Supporting information for

Synthesis of Carboxylate-bridged Iron-thiolate Clusters from Alcohols/Aldehydes or Carboxylate salts

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Contents

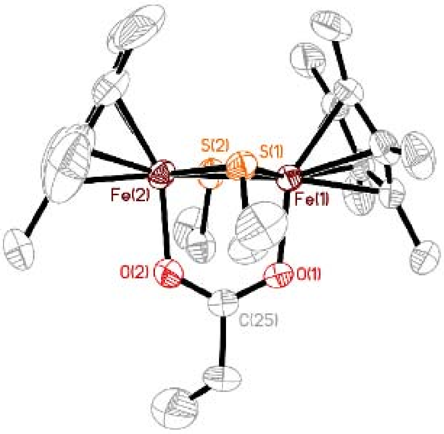

Fig S1 ORTEP (ellipsoids at 30% probability) diagram of **4**. All hydrogen atoms as well as the PF_6^- anions are omitted for clarity. Disorder is omitted for clarity. Selected bond length (Å), Bond Angles and Plane Angles (deg): Fe(1)–Fe(2) 2.6166(9), Fe(1)–S(1) 2.2124(13), Fe(1)–S(2) 2.2084(13), Fe(1)–O(1) 1.978(3), Fe(2)–S(1) 2.1968(13), Fe(2)–S(2) 2.2073(14), Fe(2)–O(2) 1.980(3), Fe(2)–S(1)–Fe(1) 72.80(4), Fe(2)–S(2)–Fe(1) 72.68(4), O(2)–C(25)–O(1) 125.4(4), Cp*(1)-Cp*(2) 54.646(204), S(1)Fe(2)Fe(1)-Fe(2)O(2)O(1)Fe(1) 85.793(61), O(2)C(25)O(1)-Fe(2)O(2)O(1)Fe(1) 0.881(422).

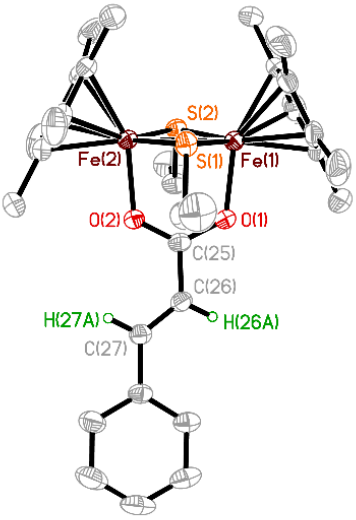

Fig. S2 ORTEP (ellipsoids at 30% probability) diagram of **8**. All hydrogen atoms as well as the PF_6^- anions are omitted for clarity. Selected bond length (Å), Bond Angles and Plane Angles (deg): Fe(1)–Fe(2) 2.6195(7), Fe(1)–S(1) 2.2068(11), Fe(1)–S(2) 2.2194(11), Fe(1)–O(1) 1.963(3), Fe(2)–S(1) 2.2184(11), Fe(2)–S(2) 2.2104(10), Fe(2)–O(2) 1.978(2), Fe(2)–S(1)–Fe(1) 72.59(3), Fe(2)–S(2)–Fe(1) 72.50(3), O(2)–C(25)–O(1) 126.0(3), Cp*(1)-Cp*(2) 55.112(109), S(1)Fe(2)Fe(1)-Fe(2)O(2)O(1)Fe(1) 86.774(61), O(2)C(25)O(1)-Fe(2)O(2)O(1)Fe(1) 3.128(462).

Table S1 Crystal Data and Structure Refinement for complexes **4** and **8**.

	4	**8**
Formula	$C_{27}H_{45}F_6Fe_2O_2PS_2$	$C_{33}H_{47}F_6Fe_2O_2PS_2$
Formula weigh	722.42	796.50
Crystal dimensions (mm^3)	0.20×0.22×0.6	0.24×0.26×0.16
Crystal system	Tetragonal	Monoclinic
Space group	$P4_12_12$	$P2_1/c$
a (Å)	13.0082(4)	15.237(2)
b (Å)	13.0082(4)	14.235(2)
c (Å)	38.517(3)	17.525(3)
α (°)	90.00	90.00
β (°)	90.00	106.440(8)
γ (°)	90.00	90.00
Volume ($Å^3$)	6517.6(5)	3645.8(10)
Z	8	4
T (K)	298(2)	298(2)
D calcd (g cm^{-3})	1.472	1.451
μ (mm^{-1})	1.125	1.013
F (000)	3008	1656
No. Of rflns. collected	44596	17495
No. Of indep. Rflns. /Rint	5745 / 0.0478	6344 / 0.0531
No. Of obsd. Rflns. [$I > 2\sigma(I)$]	4899	4660
Data / restraints / parameters	5745 / 12 / 355	6344 / 0 / 399
R_1, ^{a} /wR_2 ^{b} [$I > 2\sigma(I)$]	0.0471 / 0.1290	0.0482 / 0.1278
R_1, ^{a} /wR_2 ^{b} (all data)	0.0574 / 0.1355	0.0689 / 0.1394
GOF (on F^2)	1.000	1.000
Largest diff. Peak and hole (e $Å^{-3}$)	0.479 / -0.362	0.501 / -0.258

$^a R_1 = \Sigma Fo - |F_c /\Sigma|F_o|$. $^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

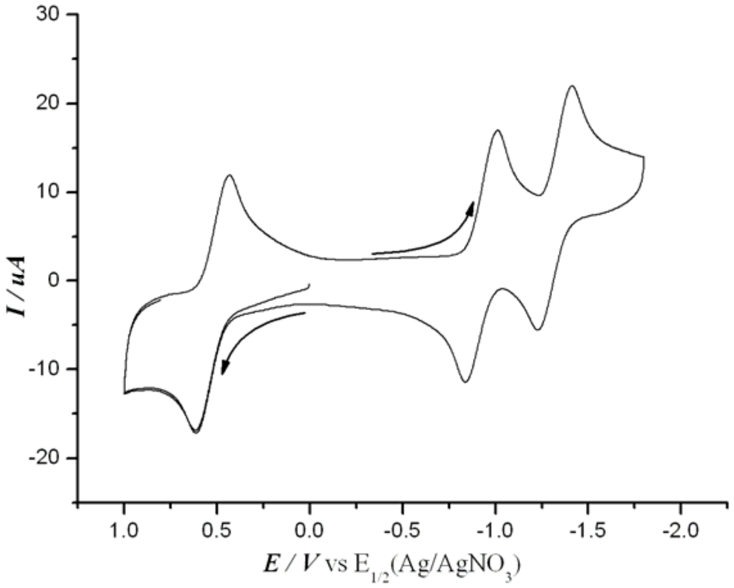

Fig S3 Cyclic voltammograms of complex **2.** The scan rate is 0.100V.s^{-1}, and the reference electrode is Ag/AgNO$_3$

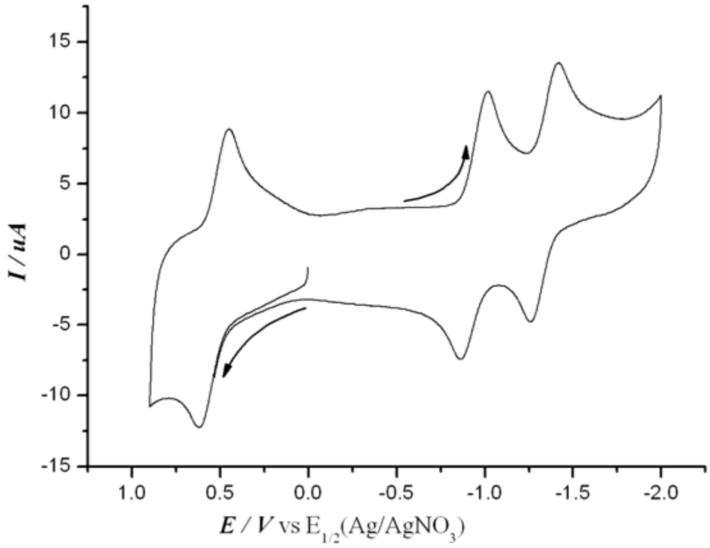

Fig S4 Cyclic voltammograms of complex **6.** The scan rate is 0.100V.s^{-1}, and the reference electrode is Ag/AgNO$_3$

The calculation of the magnetic moments and magnetic susceptibility

According to the standard Evans method, the molar paramagnetic susceptibility illustrated in the following equation:

$$\chi_M^P = \frac{3\Delta f M^P}{2\pi f m} + \frac{\chi^0 M^P (d_0 - d_s)}{m} + \chi^0 M^P \qquad (1)$$

where,

χ_M^P = Molar paramagnetic susceptibility in cm^{-3}. mol^{-1};

Δf = Frequency difference between the two peaks of the inner and outer tube in Hz;

M^P = Molecular weight of the substance in g. mol^{-1};

f = Frequency of the NMR instrument in Hz;

m = Mass of the substance in 1 mL of solution in g. mol^{-1};

χ^0 = Mass susceptibility of the solvent in cm^{-3}. mol^{-1};

d_0 = Density of the solvent in g. mol^{-3};

d_s = Density of the solution in g. mol^{-3};

Since the tested solutions were dilute (0.8, 1.6, 2.4 mM), the densities of the solvent, and the solution are considered to be almost equal, and so the $(d_0 - d_s)/m$ is neglected. Since the same solvent is used in both tubes the solvent correction is also avoided. As shown in Fig S5, there was no shifting about H single of tetramethylsilane (TMS) after adding the complex **2** into a solution of $CDCl_3$ and TMS (still located at δ = 0), which meant that Δf = 0. So, χ_M^P = 0.

To calculate the magnetic moment (μ_{eff}) of complexes **2**, the general equation was used.

$$\mu_{eff} = \sqrt{8.\chi_M^P.T}$$

Because of χ_M^P = 0, μ_{eff} = 0.

According to the following equation

$$\mu_{eff} = \sqrt{4S(S+1)}$$

So, S = 0. Unpaired electron n = 0. It could be concluded that carboxylate-bridged complex **2** was diamagnetic with low spin. The distances of Fe-O (carboxylate) of the complexes in this context were almost 1.97 Å, smaller than the distance of 2.00-2.10 Å (the distances of Fe-O (carboxylate) of all known the carboxylate-bridged diiron complexes), which indirectly showed they were low spin.

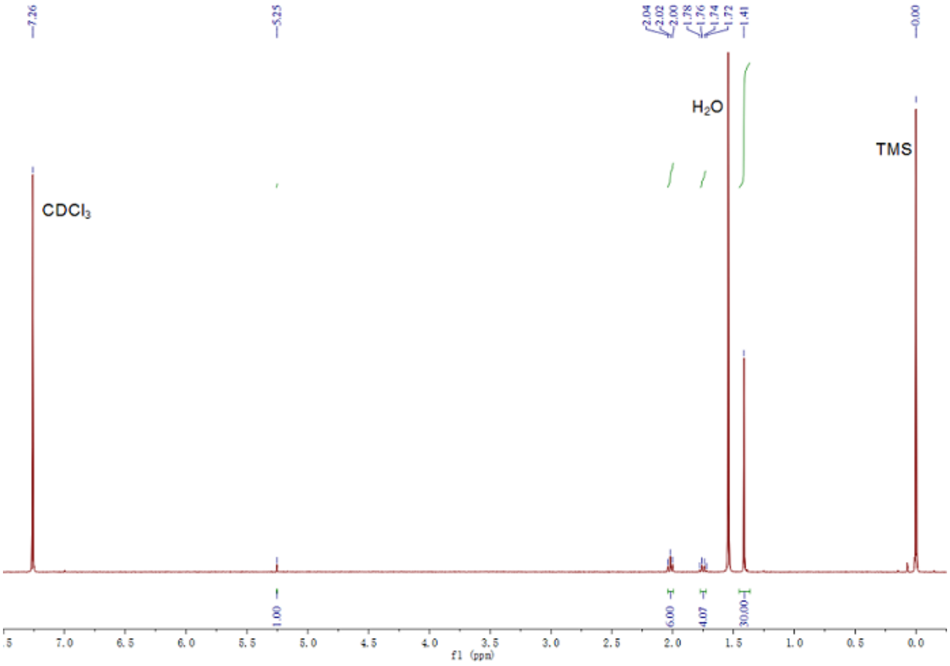

Fig S5 ^{1}H NMR of complex **2** added TMS