

## Supporting Information for

### Room-Temperature Magnetism in the Crystal of a 1,6-Heptadiyne Derivative and the Processable Polymer

Manyu Chen<sup>a</sup>, Guangze Hu<sup>a</sup>, Zuping Xiong<sup>a</sup>, Haoyuan Hu<sup>a</sup>, Jing Zhi Sun<sup>\*a</sup>, Haoke Zhang<sup>\*a,b</sup>, Ben Zhong Tang<sup>\*a,c</sup>

<sup>a</sup> MOE Key Laboratory of Macromolecules Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310058, China. E-mail: [sunjz@zju.edu.cn](mailto:sunjz@zju.edu.cn); [zhanghaoke@zju.edu.cn](mailto:zhanghaoke@zju.edu.cn)

<sup>b</sup> Zhejiang-Israel Joint Laboratory of Self-Assembling Functional Materials, ZJU-Hangzhou Global Scientific and Technological Innovation Center, Zhejiang University, Hangzhou, 311215, China

<sup>c</sup> School of Science and Engineering, Shenzhen Institute of Aggregate Science and Technology, The Chinese University of Hong Kong, Shenzhen (CUHK-SZ), Guangzhou, 518172, China E-mail: [tangbenz@cuhk.edu.cn](mailto:tangbenz@cuhk.edu.cn)

Keywords: room-temperature organic ferromagnets, radicals, substituted polydiyne

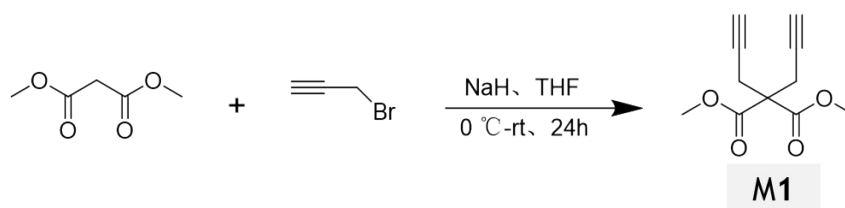
### Table of Contents

<b>Table of Contents</b> .....	1
<b>Monomer synthesis [2,2-Di-(prop-2-ynyl)-malonic acid dimethyl ester]</b> .....	2
<b>Scheme S1</b> Synthetic route to 4-substituted 1,6-heptadiyne (M1). .....	2
<b>Polymer synthesis</b> .....	2
<b>Table S1</b> Polymerization of M1 <sup>a</sup> . .....	3
<b>Figure S1</b> FTIR spectra of monomer (M1, A) and polymer (P1, B) in KBr pellets. ....	4
<b>Figure S2</b> <sup>1</sup> H NMR spectra of monomer (M1, A) and polymer (P1, B) measured in CDCl <sub>3</sub> solution. The symbol (*) refers to peak of the solvent. ....	4
<b>Figure S3</b> Magnetization–magnetic field (M–H) curve of P1 powders measured at 300 K. ....	5
<b>Figure S4</b> (A) Photograph of P1 solution in a petri-dish with tetrahydrofuran as solvent; (B) A piece of solid film of P1 made from solution casting method at room temperature. ....	5
<b>Table S2</b> The content of molybdenum, iron, cobalt, and nickel in P1 tested by inductively coupled plasma optical emission spectrometer (ICP-OES). ....	5
<b>Figure S5</b> UV-visible spectra for P1 solution samples of the as-prepared (black line) and the stored in the air for two weeks (red line). ....	6
<b>Figure S6</b> Fluorescence emission curves of P1 solution (THF, 10 <sup>-4</sup> M) and solid. (E <sub>x</sub> = 500 nm) .....	6
<b>Figure S7</b> Photos of P1 solution and solid under sunlight and 365nm ultraviolet light. ....	7

<b>Figure S8</b> Thermogravimetric curves of M1 and P1.....	7
<b>Figure S9</b> Magnetization curves of MoCl <sub>5</sub> before and after oxidation. ....	8
<b>Figure S10</b> P1 X-ray photoelectron spectrometer full spectrum. ....	8
<b>Figure S11</b> Fine spectrum of P1 iron element tested by X-ray photoelectron spectrometer. ....	9
<b>Figure S12</b> Hysteresis curve of P1 residue after heating at 500 °C for 1 h.....	9
<b>Figure S13</b> Temperature dependent magnetic properties of P1 powders. (A) and (B) are the magnetic susceptibility ( $\chi$ ) and the product ( $\chi T$ ) of magnetic susceptibility and temperature of P1. ....	10
<b>Video display of P1</b> .....	10

### Monomer synthesis [2,2-Di-(prop-2-ynyl)-malonic acid dimethyl ester]

The synthetic route is shown in Scheme S1, and the experimental procedures are described as following. 2.64 g NaH (110 mmol) was weighed in a 250 mL double-necked flask and placed in a nitrogen and ice bath environment. Under magnetic stirring, 50 mL ultra-dry THF was added dropwise, and then dimethyl malonate (6.6 g, 50 mmol) THF solution (20 mL) was added dropwise. After 1 h of reaction, the THF solution (25 mL) of bromopropyne (14.28 g, 120 mmol) was added dropwise, and the ice bath was removed after the bromopropyne solution was added dropwise. The reaction was performed at room temperature for 24 h. After the reaction was completed, washed with saturated NH<sub>4</sub>Cl solution, extracted with DCM, collected the organic phase, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, removed the solvent by rotary evaporation, and then purified by column chromatography (PE:EA = 4:1). The white solid was obtained by rotary evaporation with a yield of 52.8 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 3.76(6H, s), 2.99 (4H, d), 2.03 (2H, t). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 169.16, 78.41, 71.90, 56.55, 53.28, 22.78.



**Scheme S1** Synthetic route to 4-substituted 1,6-heptadiyne) (M1).

### Polymer synthesis

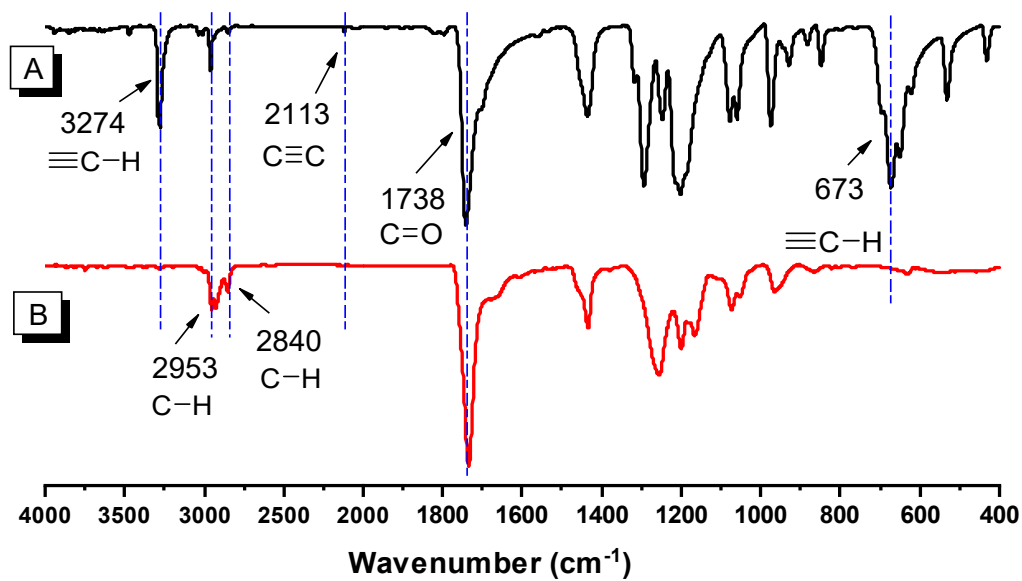
In the glove box, 0.01 mol of catalyst (MoCl<sub>5</sub>) was weighed in the polymerization tube, 0.02 mol of tetrabutyltin was taken with a micro-injector after the catalyst was added, and then 1 mL of DCE solvent was added. In another polymerization tube, 0.5 mol of monomer was weighed, 1 mL of ultra-dry DCE was added to dissolve the monomer, and then the monomer solution was transferred to the polymerization tube where the catalyst had been activated for 15 min. At the end of the reaction at the preset

temperature and time, 1 mL of methanol was added to terminate the reaction, and then the solution was then dropped into a large amount of methanol through a glass dropper and precipitated overnight. The resultant was filtered using a sand core funnel. The resultant was purified with repeated dissolving and precipitation operations for no less than 6 times, and the precipitate was dried in vacuum dry to a constant weight, and finally black powder (P1) was obtained. The synthetic procedures of the monomer and the structure characterization data of the monomer and polymer are included in Supporting Information.

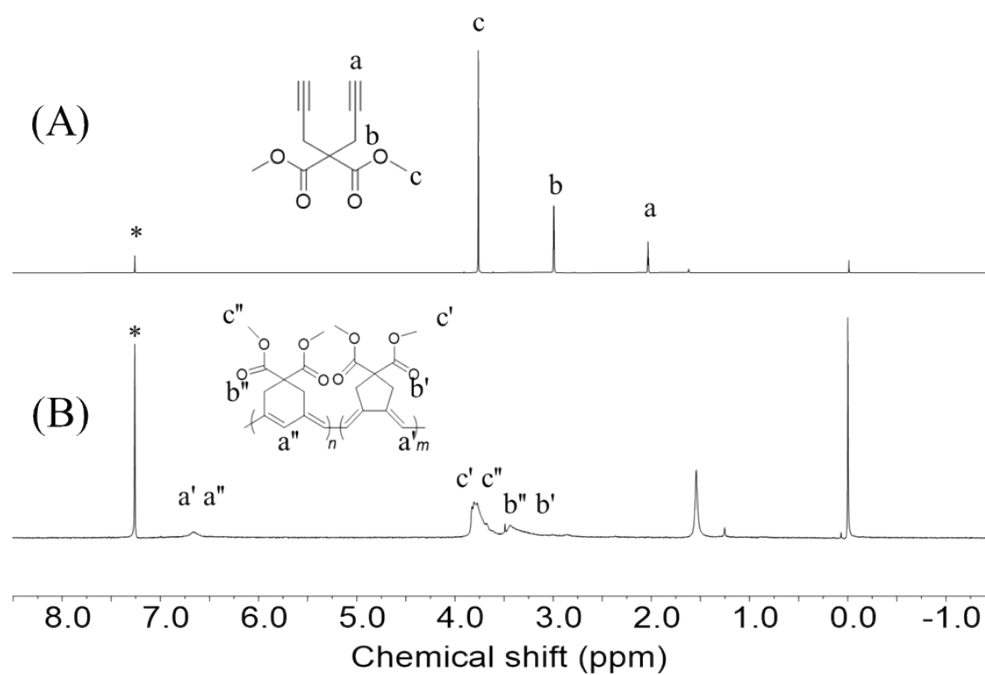
**Table S1** Polymerization of M1<sup>a</sup>.

Entry	Catalyst system	Temp. (°C)	t	Yield <sup>b</sup> (%)	M <sub>w</sub> <sup>c</sup>	PDI <sup>c</sup>
1	MoCl <sub>5</sub>	60	2 min	82.3	-	-
2	MoCl <sub>5</sub>	0	2 min	75.2	-	-
3	MoCl <sub>5</sub>	-10	3 h	42.8	14400	1.79

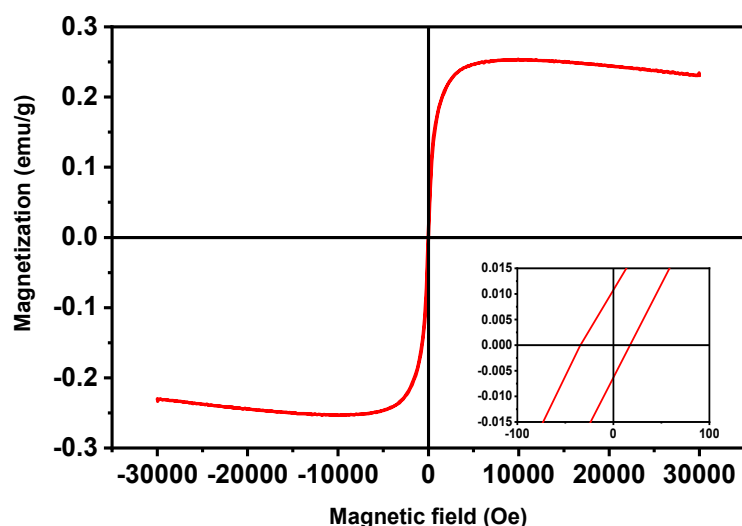
<sup>a</sup> The reaction was carried out at the desired temperature in DCE for desired times, [M] = 0.25 mol/L, [Catalyst] = 0.005 mol/L, [co-catalyst] = 0.01 mol/L. <sup>b</sup> The product was precipitated from methanol; <sup>c</sup> Estimated by GPC, PDI = poly-dispersion index. -: Indicating that the polymer is almost insoluble.



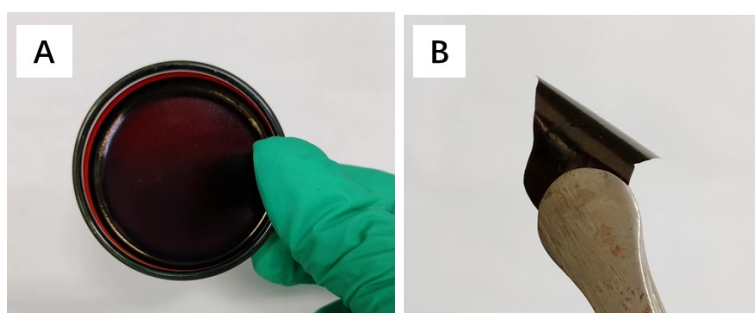
**Figure S1** FTIR spectra of monomer (M1, A) and polymer (P1, B) in KBr pellets.



**Figure S2**  $^1\text{H}$  NMR spectra of monomer (M1, A) and polymer (P1, B) measured in  $\text{CDCl}_3$  solution. The symbol (\*) refers to peak of the solvent.



**Figure S3** Magnetization–magnetic field (M–H) curve of P1 powders measured at 300 K.

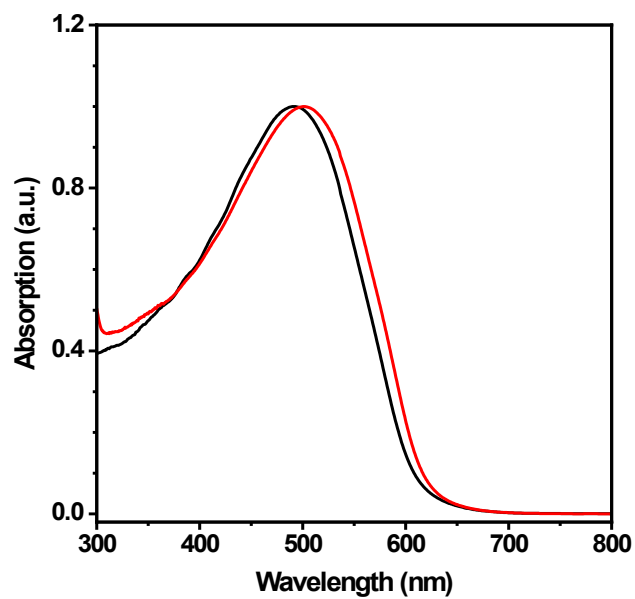


**Figure S4** (A) Photograph of P1 solution in a petri-dish with tetrahydrofuran as solvent; (B) A piece of solid film of P1 made from solution casting method at room temperature.

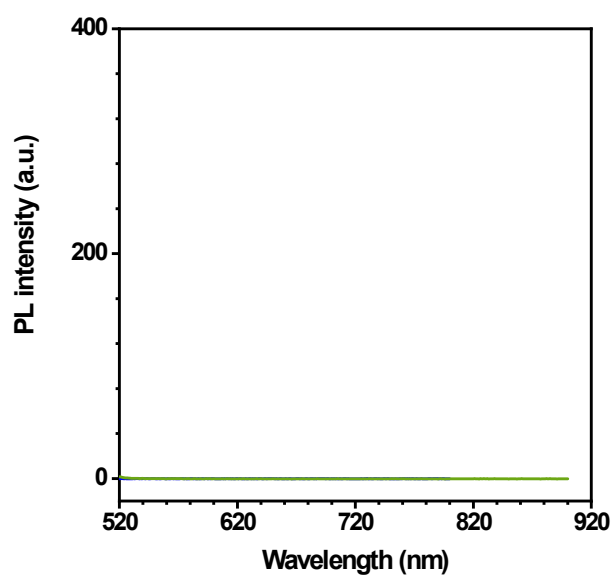
**Table S2** The content of molybdenum, iron, cobalt, and nickel in P1 tested by inductively coupled plasma optical emission spectrometer (ICP-OES).

The result showed that the content of molybdenum, iron, cobalt, and nickel in P1.

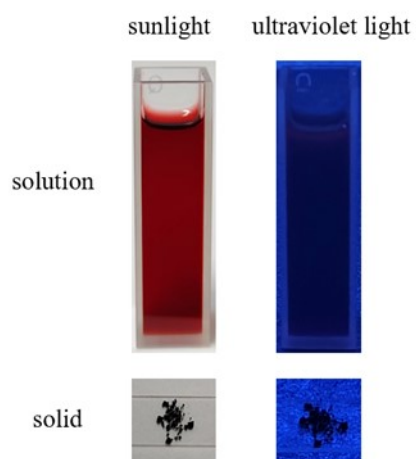
Sample number	Sample mass $m_0$ (g)	Fixed volume $V_0$ (mL)	Test elements	Test solution element concentration $C_0$ (mg/L)	Dilution factor $f$	Element	Sample element content $C_x$ (mg/kg)	Sample element content W (%)
						concentration $C_1$ (mg/L) in the original solution of the digestion solution		
P1	0.0528	25	Mo	0.242	1	0.24192301	114.5	0.01
P1	0.0528	25	Mo	0.242	1	0.24194307	114.6	0.01
P1	0.064	25	Fe	0.149	1	0.149	58.379	0.0058
P1	0.064	25	Co	0.000276	1	0.000276	0.108	0.00001
P1	0.064	25	Ni	0.00267	1	0.00267	1.043	0.0001



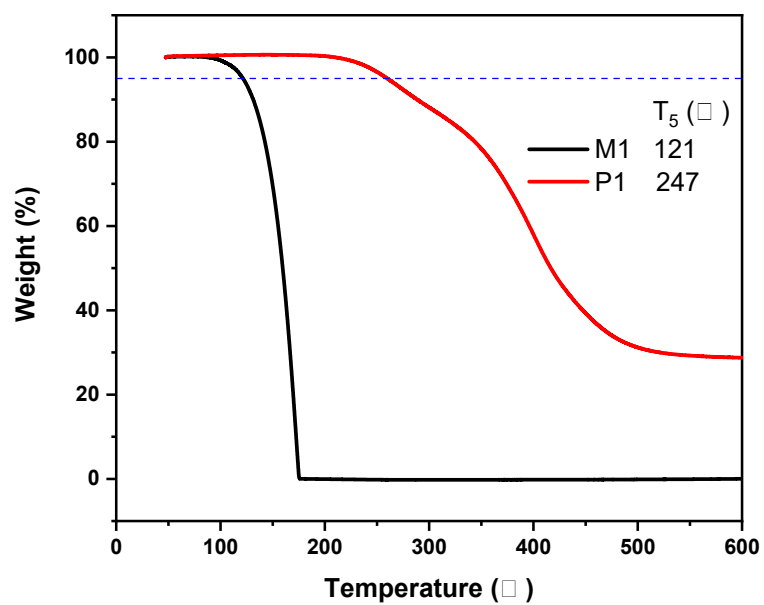
**Figure S5** UV-visible spectra for P1 solution samples of the as-prepared (black line) and the stored in the air for two weeks (red line)..



**Figure S6** Fluorescence emission curves of P1 solution (THF,  $10^{-4}$  M) and solid. ( $E_x = 500$  nm)



**Figure S7** Photos of P1 solution and solid under sunlight and 365nm ultraviolet light.



**Figure S8** Thermogravimetric curves of M1 and P1.

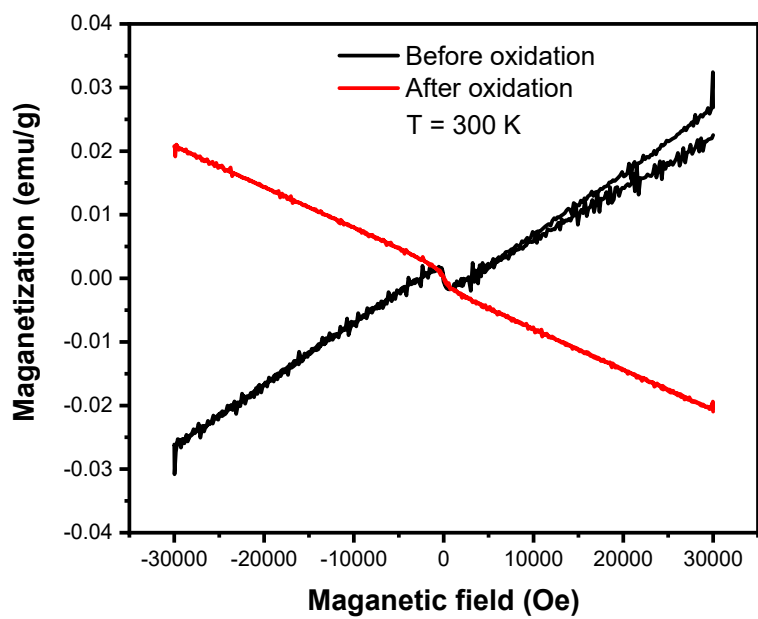


Figure S9 Magnetization curves of MoCl<sub>5</sub> before and after oxidation.

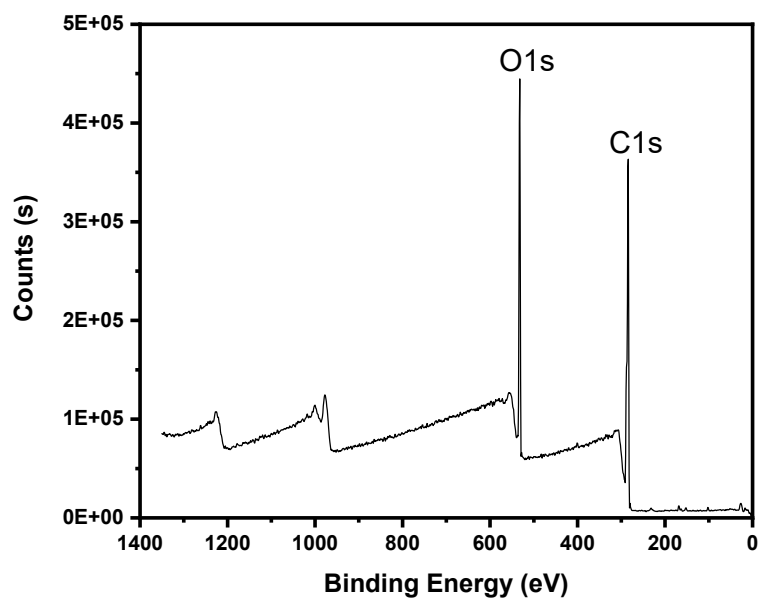
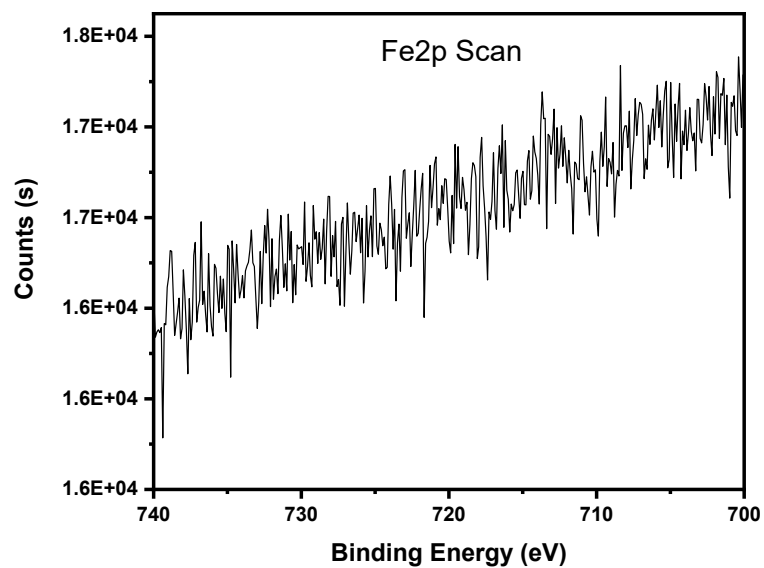
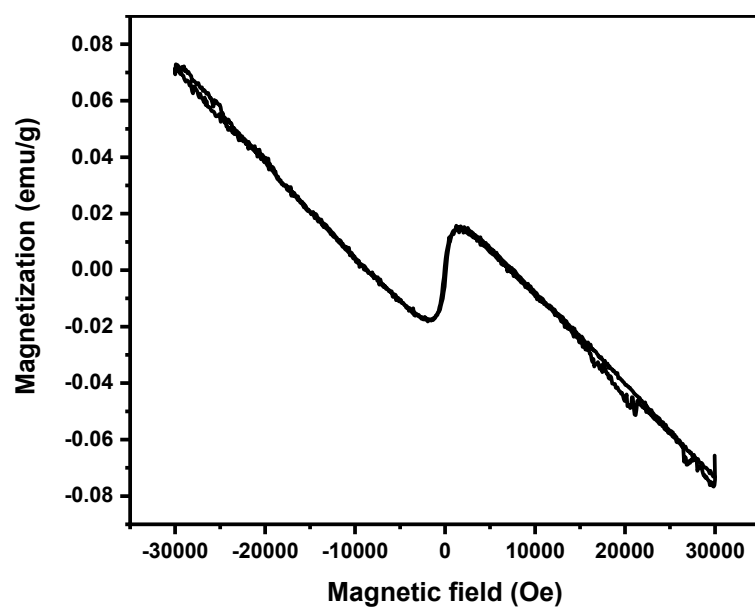


Figure S10 P1 X-ray photoelectron spectrometer full spectrum.

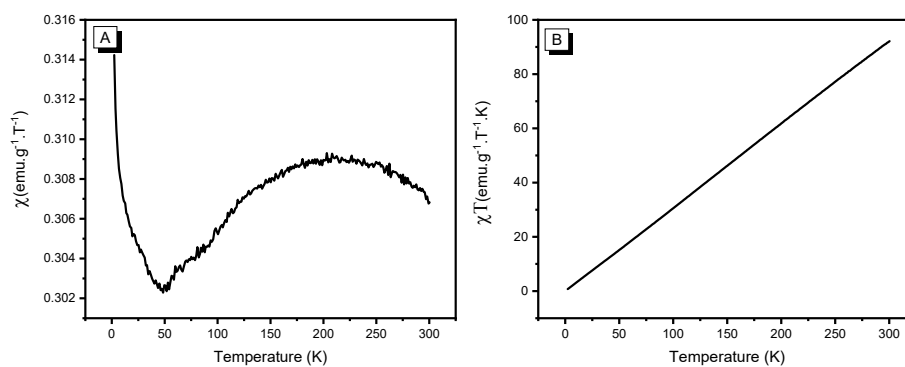




**Figure S11** Fine spectrum of P1 iron element tested by X-ray photoelectron spectrometer.



**Figure S12** Hysteresis curve of P1 residue after heating at 500 °C for 1 h.



**Figure S13** Temperature dependent magnetic properties of P1 powders. (A) and (B) are the magnetic susceptibility ( $\chi$ ) and the product ( $\chi T$ ) of magnetic susceptibility and temperature of P1.

### Video display of P1

