Electronic Supplemental Information

Synthesis and characterisation of polymeric materials consisting of {$Fe_2(CO)_5$}-unit and their relevance to the diiron sub-unit of [FeFe]-hydrogenase

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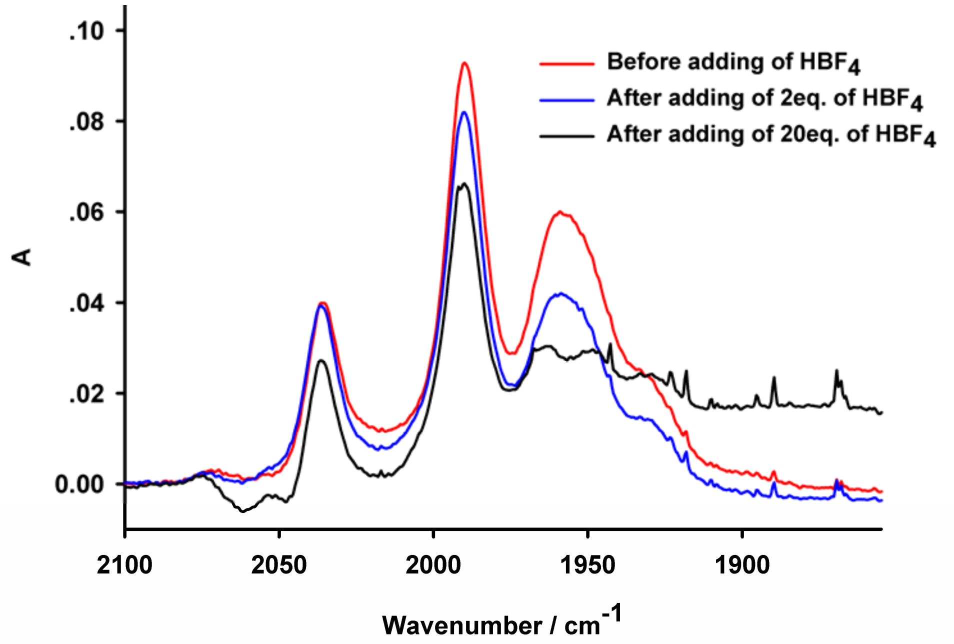


Figure S1 Variation in IR spectra (carbonyl region) of **Poly-Py** upon addition of HBF_4 in DMF under CO.

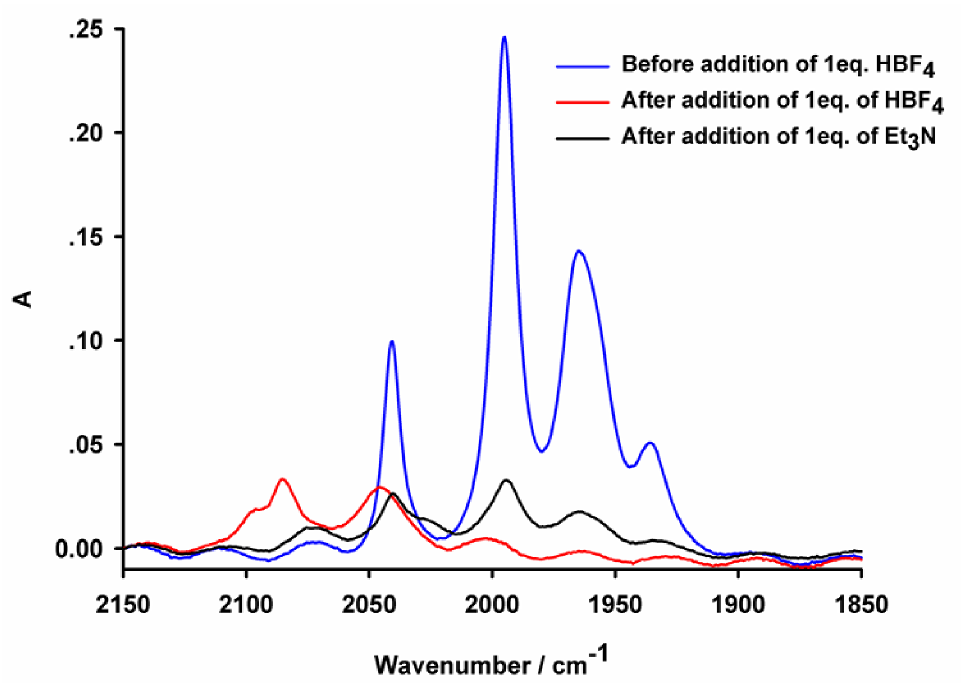


Figure S2 Variation in IR spectra (carbonyl region) of compound **3** upon addition of HBF_4 and then neutralisation by Et_3N in CH_3CN under CO.

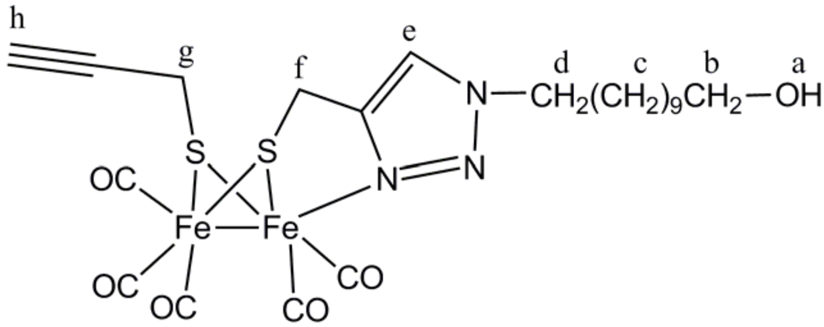


Figure S3 Schematic structure of complex **3** and the labeling scheme of its non-CO carbon atoms.

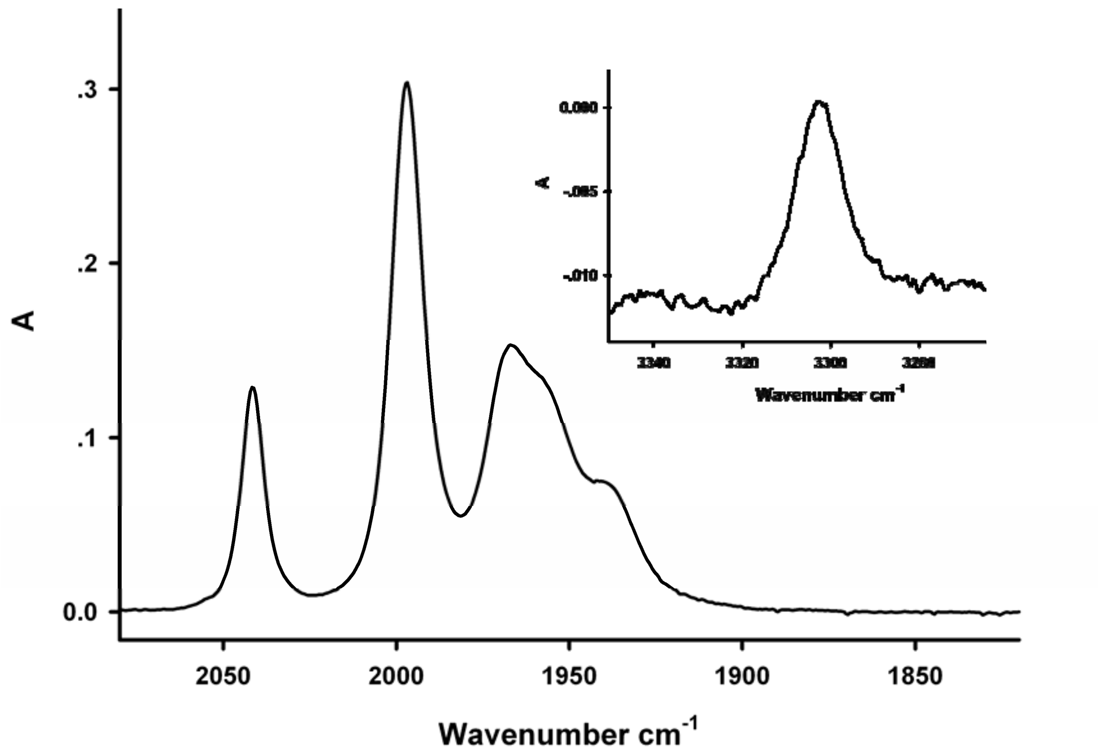


Figure S4 IR spectrum of complex **4** in DCM, inset: the absorption of alkynyl CH bond.

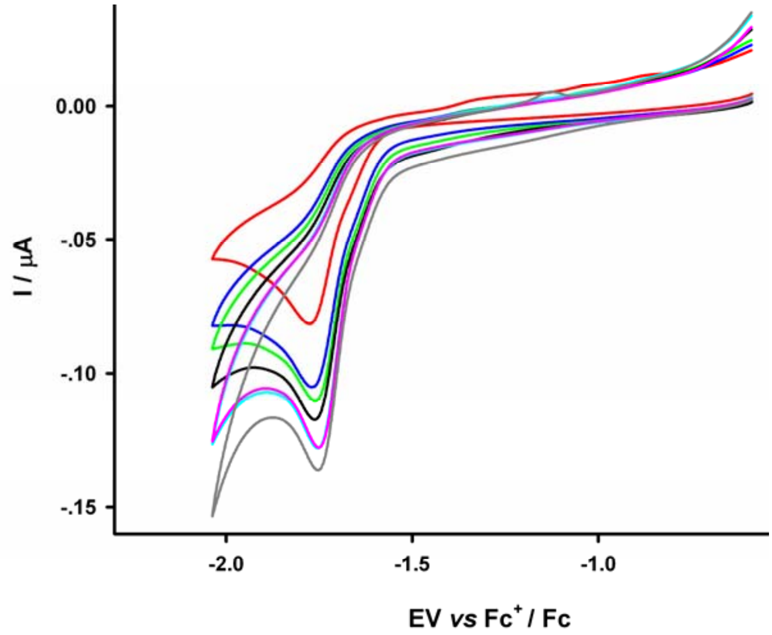
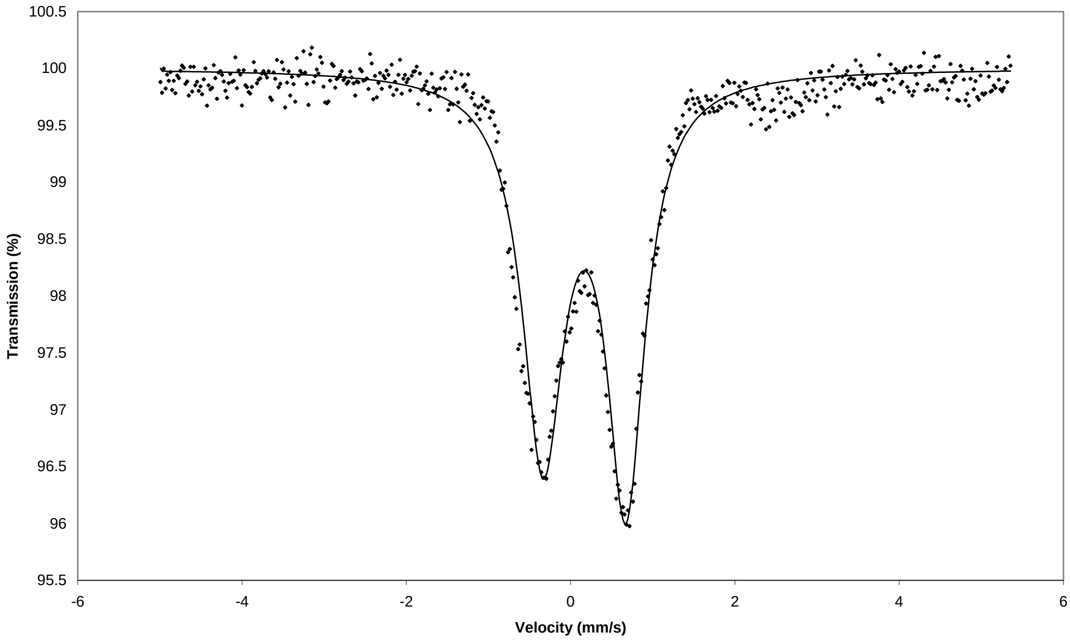


Figure S5 The cyclic voltammograms of complex **4** (5.1 mmol L^{-1}) in DMF solution in the presence of CH_3COOH (0.0, 0.5, 1.0, 2.0, 22.5, 32.5, 52.5 eq.) at a scan rate of 0.1 Vs^{-1}.



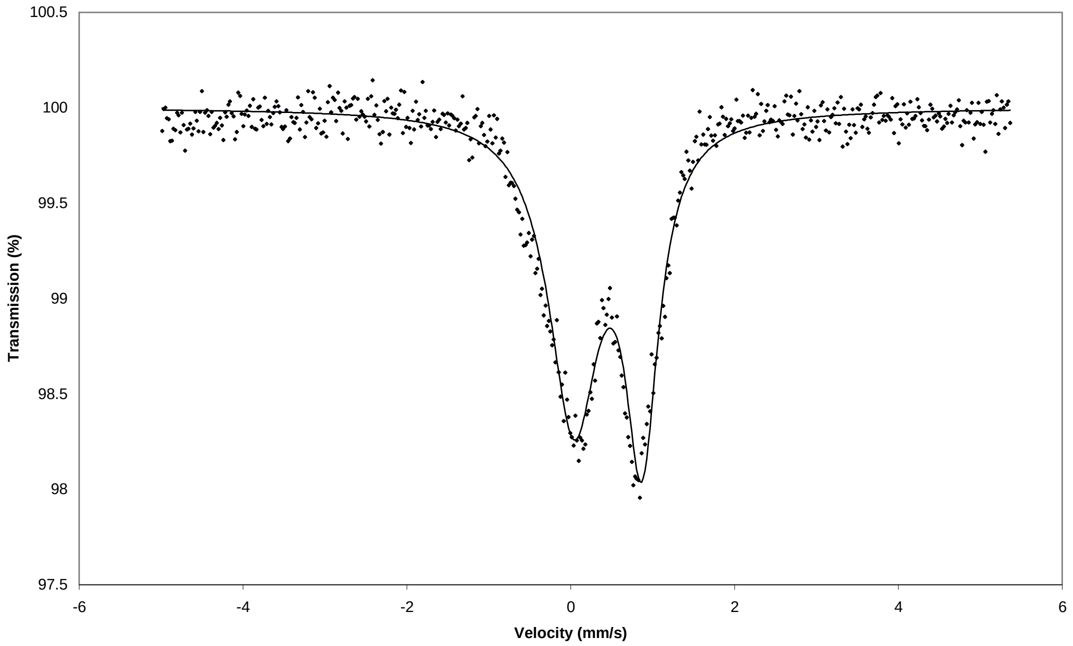


Figure S6 Mössbauer spectra of **Poly-Py** (top) and **Poly-Ph** (bottom) at 80 K.

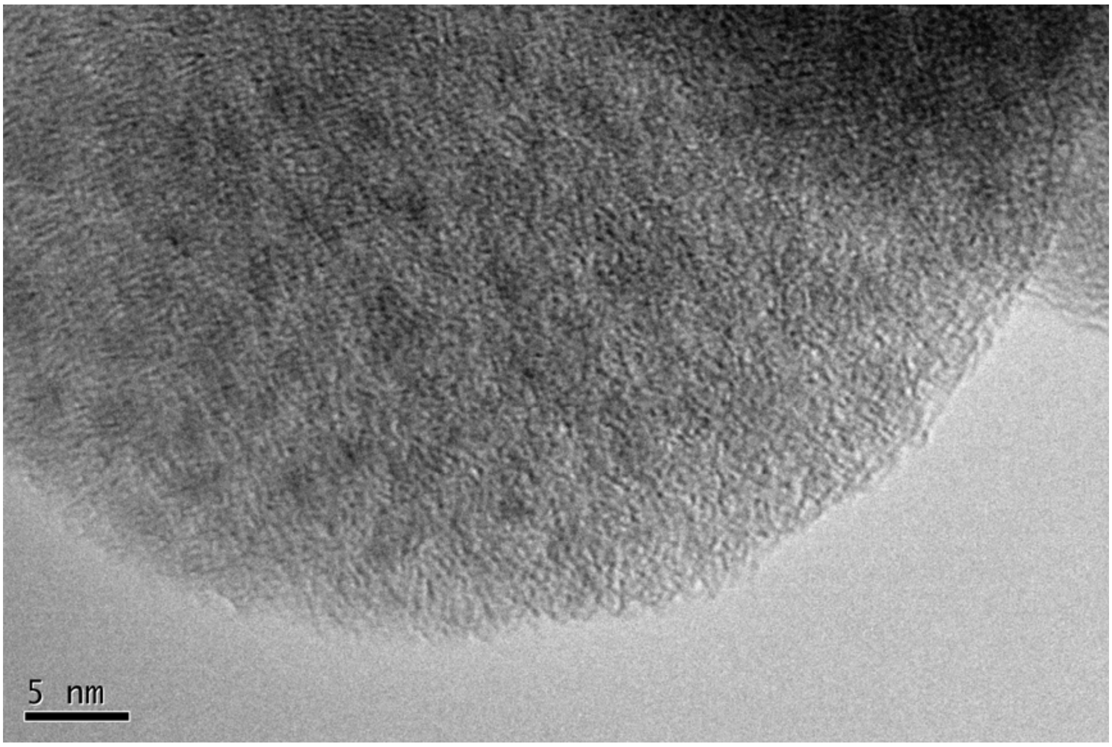


Figure S7 TEM diagram of **Poly-Ph**

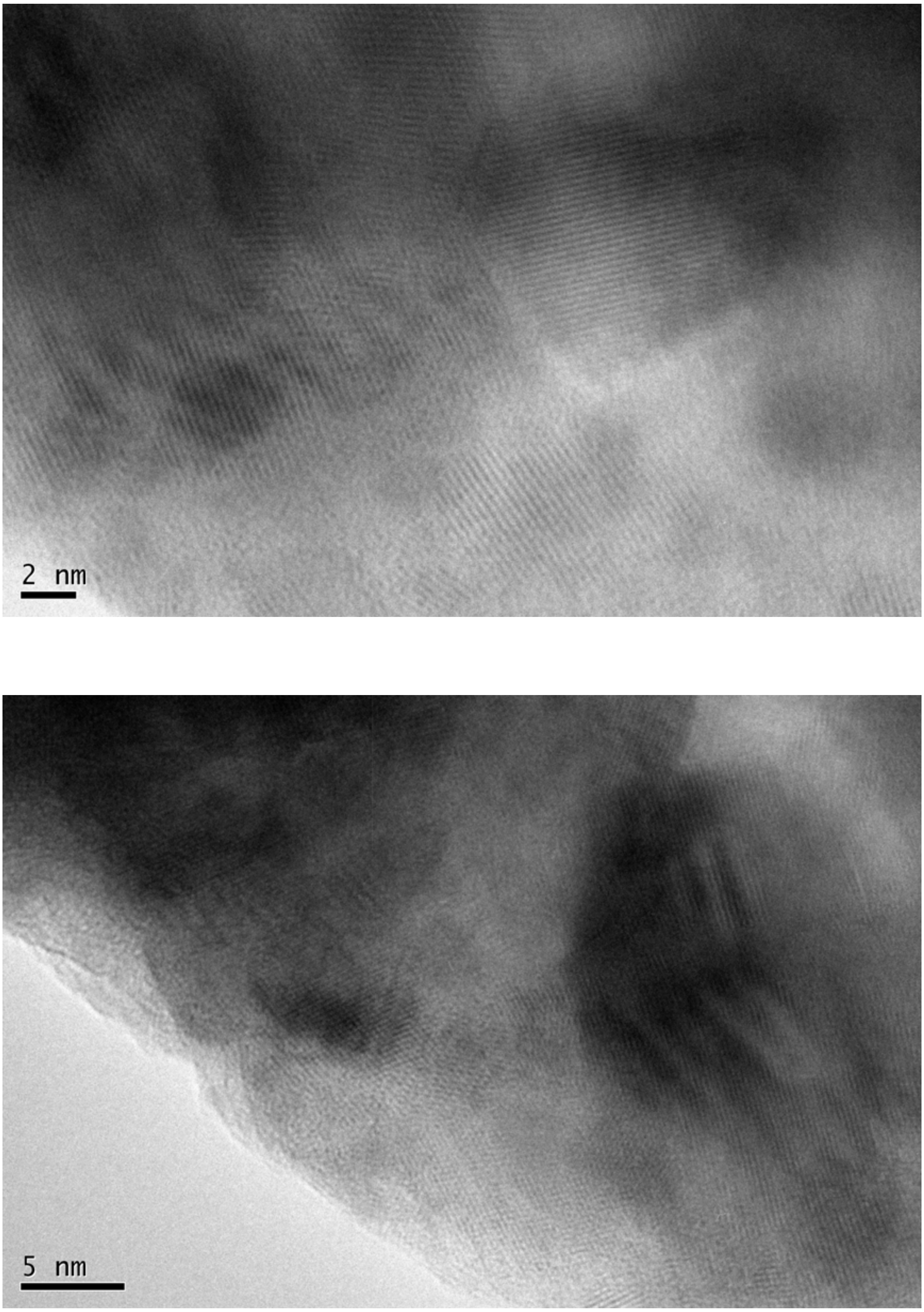


Figure S8 TEM diagrams of **Poly-Py** at two different scales.

Table S1 Bond lengths [Å] and angles [°] for complex **4**.

Fe(1)-C(3)	1.782(2)
Fe(1)-C(1)	1.785(2)
Fe(1)-C(2)	1.814(2)
Fe(1)-S(1)	2.2630(5)
Fe(1)-S(2)	2.2893(5)
Fe(1)-Fe(2)	2.5411(4)
Fe(2)-C(4)	1.7832(17)
Fe(2)-C(5)	1.7832(18)
Fe(2)-N(1)	1.9655(13)
Fe(2)-S(1)	2.2236(5)
Fe(2)-S(2)	2.2447(5)
S(1)-C(6)	1.8461(19)
S(2)-C(9)	1.8290(17)
C(1)-O(1)	1.139(2)
C(2)-O(2)	1.131(2)
C(3)-O(3)	1.138(2)
C(4)-O(4)	1.139(2)
C(5)-O(5)	1.136(2)
C(6)-C(7)	1.447(3)
C(6)-H(6A)	0.9700

C(6)-H(6B)	0.9700
C(7)-C(8)	1.171(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.486(2)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-N(1)	1.357(2)
C(10)-C(11)	1.367(2)
C(11)-N(3)	1.342(3)
C(11)-H(11)	0.9300
C(12)-N(3)	1.478(2)
C(12)-C(13)	1.501(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.375(3)
C(13)-C(18)	1.381(3)
C(14)-C(15)	1.393(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.359(4)
C(15)-H(15)	0.9300
C(16)-C(17)	1.359(4)
C(16)-H(16)	0.9300

C(17)-C(18)	1.380(3)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
N(1)-N(2)	1.3210(18)
N(2)-N(3)	1.332(2)
C(3)-Fe(1)-C(1)	91.47(9)
C(3)-Fe(1)-C(2)	98.56(9)
C(1)-Fe(1)-C(2)	102.68(10)
C(3)-Fe(1)-S(1)	160.68(7)
C(1)-Fe(1)-S(1)	85.71(7)
C(2)-Fe(1)-S(1)	100.70(7)
C(3)-Fe(1)-S(2)	92.55(6)
C(1)-Fe(1)-S(2)	152.47(7)
C(2)-Fe(1)-S(2)	103.62(7)
S(1)-Fe(1)-S(2)	81.571(16)
C(3)-Fe(1)-Fe(2)	106.93(7)
C(1)-Fe(1)-Fe(2)	97.77(6)
C(2)-Fe(1)-Fe(2)	146.72(7)
S(1)-Fe(1)-Fe(2)	54.774(13)
S(2)-Fe(1)-Fe(2)	55.085(13)
C(4)-Fe(2)-C(5)	96.32(8)
C(4)-Fe(2)-N(1)	98.62(7)

C(5)-Fe(2)-N(1)	93.80(7)
C(4)-Fe(2)-S(1)	103.31(6)
C(5)-Fe(2)-S(1)	90.05(6)
N(1)-Fe(2)-S(1)	157.17(4)
C(4)-Fe(2)-S(2)	105.27(6)
C(5)-Fe(2)-S(2)	158.34(6)
N(1)-Fe(2)-S(2)	84.76(4)
S(1)-Fe(2)-S(2)	83.442(18)
C(4)-Fe(2)-Fe(1)	151.57(6)
C(5)-Fe(2)-Fe(1)	102.65(6)
N(1)-Fe(2)-Fe(1)	101.01(4)
S(1)-Fe(2)-Fe(1)	56.238(15)
S(2)-Fe(2)-Fe(1)	56.749(13)
C(6)-S(1)-Fe(2)	113.31(7)
C(6)-S(1)-Fe(1)	109.98(6)
Fe(2)-S(1)-Fe(1)	68.988(15)
C(9)-S(2)-Fe(2)	102.32(6)
C(9)-S(2)-Fe(1)	112.25(6)
Fe(2)-S(2)-Fe(1)	68.166(14)
O(1)-C(1)-Fe(1)	178.80(18)
O(2)-C(2)-Fe(1)	178.49(19)
O(3)-C(3)-Fe(1)	179.4(2)

O(4)-C(4)-Fe(2)	177.93(18)
O(5)-C(5)-Fe(2)	178.86(18)
C(7)-C(6)-S(1)	111.05(14)
C(7)-C(6)-H(6A)	109.4
S(1)-C(6)-H(6A)	109.4
C(7)-C(6)-H(6B)	109.4
S(1)-C(6)-H(6B)	109.4
H(6A)-C(6)-H(6B)	108.0
C(8)-C(7)-C(6)	178.9(2)
C(7)-C(8)-H(8)	180.0
C(10)-C(9)-S(2)	110.07(11)
C(10)-C(9)-H(9A)	109.6
S(2)-C(9)-H(9A)	109.6
C(10)-C(9)-H(9B)	109.6
S(2)-C(9)-H(9B)	109.6
H(9A)-C(9)-H(9B)	108.2
N(1)-C(10)-C(11)	106.72(15)
N(1)-C(10)-C(9)	120.00(14)
C(11)-C(10)-C(9)	133.19(16)
N(3)-C(11)-C(10)	105.33(15)
N(3)-C(11)-H(11)	127.3
C(10)-C(11)-H(11)	127.3

N(3)-C(12)-C(13)	113.48(15)
N(3)-C(12)-H(12A)	108.9
C(13)-C(12)-H(12A)	108.9
N(3)-C(12)-H(12B)	108.9
C(13)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.7
C(14)-C(13)-C(18)	118.92(19)
C(14)-C(13)-C(12)	120.44(19)
C(18)-C(13)-C(12)	120.60(19)
C(13)-C(14)-C(15)	120.1(2)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	119.7(2)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	120.9(2)
C(15)-C(16)-H(16)	119.6
C(17)-C(16)-H(16)	119.6
C(16)-C(17)-C(18)	119.8(2)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(17)-C(18)-C(13)	120.6(2)

C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
N(2)-N(1)-C(10)	110.52(13)
N(2)-N(1)-Fe(2)	126.73(10)
C(10)-N(1)-Fe(2)	122.72(11)
N(1)-N(2)-N(3)	105.58(13)
N(2)-N(3)-C(11)	111.85(14)
N(2)-N(3)-C(12)	119.20(16)
C(11)-N(3)-C(12)	128.92(16)