Supporting Information

Ferroelectric metallomesogens composed of achiral spin crossover molecules

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Experimental Procedures

General

All chemicals were purchased from commercial sources and used without further purification. All syntheses were based on previously reported procedures and were performed under an Ar atmosphere.^{1,2}

Synthesis

OH-bzimpy. A suspension of 4-hydroxypyridine-2,6-dicarboxylic acid monohydrate (5.04 g, 27.3 mmol) and o-phenylenediamine (6.49 g, 58.7 mmol) in 85% phosphoric acid (55 ml) was heated at 220 °C for 6 h with vigorous stirring. After cooling to room temperature, the mixture was slowly poured into ice-water (400 ml), and the white precipitate was filtered off and added to hot 10% Na₂CO₃ solution (350 ml). The resulting light blue solid was filtered off and added to hot methanol saturated with Na₂CO₃. The solution was diluted with water (100 ml) and acidified with 15% hydrochloric acid to pH 1. The white precipitate was filtered off and extracted several times with boiling methanol. The collected extracts were evaporated to give the product as a colourless solid. Yield of OH-bzimpy: 6.3 g (71%). ¹H NMR (500 MHz, DMSO-d₆): δ = 7.91 (s, 2H), 7.86-7.84 (m, 4H), 7.49-7.46 (m, 4H).

3C₈-**bzimpy.** NaH (oil dispersion, 60%: 0.74 g, 18.5mmol) was washed with hexane and then suspended in dry DMF (50 ml) under Ar. To this suspension, OH-bzimpy (1.0 g, 3.07 mmol) was added and the mixture stirred at 80 °C for 2 h. 1-Bromoalkane (12.9 mmol) in dry DMF (30 ml) was added dropwise and the solution was then stirred at 100 °C for 48h. After cooling to room temperature, the solution was poured into 10% aqueous NH₄Cl (100 ml), and then extracted with CHCl₃. The extract was washed with water and saturated aqueous NaCl solution, and then dried over MgSO₄. The solvent was removed and the residue was purified by column chromatography employing silica gel with ethyl acetate/hexane (1/11) to give the product as a colourless oil. Yield of 3C₈-bzimpy: 0.41 g (20%). ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (m, 2H, Ar-H), 7.75 (s, 2H, pyridine-H), 7.38 (m, 2H, Ar-H), 7.27 (m, 4H, Ar-H), 4.63 (t, 4H, N-CH₂), 4.16 (t, 2H, O-CH₂), 1.79-0.96 (m, 36H, CH₂), 0.81 (m, 9H, CH₃).



3C₁₀-bzimpy. 3C₁₀-bzimpy was synthesized from OH-bzimpy (1.0 g, 3.07mmol) and 1-bromodecane (2.7 mL, 12.2 mmol) using the same procedure as used for 3C₈-bzimpy. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/11) as eluent to give the product as a colourless oil. Yield for 3C₁₀-bzimpy: 0.46 g (20%). ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (m, 2H, Ar-H), 7.75 (s, 2H, pyridine-H), 7.38 (m, 2H, Ar-H), 7.27 (m, 4H, Ar-H), 4.63 (t, 4H, N-CH₂), 4.16 (t, 2H, O-CH₂), 1.79-0.96 (m, 48H, CH₂), 0.81 (m, 9H, CH₃).



3C₁₂-**bzimpy.** $3C_{12}$ -bzimpy was synthesized from OH-bzimpy (1.0 g, 3.07 mmol) and 1-bromododecane (3.5 mL, 14.0 mmol) using the same procedure as used for $3C_8$ -bzimpy. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/11) as eluent to give the product as a colourless oil. Yield of $3C_{10}$ -bzimpy: 0.23 g (8.9%). ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (m, 2H, Ar-H), 7.75 (s, 2H, pyridine-H), 7.38 (m, 2H, Ar-H), 7.27 (m, 4H, Ar-H), 4.63 (t, 4H, N-CH₂), 4.16 (t, 2H, O-CH₂), 1.79-0.96 (m, 60H, CH₂), 0.81 (m, 9H, CH₃).



3C₁₄-**bzimpy.** 3C₁₄-bzimpy was synthesized from OH-bzimpy (1.0 g, 3.07 mmol) and 1-bromotetradecane (3.5 mL, 14.0 mmol) using the same procedure as used for 3C₈-bzimpy. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/11) as eluent to give the product as a colourless oil. Yield of 3C₁₄-bzimpy: 0.75 g (26.5%). ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (m, 2H, Ar-H), 7.75 (s, 2H, pyridine-H), 7.38 (m, 2H, Ar-H), 7.27 (m, 4H, Ar-H), 4.63 (t, 4H, N-CH₂), 4.16 (t, 2H, O-CH₂), 1.79-0.96 (m, 72H, CH₂), 0.81 (m, 9H, CH₃).



3C₁₆-**bzimpy.** 3C₁₆-bzimpy was synthesized from OH-bzimpy (1.0 g, 3.07 mmol) and 1-bromohexadecane (4.5 mL, 14.7 mmol) using the same procedure as used for 3C₈-bzimpy. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/11) as eluent to give the product as a colourless oil. Yield of 3C₁₆-bzimpy: 0.61 g (20%). ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (m, 2H, Ar-H), 7.75 (s, 2H, pyridine-H), 7.38 (m, 2H, Ar-H), 7.27 (m, 4H, Ar-H), 4.63 (t, 4H, N-CH₂), 4.16 (t, 2H, O-CH₂), 1.79-0.96 (m, 84H, CH₂), 0.81 (m, 9H, CH₃).



3C₁₈-**bzimpy.** 3C₁₈-bzimpy was synthesized from OH-bzimpy (1.0 g, 3.07 mmol) and 1-bromooctadecane (5.0mL, 14.9 mmol) using the same procedure as used for 3C₈-bzimpy. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/11) as eluent to give the product as a colourless oil. Yield of 3C₁₈-bzimpy: 0.36 g (10.9%). ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (m, 2H, Ar-H), 7.75 (s, 2H, pyridine-H), 7.38 (m, 2H, Ar-H), 7.27 (m, 4H, Ar-H), 4.63 (t, 4H, N-CH₂), 4.16 (t, 2H, O-CH₂), 1.79-0.96 (m, 96H, CH₂), 0.81 (m, 9H, CH₃).



[Fe(3C₈-bzimpy)₂](BF₄)₂·nH₂O (1·nH₂O). To a solution of 3C₈-bzimpy (0.203 g, 0.30 mmol) in CHCl₃/MeOH (1:1, 20 mL) was added a MeOH solution (10 mL) of Fe(BF₄) $_2$ ·6H₂O (0.050 g, 0.15 mmol). The reaction mixture was stirred at room temperature for 3 h. The resulting solution was concentrated to give the product as a red-purple solid. Yield for 1·nH₂O: 0.16 g (69%). Since the solvent water molecules gradually removed under air, the number of water molecules could not be determined. After thermal treatment at their melting points for 1 hour to remove the water molecules, the non-solvated compound 1 was obtained. Analysis (calcd., found for C₈₆H₁₂₂B₂F₈FeN₁₀O₂): C (66.32, 66.16), H (7.90, 7.80), N (8.99, 8.95).

 $[Fe(3C_{10}-bzimpy)_2](BF_4)_2 \cdot nH_2O$ (2·nH₂O). This complex was synthesized using $3C_{10}-bzimpy$ by the same procedure as employed for 1. After thermal treatment, the non-solvated compound 2 was obtained. Yield of 2: 0.18 g (70%). Analysis (calcd., found for $C_{98}H_{146}B_2F_8FeN_{10}O_2 + H_2O$): C (68.21, 68.62), H (8.53, 8.44), N (8.12, 8.14).

 $[Fe(3C_{12}-bzimpy)_2](BF_4)_2 \cdot nH_2O$ (3·nH₂O). This complex was synthesized using $3C_{12}$ -bzimpy by the same procedure as employed for 1. After thermal treatment, the non-solvated compound 3 was obtained. Yield of 3: 0.20 g (70%). Analysis (calcd., found for $C_{110}H_{170}B_2F_8FeN_{10}O_2 + H_2O$): C (69.10, 69.20), H (9.07, 8.70), N (7.33, 7.42).

 $[Fe(3C_{14}-bzimpy)_2](BF_4)_2\cdot nH_2O$ (4·nH₂O). This complex was synthesized by the same procedure as employed for 1 using $3C_{14}$ -bzimpy. After thermal treatment, the non-solvated compound 4 was obtained. Yield of 4: 0.22 g (72%). Analysis (calcd., found for $C_{122}H_{194}B_2F_8FeN_{10}O_2 + H_2O$): C (70.43, 70.54), H (9.50, 9.53), N (6.73, 6.69).

 $[Fe(3C_{16}-bzimpy)_2](BF_4)_2 \cdot 2H_2O$ (5·2H₂O). This complex was synthesized by the same procedure as employed for 1 using $3C_{16}$ -bzimpy. After thermal treatment, the non-solvated compound 5 was obtained. Yield of 5: 0.24 g (72%). Analysis (calcd., found for $C_{134}H_{218}B_2F_8FeN_{10}O_2 + H_2O$): C (71.57, 71.28), H (9.86, 9.84), N (6.23, 6.19).

 $[Fe(3C_{18}-bzimpy)_2](BF_4)_2\cdot nH_2O$ (6·nH₂O). This complex was synthesized by the same procedure as employed for 1 using $3C_{18}$ -bzimpy. After thermal treatment, the non-solvated compound 6 was obtained. Yield of 6: 0.26 g (72%). Analysis (calcd., found for $C_{146}H_{242}B_2F_8FeN_{10}O_2 + H_2O$): C (72.15, 72.63), H (9.85, 10.20), N (5.80, 5.76).

 $[Zn(3C_{16}-bzimpy)_2](BF_4)_2 \cdot nH_2O$ (7·H₂O). To a solution of 3C₁₆-bzimpy (0.0203 g, 0.30 mmol) in CHCl₃/MeOH (1:1, 20 mL) was added a MeOH solution (15 mL) of ZnCl₂ (0.020 g, 0.15 mmol) and NaBF₄ (0.033 g, 0.30 mmol). The reaction mixture was stirred at room temperature for 3 h. The resulting solution was concentrated to give the product as a white solid. Yield of $[Zn(3C_{16}-bzimpy)_2](BF_4)_2 \cdot nH_2O$: 0.24 g (71%). After thermal, treatment the non-solvated compound 7 was obtained. Analysis (calcd., found for

C₁₃₄H₂₁₈B₂F₈ZnN₁₀O₂): C (71.84, 72.03), H (9.81, 10.20), N (6.25, 6.19).

Physical Measurements

¹H NMR were recorded on a JEOL (500-ECX) instrument (500 MHz) in deuterated solvents using TMS as the internal reference. Elemental analyses (C, H, N) were carried out on a J-SCIENCE LAB JM10 analyser at the Instrumental Analysis Centre of Kumamoto University. X-ray diffraction data for the single crystal of 5 were collected with a Rigaku Saturn70 diffractometer. Crystal evaluation and data collection were performed using Mo-Ka $\lambda = 0.71075$ Å radiation. The structure was solved by direct methods (Sir 2004) and refined by full-matrix least-squares refinement using the SHELXL97 computer program. For [Zn(3C₁₆bzimpy)₂](BF₄)₂, single crystal X-ray data were recorded on a Rigaku R-AXIS RAPID 191R. Crystal evaluation and data collection were carried out using Cu-Ka $\lambda = 1.54187$ Å radiation. The structure was solved with SHELXL structure solution program using direct methods (Sir 2004) and refined with the SHELXT refinement package using least-squares minimization. The hydrogen atoms were refined geometrically by using a riding model. Differential scanning calorimetry (DSC) thermal analysis was performed on a SHIMADZU DSC50 instrument. Textures of liquid crystalline states were obtained using polarized optical microscopy (POM) on a Nippon Chemical Industrial corporation polarization microscope OPTICAL POL with a Yanagimoto factory MODEL MP-J3 micro melting point meter. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Smart Lab X-ray diffractometer (RAD-2A with a 1.5 kW Cu K_αX-ray). Circular dichroism (CD) spectra were collected with a JASCO J-820 instrument. Temperature-dependent dielectric constants in the frequency range of 100-1000 Hz were measured by an inductance capacitance and resistance (LCR) meter on a Wayne Kerr 6440B LCR meter. The determination of polarization was performed on an aixACT TF analyser 1000. SHG spectra were recorded employing a time-correlated single photon counting system (SPC130 EM, Becker&Hickle). Samples were excited by femtosecond near-IR pulses from the output of OPA (TOPAS-C, Spectra-Physics) seeded by Ti:Sapphire regenerative amplifier (Spitfire-pro, Spectra-Physics). The signals were detected by a single photo avalanche diode (PD-050-CTD) through a spectrometer (SP275, Acton Research). Temperature dependence of magnetic susceptibilities were measured on a Superconducting Quantum Interference Device (SOUID) magnetometer at field strengths of 0.5 T with a sweep mode of 5 K min⁻¹ in the temperature range of 100 to 400 K.

Compound	5·2H ₂ O
CCDC number	1416013
Chemical formula	$C_{134}H_{218}B_2F_8FeN_{10}O_3$
Formula weight / g mol ⁻¹	2246.72
T / K	93
Crystal system	Triclinic
Space group	P-1(#2)
a / Å	13.8289(14)
b / Å	17.3327(17)
c / Å	29.608(4)
lpha / °	83.044(12)
eta / \degree	80.705(9)
γ/°	69.477(10)
\dot{V} / Å ³	6543.1(14)
Z	2
F(000)	2448.00
<i>R</i> 1	0.1571
wR2	0.3436
R1 [all data]	0.2548
wR2 [all data]	0.4289
G.O.F.	1.140

Table S1. Crystal parameters for $5.2H_2O$



Fig. S1 (a) Single crystal X-ray structure of $5 \cdot 2H_2O$. (b) FeN₆ octahedron present in a molecule of $5 \cdot 2H_2O$. Colour code: Orange, Fe; red, O; blue, N; grey, C. (c) Packing structure of $5 \cdot 2H_2O$. Two alkyl chains on one side are coloured green, and four alkyl chains on the opposite side are coloured pink. H atoms, counter anions, solvent molecules are omitted for clarity.



Fig. S2 DSC curves for (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** and (f) **6** (black line: 1st cycle, red line: 2nd heating).

а









378 K

432 K

С

b



Fig. S3 POM textures of (a) 3, (b) 4 and (c) 6 (left: SmC* state, right: SmA state).



Fig. S4 Temperature-dependent PXRD patterns for (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) **6**. The inset graph shows PXRD patterns for SmC* state (red line) and SmA state (black line).



Fig. S5 CD spectra for (a) **3**, (b) **4** and (c) **6** at room temperature (blue line: Cr state, red line: SmC* state). The SmC* sample was prepared by cooling after melting.



Fig. S6 Temperature-dependent dielectric constants of (a) **3**, (b) **4**, (c) **5** and (d) **6** (black line: 100 Hz, red line: 1 kHz).



Fig. S7 Temperature-dependent *P-E* hysteresis curves for (a) **3**, (b) **4** and (d) **6** (blue line: Cr state, red line: SmC* state).



Fig. S8 Results of SHG experiments for (a) **3**, (b) **4** and (c) **6** at room temperature ($\lambda_{ex} = 1080$ nm, black plot: Cr state, red plot: SmC* state). The SmC* sample for this measurement was prepared by cooling to room temperature after melting.



Fig. S9 $\chi_m T$ vs T plots for (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** and (f) **6** (black plot: virgin sample, red plot: sample after melting).



Fig. S10 $\chi_m T$ vs *T* plots for (a) **5** and (b) **6** (red plot: heating, blue plot: cooling); the black plot is derived from the DSC study.



Fig. S11 Mössbauer spectra for **5** at 100 K (top: specrum before removing solvent, bottom: spectrum after removing solvent).

Table S2. The Mössbauer fitting parameters for **5**.

Compound		I.S. / mm s ⁻¹	Q.S. / mm s ⁻¹	Area ratio / %
5 (before removing solvent)	Fe ^{II} (LS)	0.34	0.58	100.0
5 (after removing solvent)	Fe ^{II} (LS)	0.26	0.50	68.9
	Fe ^{II} (HS)	0.96	2.79	31.1



Fig. S12 Structure of (a) $[Fe(1C_{16}-bzimpy)_2](BF_4)_2$ and (b) $[Fe(2C_{16}-bzimpy)_2](BF_4)_2$.

Compound	7·H ₂ O
CCDC number	1908948
Chemical formula	$C_{134}H_{218}B_2F_8ZnN_{10}O_3$
Formula weight / g mol ⁻¹	2256.25
T/K	200
Crystal system	Triclinic
Space group	P-1(#2)
<i>a</i> / Å	14.063(4)
b / Å	17.387(4)
c / Å	29.844(8)
lpha / °	82.385(6)
eta / $^\circ$	82.783(7)
y / °	68.932(5)
$V/Å^3$	6725.38(3)
Z	2
F(000)	2456.00
<i>R</i> 1	0.1230
w <i>R</i> 2	0.3126
R1 [all data]	0.1755
wR2 [all data]	0.3473
G.O.F.	1.066

Table S3. Crystal parameters for $7 \cdot H_2O$.



Fig. S13 (a) Single crystal X-ray structure of $7 \cdot H_2O$. Colour code: Yellow, Zn; red, O; blue, N; grey, C. (b) Packing structure of $7 \cdot H_2O$. Two alkyl chains on one side are coloured green, and four alkyl chains on the opposite side are coloured pink. H atoms, counter anions, solvent molecules are omitted for clarity.



Fig. S14 DSC curve and phase transition temperature in the 2nd heating mode of **7** (black line: 1st cycle, red line: 2nd heating).



Fig. S15 (a) POM textures for the SmC* state at 418 K and (b) the SmA state at 445 K in 7. (c) CD spectra for 7 at 298 K (blue line: Cr state, red line: SmC* state). The spectrum for the SmC* state was obtained using the sample cooled to room temperature after melting. The observed fingerprint-shape texture in the SmC* state was maintained at room temperature. (d) Temperature-dependent PXRD patterns for 7. The inset shows the PXRD patterns for SmC* (red line) and SmA (black line) states.



Fig. S16 Dielectric constant of 7 (black line: 100 Hz, red line: 1 kHz).



Fig. S17 (a) Temperature-dependent P - E hysteresis curves for **7** at 100 kHz (blue line: 298 K (Cr state), red line: 350 K (SmC* state)). (b) Result of SHG experiment on **7** at 298 K. The SmC* sample for this measurement was prepared by cooling to room temperature after melting.

Reference

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