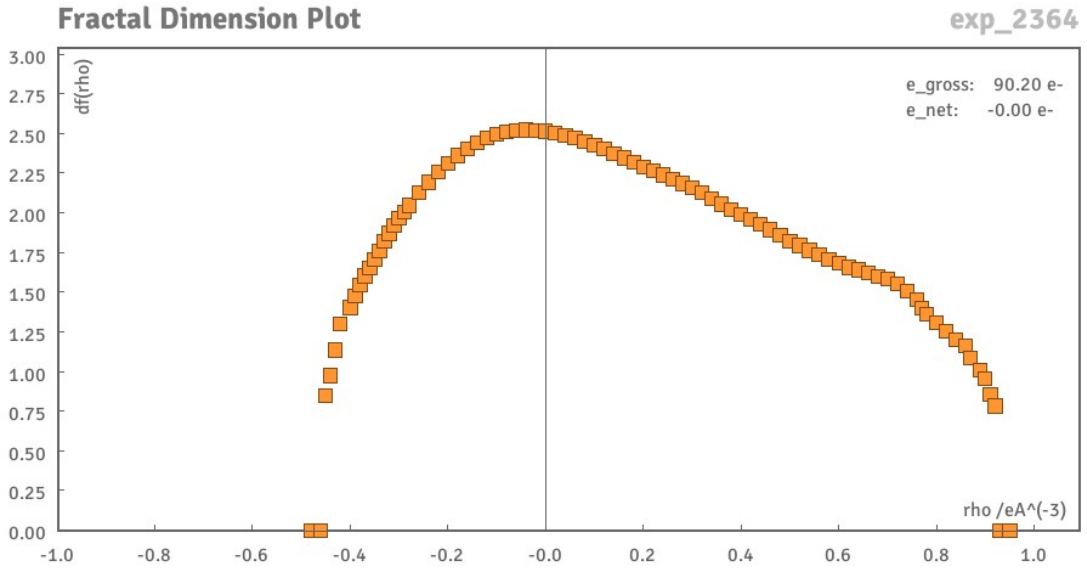
Supplementary Information

^{57}Fe Mössbauer Spectroscopy and High-Pressure Structural Analysis for Mechanism of Pressure-Induced Unique Magnetic Behaviour in (cation)[$Fe^{II}Fe^{III}(dto)_3$] (cation = Ph_4P and $^{n}PrPh_3P$; dto = 1,2-dithiooxalato)

Ryosuke Taniai,[a] Tsubasa Endo,[a] Takuya Kanetomo,[a,*] Atsushi Okazawa,[b] Hirokazu Kadobayashi,[c] Saori I. Kawaguchi,[c] and Masaya Enomoto[a,*]

[a] Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
[b] Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
[c] Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Sayo, Hyogo 679-5198, Japan

a)



b)

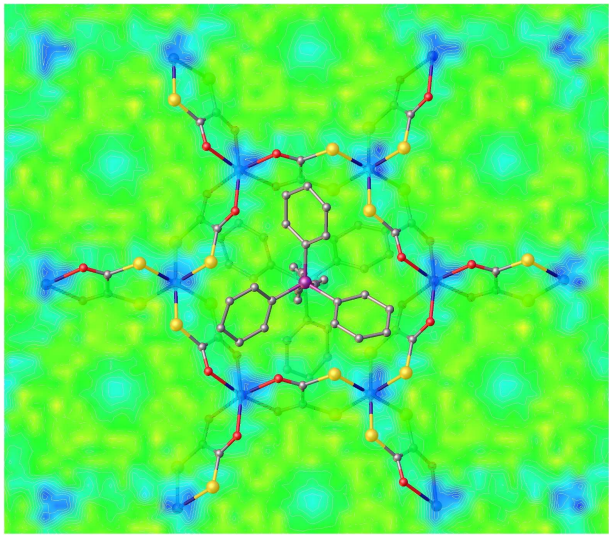


Fig. S1. (a) The fractal dimension distribution of residual electron density and (b) residual

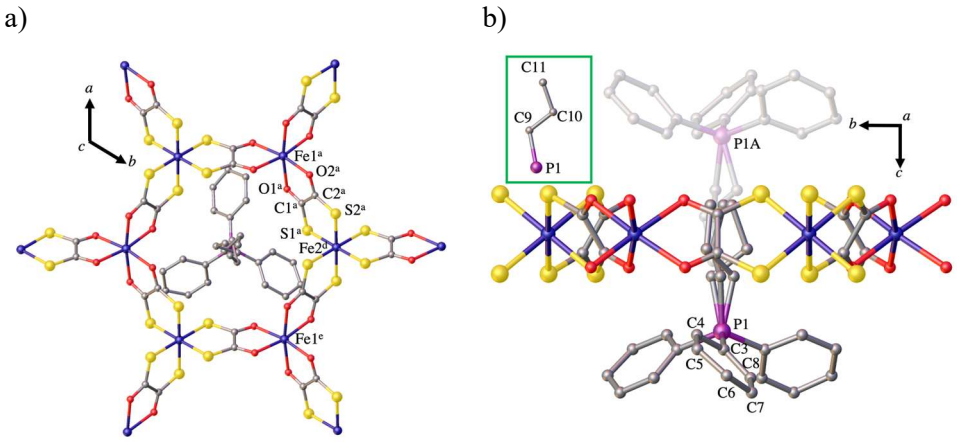


Fig. S2. (a) Coordination environment of O_6 and S_6 atoms for the two Fe ions in **1**. Symmetry code: (a) 1+*x*, 1+*y*, +*z*; (d) 2–*y*, 1+*x* –*y*, +*z*; (e) 1+*y*–*x*, 2–*x*, +z. Color codes: gray, red, yellow, purple, and navy represent C, O, S, P, and Fe atoms, respectively. (b) Penetrated $^{n}PrPh_3P$ cation in the anion layer. One of the disordered states is shown in bright colors, while the other state is shown in a pale color. The inset shows the labels of atoms in the penetrated phenyl ring of the cation.

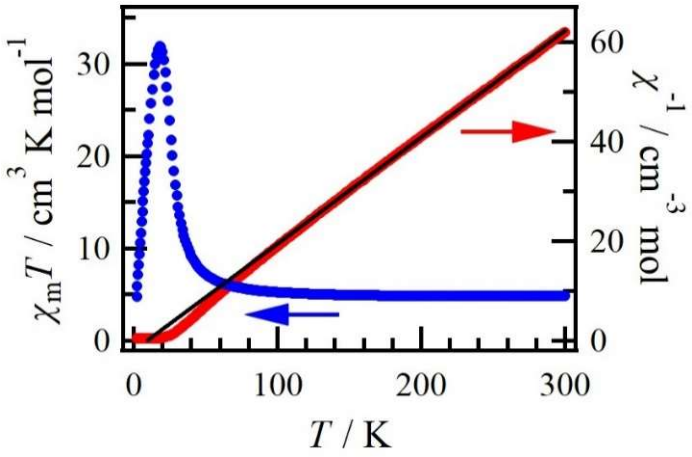


Fig. S3. Temperature dependence of $\chi_m T$ (blue) and χ^{-1} (red) for ($^{n}PrPh_3P$)[$Fe^{II}Fe^{III}$(dto)$_3$] (**3**) measured at the magnetic field of 5000 Oe in the temperature range of 2–300 K. A solid line represents the simulation derived from the Curie-Weiss equation.

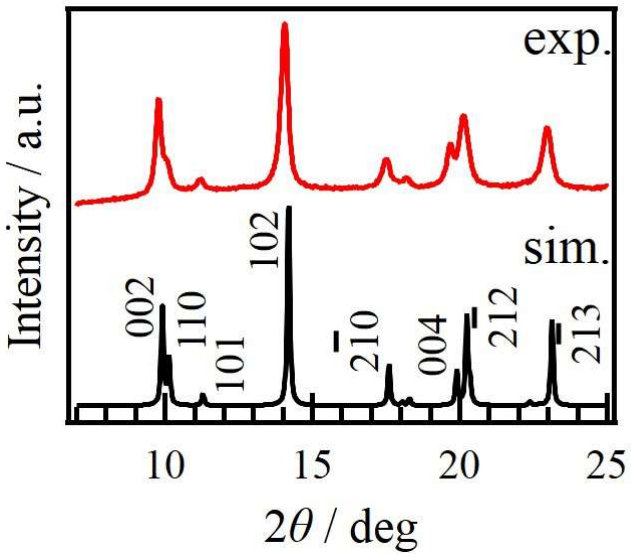


Fig. S4. Experimental result of powder pattern for (^{n}PrPh$_3$P)[Fe^{II}Fe^{III}(dto)$_3$] (**3**) at room temperature (red line) and simulated pattern from SCXRD at 93 K (black line). Both of experiments were performed under ambient pressure.

Table S1. Selected cell parameters at each pressure for **2**.

Pressure / GPa	*a* /Å	*c* /Å	*V* / Å^3
1.0×10^{-4}	10.125(2)	18.447(3)	1637.8(4)
0.523(7)	9.911(2)	17.965(5)	1528.2(5)
0.668(3)	9.886(1)	17.867(4)	1512.4(4)
0.78(2)	9.854(1)	17.834(4)	1499.7(4)
0.88(5)	9.824(1)	17.757(4)	1484.2(4)
1.10(4)	9.789(1)	17.665(4)	1466.0(4)
1.308(3)	9.7537(9)	17.571(3)	1447.6(3)
1.53(8)	9.7188(6)	17.473(2)	1429.3(2)
1.77(4)	9.684(1)	17.372(3)	1410.7(3)
2.12(6)	9.655(1)	17.266(4)	1393.9(4)
3.2(1)	9.5716(9)	16.997(3)	1348.5(3)
4.2(1)	9.4950(9)	16.783(3)	1310.4(3)
5.2(1)	9.4319(9)	16.617(3)	1280.2(3)

Table S2. Selected cell parameters at each pressure for **3**.

Pressure / GPa	*a* /Å	*c* /Å	*V* /Å^3
1.0×10^{-4}	10.127(2)	18.049(4)	1603.1(5)
0.46(3)	9.949(2)	17.526(5)	1502.3(6)
0.60(2)	9.925(3)	17.46(1)	1489.5(9)
0.67(1)	9.905(3)	17.40(1)	1479(1)
0.86(2)	9.873(3)	17.28(1)	1459(1)
0.96(2)	9.852(3)	17.23(1)	1448(1)
1.13(3)	9.825(3)	17.15(1)	1434(1)
1.40(3)	9.783(2)	17.037(7)	1412.1(7)
1.61(3)	9.753(2)	16.964(8)	1397.5(8)
1.91(4)	9.720(3)	16.842(5)	1378.0(7)
2.08(3)	9.701(4)	16.806(6)	1369.8(8)
2.52(3)	9.648(3)	16.71(1)	1347(1)
3.09(6)	9.583(3)	16.58(2)	1319(1)
4.01(5)	9.503(3)	16.41(1)	1283.8(9)
5.13(9)	9.447(6)	16.21(2)	1253(2)