## **Supporting Information**

## Homochiral Iron(II)-based metal-organic nanotubes: metamagnetism and selective nitric oxide adsorption in confined channel

Jia-Ge Jia, Jian-Shen Feng, Xin-Da Huang, Song-Song Bao,\* and Li-Min Zheng\* State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China; E-mail: Imzheng@nju.edu.cn, baososo@nju.edu.cn

## **Experimental Section**

Materials and measurements. All starting materials were commercially without further purification. (S)-, (R)-(1-phenylethylamino)available methylphosphonic acid (pempH<sub>2</sub>) were prepared by reactions of (S)- or (R)-1-phenylethylamine, diethyl phosphite and paraformaldehyde, according to the literature method.<sup>1</sup> The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a Bruker Tensor 27 spectrometer with pressed KBr pellets. The powder XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer. The UV/Vis spectra were measured on a Perkin Elmer Lambda 950 UV/VIS/NIR spectrometer using powder samples. CD spectra were measured on a JASCO J-720W spectrophotometer at room temperature. Thermogravimetric analyses were performed on a Mettler Toledo TGA/DSC instrument in the range of 30-600 °C under a nitrogen flow (20 mL/min) at a heating rate of 5 °C min<sup>-1</sup>. The gas absorption and desorption isotherms were conducted by a BELSORP-Max adsorption analyzer using easy-mode (for N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>) or detail-mode (for NO). The magnetic susceptibility data were obtained on polycrystalline samples using a Quantum Design SQUID VSM system. The data were corrected for diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constants. TG-MS measurement is carried on the NETZSCH STA 449C instrument.

Syntheses of *R*-1. *R*-pempH<sub>2</sub> (0.01 mol, 2.15 g) was dissolved in 250 mL H<sub>2</sub>O at 80 °C. After bubbling the solution with Ar for about 5 min, FeSO<sub>4</sub>·7H<sub>2</sub>O (0.01 mol, 2.78 g) and ascorbic acid (176 mg) was added, and the mixture was stirred until a clear solution was obtained. Then 8 mL piperazine (1 M) was added (pH = 5.6), and the reaction glass vial was kept at 100 °C for 1 day. Colorless needle-like crystals of compound *R*-1 were obtained. Yield: 50 %. Elemental analysis calcd (%) for C<sub>9</sub>H<sub>16</sub>FeNO<sub>5</sub>P: C, 35.44; H, 5.29; N, 4.59 %; found: C, 35.45; H, 5.31; N, 4.55 %. IR (KBr, cm<sup>-1</sup>): 3587 (w), 3297(m), 3130(w), 2912(w), 1715(w), 1622(w), 1495(m), 1458(w), 1377(m), 1319(w), 1278(m), 1196(w),

1113(w), 1092(s), 1061(s), 1011(w), 987(s), 945(w), 891(w), 841(m), 770(m), 704(m), 577(w), 550(m), 486(m).

**Syntheses of S-1. S-1** was prepared using a similar procedure to *R*-1 except that *R*-pempH<sub>2</sub> was replaced by *S*-pempH<sub>2</sub>. Yield: 51%. Elemental analysis calcd (%) for C<sub>9</sub>H<sub>16</sub>FeNO<sub>5</sub>P: C, 35.44; H, 5.29; N, 4.58%. Found: C, 35.42; H, 5.32; N, 4.60%. IR (KBr, cm<sup>-1</sup>): 3587 (w), 3298(m), 3130(w), 2912(w), 1715(w), 1621(w), 1495(m), 1458(w), 1377(m), 1319(w), 1278(m), 1196(w), 1114(w), 1092(s), 1061(s), 1011(w), 987 (s), 945(w), 891(w), 841(m), 770(m), 704(m), 577(w), 550(m), 486(m).

**Preparation of** *R***-1-de:** The dehydrated sample was obtained by heating *R*-1 (200 mg) in a adsorption tube or schlenk flask under vacuum at 100 °C for about 2 hours. After cooling down to room temperature and filling with Ar gas, the sample was kept in the glove box for further measurements.

**Preparation of** *R***-1-de-NO:** The dehydrated sample was transferred to a schlenk flask. The flask was flushed three times with nitric oxide and left overnight filled with the gas (1 atm). The color changed from white to black rapidly upon NO adsorption. Then, the flask containing the sample was filled fully with Ar, and was kept in the glove box to further studies

**Preparation of** *R***-1-de-NO-de:** The *R***-1-de-NO** sample was transferred to the adsorption tube and heated under vacuum at 140, 180, 200 °C for about 2 hours. And then, filling full with Ar, the sample was kept in the glove box to further studies.

**Crystallographic studies.** Single crystals of dimensions  $1.00 \times 0.20 \times 0.20$  mm<sup>3</sup> for *R*-1 and  $0.20 \times 0.10 \times 0.08$  mm<sup>3</sup> for *S*-1 were used for data collections on a Bruker APEX II (for *R*-1) or Bruker APEX DUO (for *S*-1) diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Hemisphere of data were collected in the  $\theta$  range of 1.28–28.19 for *R*-1, 2.22–28.19 for *S*-1. The structures were solved by direct method and refined on F<sup>2</sup> by full-matrix least squares using SHELXTL.<sup>2</sup> All the non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically. All hydrogen

atoms were either put in calculated positions or found from the difference Fourier maps and refined isotropically. CCDC 1874963-1874964 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

EXAFS measurements and data analyses. The EXAFS measurements at the Fe-K edge (7112 eV) were carried out in transmission mode at the beamline BL14W1 in Shanghai Synchrotron Radiation Facility (SSRF) in China. The storage ring of NSRL was run at 3.5 GeV, which is the highest value in the medium-energy light source. A double crystal Si(111) monochromator was used. The iron foils standard were purchased from the commercial source. In a typical experiment, about 20 mg of sample was ground into fine powder and mixed with ca. 130 mg of BN and then pulled out 23 mg to press into a 5.0 mm diameter circular sample holder, which encapsulated by KAPTON film to prevent the oxidation of samples. The spectrum of iron foil was recorded periodically to check the energy calibration, and the first derivative of the iron foil K-edge spectrum at 7112 eV were used to define the zero-energy reference point. The XANES spectra were background subtracted and were normalized to the edge step at the beginning of the EXAFS oscillations in order to make a meaningful comparison of the intensity of the pre-edge features. The EXAFS signals,  $\chi(k)$ , were extracted from the absorption raw data,  $\mu(E)$ , ATHENA 0.9.25 program<sup>3</sup> choosing the energy edge value ( $E_0$ ) at the maximum derivative. The quantitative analysis was carried out with the IFEFFIT 1.2.12-ARTEMIS 0.9.25 programs<sup>4</sup> with the atomic models described below. Theoretical EXAFS signals were computed with the FEFF8.0 code<sup>5</sup> using muffin-tin potentials and the Hedin-Lunqvist approximation for the energy-dependent part. The free-fitting parameters used in the analysis were:  $S_0^2$  (common amplitude parameter),  $\Delta E_0$  (the refinement of the edge position), R (the interatomic distance) and  $\sigma^2$  (the Debye-Waller factor). The structural parameters were determined by a curve-fitting procedure in R space by using the ARTEMIS program and USTCXAFS software packages. The employed fitting ranges are summarized in Tables S3. The intrinsic reduction factor  $S_0^2$ , the edge-energy shift  $\Delta E_0$ , the coordination number N, the inter-atomic distance R and the mean-square relative displacement  $\sigma^2$  were fitted. The results concerning N and R are summarized in Table S4.

## **Reference:**

- M. I. Kabachnik, T. Y. Medved', G. K. Kozlova, V. S. Balabukha, E. A.
   Mironova, L. I. Tikhonova, *Izvest. Akad. Nauk SSSR, Ser. Khim.* **1960**, 651.
- 2 SHELXTL (version 5.0), *Reference Manual*, Siemens Industrial Automation, Analytical Instruments, Madison, WI, **1995.**
- 3 B. Ravel, M. J. Newville, *Synchrotron Radiat.* **2005**, 12, 537–541.
- 4 M. J. Newville, *Synchrotron Radiat.* **2001**, 8, 322–324.
- J. M. De Leon, J. J. Rehr, S. I. Zabinsky, R. C. Albers, *Phys. Rev. B* 1991, 44, 4146.

	<i>R-</i> 1	S-1
Formula	C <sub>9</sub> H <sub>16</sub> NO <sub>5</sub> PFe	C <sub>9</sub> H <sub>16</sub> NO <sub>5</sub> PFe
Μ	305.05	305.05
temperature	296 K	123 K
crystal size [mm]	1.00×0.20×0.20	0.20×0.10×0.08
crystal system	Hexagonal	Hexagonal
space group	P63	P63
a [Å]	18.4179(4)	18.3354(4)
<i>b</i> [Å]	18.4179(4)	18.3354(4)
<i>c</i> [Å]	6.1607(3)	6.1492(3)
α [°]	90	90
β[°]	90	90
γ [°]	120	120
∨[ų]	1809.84(10)	1790.32(10)
Ζ	6	6
<i>D</i> <sub>c</sub> [g cm <sup>-3</sup> ]	1.679	1.698
$\mu$ [mm <sup>-1</sup> ]	1.391	1.406
<i>F</i> (000)	948	948
R <sub>int</sub>	0.0164	0.1255
T <sub>max</sub> , T <sub>min</sub>	0.7683, 0.3368	0.8958, 0.7663
GoF on F <sup>2</sup>	1.061	1.073
R1, wR2 <sup>[a]</sup> [ <i>I&gt;2o</i> ( <i>I</i> )]	0.0167, 0.0438	0.0633, 0.1568
(all data)	0.0172, 0.0440	0.0831, 0.1686
Flack parameter	0.016(10)	0.04(4)
( $arDelta ho$ )max, ( $arDelta ho$ )min [e Å <sup>-3</sup> ]	0.296, -0.181	0.650, -0.759
CCDC	1874963	1874964

**Table S1.** Crystallographic data and structure refinement parameters for compounds **1**.

 ${}^{\mathrm{a}}R_{1} = \Sigma ||F_{\mathrm{o}}| - |F_{\mathrm{c}}||/\Sigma |F_{\mathrm{o}}|, \ \mathrm{w}R_{2} = [\Sigma \mathrm{w}(F_{\mathrm{o}}{}^{2} - F_{\mathrm{c}}{}^{2})^{2}/\Sigma \mathrm{w}(F_{\mathrm{o}}{}^{2})^{2}]^{1/2}$ 

	S-1	<i>R-</i> 1
Fe1-O1A	2.044(4)	2.0451(11)
Fe1-O3	2.078(4)	2.0778(10)
Fe1-O2B	2.140(4)	2.1367(9)
Fe1-O2W	2.186(5)	2.1965(11)
Fe1-O1W	2.237(4)	2.2506(9)
Fe1-N1	2.289(5)	2.2994(12)
O1A-Fe1-O3	170.93(17)	170.20(4)
O1A-Fe1-O2B	97.78(16)	98.16(4)
O3-Fe1-O2B	88.92(15)	89.53(4)
O1A-Fe1-O2W	88.97(19)	88.46(5)
O3-Fe1-O2W	84.01(19)	84.48(5)
O2B-Fe1-O2W	98.12(17)	97.62(4)
O1A-Fe1-O1W	86.66(18)	86.09(4)
O3-Fe1-O1W	87.34(17)	86.89(4)
O2B-Fe1-O1W	172.63(16)	172.94(4)
O2W-Fe1-O1W	87.80(16)	88.09(4)
O1A-Fe1-N1	105.25(18)	105.73(5)
O3-Fe1-N1	81.10(18)	80.54(4)
O2B-Fe1-N1	86.99(18)	87.55(4)
O2W-Fe1-N1	164.17(19)	164.12(5)
O1W-Fe1-N1	86.16(17)	85.87(4)

Table S2. Selected bond lengths (Å) and angles (°) of compounds 1

Symmetry codes: A: x, y, -1+z; B: x, y, 1+z

**Table S3.** Forward Fourier transform and backward Fourier transform selectedparameters of the Fe-N/O first shell at Fe-K edge of *R*-1.

Sample	Shell	K-range	Window	R-range	Window
			type		type
<i>R</i> -1	Fe-O/N	2.313 - 12.900	Hanning	1.06 - 1.97	Hanning
<i>R</i> -1-de	Fe-O/N	2.497 - 11.656	Hanning	1.02 - 1.98	Hanning
<i>R</i> -1-de-NO	Fe-O/N	2.488 - 11.656	Hanning	1.07 - 1.91	Hanning
<b><i>R</i>-1-de-NO</b> -200°C	Fe-O/N	2.497 - 11.656	Hanning	1.07 - 1.95	Hanning

Sample	Shell	R	Ν	<b>S</b> 0 <sup>2</sup>	ΔE <sub>0</sub>	ΔR	σ²	R-factor	
D 1	Fe-O	2.08	5	1.0	$3.4 \pm 0.3$	0.004 ± 0.005	0.011 ± 0.00090	0.0045	
<i>R</i> -1	Fe-N	2.28	1	1.0	1.7 ± 2.2	-0.023 ± 0.019	0.0030 ± 0.0032	0.0045	
P1 do	Fe-O	2.02	4	1.0	2.9± 0.4	-0.052 ± 0.001	0.011 ± 0.00120	0.0010	
R-1-ae	Fe-N	2.23	1	1.0	2.5 ± 2.2	-0.065 ± 0.010	0.0062 ± 0.0045	- 0.0019	
R1 do NO	Fe-O	2.08	4	1.0	1.4 ± 0.6	0.01 ± 0.006	0.0211 ± 0.0012	0.0012	
<i>R</i> -1-de-NU	Fe-N	2.01	2	1.0	5.3 ± 2.9	-0.29 ± 0.004	0.0047 ± 0.0006	- 0.0012	
<i>R</i> -1-de-NO-	Fe-O	2.02	4	1.0	3.1 ± 0.3	-0.052 ± 0.005	0.0106 ± 0.0008	0 0029	
200°C	Fe-N	2.23	1	1.0	2.1 ± 1.6	-0.062± 0.018	0.0052 ± 0.0028	- 0.0036	

**Table S4**. Local structural fitting parameters of the Fe-O and Fe-N shells aroundFe in *R*-1 and related samples.

Table S5. The half-height of the normalized edge-jump of R-1 and related samples

Sample	Edge energy (eV)	Sample	Edge energy (eV)
Fe-foil	7111.2	<i>R</i> -1-de-NO	7123.9
Fe <sub>2</sub> O <sub>3</sub>	7126.2	<b><i>R</i>-1-de-NO</b> -140℃	7122.2
<i>R</i> -1	7120.6	<b><i>R</i>-1-de-NO</b> -180℃	7121.6
<i>R</i> -1-de	7119.8	<b><i>R</i>-1-de-NO</b> -200℃	7119.8

**Table S6.** The peak position of the XPS Fe 2p and 3p peak for *R*-1 and related samples

Sample		<i>R</i> -1	<i>R</i> -1-de	<i>R</i> -1-de-NO	<b><i>R</i>-1-de-NO</b> -200℃
	Fe2p <sub>1/2</sub>	723	723.67	724.37	723.25
Peak positions(eV)	Fe2p <sub>3/2</sub>	709.75	709.87	710.4	709.87
	Fe3p	54.4	54.5	55.13	54.4

Sample	formula		C /%	N/%	
	Tormula	Found	calculated	Found	calculated
<i>R</i> -1	Fe(pemp)(H <sub>2</sub> O) <sub>2</sub>	35.45	35.44	4.54	4.59
<i>R</i> -1-de	Fe(pemp)	39.48	40.18	5.16	5.21
<i>R</i> -1-de-NO	Fe(pemp)(NO) <sub>0.67</sub>	37.18	37.39	7.92	8.09
<b><i>R</i>-1-de-NO</b> -200°C	Fe(pemp)	39.71	40.18	4.99	5.21

Table S7. The element analyses of C and N for *R*-1, *R*-1-de, *R*-1-de-NO and *R*-1-de-NO-200°C



Figure S1. Powder XRD patterns of 1.



Figure S2. The IR spectra of 1



Figure S3. The CD spectra of 1.



**Figure S4.** The UV-vis absorption spectra of **1.** The UV-vis absorption spectra were translated from the diffuse reflectance spectra using Kubelka-Munk function  $(F(R) = (1 - R)^2/2R)$ .



**Figure S5.** Packing diagram of *R***-1** viewed along the *b*-axis (a) and *c*-axis (b). Color codes: Fe dark yellow, P pink, C gray, N blue, O red, H turqoise. All H atoms are omitted for clarity. The angle of C-H… $\pi$  interaction is 148.21°.



**Figure S6.** The plots of  $\chi_{M^{-1}}$  versus *T* for *R*-1. The red curve means the best fitting of the plot of  $\chi_{M^{-1}}$  vs. *T* above 100 K to the Curie–Weiss law.



**Figure S7.** The magnetic exchange interactions over the O-P-O bridges in compound **1**. Considering that the neighboring Fe····Fe distance over O1-P1-O3 (mode B, 6.161 Å) is much larger than those over O1-P1-O2 (mode A, 5.018 Å) and O2-P1-O3 (mode C, 5.018 Å), the magnetic interactions in mode B ( $J_2$ ) should be much weaker than those in modes A ( $J_1$ ) and C( $J_3$ ), e.g.  $IJ_1I\approx IJ_3I > IJ_2I$ . Assuming that the  $J_2$  is negligible, a two-dimensional antiferromagnetic exchange model of a square lattice can be used to fit the magnetic data, where J is defined by the spin Hamiltonian  $H = \sum_{NN} JS_i S_j$  (ref: S. Konar et al. Eur. J. Inorg. Chem. 2004, 4202-4208; J. Curély, Physica B, 1998, 254, 277–297).



**Figure S8.** The isothermal field dependence of magnetization for *R*-1 at 2.0 K. Insert: the  $d_M/d_H$  vs *H* plot.



Figure S9. The magnetic susceptibility of *R*-1 under different fields.



**Figure S10.** The in-phase ( $\chi$ ') and out-of-phase ( $\chi$ '') signals versus *T* plots of *R*-**1** at indicated frequencies.



**Figure S11.** Variable-temperature magnetic susceptibilities for **S-1.** Inset: The isothermal field dependence of magnetization for **S-1** at 2 K.



Figure S12. TGA curves of compounds 1.



Figure S13. Top: The powder XRD patterns of *R*-1 before and after thermal treatment at different temperature for 2 h. Bottom: The powder XRD patterns of *R*-1, *R*-1-de and rehydrated samples after soaking *R*-1-de in de-oxygenated water for 24 h at different temperatures.



**Figure S14.** Top: Variable-temperature magnetic susceptibilities for *R*-1-de (Insert: The plots of  $\chi_{M^{-1}}$  versus *T*); Bottom: The isothermal field dependence of magnetization for *R*-1-de at 2 K.



**Figure S15.** The Fe-K edge k<sup>3</sup>-weight EXAFS signals taken at room temperature for *R*-1, *R*-1-de, *R*-1-de-NO and *R*-1-de-NO thermally treated at different temperatures.



Figure S16. Fourier transformed space (R space) for *R*-1, *R*-1-de, *R*-1-de-NO and *R*-1-de-NO-200°C.



**Figure S17.** (a) A comparison of the NO adsorption/desorption isotherms of the dehydrated sample *R*-1-de at 298 K and 196 K. (b) A comparison of the NO adsorption/desorption isotherms of the dehydrated samples *R*-1-de and *S*-1-de at 298 K.



**Figure S18.** A comparison of the NO adsorption/desorption isotherms of the dehydrated samples *R*-1-de [Fe(pemp)], Co(pemp) and Ni(pemp) at 298 K.



**Figure S19.** IR spectra of *R***-1-de**, *R***-1-de**-NO and *R***-1-de**-NO thermally treated at 140 °C, 180 °C and 200 °C for about 2 hours.



**Figure S20.** UV-vis spectra of *R*-1, *R*-1-de, *R*-1-de-NO and *R*-1-de-NO thermally treated at 200 °C for about 2 hours.



**Figure S21.** Top: Variable-temperature magnetic susceptibilities for *R*-1-de-NO Insert: The  $\chi M^{-1}$  versus *T* plot; Bottom: Variable-temperature magnetic susceptibilities for *R*-1-de-NO-200. Insert: The  $\chi M^{-1}$  versus *T* plot.



Figure S22. The TG-MS of the NO adsorption sample *R*-1-de-NO.



Figure S23. The in-situ variable temperature IR spectra of *R*-1-de-NO in vacuum.



**Figure S24.** The temperature dependent variation of the intensities for the peaks at 1705, 1788 and 2216 cm<sup>-1</sup>.



**Figure S25.** The proposed mechanism for the formation of the intermediate during the release of NO upon heating the sample of *R*-1-de-NO.



Figure S26. The Fe 2p (top) and Fe 3p (bottom) XPS spectra of *R*-1, *R*-1-de, *R*-1-de-NO and *R*-1-de-NO-200°C.



**Figure S27.** The NO adsorption (filled) and desorption (open) isotherms for dehydrated sample *R*-1-de for four cycles. For the first cycle, the sample was activated at 100 °C to remove all coordination water molecules. For the second to fourth cycles, the sample was activated at 200 °C to remove all NO molecules.



**Figure S28.** Powder XRD patterns of *R*-1, *R*-1-de, *R*-1-de-NO (after NO adsorption), *R*-1-de-NO-200 (after activation at 200 °C to release NO), and *R*-1-de-NO-200-soak (after soaking the four cycled *R*-1-de-NO-200 in de-oxygenated water for 24h at 60 °C).