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Supporting Information

Amphiphilic Iron(II) Spin Crossover Coordination Polymers: Crystal Structures and Phase Transition Properties

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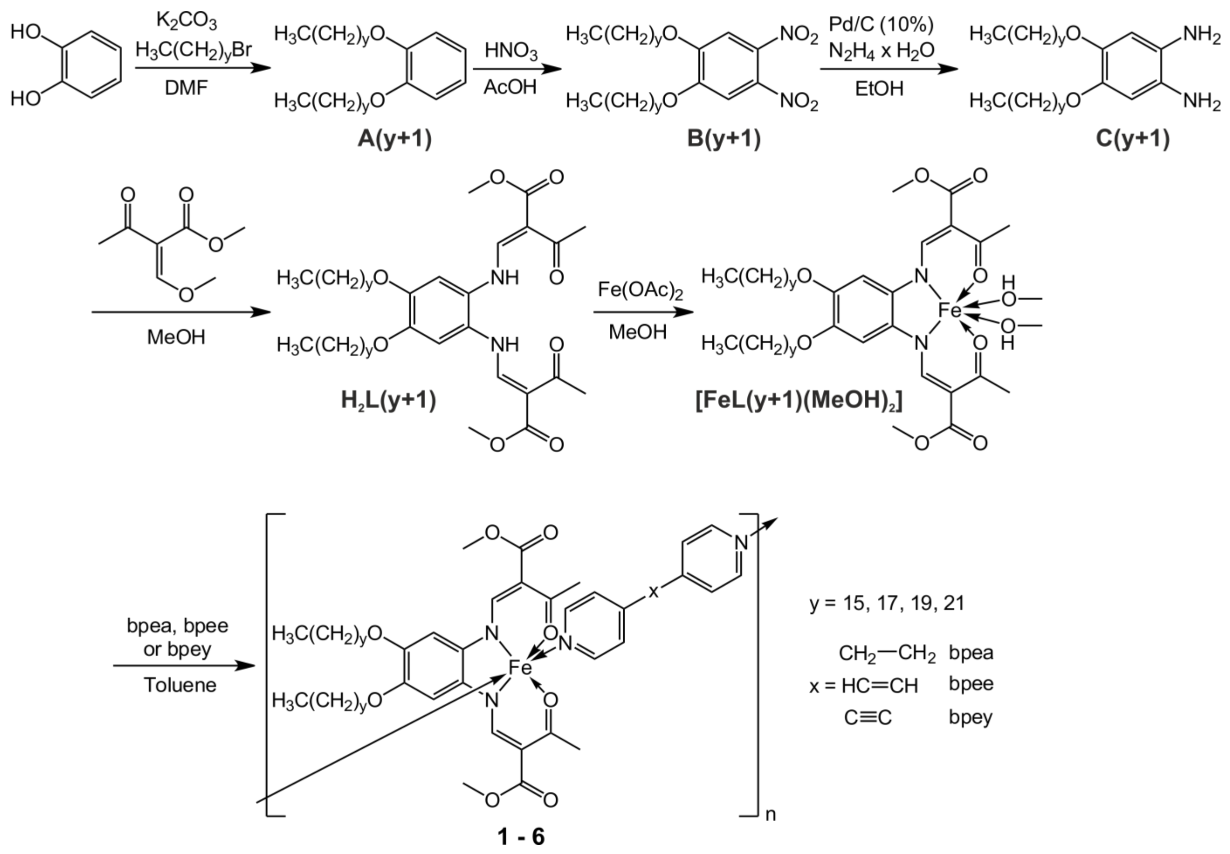
Scheme S1. Synthesis of the ligands and the resulting complexes **1 – 6**.



Experimental Section

Infrared Spectroscopy: Transmission infrared spectra were collected using a PerkinElmer Spectrum 100 FT-IR (ATR). The samples were measured as solids.

Elemental Analysis: Carbon, hydrogen and nitrogen contents were measured using a Vario EL III. The samples were prepared in tin boats. All samples were measured at least twice and the average was used. Acetanilide (Merck) was used as standard.

Mass Spectrometry: Mass spectra were recorded with a MS8500 sector field mass spectrometer from Thermo Finnigan. Direct injection was used and the measurement was done in a temperature range of room temperature to 330 °C.

Nuclear Magnetic Resonance Spectroscopy: The NMR spectra were recorded with a Varian Unity Inova 300 spectrometer from Agilent Technologies at 300 MHz. The samples were dissolved in $CDCl_3$ and their signals were calibrated to the residual signals of the solvent.

Magnetic Measurements: Magnetic measurements were collected using a SQUID MPMS-XL5 instrument from Quantum Design. A field of 1.0 T was applied and the samples were measured from 200 K to 400 K to 50 K to 400 K in sweep mode with a sweep velocity of 2K/min. Gelatine capsules in a plastic straw were used for sample preparation. Moreover, $K_3[Fe(CN)_6]$ was added as a paramagnetic standard to bypass center problems. The diamagnetic parts of the sample holder, the organic ligand and additional paramagnetic parts of the standard were corrected afterwards by using tabulated Pascal's constants (ligand)[1] or measured values (sample holder, $K_3[Fe(CN)_6]$).

Mössbauer Spectroscopy: ^{57}Fe Mössbauer spectra were recorded in transmission geometry at constant acceleration using a conventional Mössbauer spectrometer with a 50 mCi $^{57}Co(Rh)$ source. The samples were prepared under argon atmosphere. The spectra were fitted using Recoil 1.05 Mössbauer analysis software.[2] Isomer shift values were reported with respect to α-Fe as a reference at room temperature.

Thermogravimetric Analysis*:* Thermogravimetric analysis was done with a Netzsch TG 209 F1 Libra under nitrogen atmosphere using 4 mg – 10 mg of the sample with a heating rate of 10 K min^{-1}.

Differential Scanning Calorimetry: The samples were measured with a Mettler Toledo 821c calorimeter under nitrogen atmosphere (50 mL min^{-1}). 5 mg – 10 mg of the samples were prepared in an aluminum boat (0.04 mL) and the heat rate was set to 10 K min^{-1}.

Single Crystal X-ray Diffraction: The X-ray crystal analysis of **[FeL(20)(MeOH)2]** and **4·tol** were done on a STOE StadiVari diffractometer, the one of **6·tol** was done on a Bruker D8 Quest diffractometer. Both were using graphite-monochromatic Mo-K_α radiation. The data were corrected for Lorentzian and polarization effects. The structures were solved by direct methods (SIR-97, SIR2014)[3,4] and refined by full matrix-least square techniques against F_o^2 (SHELXL-97)[5] Hydrogen atoms were included at calculated positions with fixed displacement parameters. Due to a strong disorder in **6·tol** the included solvent could not be solved and was squeezed with PLATON.[6] ORTEP-III[7] was used for the presentation of the asymmetric unit of the crystal structure, SCHAKAL-99[8] to illustrate the molecular packing. Powder pattern were calculated from the x-ray crystal data by using Mercury. [9] The supplementary crystallographic data for **[FeL(20)(MeOH)$_2$]** (CCDC number 1835195), for **6·tol** (CCDC number 1835196), and for **6·tol** (CCDC number 1044903) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray Powder Diffraction: XRPD measurements were done on a STOE Stadi P diffractometer in transmission geometry with Cu-K_α radiation and a Mythen1K detector. The grinded samples were prepared in glass capillaries under argon flow. Temperature dependent XRPD measurements were done on an X'Pert MPD Pro diffractometer from Panalytical (Bragg-Brentano geometry). Cu-K_α radiation was used. The samples were measured on a flat plate under nitrogen atmosphere in an XRK-900 chamber from Anton Paar.

Polarized Optical Microscopy: The micrographs were taken on a Nikon DIAPHOT 300 microscope using a Nikon Digital Camera DXM1200 and Nikon ACT-1 software. For temperature control a Mettler Toledo FP82HT Hot Stage was used. The samples were prepared between two glass plates and sealed with glue under argon atmosphere.

Scanning Electron Microscope: Scanning electron microscopy images were taken with a Zeiss LEO 1530. The samples were prepared on carbon tape.

Spin coating: Spin coating was done with 0.2 mg/mL, 1.0 mg/mL, 5 mg/mL, and 10 mg/mL solutions of **7** in toluene. The spin speed was 2000 rpm or 5000 rpm. The substrates were silicon wafers or glass slides (Menzel glass) which were first cleaned with acetone under ultrasonication for 10 min, then with a 1 vol% Hellmanex III (Hellma, Müllheim, Germany) solution at room temperature under ultrasonication for 10 min, then ultrasonicated twice in Milli-Q water for 10 min and finally ultrasonicated in iso-propanol for another 10 min. They were dried under nitrogen flow and then either put on a hotplate or put in an ozone oven. Some of them were then functionalized with octadecyltrichlorosilane (ODTS) after the ozone treatment and also dried on the hotplate.

Delamination procedure: 4 was dispersed in degassed iso-octane, vortexed, and ultrasonicated for about 1 min. One drop of the dispersion was then applied on a freshly prepared mica plate and used for AFM measurements.

AFM measurements: AFM measurements of **7** were done on a commercially available Dimension™ 3100 AFM from Veeco Instruments equipped with a Nanoscope® V controller (USA) and a hybrid XYZ closed loop scanner. The micro cantilevers (OTESPA-R3) were purchased from Bruker. The images were recorded with 512 rows and 512 pixels. The set point amplitude was 500 mV and the drive amplitude 380 mV. The scan rate was 0.4 Hz for the images with a resolution of 20x20 µm and 10x10 µm, and 1.0 Hz for the images with a resolution of 1x1 µm. AFM images were processed with Gwyddion 2.50.[10] The data was leveled by mean plane subtraction and flattened by subtracting a third order polynomial background. The fast scanning x-axis was corrected with a median of differences algorithm. The minimum of the data values was then shifted to zero. AFM measurements of the delaminated crystals of **4** were done on a commercially available Dimension Icon from Bruker in tapping mode under air. The micro cantilevers (AC160TS) were purchased from Oxford Instruments. The images were recorded with 512 rows and 512 pixels. AFM images were first processed with NanoScope Analysis 1.80. The data was leveled with a first order plane fit and a first order flattening in histogram mode. The data was then further processed with Gwyddion 2.50[10] where the minimum of the data values was shifted to zero.

Transmission electron microscopy: Transmission electron microscopy was made at a Zeiss CEM902 electron microscope (Zeiss, Oberkochen, Germany). The complex was dissolved/dispersed in toluene/iso-octane applying vortex. The solution was dropped on a copper grid (mesh 200, Science Services, Munich). Electron acceleration voltage was set to 80 kV. Micrographs were taken with a MegaView III / iTEM image acquiring and processing system from Olympus Soft Imaging Systems (OSIS, Münster, Germany) and an Orius 830 SC200W / DigitalMicrograph system from Gatan (Munich, Germany).

General: The syntheses of the iron complexes were carried out under an argon atmosphere (argon 5.0) using Schlenk tube techniques. Apart from this, the μ-O-complexes were dissolved in toluene under air. The solvents were purified as described in the literature[11] and distilled under an atmosphere of argon or saturated with argon over one hour. When argon is used for the synthesis of the intermediate products, it is described in the text. The alkylbromide, bpea and bpee are commercial products (Sigma-Aldrich) and were used as received. The syntheses of 1,2-di(4-pyridyl)ethyne,[12] methoxymethylenemethylaceto-acetate,[13] iron(II) acetate,[43] and **[FeL(16)(MeOH)$_2$]** [14] are described in literature.

1,2-Dioctadecyloxybenzene (A(18)): 1,2-dihydroxybenzene (5.03 g, 45.68 mmol) was mixed with K_2CO_3 (15.90 g, 115.05 mmol, 2.5 eq.) in DMF (500 mL) and stirred for 1 h at room temperature. 1-bromooctadecane (33.50 g, 100.48 mmol, 2.2 eq.) was added and it was heated to 100 °C for 35 h. The mixture was filtrated, washed with H_2O (3x200 mL). It was recrystallized from an EtOH/H_2O (120 mL/60 mL) solution, filtrated, washed with EtOH (60 mL) and dried on air to obtain a white powder. Yield: 18.09 g (65%) $C_{42}H_{78}O_2$ (615.07): calcd. C 82.02, H 12.78; found C 81.74, H 12.71. MS (DEI-(+)): *m/z* (%) 614 (92) $[M]^+$, 362 (20), 110 (100). ^{1}H-NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.88 (t, *J* = 6.5 Hz, 6 H, CH_3), 1.18-1.40 (m, 56 H, CH_2), 1.41-1.52 (m, 4 H, CH_2), 1.74-1.87 (m, 4 H, CH_2), 3.99 (t, *J* = 6.6 Hz, 4 H, CH_2O), 6.88 (s, 4 H, H_{ar}) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$, 296 K): δ = 14.3 (CH_3), 22.8 (CH_2), 26.2 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 69.4 (CH_2O), 114.2 (C_{ar}), 121.1 (C_{ar}), 149.4 (C_{ar}-O) ppm.

1,2-Diicosyloxybenzene (A(20)): 1,2-dihydroxybenzene (2.37 g, 21.52 mmol) was mixed with K_2CO_3 (7.52 g, 54.41 mmol, 2.5 eq.) in DMF (250 mL) and stirred for 45 min at room temperature. 1-bromoeicosane (17.00 g, 47.03 mmol, 2.2 eq.) was added and it was heated to 95 °C for 44 h. The mixture was filtrated, washed with H_2O (2x50 mL) and EtOH (100 mL). It was recrystallized from an EtOH/H_2O (80 mL/40 mL) solution, filtrated, washed with EtOH (30 mL) and dried on air to obtain a white powder. Yield: 11.10 g (77 %). $C_{46}H_{86}O_2$ (671.17): calcd. C 82.32, H 12.92; found C 79.78, H 12.85. MS (DEI-(+)): *m/z* (%) 671 (100) $[M]^+$, 324 (93), 110 (53). ^{1}H-NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.88 (t, *J* = 6.0 Hz, 6 H, CH_3), 1.18-1.40 (m, 64 H, CH_2), 1.41-1.52 (m, 4 H, CH_2), 1.74-1.87 (m, 4 H, CH_2), 3.99 (t, *J* = 6.5 Hz, 4 H, CH_2O), 6.88 (s, 4 H, H_{ar}) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$, 296 K): δ = 14.3 (CH_3), 22.8 (CH_2), 26.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 69.4 (CH_2O), 114.3 (C_{ar}), 121.1 (C_{ar}), 149.4 (C_{ar}-O) ppm.

1,2-Didocosyloxybenzene (A(22)): 1,2-dihydroxybenzene (10 g, 0.09 mol) was mixed with K_2CO_3 (31.21 g, 0.226 mol, 2.5 eq.) in DMF (650 mL) and stirred for 1 h at room temperature. 1-bromodocosane (70.75 g, 0.182 mol, 2 eq.) was added and it was heated to 80 °C for 17 h. The mixture was poured into 6 L H_2O and stirred for 4 days at room temperature. After filtrating and washing the white precipitate with H_2O (100 mL) and EtOH (200 mL), it was recrystallized 4 times in EtOH (500 mL) to obtain white fine crystalline powder. Yield: 38.6 g (58.9 %). $C_{50}H_{94}O_2$ (727.28): calcd. C 82.57, H 13.03; found C 82.68, H 13.58. MS (DEI+): *m/z* (%) = 727 (100) $[M]^+$, 419 (14), 110 (47). ^1H NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.86 (t, *J* = 6.3 Hz, 6H, CH_3), 1.21–1.30 (m, 72 H, CH_2), 1.41–1.47 (m, 4H, CH_2), 1.74–1.83 (m, 4H, CH_2), 3.97 (t, 4H, *J* = 6.0 Hz CH_2O) 6.81–6.85 (m, 4 H, H_{ar}) ppm.

1,2-Dinitro-4,5-dioctadecyloxybenzene (B(18)): **A(18)** (17.65 g, 28.70 mmol) was suspended in acetic acid (215 mL) and stirred for 1 h. Nitric acid (68 %, 50 mL) was added dropwise. Then fuming nitric acid (>90 %, 180 mL) was added dropwise over 1 h and it was heated shortly to 60 °C to obtain a yellow suspension. The mixture was stirred for 25 h at room temperature. It was poured over ice water (4 L) and stirred for some minutes. It was filtrated, washed neutral with H_2O (5 L) and recrystallized from EtOH (280 mL). It was filtrated again, washed with EtOH (60 mL) and dried on air to obtain a yellow powder. Yield: 17.36 g (86 %). $C_{42}H_{76}N_2O_6$ (705.06): calcd. C 71.55, H 10.86, N 3.97; found C 71.52, H 11.40, N 3.92. MS (DEI-(+)): *m/z* (%) 704 (55) $[M]^+$, 57 (100) $[C_4H_9^\bullet]^+$. ^1H-NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.88 (t, *J* = 6.9 Hz, 6 H, CH_3), 1.16-1.41 (m, 64 H, CH_2), 1.42-1.54 (m, 4 H, CH_2), 1.79-1.93 (m, 4 H, CH_2), 4.10 (t, *J* = 6.4 Hz, 4 H, CH_2O), 7.29 (s, 2 H, H_{ar}) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$, 296 K): δ = 14.3 (CH_3), 22.8 (CH_2), 26.0 (CH_2), 28.9 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 70.4 (CH_2O), 108.1 (C_{ar}-H), 136.6 (C_{ar}-NO_2), 151.9 (C_{ar}-O) ppm.

1,2-Dinitro-4,5-diicosyloxybenzene (B(20)): **A(20)** (10.70 g, 15.94 mmol) was suspended in acetic acid (130 mL) and stirred for 1 h. Nitric acid (68 %, 30 mL) was added dropwise and it was heated shortly to 60 °C to obtain a yellow suspension. Then fuming nitric acid (>90 %, 110 mL) was added dropwise over 45 min and the mixture was stirred for 20 h at room temperature. It was poured over ice water (3 L) and stirred for some minutes. It was filtrated, washed neutral with H_2O (3 L) and recrystallized from EtOH (170 mL). It was filtrated again, washed with EtOH (40 mL) and dried on air to obtain a yellow powder. Yield: 9.95 g (82 %). $C_{46}H_{84}N_2O_6$ (761.17): calcd. C 72.58, H 11.12, N 3.68; found C 73.62, H 11.68, N 2.81. MS (DEI-(+)): *m/z* (%) 761 (19) $[M]^+$, 325 (95), 57 (100). ^1H-NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.88 (t, *J* = 6.4 Hz, 6 H, CH_3), 1.15-

1.41 (m, 64 H, CH_2), 1.42-1.54 (m, 4 H, CH_2), 1.79-1.91 (m, 4 H, CH_2), 4.09 (t, J = 6.2 Hz, 4 H, CH_2O), 7.29 (s, 2 H, H_{ar}) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$, 296 K): δ = 14.3 (CH_3), 22.8 (CH_2), 26.0 (CH_2), 28.8 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 32.1 (CH_2), 70.3 (CH_2O), 108.0 (C_{ar}-H), 136.6 (C_{ar}-NO_2), 151.9 (C_{ar}-O) ppm.

1,2-Dinitro-4,5-didocosyloxybenzene (B(22)): **A(22)** (25.02 g, 0.03 mol) was suspended in acetic acid (300 mL) for 1 h. nitric acid (68%, 70 mL) was added dropwise and heated shortly to 60 °C to obtain a yellow suspension. Over 1.5 h, fuming nitric acid (>90 %, 250 mL) was added dropwise and the mixture was stirred for 2 d at room temperature. It was poured into ice water (2.5 L) and stirred for 15 min. It was filtered off, washed neutral and dried on air. Recrystallization from EtOH (700 mL) gave a yellow powder. Yield: 24.1 g (85.0 %). $C_{50}H_{92}N_2O_6$ (817.28): calcd. C 73.48, H 11.35, N 3.43; found C 72.85, H 11.80, N 3.95. MS (DEI+): *m/z* (%) = 817 (100) $[M]^+$, 476 (10). ^{1}H NMR (300 MHz, $CDCl_3$, 296 K,): δ = 0.81 (t, J = 7.0 Hz, 6 H, CH_3), 1.05–1.51 (m, 80 H, CH_2), 1.80 (quint, J = 7.0 Hz, 4 H, CH_2), 4.02 (t, J = 7.0 Hz, 4 H, CH_2O), 7.3 (s, 2 H, H_{ar}).

1,2-Diamino-4,5-dioctadecyloxybenzene (C(18)): **B(18)** (17.10 g, 24.25 mmol) and Pd/C (1.21 g, 10 %) were suspended in degassed EtOH (600 mL) under argon. Hydrazine monohydrate (65 mL, 1.24 mol, 50 eq.) was added dropwise and it was heated to reflux for 22 h. The Pd/C was removed by hot filtration over Celite® 545. After 1 d at -30 °C, the yellow-white precipitate was filtrated, washed with EtOH (3x15 mL) and dried under vacuum to obtain a white powder. Yield: 13.03 g (83 %). $C_{42}H_{80}N_2O_2$ (645.10): calcd. C 78.20, H 12.50, N 4.34; found C 78.18, H 13.44, N 4.37. MS (DEI-(+)): *m/z* (%) 644 (100) $[M]^+$, 629 (9) $[M - NH_2]^+$, 392 (16) $[M - C_{18}H_{37}^{\bullet}]^+$.

1,2-Diamino-4,5-diicosyloxybenzene (C(20)): **B(20)** (9.50 g, 12.48 mmol) and Pd/C (0.60 g, 10 %) were suspended in degassed EtOH (300 mL) under argon. Hydrazine monohydrate (30 mL, 625 mmol, 50 eq.) was added dropwise and it was heated to reflux for 23 h. The Pd/C was removed by hot filtration over Celite® 545. After 1 d at -30 °C, the yellow-white precipitate was filtrated, washed with EtOH (2x10 mL) and dried under vacuum to obtain a pale yellow powder. Yield: 6.40 g (73 %). $C_{46}H_{88}N_2O_2$ (701.20): calcd. C 78.79, H 12.65, N 4.00; found C 78.00, H 12.77, N 3.49. MS (DEI-(+)): *m/z* (%) 700 (100) $[M]^+$, 685 (25) $[M - NH_2]^+$, 420 (8) $[M - C_{20}H_{41}^{\bullet}]^+$.

1,2-Diamino-4,5-didocosyloxybenzene (C(22)): **B(22)** (12.25 g, 14.99 mmol) and Pd/C (0.75 g, 10 %) were suspended in degassed EtOH (350 mL) under argon. Hydrazine monohydrate (35 mL, 722 mmol, 48 eq.) was added dropwise and it was heated to reflux for 18 h. The Pd/C was removed by hot filtration over Celite® 545. After 2 d at -30 °C, the white precipitate was filtrated, washed with EtOH (2x10 mL) and dried under vacuum to obtain a white powder. Yield: 7.59 g (67 %). $C_{50}H_{96}N_2O_2$ (757.31): calcd. C 79.30, H 12.78, N 3.70; found C 78.94, H 12.52, N 3.77.

$H_2L(18)$: **C(18)** (4.00 g, 6.20 mmol) and methoxymethylenemethylacetoacetate (3.00 g, 18.97 mmol) were suspended in MeOH (500 mL) under argon and it was heated to reflux for 16 h. After 1 d at 4 °C, the product was filtrated, washed with MeOH (2x50 mL) and dried on air to obtain a yellow powder. Yield: 5.35 g (96 %). $C_{54}H_{92}N_2O_8$ (897.32): calcd. C 72.28, H 10.33, N 3.12; found C 72.08, H 10.60, N 3.17. MS (DEI-(+)): *m/z* (%) 896 (5) $[M]^+$, 755 (100) $[M - C_6H_8NO_3^\bullet]^+$. IR: $\tilde{\upsilon}$ = 1706 (s) (C=O), 1629 (s) (N-H), 1603 (s) (C=O) cm^{-1}. ^1H-NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.88 (t, *J* = 6.5 Hz, 6 H, CH_3), 1.14-1.41 (m, 64 H, CH_2), 1.42-1.55 (m, 4 H, CH_2), 1.75-1.90 (m, 4 H, CH_2), 2.55 (s, 6 H, CH_3), 3.78 (s, 6 H, CH_3), 4.01 (t, *J* = 6.3 Hz, 4 H, CH_2O), 6.74 (s, 2 H, H_{ar}), 8.26 (d, *J* = 12.3 Hz, 2 H, CH), 12.89 (d, *J* = 12.4, 2 H, NH) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$, 296 K): δ = 14.3 (CH_3), 22.8 (CH_2), 26.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 31.2 (CH_3) 32.1 (CH_2), 51.4 (CH_3), 70.3 (CH_2O), 103.6 (C_q), 106.7 (C_{ar}-H), 125.0 (C_{ar}-N), 148.7 (C_{ar}-O), 154.3 (CH), 167.4 (O-C=O), 200.3 (C=O) ppm.

$H_2L(20)$: **C(20)** (2.51 g, 3.58 mmol) and methoxymethylenemethylacetoacetate (1.70 g, 10.75 mmol) were suspended in MeOH (300 mL) under argon and it was heated to reflux for 19 h. The product was filtrated, washed with MeOH (2x15 mL) and recrystallized from MeOH (120 mL). It was filtrated again and dried on air to obtain a yellow powder. Yield: 2.48 g (73 %). $C_{58}H_{100}N_2O_8$ (953.42): calcd. C 73.07, H 10.57, N 2.94; found C 73.10, H 10.63, N 2.90. MS (DEI-(+)): *m/z* (%) 952 (5) $[M]^+$, 811 (100) $[M - C_6H_8NO_3^\bullet]^+$. IR: $\tilde{\upsilon}$ = 1712 (s) (C=O), 1619 (s) (N-H), 1600 (s) (C=O) cm^{-1}. ^1H-NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.88 (t, *J* = 6.3 Hz, 6 H, CH_3), 1.13-1.41 (m, 64 H, CH_2), 1.42-1.55 (m, 4 H, CH_2), 1.75-1.89 (m, 4 H, CH_2), 2.55 (s, 6 H, CH_3), 3.78 (s, 6 H, CH_3), 4.01 (t, *J* = 6.2 Hz, 4 H, CH_2O), 6.74 (s, 2 H, H_{ar}), 8.26 (d, *J* = 12.4 Hz, 2 H, CH), 12.88 (d, *J* = 12.5, 2 H, NH) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$, 296 K): δ = 14.3 (CH_3), 22.8 (CH_2), 26.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 31.2 (CH_3) 32.1 (CH_2), 51.4 (CH_3), 70.3 (CH_2O), 103.6 (C_q), 106.7 (C_{ar}-H), 125.0 (C_{ar}-N), 148.7 (C_{ar}-O), 154.3 (CH), 167.4 (O-C=O), 200.3 (C=O) ppm.

$H_2L(22)$: **C(22)** (2.40 g, 3.17 mmol) and methoxymethylenemethylacetoacetate (1.59 g, 10.05 mmol) were suspended in MeOH (250 mL) under argon and it was heated to reflux for 18 h. The product was filtrated, washed with MeOH (2x15 mL) and recrystallized from MeOH (120 mL). It was filtrated again, washed with MeOH (2x15 mL) and dried on air to obtain a yellow powder. Yield: 2.88 g (90 %). $C_{62}H_{108}N_2O_8$ (1009.53): calcd. C 73.76, H 10.78, N 2.77; found C 73.48, H 10.42, N 2.87. IR: $\tilde{\upsilon}$ = 1706 (s) (C=O), 1620 (s) (N-H), 1603 (s) (C=O) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$, 296 K): δ = 0.88 (t, J = 6.0 Hz, 6 H, CH_3), 1.11-1.41 (m, 72 H, CH_2), 1.42-1.54 (m, 4 H, CH_2), 1.74-1.91 (m, 4 H, CH_2), 2.55 (s, 6 H, CH_3), 3.78 (s, 6 H, CH_3), 4.01 (t, J = 5.7 Hz, 4 H, CH_2O), 6.74 (s, 2 H, H_{ar}), 8.26 (d, J = 12.2 Hz, 2 H, CH), 12.89 (d, J = 12.4, 2 H, NH) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$, 296 K): δ = 14.3 (CH_3), 22.8 (CH_2), 26.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 31.2 (CH_3) 32.1 (CH_2), 51.4 (CH_3), 70.2 (CH_2O), 103.6 (C_q), 106.6 (C_{ar}-H), 125.0 (C_{ar}-N), 148.7 (C_{ar}-O), 154.3 (CH), 167.4 (O-C=O), 200.3 (C=O) ppm.

[FeL(18)(MeOH)$_2$]: **H_2L(18)** (3.01 g, 3.35 mmol) and iron(II) acetate (1.44 g, 8.28 mmol, 2.5 eq.) were suspended in MeOH (190 mL) and heated to reflux for 6 h. It was filtrated and washed with MeOH (2x15 mL) and dried under vacuum to obtain a brown powder. Yield: 3.24 g (96 %): $C_{56}H_{98}FeN_2O_{10}$ (1015.23): calcd. C 66.25, H 9.73, N 2.76; found C 66.44, H 9.80, N 2.92. MS (DEI-(+)): m/z (%) 950 (100) $[M - 2xMeOH]^+$, 892 (63) $[M - 2xMeOH - C_2H_3O_2^{\bullet}]^+$. IR: $\tilde{\upsilon}$ = 3342 (b) (O-H), 1696 (s) (C=O), 1574 (s) (C=O) cm^{-1}.

[FeL(20)(MeOH)$_2$]: **H_2L(20)** (1.00 g, 1.05 mmol) and iron(II) acetate (0.44 g, 2.52 mmol, 2.4 eq.) were suspended in MeOH (55 mL) and heated to reflux for 3 h. It was filtrated and washed with MeOH (2x5 mL) and dried under vacuum to obtain a brown powder. Yield: 0.95 g (84 %): $C_{60}H_{106}FeN_2O_{10}$ (1071.34): calcd. C 67.27, H 9.97, N 2.61; found C 67.70, H 9.43, N 2.63. MS (DEI-(+)): m/z (%) 1006 (100) $[M - 2xMeOH]^+$, 948 (63) $[M - 2xMeOH - C_2H_3O_2^{\bullet}]^+$. IR: $\tilde{\upsilon}$ = 3365 (b) (O-H), 1698 (s) (C=O), 1576 (s) (C=O) cm^{-1}.

[FeL(20)(MeOH)$_2$]: **3** (61 mg, 0.05 mmol) was dissolved in toluene (21 mL) and heated to reflux for some minutes. A reservoir with MeOH (20 mL) was put on top and after some days very few crystals suitable for single crystal X-ray diffraction were obtained.

[FeL(22)(MeOH)$_2$]: **H_2L(22)** (2.59 g, 2.57 mmol) and iron(II) acetate (1.08 g, 6.17 mmol, 2.4 eq.) were suspended in MeOH (130 mL) and heated to reflux for 6 h. It was filtrated and washed with MeOH (2x7 mL) and dried under vacuum to obtain a brown powder. Yield: 2.43 g (84 %): $C_{64}H_{114}FeN_2O_{10}$ (1127.44): calcd. C 68.18, H 10.19, N 2.48; found C 70.85, H 10.57, N 2.75. MS (DEI-(+)): m/z (%) 1062 (20) $[M - 2xMeOH]^+$, 1004 (28) $[M - 2xMeOH - C_2H_3O_2^{\bullet}]^+$, 43 (100) $[C_3H_7^{\bullet}]^+$. IR: $\tilde{\upsilon}$ = 3360 (b) (O-H), 1696 (s) (C=O), 1571 (s) (C=O) cm^{-1}.

[FeL(16)bpey]$_n$ (1): **[FeL(16)(MeOH)$_2$]** (515 mg, 0.54 mmol) and bpey (390 mg, 2.16 mmol, 4.0 eq.) were dissolved in toluene (7 mL) and heated to reflux for 2 h. After 2 days at room temperature it was filtrated and washed with toluene (2x1.5 mL) and dried under vacuum to obtain a black, crystalline powder. Yield: 267 mg (46 %): $C_{62}H_{90}FeN_4O_8$ (1075.25): calcd. C 69.26, H 8.44, N 5.21; found C 68.69, H 7.82, N 5.32. MS (DEI-(+)): *m/z* (%) 894 (18) [M - bpey]$^+$, 836 (8) [M - bpey - $C_2H_3O_2^{\bullet}$]$^+$, 44 (100) [$C_3H_7^{\bullet}$]$^+$. IR: $\tilde{\upsilon}$ = 1685 (s) (C=O), 1595 (s) (C=O) cm^{-1}.

[FeL(18)bpey]$_n$ (2): **[FeL(18)(MeOH)$_2$]** (636 mg, 0.63 mmol) and bpey (471 mg, 6.17 mmol, 4.2 eq.) were dissolved in toluene (8 mL) and heated to reflux for 5 h. After 2 days at room temperature it was filtrated and washed with toluene (2x1.5 mL) and dried under vacuum to obtain a black, crystalline powder. Yield: 575 mg (81 %): $C_{66}H_{98}FeN_4O_8$×0.25 toluene (1154.39): calcd. C 70.49, H 8.73, N 4.85; found C 70.57, H 9.06, N 4.93. MS (DEI-(+)): *m/z* (%) 950 (62) [M - bpey]$^+$, 892 (17) [M - bpey - $C_2H_3O_2^{\bullet}$]$^+$, 57 (100) [$C_4H_9^{\bullet}$]$^+$. IR: $\tilde{\upsilon}$ = 1685 (s) (C=O), 1600 (s) (C=O) cm^{-1}.

[FeL(20)bpey]$_n$ (3): **[FeL(20)(MeOH)$_2$]** (342 mg, 0.32 mmol) and bpey (345 mg, 1.92 mmol, 6.0 eq.) were dissolved in toluene (5 mL) and heated to reflux for 2 h. After 2 days at room temperature it was filtrated and washed with toluene (2x1.0 mL) and dried under vacuum to obtain a black, crystalline powder. Yield: 267 mg (70 %): $C_{70}H_{106}FeN_4O_8$×0.50 toluene (1233.53): calcd. C 71.57, H 8.99, N 4.54; found C 71.79, H 9.09, N 4.59. MS (DEI-(+)): *m/z* (%) 1006 (18) [M - bpey]$^+$, 948 (16) [M - bpey - $C_2H_3O_2^{\bullet}$]$^+$, 43 (100) [$C_3H_7^{\bullet}$]$^+$. IR: $\tilde{\upsilon}$ = 1688 (s) (C=O), 1600 (s) (C=O) cm^{-1}.

[FeL(22)bpey]$_n$ (4): **[FeL(22)(MeOH)$_2$]** (469 mg, 0.42 mmol) and bpey (456 mg, 2.50 mmol, 6.0 eq.) were dissolved in toluene (6 mL) and heated to reflux for 2 h. After 2 days at room temperature it was filtrated and washed with toluene (3x1.0 mL) and dried under vacuum to obtain a black, crystalline powder. Yield: 338 mg (67 %): $C_{74}H_{116}FeN_4O_8$×1.00 toluene (1335.70): calcd. C 72.84, H 9.21, N 4.19; found C 72.80, H 9.28, N 4.22. MS (DEI-(+)): *m/z* (%) 1062 (6) [M - bpey]$^+$, 1004 (19) [M - bpey - $C_2H_3O_2^{\bullet}$]$^+$, 43 (100) [$C_3H_7^{\bullet}$]$^+$. IR: $\tilde{\upsilon}$ = 1682 (s) (C=O), 1598 (s) (C=O) cm^{-1}.

[FeL(22)bpey]$_n$·toluene (4·tol): **[FeL(22)(MeOH)$_2$]** (35 mg, 0.03 mmol) and bpey (34 mg, 0.19 mmol, 6.0 eq.) were dissolved in toluene (15 mL) and heated to reflux for 2 min. A reservoir with acetonitrile (17 mL) was put on top and after some days very few crystals suitable for single crystal X-ray diffraction were obtained.

[FeL(22)bpee]$_n$ (5): **[FeL(22)(MeOH)$_2$]** (457 mg, 0.41 mmol) and bpee (148 mg, 0.81 mmol, 2.0 eq.) were dissolved in toluene (5 mL) and heated to reflux for 2 h. After 6 days at room temperature it was filtrated and washed with toluene (2x1.0 mL) and dried under vacuum to obtain a black, crystalline powder. Yield: 338 mg (67 %): $C_{74}H_{116}FeN_4O_8$×1.00 toluene (1337.72): calcd. C 72.73, H 9.34, N 4.19; found C 72.87, H 10.04, N 4.00. MS (DEI-(+)): *m/z* (%) 1062 (4) [M - bpee]$^+$, 1004 (11) [M - bpee - $C_2H_3O_2^{\bullet}$]$^+$, 43 (100) [$C_3H_7^{\bullet}$]$^+$. IR: $\tilde{\upsilon}$ = 1685 (s) (C=O), 1603 (s) (C=O) cm^{-1}.

[FeL(22)bpea]$_n$ (6): **[FeL(22)(MeOH)$_2$]** (522 mg, 0.49 mmol) and bpea (182 mg, 0.99 mmol, 2.0 eq.) were dissolved in toluene (5 mL) and heated to reflux for 2 h. After 3 days at room temperature it was filtrated and washed with toluene (2x1.0 mL) and dried under vacuum to obtain a reddish-brown, crystalline powder. Yield: 422 mg (69 %): $C_{74}H_{118}FeN_4O_8$×1.00 toluene (1339.73): calcd. C 72.62, H 9.48, N 4.18; found C 72.84, H 10.08, N 4.13. MS (DEI-(+)): *m/z* (%) 1062 (30) [M - bpea]$^+$, 1004 (37) [M - bpea - $C_2H_3O_2^{\bullet}$]$^+$, 57 (100) [$C_4H_9^{\bullet}$]$^+$. IR: $\tilde{\upsilon}$ = 1687 (s) (C=O), 1604 (s) (C=O) cm^{-1}.

[FeL(22)bpea]$_n$ (6·tol): **[FeL(22)(MeOH)$_2$]** (0.18 g, 0.16 mmol) and bpea (0.35 g, 1.92 mmol, 12.0 eq.) were dissolved in toluene (8.5 mL) and heated to reflux for 1.5 h. After cooling to room temperature, black needle-like crystals were filtrated and dried under vacuum. The crystals obtained were suitable for single crystal X-ray diffraction. Yield: 120 mg (60 %): $C_{74}H_{118}FeN_4O_8$×0.3 toluene (1278.31): calcd. C 71.24, H 9.53, N 4.48; found C 71.72, H 9.51, N 4.38.

[μ-O-((FeL(16))$_2$] (7): **[FeL(16)(MeOH)$_2$]** was dissolved in toluene under air and refluxed for 2 h. After some days the solvent evaporated and a dark brown powder was obtained. Yield: 185 mg (100 %): $C_{100}H_{164}Fe_2N_4O_{17}$ (1806.08): calcd. C 66.50, H 9.15, N 3.10; found C 66.46, H 9.34, N 3.07.

[μ-O-((FeL(18))$_2$] (8): **[FeL(18)(MeOH)$_2$]** was dissolved in toluene under air and refluxed for 3 h. After some days the solvent evaporated and a dark brown powder was obtained. Yield: 121 mg (89 %): $C_{108}H_{180}Fe_2N_4O_{17}$ (1918.29): calcd. C 67.62, H 9.46, N 2.92; found C 67.20, H 9.94, N 3.00.

[μ-O-((FeL(20))$_2$] (9): **[FeL(20)(MeOH)$_2$]** was dissolved in toluene under air and refluxed for 2 h. After some days the solvent evaporated and a dark brown powder was obtained. Yield: 216 mg (97 %): $C_{116}H_{196}Fe_2N_4O_{17}$ (2030.50): calcd. C 68.62, H 9.73, N 2.76; found C 68.05, H 9.67, N 2.78.

[μ-O-((FeL(22))$_2$] (10): **[FeL(22)(MeOH)$_2$]** was dissolved in toluene under air and refluxed for 2 h. After some days the solvent evaporated and a dark brown powder was obtained. Yield:

156 mg (81 %): $C_{124}H_{212}Fe_2N_4O_{17}$ (2142.72): calcd. C 69.51, H 9.97, N 2.61; found C 69.07, H 9.82, N 2.69.

Table S1. Crystallographic data of **[FeL(20)(MeOH)$_2$]**, **4·tol** and **6·tol**.

Compound	**[FeL(20)(MeOH)$_2$]**	**4·tol**	**6·tol**
CCDC	1835195	1835196	1044903
empirical formula	$C_{60}H_{106}FeN_2O_{10}$	$C_{74}H_{114}FeN_4O_8 \cdot C_7H_8$	$C_{74}H_{118}FeN_4O_8$
formula weight / g mol^{-1}	1071.36	1335.73	1247.57
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	8.1994(6)	8.9330(6)	8.8292(5)
b / Å	10.9932(8)	13.125(1)	13.3483(8)
c / Å	35.441(2)	35.302(3)	38.144(2)
α / °	87.909(5)	95.974(6)	100.300(3)
β / °	84.165(5)	95.177(6)	90.396(3)
γ / °	68.887(5)	73.555(6)	104.379(3)
V / Å^3	2964.7(4)	3951.0(5)	4278.2(4)
Z	2	2	2
$\rho_{calc.}$ / g cm^{-3}	1.200	1.123	0.969
μ / mm^{-1}	0.311	0.245	0.222
crystal size / mm	0.459×0.189×0.169	0.204×0.119×0.115	0.303×0.139×0.024
T / K	133 K	133 K	200 K
λ / Å	Mo-K_α 0.71073	Mo-K_α 0.71069	Mo-K_α 0.71073
θ-range / °	1.2-28.5	1.2-28.6	2.2-23.4
measured reflections	25667	36530	56143
independent reflections	12111	17564	11638
parameters	660	847	790
R	0.0919	0.1706	0.0757
wR^2	0.2604	0.4733	0.1952
S	0.88	1.28	1.00

Figure S1. Powder X-ray diffraction patterns of **7 – 10** in the range of 2° – 30° 2*θ* at room temperature.

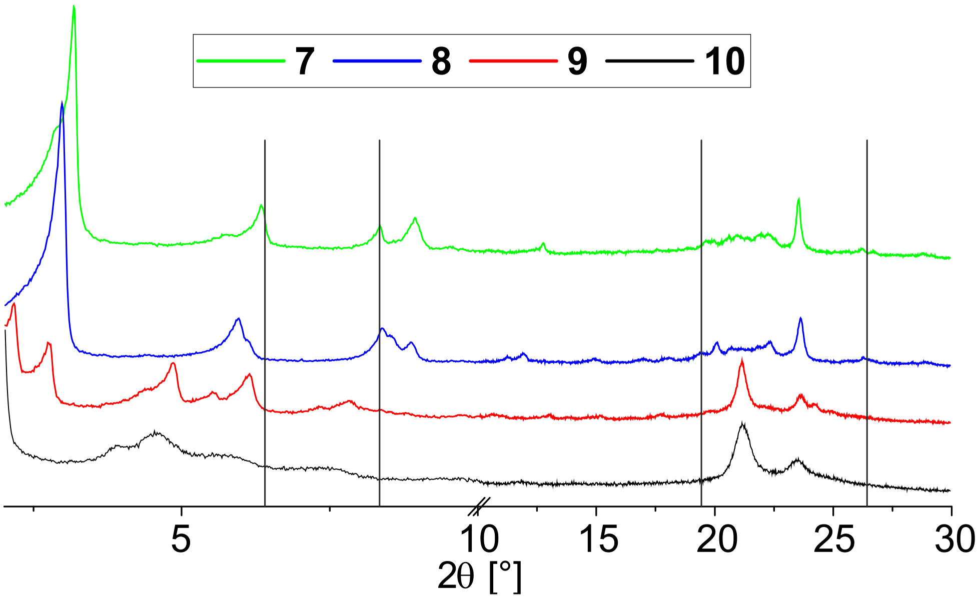


Figure S2. Magnetic measurements of **1 – 4** (top) and **4 – 6** (bottom) with $\chi_M T$ plotted against T.

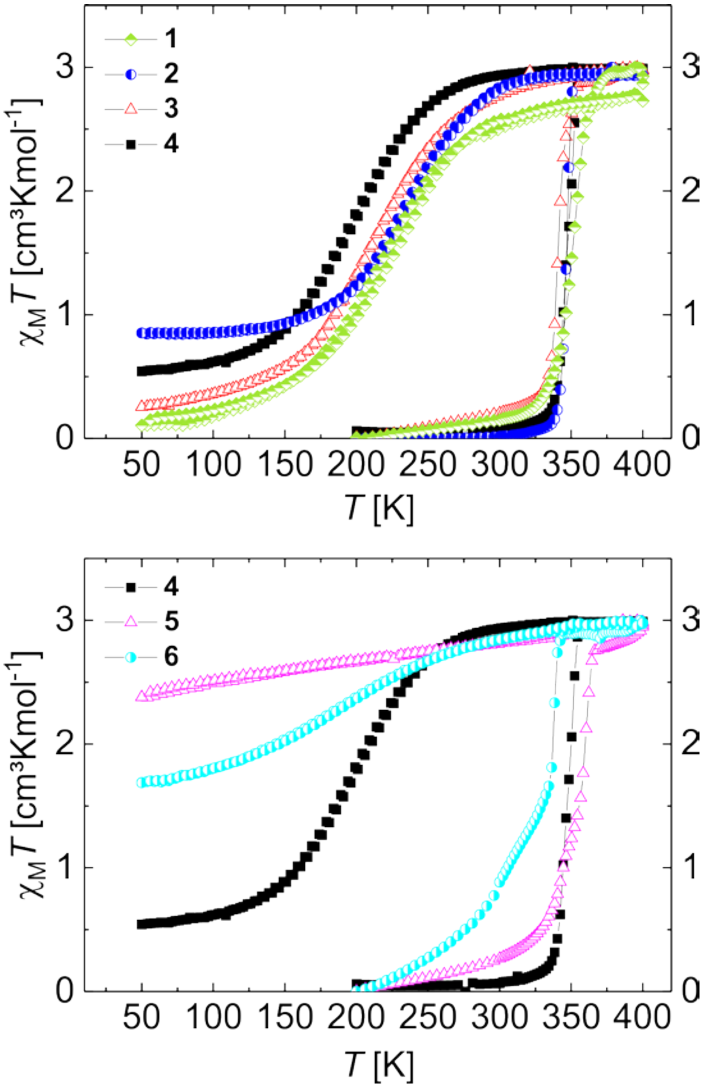


Figure S3. Mössbauer spectra of **7 – 10** measured at room temperature.

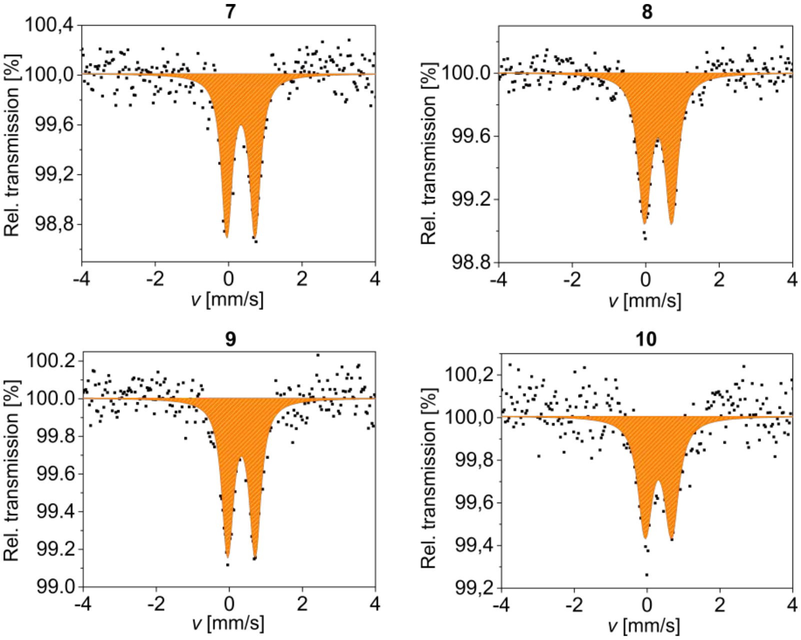


Figure S4. Magnetic measurement of **2** with γ_{HS} plotted against *T*. Measured only up to 354 K (left) and measured with 3 repeating temperature cycles (right).

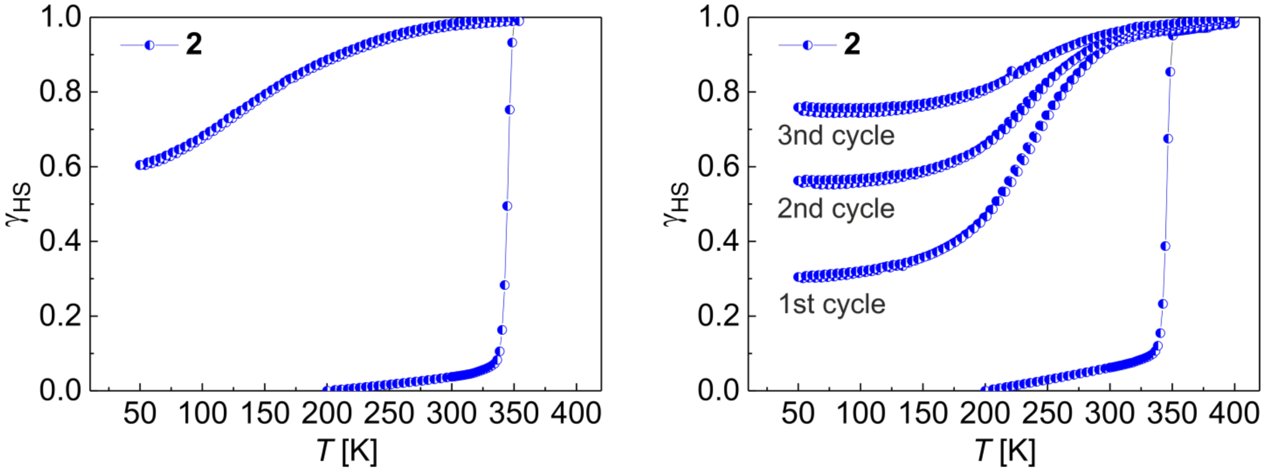


Figure S5. Results from TGA measurements of the complexes **1 – 6**.

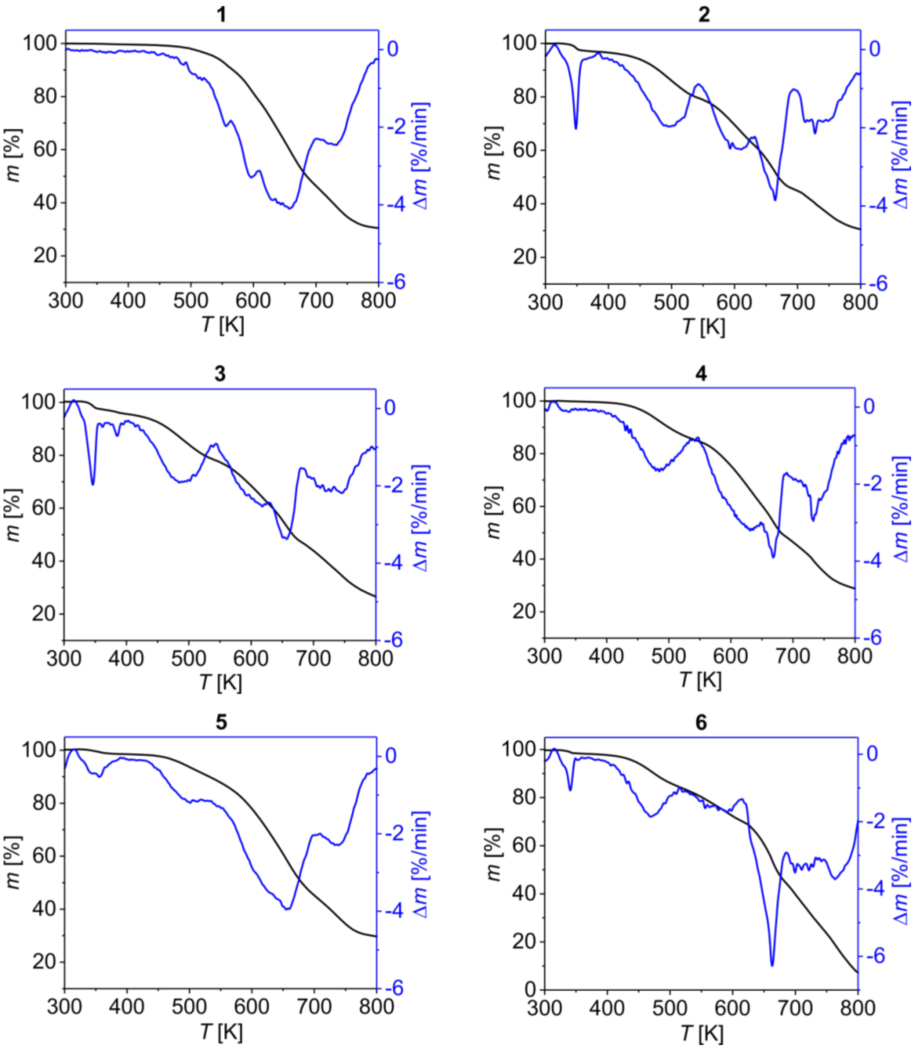


Table S2. Correlation between the weight loss due to solvent loss in TGA and elemental analysis.

Compound	Weight loss (TGA) [wt%]	Additional toluene (Elemental Analysis)	Weight portion toluene (Elemental Analysis) [wt%]	Temperature of weight loss (TGA) [K]	$T_{1/2}$ (Magnetic measurement) [K]
1	-	-	-	-	354
2	2.56	0.25	2.00	349	347
3	2.40	0.50	3.73	346	340
4	-	1.00	6.90	-	344/351
5	1.29	1.00	6.89	349	340/369
6	1.27	1.00	6.88	341	338

Figure S6. DSC measurements of **1 – 6** in the heating and cooling mode (first cycle: black, second cycle: red).

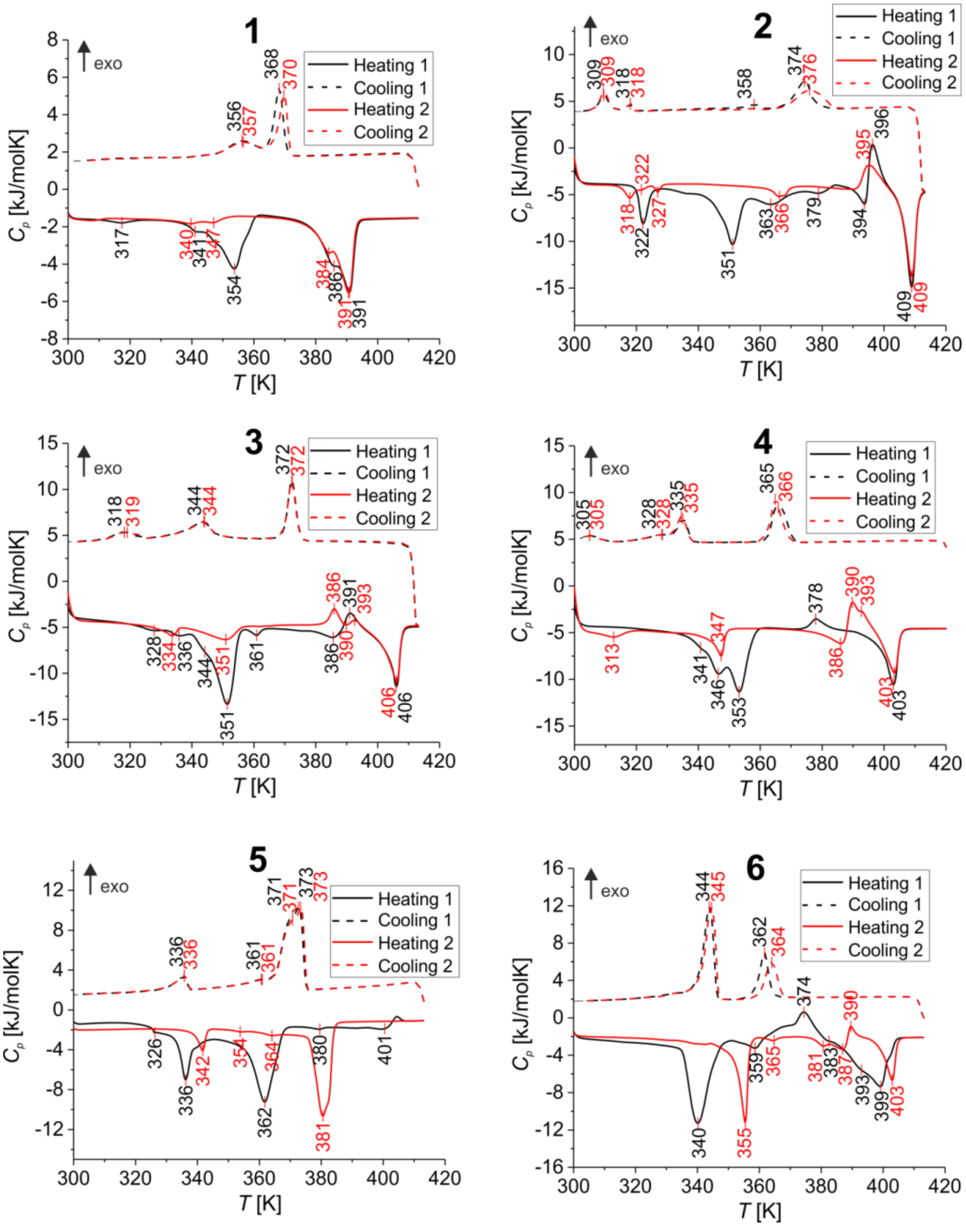


Figure S7. Temperature dependent powder X-ray diffraction patterns of **1** and **3** displayed in the 2.0° – 3.5° 2θ range and **6** displayed in the 1.5° – 3.0° 2θ range. The temperatures were selected based on the DSC measurements and the phase transitions observed therein.

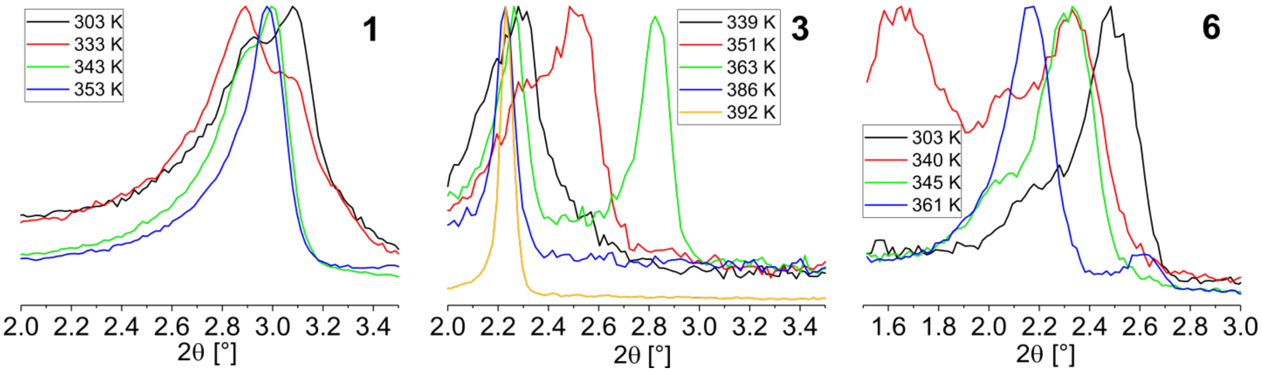


Figure S8. Temperature dependent PXRD patterns of **1** – **6** displayed in the 1.5° – 30° 2θ range.

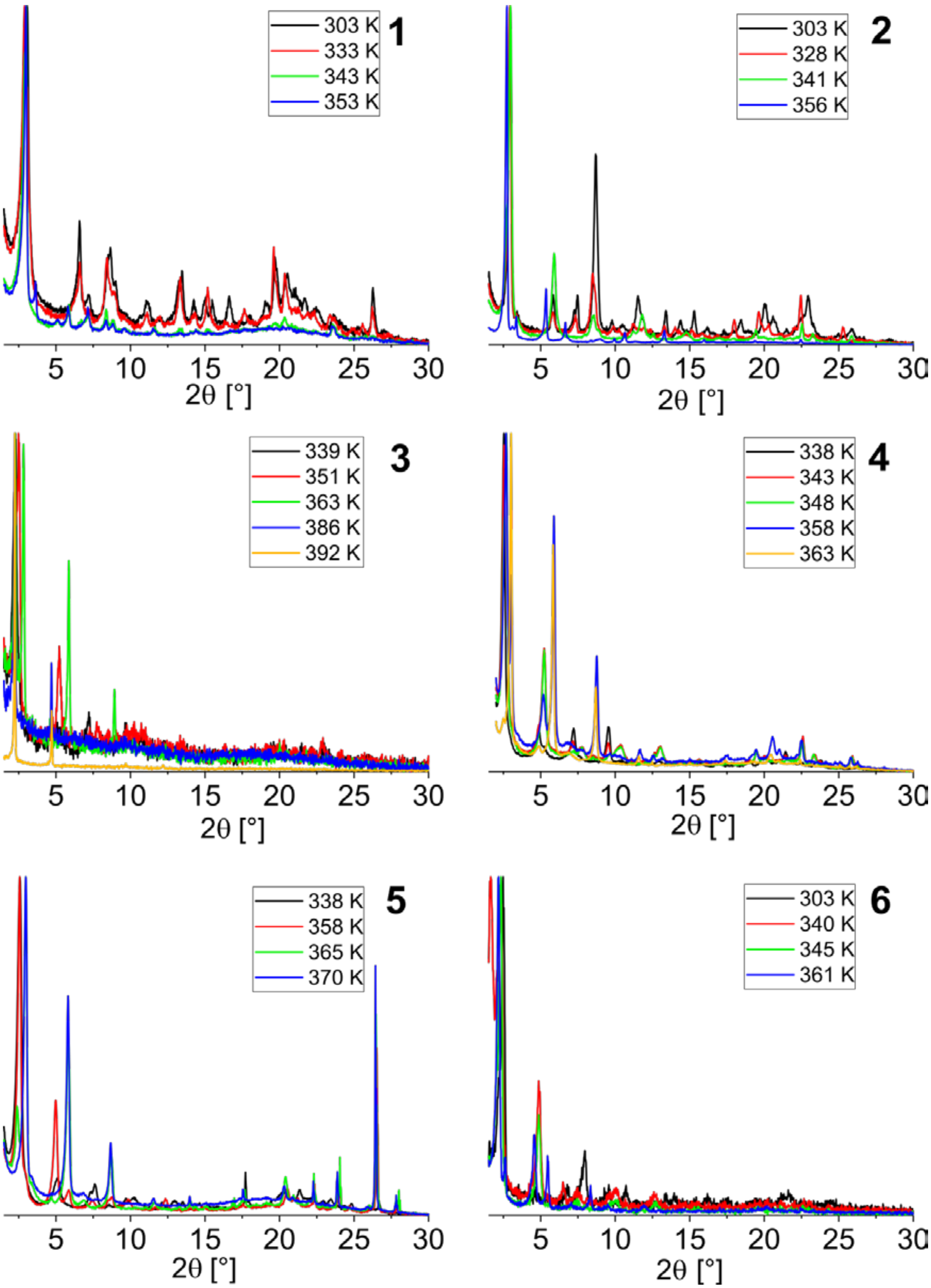


Figure S9. Temperature dependent XRPD patterns of **1** displayed in the 1.5° – 30° 2θ range at 303 K before annealing (1st cycle), after annealing at 413 K (2nd cycle) and after second annealing at 373 K (3rd cycle). Inset: zoomed 2.0° – 3.5° 2θ range.

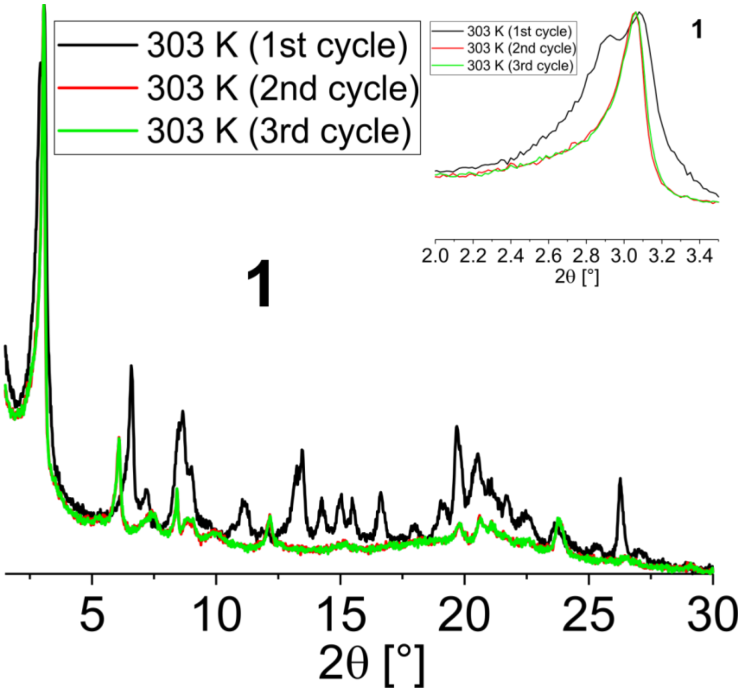


Figure S10. POM micrographs of **1**. All images were taken under crossed polarised light. Left: with retardation plate, right: without retardation plate. A) and B): crystalline powder from synthesis; C) and D): after phase transition; E) and F): melted sample; G) and H): formation of birefringent domains after cooling down.

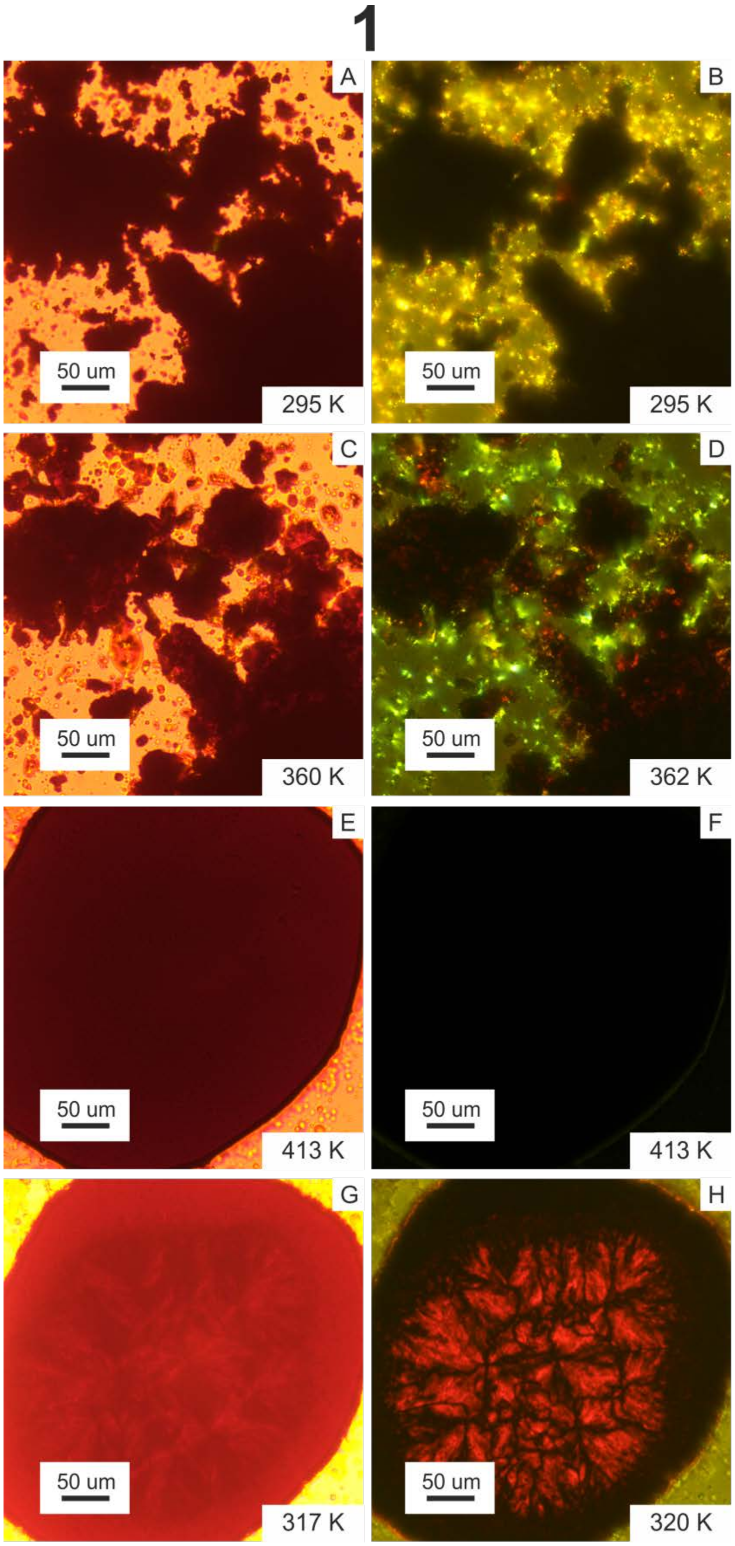


Figure S11. POM micrographs of **2**. All images were taken under crossed polarised light. Left: with retardation plate, right: without retardation plate. A) and B): crystalline powder from synthesis; C) and D): after phase transition; E) and F): melted sample; G) and H): formation of birefringent domains after cooling down.

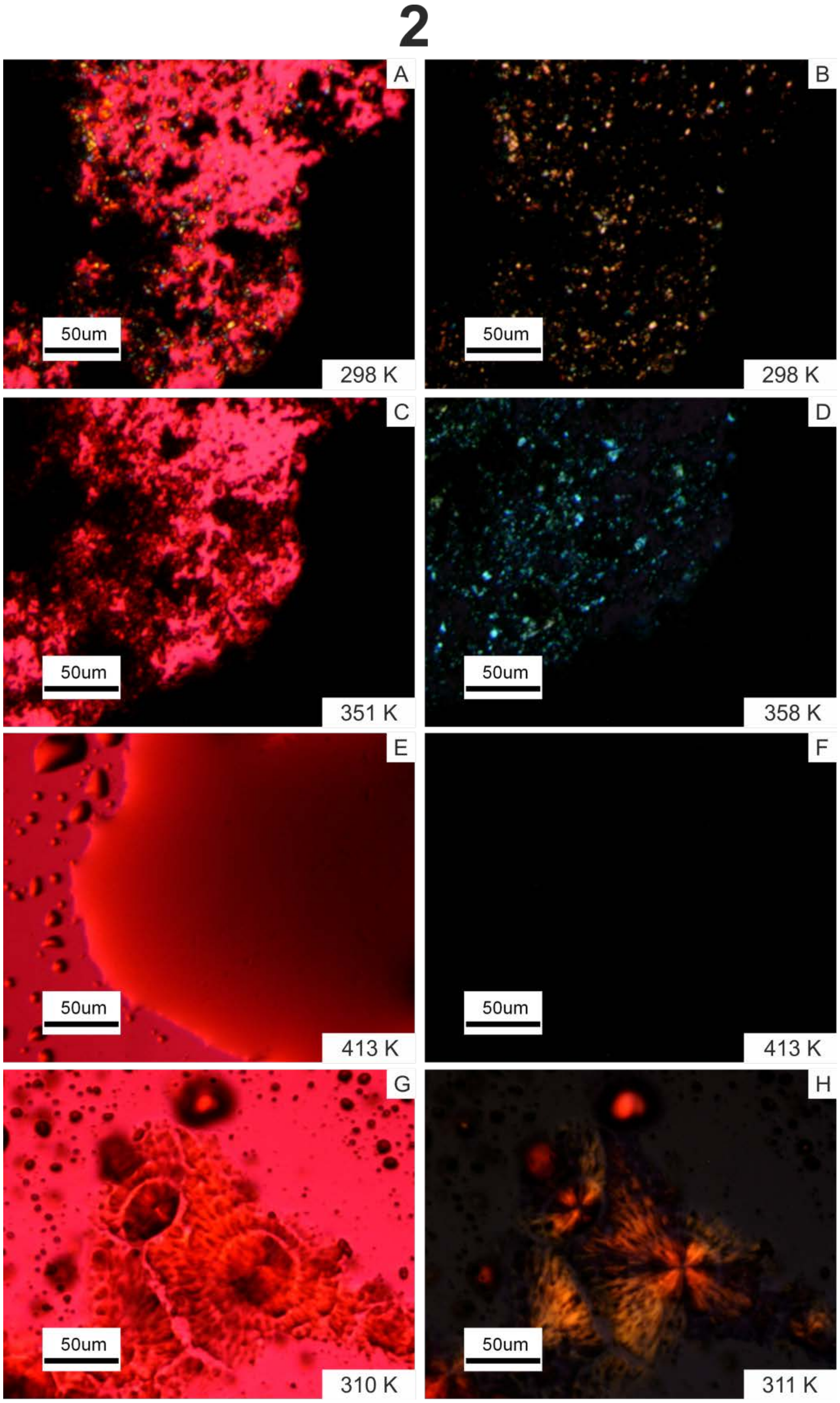


Figure S12. POM micrographs of **3**. All images were taken under crossed polarised light. Left: with retardation plate, right: without retardation plate. A) and B): crystalline powder from synthesis; C) and D): after phase transition; E) and F): melted sample; G) and H): formation of birefringent domains after cooling down.

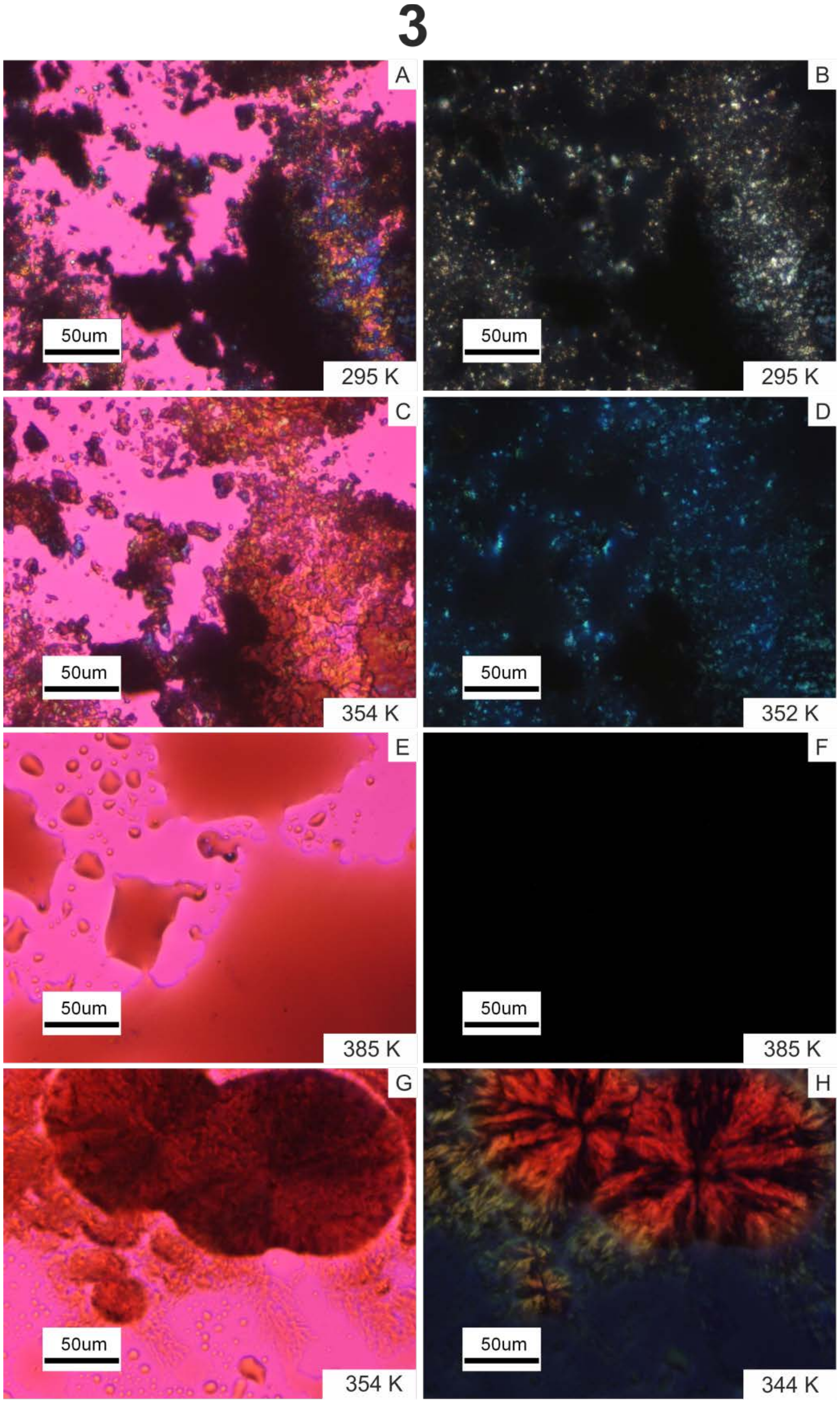


Figure S13. POM micrographs of **5**. All images were taken under crossed polarised light. Left: with retardation plate, right: without retardation plate. A) and B): crystalline powder from synthesis; C) and D): after phase transition; E) and F): melted sample; G) and H): formation of birefringent domains after cooling down.

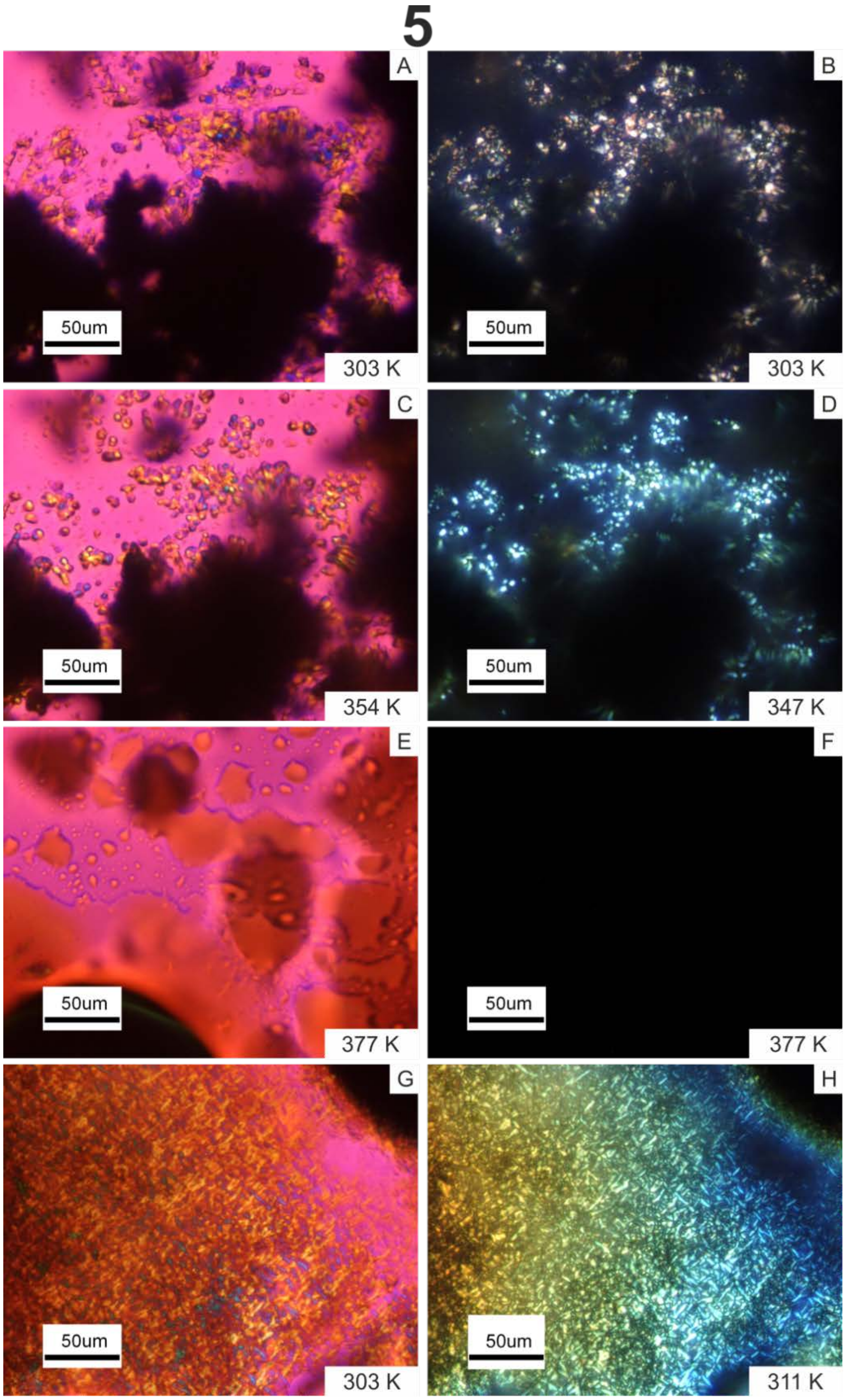


Figure S14. POM micrographs of **6**. All images were taken under crossed polarised light. Left: with retardation plate, right: without retardation plate. A) and B): crystalline powder from synthesis; D): after phase transition; E) and F): melted sample; G) and H): formation of birefringent domains after cooling down.

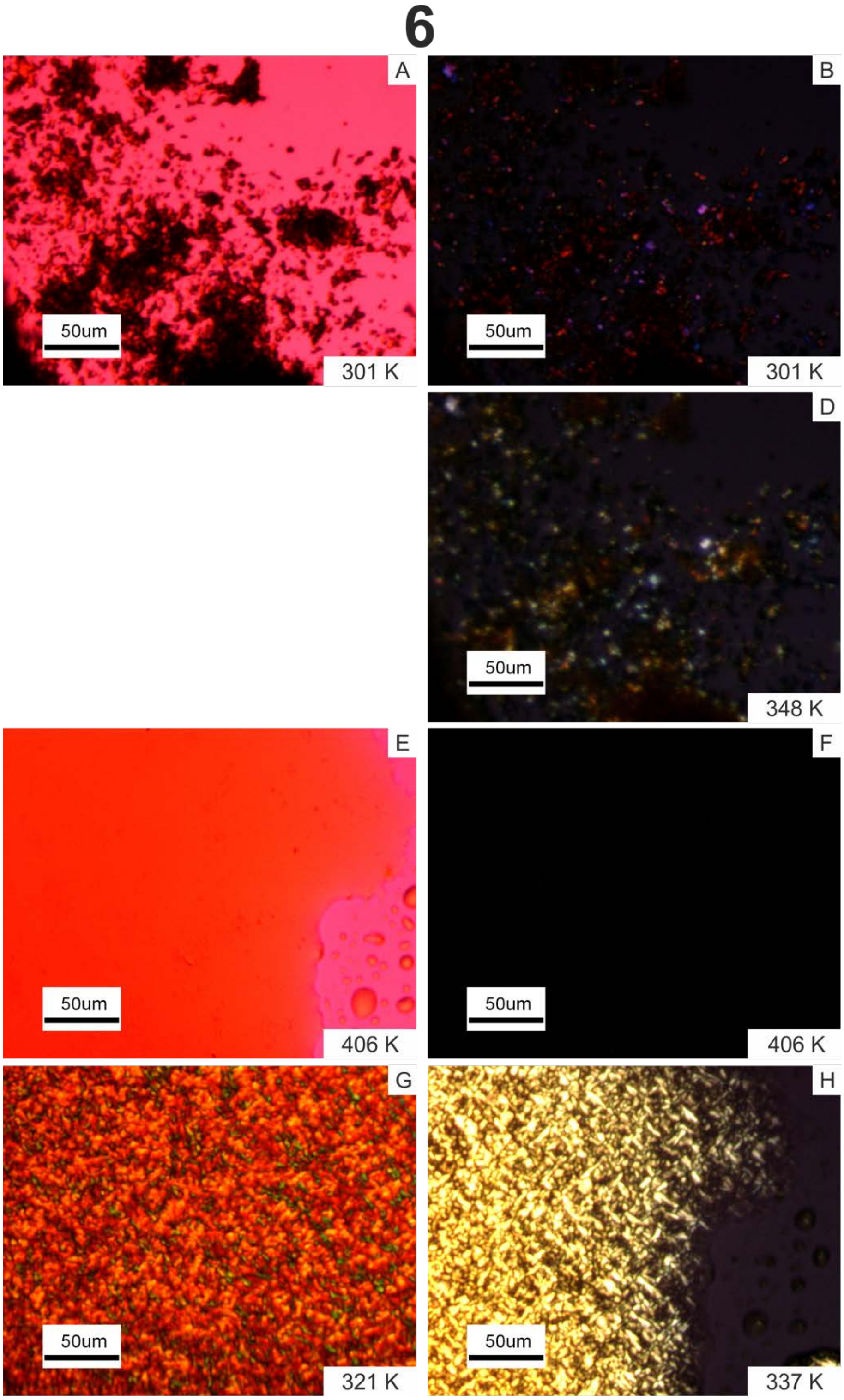
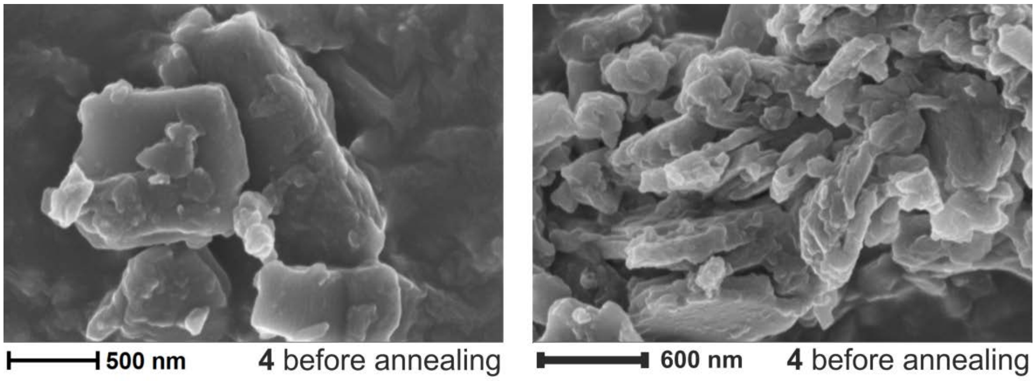
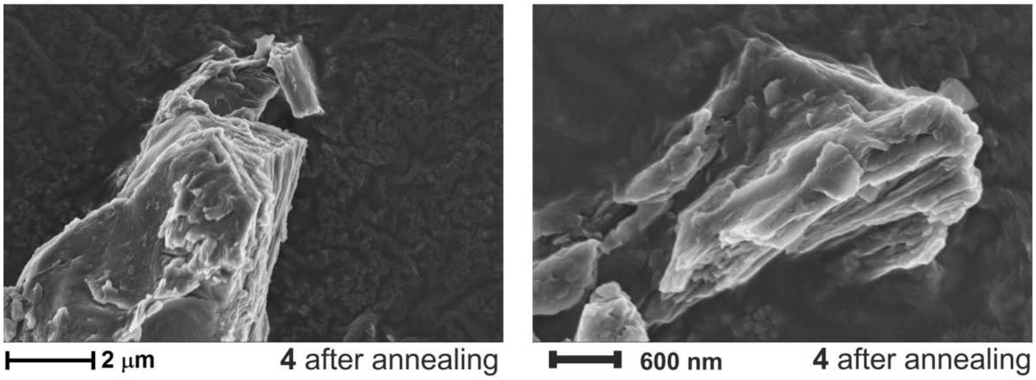


Figure S15. SEM measurements of **4** (top: sample before annealing, bottom: sample after annealing).



4 before annealing **4** before annealing



4 after annealing **4** after annealing

Figure S16. AFM images of **7** with corresponding height profiles and different resolutions. The spin coating parameters were varied from 0.2 mg/mL with 2000 rpm (A1) to 1.0 gm/mL with 2000 rpm (B1 and B2) to 5.0 mg/mL with 2000 rpm (C1 and C2) to 10.0 mg/mL with 2000 rpm (D1 and D2) to 10.0 mg/mL with 5000 rpm (E1 and E2).

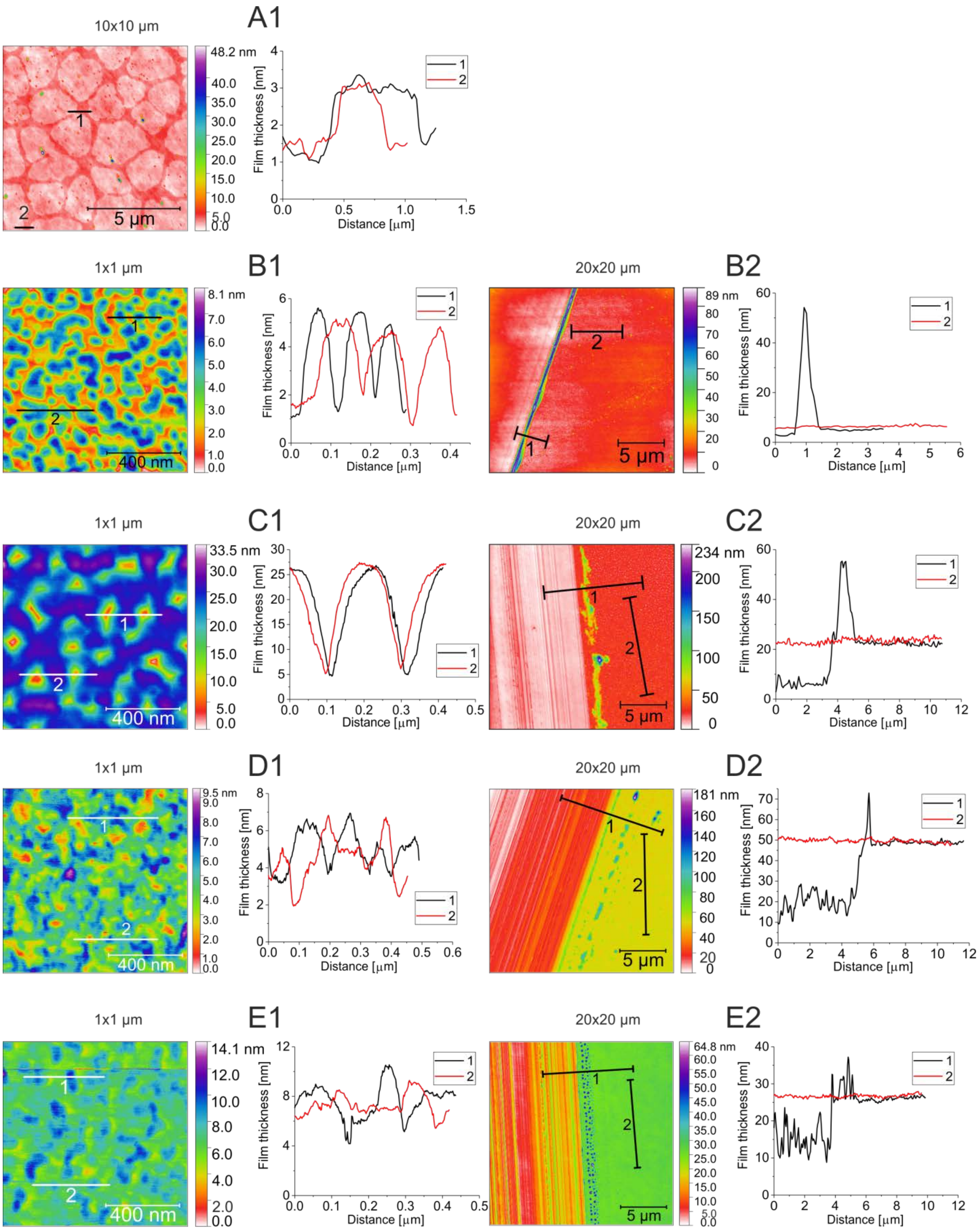
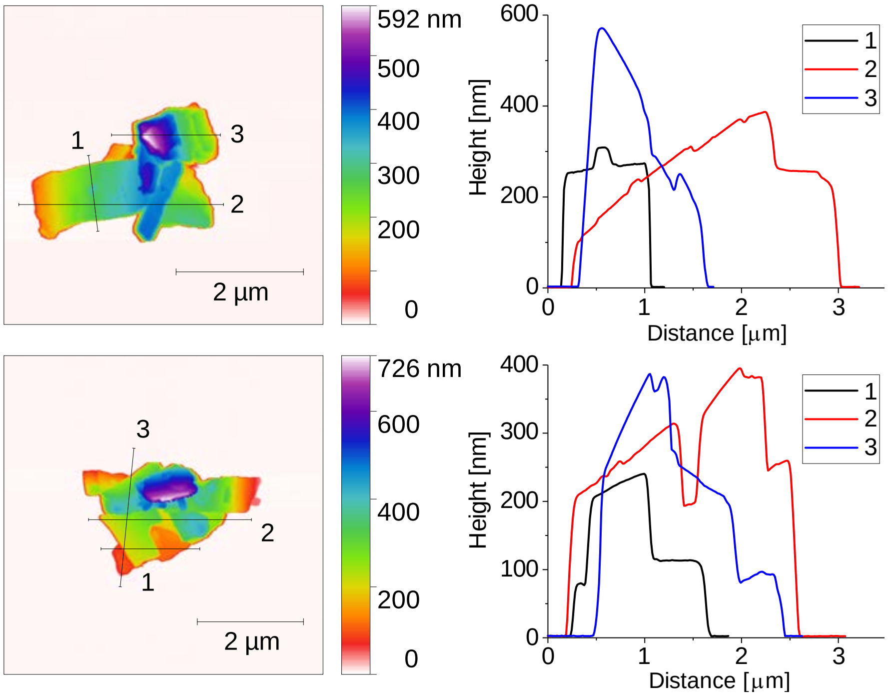


Figure S17. AFM images of **4** with the corresponding height profiles.



References

1 O. Kahn, *Molecular Magnetism*, VCH, New York, N.Y, 1993.

2 K. Lagarec and D. G. Rancourt, *Recoil, mössbauer spectral analysis software for windows 1.0*, Department of Physics, University of Ottawa, Canada, 1998.

3 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, SIR97: a new tool for crystal structure determination and refinement, *J. Appl. Cryst.*, 1999, **32**, 115–119.

4 M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone and G. Polidori, Crystal structure determination and refinement viaSIR2014, *J. Appl. Cryst*, 2015, **48**, 306–309.

5 G. Sheldrick, A short history of SHELX, *Acta Cryst. A*, 2008, **64**, 112–122.

6 A. L. Spek, *PLATON - A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2008.

7 L. Farrugia, ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI), *J. Appl. Cryst.*, 1997, **30**, 565.

8 E. Keller, *Schakal-99*, University of Freiburg, Freiburg, Germany, 1999.

9 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shilds, R. Taylor, M. Towler and J. van de Streek, Mercury, *J. Appl. Cryst.*, 2006, **39**, 453–457.

10 D. Nečas and P. Klapetek, Gwyddion, *Cent. Eur. J. Phys.*, 2012, **10**, 181–188. DOI: 10.2478/s11534-011-0096-2.

11 H. G. O. Becker, *Organikum*. Organisch-chemisches Grundpraktikum, Johann Ambrosius Barth, Berlin, 19th edn., 1993.

12 M. Tanner and A. Ludi, A facile synthesis of 4,4'-dipyridylacetylene, *Chimia*, 1980, **34**, 23–24.

13 W. Bauer, T. Ossiander and B. Weber, A Promising New Schiff Base-like Ligand for the Synthesis of Octahedral Iron(II) Spin Crossover Complexes, *Z. Naturforsch. B*, 2010, **2010**, 323–328.

14 S. Schlamp, B. Weber, A. D. Naik and Y. Garcia, Cooperative spin transition in a lipid layer like system, *Chem. Commun*, 2011, **47**, 7152–7154.