

Supplementary Information for

“Antiferromagnetism in Two-Dimensional Polyradical Nanosheets”

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Materials and Reagents

1,2,4,5-tetrachlorobenzene (>99.0%) was purchased from TCI. CHCl_3 ($\geq 99.0\%$) was purchased from Sinopharm. Tetrahydrofuran (THF, 99.5%, super dry) and trimethylamine (TEA, 99%) were purchased from J&K. AlCl_3 (anhydrous, $\geq 99.0\%$), CH_2Cl_2 ($\geq 99.5\%$), pyridine ($\geq 99.0\%$) were purchased from General-Reagent. I_2 (99%), *n*-BuLi (2.5M in hexane), ethynyltrimethylsilane (98%+), $(\text{PPh}_3)_4\text{Pd}$ (9.2% Pd), CuI (98%+), tetrabutylammonium fluoride (TBAF, 1M in THF), *p*-chloranil (97%+) and $\text{Cu}(\text{OAc})_2$ (98%+) were purchased from Adamas. All reagents were used as received.

Instrumentation and Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 400 Ultrashield NMR spectrometer. Elemental analysis was performed on a Carlo-Erba 1106 (for C, H, and N) and a Metrohm 905 Titrando (for Cl and I). XRD pattern was obtained on a Rigaku-TTR3 X-ray diffractometer. FT-IR spectrum was obtained on a Nicolet 8700. SEM images were obtained on a FEI Helios Nanolab 600i. The OMP sample was dispersed in EtOH via sonication and then dropped onto a carbon mesh grid (purchased from Beijing Zhongjingkeyi Technology Co., Ltd) and dried at room temperature. The carbon grid was attached to an aluminum sample holder without gold coating and then directly placed into the instrument. TEM, STEM and EDX mapping images were obtained on a Tecnai G2 F20 (acceleration voltage: 200 kV). For TEM observations, the carbon mesh grid with the sample was obtained the same as that for SEM. AFM images were obtained on a Bruker Multimode 8. For

AFM measurements, the dispersion of the sample used for TEM and SEM observations was dropped onto freshly cleaved mica. The residual solvent was removed via evaporation at room temperature. Optical microscopy images were obtained on a MV3000 microscope. XPS spectra were obtained on an ESCALAB 250Xi. ESR measurements were performed on a Bruker EMX plus X-band spectrometer from 1.8 to 300 K. SQUID measurements were performed using a Quantum Design MPMS7 SQUID magnetometer. Temperature evolution of the χ was measured in a sweep mode over a temperature range from 2 to 300 K in a field after cooling in the field.

Synthetic procedures

Synthesis of tris(2,3,5,6-tetrachlorophenyl)methane (2): 1,2,4,5-Tetrachlorobenzene (**1**; 9.6 g, 44 mmol), AlCl₃ (0.75 g, 5.6 mmol), and CHCl₃ (0.6 mL, 7.4 mmol) were mixed in a glass pressure vessel and heated at 160°C for 45 min in an oil bath. The mixture was then poured into cracked ice and 50 mL of HCl (1M) and then extracted with CHCl₃ (3×60 mL). The organic phase was washed with deionized water twice, then 2% aqueous NaHCO₃, and finally dried with anhydrous Na₂SO₄ overnight. After evaporation of the solvent, the residue was then purified by column chromatography eluting with *n*-hexane to yield 1.59 g of **2** (33% yield based on CHCl₃) as white crystals. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (s, 3H), 6.98 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 138.6, 134.4, 133.6, 133.3, 132.4, 130.4, 56.0. Elemental analysis: Calcd. for C₁₉H₄Cl₁₂: C, 34.70; H, 0.61; Cl, 64.69. Found: C,

35.02; H, 0.57; Cl, 63.79.

Synthesis of tris(4-iodo-2,3,5,6-tetrachlorophenyl)methane (3): To a 200 ml Schlenk flask, 1.32g of **2** (2 mmol) was added under argon atmosphere. 80 mL of dry THF was then added. The solution was cooled to -78°C and 5 mL of *n*-BuLi (2.5M in hexane, 12.5 mmol) was slowly added. The solution was stirred for 2 h at -78 °C and then 6.35 g of I₂ (25 mmol) was added. The mixture was warmed to room temperature gradually and stirred overnight. Then 30 mL of saturated Na₂S₂O₃•5H₂O solution was added to quench the reaction. The mixture was filtered through a 0.22 μm membrane. The solid was washed with CH₂Cl₂ and *n*-hexane and then dried under vacuum at 60°C overnight. Finally, 1.73g of white powder **3** was obtained (83% yield). ¹H NMR (400 MHz, THF-*d*₈): δ 6.99 (s, 1H). Elemental analysis: Calcd. for C₁₉H₁Cl₁₂I₃: C, 22.04; H, 0.10; Cl, 41.09; I, 36.77. Found: C, 22.88; H, <0.30; Cl, 40.57; I, 35.63.

Synthesis of tris(2,3,5,6-tetrachloro-4-((trimethylsilyl)ethynyl)phenyl)methane (4): Under argon atmosphere, 1.035g of **3** (1mmol), 80 mg of CuI (0.4 mmol), 240 mg of (PPh₃)₄Pd (02 mmol), 30 mL of dry THF, 1.7 mL of TEA (12 mmol) and 0.5 mL of ethynyltrimethylsilane (3.5 mmol) were mixed in a glass pressure vessel and heated at 80°C for 24 h in an oil bath. After cooling to room temperature, the mixture was extracted with CH₂Cl₂ and 6M HCl. The organic phase was separated, washed with deionized water for three times and then dried with anhydrous Na₂SO₄ overnight. After evaporation of the solvent, the residue was then purified by column chromatography eluting with *n*-hexane to yield 116 mg of **4** (12% yield) as white crystals. ¹H NMR (400 MHz, CDCl₃): δ 6.95 (s, 1H), 0.30 (s, 27H). ¹³C NMR (100

MHz, CDCl₃): δ 137.7, 136.0, 134.9, 134.4, 133.3, 125.0, 109.8, 97.7, 56.7, -0.4.

Elemental analysis: Calcd. for C₃₄H₂₈Cl₁₂Si₃: C, 43.15; H, 2.98; Cl, 44.96. Found: C, 43.94; H, 3.06; Cl, 44.82

Synthesis of tris(2,3,5,6-tetrachloro-4-ethynylphenyl)methyl radical (5): To a solution of **4** (19 mg, 20 μ mol) in 100 mL of CH₂Cl₂, 200 μ L of TBAF (1M in THF, 200 μ mol) was added. The solution was stirred in the dark for 1 h and 60 mg of *p*-chloranil (240 μ mol) was then added. The solution was stirred in the dark for 2h to obtain **5**. The solution containing **5** was directly used for the synthesis of OMP without further purification.

Synthesis of organic magnetic polyradical (OMP) nanosheets: The solution of **5** was poured into a glass cylinder with a diameter of 75 mm. 50 mL of deionized water was added and a two-phase interface was formed. Then an aqueous solution (50 mL) of copper acetate (0.01 M) and pyridine (0.25 M) was added dropwise to the water phase. The reaction system was kept in the dark for one week without any disturbance and a dark brown film of OMP was obtained at the interface. The water phase was replaced with 1M HCl and then deionized water, while the organic phase was replaced with pure CH₂Cl₂. The mixture was through a 0.22 μ m membrane and the solid was washed with deionized water, EtOH and CH₂Cl₂. Finally, after drying under vacuum at 50°C overnight, 6.1 mg of OMP was obtained (42% yield).

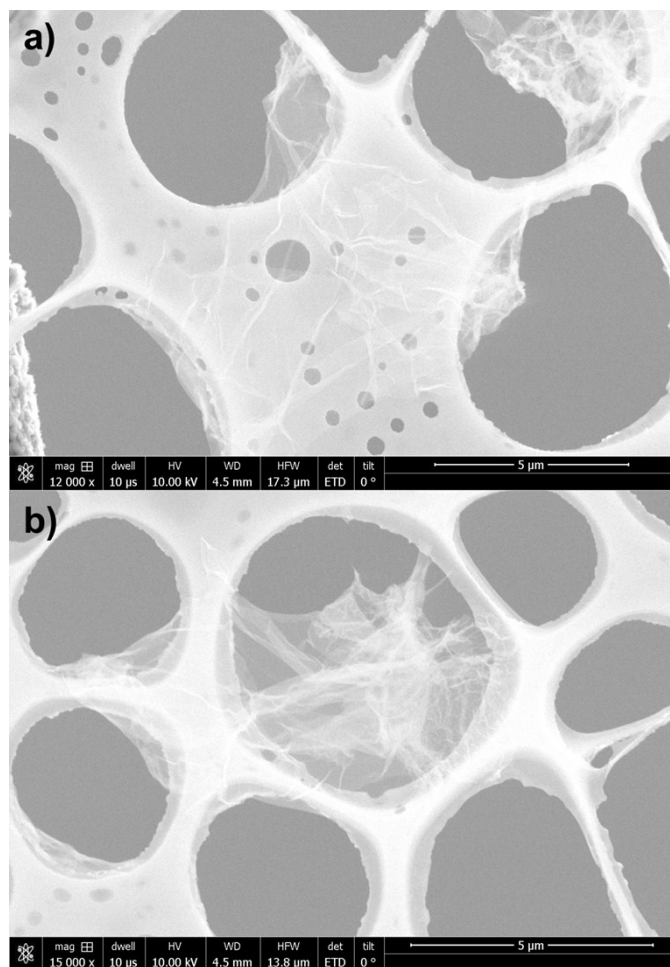


Fig. S1 a and b more scanning electron microscopy (SEM) images of OMP nanosheets.

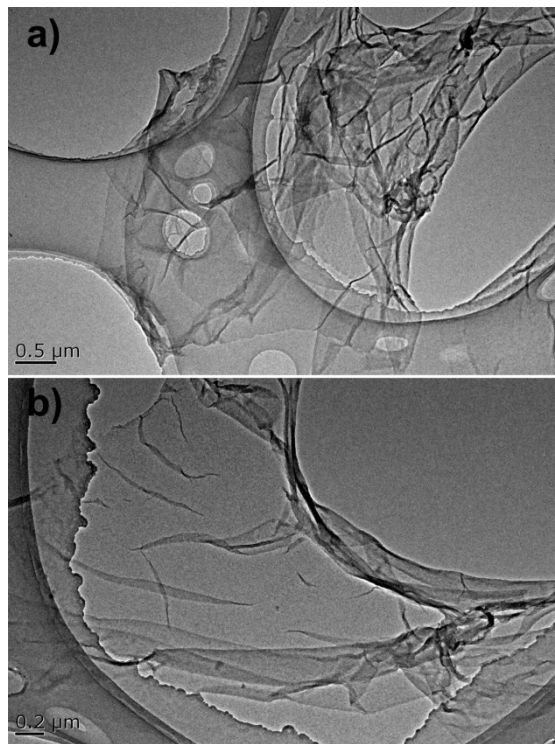


Fig. S2 a and b more transmission electron microscopy (TEM) images of OMP nanosheets.

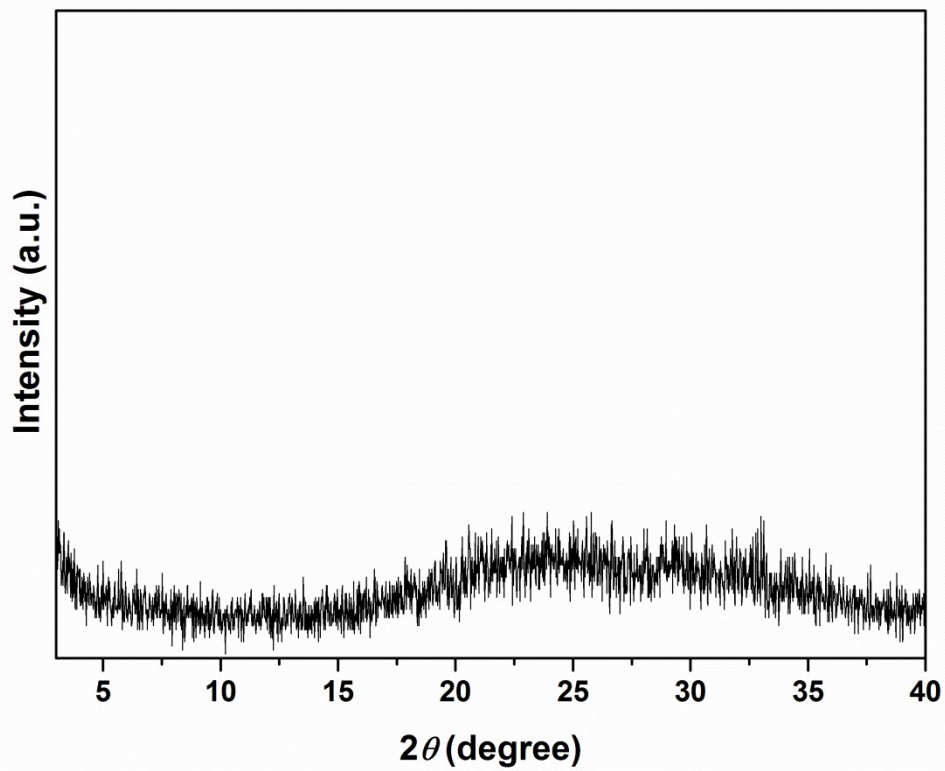


Fig. S3 XRD pattern of OMP.

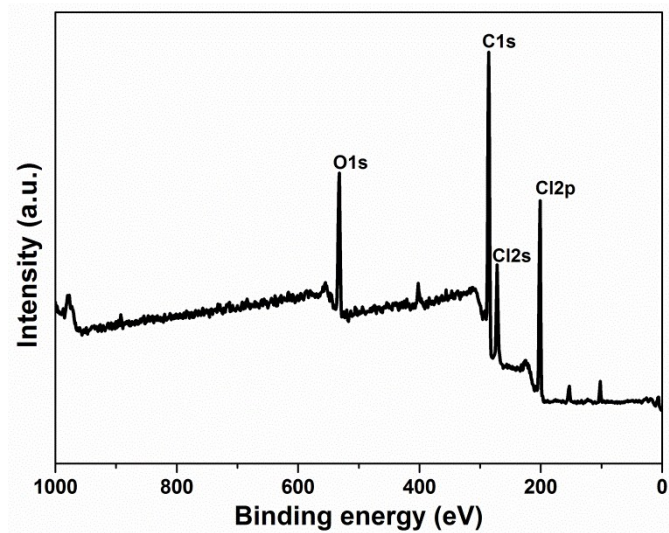


Fig. S4 Complete X-ray photoelectron spectroscopy (XPS) spectrum of OMP.

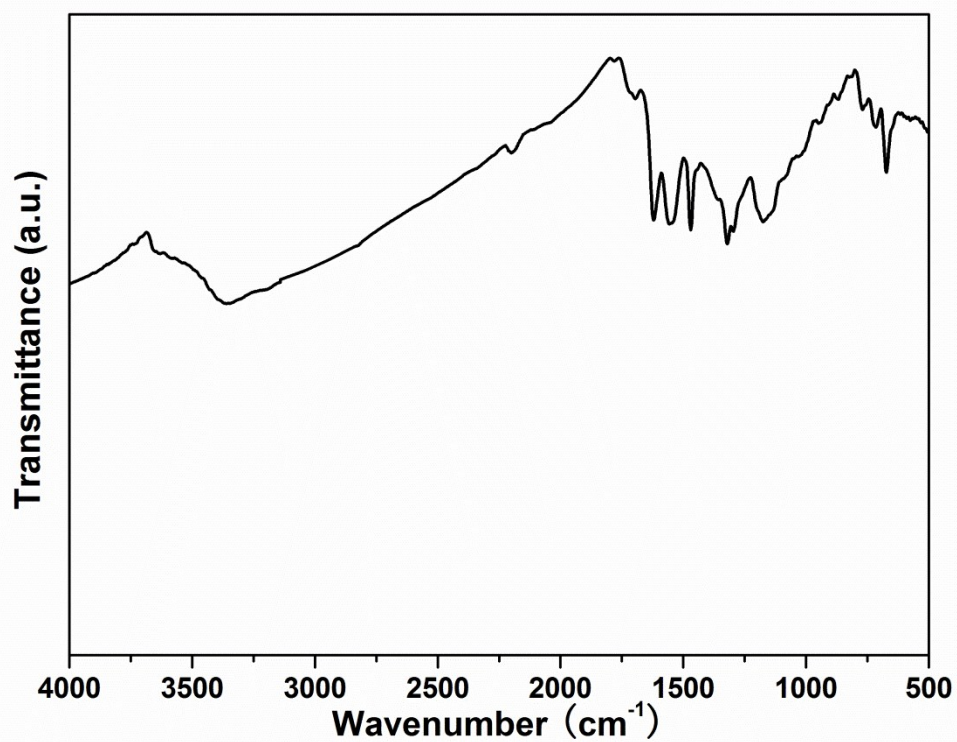


Fig. S5 FT-IR spectrum of OMP.

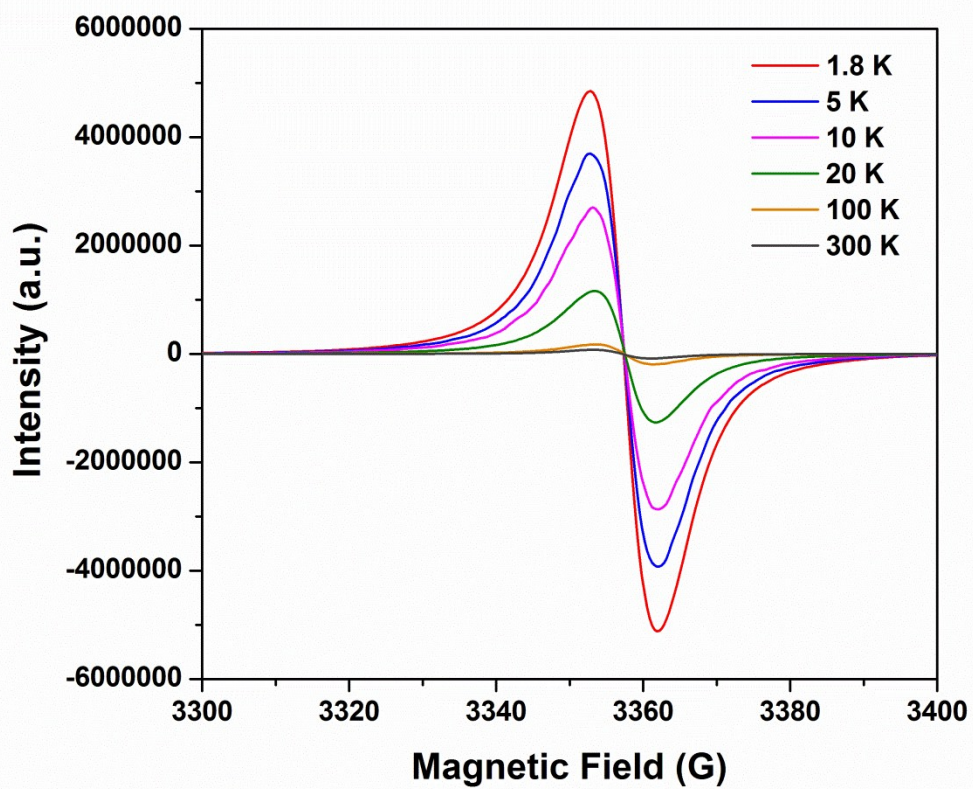


Fig. S6 Electron spin resonance (ESR) spectra of OMP at various temperatures.

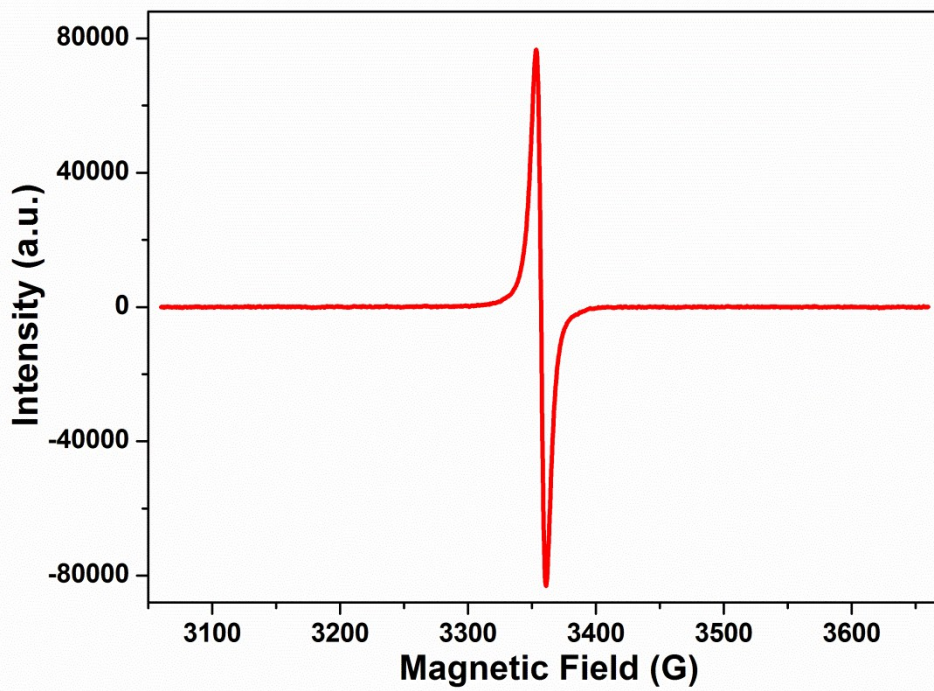


Fig. S7 ESR spectrum of OMP in wide magnetic field from 3060 to 3660 G at 300 K.

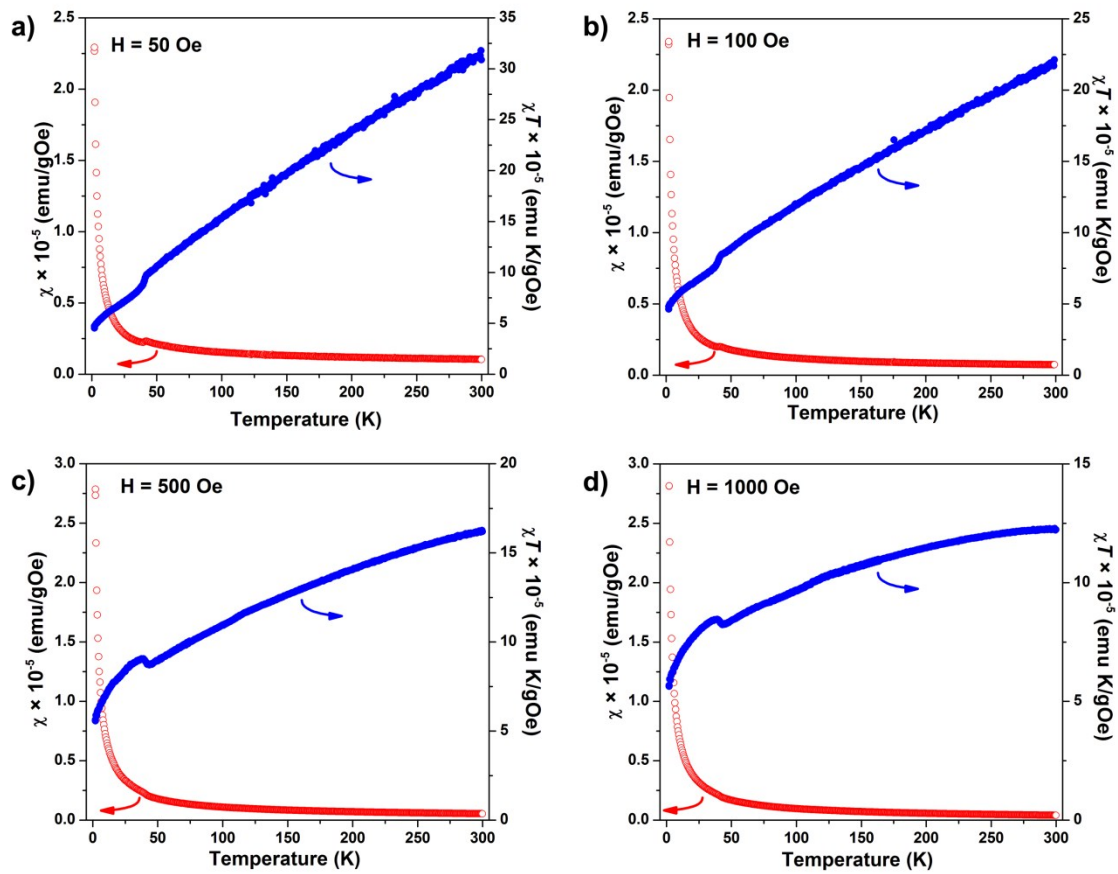


Fig. S8 χ - T and χT - T curves of OMP under various fields.