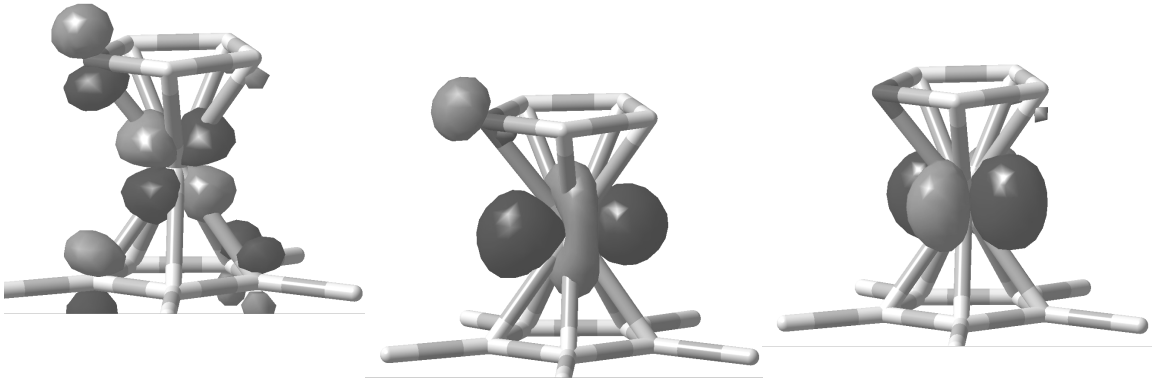
Supporting Information: atomic coordinates of optimized geometries, absolute total energies for azaferrocenes, UV-Vis spectra of III, deconvoluted photoelectron spectra, X-ray diffraction data for II.

(x,y,z, in Angstroms for fully optimized geometry; torsional angles in deg; total conformer energies at B3LYP/6-31G* level in a.u.)

(I) PMAF NIMAG=0

	x	y	z
c	2.158776	1.102063	0.340347
h	2.171010	2.104431	0.747777
c	2.164780	0.707936	-1.026697
h	2.168939	1.359304	-1.890470
c	2.164393	-0.716635	-1.021716
h	2.168175	-1.373984	-1.880932
c	2.158253	-1.101216	0.348046
h	2.170135	-2.100745	0.762400
c	-1.114033	0.726920	1.015928
c	-1.114398	-0.709022	1.028241
c	-1.162527	-1.164540	-0.331199
c	-1.187846	-0.009923	-1.185211
c	-1.161966	1.159089	-0.351124
c	-1.099441	1.612089	2.229870
h	-0.509804	1.172463	3.040168
h	-0.670339	2.594891	2.009910
h	-2.117159	1.776501	2.610017
c	-1.099437	-1.572987	2.257326
h	-0.501069	-1.124219	3.056145
h	-2.116053	-1.722548	2.646424
h	-0.679737	-2.562884	2.051774
c	-1.237783	-2.594841	-0.785889
h	-0.759531	-2.736808	-1.760588
h	-0.749365	-3.272897	-0.078971
h	-2.282412	-2.921332	-0.883746
c	-1.300145	-0.022490	-2.683848
h	-0.828676	-0.909655	-3.119010
h	-2.352576	-0.023047	-3.000226
h	-0.825101	0.855247	-3.133990
c	-1.235917	2.581436	-0.830314
h	-0.751811	3.271531	-0.132150
h	-0.752384	2.707273	-1.804624
h	-2.280241	2.905361	-0.939209
fe	0.495135	-0.000364	-0.022048
n	2.146889	0.003328	1.178566

total energy= -1863.3296157



LUMO HOMO HOMO-1

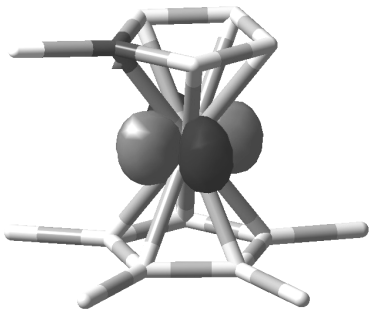
Frontier MO for PMAF. Hydrogen atoms are omitted for clarity.

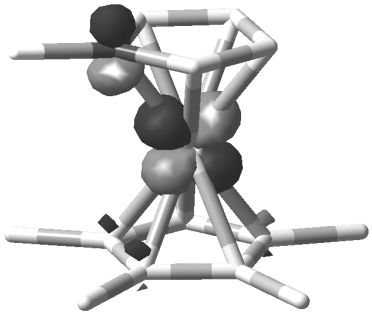
(IV) PMAF-BH3 NIMAG=0

	x	y	z
c	7.856985	2.703877	24.473780
h	7.507447	2.715098	25.495064
c	8.312704	1.633847	23.667771
h	8.432538	0.606128	23.980589
c	8.588943	2.179487	22.379562
h	8.961885	1.651448	21.513242
c	8.290413	3.560787	22.450293
h	8.322734	4.326479	21.690058
c	10.860992	4.066192	25.271066
c	11.130883	4.641817	23.982891
c	11.609524	3.599530	23.123351
c	11.633063	2.377183	23.876978
c	11.174218	2.668917	25.206243
c	10.382345	4.825096	26.475843
h	9.611824	5.554345	26.210481
h	9.954338	4.158013	27.230236
h	11.215474	5.363631	26.947526
c	10.979459	6.094978	23.634279
h	10.071134	6.520174	24.069723
h	11.838957	6.670330	24.004300
h	10.923657	6.247737	22.552304
c	12.058943	3.760040	21.698461
h	11.860614	2.861332	21.105254
h	11.555780	4.597896	21.206663

h	13.139313	3.952101	21.650144
c	12.128372	1.046064	23.385892
h	11.969337	0.923563	22.309787
h	13.206124	0.939045	23.570127
h	11.628584	0.213118	23.890703
c	11.090369	1.686705	26.340377
h	10.322952	1.970503	27.066759
h	10.855133	0.676996	25.988232
h	12.046459	1.630846	26.878177
b	7.219108	5.280312	24.187777
h	7.788444	6.136229	23.541097
h	6.035252	5.215256	23.922928
h	7.417362	5.369139	25.383007
fe	9.731951	3.139245	23.820515
n	7.839042	3.872010	23.724910

total energy= -1889.7322342



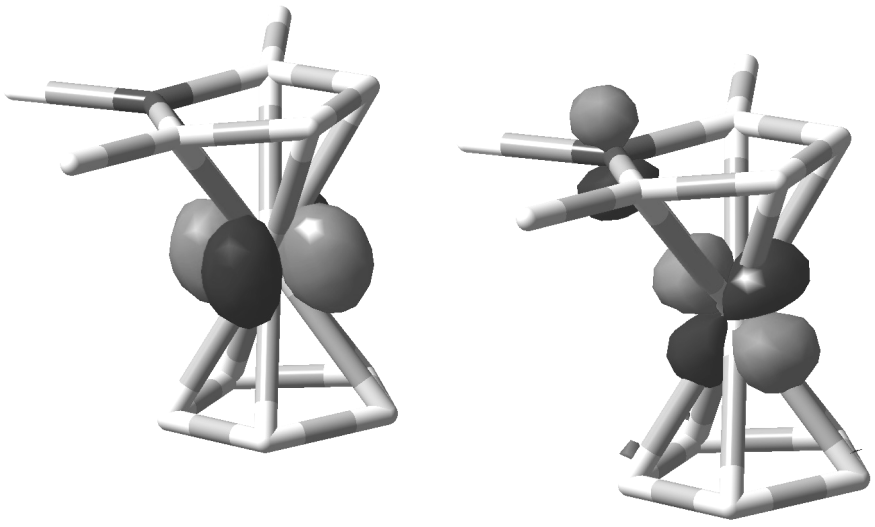


Frontier orbitals: HOMO LUMO

(II) DMAF-BH3 NIMAG=0

	x	y	z
c	1.705163	-1.078785	-1.138185
c	0.883341	-2.153644	-0.713966
h	0.353568	-2.832381	-1.368152
c	0.883587	-2.155574	0.708018
h	0.353927	-2.836034	1.360503
c	1.705465	-1.081789	1.134830
c	-0.470740	1.457204	-0.729883
c	-0.453060	1.476257	0.697577
c	-1.317692	0.443290	1.162590
c	-1.867898	-0.219932	0.024022
c	-1.347002	0.412558	-1.145198
n	3.261962	0.779896	0.000947
h	3.066707	1.429760	1.005337
h	4.355711	0.246440	0.000702
h	3.067531	1.432341	-1.001871
fe	0.186216	-0.345208	-0.000432
n	2.197518	-0.427160	-0.000884
h	-1.502334	0.185828	2.197686
h	-2.548785	-1.060969	0.043857
h	-1.558370	0.127611	-2.167909
h	0.118381	2.094522	-1.375640
h	0.153338	2.129206	1.310892
c	2.139330	-0.733069	-2.525778
h	3.176906	-1.050893	-2.683551
h	1.504955	-1.247635	-3.253720
h	2.100135	0.342506	-2.705340
c	2.139158	-0.738646	2.523239
h	1.508512	-1.259683	3.249819
h	3.178786	-1.050736	2.678746
h	2.093633	0.336016	2.707044

total energy= -1772.0466722



Frontier orbitals: HOMO LUMO

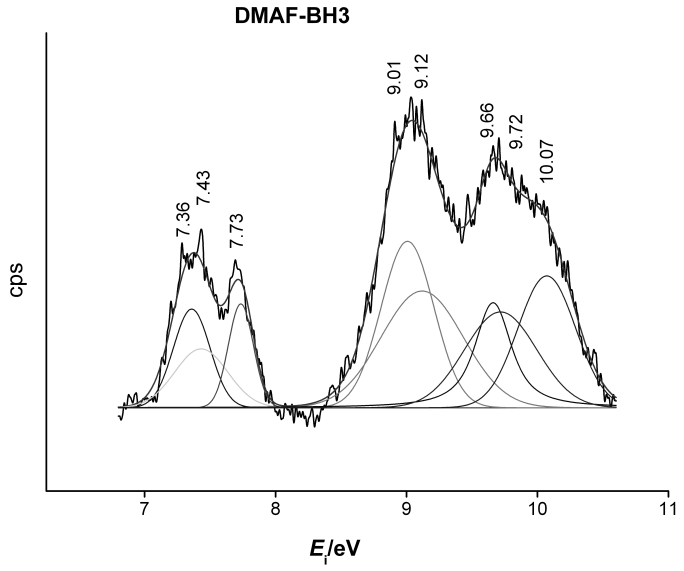


Fig. S1 Deconvoluted HeI spectrum of DMAF-BH3

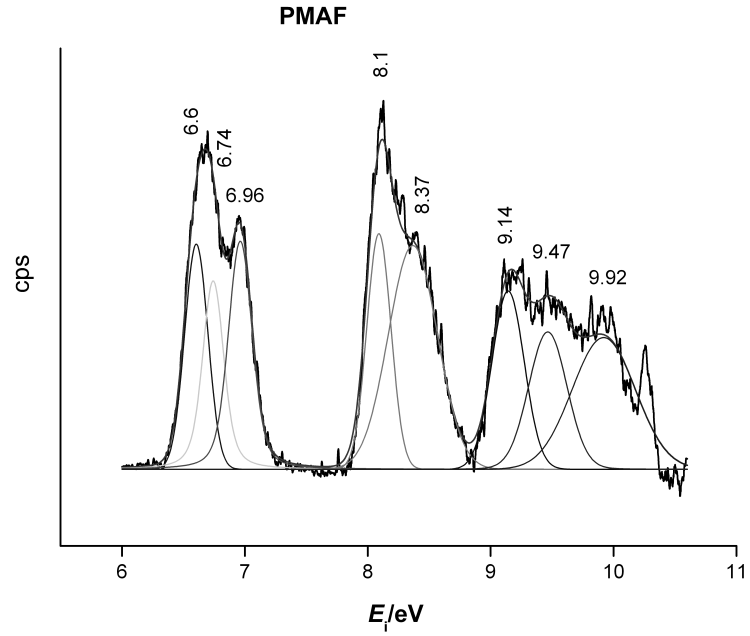


Fig. S2 Deconvoluted HeI spectrum of PMAF

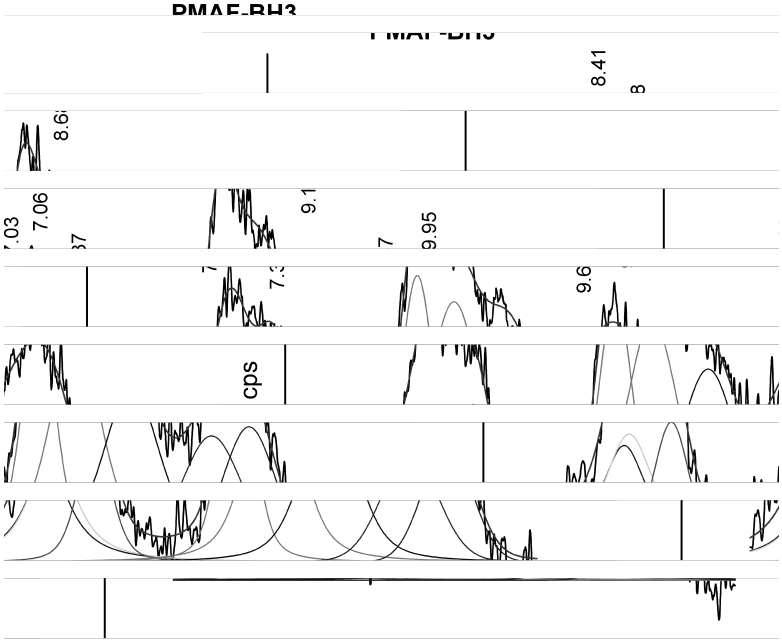


Fig. S3 Deconvoluted HeI spectrum of PMAF-BH3

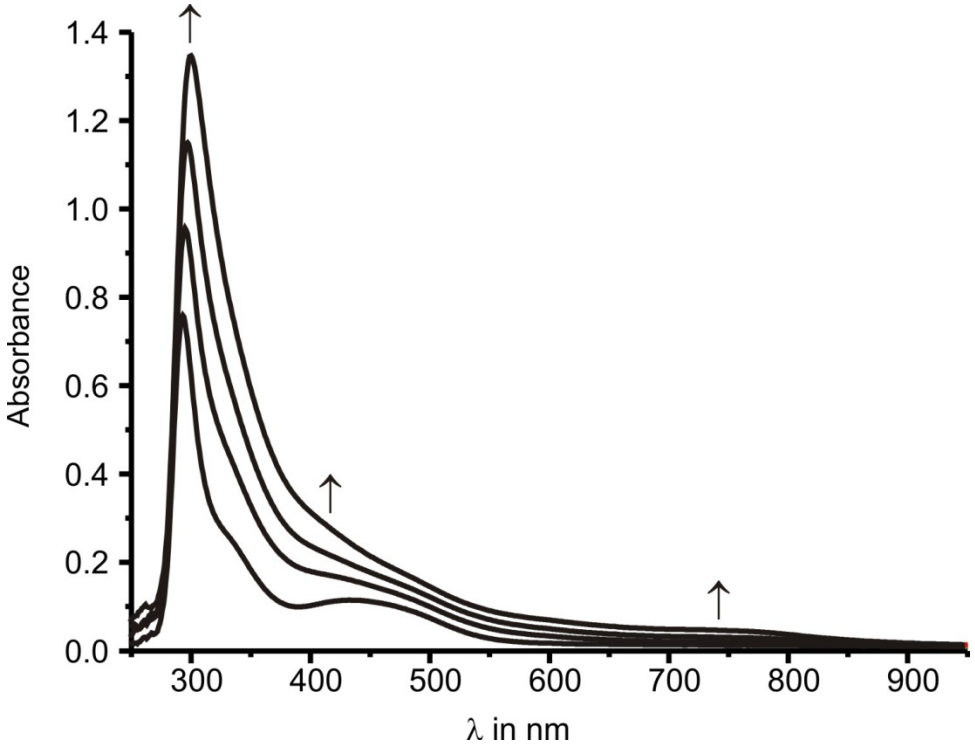


Fig. S4 Changes in the UV-Vis spectrum of **III** (PMAF) during oxidation in a OTTLE cell. Arrows indicate bands due to molecular ion. Conditions: DCE as solvent and $[NBu_4]^+$ $[B\{C_6H_3(CF_3\text{-}3,5)\}]^-$ as supporting electrolyte.

Table S1 Deconvolution parameters

Sample	Voigt profile parameters			
	CenterGrvty / eV	MaxHeight	AreaFit	FWHM / eV
DMAF-BH_3	7.36 7.43 7.73 9.01 9.12 9.66 9.72 10.07	0.12 0.07 0.12 0.20 0.14 0.13 0.12 0.16	0.046 0.035 0.035 0.091 0.093 0.080 0.072 0.085	0.33 0.48 0.22 0.47 0.74 0.33 0.65 0.52
PMAF	6.60 6.74 6.96 8.10 8.37 9.14 9.47 9.92	0.29 0.25 0.29 0.31 0.29 0.23 0.18 0.17	0.083 0.085 0.102 0.087 0.132 0.079 0.069 0.103	0.22 0.20 0.23 0.23 0.47 0.31 0.37 0.60
PMAF-BH_3	7.03 7.06 7.37 8.41 8.68 9.10 9.67 9.95	0.06 0.07 0.07 0.14 0.12 0.09 0.06 0.07	0.036 0.039 0.026 0.048 0.068 0.056 0.035 0.032	0.39 0.41 0.29 0.28 0.44 0.47 0.49 0.42

The fitting procedure was applied to regions of interest in the original spectra: for DMAF–BH_3 6.7 - 10.5 eV, for PMAF and PMAF–BH_3 6.5 - 10.5 eV region. The number of points used was 5000 per spectrum by interpolation. The spectra were smoothed by Savitzky-Golay filter, using local regression of 20 points by third-order polynomial. Baseline was subtracted from the original spectra, using exponential growth function (y = y0 + Ae^/(x/t0)) applied to 4 points, which represent local minima in each spectrum. Finally, each spectrum was fitted to 8 Voigt profile functions.
Initial parameters were selected according to theoretical predictions.

Table S2. Crystal data and structure refinement for DMAF-BH_3 (II)

Identification code	towson10	
Empirical formula	C11 H16 B Fe N	
Formula weight	228.91	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/m$	
Unit cell dimensions	a = 6.8884(4) Å	□= 90°
	b = 10.1248(5) Å	□= 100.8890(10)°
	c = 7.7647(4) Å	□ = 90°
Volume	531.79(5) $Å^3$	
Z	2	
Density (calculated)	1.430 g/cm^3	
Absorption coefficient	1.374 mm^{-1}	
F(000)	240	
Crystal size	0.28 x 0.28 x 0.20 mm^3	
Theta range for data collection	2.67 to 25.39°	
Index ranges	-8<=h<=8, -12<=k<=12, -9<=l<=9	
Reflections collected	4968	
Independent reflections	1040 [R(int) = 0.0139]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7707 and 0.6997	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	1040 / 0 / 111
Goodness-of-fit on F^2	1.145
Final R indices [I>2sigma(I)]	R1 = 0.0183, wR2 = 0.0508
R indices (all data)	R1 = 0.0187, wR2 = 0.0510
Largest diff. peak and hole	0.211 and -0.197 e $Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for towson10. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	831(1)	2500	3123(1)	25(1)
Fe(1')	5646(19)	2500	3085(16)	44(6)
N(1)	2700(2)	2500	1400(2)	25(1)
C(1)	2982(2)	14(2)	1748(2)	37(1)
C(2)	3034(2)	1374(2)	2467(2)	31(1)
C(3)	3578(2)	1803(2)	4227(2)	39(1)
C(4)	-2068(3)	2500	1828(3)	31(1)
C(5)	-1678(2)	1364(2)	2902(2)	34(1)
C(6)	-1035(2)	1799(2)	4658(2)	39(1)
B(1)	2240(3)	2500	-694(3)	29(1)

Table S4. Bond lengths [Å] and angles [°] for towson10.

Fe(1)-N(1)	2.0243(15)	N(1)-C(2)#1	1.4023(17)
Fe(1)-C(2)	2.0379(13)	N(1)-B(1)	1.597(2)
Fe(1)-C(2)#1	2.0379(13)	C(1)-C(2)	1.484(2)
Fe(1)-C(6)	2.0384(14)	C(1)-H(1C)	0.97(2)
Fe(1)-C(6)#1	2.0385(14)	C(1)-H(1B)	0.94(2)
Fe(1)-C(3)#1	2.0493(14)	C(1)-H(1A)	0.946(19)
Fe(1)-C(3)	2.0493(14)	C(2)-C(3)	1.415(2)
Fe(1)-C(5)	2.0559(14)	C(3)-C(3)#1	1.412(4)
Fe(1)-C(5)#1	2.0559(14)	C(3)-H(3)	0.879(19)
Fe(1)-C(4)	2.0591(19)	C(4)-C(5)#1	1.4159(19)
Fe(1')-C(3)	1.947(12)	C(4)-C(5)	1.4159(19)
Fe(1')-C(3)#1	1.947(12)	C(4)-Fe(1')#4	2.003(13)
Fe(1')-C(4)#2	2.003(13)	C(4)-H(4)	0.89(3)
Fe(1')-C(2)	2.107(11)	C(5)-C(6)	1.422(2)
Fe(1')-C(2)#1	2.107(11)	C(5)-Fe(1')#4	2.200(11)
Fe(1')-N(1)	2.197(13)	C(5)-H(5)	0.946(18)
Fe(1')-C(5)#2	2.200(11)	C(6)-C(6)#1	1.419(4)
Fe(1')-C(5)#3	2.200(11)	C(6)-Fe(1')#4	2.483(12)
Fe(1')-C(6)#2	2.483(12)	C(6)-H(6)	0.943(19)
Fe(1')-C(6)#3	2.483(12)	B(1)-H(1E)	1.10(2)
N(1)-C(2)	1.4022(17)	B(1)-H(1D)	1.08(3)

N(1)-Fe(1)-C(2)	40.38(4)	C(2)#1-Fe(1)-C(3)#1	40.50(6)
N(1)-Fe(1)-C(2)#1	40.39(4)	C(6)-Fe(1)-C(3)#1	120.65(6)
C(2)-Fe(1)-C(2)#1	68.01(8)	C(6)#1-Fe(1)-C(3)#1	105.66(6)
N(1)-Fe(1)-C(6)	159.46(5)	N(1)-Fe(1)-C(3)	67.92(6)
C(2)-Fe(1)-C(6)	122.21(6)	C(2)-Fe(1)-C(3)	40.50(6)
C(2)#1-Fe(1)-C(6)	157.27(6)	C(2)#1-Fe(1)-C(3)	67.98(6)
N(1)-Fe(1)-C(6)#1	159.46(5)	C(6)-Fe(1)-C(3)	105.66(6)
C(2)-Fe(1)-C(6)#1	157.27(6)	C(6)#1-Fe(1)-C(3)	120.65(6)
C(2)#1-Fe(1)-C(6)#1	122.21(6)	C(3)#1-Fe(1)-C(3)	40.31(11)
C(6)-Fe(1)-C(6)#1	40.74(10)	N(1)-Fe(1)-C(5)	125.05(5)
N(1)-Fe(1)-C(3)#1	67.92(6)	C(2)-Fe(1)-C(5)	108.68(6)
C(2)-Fe(1)-C(3)#1	67.98(6)	C(2)#1-Fe(1)-C(5)	161.05(6)

C(6)-Fe(1)-C(5)	40.64(6)	C(3)-Fe(1')-C(5)#2	122.3(2)
C(6)#1-Fe(1)-C(5)	68.32(6)	C(3)#1-Fe(1')-C(5)#2	155.9(6)
C(3)#1-Fe(1)-C(5)	157.34(7)	C(4)#2-Fe(1')-C(5)#2	39.0(2)
C(3)-Fe(1)-C(5)	122.51(7)	C(2)-Fe(1')-C(5)#2	113.11(15)
N(1)-Fe(1)-C(5)#1	125.05(5)	C(2)#1-Fe(1')-C(5)#2	163.3(6)
C(2)-Fe(1)-C(5)#1	161.05(6)	N(1)-Fe(1')-C(5)#2	130.7(4)
C(2)#1-Fe(1)-C(5)#1	108.68(6)	C(3)-Fe(1')-C(5)#3	155.9(6)
C(6)-Fe(1)-C(5)#1	68.32(6)	C(3)#1-Fe(1')-C(5)#3	122.3(2)
C(6)#1-Fe(1)-C(5)#1	40.64(6)	C(4)#2-Fe(1')-C(5)#3	39.0(2)
C(3)#1-Fe(1)-C(5)#1	122.51(7)	C(2)-Fe(1')-C(5)#3	163.3(6)
C(3)-Fe(1)-C(5)#1	157.34(7)	C(2)#1-Fe(1')-C(5)#3	113.11(15)
C(5)-Fe(1)-C(5)#1	68.01(9)	N(1)-Fe(1')-C(5)#3	130.7(4)
N(1)-Fe(1)-C(4)	110.88(7)	C(5)#2-Fe(1')-C(5)#3	63.0(4)
C(2)-Fe(1)-C(4)	125.25(6)	C(3)-Fe(1')-C(6)#2	110.9(4)
C(2)#1-Fe(1)-C(4)	125.25(6)	C(3)#1-Fe(1')-C(6)#2	124.4(6)
C(6)-Fe(1)-C(4)	67.98(7)	C(4)#2-Fe(1')-C(6)#2	60.3(3)
C(6)#1-Fe(1)-C(4)	67.98(7)	C(2)-Fe(1')-C(6)#2	128.65(19)
C(3)#1-Fe(1)-C(4)	159.67(5)	C(2)#1-Fe(1')-C(6)#2	159.0(4)
C(3)-Fe(1)-C(4)	159.67(5)	N(1)-Fe(1')-C(6)#2	162.5(2)
C(5)-Fe(1)-C(4)	40.25(5)	C(5)#2-Fe(1')-C(6)#2	34.68(19)
C(5)#1-Fe(1)-C(4)	40.25(5)	C(5)#3-Fe(1')-C(6)#2	58.4(3)
C(3)-Fe(1')-C(3)#1	42.5(3)	C(3)-Fe(1')-C(6)#3	124.4(6)
C(3)-Fe(1')-C(4)#2	158.74(15)	C(3)#1-Fe(1')-C(6)#3	110.9(4)
C(3)#1-Fe(1')-C(4)#2	158.74(15)	C(4)#2-Fe(1')-C(6)#3	60.3(3)
C(3)-Fe(1')-C(2)	40.6(2)	C(2)-Fe(1')-C(6)#3	159.0(4)
C(3)#1-Fe(1')-C(2)	68.5(4)	C(2)#1-Fe(1')-C(6)#3	128.65(19)
C(4)#2-Fe(1')-C(2)	127.2(5)	N(1)-Fe(1')-C(6)#3	162.5(2)
C(3)-Fe(1')-C(2)#1	68.5(4)	C(5)#2-Fe(1')-C(6)#3	58.4(3)
C(3)#1-Fe(1')-C(2)#1	40.6(2)	C(5)#3-Fe(1')-C(6)#3	34.68(19)
C(4)#2-Fe(1')-C(2)#1	127.2(5)	C(6)#2-Fe(1')-C(6)#3	33.20(19)
C(2)-Fe(1')-C(2)#1	65.5(4)	C(2)-N(1)-C(2)#1	108.75(16)
C(3)-Fe(1')-N(1)	66.3(4)	C(2)-N(1)-B(1)	125.48(8)
C(3)#1-Fe(1')-N(1)	66.3(4)	C(2)#1-N(1)-B(1)	125.48(8)
C(4)#2-Fe(1')-N(1)	115.6(6)	C(2)-N(1)-Fe(1)	70.33(8)
C(2)-Fe(1')-N(1)	38.0(2)	C(2)#1-N(1)-Fe(1)	70.33(8)
C(2)#1-Fe(1')-N(1)	38.0(2)	B(1)-N(1)-Fe(1)	130.11(12)

C(2)-N(1)-Fe(1')	67.56(17)	C(5)#1-C(4)-H(4)	125.69(10)
C(2)#1-N(1)-Fe(1')	67.56(17)	C(5)-C(4)-H(4)	125.69(10)
B(1)-N(1)-Fe(1')	126.1(3)	Fe(1')#4-C(4)-H(4)	112.2(17)
Fe(1)-N(1)-Fe(1')	103.8(3)	Fe(1)-C(4)-H(4)	125.0(16)
C(2)-C(1)-H(1C)	110.2(12)	C(4)-C(5)-C(6)	107.66(14)
C(2)-C(1)-H(1B)	109.0(11)	C(4)-C(5)-Fe(1)	70.00(9)
H(1C)-C(1)-H(1B)	108.3(16)	C(6)-C(5)-Fe(1)	69.02(8)
C(2)-C(1)-H(1A)	109.2(12)	C(4)-C(5)-Fe(1')#4	63.0(3)
H(1C)-C(1)-H(1A)	110.7(15)	C(6)-C(5)-Fe(1')#4	83.6(3)
H(1B)-C(1)-H(1A)	109.4(16)	Fe(1)-C(5)-Fe(1')#4	113.8(2)
N(1)-C(2)-C(3)	107.78(14)	C(4)-C(5)-H(5)	124.8(10)
N(1)-C(2)-C(1)	122.86(12)	C(6)-C(5)-H(5)	127.6(10)
C(3)-C(2)-C(1)	129.11(14)	Fe(1)-C(5)-H(5)	125.0(10)
N(1)-C(2)-Fe(1)	69.29(8)	Fe(1')#4-C(5)-H(5)	119.6(10)
C(3)-C(2)-Fe(1)	70.19(8)	C(6)#1-C(6)-C(5)	108.04(9)
C(1)-C(2)-Fe(1)	130.31(10)	C(6)#1-C(6)-Fe(1)	69.63(5)
N(1)-C(2)-Fe(1')	74.5(3)	C(5)-C(6)-Fe(1)	70.34(8)
C(3)-C(2)-Fe(1')	63.6(3)	C(6)#1-C(6)-Fe(1')#4	73.40(9)
C(1)-C(2)-Fe(1')	123.1(2)	C(5)-C(6)-Fe(1')#4	61.7(3)
Fe(1)-C(2)-Fe(1')	106.5(2)	Fe(1)-C(6)-Fe(1')#4	103.7(3)
C(3)#1-C(3)-C(2)	107.85(10)	C(6)#1-C(6)-H(6)	126.1(11)
C(3)#1-C(3)-Fe(1')	68.74(15)	C(5)-C(6)-H(6)	125.9(11)
C(2)-C(3)-Fe(1')	75.8(3)	Fe(1)-C(6)-H(6)	125.1(11)
C(3)#1-C(3)-Fe(1)	69.84(5)	Fe(1')#4-C(6)-H(6)	130.8(12)
C(2)-C(3)-Fe(1)	69.32(8)	N(1)-B(1)-H(1E)	108.1(10)
Fe(1')-C(3)-Fe(1)	112.4(3)	N(1)-B(1)-H(1D)	109.3(15)
C(3)#1-C(3)-H(3)	129.8(12)	H(1E)-B(1)-H(1D)	111.8(12)
C(2)-C(3)-H(3)	122.2(12)		
Fe(1')-C(3)-H(3)	124.8(12)		
Fe(1)-C(3)-H(3)	122.8(12)		
C(5)#1-C(4)-C(5)	108.60(19)		
C(5)#1-C(4)-Fe(1')#4	78.0(2)		
C(5)-C(4)-Fe(1')#4	78.0(2)		
C(5)#1-C(4)-Fe(1)	69.75(9)		
C(5)-C(4)-Fe(1)	69.75(9)		
Fe(1')#4-C(4)-Fe(1)	122.8(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z #2 x+1,y,z #3 x+1,-y+1/2,z

#4 x-1,y,z

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for towson10. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	18(1)	41(1)	18(1)	0	5(1)	0
Fe(1')	38(8)	64(10)	30(8)	0	7(5)	0
N(1)	20(1)	35(1)	22(1)	0	7(1)	0
C(1)	35(1)	39(1)	41(1)	13(1)	16(1)	8(1)
C(2)	20(1)	47(1)	27(1)	9(1)	8(1)	6(1)
C(3)	21(1)	72(1)	25(1)	10(1)	3(1)	6(1)
C(4)	20(1)	42(1)	30(1)	0	4(1)	0
C(5)	24(1)	38(1)	40(1)	3(1)	10(1)	-2(1)
C(6)	29(1)	61(1)	32(1)	11(1)	14(1)	1(1)
B(1)	34(1)	34(1)	19(1)	0	6(1)	0

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for towson10.

	x	y	z	U(eq)
H(4)	-2460(40)	2500	670(40)	42(7)
H(1C)	1760(30)	-130(20)	900(20)	53(5)
H(1B)	3020(30)	-590(20)	2670(20)	50(5)
H(3)	3770(30)	1247(19)	5110(30)	47(5)
H(5)	-1800(20)	484(18)	2490(20)	40(4)
H(1E)	1340(30)	1620(20)	-1140(30)	57(5)
H(1A)	4100(30)	-117(19)	1220(20)	48(5)
H(6)	-660(30)	1251(19)	5650(20)	51(5)
H(1D)	3610(40)	2500	-1170(40)	62(8)