

# Supporting information of

## Antiferromagnetic spin-1 large-*D* phase in organic spin-chain crystals

Zhihao Li,<sup>1,2</sup> Yihao Wang,<sup>1,2</sup> Yuyan Han,<sup>1</sup> Meng Song,<sup>1,2</sup> Jiangpeng Song,<sup>1,2</sup> Junbo Li,<sup>1,2</sup> Yongliang Qin,<sup>1</sup> Langsheng Ling,<sup>1</sup> Wei Tong,<sup>1</sup> Yuxian Guo,<sup>3</sup> Zan Du,<sup>1,2</sup> Lei Zhang,<sup>1</sup> Wenhua Zhang,<sup>4\*</sup> Yimin Xiong,<sup>5,6‡</sup> Liang Cao,<sup>1†</sup>

*1 Anhui Province Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei, Anhui 230031, China*

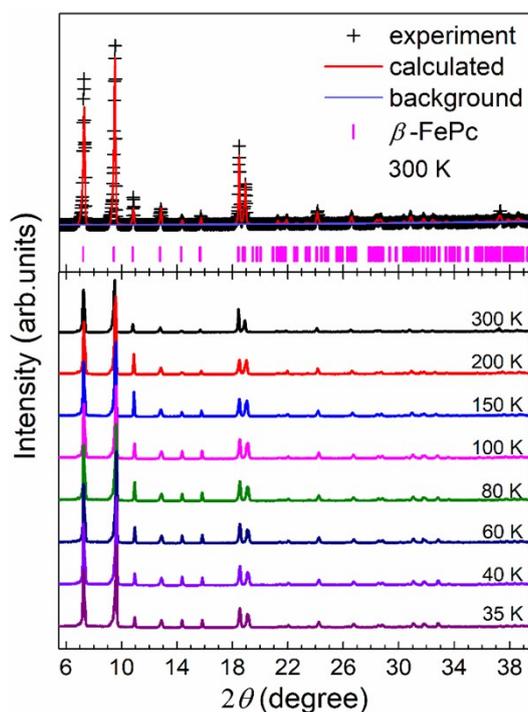
*2 University of Science and Technology of China, Hefei, Anhui 230026, China*

*3 School of Mathematics & Physics, Anhui Jianzhu University, Hefei, 230601, China*

*4 National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China*

*5 Department of Physics, School of Physics and Optoelectronics Engineering, Anhui University, Hefei 230601, P. R. China*

*6 Hefei National Laboratory, Hefei 230028, China*

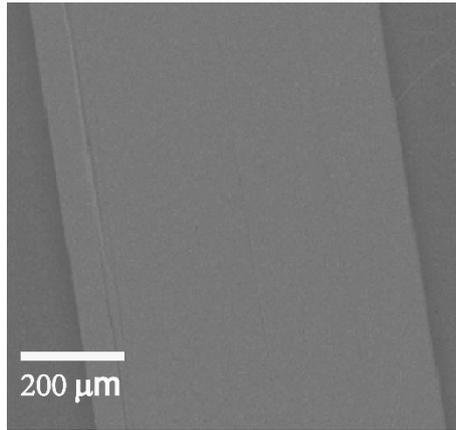


**Figure S1.** XRD pattern for pulverized  $\beta$ -FePc single crystal samples at different temperature. The red, blue and pink lines in the top picture are the calculated intensity, estimated background and Bragg diffraction peaks obtained by GSAS software, respectively.

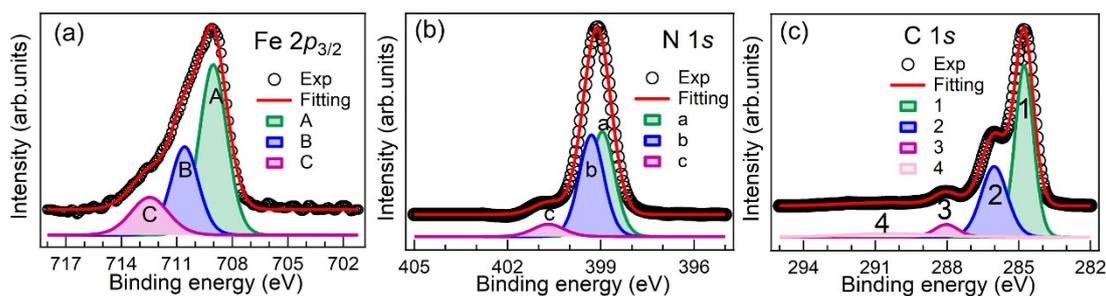
To investigate the influence of temperature on molecular stacking arrangement in  $\beta$ -FePc crystals, which can significantly affect the physical and chemical properties of molecular aggregates, XRD measurements were performed on pulverized single crystal samples at temperature ranging from 300 K to 35 K. The structure parameters at different temperature, which were calculated from diffraction data by using GSAS software, are summarized in Table S1.

**Table S1 | The structure parameters of  $\beta$ -FePc crystal at different temperature**

T (K)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)
300	19.45	4.80	14.63	120.77
200	19.42	4.81	14.63	120.74
150	19.39	4.81	14.66	120.70
100	19.36	4.81	14.66	120.62
80	19.34	4.82	14.66	120.64
60	19.32	4.82	14.66	120.60
40	19.33	4.81	14.66	120.58
35	19.32	4.82	14.66	120.61



**Figure S2.** Scanning electron microscope of the  $bc$  plane of a thinner  $\beta$ -FePc single crystal.

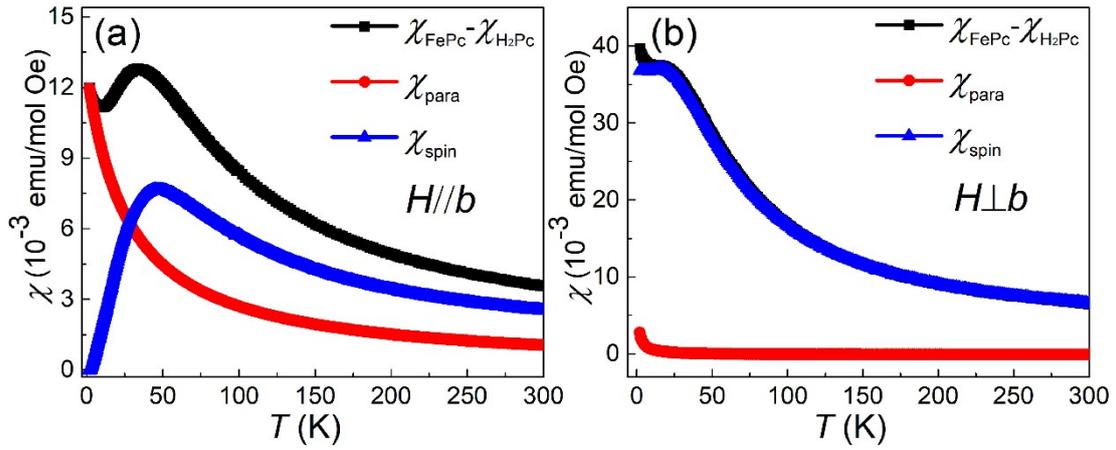


**Figure S3.** (a) Fe  $2p_{3/2}$ , (b) N  $1s$  and (c) C  $1s$  X-ray photonemission (XPS) spectrum of  $\beta$ -FePc crystal. The black circles represent the experiment data, the greenish, bluish and pinkish lines are the components (Gaussian line shape) according to signal deconvolution, and the solid red line is the sum of these components. The Shirley background was subtracted from all the spectrums.

As shown in Fig. S3 (a), the Fe  $2p_{3/2}$  core level spectrum features two main peaks A and B and a satellite C. The de-convoluted component peak positions and their full width at half maximum (FWHM) are summarized in Table S2. As shown in Fig. S2 (b), the N $1s$  core level spectrum is de-convoluted in three components. Peak a and peak b are attributed to different photoexcitation, respectively from the two non-equivalent pyrrole ring nitrogen atoms and bridged position nitrogen atoms. The component c corresponds to the shake-up satellite at higher binding energy. The C  $1s$  spectrum has been de-convoluted in four components (1, 2, 3 and 4). The main component 1 is attributed to the benzene carbons (C-C) and component 2 is attributed to the pyrrole carbons (C-N) of the FePc molecule. The components 3 and 4 correspond to the shake-up satellites of the components 1 and 2, respectively. According to these fitting results, the atomic ratio of Fe:N:C estimated of Fe  $2p$ , N  $1s$  and C  $1s$  is 1:7.4:33.1 by using relative integrated area, which is close to stoichiometric ratio of 1: 8: 32.

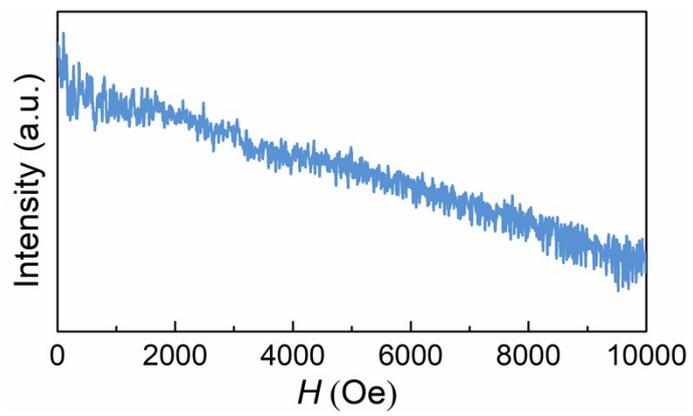
Table S2. Binding energies (BE) and FWHM for the peak components of the Fe  $2p_{3/2}$ , N  $1s$  and C  $1s$  photoemission spectra of  $\beta$ -FePc crystal.

Spectrum	Fe 2p			N 1s			C 1s			
Peak	A	B	C	a	b	c	1	2	3	4
BE (eV)	709	710.6	712.5	398.9	399.3	400.7	284.8	286.0	288.0	290.3
FWHM (eV)	1.74	1.76	2.32	0.93	0.94	1.17	0.91	1.29	1.18	4.50

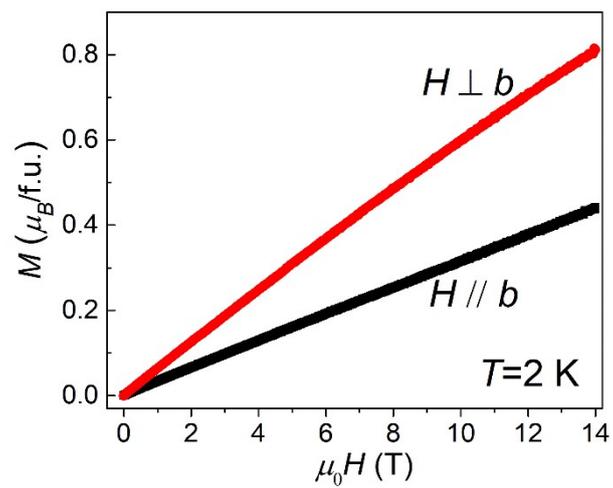


**Figure S4.** Spin susceptibility  $\chi_{\text{spin}}$  obtained by subtracting for anisotropy  $\chi_{\text{H}_2\text{Pc}}$  and  $\chi_{\text{para}}$  for  $H//b$  (a) and  $H \perp b$  (b), respectively.

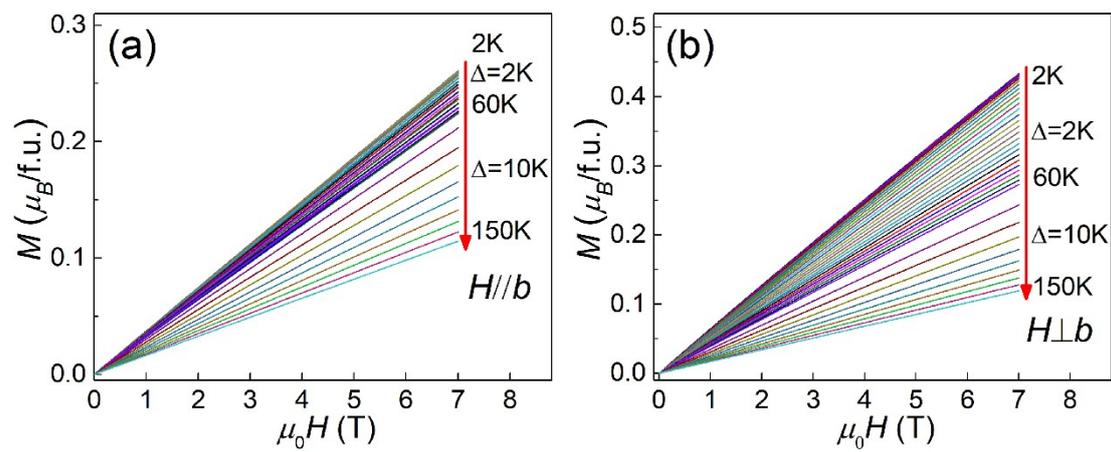
Since the large single ion anisotropy ( $D$ ) in FePc, the spin contribution  $\chi_{\text{spin}}$  should go to zero and close to a constant for  $H//b$  and  $H \perp b$ , respectively. Therefore, after subtracting the diamagnetic susceptibility  $\chi_{\text{H}_2\text{Pc}}$ , the paramagnetic contribution  $\chi_{\text{para}}$  was fitted by Curie-Weiss Law  $\chi_{\text{para}} = C/(T-\theta)$  for  $H//b$  and with an additional constant  $\chi_0$  for  $H \perp b$  at low temperature, as shown in Figure S3. The extrinsic Curie constant  $C$  and Curie-Weiss temperature  $\theta$  are 0.343 emu K/mol Oe and -26.8 K for  $H//b$  and  $6.02 \times 10^{-3}$  emu K/mol Oe and -0.198 K for  $H \perp b$ . Finally, by subtracting the  $\chi_{\text{para}}$ , the spin susceptibility  $\chi_{\text{spin}}$  is obtained.



**Figure S5.** ESR spectrum of  $\beta$ -FePc single crystal at 1.8 K with 9.4 GHz frequency.



**Figure S6.** Field dependence of molar magnetization at 2 K with  $H \perp b$  or  $H // b$  axis.



**Figure S7.** Isothermal magnetization of  $\beta$ -FePc crystal for  $H//b$  (a) and  $H \perp b$  (b).