

Electronic supplementary information

Proton-coupled electron transfer in the reduction of diiron hexacarbonyl complexes and its enhancement on electrocatalytic reduction of proton caused by a pendant basic group

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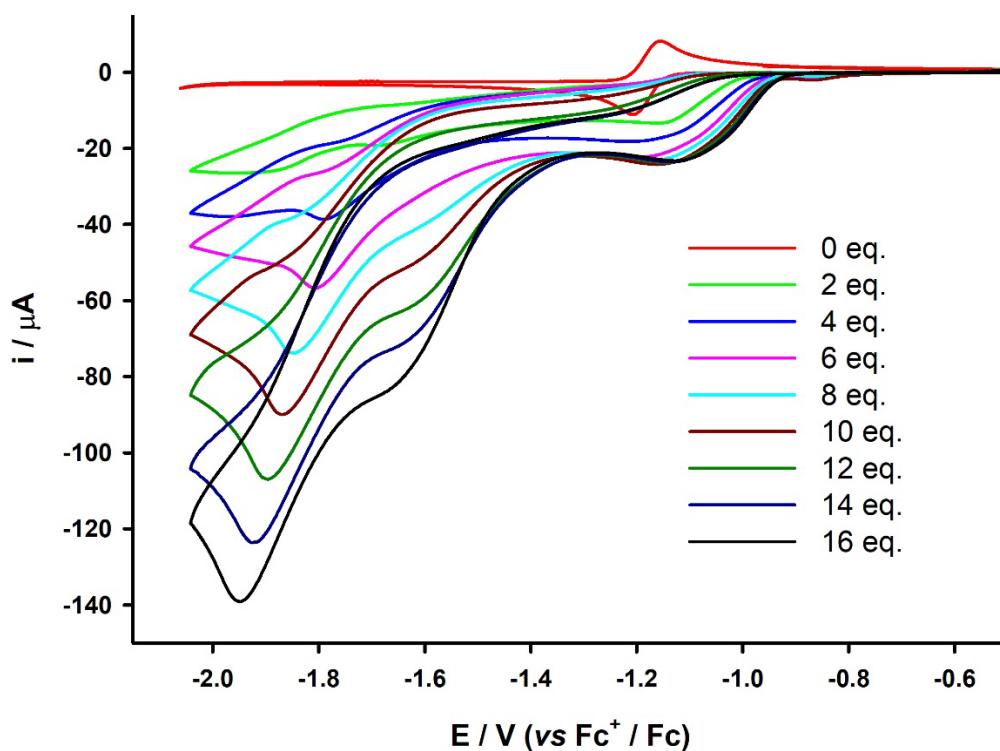
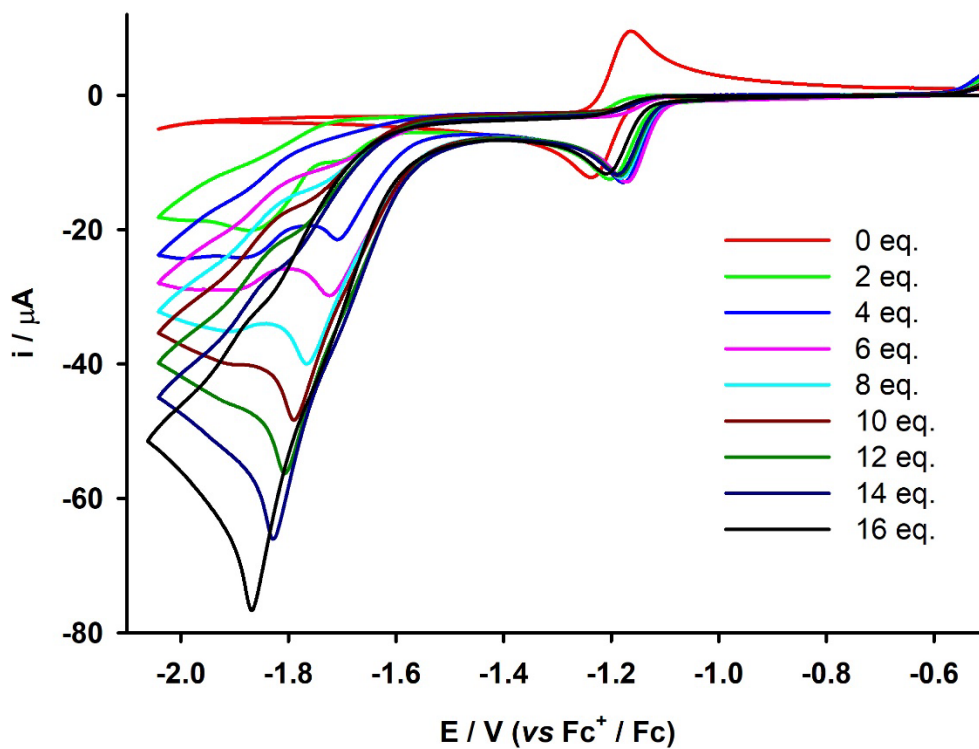


Fig. S1 CVs of complex **2** ($c = 2.86 \text{ mmol L}^{-1}$) in 0.1 mol L^{-1} $[\text{NnBu}_4]\text{BF}_4/\text{MeCN}$ solution upon successive addition of CF_3COOH (scanning rate = 0.1 V s^{-1}): 0, 2, 4, 6, 8, 10, 12, 14 and 16 equivalents.



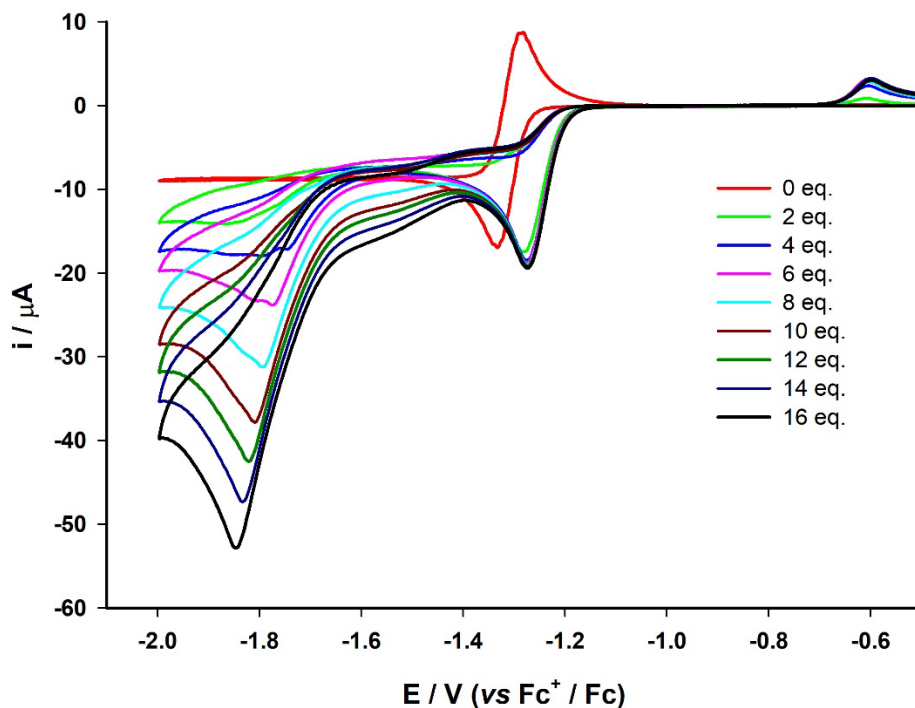


Fig. S2 CVs of complexes **3** (up) and **4** (down) ($c = 2.86 \text{ mmol L}^{-1}$) in 0.1 mol L^{-1} $[\text{NnBu}_4]\text{BF}_4/\text{MeCN}$ solution upon successive addition of CF_3COOH (scanning rate = 0.1 V s^{-1}): 0, 2, 4, 6, 8, 10, 12, 14 and 16 equivalents.

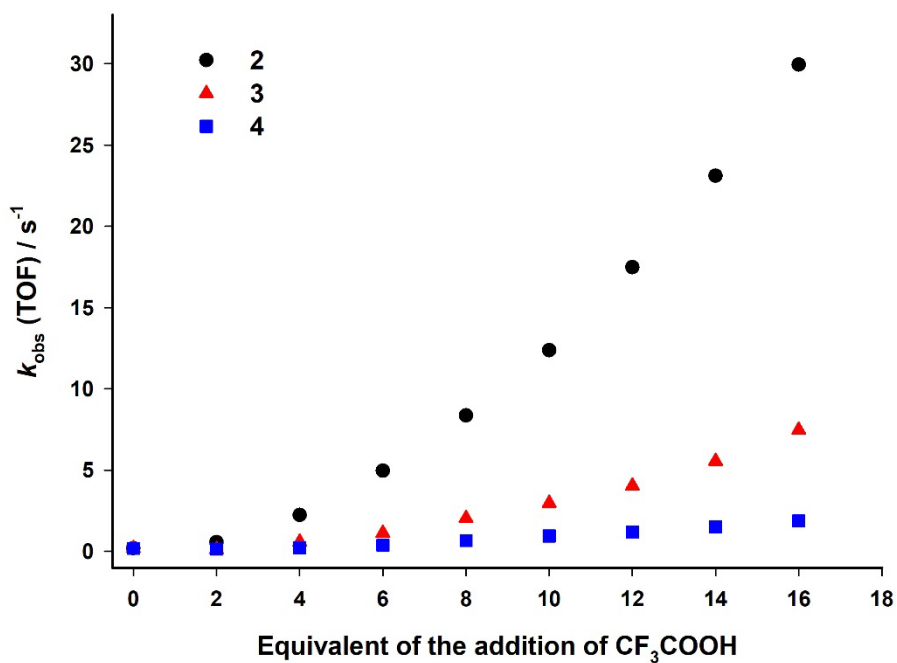


Fig. S3 Plots of k_{obs} (TOF) against the addition of CF_3COOH of complexes **2–4** ($c = 2.86 \text{ mmol L}^{-1}$) at a scanning rate of 0.1 V s^{-1} .

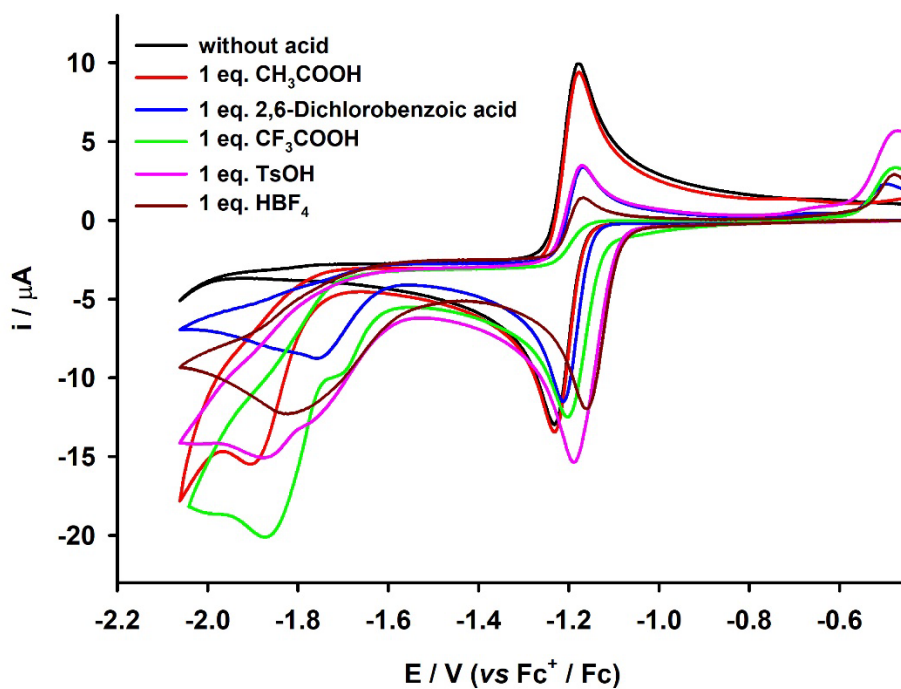


Fig.S4 CVs of complex **3** with 1 eq. of various acids in 0.1 mol L^{-1} $[\text{NBut}_4]\text{BF}_4$ / acetonitrile at room temperature.

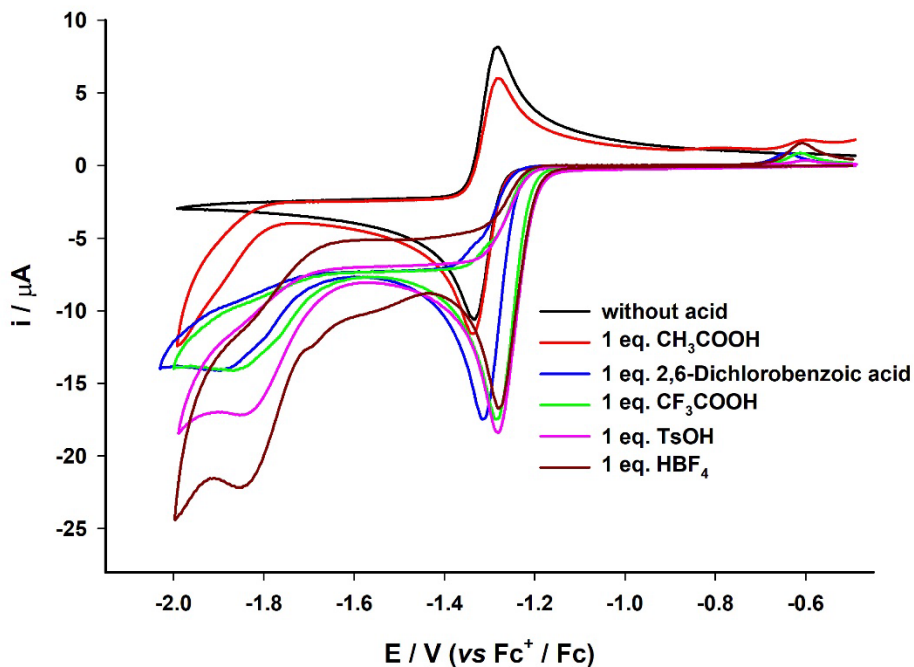


Fig.S5 CVs of complex **4** with 1 eq. of various acids in 0.1 mol L^{-1} $[\text{NBut}_4]\text{BF}_4$ / acetonitrile at room temperature.

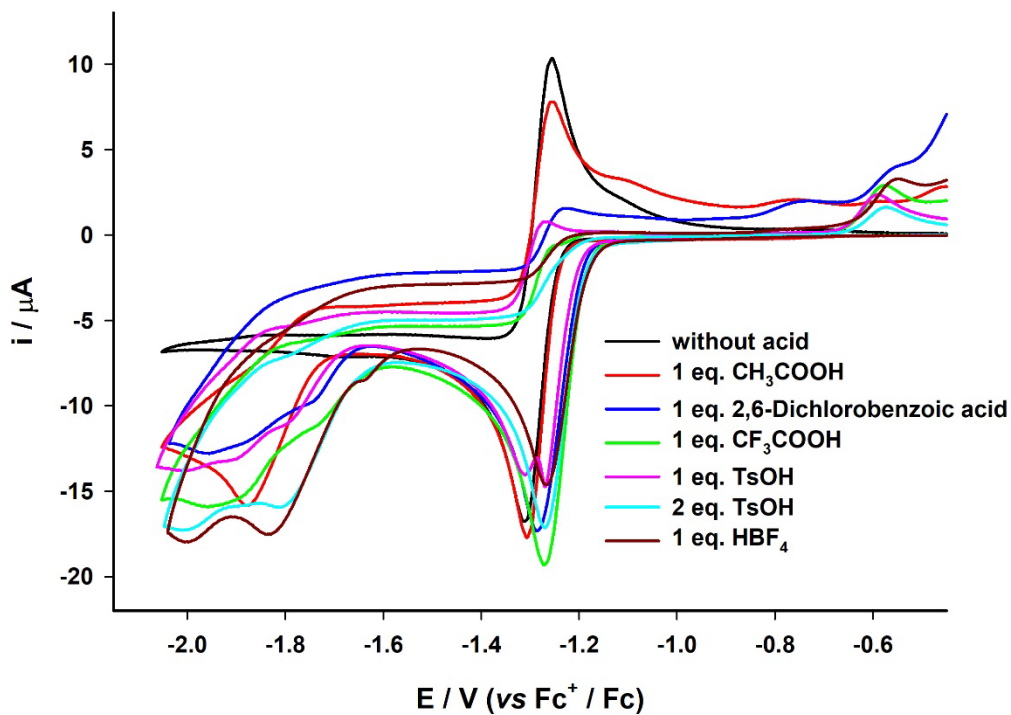


Fig.S6 CVs of complex **5** with 1 eq. of various acids in 0.1 mol L^{-1} $[\text{NBut}_4]\text{BF}_4$ / acetonitrile at room temperature.

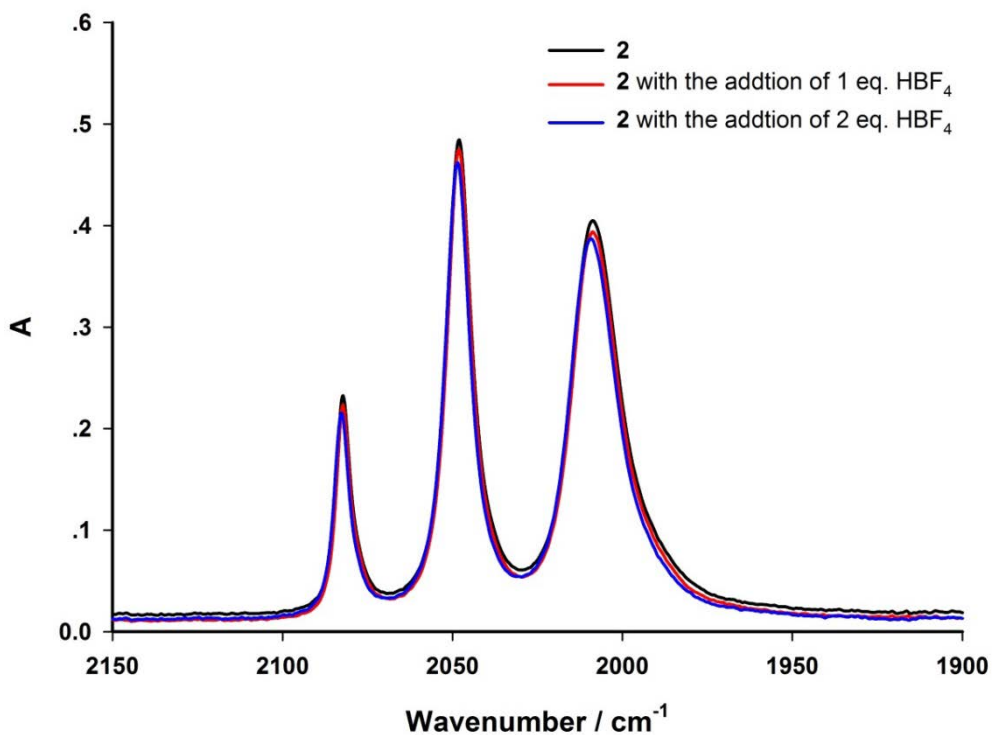


Fig.S7 FTIR spectra of complex **2** with the addition of HBF_4 in CH_2Cl_2 .

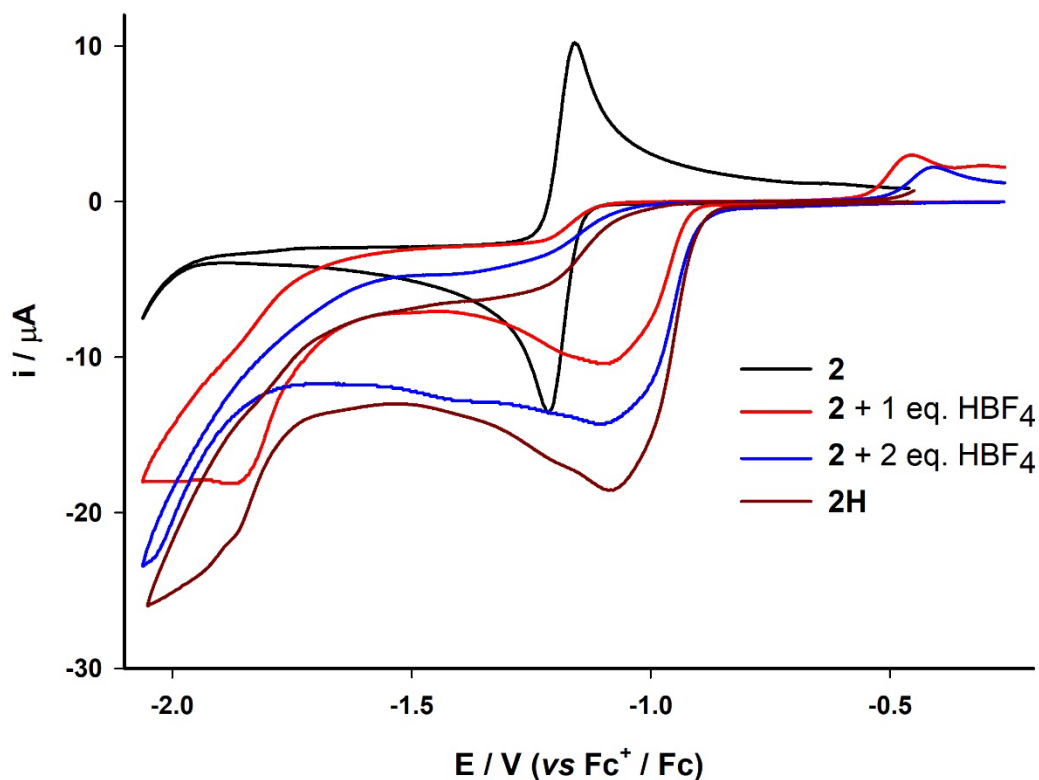


Fig.S8 Comparison of CVs of **2**, **2** with the addition of HBF₄ and **2H**.

Comparison of the catalytic turnover frequency (TOF) between complexes **2** and **3** in the presence of CF₃COOH.

As shown in Fig. 3, the catalytic peak current (i_{cat}) increased almost linearly with acid concentration, indicating that at fixed catalyst concentration the reaction is first order with respect to acid concentration. Thus, the catalytic turnover frequency (TOF) of complexes **2–4** can be calculated by the following equation ^[1]:

$$\frac{i_{\text{cat}}}{i_{\text{p}}} = \frac{n}{0.446} \sqrt{\frac{RTk_{\text{obs}}}{Fv}}$$

where i_{cat} is the peak current in presence of acid, i_{p} is the peak current in the absence of acid, n is the number of electrons involved in the catalytic process, k_{obs} (turn over frequency, TOF) is the observed rate constant, R is ideal gas constant, T is temperature in Kelvin (298 K), F is Faraday's constant, and v is the scanning rate. According to this equation, the values of TOF for complexes **2–4** with different equivalent of CF₃COOH can be calculated and showed in Fig. S3.

Table S1. Crystallographic details for complexes **2–4**.

Complex	2	3	4
CCDC number	1847707	1847708	1847709
Chemical formula	2(C ₂₄ H ₁₀ Fe ₂ N ₂ O ₁₀ S ₂)•CH ₂ Cl ₂	C ₂₈ H ₁₆ Fe ₂ O ₁₂ S ₂	C ₂₆ H ₁₆ Fe ₂ O ₈ S ₂
Formula weight	1409.25	720.23	632.21
Crystal size (mm)	0.30×0.24×0.21	0.35×0.28×0.25	0.42×0.33×0.28
Temperature (K)	296(2)	296(2)	293(2)
Radiation	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	P2(1)/n	P2(1)/c	Pnma
<i>a</i> (Å)	17.687(4)	12.040(2)	12.3381(6)
<i>b</i> (Å)	16.553(4)	17.033(3)	19.4322(10)
<i>c</i> (Å)	18.948(4)	15.155(3)	10.9337(8)
<i>α</i> (°)	90	90	90
<i>β</i> (°)	91.001(3)	101.646(2)	90
<i>γ</i> (°)	90	90	90
V(Å ³)	5547(2)	3043.8(9)	2621.4(3)
Z	4	4	4
ρ (calc) (g/cm ³)	1.688	1.572	1.602
F (000)	2824	1456	1280
Absorp.coeff. (mm ⁻¹)	1.352	1.152	1.314
θ range (deg)	2.30 to 28.32	2.31 to 29.01	3.25 to 26.00
Reflns collected	51779 (R _{int} = 0.0589)	28548 (R _{int} = 0.0265)	7106 (R _{int} = 0.0308)
Indep. reflns	13688	7894	2656
Refns obs. [<i>I</i> > 2 σ (<i>I</i>)]	8328	5753	1930
Data/restr/paras	13688/0/748	7894/0/399	2656/0/181
GOF	1.016	1.036	1.092

$R_1/wR_2 [I > 2\sigma(I)]$	0.0479/0.1085	0.0375/0.0952	0.0452/0.0935
R_1/wR_2 (all data)	0.0957/0.1276	0.0603/0.1125	0.0730/0.1058
Large peak and hole ($e/\text{\AA}^3$)	1.233/-0.958	0.474/-0.358	0.719/-0.364

Reference

1. M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois and D. L. DuBois, *Science*, 2011, **333**, 863-866.