Supporting Information

Homochiral 3D framework of mechanically interlocked 1D loops with solvent-dependent spin-state switching behaviors

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TABLE OF CONTENTS

Experimental Details
Materials and methodsS4
Synthetic procedures
Single-crystal X-ray diffractometry S6
Additional Tables
Table S1. Crystallographic data and refinement parameters for 1·CH ₃ CN and 1·CH ₃ OH······S7
Table S2. Internal angles and dimensions in $1 \cdot CH_3CN$ and $1 \cdot CH_3OH$ at variable temperatures
Table S3. The distance between the neighboring 1D corner-sharing looped structures in $1 \cdot CH_3CN$ and
1·CH ₃ OH at variable temperatures
Table S4. The included angle in 1·CH ₃ CN and 1·CH ₃ OH at variable temperatures ·······S8
Table S5. The size of 1D open channels in 1·CH ₃ CN and 1·CH ₃ OH at variable temperatures
Table S6. Structural parameters for the mechanical interactions at variable temperatures ••••••••••••••••••••••••••••••••••••
Table S7. Selected Bond Lengths (Å) and Angles (°) for 1·CH ₃ CN S9
Table S8. Selected Bond Lengths (Å) and Angles (°) for 1·CH ₃ OH S10
Additional Figures
Figure S1. The remarkable color variation of 1·CH ₃ CN and 1·CH ₃ OH between HS and LS states ····S11
Figure S2. Comparison of the PXRD patterns of 1·CH ₃ CN and 1·CH ₃ OH measured from respective
bulk polycrystalline-sample and the simulated result based on single-crystal structure
Figure S3. Elemental mapping photographs and SEM image of single crystal of 1·CH ₃ CNS12
Figure S4. Elemental mapping photographs and SEM image of single crystal of 1·CH ₃ OH ·······S12
Figure S5. Thermogravimetric plots of 1·CH ₃ CN and 1·CH ₃ OH ······S13
Figure S6. The general view of internal angles and dimensions in 1
Figure S7. A possible interlocking process of 1
Figure S8. The constructing of the right triangle to calculate the distance between the neighboring 1D
corner-sharing looped structures in 1
Figure S9. The view of the 1D open channels in the title 3D MIS framework
Figure S10. The stick and its simplified views of the linear poly[<i>n</i>]catenane structure in 1S15
Figure S11. The mechanically interlocked loops with three kinds of mechanical interactions and the
perspective view of the three kinds of interactions in 1
Figure S12. Topological representation of the interlocked right-handed helical chains viewed along b-
axis and in the <i>ac</i> plane in 1S16
Figure S13. The interlocking of four neighboring right-handed helical chains viewed along <i>b</i> -axis and
in the <i>ac</i> plane in 1S17

Figure S14. The SHG signals of 1·CH ₃ CN, 1·CH ₃ OH, <i>R</i> -L2 and KDPS17
Figure S15. View of the spin-state ordering of 1·CH ₃ OH at 160 K ······S18
Figure S16. Schematic representation of spin-state conversions of Fe ^{II} ions in $1 \cdot CH_3OH \cdots S18$
Figure S17. Enlarged view of the hysteresis loop of 6 K of 1 · CH ₃ OH ·······S18
Figure S18. Comparison of the PXRD patterns of $1 \cdot C_2 H_5 OH$ and $1 \cdot C_3 H_7 OH$ measured from respective
bulk polycrystalline-sample and the simulated result based on single-crystal structure
Figure S19. Powder X-ray diffraction of desolvated phase 1 and 1·H ₂ O ······S19
Figure S20. Normalized variable temperature $\chi_M T$ versus T plots for 1·CH ₃ CN, 1, 1·H ₂ O, 1·CH ₃ OH,
1·C ₂ H ₅ OH and 1·C ₃ H ₇ OH
Figure S21. The corresponding $d(\chi_M T)/dT$ versus T plots for 1·CH ₃ CN, 1·CH ₃ OH, 1·C ₂ H ₅ OH and
1·C ₃ H ₇ OH
Figure S22. IR spectra of 1·CH ₃ CN, 1·CH ₃ OH and ligand <i>R</i> -L2······S21
Figure S23. UV-vis spectra of 1·CH ₃ CN, 1·CH ₃ OH and ligand <i>R</i> -L2
Figure S24. ¹ H NMR spectra of ligand <i>R</i> -L2
References

Experimental Details

Materials and methods

All chemical reagents were commercially available and used as purchased. Powder X-ray diffraction (PXRD) data were collected on a PANalytical diffractometer with Cu $K\alpha$ ($\lambda = 1.54056$ Å) radiation. The C, H, and N microanalyses were measured on a EUROVECTER EA3000 analyzer. Fourier transform infrared (FT-IR) spectra were performed on a Nicolet IS10 FT-IR spectrometer in the range of 4000-400 cm⁻¹ with KBr pellets. Thermogravimetric (TG) analyses were recorded on a TG-DTA 6200 instrument under a flowing nitrogen atmosphere in the temperature range 20-700 °C at a heating rate of 10 °C min⁻¹. The ¹H NMR spectrum was measured by a Bruker Avance 400 MHz spectrometer. Magnetic susceptibility measurements of the polycrystalline samples were measured on a Quantum Design MPMS XL7 magnetometer operating in the successive cooling/heating cycle with a scan rate of 1 K min⁻¹. Field-emission scanning electron microscopy (FE-SEM) images were tested on a JSM-7500F scanning electron microscope with an accelerating voltage of 5.0 kV. UV-Vis spectra were obtained from a TU-1950 UV-Vis spectrophotometer with BaSO₄ as reference. Solid-state circular dichroism (CD) spectra were carried out on a Jasco-810 spectropolarimeter with respective bulk sample using dried KBr pellets and the weight ratio are adopted as: 1·CH₃CN : KBr = 1:800, 1·CH₃OH : KBr = 1:600, *R*-L2 : KBr = 1:600. Second harmonic generation (SHG) signals of title compounds and KDP (particle size range of 30–70 μm) were performed on a Q-switched Nd:YAG solid-state laser at room temperature with a wavelength of 1064 nm.

Synthetic procedures

Synthesis of *R*-2,2'-bis(methoxymethoxy)-6,6'-bis(4-pyridylethynyl)-1,1'-binaphth-yl (*R*-L2): The ligand *R*-L2 was synthesized according to the published references.^{1,2} Elemental analysis (%) calcd for $C_{38}H_{28}N_2O_4$: C, 79.15; H, 4.89; N, 4.86. Found: C, 79.23; H, 4.87; N, 4.83. ¹H NMR (400 MHz, CDCl₃, ppm), δ : 8.61–8.59 (m, 4H, ArH), δ : 8.14 (d, 2H, ArH), δ : 7.98–7.96 (d, 2H, ArH), δ : 7.65–7.63 (d, 2H, ArH), δ : 7.40–7.38 (m, 4H, ArH), δ : 7.35–7.33 (dd, 2H, ArH), δ : 7.15–7.13 (d, 2H, ArH), δ : 5.15–5.13 (d, 2H, -CH₂–), δ : 5.03–5.01 (d, 2H, -CH₂–), δ : 3.18 (s, 6H, -CH₃). IR (KBr pellet, cm⁻¹): 2208 (m), 2068 (w), 1927 (w), 1735 (w), 1620 (m), 1594 (s), 1536 (w), 1473 (m), 1405 (m), 1370 (w), 1348 (m), 1301 (w), 1244 (m), 1194 (m), 1150 (s), 1069 (s), 1026 (s), 968

(w), 921 (w), 889 (w), 874 (w), 819 (s), 729 (w), 692 (m), 669 (w), 626 (w), 591 (w), 556 (m), 542 (s), 500 (m), 448 (w), 427 (m).

Preparation of $[Fe(NCBH_3)_2(R-L2)_2] \cdot 6CH_3CN (1 \cdot CH_3CN)$: An acetonitrile solution (6.0 mL) of $FeSO_4 \cdot 7H_2O$ (0.0278 g, 0.1 mmol) and NaNCBH₃ (0.0157 g, 0.25 mmol) in the presence of 5.5 mg ascorbic acid was added to the bottom of a test tube, 4.0 mL acetonitrile was added as the buffer layer, and then upon which another acetonitrile solution (5.0 mL) containing *R*-L2 (0.0288 g, 0.05 mmol) was carefully layered. The test tube was sealed and kept undisturbedly, and orange crystals were obtained in half a day. Yield: 25 mg (~ 65% based on the ligand *R*-L2). Elemental analyses (%) calcd for C₉₀H₈₀N₁₂FeB₂O₈: C, 70.42; H, 5.25; N, 10.95. Found: C, 70.53; H, 5.17; N, 10.62. The final formula of $1 \cdot CH_3CN$ was confirmed as $[Fe(NCBH_3)_2(R-L2)_2] \cdot 6CH_3CN$ by thermogravimetric analysis. IR (KBr pellet, cm⁻¹): 2341 (m), 2207 (m), 2182 (m), 1605 (s), 1536 (w), 1474 (m), 1349 (m), 1303 (w), 1241 (m), 1217 (w), 1199 (w), 1150 (m), 1115 (w), 1071 (m), 1014 (s), 968 (w), 922 (w), 890 (w), 826 (s), 733 (w), 695 (w), 669 (w), 598 (w), 557 (w), 542 (m), 502 (w), 432 (w).

Yellow crystals of $1 \cdot CH_3OH$ were obtained *via* the solvent-treating process by immersing the crystals of $1 \cdot CH_3CN$ in pure methanol for one day in a 1.5 mL sample-tube, during which the methanol solution was replaced with pure methanol every three hours. Elemental analyses (%) calcd for $C_{86}H_{94}N_6FeB_2O_{16}$: C, 66.85; H, 6.13; N, 5.44. Found: C, 66.98; H, 6.07; N, 5.46. Thermogravimetric and elemental analyses jointly fix the final formula of $1 \cdot CH_3OH$ as $[Fe(NCBH_3)_2(R-L2)_2] \cdot 8CH_3OH$. IR (KBr pellet, cm⁻¹): 2346 (w), 2337 (w), 2207 (m), 2183 (w), 1605 (s), 1535 (w), 1473 (m), 1350 (m), 1304 (w), 1241 (m), 1218 (w), 1200 (w), 1151 (s), 1114 (w), 1070 (m), 1015 (s), 968 (w), 920 (w), 890 (w), 827 (s), 734 (w), 694 (w), 669 (w), 599 (w), 556 (w), 542 (m), 501 (m), 430 (w).

The products $1 \cdot H_2O$, $1 \cdot C_2H_5OH$ and $1 \cdot C_3H_7OH$ were obtained following the procedure preparing $1 \cdot CH_3OH$ except for the use of distilled water, ethanol and *n*-propanol as solvents, respectively. Crystals of 1 were prepared by placing crystals of $1 \cdot CH_3CN$ in vacuum oven at 80 °C overnight.

Single-crystal X-ray diffractometry (SCXRD)

Variable-temperature single-crystal X-ray diffraction (SCXRD) experiments at 100 K, 160 K, 240 K for 1·CH₃CN and 1·CH₃OH were performed on a Bruker D8 VENTURE PHOTON II diffractometer equipped with a microfocus radiation source (Cu-Ka, $\lambda = 1.54178$ Å). The title mechanically interlocked structures were solved by the direct method and refined by full-matrix least-squares on F^2 with SHELXL software package.³ In the final refinement, the reflection contributions of highly disordered solvent molecules were removed using the OLEX2 solvent MASK routine (similar to PLATON/SQUEEZE).⁴ All hydrogen atoms were fixed in the calculated positions and refined using a riding model. The weak diffraction intensity to the resolution higher than 1.0 Å of single crystal is responsible for the corresponding alert: the value of sin(theta_max)/wavelength is less than 0.550 or 0.575. For 1·CH₃CN, the O8-C78 section was refined isotropically and split as O8A-C78A, O8B-C78B at 100, 160 and 240 K, and C72 at 240 K was also refined isotropically. Other non-hydrogen atoms were refined anisotropically. The contributions of 668.0 (100 K), 674.4 (160 K), 728.0 (240 K) electrons were removed from the unitcell contents. The crystal data and structure refinement results revealed that the presence of $7.5 \sim 8.0$ acetonitrile molecules per formula unit. However, TG and elemental analyses showed that the number of acetonitrile molecules might be 6 for the empirical formula of [Fe(NCBH₃)₂(R- $L_{2_2} \rightarrow CH_3 CN (C_{90}H_{80}N_{12}FeB_2O_8)$. This might be attributed to the weathering of the test samples. For 1. CH₃OH, C156 at 160 K was refined isotropically and other non-hydrogen atoms were refined anisotropically. The contributions of 848.0 (100 K), 868.3 (160 K), 774.6 (240 K) electrons were removed from the unit-cell contents, corresponding to $10.5 \sim 12$ methanol molecules per formula unit. However, TG and elemental analyses showed the number of methanol molecules might be 8 for the empirical formula of [Fe(NCBH₃)₂(*R*-L2)₂]·8CH₃OH (C₈₆H₉₄N₆FeB₂O₁₆). This also might be attributed to the weathering of the test samples. The final formulas were determined by the combination of SCXRD analyses, elemental data and TG data. Crystallographic parameters and structural refinement results were summarized in Table S1. Selected bond lengths and angles are listed in Table S7 and Table S8. CCDC 1942449 (100 K), 1966026 (160 K), 1942451 (240 K) for 1·CH₃CN and 1942452 (100 K), 1942453 (160 K), 1942454 (240 K) for 1·CH₃OH contain the supplementary crystallographic data and can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif.

Additional Tables

Table S1. Crystallographic data and refinement parameters for $1 \cdot CH_3CN$ and $1 \cdot CH_3OH$ (The formula and formula weight containing six acetonitrile molecules for $1 \cdot CH_3CN$ and eight methanol molecules for $1 \cdot CH_3OH$ at 100 K, 240 K, and sixteen methanol molecules at 160 K).

Compound	1·CH ₃ CN			1·CH ₃ OH		
<i>T/</i> K	100 K	160 K	240 K	100 K	160 K	240 K
formula	$C_{90}H_{80}N_{12}FeB_2O_8\\$	$C_{90}H_{80}N_{12}FeB_2O_8\\$	$C_{90}H_{80}N_{12}FeB_2O_8\\$	$C_{86}H_{94}N_{6}FeB_{2}O_{16}$	$C_{172}H_{188}N_{12}Fe_2B_4O_{32}$	$C_{86}H_{94}N_{6}FeB_{2}O_{16}$
$M_{\rm r}/{ m g}~{ m mol}^{-1}$	1535.14	1535.14	1535.14	1545.16	3090.33	1545.16
space group	<i>C</i> 2	C2	<i>C</i> 2	<i>C</i> 2	$P2_1$	<i>C</i> 2
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	31.9544(10)	32.027(15)	32.761(8)	31.8352(13)	18.080(6)	32.45(2)
b/Å	16.4618(5)	16.64(1)	16.907(4)	16.6477(6)	16.715(6)	16.983(9)
c/Å	17.8159(5)	17.903(8)	18.032(4)	17.9355(6)	32.015(8)	18.105(14)
α/deg	90	90	90	90	90	90
β/deg	104.814(2)	105.183(14)	106.009(9)	105.495(2)	106.028(12)	106.85(4)
γ/deg	90	90	90	90	90	90
$V/Å^3$	9060.1(5)	9208(8)	9600(4)	9160.0(6)	9299(5)	9550(11)
Ζ	4	4	4	4	2	4
$D_{\rm calcd}/{ m g~cm^{-3}}$	0.941	0.926	0.887	0.935	0.921	0.896
μ/mm^{-1}	1.704	1.677	1.608	1.686	1.661	1.617
F(000)	2668	2668	2660	2688	2688	2688
$R1 \ (I \ge 2\sigma(I))^a$	0.0695	0.0655	0.0774	0.0712	0.0597	0.0619
wR2 (all data) ^b	0.1967	0.1920	0.2429	0.2000	0.1619	0.1763
Flack parameter	0.091(9)	0.129(7)	0.100(10)	0.002(8)	0.056(4)	0.075(7)
CCDC	1942449	1966026	1942451	1942452	1942453	1942454

Table S2. Internal angles and dimensions in 1·CH₃CN and 1·CH₃OH at variable temperatures.

	Т	internal angles (°)		diagonal dimensio	ons (Å)
	(17)	(LE L			5115 (71)
	(K)	ZLFeL	∠FeLFe	FeFe	L…L
1·CH ₃ CN	240	68.87(1), 69.636(11)	110.557(12), 110.869(12)	22.4057(47)	15.4747(25)
	160	67.362(10), 67.949(10)	112.218(12), 112.442(12)	22.2711(74)	14.9258(46)
	100	67.172(8), 67.003(9)	112.177(10), 112.59(1)	22.2456(24)	14.8906(3)
1·CH₃OH	240	70.520(12), 70.711(12)	109.317(14), 109.428(14)	22.2002(134)	15.7245(82)
	160	72.177(5), 73.543(5)	107.309(6), 106.961(6)	21.7953(41)	16.0856(44)
		68.019(5), 67.454(5)	111.590(7), 112.912(7)	22.4452(44)	15.0663(41)
	100	69.325(7), 69.346(7)	110.554(8), 110.727 (8)	22.1765(18)	15.3396(4)

	<i>T</i> (K)	heta (°)	$\sin \theta$	c (Å)	d (Å)	
1·CH ₃ CN	240	29.683	0.4952	11.4739	5.68	
	160	29.517	0.4927	11.2515	5.54	
	100	29.064	0.4858	11.2727	5.48	
1∙CH₃OH	240	28.917	0.4835	11.1972	5.41	
	160	28.950	0.4840	10.8652	5.26	
		28.458	0.4765	11.3271	5.40	
	100	28.328	0.4745	11.1917	5.31	

Table S3. The distance between the neighboring 1D corner-sharing looped structures in 1·CH₃CN and 1·CH₃OH at variable temperatures.

Table S4. The included angle in 1·CH₃CN and 1·CH₃OH at variable temperatures.

<i>T</i> (K)	included angle (°)
240	56.462(20)
160	56.592(14)
100	56.104(10)
240	57.343(16)
160	56.802(10)
100	56.974(7)
	Т (К) 240 160 100 240 160 100

Table S5. The size of 1D open channels in 1·CH₃CN and 1·CH₃OH at variable temperatures.

	Т, К	void channel percent, %	void unit cell volume, Å ³	dimension, $Å \times Å$
1·CH ₃ CN	240	35.5	3412.3	9.6805 × 6.8592
	160	33.7	3099.1	9.7091 × 6.5995
	100	32.5	2944.9	9.1951 imes 6.0637
1∙СН₃ОН	240	36.5	3486.9	10.2412×6.5241
	160	34.9	3243.4	10.1658 × 6.1033
	100	34.6	3165.3	10.3348×5.8719

	<i>Т</i> , К	C–H··· π interactions, Å (A)	$\pi \cdot \cdot \pi$ interactions, Å (B)	C–H··· π interactions, Å (C)
1·CH ₃ CN	240	2.9479(5), 3.2904(6)	4.4842(9)	3.1659(6), 3.7271(7)
	160	2.7692(10), 3.3768(13)	4.4639(18)	3.0338(12), 3.8222(13)
	100	2.7362(1), 3.2892(1)	4.4284(1)	3.0537(1), 3.8535(1)
І∙СН₃ОН	240	2.8272(19), 2.9128(21)	4.0960(28)	4.0722(28), 4.0863(30)
	160	2.7687(9), 2.7941(9),	4.4709(15)	3.0518(9), 3.3978(7),
		2.8988(9), 3.6223(11)		3.9328(9), 4.0587(13)
	100	2.7780(1), 2.8074(1)	3.8592(1)	4.4635(1), 4.6462(2)

Table S6. Structural parameters for the mechanical interactions at variable temperatures.

Table S7. Selected Bond Lengths (Å) and Angles (°) for $1{\cdot}CH_3CN.$

1·CH ₃ CN	100 K	160 K	240 K	
Fe1-N1	1.890(14)	1.829(11)	2.010(15)	
Fe1-N2	1.960(15)	1.997(11)	2.071(15)	
Fe1-N3	2.003(11)	2.063(10)	2.177(13)	
Fe1-N4	1.989(9)	2.009(9)	2.242(12)	
Fe1-N5	2.000(8)	2.004(7)	2.195(11)	
Fe1-N6	2.012(9)	2.039(8)	2.221(10)	
N1-Fe1-N3	91.8(5)	92.4(5)	90.4(5)	
N1-Fe1-N4	89.7(5)	90.0(4)	89.9(6)	
N1-Fe1-N5	89.5(5)	90.7(4)	89.5(5)	
N1-Fe1-N6	91.6(5)	89.5(4)	89.2(5)	
N2-Fe1-N3	89.8(5)	90.6(4)	88.0(6)	
N2-Fe1-N4	88.7(4)	87.0(4)	91.8(6)	
N2-Fe1-N5	88.8(5)	89.0(4)	89.7(6)	
N2-Fe1-N6	90.1(5)	90.7(4)	91.7(5)	
N3-Fe1-N6	89.0(4)	91.4(4)	88.7(4)	
N4-Fe1-N5	88.0(4)	87.5(3)	86.1(4)	
N4-Fe1-N6	91.2(4)	91.3(3)	92.5(4)	
N5-Fe1-N3	91.7(4)	89.8(4)	92.7(5)	
$\langle d_{\rm Fe1-N} \rangle^a$	1.976	1.990	2.153	
$\Sigma_{\rm Fel}{}^b$	12.90	14.30	18.00	

 $a(d_{Fe-N})$: the average Fe–N bond lengths. $b\Sigma_{Fe}$: the sum of the deviations of N–Fe–N angles from 90°.^{5,6}

1-СН ₃ ОН	100 K	160 K	240 K
Fe1-N1 / Fe2-N7	1.996(8)	2.085(2) / 1.9395(19)	2.061(9)
Fe1-N2 / Fe2-N8	1.968(9)	2.084(2) / 1.9268(19)	2.180(9)
Fe1-N3 / Fe2-N9	2.000(7)	2.187(2) / 2.0217(19)	2.205(7)
Fe1-N4 / Fe2-N10	2.025(9)	2.198(2) / 2.0113(19)	2.196(7)
Fe1-N5 / Fe2-N11	2.021(7)	2.173(2) / 2.0026(18)	2.198(6)
Fe1-N6 / Fe2-N12	2.047(8)	2.183(2) / 2.0073(19)	2.208(6)
N1-Fe1-N3 / N7-Fe2-N9	91.1(3)	86.74(8) / 92.78(8)	92.6(3)
N1-Fe1-N4 / N7-Fe2-N10	89.3(3)	90.72(9) / 89.85(8)	90.5(3)
N1-Fe1-N5 / N7-Fe2-N11	90.2(3)	92.74(9) / 90.21(8)	89.3(3)
N1-Fe1-N6 / N7-Fe2-N12	86.8(3)	91.16(9) / 89.53(8)	87.7(3)
N2-Fe1-N3 / N8-Fe2-N9	88.3(3)	91.83(8) / 87.80(8)	86.5(3)
N2-Fe1-N4 / N8-Fe2-N10	91.3(4)	90.79(9) / 89.67(8)	90.5(3)
N2-Fe1-N5 / N8-Fe2-N11	90.1(3)	89.37(9) / 92.32(8)	90.8(3)
N2-Fe1-N6 / N8-Fe2-N12	92.9(3)	86.74(9) / 87.94(8)	92.2(3)
N4-Fe1-N5 / N10-Fe2-N11	90.0(3)	91.54(8) / 90.00(7)	89.9(2)
N4-Fe1-N6 / N10-Fe2-N12	90.5(3)	87.91(8) / 90.99(7)	92.1(3)
N5-Fe1-N3 / N11-Fe2-N9	91.0(3)	86.45(8) / 87.77(7)	91.6(2)
N6-Fe1-N3 / N12-Fe2-N9	88.5(3)	94.27(8) / 91.26(7)	86.6(2)
$\langle d_{Fe1-N} \rangle / \langle d_{Fe2-N} \rangle^a$	2.009	2.152 / 1.984	2.175
$\Sigma_{\rm Fe1}$ / $\Sigma_{\rm Fe2}{}^b$	14.2	25.7 / 15.0	20.3

Table S8. Selected Bond Lengths (Å) and Angles (°) for $1 \cdot CH_3OH$.

 a (d_{Fe-N}): the average Fe-N bond lengths. ${}^{b}\Sigma_{Fe}$: the sum of the deviations of N-Fe-N angles from 90°.^{5,6}

Additional Figures



Figure S1. The remarkable color variation of 1·CH₃CN and 1·CH₃OH between HS and LS states.



Figure S2. Comparison of the PXRD patterns of 1·CH₃CN and 1·CH₃OH measured from respective bulk polycrystalline-sample and the simulated result based on single-crystal structure.



Figure S3. Elemental mapping photographs (C, N, O, B and Fe) and SEM image of single crystal of 1·CH₃CN.



Figure S4. Elemental mapping photographs (C, N, O, B and Fe) and SEM image of single crystal of 1·CH₃OH.



Figure S5. Thermogravimetric plots of $1 \cdot CH_3CN$ (left) and $1 \cdot CH_3OH$ (right), corresponding to six acetonitrile (calcd 16.04 %) and eight methanol molecules (calcd 16.59 %), respectively.



Figure S6. The general view of internal angles and dimensions in **1** (the internal angles and dimensions are marked). Color codes, Fe: sky blue, N: blue, C: grey, O: red, B: yellow. Hydrogen atoms are omitted for clarity.



Figure S7. A possible interlocking process of **1**. The identical 1D loops are shown in two different colors for better view.



Figure S8. The constructing of the right triangle to calculate the distance between the neighboring 1D corner-sharing looped structures in **1**.



Figure S9. The view of the 1D open channels (pink) in the title 3D MIS framework. Color codes, Fe: sky blue; N, C, B, O and H atoms are grey-coloured to assist the viewer.



Figure S10. The stick (top) and its simplified views (bottom) of the linear poly[*n*]catenane structure in1. Hydrogen atoms and the MOMO groups are omitted for clarity.



Figure S11. The mechanically interlocked loops with three kinds of mechanical interactions showing the ABAC… manner (a) and perspective view of the three kinds of interactions (b) in **1**. Hydrogen atoms and the MOMO groups are omitted for clarity.



Figure S12. Topological representation of the interlocked right-handed helical chains viewed along *b*-axis (a, b) and in the *ac* plane (c) in **1**. The yellow tubes represent the helical axes and the identical 1D loops are marked in red and blue for better view.



Figure S13. The interlocking of four neighboring right-handed helical chains viewed along *b*-axis (a, d) and in the *ac* plane (b, c) in **1**. The yellow tubes represent the helical axes and the identical 1D loops are marked in red and blue for better view.



Figure S14. The SHG signals of 1·CH₃CN, 1·CH₃OH, *R*-L2 and KDP.



Figure S15. View of the spin-state ordering of **1**•**CH**₃**OH** at 160 K, corresponding to the magnetic phases of HS^{0.5}LS^{0.5} (HS-Fe1 ions: yellow balls, LS-Fe2 ions: purple balls).



Figure S16. Schematic representation of the spin-state conversions of Fe^{II} ions in **1**·**CH**₃**OH** from 240 K to 100 K in a single layer, corresponding to the magnetic phases sequence of $HS^{1.0} \leftrightarrow HS^{0.5}LS^{0.5} \leftrightarrow LS^{1.0}$ (HS-Fe ions: yellow balls, LS-Fe ions: purple balls).



Figure S17. Enlarged view of the hysteresis loop of 6 K of 1 ·CH₃OH in the first-step spin transition (

 $T_{\rm C1}\downarrow = 176 \text{ K}, \ T_{\rm C1}\uparrow = 182 \text{ K}).$



Figure S18. Comparison of the PXRD patterns of $1 \cdot C_2 H_5 OH$ and $1 \cdot C_3 H_7 OH$ measured from respective bulk polycrystalline-sample and the simulated result based on single-crystal structure.



Figure S19. Powder X-ray diffraction of desolvated phase 1 and 1·H₂O.



Figure S20. Normalized variable temperature $\chi_M T$ versus T plots for 1·CH₃CN, 1, 1·H₂O, 1·CH₃OH, 1·C₂H₅OH and 1·C₃H₇OH.



Figure S21. The corresponding $d(\chi_M T)/dT$ versus T plots for $\mathbf{1} \cdot \mathbf{CH}_3 \mathbf{CN}$ ($^T_{C\downarrow} = ^T_{C\uparrow} = 180$ K), $\mathbf{1} \cdot \mathbf{CH}_3 \mathbf{OH}$ ($^T_{C\downarrow\downarrow} = 176$ K, $^T_{C\uparrow\uparrow} = 182$ K; $^T_{C2\downarrow} = ^T_{C2\uparrow} = 143$ K), $\mathbf{1} \cdot \mathbf{C}_2 \mathbf{H}_5 \mathbf{OH}$ ($^T_{C\downarrow} = ^T_{C\uparrow} = 177$ K) and $\mathbf{1} \cdot \mathbf{C}_3 \mathbf{H}_7 \mathbf{OH}$ ($^T_{C\downarrow} = ^T_{C\uparrow} = 159$ K).



Figure S22. IR spectra of 1·CH₃CN, 1·CH₃OH and ligand *R*-L2.



Figure S23. UV-vis spectra of $1 \cdot CH_3CN$, $1 \cdot CH_3OH$ and ligand *R*-L2 in the solid state. The strong absorption band of ligand *R*-L2 was obtained between 270 and 380 nm, while the broader absorption bands in the range of 260–500 nm were found in $1 \cdot CH_3CN$ and $1 \cdot CH_3OH$.



Figure S24. ¹H NMR spectra of ligand *R*-L2 (inset: the structure of ligand *R*-L2). ¹H NMR (400 MHz, CDCl₃, ppm), δ: 8.61–8.59 (m, 4H, ArH), δ: 8.14 (d, 2H, ArH), δ: 7.98–7.96 (d, 2H, ArH), δ: 7.65–7.63 (d, 2H, ArH), δ: 7.40–7.38 (m, 4H, ArH), δ: 7.35–7.33 (dd, 2H, ArH), δ: 7.15–7.13 (d, 2H, ArH), δ: 5.15–5.13 (d, 2H, -CH₂–), δ: 5.03–5.01 (d, 2H, -CH₂–), δ: 3.18 (s, 6H, -CH₃).

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