Electronic Supplementary Information for:

Mesogenic Gold Complexes Showing Aggregation-Induced Enhancement of Phosphorescence in Both Crystalline and Liquid-Crystalline Phases

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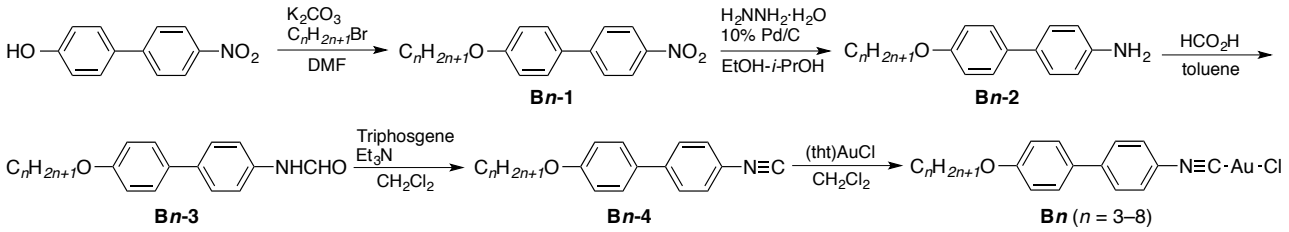
1. Synthesis

General. Gold complexes used in this study were synthesized according to the previous report with some modifications,[1] as shown in Scheme S1. All solvents and reagents used were reagent grade and commercially available, and were used without further purification unless otherwise stated. ^{1}H spectra were recorded using a JEOL ECS-400 spectrometer at 400 MHz in $CDCl_3$. Chemical shifts are reported in parts per million (ppm), using the residual proton in the NMR solvent as an internal reference. Infrared spectra (IR) were observed by a KBr disk method with an FT/IR-610 (JASCO), and all spectra were reported in wavenumber (cm^{-1}). High resolution mass spectra (HRMS) were taken with a JEOL JMS-700 spectrometer. Elemental analyses were conducted with a MICRO CORDER, JM10 (J-SCIENCE).



Scheme S1 Synthetic pathway to mesogenic Au complexes **B*n***

Synthesis of 4-propoxy-4'-nitrobiphenyl (B3-1). In a 50 mL two-necked round-bottomed flask, 4-hydroxy-4'-nitrobiphenyl (0.95 g, 4.4 mmol), 1-bromopropane (0.69 g, 5.6 mmol) and potassium carbonate (0.69 g, 5.0 mmol) were added to DMF (15 mL), and the resultant mixture was stirred at 90 °C for 22 h. The reaction mixture was poured into H_2O and the crude product was extracted with AcOEt. The organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (eluent: CH_2Cl_2) to obtain **B3-1** (1.1 g, 4.3 mmol, 96%) as yellow solid. ^{1}H NMR ($CDCl_3$, δ): 8.27 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 7.69 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.57 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.01 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 3.98 (t, J = 6.7 Hz, 2H, OCH_2), 1.85 (qt, J = 7.5, 6.7 Hz, 2H, OCH_2CH_2), 1.06 (t, J = 7.5 Hz, 3H, CH_3).

B*n*-1 (*n* = 4–8). According to the above procedure, **B*n*-1** (n = 4–8) was obtained from the corresponding materials in 94–98% yields.

4-Butoxy-4'-nitrobiphenyl (B4-1). Yield: 94%. ^{1}H NMR ($CDCl_3$, δ): 8.27 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 7.69 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.57 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.01 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 4.03 (t, J = 6.3 Hz, 2H, OCH_2), 1.81 (tt, J = 7.1, 6.3 Hz, 2H, OCH_2CH_2), 1.52 (qt, J = 7.5, 7.1 Hz, 2H, $OCH_2CH_2CH_2$), 1.00 (t, J = 7.5 Hz, 3H, CH_3).

4-Nitro-4'-pentyloxybiphenyl (B5-1). Yield: 97%. ^{1}H NMR ($CDCl_3$, δ): 8.26 (d, J = 8.6 Hz, 3,5-*H* in biphenyl), 7.69 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.57 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.01 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.02 (t, J = 6.3 Hz, 2H, OCH_2), 1.82 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.51–1.35 (m, 4H, $OCH_2CH_2CH_2CH_2$), 0.95 (t, J = 7.5 Hz, 3H, CH_3).

4-Hexyloxy-4'-nitrobiphenyl (B6-1). Yield: 95%. ^{1}H NMR ($CDCl_3$, δ): 8.27 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 7.69 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.57 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.01 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 4.02 (t, J = 6.3 Hz, 2H, OCH_2), 1.82 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.53–1.44 (m, 2H, $OCH_2CH_2CH_2$), 1.40–1.32 (m, 4H, $O(CH_2)_3CH_2CH_2$), 0.92 (t, J = 7.5 Hz, 3H, CH_3).

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[1] (a) M. Benouazzane, S. Coco, P. Espinet, J. M. Martin-Alvarez, *J. Mater. Chem.*, 1995, **5**, 441–445; (b) K. Fujisawa, Y. Okuda, Y. Izumi, A. Nagamatsu, Y. Rokusha, Y. Sadaike, O. Tutsumi, *J. Mater. Chem. C*, 2014, **2**, 3549–3555.

4-Heptyloxy-4'-nitrobiphenyl (B7-1). Yield: 98%. ^{1}H NMR ($CDCl_3$, δ): 8.27 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 7.69 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.57 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.01 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 4.01 (t, J = 6.7 Hz, 2H, OCH_2), 1.82 (tt, J = 7.1, 6.7 Hz, 2H, OCH_2CH_2), 1. 53–1.42 (m, 2H, $OCH_2CH_2CH_2$), 1.41–1.25 (m, 6H, $OCH_2CH_2CH_2(CH_2)_3$), 0.90 (t, J = 7.1 Hz, 3H, CH_3).

4-Nitro-4'-octyloxybiphenyl (B8-1). Yield: 94%. ^{1}H NMR ($CDCl_3$, δ): 8.27 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 7.69 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.57 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.01 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.01 (t, J = 6.7 Hz, 2H, OCH_2), 1.82 (tt, J = 7.1, 6.7 Hz, 2H, OCH_2CH_2), 1.53–1.43 (m, 2H, $OCH_2CH_2CH_2$), 1.41–1.25 (m, 8H, $OCH_2CH_2CH_2(CH_2)_4$), 0.89 (t, J = 7.5 Hz, 3H, CH_3).

Synthesis of 4-amino-4'-propoxybiphenyl (B3-2). In a 50 mL two-necked round-bottomed flask, 4-propoxy-4'-nitrobiphenyl (**B3-1**, 1.1 g, 4.2 mmol), hydrazine monohydrate (2.2 g, 43 mmol) and 10% Pd/C (79 mg) were added to ethanol (20 mL), and the mixture was refluxed for 40 min. The solid in the reaction mixture was filtered off and the filtrate was evaporated *in vacuo*. The residue was dissolved in AcOEt, and washed with H_2O and brine. After the organic layer was dried over with anhydrous sodium sulfate, the solvent was evaporated completely to give the **B3-2** in 92% yield (0.42 g, 1.7 mmol) as a white solid. ^{1}H NMR ($CDCl_3$, δ): 7.44 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.36 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 6.93 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.74 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 3.95 (t, J = 6.3 Hz, 2H, OCH_2), 3.69 (brs, 2H, NH_2), 1.82 (qt, J = 7.5, 6.3 Hz, 2H, OCH_2CH_2), 1.05 (t, J = 7.5 Hz, 3H, CH_3).

B*n*-2 (*n* = 4–8). According to the above procedure, **B*n*-2** (*n* = 4–8) was obtained from the corresponding materials in 91–95% yields.

4-Amino-4'-butoxybiphenyl (B4-2). Yield: 92%. ^{1}H NMR ($CDCl_3$, δ): 7.44 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.36 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 6.93 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.74 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 3.99 (t, J = 6.7 Hz, 2H, OCH_2), 3.69 (brs, 2H, NH_2), 1.78 (tt, J = 7.1, 6.7 Hz, 2H, OCH_2CH_2), 1.51 (qt, J = 7.5, 7.1 Hz, 2H, $OCH_2CH_2CH_2$), 0.98 (t, J = 7.5 Hz, 3H, CH_3).

4-Amino-4'-pentyloxybiphenyl (B5-2). Yield: 95%. ^{1}H NMR ($CDCl_3$, δ): 7.44 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.36 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 6.93 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.74 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 3.98 (t, J = 6.3 Hz, 2H, OCH_2), 3.69 (brs, 2H, NH_2), 1.80 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.50–1.34 (m, 4H, $OCH_2CH_2(CH_2)_2$), 0.94 (t, J = 7.1 Hz, 3H, CH_3).

4-Amino-4'-hexyloxybiphenyl (B6-2). Yield: 95%. ^{1}H NMR ($CDCl_3$, δ): 7.44 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.36 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 6.93 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.74 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 3.98 (t, J = 6.3 Hz, 2H, OCH_2), 3.69 (brs, 2H, NH_2), 1.79 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.51–1.43 (m, 2H, $OCH_2CH_2CH_2$), 1.38–1.30 (m, 4H, $OCH_2CH_2CH_2(CH_2)_2$), 0.91 (t, J = 7.1 Hz, 3H, CH_3).

4-Amino-4'-heptyloxybiphenyl (B7-2). Yield: 94%. ^{1}H NMR ($CDCl_3$, δ): 7.44 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.36 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 6.93 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.74 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 3.97 (t, J = 6.3 Hz, 2H, OCH_2), 3.69 (brs, 2H, NH_2), 1.80 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.52–1.41 (m, 2H, $OCH_2CH_2CH_2$), 1.40–1.25 (m, 6H, $OCH_2CH_2CH_2(CH_2)_3$), 0.90 (t, J = 6.7 Hz, 3H, CH_3).

4-Amino-4'-octyloxybiphenyl (B8-2). Yield: 91%. ^{1}H NMR ($CDCl_3$, δ): 7.44 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.36 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 6.93 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.74 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 3.98 (t, J = 6.3 Hz, 2H, OCH_2), 3.69 (brs, 2H, NH_2), 1.79 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.50–1.43 (m, 2H, $OCH_2CH_2CH_2$), 1.39–1.24 (m, 8H, $OCH_2CH_2CH_2(CH_2)_4$), 0.89 (t, J = 6.7 Hz, 3H, CH_3).

Synthesis of *N*-(4'-propoxy-1,1'-biphenyl-4-yl)formamide (B3-3). In a 50 mL two-necked round-bottomed flask, 4-amino-4'-propoxybiphenyl (**B3-2**, 0.92 g, 4.1 mmol), and formic acid (3.0 g, 65 mmol) were dissolved in toluene (15 mL), and the solution was refluxed for 30 min. After the reaction mixture was cooled down to room temperature, a precipitate formed was collected to obtain the title compound **B3-3** in 81% yield (0.84 g, 3.3 mmol) as a mixture of rotamers at the *N*H–*C*HO single bond as a white rod-like crystal. ^{1}H NMR ($CDCl_3$, δ): 8.71 (d, J = 12 Hz, 1H; (*E*)-C*H*O), 8.41 (d, J = 1.8 Hz, 1H, (*Z*)-C*H*O), 7.61–7.45 (m, 9H, (*E*)-N*H*, 2,6-*H*, 2',6'-*H*, (*Z*)-3',5'-*H* in biphenyl), 7.17 (brs, 1H, (*Z*)-N*H*), 7.12 (d, J = 8.6 Hz, 4H, (*E*)-3',5'-H in biphenyl), 7.00–6.94 (m, 4H, 3,5-*H* in biphenyl), 3.96 (t, J = 6.7 Hz, 2H, OCH_2), 3.961 (t, J = 6.7 Hz, 2H, OCH_2), 1.836 (tt, J = 7.1, 6.7 Hz, 2H, OCH$_2$CH_2), 1.832 (tt, J = 7.5, 6.7 Hz, OCH$_2$CH_2), 1.06 (t, J = 7.1 Hz, 3H, CH_3), 1.05 (t, J = 7.5 Hz, 3H, CH_3).

B*n*-3 (*n* = 4–8). According to the above procedure, **B*n*-3** (n = 4–8) was obtained from the corresponding materials in 70–88% yields.

***N*-(4'-Butoxy-1,1'-biphenyl-4-yl)formamide (B4-3).** Yield: 70%. ^{1}H NMR ($CDCl_3$, δ): 8.71 (d, J = 11Hz, 1H, (*E*)-C*H*O), 8.41 (d, J = 1.8 Hz, 1H, (*Z*)-C*H*O), 7.65–7.45 (m, 9H, (*E*)-N*H*, 2,6-*H*, 2',6'-*H* in biphenyl), 7.17 (brs, 1H, (*Z*)-N*H*), 7.12 (d, J = 8.6 Hz, 4H, (*E*)-3',5'-*H* in biphenyl), 7.00–6.92 (m, 4H, 3,5-*H* in biphenyl), 4.01 (t, J = 6.7 Hz, 2H, OCH_2), 4.00 (t, J = 6.3 Hz, 2H, OCH_2), 1.793 (tt, J = 7.1, 6.7 Hz, 2H, OCH$_2$CH_2), 1.791 (tt, J = 7.1, 6.3 Hz, 2H, OCH$_2$CH_2), 1.51 (qt, J = 7.5, 7.1 Hz, 4H, OCH$_2$CH$_2$CH_2), 0.95 (t, J = 7.5 Hz, 6H, CH_3).

***N*-(4'-Pentyloxy-1,1'-biphenyl-4-yl)formamide (B5-3).** Yield: 74%. ^{1}H NMR ($CDCl_3$, δ): 8.71 (d, J = 11 Hz, 1H, (*E*)-C*H*O), 8.41 (d, J = 1.8 Hz, 1H, (*Z*)-C*H*O), 7.61–7.45 (m, 9H, (*E*)-N*H*, 2,6-*H*, 2',6'-*H* in biphenyl), 7.19 (brs, 1H, (*Z*)-N*H*), 7.12 (d, J = 8.8 Hz, 4H, (*E*)-3',5'-H in biphenyl), 6.99–6.93 (m, 4H, 3,5-*H* in biphenyl), 4.00 (t, J = 6.7 Hz, 2H, OCH_2), 3.99 (t, J = 6.7 Hz, 2H, OCH_2), 1.81 (tt, J = 7.1, 6.7 Hz, 4H, OCH$_2$CH_2), 1.51–1.34 (m, 8H, OCH$_2$CH$_2$ (CH_2)$_2$), 0.94 (t, J = 7.5 Hz, 6H, CH_3).

***N*-(4'-Hexyloxy-1,1'-biphenyl-4-yl)formamide (B6-3).** Yield: 82%. ^{1}H NMR ($CDCl_3$, δ): 8.71 (d, J = 12 Hz, 1H, (*E*)-C*H*O), 8.41 (d, J = 1.3 Hz, 1H, (*Z*)-C*H*O), 7.62–7.46 (m, 9H, (*E*)-N*H*, 2,6-*H*, 2',6'-*H* in biphenyl), 7.13 (brs, 1H, (*Z*)-N*H*), 7.12 (d, J = 8.2 Hz, 4H, (*E*)-3',5'-*H* in biphenyl), 6.99–6.94 (m, 4H, 3,5-*H* in biphenyl), 4.00 (t, J = 6.3 Hz, 2H, OCH_2), 3.99 (t, J = 6.3 Hz, 2H, OCH_2), 1.81 (tt, J = 7.5, 6.3 Hz, 4H, OCH$_2$CH_2), 1.52–1.43 (m, 4H, OCH$_2$CH$_2$CH_2), 1.40–1.30 (m, 8H, OCH$_2$CH$_2$CH$_2$(CH_2)$_2$), 0.91 (t, J = 7.1 Hz, 6H, CH_3).

***N*-(4'-Heptyloxy-1,1'-biphenyl-4-yl)formamide (B7-3).** Yield: 74%. ^{1}H NMR ($CDCl_3$, δ): 8.71 (d, J = 12 Hz, 1H, (*E*)-C*H*O), 8.41 (d, J = 1.8 Hz, 1H, (*Z*)-C*H*O), 7.60–7.41 (m, 9H, (*E*)-N*H*, 2,6-*H*, 2',6'-*H* in biphenyl), 7.13 (brs, 1H, (*Z*)-N*H*), 7.11 (d, J = 6.8 Hz, 4H, (*E*)-3',5'-*H* in biphenyl), 6.99–6.95 (m, 4H, 3,5-*H* in biphenyl), 4.00 (t, J = 6.7 Hz, 2H, OCH_2), 3.99 (t, J = 6.7 Hz, 2H, OCH_2), 1.80 (tt, J = 7.1, 6.7 Hz, 4H, OCH$_2$CH_2), 1.52–1.42 (m, 4H, OCH$_2$CH$_2$CH_2), 1.41–1.25 (m, 12H, OCH$_2$CH$_2$CH$_2$(CH_2)$_3$), 0.90 (t, J = 6.7 Hz, 6H, CH_3).

***N*-(4'-Octyloxy-1,1'-biphenyl-4-yl)formamide (B8-3).** Yield: 88%. ^{1}H NMR ($CDCl_3$, δ): 8.71 (d, J = 12 Hz, 1H, (*E*)-C*H*O), 8.41 (d, J = 1.4 Hz, 1H, (*Z*)-C*H*O), 7.60–7.47 (m, 9H, (*E*)-N*H*, 2,6-*H*, 2',6'-*H* in biphenyl), 7.15 (brs, 1H, (*Z*)-N*H*), 7.12 (d, J = 6.8 Hz, 4H, (*E*)-3',5'-*H* in biphenyl), 6.99–6.94 (m, 4H, 3,5-*H* in biphenyl), 4.00 (t, J = 6.7 Hz, 2H, OCH_2), 3.99 (t, J = 6.7 Hz, 2H, OCH_2), 1.81 (tt, J = 7.1, 6.7 Hz, 4H, OCH$_2$CH_2), 1.51–1.43 (m, 4H, OCH$_2$CH$_2$CH_2), 1.41–1.24 (m, 16H, OCH$_2$CH$_2$CH$_2$(CH_2)$_4$), 0.89 (t, J = 7.1 Hz, 6H, CH_3).

Synthesis of 4-isocyano-4'-propoxybiphenyl (B3-4). In a 50 mL two-necked round-bottomed flask, fleshly prepared **B3-3** (0.31 g, 1.2 mmol), and triethylamine (0.38 g, 3.8 mmol) were dissolved in dichloromethane (10 mL). To the resultant solution, a solution of triphosgene (0.19 g, 0.64 mmol) in dichloromethane (5.0

mL) were added, and the solution was stirred at room temperature for 45 min under argon. After the solid was filtered off and the solvent was evaporated, the crude product obtained was purified by a silica-gel column chromatography (eluent: CH_2Cl_2) to obtain **B3-4** (0.21 g, 0.92 mmol) in 75% yield as a white solid. ^{1}H NMR ($CDCl_3$, δ): 7.56 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.49 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.41 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 6.98 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 3.97 (t, J = 6.3 Hz, 2H, OCH_2), 1.84 (qt, J = 7.5, 6.3 Hz, 2H, OCH_2CH_2), 1.06 (t, J = 7.5 Hz, 3H, CH_3).

B*n*-4 (*n* = 4–8). According to the above procedure, **B*n*-4** (n = 4–8) was obtained from the corresponding materials in 63–87% yields.

4-Butoxy-4'-isocyanobiphenyl (B4-4). Yield: 86%. ^{1}H NMR ($CDCl_3$, δ): 7.56 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.49 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.41 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.98 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.01 (t, J = 6.3 Hz, 2H, OCH_2), 1.80 (tt, J = 7.0, 6.3 Hz, 2H, OCH_2CH_2), 1.51 (qt, J = 7.5, 7.0 Hz, 2H, $OCH_2CH_2CH_2$), 0.99 (t, J = 7.5 Hz, 3H, CH_3).

4-Isocyano-4'-pentyloxybiphenyl (B5-4). Yield: 63%. 7.56 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.49 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.41 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 6.98 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 4.00 (t, J = 6.3 Hz, 2H, OCH_2), 1.81 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.50–1.35 (m, 4H, $OCH_2CH_2(CH_2)_2$), 0.94 (t, J = 7.1 Hz, 3H, CH_3).

4-Hexyloxy-4'-isocyanobiphenyl (B6-4). Yield: 66%. ^{1}H NMR ($CDCl_3$, δ): 7.56 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.49 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.41 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.98 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.00 (t, J = 6.3 Hz, 2H, OCH_2), 1.79 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.52–1.44 (m, 2H, $OCH_2CH_2CH_2$), 1.41–1.31 (m, 4H, $OCH_2CH_2CH_2(CH_2)_2$), 0.92 (t, J = 7.1 Hz, 3H, CH_3).

4-Heptyloxy-4'-isocyanobiphenyl (B7-4). Yield: 87%. ^{1}H NMR ($CDCl_3$, δ): 7.56 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.49 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.41 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 6.98 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.00 (t, J = 6.3 Hz, 2H, OCH_2), 1.81 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.51–1.27 (m, 8H, $OCH_2CH_2(CH_2)_4$), 1.06 (t, J = 6.7 Hz, 3H, CH_3).

4-Isocyano-4'-octyloxybiphenyl (B8-4). Yield: 83%. ^{1}H NMR ($CDCl_3$, δ): 7.56 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.49 (d, J = 9.1 Hz, 2H, 2,6-*H* in biphenyl), 7.41 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 6.98 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 4.00 (t, J = 6.3 Hz, 2H, OCH_2), 1.81 (tt, J = 6.7, 6.3 Hz, 2H, OCH_2CH_2), 1.52–1.43 (m, 2H, $OCH_2CH_2CH_2$), 1.38–1.24 (m, 8H, $OCH_2CH_2CH_2(CH_2)_4$), 0.89 (t, J = 6.7 Hz, 3H, CH_3).

Synthesis of (4-isocyano-4'-propoxy-1,1'-biphenyl)gold(I) chloride (B3). In 50 mL round-bottomed flask, isocyanide ligand (**B3-4**, 81 mg, 0.36 mmol), and (tht)AuCl (tht: tetrahydrothiophene; 0.13 g, 0.42 mmol) were dissolved in dichloromethane. After the reaction mixture was stirred at room temperature for 10 min, the solvent was removed under reduced pressure to give the crude product. The crude product was washed with diethyl ether three times, and then was purified by a column chromatography on silica-gel (eluent: CH_2Cl_2). The product was further purified by recrystallization from a mixed solvent of hexane and dichloromethane to afford gold(I) complex (**B3**, 0.12 g, 0.25 mmol) in 71% yield as a pale-yellow plate crystal. m.p.: 218 °C. ^{1}H NMR ($CDCl_3$, δ): 7.67 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 7.56 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.52 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.00 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 3.98 (t, J = 6.7 Hz, 2H, OCH_2), 1.84 (qt, J = 7.1, 6.7 Hz, 2H, OCH_2CH_2), 1.06 (t, J = 7.1 Hz, 3H, CH_3). IR (KBr): ν 3043, 2967, 2880, 2224, 1493, 1294, 1176, 1011, 970 cm^{-1}. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{16}H_{15}AuClNO$ 469.0508; Found 469.0524. Anal. Calcd for $C_{16}H_{15}AuClNO$: C, 40.91; H, 3.22; N, 2.98. Found: C, 40.60; H, 2.95; N, 2.96.

B*n* (*n* = 4–8). According to the above procedure, **B*n*** (*n* = 4–8) was obtained from the corresponding materials in 40–84% yields.

(4-Butoxy-4'-isocyano-1,1'-biphenyl)gold(I) chloride (B4). Yield: 83%. m.p. 170 °C. ^{1}H NMR ($CDCl_3$, δ): 7.67 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 7.56 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.52 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.00 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.02 (t, J = 6.3 Hz, 2H, OCH_2), 1.80 (tt, J = 7.5, 6.3 Hz, 2H, OCH_2CH_2), 1.51 (tq, J = 7.5, 7.1 Hz, 2H, $OCH_2CH_2CH_2$), 0.99 (t, J = 7.1 Hz, 3H, CH_3). IR (KBr): ν 3042, 2957, 2870, 2220, 1492, 1246, 1067, 910 cm^{-1}. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{17}H_{17}AuClNO$ 483.0664; Found 483.0679. Anal. Calcd for $C_{17}H_{17}AuClNO$: C, 42.21; H, 3.54; N, 2.90. Found: C, 41.82; H, 3.24; N, 2.85.

(4-Isocyano-4'-pentyloxy-1,1'-biphenyl)gold(I) chloride (B5). Yield: 83%. m.p. 141 °C. ^{1}H NMR ($CDCl_3$, δ): 7.67 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 7.56 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.52 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.00 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 4.01 (t, J = 6.7 Hz, 2H, OCH_2), 1.82 (tt, J = 7.1, 6.7 Hz, 2H, OCH_2CH_2), 1.51–1.34 (m, 4H, $CH_2CH_2CH_3$), 0.94 (t, J = 7.5 Hz, 3H, CH_3). IR (KBr): ν 3035, 2956, 2220, 1607, 1474, 1255, 1031, 891 cm^{-1}. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{18}H_{19}AuClNO$ 497.0821; Found 497.0817. Anal. Calcd for $C_{18}H_{19}AuClNO$: C, 43.43; H, 3.85; N, 2.81. Found: C, 43.14; H, 3.36; N, 2.82.

(4-Hexyloxy-4'-isocyano-1,1'-biphenyl)gold(I) chloride (B6). Yield: 84%. m.p. 141 °C. ^{1}H NMR ($CDCl_3$, δ): 7.67 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 7.56 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.52 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.00 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.01 (t, J = 6.3 Hz, 2H, OCH_2), 1.81 (tt, J = 7.5, 6.3 Hz, 2H, OCH_2CH_2), 1.54–1.42 (m, 2H, $OCH_2CH_2CH_2$), 1.40–1.31 (m, 4H, $O(CH_2)_3CH_2CH_2$), 0.91 (t, J = 7.1 Hz, 3H, CH_3). IR (KBr): ν 3035, 2954, 2220, 1494, 1222, 1128, 1034, 994 cm^{-1}. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{19}H_{21}AuClNO$, 511.0977; found, 511.0995. Anal. Calcd for $C_{19}H_{21}AuClNO$: C, 44.59, H: 4.14, N: 2.74. Found, C, 44.25; H, 3.93; N, 2.78.

(4-Heptyloxy-4'-isocyano-1,1'-biphenyl)gold(I) chloride (B7). Yield: 40%. m.p. 130 °C. ^{1}H NMR ($CDCl_3$, δ): 7.67 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 7.56 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.52 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.01 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 4.01 (t, J = 6.7 Hz, 2H, OCH_2), 1.81 (tt, J = 7.1, 6.7 Hz, 2H, OCH_2CH_2), 1.51–1.27 (m, 8H, $OCH_2CH_2(CH_2)_4$), 0.90 (t, J = 6.7 Hz, 3H, CH_3). IR (KBr): ν 3034, 2953, 2220, 1495, 1254, 1127, 1040, 989 cm^{-1}. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{20}H_{23}AuClNO$, 525.1134; found, 525.1126. Anal. Calcd for $C_{20}H_{23}AuClNO$: C, 45.68, H, 4.41; N, 2.66. Found, C, 45.35; H, 3.93; N, 2.68.

(4-Isocyano-4'-octyloxy-1,1'-biphenyl)gold(I) chloride (B8). Yield: 83%. m.p. 133 °C. ^{1}H NMR ($CDCl_3$, δ): 7.67 (d, J = 8.6 Hz, 2H, 3',5'-*H* in biphenyl), 7.56 (d, J = 8.6 Hz, 2H, 2',6'-*H* in biphenyl), 7.52 (d, J = 8.6 Hz, 2H, 2,6-*H* in biphenyl), 7.00 (d, J = 8.6 Hz, 2H, 3,5-*H* in biphenyl), 4.01 (t, J = 6.3 Hz, 2H, OCH_2), 1.81 (tt, J = 7.1, 6.3 Hz, 2H, OCH_2CH_2), 1.52–1.43 (m, 2H, $OCH_2CH_2CH_2$), 1.41–1.24 (m, 8H, $O(CH_2)_3(CH_2)_4$), 0.89 (t, J = 7.1 Hz, 3H, CH_3). IR (KBr): ν 3035, 2955, 2221, 1496, 1224, 1128, 1034, 851 cm^{-1}. HRMS (FAB) *m/z* $[M]^+$ calcd for $C_{21}H_{25}AuClNO$, 539.1290; found, 539.1305. Anal. Calcd for $C_{21}H_{25}AuClNO$: C, 46.72; H, 4.67; N, 2.59. Found, C, 46.30; H, 4.30; N, 2.51.

2. X-Ray Crystallography

Single crystals were obtained by slow evaporation from the mixed solvent system of ethanol and dichloromethane. The X-ray diffraction measurement was carried out at room temperature (296 K). The crystal structures of gold complexes and packing structures of **B3**–**B8** are shown in Fig. S1 and S2, respectively, and their crystallographic data are summarized in Table S1. The crystal data of mesogenic Au complexes **B3**–**B8** reported in this paper have been indexed and are included in the Cambridge Crystallographic Centre (CCDC) database with the following reference umber: CCDC 1482940–1482945. The indexed database contains additional supplementary crystallographic data for this paper and may be accessed without charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html. The CCDC may be contacted by mail at 12 Union Road, Cambridge CB2 1EZ, U.K., by fax at (44) 1223-336-033, or by e-mail at deposit@ccdc.cam.ac.uk.

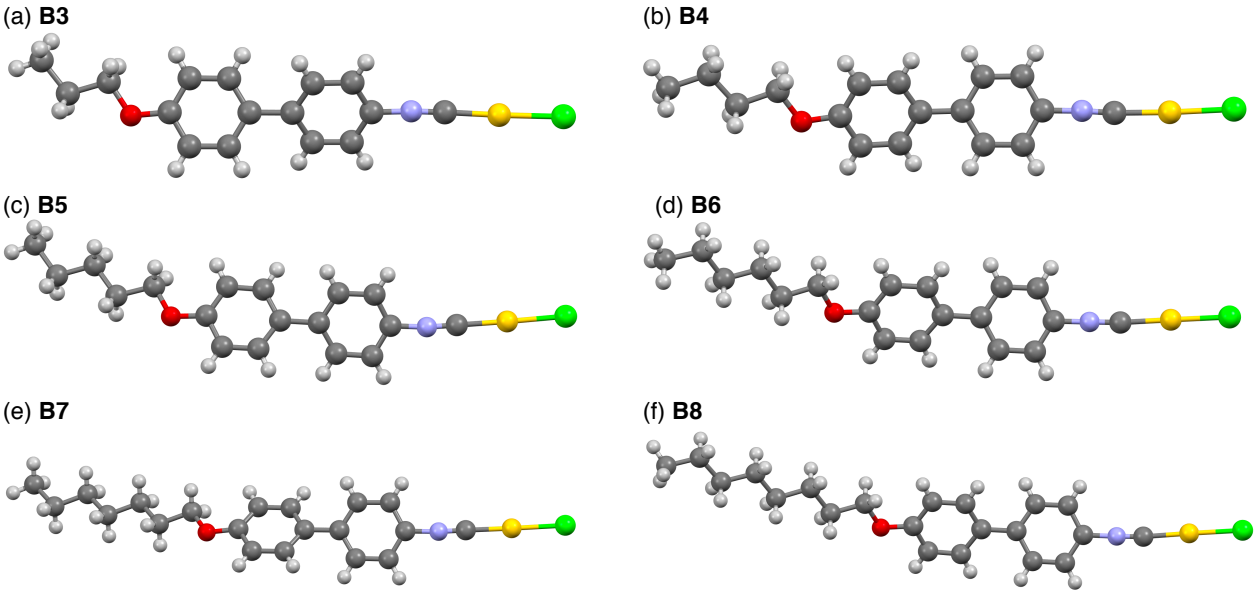


Fig. S1 Molecular structures of Au complexes. Colour legends: grey, carbon; red, oxygen; blue, nitrogen; green, chlorine; yellow, gold.

Table S1 Crystallographic data for mesogenic Au complexes **B3–B8**.

Complex	**B3**	**B4**	**B5**
CCDC number	1482940	1482941	1482942
Empirical Formula	$C_{16}H_{15}AuClNO$	$C_{17}H_{17}AuClNO$	$C_{18}H_{19}AuClNO$
Formula Weight	469.71	483.73	497.76
Temperature [K]	296	296	296
Crystal Colour / Habit	Colourless / plate	Colourless / plate	Colourless / plate
Crystal Size [mm]	0.30 × 0.20 × 0.05	0.60 × 0.10 × 0.10	0.30 × 0.20 × 0.04
Crystal System	Monoclinic	Triclinic	Monoclinic
Space group	*C*1 $2_1/c$ 1	*P*-1	*P*1 $2_1/c$ 1
a [Å]	10.0233(6)	10.2724(5)	35.545(9)
b [Å]	7.3836(5)	13.7308(7)	7.0033(17)
c [Å]	20.4729(13)	14.1704(7)	6.8729(16)
α [°]	90	61.476(1)	90
β [°]	71.090(9)	71.000(2)	92.118(5)
γ [°]	90	69.885(2)	90
V [Å^3]	1512.75(17)	1617.15(14)	1709.7(7)
Z	4	4	4
Crystal density [g cm^{-3}]	2.062	1.987	1.934
R [$F^2 > 2\sigma(F^2)$][a]	0.0401	0.0360	0.0531
$wR(F^2)$[b]	0.1029	0.1207	0.1811

Complex	**B6**	**B7**	**B8**
CCDC number	1482943	1482944	1482945
Empirical Formula	$C_{19}H_{21}AuClNO$	$C_{20}H_{23}AuClNO$	$C_{21}H_{25}AuClNO$
Formula Weight	511.78	525.81	539.84
Temperature [K]	296	296	296
Crystal Colour / Habit	Colourless / plate	Colourless / plate	Colourless / plate
Crystal Size [mm]	0.30 × 0.20 × 0.05	0.15 × 0.12 × 0.05	0.28 × 0.18 × 0.03
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	*C*1 $2_1/c$ 1	*P*1 $2_1/c$ 1	*P*1 $2_1/c$ 1
a [Å]	76.128(14)	78.931(9)	42.33(2)
b [Å]	7.0364(13)	7.0341(8)	7.082(3)
c [Å]	6.8648(12)	6.8739(8)	6.912(3)
α [°]	90	90	90
β [°]	91.305(4)	91.828(3)	91.738(9)
γ [°]	90	90	90
V [Å^3]	3676.3(12)	3814.5(8)	2071.1(17)
Z	8	8	4
Crystal density [g cm^{-3}]	1.849	1.831	1.731
R [$F^2 > 2\sigma(F^2)$][a]	0.0864	0.0460	0.0727
$wR(F^2)$[b]	0.2309	0.1693	0.2207

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = \{[\Sigma w(|F_o| - |F_c|)]/\Sigma w|F_o|\}^{1/2}$.

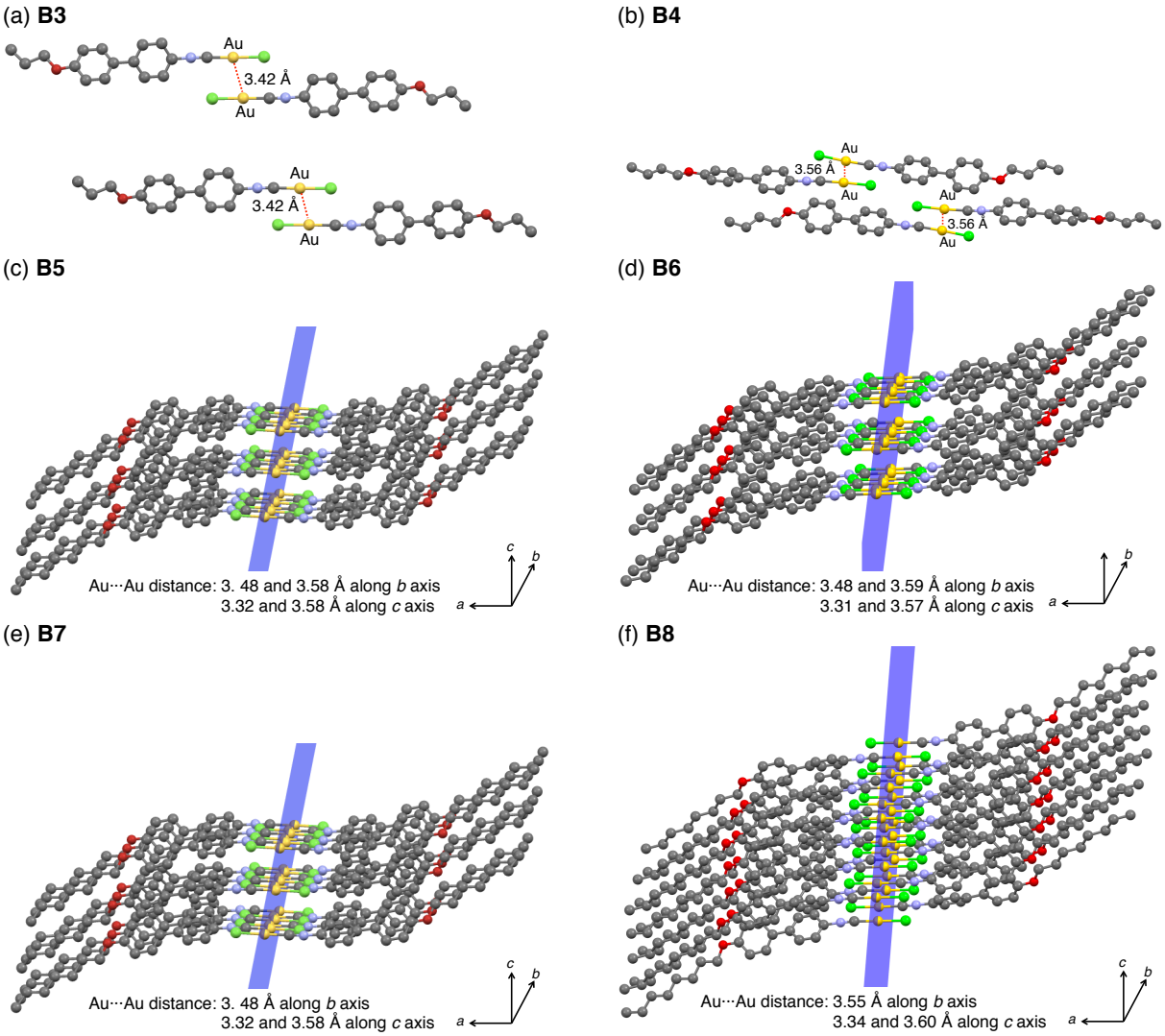


Fig. S2 Crystal packing structures of **B3**–**B8**. Hydrogen atoms are omitted for clarity. Blue square sheets indicate a two-dimensional plane consisted of Au atoms. Hydrogen atoms are omitted for clarity. Colour legends: grey, carbon; red, oxygen; blue, nitrogen; green, chlorine; yellow, gold. Blue planes indicate a two-dimensional plane, in where Au atoms are arranged by Au/Au interaction.

3. Thermal properties

Thermal properties of the complexes were evaluated by TG-DTA (Shimadzu, DTG-60AH) at a heating rate of 5.0 °C min^{-1} (Fig. S3). Thermal decomposition temperature is defined as the temperature that 5% weight loss occurred, and are summarized in the main text.

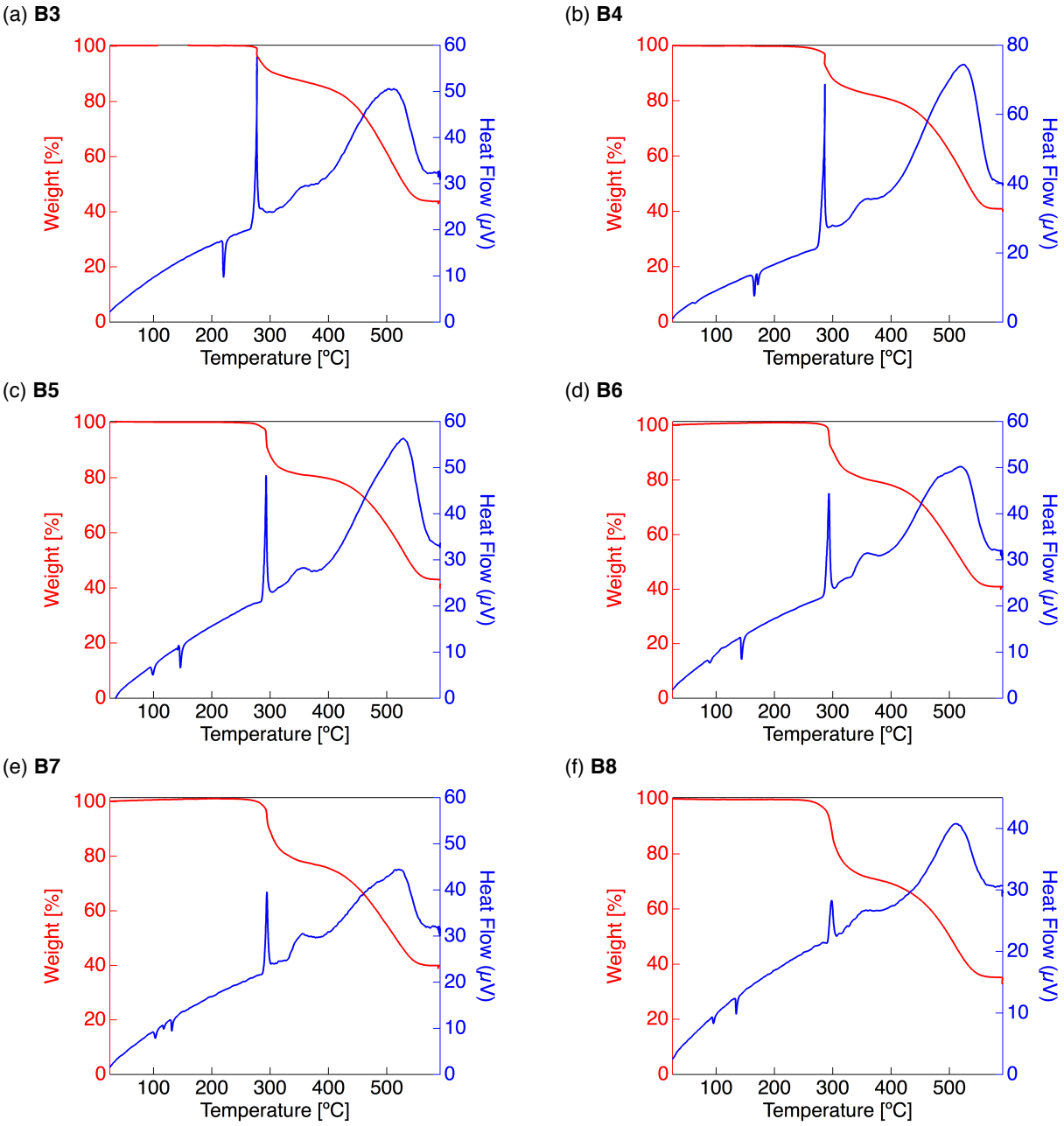


Fig. S3 TG-DTA thermograms of **B3**–**B8** in air. Heating rate was 5.0 °C min^{-1}.

4. Phase transition properties

The phase transition behaviour of the complexes was determined by DSC (SII X-DSC7000) at a scanning rate of 5.0 °C min^{-1} (Fig. S4). At least three scans were performed to ensure reproducibility.

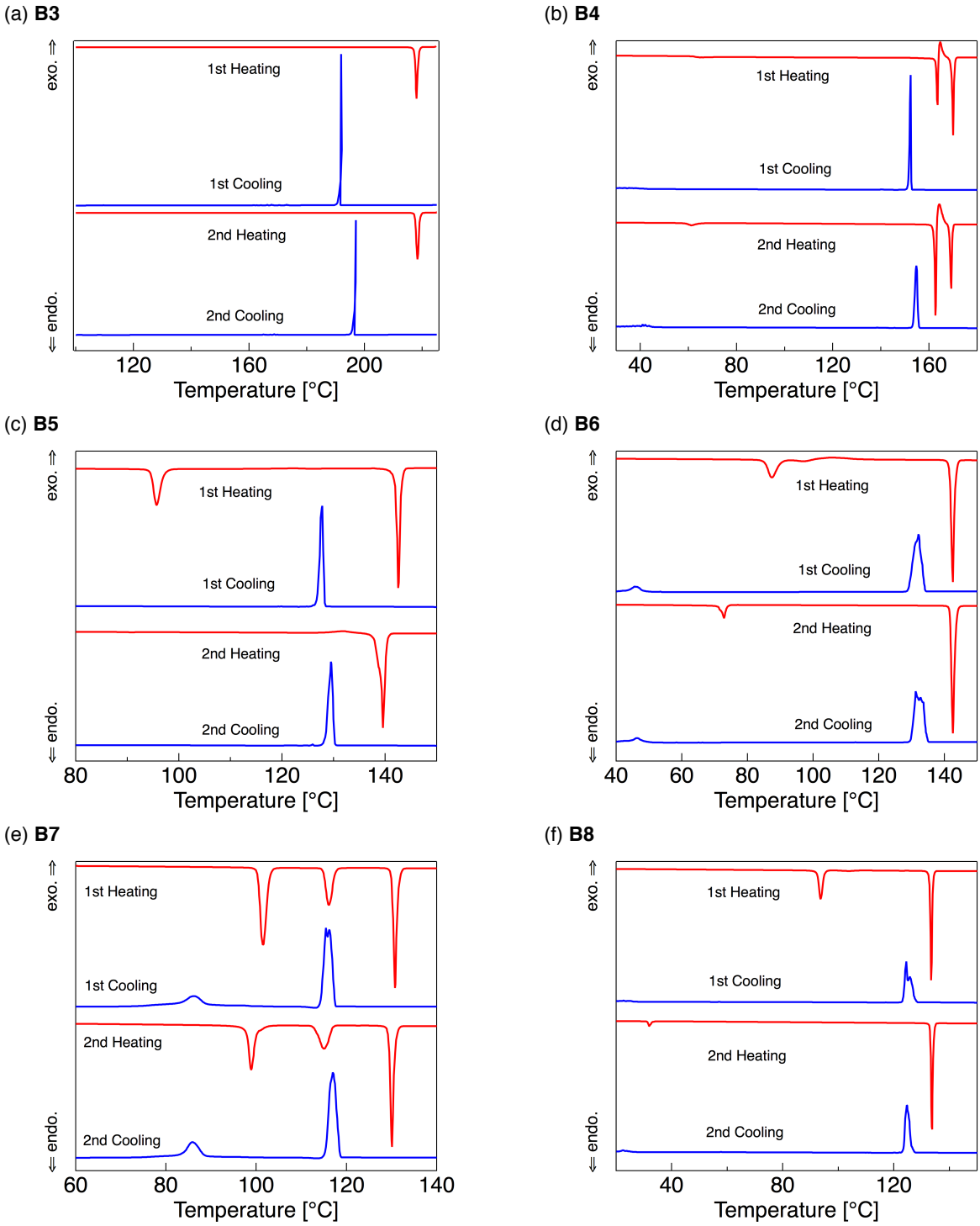


Fig. S4 DSC thermograms of **B3**–**B8**: Scanning rate = 5.0 °C min^{-1}.

Table S2 Thermodynamic parameters of the complexes.

Complex	Phase transition temperature [°C]			ΔH [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]
B3	Heating	Cry_1 – Sme A	218	32.0	65.2
	Cooling	Sme A – Cry_x	190	–34.4	–73.5
B4	Heating	Cry_1 – Cry_2	60	2.2	6.7
		Cry_2 – Cry_3	163	23.5	53.9
		Cry_3 – Sme A	170	14.4	32.4
	Cooling	Sme A – Cry_2	157	–23.6	–54.8
		Cry_4 – Cry_x	46	–2.9	–8.9
B5	Heating	Cry_1 – Sme A	143	21.6	51.8
	Cooling	Sme A – Cry_x	130	–18.1	–44.9
B6	Heating	Cry_1 – Cry_2	72	4.4	13
		Cry_2 – Sme A	142	24.1	58.0
	Cooling	Sme A – Cry_3	135	–23.5	–57.7
		Cry_3 – Cry_x	49	–3.2	–9.9
B7	Heating	Cry_1 – Cry_2	99	9.0	24
		Cry_2 – Cry_3	114	6.84	17.7
		Cry_3 – Sme A	130	14.9	36.9
	Cooling	Sme A – Cry_4	119	–5.19	–14.3
		Cry_4 – Cry_x	89	–20	–51
B8	Heating	Cry_1 – Cry_2	31	1.4	4.5
		Cry_2 – Sme A	133	26.0	64.0
	Cooling	Sme A – Cry_x	126	–25.2	–63.1

Abbreviations: Cry, crystalline; Sme A, smectic A phase.

5. Powder X-ray diffraction

Powder X-ray diffractometry (XRD) was performed on Rigaku Ultima IV, XRD-DSC II with D/tex-Ultra detector for the small angle region or with a scintillation counter for the wide angle region. The temperature was controlled with a built-in DSC unit (Rigaku, ThermoPlus2, DSC8230) at the scanning rate of 10 °C min^{-1}.

Fig. S5 shows diffraction patterns in a small-angle region: the diffraction angle and the estimated interlayer spacing were listed in Table S3.

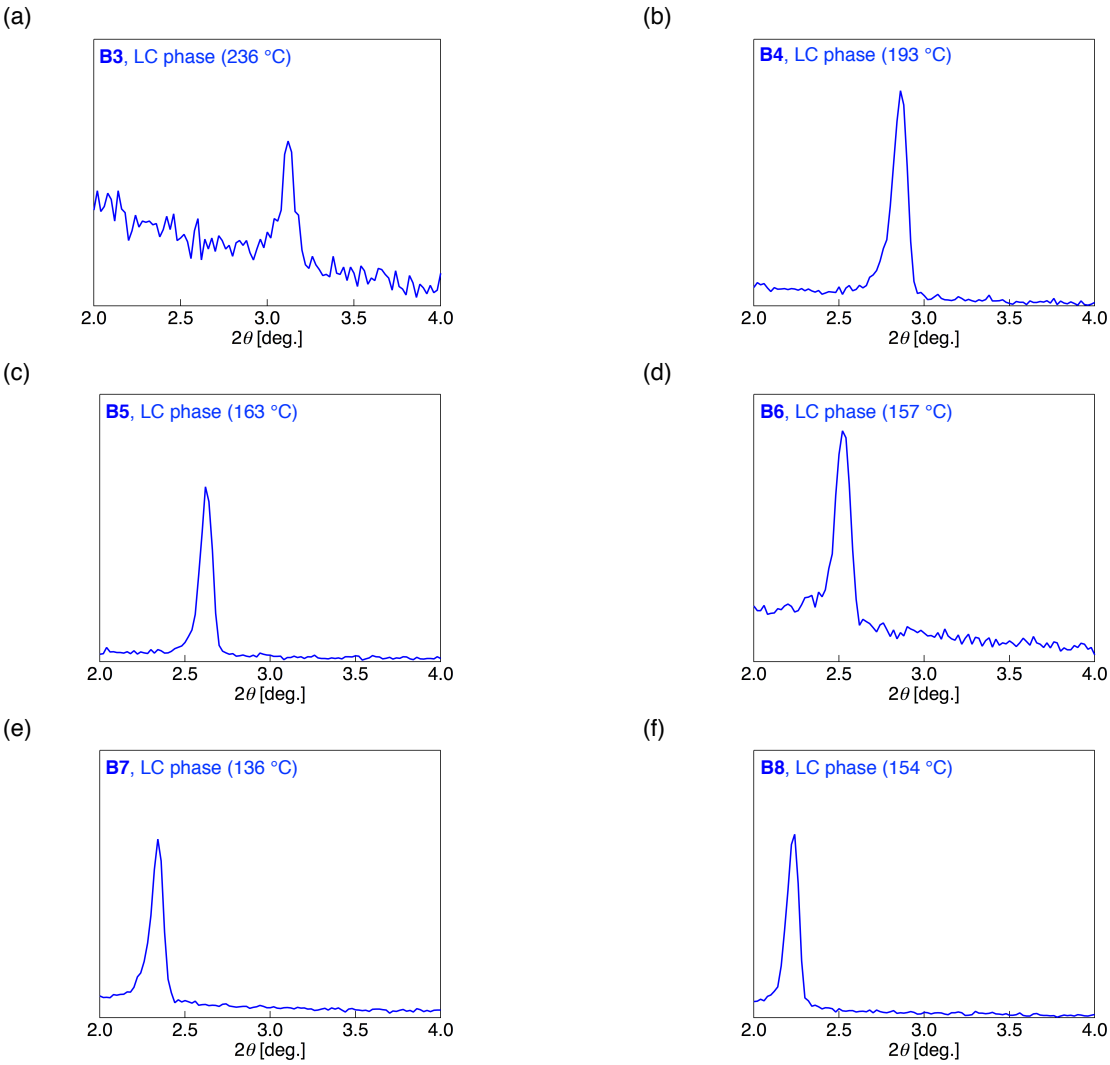


Fig. S5 Small-angle XRD patterns in the Sme A phase.

Table S3 Diffraction data and the corresponding interlayer spacing length.

Complex	Diffraction angle (2θ) [°]	Interlayer spacing in LC phase [Å]
B3	3.12	28.3
B4	2.86	30.8
B5	2.62	33.6
B6	2.52	35.0
B7	2.34	37.7
B8	2.24	39.4

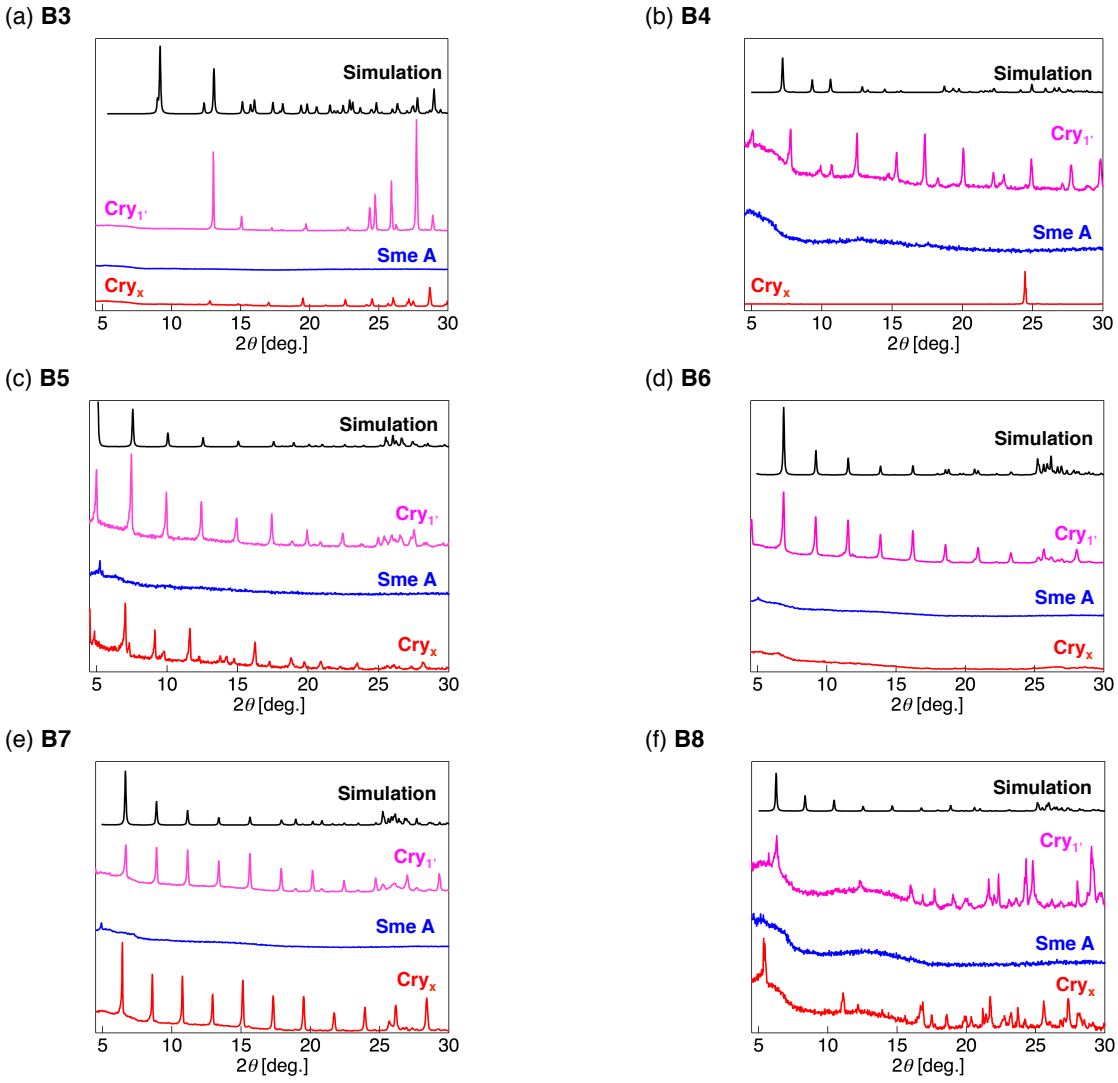


Fig. S6 Wide-angle XRD patterns. $Cry_{1'}$: crystalline phase after grinding single crystals, Cry_x: crystal frozen from Sme A phase.

6. Photophysical properties

UV-Vis absorption and steady-state photoluminescence spectra were recorded on a JASCO V-550 absorption spectrophotometer and a Hitachi F-7000 fluorescence spectrophotometer, respectively. Photoluminescent quantum yields were determined by a calibrated integrating sphere system (Hitachi). Photoluminescent decay profiles were measured by using a Nd:YAG laser (Continum, Minilite II, λ = 337 nm; pulse width = 4 ns, fwhm; repetition rate = 10 Hz). The decay profiles were recorded with a streak camera (Hamamatsu, C7700).

Absorption and photoluminescence spectra in dilute chloroform solution

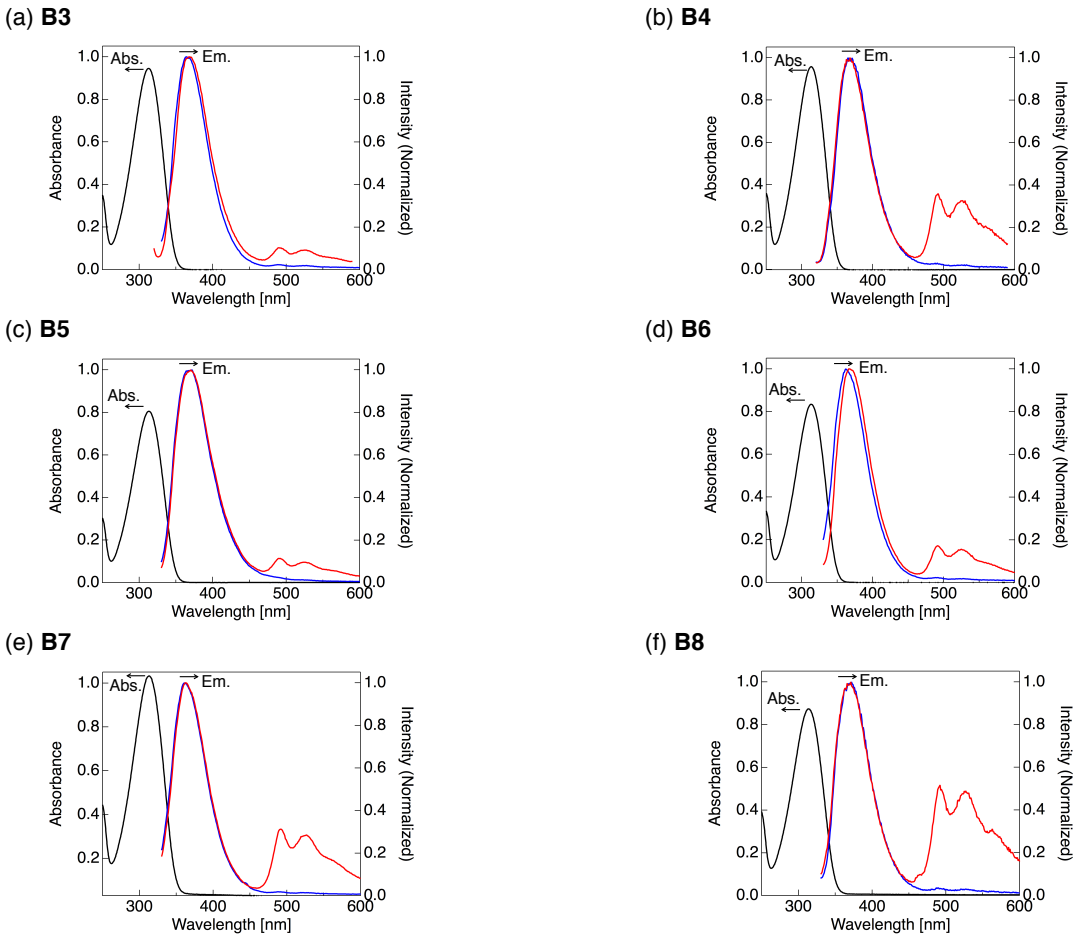


Fig. S7 Absorption (3.0×10^{-5} mol L^{-1}) and corrected photoluminescence spectra (λ_{ex} = 313 nm, 3.0×10^{-6} mol L^{-1}) in $CHCl_3$ solution: black, absorption spectra; blue, photoluminescence spectra in air; red, photoluminescence spectra in degassed solution.

Excitation and photoluminescence spectra in crystalline phase

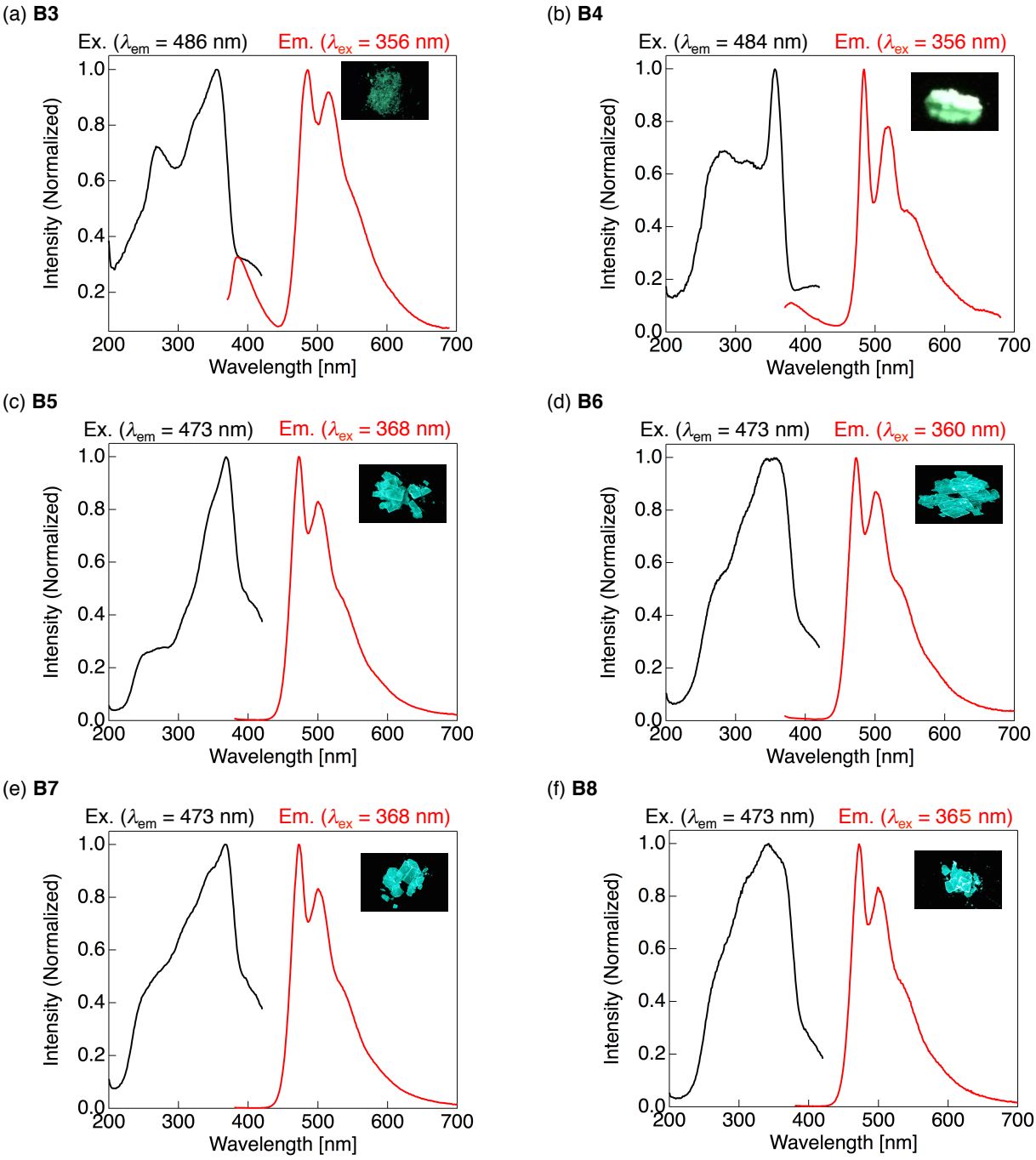


Fig. S8 Excitation (black) and corrected emission spectra (red) in crystal of **B3**–**B8**. Inset: photographs of crystal taken under UV irradiation at 365 nm.

Photoluminescence Lifetime

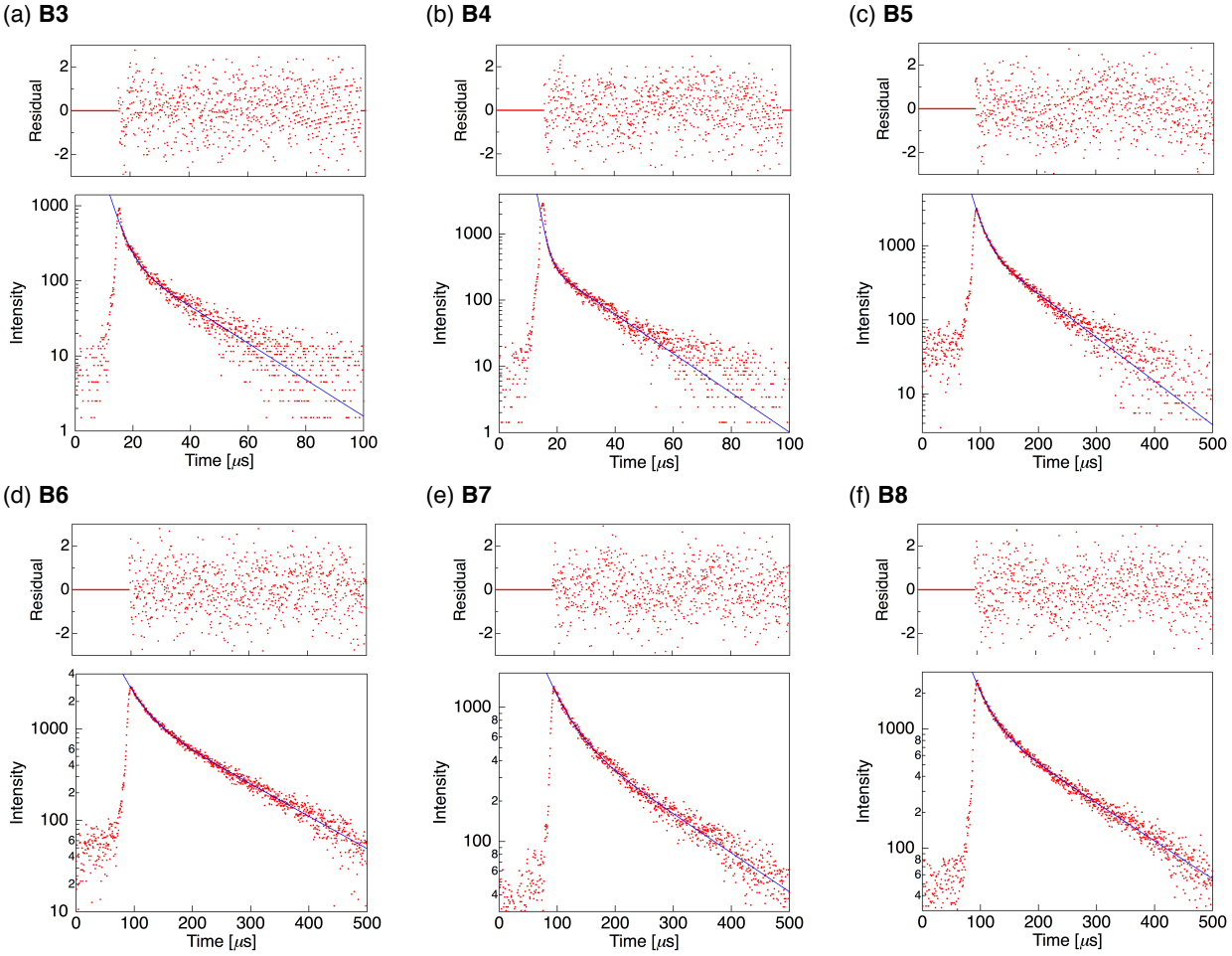


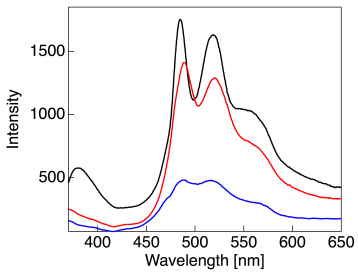
Fig. S9 Photoluminescence decay profiles of **B3**–**B8** observed in a wavelength range of 450–600 nm at room temperature in air. The measurement was carried out using a laser pulse at 355 nm (4 ns, fwhm; 10 Hz).

Table S4 Photoluminescence lifetime and quantum yield.

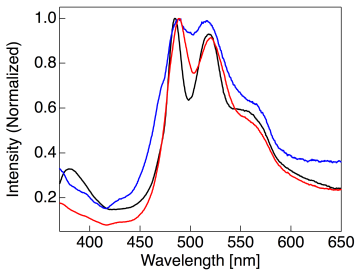
Complex	Lifetime [μs] (amplitude [%])	Quantum yield [%]
B3	3.22 (99), 17.9 (1)	5
B4	1.68 (99), 14.6 (1)	12
B5	14.0 (99), 73.7 (1)	34
B6	26.2 (95), 123 (5)	37
B7	31.3 (93), 150 (7)	60
B8	24.9 (96), 137 (4)	66

Photoluminescence behaviour in LC phases

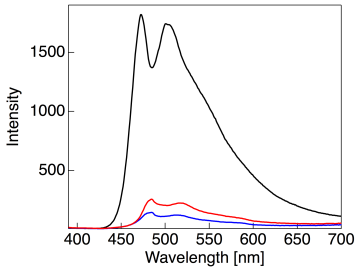
(a) **B4**



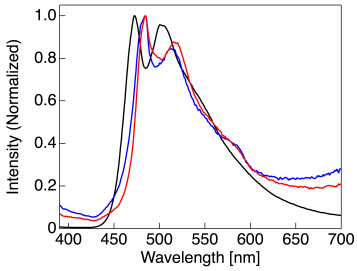
(b) **B4** (normalized)



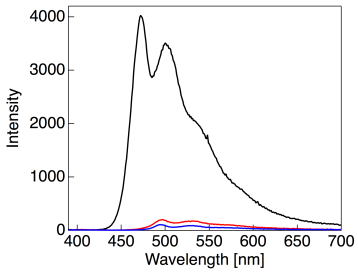
(c) **B5**



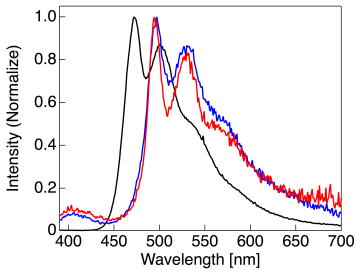
(d) **B5** (normalized)



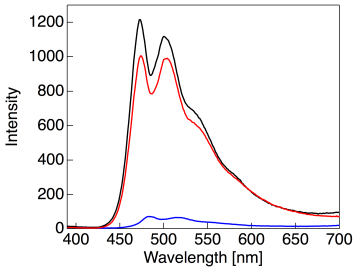
(e) **B6**



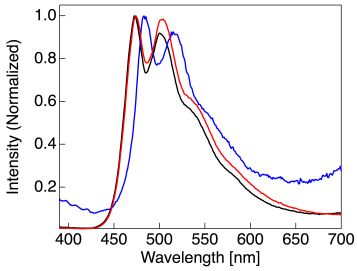
(f) **B6** (normalized)



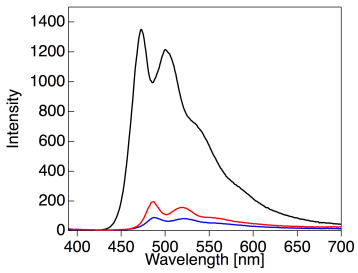
(g) **B7**



(h) **B7** (normalized)



(i) **B8**



(j) **B8** (normalized)

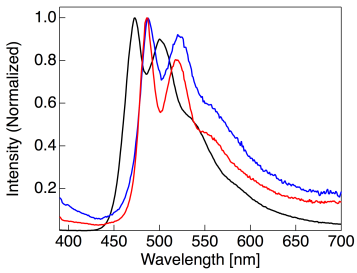


Fig. S10 Photoluminescence spectra of **B4**–**B8** in Cry_1 (black), Sme A (blue) and Cry_x phases (red).