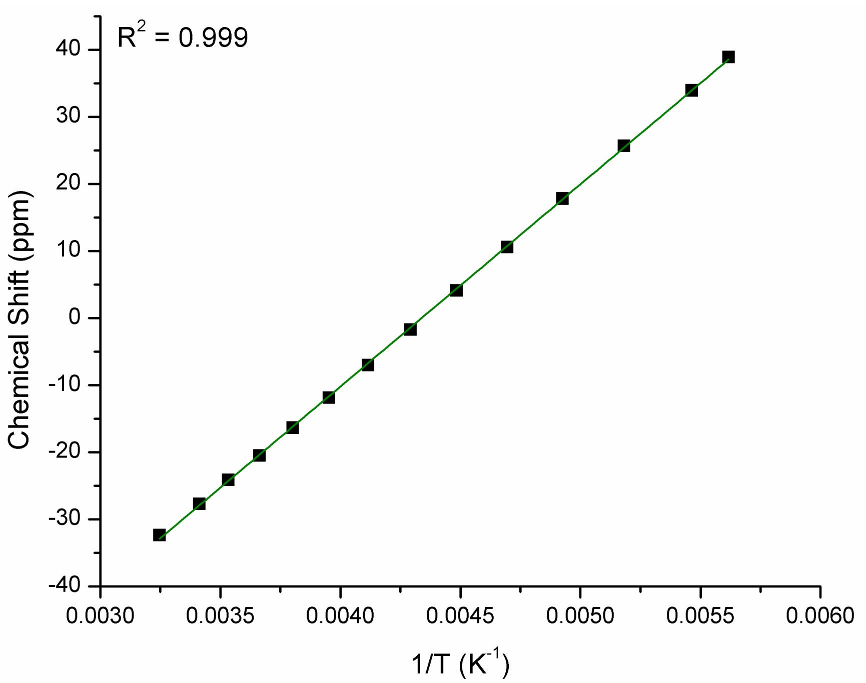


Figure S3: Linear dependence of the chemical shift of the fluorine resonance in **11** with inverse temperature, showing Curie behavior.

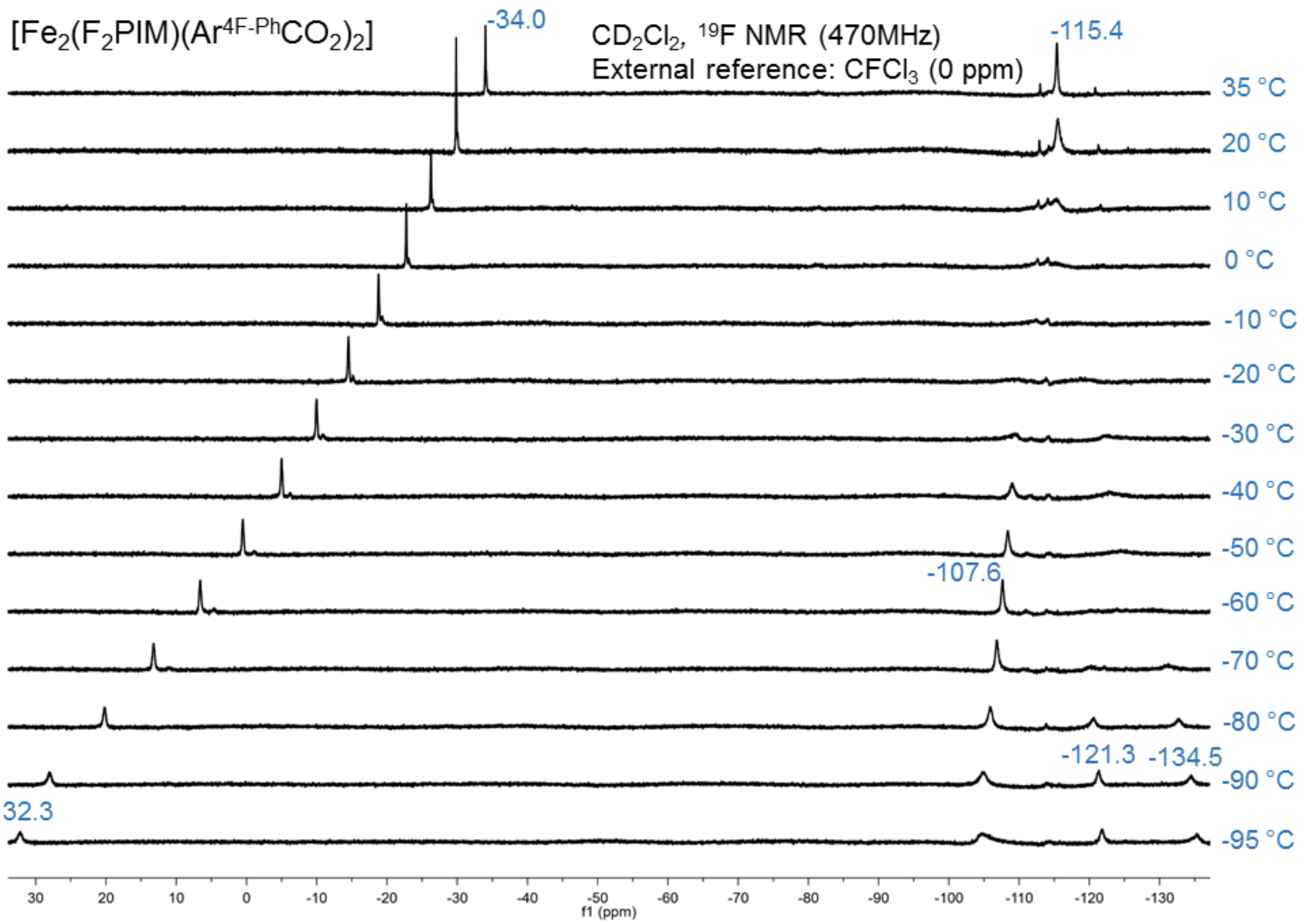


Figure S4: VT ^{19}F-NMR (470 MHz) of **12** in CD_2Cl_2. Minor impurities are observed at higher temperatures.

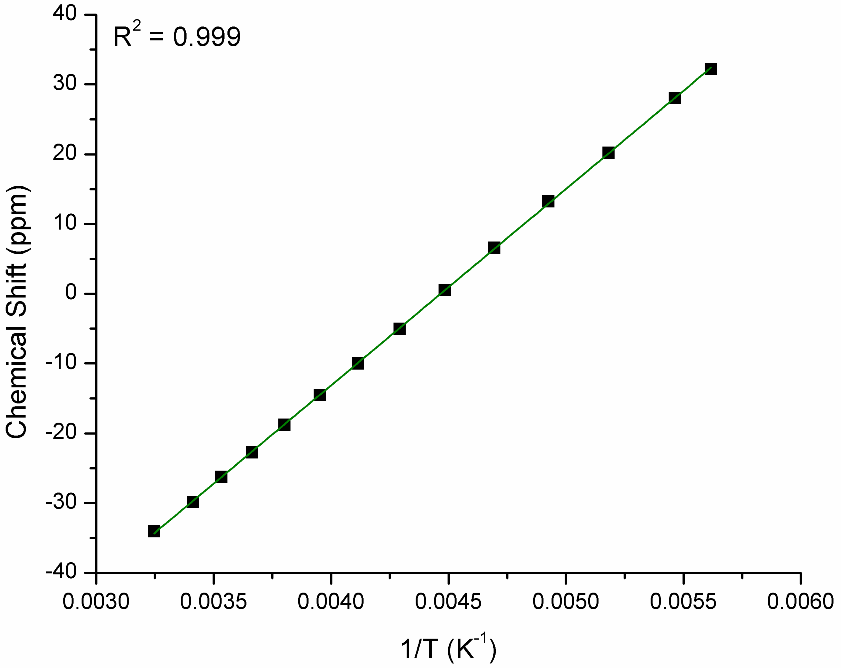


Figure S5: Linear dependence of the chemical shift of the 4-fluorophenoxide fluorine resonance in **12** with inverse temperature, showing Curie behavior.

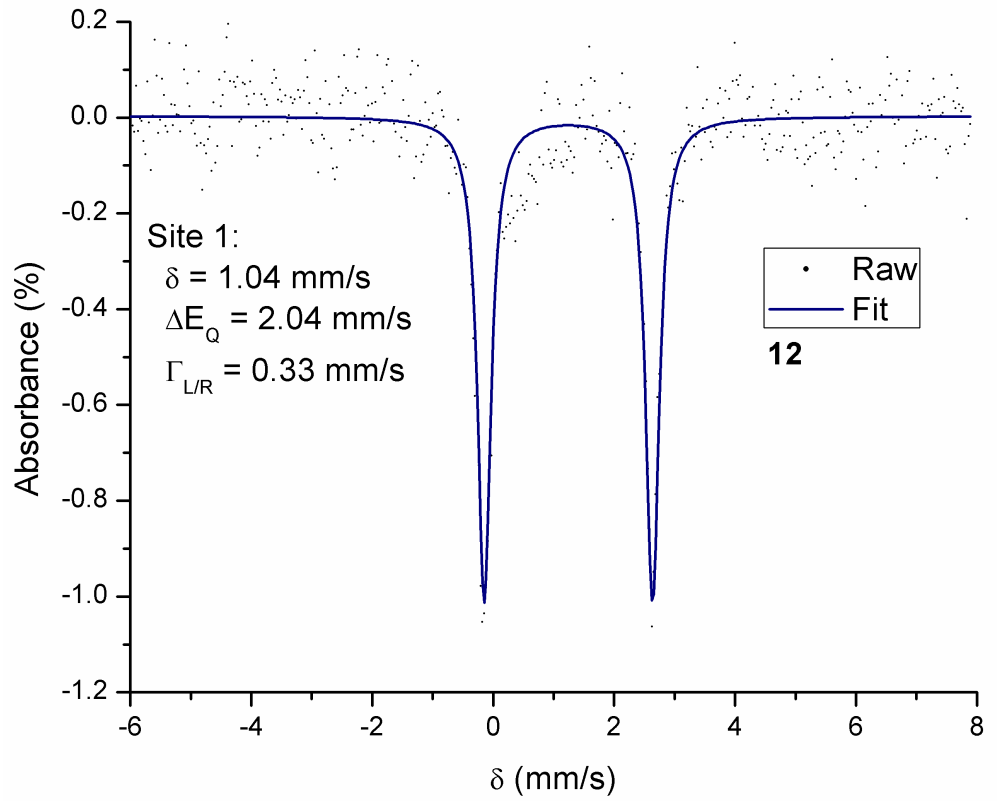


Figure S6: Mössbauer spectra of **12**.

Table S1: X-ray Data Collection and Refinement Parameters for **H_2PIM**, **H_2F_2PIM**, and **10**.

	H_2PIM	**H_2F_2PIM**	**10**
Empirical formula	$C_{42}H_{34}N_2O_5S\cdot(CH_2Cl_2)_{0.127}$ $(C_3H_6O)_{0.873}$	$C_{40}H_{28}F_2N_2O_5S\cdot(CHCl_3)_{1.063}$ $(C_6H_6)_{0.065}(C_5H_{10})_{0.125}$	$[Fe_2C_{80}H_{54}F_4N_2O_9S]$ $\cdot(CH_2Cl_2)_{1.223}$ $(C_5H_{12})_{0.281}$
Formula weight	740.25	825.64	1560.44
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 11.961(2) Å b = 14.415(3) Å c = 42.946(8) Å	a = 12.5668(11) Å b = 34.957(3) Å c = 18.1763(16) Å β = 90.0110(10) °	a = 19.2065(12) Å b = 13.5135(8) Å c = 27.8480(17) Å β = 99.2830(10) °
Volume (Å^3)	7404(2)	7984.9(12)	7133.2(8)
Z	8	8	4
Calculated density (g/mm^3)	1.328	1.374	1.422
Absorption coefficient (mm^{-1})	0.159	0.351	0.600
F(000)	3114	3389	3133
Crystal size (mm^3)	0.58 x 0.21 x 0.19	0.44 x 0.18 x 0.04	0.43 x 0.24 x 0.10
Θ range for data collection	1.49 to 27.31°	1.62 to 29.62°	1.68 to 29.44°
Index ranges	-15<=h<=15 -18<=k<=18 -55<=l<=55	-17<=h<=17 -48<=k<=48 -25<=l<=25	-25<=h<=26 -18<=k<=18 -38<=l<=38
Reflections collected	133257	172747	145354
Independent reflections	16578 [R(int) = 0.0893]	22377 [R(int) = 0.0664]	19473 [R(int) = 0.0513]
Completeness to Θ	99.4%	100.0%	100.0%
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical
Max. and min. transition	0.7455 and 0.6159	0.7370 and 0.6546	0.7459 and 0.6856
Data / restraints / parameters	16578 / 44 / 1005	22377 / 609 / 1229	19473 / 180 / 1014
Goodness-of-fit on F^2	1.104	1.085	1.154
Final R indicies [I>2σ (I)]	R1 = 0.0721, wR2 = 0.1937	R1 = 0.0606, wR2 = 0.1561	R1 = 0.0759, wR2 = 0.2106
R indicies (all data)	R1 = 0.0827, wR2 = 0.2000	R1 = 0.0852, wR2 = 0.1703	R1 = 0.0967, wR2 = 0.2224
Flack parameter	0.02(9)		
BASF value		0.18261(74)	
Largest diff. peak and hole (eÅ^3)	0.976 and -0.504	0.943 and -0.729	1.741 and -1.583

Table S2: X-ray Data Collection and Refinement Parameters for **11** and **12**.

	11	**12**
Empirical formula	$[Fe_2C_{82}H_{60}F_2N_2O_9S]$ $\cdot(CH_2Cl_2)_2(C_5H_{12})_{0.5}$	$[Fe_2C_{78}H_{48}F_6N_2O_9S]\cdot(CH_2Cl_2)_2$
Formula weight	1586.95	1584.80
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P$\bar{1}$
Unit cell dimensions	a = 29.279(3) Å b = 15.9399(16) Å c = 34.344(4) Å β = 114.405(2) °	a = 14.0897(9) Å b = 14.7198(9) Å c = 17.4942(11) Å α = 100.7350(10) ° β = 102.7140(10) ° γ = 94.7000(10) °
Volume (Å^3)	14596(3)	3448.6(4)
Z	8	2
Calculated density (g/mm^3)	1.442	1.526
Absorption coefficient (mm^{-1})	0.637	0.685
F(000)	6541	1616
Crystal size (mm^3)	0.50 x 0.40 x 0.05	0.58 x 0.55 x 0.12
Θ range for data collection	1.49 to 29.61 °	1.67 to 29.54 °
Index ranges	-40<=h<=39 -22<=k<=21 -46<=l<=47	-19<=h<=19 -20<=k<=20 -23<=l<=24
Reflections collected	142048	70296
Independent reflections	20367 [R(int) = 0.0601]	18887 [R(int) = 0.0419]
Completeness to Θ	100.0%	99.9%
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transition	0.7459 and 0.6380	0.7459 and 0.6232
Data / restraints / parameters	20367 / 198 / 1043	18887 / 308 / 999
Goodness-of-fit on F^2	1.039	1.045
Final R indicies [I>2σ (I)]	R1 = 0.0680, wR2 = 0.1743	R1 = 0.0667, wR2 = 0.1789
R indicies (all data)	R1 = 0.1001, wR2 = 0.2000	R1 = 0.1137, wR2 = 0.2142
Largest diff. peak and hole (eÅ^3)	1.458 and -1.742	1.364 and -1.821

[a] Hydrogen atoms were not modeled at all positions (see refinement details).

Refinement details for H_2PIM: Crystals of H_2PIM grew from an acetone solution of waste dizinc PIM complexes. H_2PIM crystallizes in the space group $P2_12_12_1$ and a Flack parameter of 0.02 confirms the absolute configuration of the crystal structure model. A minor inversion twin was modeled and refined to a 1.6% contribution. Two molecules of H_2PIM are contained within the asymmetric unit. Both molecules conform such that the diphenyl sulfone unit and dibenzyl ether unit conform in opposite directions (Figure S8, right). The two molecules differ by the solvent occupancy within the cavity of the macrocycle. Molecule 1 contains an acetone molecule with a C=O unit pointing towards the sulfone. Molecule 2 also contains an acetone, but is disordered between the acetone (74.6%) and a CH_2Cl_2 (25.4%). Standard uncertainties for the anisotropic displacement parameter (ADP) restraints SIMU and DELU for the acetone were set to 0.01 and 0.0025 for this disorder. The CH_2Cl_2 ADPs were set to be equal. The CH_2Cl_2 C-Cl and Cl-Cl bond distances were fixed to ideal values of 1.77 and 2.93 Å, respectively. The two acetone molecules 1,2 and 1,3 distances were restrained to be similar. The molecule 1's acetone methyl hydrogens were found on one side and disordered on the other. For molecule 2's acetone, the methyl hydrogens were modeled to be disordered. The methyl hydrogen atoms on both molecules were found. Intramolecular OH---N hydrogen bonds within the salicylideneimine units were found with O---N distances of 2.588(5), 2.588(2), 2.574(5), and 2.591(5) Å. H2PIM molecules stack in the crystal lattice to form porous columns along a (Figure S9).

Figure S7: Crystal structure of H_2PIM (left) and a second view (right), which highlights the conformation of the diphenylsulfone and dibenzyl ether units. Ellipsoids are drawn at 50% and solvent molecules and the second molecule in the asymmetric unit have been left out for clarity.

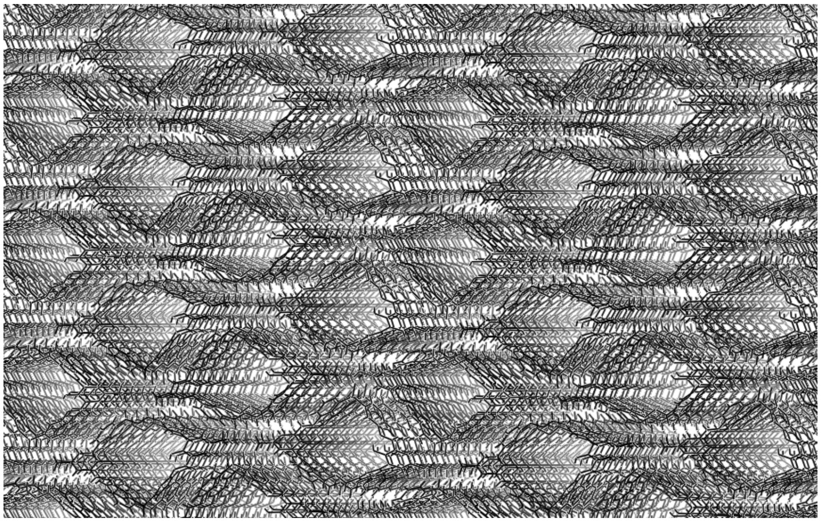


Figure S8: Porous columns of stacked H_2PIM molecules along a in the crystal lattice. Solvent molecules were removed for clarity.

Refinement details for H_2F_2PIM: Crystals of H_2F_2PIM were obtained by layering pentane over a solution of H_2F_2PIM in benzene and chloroform. The space group of the crystals is $P2_1/c$ with β very close to 90 ° (90.0110(10) °). As such, the crystals were found to be pseudomerohedrally twinned (twin law = -1 0 0 0 -1 0 0 0 1) with a minor twin component of 18.3%. Like H_2PIM, two molecules are contained in the asymmetric unit and OH hydrogens were found with OH---N intramolecular hydrogen bonding (O---N dist = 2.576(3) 2.593(3), 2.615(3),and 2.593(3) Å). The cavity of the macrocycles are filled with $CHCl_3$ molecules disordered across two positions. The major component percentages of these disorders are 71.2% and 83.2% in each molecule. C-H---O non-standard hydrogen bonds may aid in the preferred orientation of the 83.2% occupied $CHCl_3$ as suggested by the metric parameters of that contact (C---O dist = 2.931(4), C-H---O = 2.264, C-H---O ∠ = 123.1 °). In one molecule, a benzyl linker $-C_6H_4-$ ring is disordered across two positions with a major component refining to 60.8%. A complicated free solvent disorder near an inversion center was found and modeled to a pentane (24.9%), benzene (13.0%), and $CHCl_3$ (12.5%). Bond distance and angle restraints were applied on all solvent molecules. Bond distances of the two $CHCl_3$ molecules were restrained to be similar. Pentane 1,2 and 1,3 distances were fixed to ideal values of 1.54 and 2.52 Å and $CHCl_3$ C-Cl and Cl-Cl distances were fixed to 1.767 and 2.90 Å, respectively. The benzene 1,2 and 1,3 distances were fixed to be 1.40 and 2.42 Å, respectively, and 6 atoms were forced to be lie in the same plane. The ADPs of disordered atoms were restrained to be similar using SIMU and DELU with non-default standard uncertainties set between 0.05 and 0.001. For the benzyl linker disorder, bond distances were restrained to be similar and for ADPs, SIMU and DELU commands were applied. In addition, the ADPs of C115 and 15b were set to be the same. The conformation of the macrocycle is the same as that in the structure of H_2PIM.

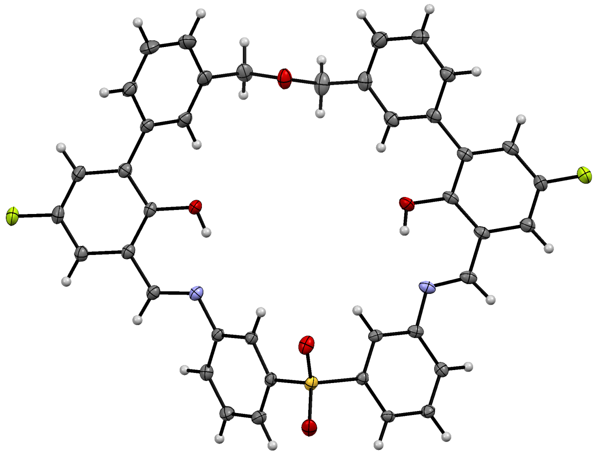
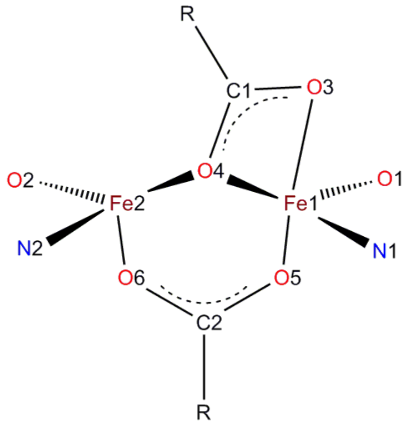


Figure S9: Crystal structure of H_2F_2PIM with ellipsoids drawn at 50% and solvent molecules and the second molecule in the asymmetric unit left out for clarity.

Table S1: Selected Bond Distances and Angles for Compound **10**.



Bond Distances (Å)[a]			
Fe1---Fe2	3.5680(7)	Fe1-O3	2.535(2)
Fe1-O1	1.881(2)	Fe2-O2	1.877(2)
Fe1-N1	2.051(3)	Fe2-N2	2.032(3)
Fe1-O4	2.043(2)	Fe2-O4	2.055(2)
Fe1-O5	2.026(2)	Fe2-O6	1.973(2)
Bond Angles (°)[a]			
O1-Fe1-N1	91.3(1)	O2-Fe2-N2	93.1(1)
O1-Fe1-O3	92.14(9)	O2-Fe2-O4	108.7(1)
O1-Fe1-O4	135.6(1)	O2-Fe2-O6	124.8(1)
O1-Fe1-O5	95.3(1)	N2-Fe2-O4	121.2(1)
N1-Fe1-O3	105.5(1)	N2-Fe2-O6	116.8(1)
N1-Fe1-O4	124.4(1)	O4-Fe2-O6	94.5(1)
N1-Fe1-O5	110.6(1)	Fe1-O4-Fe2	121.0(1)
O3-Fe1-O4	56.10(8)	Fe1-O4-C1	102.2(2)
O3-Fe1-O5	142.88(9)	Fe2-O4-C1	132.9(2)
O4-Fe1-O5	95.2(1)		

[a] The number scheme used matches the cartoon above and the numbers are not necessarily the numbers assigned in the X-ray structure.

*Refinement details for **10**:* Complex **10** crystallizes in P2$_1$/c with a free CH_2Cl_2 in the lattice as well as a three part solvent disorder near an inversion center consisting of a pentane (28.1%) and two CH_2Cl_2 molecules (11.4 and 10.8%). The disordered solvent molecule 1,2 and 1,3 distances were fixed to ideal values and the ADPs were restrained to be similar using SIMU and DELU commands with standard uncertainties set to 0.005. No hydrogen atoms were modeled for the three-part disorder. A residual electron density peak of 1.741 eÅ^3 remains in close proximity to a disordered CH_2Cl_2 chlorine atom. The non-disordered CH_2Cl_2 sits close by to an inversion center and likely plays a significant role in packing as suggested by a network of close contacts (Figure S11).

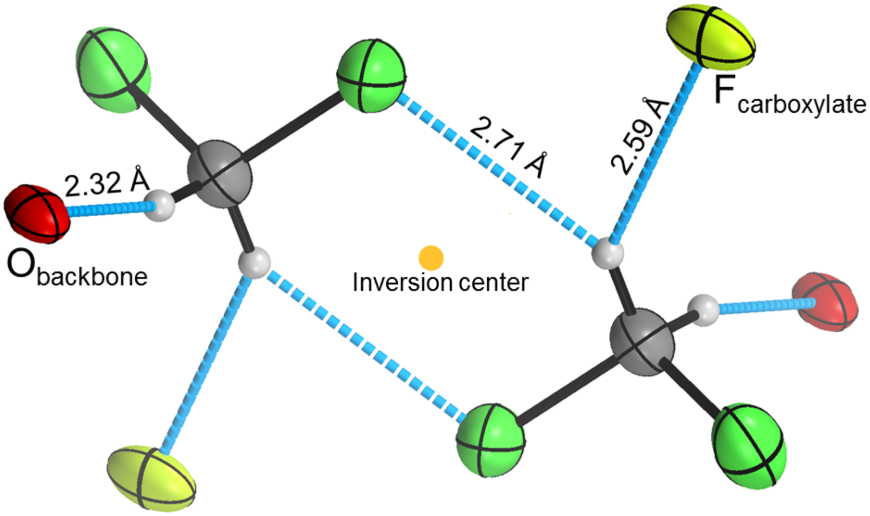
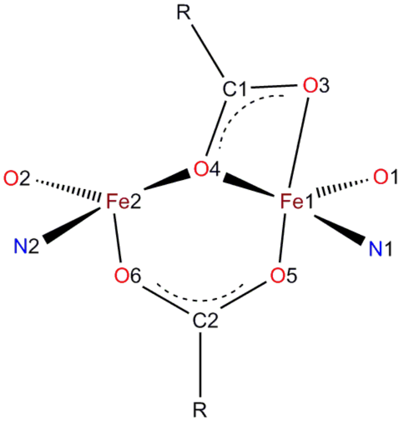


Figure S10: Short contacts about an inversion center in the lattice of the crystals of **10** that may be important for packing.

Table S5: Selected Bond Distances and Angles for Compound **11**.



Bond Distances (Å)[a]			
Fe1---Fe2	3.5648(8)	Fe1-O3	2.443(2)
Fe1-O1	1.883(3)	Fe2-O2	1.886(3)
Fe1-N1	2.042(3)	Fe2-N2	2.031(3)

Fe1-O4	2.062(2)	Fe2-O4	2.038(2)
Fe1-O5	2.028(2)	Fe2-O6	1.991(2)
	Bond Angles (°)[a]		
O1-Fe1-N1	91.8(1)	O2-Fe2-N2	93.1(1)
O1-Fe1-O3	94.9(1)	O2-Fe2-O4	111.6(1)
O1-Fe1-O4	138.2(1)	O2-Fe2-O6	123.3(1)
O1-Fe1-O5	96.1(1)	N2-Fe2-O4	116.6(1)
N1-Fe1-O3	93.3(1)	N2-Fe2-O6	113.0(1)
N1-Fe1-O4	118.0(1)	O4-Fe2-O6	100.4(1)
N1-Fe1-O5	122.4(1)	Fe1-O4-Fe2	120.8(1)
O3-Fe1-O4	57.41(9)	Fe1-O4-C1	98.7(2)
O3-Fe1-O5	142.2(1)	Fe2-O4-C1	129.9(2)
O4-Fe1-O5	91.7(1)		

[a] The number scheme used matches the cartoon above and the numbers are not necessarily the numbers assigned in the X-ray structure.

*Refinement details for **11**:* Complex **11** crystallizes in C2/c and the diiron complex refined without any special treatment, however a few solvent molecules were present in the lattice. At one site by a glide plane in the ac plane, a CH_2Cl_2 molecule (45.8%) is disordered with a pentane that lies across an inversion center on the glide plane. Thus, the pentane (54.2%) exists in two parts (27.1% each) related to each other by the inversion center. A depiction of the disorder can be found in Figure S12. The pentane was modeled by fixing 1,2 and 1,3 distances to idealized values and ADPs fixed to be similar. The CH_2Cl_2 distances were restrained to be similar to the other CH_2Cl_2 molecules in the lattice. Another CH_2Cl_2 molecule was found to sit on a 2-fold axis along b and was modeled accordingly using the PART -1 command. This CH_2Cl_2 molecule packs between two fluorine atoms on two separate macrocycles across the 2-fold axis. A disordered CH_2Cl_2 molecule was found in a general position and was modeled to a two part disorder with the main component refining to 58.5% occupancy. The ADPs of the atoms in this disorder were fixed to be the same. A high residual electron density peak of 1.458 eÅ^3 remains less than 0.9 Å from a Cl atom in this disorder. In terms of packing interactions, a π-π stacking interaction is present between two molecules of **11** across an inversion center.

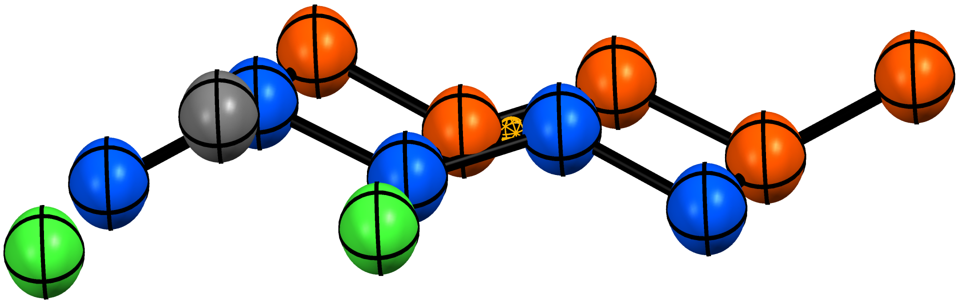


Figure S11: Three part disorder in the crystal structure of **11** involving a CH_2Cl_2 and a pentane disordered at an inversion center (blue and orange). The inversion center is colored yellow.

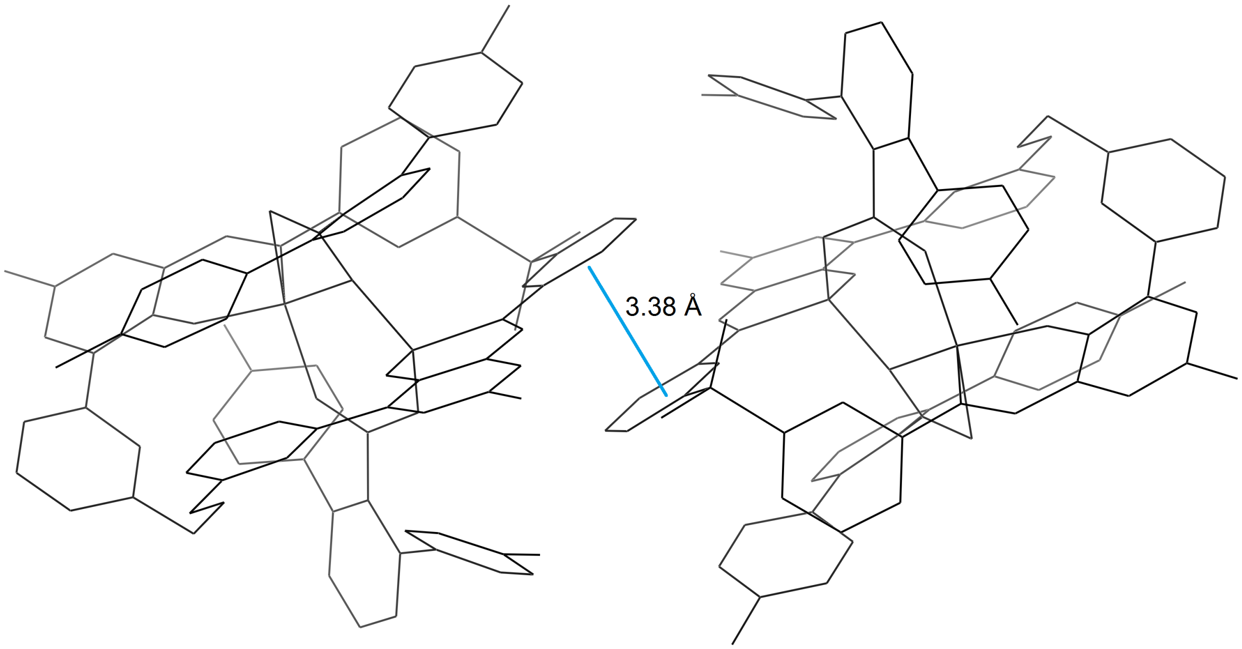
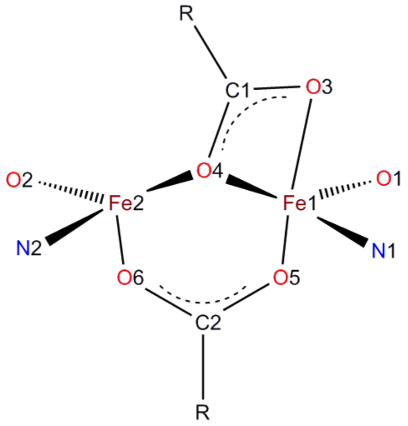


Figure S12: The π-π stacking interaction between molecules of **11**.

Table S6: Selected Bond Distances and Angles for Compound **12**.



Bond Distances (Å)^{a}			
Fe1---Fe2	3.6387 (6)	Fe1-O3	2.348(3)
Fe1-O1	1.900(3)	Fe2-O2	1.888(3)
Fe1-N1	2.054(3)	Fe2-N2	2.024(3)
Fe1-O4	2.103(2)	Fe2-O4	2.039(2)
Fe1-O5	2.048(3)	Fe2-O6	1.955(3)
Bond Angles (°)^{a}			
O1-Fe1-N1	90.4(1)	O2-Fe2-N2	94.9(1)
O1-Fe1-O3	97.4(1)	O2-Fe2-O4	104.0(1)
O1-Fe1-O4	141.8(1)	O2-Fe2-O6	129.8(1)
O1-Fe1-O5	97.9(1)	N2-Fe2-O4	117.8(1)
N1-Fe1-O3	96.5(1)	N2-Fe2-O6	114.3(1)
N1-Fe1-O4	119.1(1)	O4-Fe2-O6	97.3(1)
N1-Fe1-O5	114.0(1)	Fe1-O4-Fe2	122.9(1)

O3-Fe1-O4	58.3(1)	Fe1-O4-C1	95.4(2)
O3-Fe1-O5	145.6(1)	Fe2-O4-C1	133.8(2)
O4-Fe1-O5	91.6(1)		

[a] The number scheme used matches the cartoon above and the numbers are not necessarily the numbers assigned in the X-ray structure.

*Refinement details for **12**:* Complex **12** crystallizes with two free CH_2Cl_2 molecules, one of which was modeled to with no disorder and the other which was disordered across two positions (main component = 55.7%). The 1,2 and 1,3 distances in the disordered CH_2Cl_2 were restrained to be similar and the ADPs were fixed to be equal. One 4-fluorophenyl group of an $Ar^{4F\text{-}Ph}$- wing was modeled to a two part disorder corresponding to an aryl-aryl C-C bond rotation. The main component refined to a final occupancy of 50.9%. The 1,2 and 1,3 distances of the 4-fluorophenyl groups were restrained to be similar and the ADPs were restrained to be similar using SIMU and DELU with standard uncertainties set at 0.01 and 0.0025, respectively. As with **10** and **11**, CH_2Cl_2 molecules appear to be involved in packing interactions. The non-disordered CH_2Cl_2 molecule has close contacts with two fluorine atoms and one oxygen atom between two diiron complexes in the lattice.

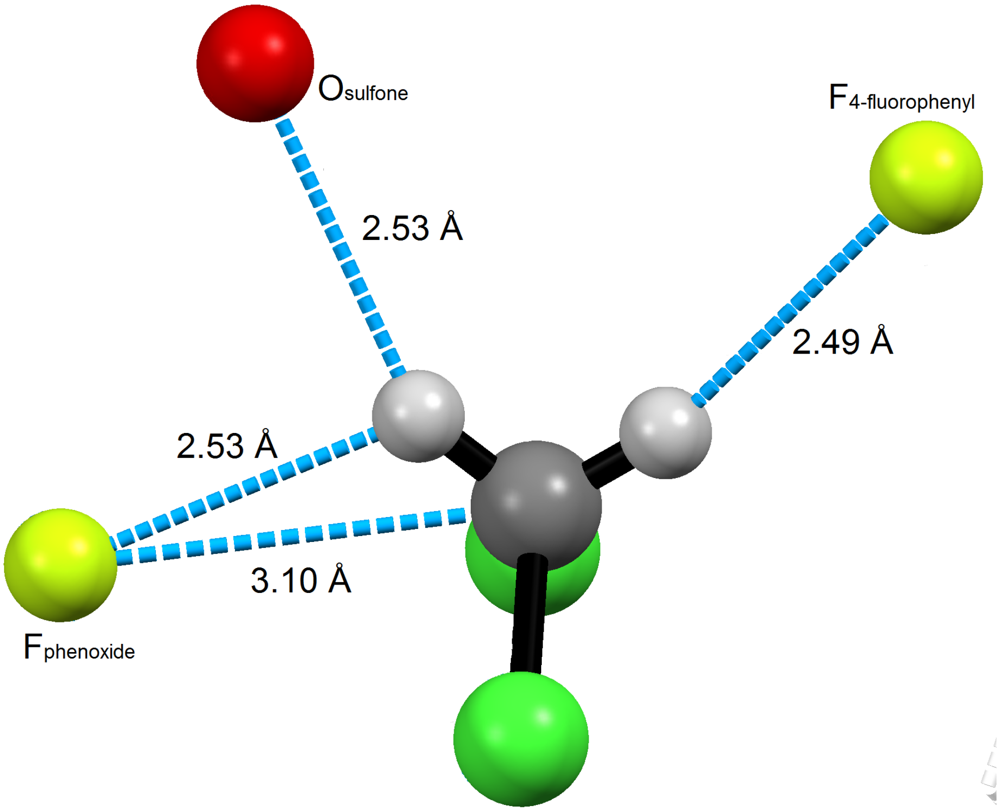
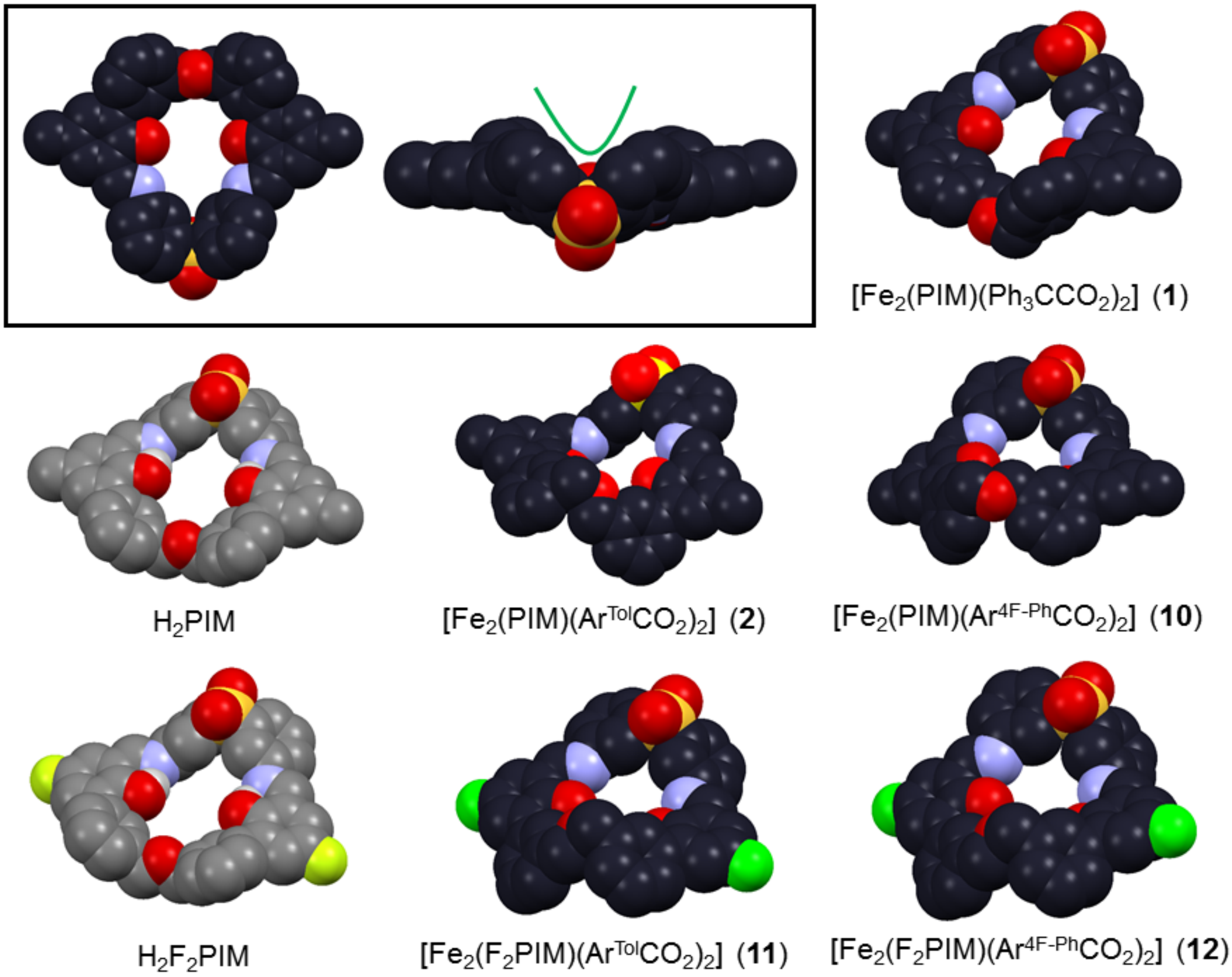


Figure S13: Short contacts in the lattice of the crystals of **12** that may be important for packing.



$[Fe_2(PIM)(Ph_3CCO_2)_2]$ (**1**)

H_2PIM

$[Fe_2(PIM)(Ar^{Tol}CO_2)_2]$ (**2**)

$[Fe_2(PIM)(Ar^{4F\text{-}Ph}CO_2)_2]$ (**10**)

H_2F_2PIM

$[Fe_2(F_2PIM)(Ar^{Tol}CO_2)_2]$ (**11**)

$[Fe_2(F_2PIM)(Ar^{4F\text{-}Ph}CO_2)_2]$ (**12**)

Figure S14: Space-filling models of the PIM and F_2PIM macrocycles showing the conformation in the solid-state. The inset shows the wedge-shape (curved green line) that is formed from the conformation of the diphenylsulfone linker. Structures with light grey carbons correspond to the free ligands and structures with dark grey carbons correspond to the ligands bound to iron. The iron atoms and carboxylate ligands are removed for clarity.

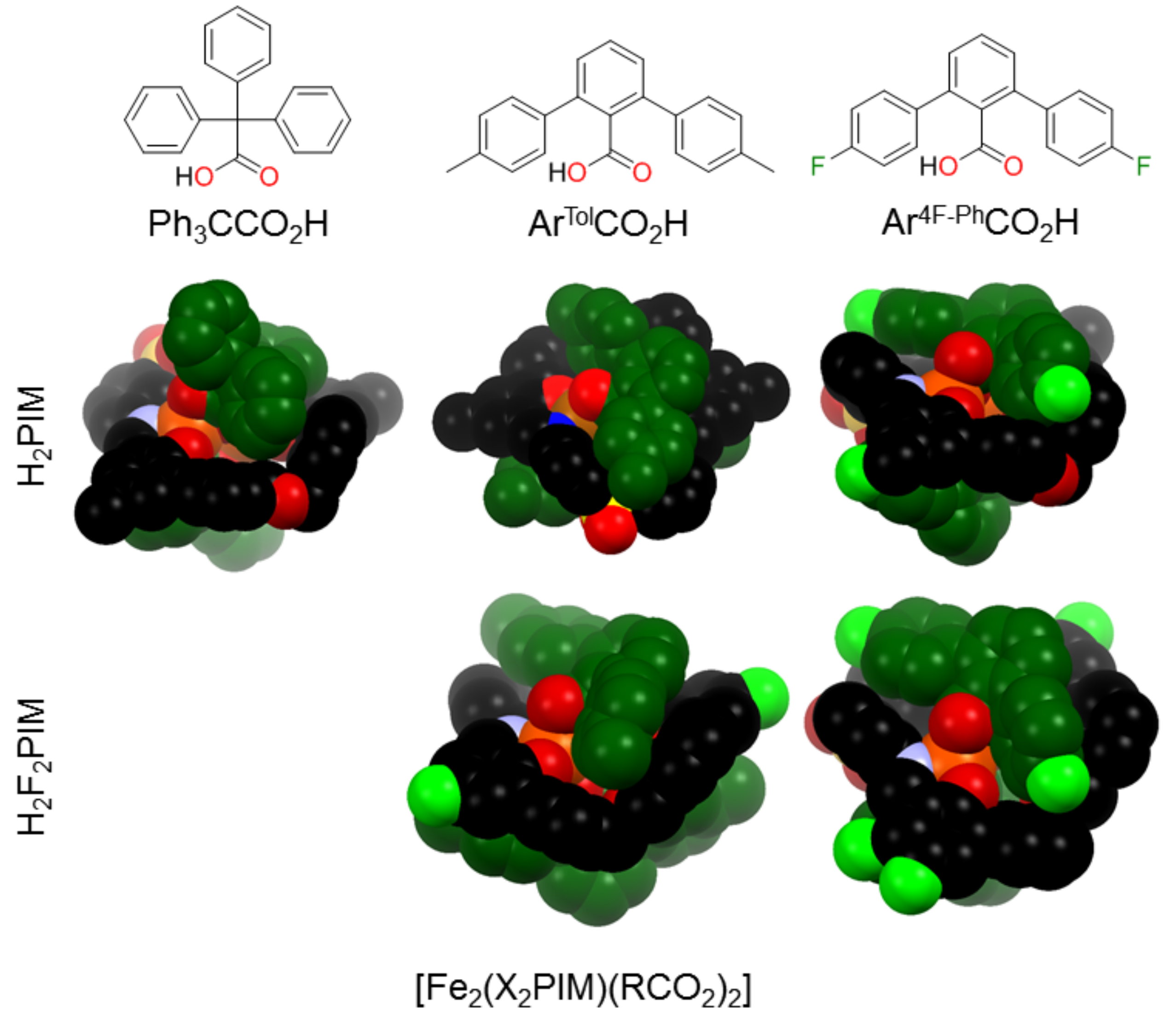


Figure S15: Space-filling models of **1-2**, and **10-12**. The models with *m*-terphenyl groups show how the *m*-terphenyl group of the μ-η^1:η^2 bridging carboxylate fits along the cavity of the wedge conformation of the macrocycle. In these cases, the *m*-terphenyl group of the μ-η^1:η^1 bridging carboxylate lies perpendicular to the *m*-terphenyl group of the μ-η^1:η^2 bridging carboxylate. The complex with the trityl carboxylate does not follow these trends, likely do to differences in steric bulk.