Supporting Information

Self-assembly of hydrogen-bonded fibrous Fe^{II} triazole complexes and their spin crossover characteristics in organic media.

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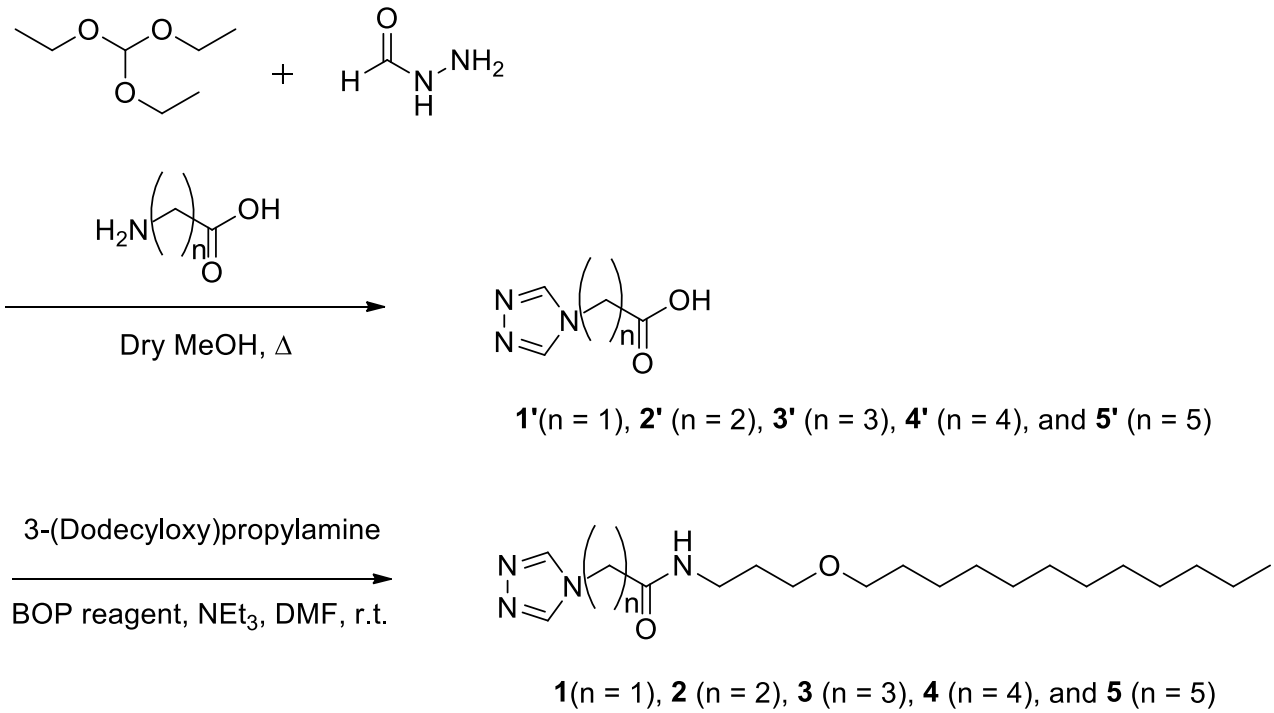
1. Synthesis of ligand 1 – 5 and iron(II) triazole complexes[1]



1'(n = 1), **2'** (n = 2), **3'** (n = 3), **4'** (n = 4), and **5'** (n = 5)

1(n = 1), **2** (n = 2), **3** (n = 3), **4** (n = 4), and **5** (n = 5)

Scheme S1 Synthesis of ligand **1** – **5** and iron(II) triazole complexes

Materials. Pyrogen-free Milli-Q water was obtained from Millipore Direct Q3-UV purification units. Anhydrous chloroform and methanol were obtained by distillation over calcium chloride ($CaCl_2$, Kishida Chemical Co.,Ltd, Osaka, Japan) and calcium hydride (CaH_2, Wako Pure Chemical Industries, Ltd., Osaka, Japan), respectively. Acetone (Kishida Chemical Co.,Ltd, Osaka, Japan), hexane (Kishida Chemical Co.,Ltd, Osaka, Japan), ethyl acetate (Kishida Chemical Co.,Ltd, Osaka, Japan), chloroform ($CHCl_3$, Kishida Chemical Co.,Ltd, Osaka, Japan), and ethylacetate (Kishida Chemical Co.,Ltd, Osaka, Japan) were used without further purification. Unless indicated otherwise, all other chemicals were used without purification.

2-(4H-1,2,4-triazol-4-yl)acetic acid (1'). A solution of 105 mmol of triethyl orthoformate (TCI, Tokyo, Japan) and 60 mmol of formylhydrazine (Sigma-Aldrich Co. LLC, St. Louis, MO, USA) in 100 mL of anhydrous methanol (distilled) was refluxed for 3.5 h under N_2. Then 30 mmol of glysine (Kishida Chemical Co.,Ltd, Osaka, Japan) was passed into the solution. Finally, the solution was refluxed for 75 h. The solvent was then removed under reduced pressure. The powder was washed in Acetone and colorless powder was obtained. Yeild 1.7 g (63 %), ^{1}H NMR (CD_3OD), δ(ppm) 3.2 (-CH_2-, 2H), 4.86 (COO<u>H</u>, 1H), 8.41 (Trz, 2H)

***N*-(3-Dodecyloxy-propyl)-1,2,4-triazole-4-yl-acetoamido (1).** 12.3 mmol of Benzotriazole-1yloxy-tris(dimethylamino)phosphonium hexafluorophosphate (TCI, Tokyo, Japan) and 19.0 mmol of triethylamine (Kishida Chemical Co.,Ltd, Osaka, Japan) were added to 12.3 mmol **1'** in 50 mL dimethyl formamide (distilled). 12.3 mmol of 3-(dodecyloxy)propylamine (Acros Organics, Geel, Belgiumin) 150 mL DMF was dropped into the **1'** solution under an ice bath. The mixture was stirred for 2 days. The solvent was then removed under reduced pressure. The obtained oil was washed in 100 mL Hexane and recrystallized in 100 mL ethyl acetate. The colorless powder was purified by silica gel column chromatography ($CHCl_3$: CH_3OH = 5: 1). Yeild 0.36 (17 %); FT-IR (BaF_2), λ^{-1}(cm^{-1}) 3349 (ν(N-H)), 2923, 2849 (ν(C-H)), 1678 (ν(C=O)), 1538 (δ(N=H)), 1465 (ν(C=N)), 1113 (ν(C-O-C))); ^{1}H

NMR($CDCl_3$), δ 0.88 (CH_3-, 3H), 1.25-1.27 (-CH_2-, 18H), 1.52 (-NH-C<u>H</u>$_2$-, 2H), 1.77 (-O-CH_2-C<u>H</u>$_2$-CH_2-NH-, 2H), 3.37 (-O-C<u>H</u>$_2$-CH_2-CH_2-NH-, 2H), 3.45 (-CH_2-O-, 2H), 3.52 (-C<u>H</u>$_2$-NH-, 2H) , 4.64 (-C<u>H</u>$_2$-Trz), 6.71 (-N<u>H</u>-CO-, 1H), 8.23 (Trz, 2H)

3-(4H-1,2,4-triazol-4-yl)propanoic acid (2'). A solution of 90 mmol of triethyl orthoformate (TCI, Tokyo, Japan) and 60 mmol of formylhydrazine (Sigma-Aldrich Co. LLC, St. Louis, MO, USA) in 100 mL of anhydrous methanol (distilled) was refluxed for 4 h under N_2. Then 30 mmol of β-alanine (Kishida Chemical Co.,Ltd, Osaka, Japan) was passed into the solution. Finally, the solution was refluxed for 35 h. The solvent was then removed under reduced pressure. The powder was washed in 150 mL Acetone and colorless powder was obtained. Yeild 2.7 g (63 %), FT-IR (BaF_2), λ^{-1}(cm^{-1}) 1718 (ν(C=O)), 1503, 1444 (ν(C=N)), 1257 (ν(C=O)); ^{1}H NMR($CDCl_3$), δ 2.85 (C<u>H</u>$_2$-COOH, 2H), 4.38 (-C<u>H</u>$_2$-Trz, 2H), 8.53 (Trz, 2H)

***N*-(3-(Dodecyloxy)propyl)-3-(4H-1,2,4-triazol-4-yl)propanamide (2).** 19.0 mmol of Benzotriazole-1yloxy-tris(dimethylamino)phosphonium hexafluorophosphate (TCI, Tokyo, Japan) and 28.5 mmol of triethylamine (Kishida Chemical Co.,Ltd, Osaka, Japan) were added to 19.0 mmol **2'** in 50 mL DMF. 19.0 mmol of 3-(dodecyloxy)propylamine (Acros Organics, Geel, Belgiumin) in 30 mL DMF was dropped into the **2'** solution under ice bath. The mixture was stirred for 1 day. The solvent was then removed under reduced pressure. The obtained oil was dissolved in 100 mL $CHCl_3$, washed in 100 mL water three times, and dried by anhydrous Na_2SO_4 (Kishida Chemical Co.,Ltd, Osaka, Japan). The solvent was then removed under reduced pressure. The colorless powder was isolated by silica gel column chromatography ($CHCl_3$: CH_3OH = 5: 1). The powder was recrystallized in 10 mL $CHCl_3$ and 150 mL Hexane. Yeild 4.3 g (62 %); FT-IR (BaF_2), λ^{-1}(cm^{-1}) 3296, 3103 (ν(N-H)), 2923, 2851 (ν(C-H)), 1635 (ν(C=O)), 1557 (δ(N=H)), 1524, 1466 (ν(C=N)), 1118 (ν(C-O-C))); ^{1}H NMR($CDCl_3$), δ 0.86 (CH_3-, 3H), 1.28-1.30 (-CH_2-, 18H), 1.54 (-C<u>H</u>$_2$-CH_2-O-, 2H), 1.74 (-O-CH_2-C<u>H</u>$_2$-CH_2-NH-, 2H), 2.60 (-CO-C<u>H</u>$_2$-CH_2-Trz, 2H), 3.36-3.41 (-O-C<u>H</u>$_2$-CH_2-CH_2-NH-, -CH_2-O-, 4H), 3.50 (-O-CH_2-CH_2-C<u>H</u>$_2$-NH-, 2H), 4.40 (-CH_2-Trz), 6.49 (-N<u>H</u>-CO-, 1H), 8.21 (Trz, 2H)

4-(4H-1,2,4-triazol-4-yl)butanoic acid (3'). A solution of 90 mmol of triethyl orthoformate (TCI, Tokyo, Japan) and 60 mmol of formylhydrazine (Sigma-Aldrich Co. LLC, St. Louis, MO, USA) in 100 mL of anhydrous methanol (distilled) was refluxed for 4 h under N_2. Then 30 mmol of γ-amino-n-butanoic acid (TCI, Tokyo, Japan) was passed into the solution. Finally, the solution was refluxed for 4 days. The solvent was then removed under reduced pressure. The oil was washed in 300 mL hot ethylacetate and pale gray powder was obtained. The powder was recrystallized in 900 mL acetonitrile. Yeild 1.9 g (40 %), ^{1}H NMR(CD_3OD), δ 2.04-2.13 (-CH_2-, 2H), 2.33 (C$\underline{H}_2$-COOH, 2H), 4.18 (-C$\underline{H}_2$-Trz, 2H), 8.55 (Trz, 2H)

***N*-(3-(Dodecyloxy)propyl)-3-(4H-1,2,4-triazol-4-yl)propanamide (3).** 12.1 mmol of Benzotriazole-1yloxy-tris(dimethylamino)phosphonium hexafluorophosphate (TCI, Tokyo, Japan) and 18.2 mmol of triethylamine (Kishida Chemical Co.,Ltd, Osaka, Japan) were added to 12.0 mmol **3'** in 50 mL DMF. 12.1 mmol of 3-(dodecyloxy)propylamine (Acros Organics, Geel, Belgiumin) in 20 mL DMF was dropped into the **3'** solution under ice bath. The mixture was stirred for 5 days. The solvent was then removed under reduced pressure. The obtained oil was dissolved in 100 mL $CHCl_3$, washed in 100 mL water three times, and dried by anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. The colorless powder was isolated by silica gel column chromatography ($CHCl_3$: CH_3OH = 5: 1). Yeild 3.8 g (83 %); FT-IR (CaF_2), λ^{-1}(cm^{-1}) 3297, 3103 (ν(N-H)), 2923, 2852 (ν(C-H)), 1636 (ν(C=O)), 1557 (δ(N=H)), 1524, 1466 (ν(C=N)), 1118 (ν(C-O-C))); ^{1}H NMR($CDCl_3$), δ 0.88 (CH_3-, 3H), 1.26-1.30 (-CH_2-, 18H), 1.54 (--C$\underline{H}_2$-CH_2-O, 2H), 1.78 (-O-CH_2-C$\underline{H}_2$-CH_2-NH-, 2H), 2.12-2.15 (-CO-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-Trz, 4H), 3.36-3.42 (-O-C$\underline{H}_2$-CH_2-CH_2-NH-, -CH_2-O-, 4H), 3.50 (-C$\underline{H}_2$-NH-, 2H), 4.15 (-CH_2-Trz), 6.58 (-N$\underline{H}$-CO-, 1H), 8.17 (Trz, 2H)

5-(4H-1,2,4-triazol-4-yl)pentanoic acid (4'). A solution of 40 mmol of triethyl orthoformate (TCI, Tokyo, Japan) and 30 mmol of formylhydrazine (Sigma-Aldrich Co. LLC, St. Louis, MO, USA) in 50 mL of anhydrous methanol (distilled) was refluxed for 4.5 h under N_2. Then 20 mmol of δ-amino-n-

valeric acid (Acros Organics, Geel, Belgiumin) was passed into the solution. Finally, the solution was refluxed for 5 days. The solvent was then cooled at room temperature and the precipitation was filtered. The colorless powder was washed in 200 mL acetone. Yeild 2.3 g (69 %), ^{1}H NMR(CD_3OD), δ 1.59 (-C<u>H</u>$_2$-CH_2-COOH, 2H), 1.86 (-C<u>H</u>$_2$-CH_2-Trz, 2H), 2.32 (-C<u>H</u>$_2$-COOH, 2H), 4.13-4.5 (-C<u>H</u>$_2$-Trz, 2H) , 4.87 (-COO<u>H</u>, 1H), 8.54 (Trz, 2H).

***N*-(3-(Lauryloxy)propyl)-4-(4H-1,2,4-triazol-4-yl)pentanamide (4).** 13.8 mmol of Benzotriazole-1yloxy-tris(dimethylamino)phosphonium hexafluorophosphate (TCI, Tokyo, Japan) and 20.7 mmol of triethylamine (Kishida Chemical Co.,Ltd, Osaka, Japan) were added to 13.8 mmol **4'** in 50 mL DMF. 13.8 mmol of 3-(dodecyloxy)propylamine (Acros Organics, Geel, Belgiumin) in 20 mL DMF was dropped into the **4'** solution under ice bath. The mixture was stirred for 5 days. The solvent was then removed under reduced pressure. The obtained oil was dissolved in 50 mL $CHCl_3$, washed in 50 mL water three times, and dried by anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. The colorless powder was isolated by silica gel column chromatography ($CHCl_3$: CH_3OH = 10: 1→3:1). Yeild 3.9 g (71 %); FT-IR (CaF_2), λ^{-1}(cm^{-1}) 3296, 3100 (ν(N-H)), 2924, 2854 (ν(C-H)), 1656 (ν(C=O)), 1540 (δ(N=H)), 1461 (ν(C=N)), 1113 (ν(C-O-C))); ^{1}H NMR($CDCl_3$), δ 0.88 (CH_3-, 3H), 1.25-1.29 (-CH_2-, 18H), 1.55 (-C<u>H</u>$_2$-CH_2-O, 2H), 1.68 (-CO-CH_2-C<u>H</u>$_2$-, 2H), 1.75 (-O-CH_2-C<u>H</u>$_2$-CH_2-NH-, 2H), 1.86 (-C<u>H</u>$_2$-CH_2-Trz, 2H), 2.18 (-CO-CH_2-, 2H), 3.34-3.37 (-O-C<u>H</u>$_2$-CH_2-CH_2-NH-, -CH_2-O-, 4H), 3.40 (-C<u>H</u>$_2$-NH-, 2H), 4.04 (-CH_2-Trz), 6.32 (-N<u>H</u>-CO-, 1H), 8.17 (Trz, 2H)

6-(4H-1,2,4-triazol-4-yl)hexanoic acid (5'). A solution of 105 mmol of triethyl orthoformate (TCI, Tokyo, Japan) and 60 mmol of formylhydrazine (Sigma-Aldrich Co. LLC, St. Louis, MO, USA) in 50 mL of anhydrous methanol (distilled) was refluxed for 4.5 h under N_2. Then 20 mmol of ε-amino-n-caproic acid (TCI, Tokyo, Japan) was passed into the solution. Finally, the solution was refluxed for 2 days. The solvent was then cooled at room temperature and the precipitation was filtered. The colorless powder was recrystallized in acetone. Yeild 3.3 g (82 %), FT-IR (KBr), λ^{-1}(cm^{-1}) 3132 (ν(C-H)$_{Trz}$), 2943 (1718 (ν(C-H)$_{CH2}$), 1682 (ν(C=O)), 1530, 1466 (ν(C=N)), 1284 (ν(C=O)); ^{1}H NMR(D_2O), δ 1.25 (-C<u>H</u>$_2$-

CH_2-CH_2-COOH, 2H), 1.58 (-C<u>H</u>$_2$-CH_2-COOH, 2H), 1.82 (-C<u>H</u>$_2$-CH_2-Trz, 2H), 2.33 (-C<u>H</u>$_2$-COOH, 2H), 4.12 (-C<u>H</u>$_2$-Trz, 2H) , 4.87 (-COO<u>H</u>, 1H), 8.47 (Trz, 2H).

***N*-(3-(Lauryloxy)propyl)-5-(4H-1,2,4-triazol-4-yl)hexanamide (5).** 5.0 mmol of Benzotriazole-1yloxy-tris(dimethylamino)phosphonium hexafluorophosphate (TCI, Tokyo, Japan) and 18.2 mmol of triethylamine (Kishida Chemical Co.,Ltd, Osaka, Japan) were added to 5.0 mmol **5'** in 30 mL DMF. 5.0 mmol of 3-(dodecyloxy)propylamine (Acros Organics, Geel, Belgiumin) in 20 mL DMF was dropped into the **5'** solution under ice bath. The mixture was stirred for 4 days. The solvent was then removed under reduced pressure. The obtained oil was dissolved in 100 mL $CHCl_3$, washed in 100 mL NaHCO3 aq., and 100 mL saturated NaCl aq. (x3), and dried by anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. The colorless powder was isolated by silica gel column chromatography ($CHCl_3$: CH_3OH = 5: 1). Yeild 1.70 g (83 %); FT-IR (CaF_2), λ^{-1}(cm^{-1}) 3323, 3109 (ν(N-H)), 2925, 2850 (ν(C-H)), 1634 (ν(C=O)), 1531 (δ(N=H)), 1467 (ν(C=N)), 1116 (ν(C-O-C))); ^{1}H NMR($CDCl_3$), δ 0.88 (CH_3-, 3H), 1.25-1.30 (-CH_2-, CO-CH_2-CH_2-C<u>H</u>$_2$-, 20H), 1.56 (-C<u>H</u>$_2$-CH_2-O, 2H), 1.67 (-CO-CH_2-C<u>H</u>$_2$-, 2H), 1.74 (-O-CH_2-C<u>H</u>$_2$-CH_2-NH-, 2H), 1.83 (-C<u>H</u>$_2$-CH_2-Trz, 2H), 2.13 (-CO-CH_2-, 2H), 3.34-3.41 (-O-C<u>H</u>$_2$-CH_2-CH_2-NH-, -CH_2-O-, 4H), 3.51 (-C<u>H</u>$_2$-NH-, 2H), 4.04 (-CH_2-Trz), 6.23 (-N<u>H</u>-CO-, 1H), 8.16 (Trz, 2H)

Synthesis of Iron triazole complexes ([Fe(1)$_3$]Cl$_2$, [Fe(2)$_3$]Cl$_2$, [Fe(3)$_3$]Cl$_2$, [Fe(4)$_3$]Cl$_2$, and [Fe(5)$_3$]Cl$_2$). [Fe^{II}(**L**)$_3$]Cl_2 (**L** = **1** – **5**) were prepared by adding 163 μmol of lipophilic triazole ligands, dissolved in 1 mL of dry methanol, to a solution of 51 μmol of iron(II) chloride 4 hydrate (Kishida Chemical Co.,Ltd, Osaka, Japan) and 51 μmol of ascorbic acid (Kishida Chemical Co.,Ltd, Osaka, Japan) in 1 mL of dry methanol. The colorless powders were precipitated within several minutes. The suspensions were kept in freezer (-20° C) overnight. The purple precipitates were centrifuged at 5000 rpm for 1 hr and washed in dry methanol (x2). Purple powders were formed after drying in vacuo. [Fe(**1**)$_3$]Cl_2, Yeild, 27 mg (44 %). Anal. Calcd for $C_{57}H_{108}N_{12}O_6Cl_2Fe$+1.5$H_2O$: C, 56.52; H, 9.24; N,

13.88. Found: C, 56.57; H, 9.00; N, 13.88.; [Fe(**2**)$_3$]Cl_2, Yeild, 35 mg (54 %). Anal. Calcd for $C_{60}H_{114}N_{12}O_6Cl_2Fe+2H_2O$: C, 57.08; H, 9.42; N, 13.31. Found: C, 57.16; H, 9.19; N, 13.21.; [Fe(**3**)$_3$]Cl_2, Yeild, 44 mg (63 %). Anal. Calcd for $C_{63}H_{120}N_{12}O_6Cl_2Fe+H_2O$: C, 58.82; H, 9.56; N, 13.07. Found: C, 58.74; H, 9.29; N, 13.01.; [Fe(**4**)$_3$]Cl_2, Yeild, 42 mg (60 %). Anal. Calcd for $C_{66}H_{126}N_{12}O_6Cl_2Fe+5H_2O$: C, 56.60; H, 9.79; N, 12.00. Found: C, 56.69; H, 9.45; N, 11.94.; [Fe(**5**)$_3$]Cl_2, Yeild, 25 mg (33 %). Anal. Calcd for $C_{69}H_{132}N_{12}O_6Cl_2Fe+1.5H_2O$: C, 60.07; H, 9.86; N, 12.18. Found: C, 59.93; H, 9.55; N, 12.01.

2. Transmission electron micrographs of iron triazole complexes

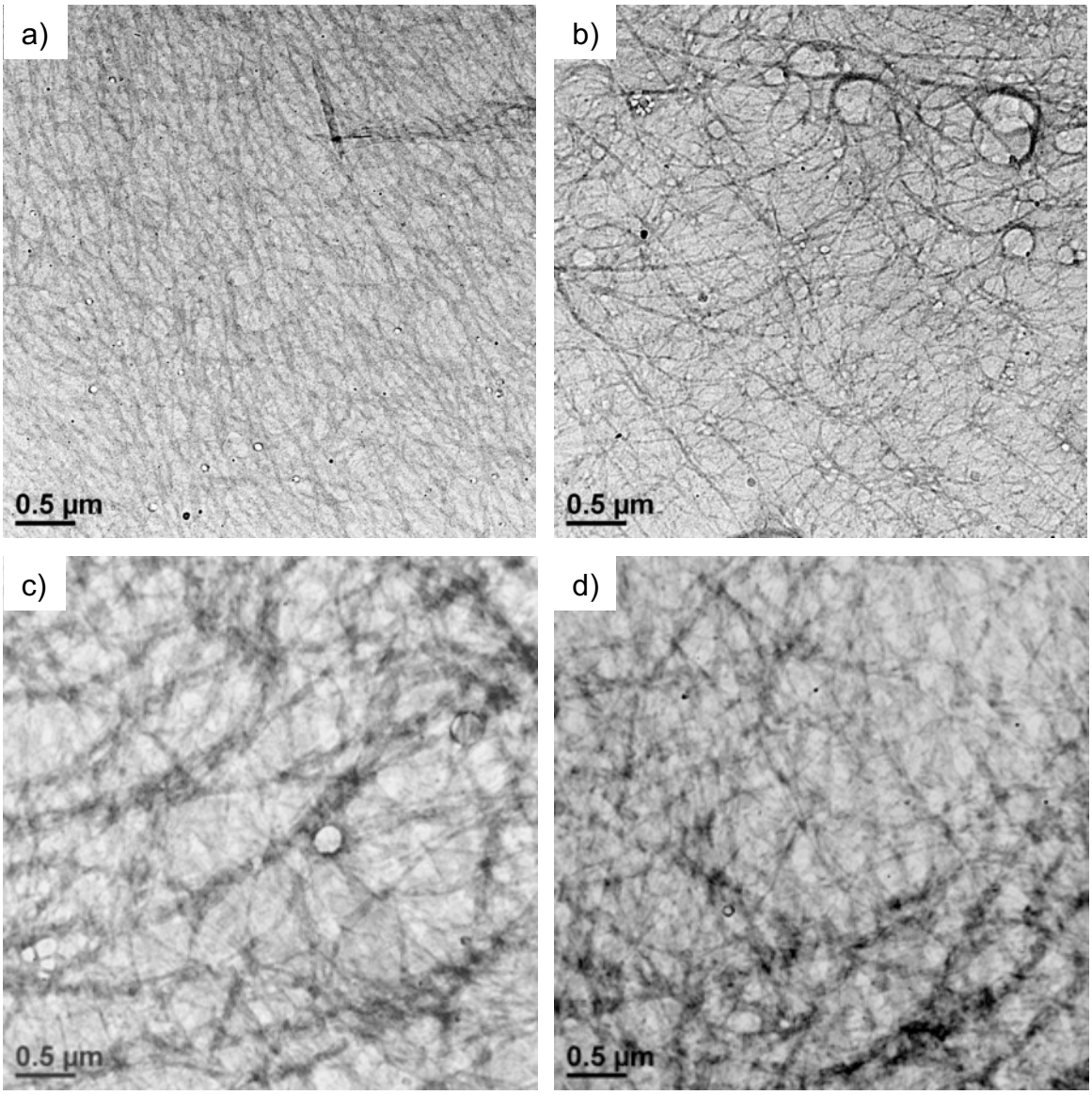


Figure S1 TEM image of $[Fe(\mathbf{2})_3]Cl_2$ (a), $[Fe(\mathbf{3})_3]Cl_2$ (b), $[Fe(\mathbf{4})_3]Cl_2$ (c), and $[Fe(\mathbf{5})_3]Cl_2$ (d) (5 unit mM) transferred on a carbon-coated TEM grid.

Figure S1 shows TEM images of $[Fe(\mathbf{2})_3]Cl_2$ (Figure S1a), $[Fe(\mathbf{3})_3]Cl_2$ (Figure S1b), $[Fe(\mathbf{4})_3]Cl_2$ (Figure S1c), and $[Fe(\mathbf{5})_3]Cl_2$ (Figure S1d) transferred on carbon coated copper grid.[2] On all the samples, networks of fibrous nanoassemblies with widths of 10 – 50 nm are abundantly seen. The nanoassemblies are similar to that of $[Fe^{II}(\mathbf{1})_3]Cl_2$ with jelly-like phase. As the observed widths

correspond to the bimolecular length of ligands (**2** , 27.1 Å; **3**, 29.0 Å; **4,** 30.0 Å; **5**, 31.5 Å, estimated by the Corey-Pauling-Koltun (CPK) model), they must be dispersed as the bundle of the linear complexes.

In addition, the network structure of $[Fe^{II}(\mathbf{4})_3]Cl_2$ and $[Fe^{II}(\mathbf{5})_3]Cl_2$ aggregates with widths of 30 – 50 nm were seen. While $[Fe^{II}(\mathbf{4})_3]Cl_2$ and $[Fe^{II}(\mathbf{5})_3]Cl_2$ exist in a dispersed solution state in chloroform, fiber-like structures analogous to those observed for $[Fe^{II}(\mathbf{1})_3]Cl_2$–$[Fe^{II}(\mathbf{3})_3]Cl_2$ were clearly observed when these complexes were transferred onto a substrate. Although the impact of solvent evaporation during the drying process cannot be disregarded, these observations indicate that the coordination polymers likely preserve their one-dimensional structures even in solution.

3. Temperature dependence of absorption intensity of low spin state in a heating-and-cooling cycle

The temperature dependence of UV-Vis spectra in chloroform was performed on the solution of iron triazole complexes. The color of $[Fe^{II}(\mathbf{L})_3]Cl_2$ below 270 K is pale purple. Both spectral changes were thermally reversible.

In the cooling process of $[Fe^{II}(\mathbf{L})_3]Cl_2$ in chloroform, the intensity of the absorption peaks at 530 nm increased (Figure S2). The absorption peak observed for $[Fe^{II}(\mathbf{L})_3]Cl_2$ at 528 nm is attributed to $^1A_1 \rightarrow {}^1T_1$ transition of the LS complex. The intensity of the absorption bands increased with respect to the decreasing temperature, and the change leveled off below 280 K. Temperature ranges of spin crossover for iron triazole complexes containing longer spacer shifted lower temperature.($[Fe^{II}(\mathbf{2})_3]Cl_2$, $T_{sc}\uparrow$ 293 K, $T_{sc}\downarrow$ 292 K, Figure S2a; $[Fe^{II}(\mathbf{3})_3]Cl_2$, $T_{sc}\uparrow$ 298 K, $T_{sc}\downarrow$ 289 K, Figure S2b; $[Fe^{II}(\mathbf{4})_3]Cl_2$, $T_{sc}\uparrow$ 292 K, $T_{sc}\downarrow$ 281 K, Figure S2c; $[Fe^{II}(\mathbf{5})_3]Cl_2$, $T_{sc}\uparrow$ 287 K, $T_{sc}\downarrow$ 282 K, Figure S2d) In addition, thermal hysteresis observed for $[Fe^{II}(\mathbf{L})_3]Cl_2$ was similar with each other (Figure S2). Therefore, all the samples likely exhibit enhanced cooperativity of iron triazole complexes, which leads to the hydrogen bonding of the amido linkage in the lipophilic part of Fe^{II} triazole complexes, resulting in the thermal hysteresis in spin crossover. It is to be noted that the spin crossover phenomena of coordination chains are regulated by the slight difference in the chemical structure of ligands.

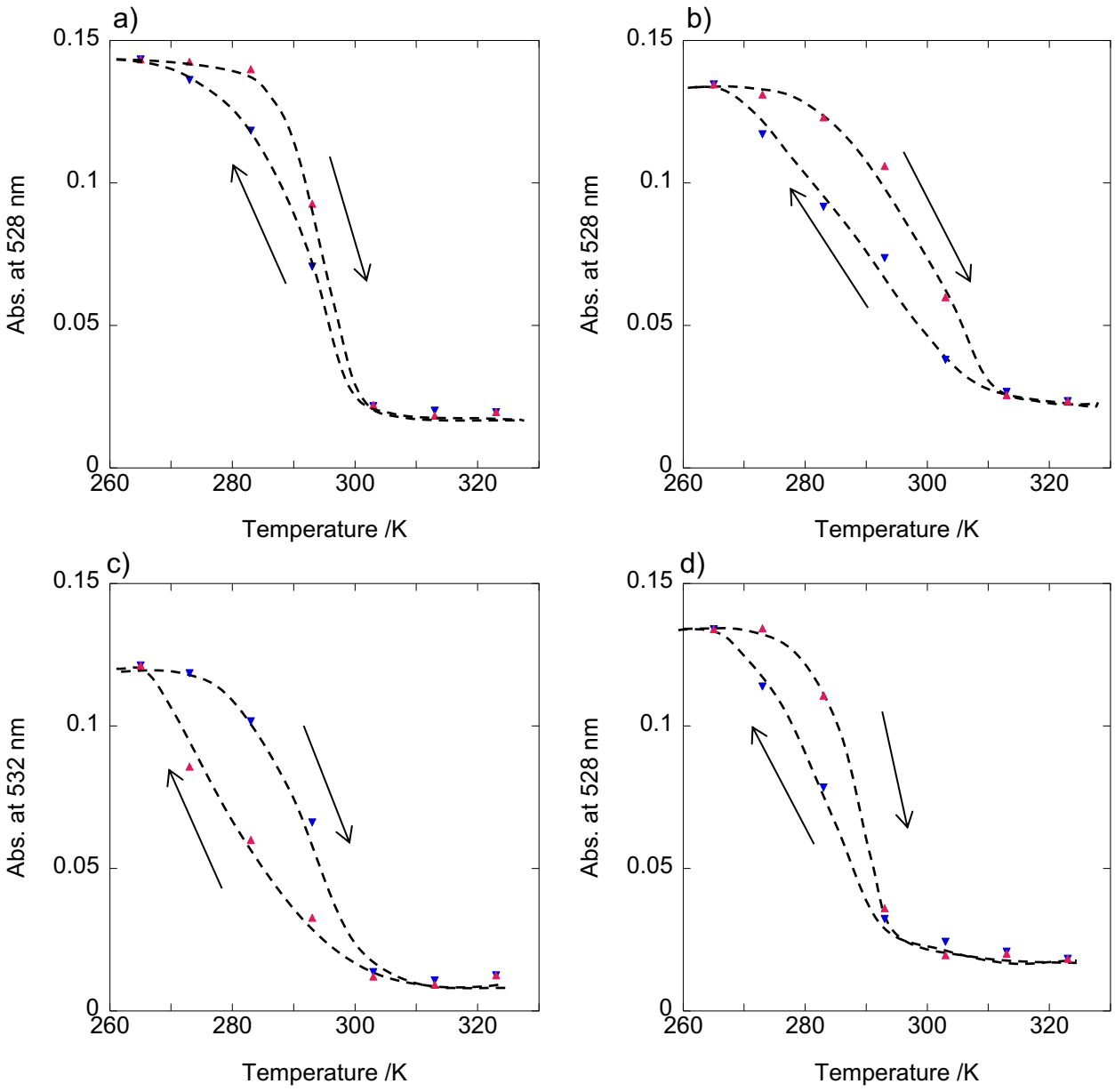


Figure S2 Temperature dependence of the absorption intensity of $^1A_1 \rightarrow {}^1T_1$ transition around 530 nm during a heating-and-cooling cycles; $[Fe(\mathbf{2})_3]Cl_2$ (a), $[Fe(\mathbf{3})_3]Cl_2$ (b), $[Fe(\mathbf{4})_3]Cl_2$ (c), and $[Fe(\mathbf{5})_3]Cl_2$ (d)

4. FT-IR spectra of iron triazole complexes

Figure S3 shows the FT-IR spectra of iron triazole complexes in chloroform. The gray regions are peaks of chloroform backgrounds. All the samples show the C=N stretching vibrations can be observed around 1415 cm^{-1} at room temperature, which indicate the presence of low spin state.[3] On the other hand, the peaks at ca. 1400 cm^{-1} can be replaced in the case of heating sample in chloroform. The shifted stretching bands of C=N units result from coordination bands of high spin state, which are elongated toward ligand field of HS state.[3] The observations of red shifted C=N stretching indicate the spin crossover phenomenon consistent with the SQUID and UV-vis spectral observations. It is noteworthy that [Fe(**3**)$_3$]Cl_2 (Figure S3c), [Fe(**4**)$_3$]Cl_2 (Figure S3d), and [Fe(**5**)$_3$]Cl_2 (Figure S3e) showed the two peak around 1400-1415 cm^{-1} at 278 K, which indicate the mixture of HS and LS state even at 278 K. The result also is consistent with lower temperature of spin crossover than that of [Fe(**1**)$_3$]Cl_2 (Figure S3a) and [Fe(**2**)$_3$]Cl_2 (Figure S3b), estimated by UV-vis spectra.

In addition, C=O stretching bands of [Fe(**1**)$_3$]Cl_2 (Figure S3a), [Fe(**2**)$_3$]Cl_2 (Figure S3b), [Fe(**3**)$_3$]Cl_2 (Figure S3c), [Fe(**4**)$_3$]Cl_2 (Figure S3d), and [Fe(**5**)$_3$]Cl_2 (Figure S3e) were observed at 1680, 1651, 1654, 1643, and 1649 cm^{-1} at 278 K, respectively. It shows hydrogen bonds among alkylchains with amido linkage were formed in triazole main chains. The C=O stretching band of [Fe(**1**)$_3$]Cl_2 was red-shifted more than the other iron triazole complexes. It indicates that [Fe(**1**)$_3$]Cl_2 strongly form not only the hydrogen bond among inter-alkyl chain, but also intermolecular interaction between amido group and halide anion, and intramolecular interaction between C=O of amido linkage and C-H of triazole ligand. When the iron triazole complexes were heated in chloroform at 323 K, C=O stretching bands of [Fe(**4**)$_3$]Cl_2 and [Fe(**5**)$_3$]Cl_2 were red-shifted at 1651 and 1654 cm^{-1}, respectively. The observation of red-shift indicates the dissociation of hydrogen bonding, whereas the bands of [Fe(**1**)$_3$]Cl_2 (Figure S3a), [Fe(**2**)$_3$]Cl_2 (Figure S3b), and [Fe(**3**)$_3$]Cl_2 (Figure S3c) remained at the same peaks of 278 K. Especially, the result of specific hydrogen bonding of [Fe(**1**)$_3$]Cl_2 seems to be controllable for spin crossover with thermal hysteresis.

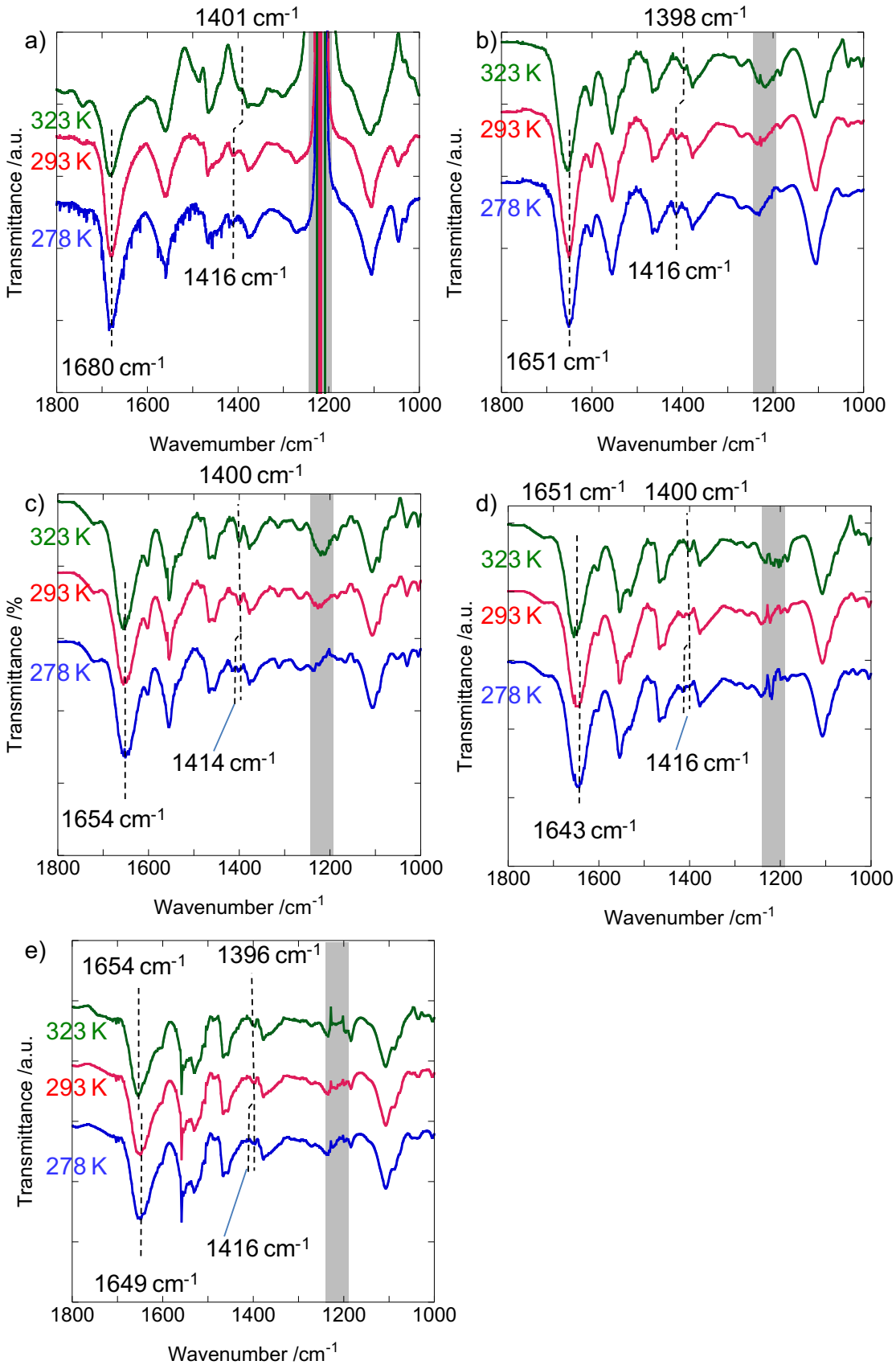


Figure S3 FT-IR spectra in the 1800 – 1000 cm^{-1} region of chloroform solution, $[Fe(\mathbf{1})_3]Cl_2$ (a), $[Fe(\mathbf{2})_3]Cl_2$ (b), $[Fe(\mathbf{3})_3]Cl_2$ (c), $[Fe(\mathbf{4})_3]Cl_2$ (d), and $[Fe(\mathbf{5})_3]Cl_2$ (e) (5 unit mM) in NaCl thin layer cell.

5. Powder X-ray Diffraction of $[Fe(2)_3]Cl_2$, $[Fe(3)_3]Cl_2$, $[Fe(4)_3]Cl_2$, and $[Fe(5)_3]Cl_2$

Figures S4 compare WAXD data obtained for $[Fe^{II}(\mathbf{L})_3]Cl_2$ at 223 K and 373 K. At room temperature, $[Fe^{II}(\mathbf{L})_3]Cl_2$ showed first-order and higher order reflections corresponding to a lamellar structure with a long period of 41.0 (Figure 5), 45.3 (Figure S4a), 39.6 (Figure S4b), 41.4 (Figure S4c), 44.4 Å (Figure S4d), respectively. Heating of $[Fe^{II}(\mathbf{L})_3]Cl_2$ sample to 373 K resulted in change of a lamellar d-spacing of 44.5 (Figure 5), 44.5 (Figure S4a), 44.1 (Figure S4b), 43.9 (Figure S4c), 44.6 Å (Figure S4d). The changed long spacing is consistent with melting of long alkyl chains. The higher order diffractions observed in the $[Fe^{II}(\mathbf{L})_3]Cl_2$ clearly showed a high structural regularity of the films. Reports on 4-alkylated triazole complexes have assumed anisotropic, rodlike structures with organic substituents that are radially attached to main chains.[3, 4] In this system, introduction of the ether linkage into the alkyl chain moiety have effectively decoupled the alignment of alkyl chains from linear Fe^{II} tris-triazole main chains, thereby allowing the formation of regular lamellar structures.[5]

In addition, the long period of $[Fe^{II}(\mathbf{2})_3]Cl_2$ showed decrease from 45.3 Å (at 223 K) to 44.5 Å (at 373 K). The smaller diffraction intensity obtained at 223 K compared to that at 373 K implies that the alkylchain layer of $[Fe^{II}(\mathbf{2})_3]Cl_2$ well accommodates each molecule and shows better perpendicular against the main chain at a lower temperature. Upon heating, however, the tilt-oriented alkylchain layer exerted a decrease in long spacing.

Thus, thermal changes in lamellar structures of nanofibrous $[Fe^{II}(\mathbf{L})_3]Cl_2$ depend on the slight difference in spacer length. The observed structural transitions are thermally reversible, and regular lamellar structures are maintained in organic media.

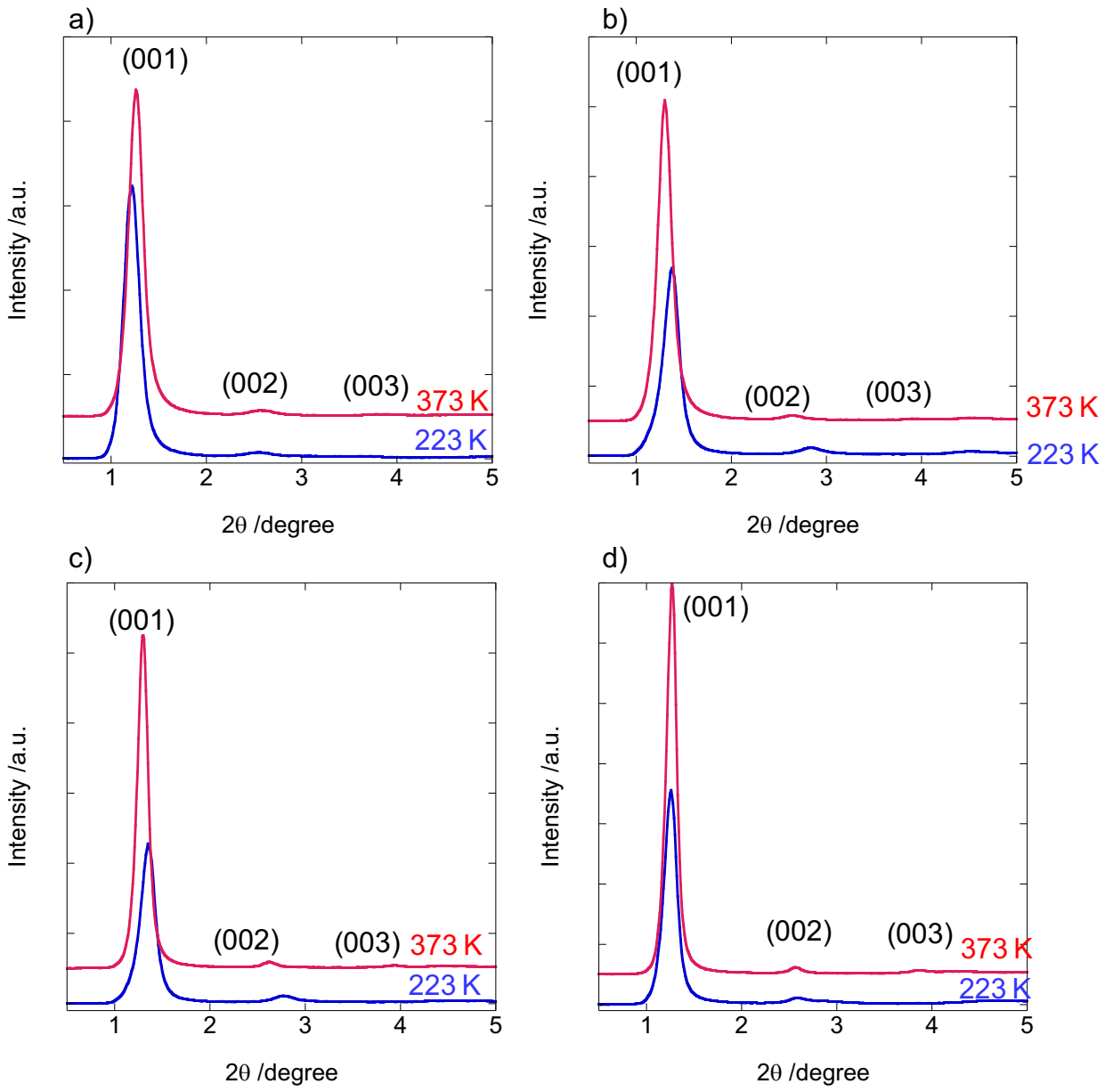


Figure S4 Wide-angle X-ray diffraction pattern of the powdered xerogel of $[Fe(\mathbf{2})_3]Cl_2$ (a), $[Fe(\mathbf{3})_3]Cl_2$ (b), $[Fe(\mathbf{4})_3]Cl_2$ (c), and $[Fe(\mathbf{5})_3]Cl_2$ (d) at 223 K and 373 K.

Reference

(1) Vos, G.; De Graaff, R. A. G.; Haasnoot, J. G.; Van Der Kraan, A. M.; De Vaal, P.; Reedijk, J. *Inorg. Chem.* **1984**, *23*, 2905.

(2) Kimizuka, N.; Shimizu, M.; Fujikawa, S.; Fujimura, K.; Sano, M.; Kunitake, T. *Chem. Lett.* **1998**, *10*, 967.

(3) Armand, F.; Badoux, C.; Bonville, P.; Ruaudel-Texier, A.; Kahn, O. *Langmuir* **1995**, *11*, 3467.

(4) Kröber, J.; Codjovi, E.; Kahn, O.; Grolière, F. *J. Am. Chem. Soc.* **1993**, *115*, 9810.; Roubeau, O.; Gomez, M. A.; Balskus, E.; Kolnaar, J. J. A.; Haasnoot, J. G.; Reedijk, J. *New J. Chem.* **2001**, *25*, 144.; (d) Roubeau, O.; Colin, A.; Schmitt, V.; Clérac, R. *Angew. Chem. Int. Ed.* **2004**, *43*, 3283.; (e) Kröber, J.; Audière, J. P.; Claude, R.; Codjovi, E.; Kahn, O.; Haasnoot, J. G.; Grolière, F.; Jay, C.; Bousseksou, A.; Linarès, J.; Varret, F.; G-Vassal, A. *Chem. Mater.* **1994**, *6*, 1404.; Fujigaya, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 14690.; Fujigaya, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 5484.; Fujigaya, T,; Jiang, D.; Aida, T. *Chem. Asian J.* **2007**, *2*, 106.; Gaspar, A. B.; Ksenofontov, V.; Seredyuk, M.; Gütlich, P. *Coord. Chem. Rev.* **2005**, *249*, 2661.

(5) Kuroiwa, K.; Shibata, T.; Sasaki, S.; Ohba, M.; Takahara, A.; Kunitake, T.; Kimizuka, N. *J. Polym. Sci. A, Polym. Chem.* **2006**, *44*, 5192.