Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Materials for:

Photoluminescent Properties of Liquid-Crystalline Gold(I) Isocyanide Complexes with a Rod-Like Molecular Structure

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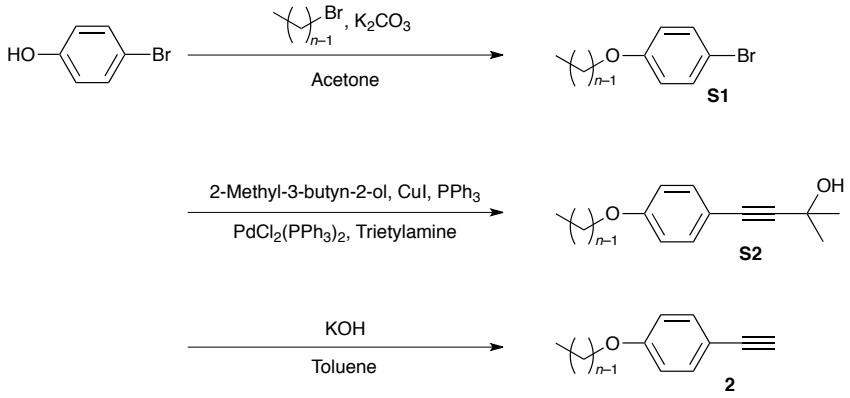
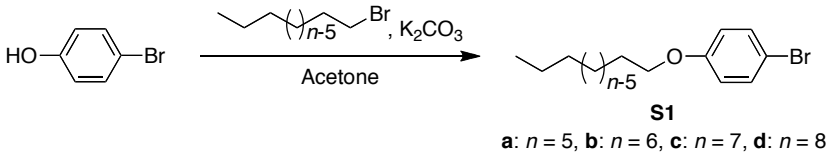
Experimental Section

General Methods and Materials. Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and were used without further purification. ^{1}H NMR spectra were recorded on a JEOL ECS-400 spectrometer at 400 MHz using the residual proton in the NMR solvent as an internal reference.

Scheme S1. Synthetic route for compound **2**.



Synthesis of S1[1]



4-bromopentyloxybenzene (S1a). 4-Bromophenol (3.0 g, 17 mmol), potassium carbonate (7.0 g, 51 mmol), and 1-bromopentane (7.7 g, 51 mmol) were added to acetone (36

mL) and refluxed for 18 h. The solid in the reaction mixture was filtered off and the filtrate was evaporated. The residue was dissolved in ethyl acetate (200 mL), washed with water (100 mL), and with brine (100 mL). The organic layer was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate (99/1)), to obtain 3.0 g (12 mmol) of the title compound in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 (dd, J = 6.9 and 1.8 Hz; 2H; 3,5-H in phenyl), 6.77 (dd, J = 6.9 and 1.8 Hz; 2H; 2,6-H in phenyl), 3.94 (t, J = 6.7 Hz; 2H; OCH_2), 1.78 (quin, J = 6.7 Hz; 2H; $OCH_2CH_2CH_2$), 1.47–1.32 (m, 4H; $OCH_2CH_2(CH_2)_2$), 0.93 (t, J = 7.1 Hz; 3H; CH_3).

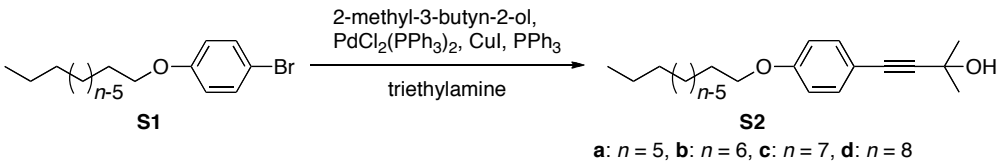
4-bromohexyloxybenzene (S1b), 4-bromoheptyloxybenzene (S1c), and **4-bromooctyloxybenzene (S1d)**. According to above procedure, compounds **S1b**, **S1c**, and **S1d** were obtained in 81%, 68%, and 90% yields, respectively.

S1b: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (dd, J = 6.9 and 1.9 Hz; 2H; 3,5-H in phenyl), 6.76 (dd, J = 7.0 and 1.9 Hz; 2H; 2,6-H in phenyl), 3.90 (t, J = 6.7 Hz; 2H; OCH_2), 1.76 (quin, J = 6.7 Hz; 2H; OCH_2CH_2), 1.52–1.28 (m, 6H; $OCH_2CH_2(CH_2)_3$), 0.90 (t, J = 6.7 Hz; 3H; CH_3).

S1c: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (dd, J = 6.7 and 2.2 Hz; 2H; 3,5-H in phenyl), 6.76 (dd, J = 6.7 and 2.2 Hz; 2H; 2,6-H in phenyl), 3.90 (t, J = 6.6 Hz; 2H; OCH_2), 1.75 (quin, J = 6.6 Hz; 2H; OCH_2CH_2), 1.49–1.23 (m, 8H; $OCH_2CH_2(CH_2)_4$), 0.88 (t, J = 6.6 Hz ; 3H; CH_3).

S1d: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 (dd, J = 6.9 and 2.2 Hz; 2H; 3,5 -H in phenyl), 6.77 (dd, J = 6.9 and 2.2 Hz, 2H; 2,6-H in phenyl), 3.91 (t, J = 6.7 Hz; 2H; OCH_2), 1.76 (quin, J = 6.8 Hz; 2H; OCH_2CH_2), 1.48–1.25 (m, 10H; $OCH_2CH_2(CH_2)_5$), 0.87 (t, J = 6.9 Hz; 3H; CH_3).

Synthesis of S2[1]



S1 **S2**

a: *n* = 5, **b**: *n* = 6, **c**: *n* = 7, **d**: *n* = 8

4-(4-Pentyloxyphenyl)-2-methylbut-3-yn-2-ol (S2a). **S1a** (1.5 g, 6.1 mmol), 2-methyl-3-butyn-2-ol (0.77 g, 9.2 mmol), bis(triphenylphosphine)palladium chloride (0.18 g, 0.18 mmol), triphenylphosphine (0.023 g, 0.12 mmol), and copper iodide (0.012 g, 0.12 mmol) were added to triethylamine (100 mL). The resultant solution was refluxed for 5 h under Ar. After the solid in the reaction mixture was removed by filtration, the reaction mixture was washed with water and brain. The organic layer was dried with anhydrous sodium sulfate and concentrated by evaporation. The crude product obtained was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 3/1), to obtain 0.65 g (2.64 mmol) of the title compound in 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (dd, J = 6.9 and 2.0 Hz; 2H; 3,5-H in phenyl), 6.81 (dd, J = 6.9 and 2.0 Hz; 2H; 2,6-H in phenyl), 3.94 (t, J = 6.8 Hz; 2H; OCH_2), 1.78 (quin, J = 6.8 Hz; 2H; OCH_2CH_2), 1.61 (s, 1H; OH), 1.62 (s, 6H; $C(CH_3)_2OH$), 1.48–1.32 (m, 4H; $OCH_2CH_2(CH_2)_2$), 0.88 (t, J = 6.9 Hz; 3H; CH_3).

4-(4-hexyloxyhexyl)-2-methylbut-3-yn-2-ol (S2b), 4-(4-heptyloxypeptyl)-2-methylbut-3-yn-2-ol (S2c), and 4-(4-octyloxyoctyl)-2-methylbut-3-yn-2-ol (S2d). According to above procedure, compounds **S2b**, **S2c**, and **S2d** were obtained in 25%, 69%, and 29% yields, respectively.

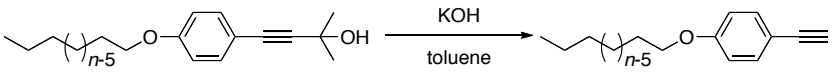
S2b: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 (dd, J = 6.8 and 2.0 Hz; 2H; 3,5-H in phenyl),

6.81 (dd, J = 6.8 and 2.0 Hz; 2H; 2,6-H in phenyl), 3.94 (t, J = 6.6 Hz; 2H; OCH_2), 1.98 (s, 1H; OH), 1.75 (quin, J = 6.6 Hz; 2H; OCH$_2$CH_2), 1.61 (s, 6H; C(CH_3)$_2$OH), 1.51–1.33 (m, 6H; OCH$_2$CH$_2$(CH_2)$_3$), 0.90 (t, J = 7.1 Hz, 3H; CH_3)

S2c: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33 (dd, J = 6.9 and 2.3 Hz; 2H; 3,5-H in phenyl), 6.81 (dd, J = 6.9 and 2.3 Hz; 2H; 2,6-H in phenyl), 3.94 (t, J = 6.7 Hz; 2H; OCH_2), 1.77 (quin, J = 6.7 Hz; 2H; OCH$_2$CH_2), 1.61 (s, 1H; OH), 1.60 (s, 6H; C(CH_3)$_2$OH), 1.47–1.24 (m , 8H; OCH$_2$CH$_2$(CH_2)$_4$), 0.89 (t, J = 7.0 Hz; 3H; CH_3)

S2d: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33 (dd, J = 6.8 and 2.1 Hz; 2H; 3,5-H in phenyl), 6.81 (dd, J = 6.8 and 1.9 Hz; 2H; 2,6-H in phenyl), 3.94 (t, J = 6.6 Hz; 2H; OCH_2), 1.77 (quin, J = 6.7 Hz; 2H; OCH$_2$CH_2), 1.62 (s, 1H; OH), 1.60 (s, 6H; C(C$\underline{H}_3$)$_2$OH), 1.48–1.25 (m, 10H; OCH$_2$CH$_2$(CH_2)$_5$), 0.88 (t, J = 6.9 Hz; 3H; CH_3)

Synthesis of 2[1]



S2 **2**

a: n = 5, **b**: n = 6, **c**: n = 7, **d**: n = 8

***p*-pentyloxyethynlbenzene (2). S2a** (550 mg, 2.2 mmol) and potassium hydroxide (510 mg, 9.1 mmol) were added to toluene (150 mL) and refluxed for 4 h. After the solid in the reaction mixture was removed by filtration, the reaction mixture was washed with water and brain. The organic layer was dried with anhydrous sodium sulfate and concentrated. The crude product obtained was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 3/1) to obtain 57 mg (0.3 mmol) of the title compound in 14% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 (dd, J = 6.8 and 2.0 Hz; 2H; 3,5-H in phenyl), 6.84 (dd, J = 6.8 and 2.0 Hz; 2H;

2,6-H in phenyl), 3.96 (t, J = 6.8 Hz; 2H; OCH_2), 3.00 (s, 1H; C≡C*H*), 1.79 (quin, J = 6.8 Hz 2H; OCH_2CH_2), 1.49–1.35 (m, 4H; $OCH_2CH_2(CH_2)_2$), 0.94 (t, J = 7.1 Hz, 3H; CH_3).

***p*-hexyloxyethynlbenzene (2b)**, ***p*-heptyloxyethynlbenzene (2c)**, and ***p*-octyloxyethynlbenzene (2d).** According to above procedure, compounds **2b**, **2c**, and **2d** were obtained in 78%, 98%, and 30% yields, respectively.

2b: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.41 (dd, J = 6.6 and 1.8 Hz; 2H; 3,5-H in phenyl), 6.83 (dd, J = 6.9 and 1.8 Hz; 2H; 2,6-H in phenyl), 3.95 (t, J = 6.6 Hz; 2H; OCH_2), 2.99 (s, 1H; C≡C*H*), 1.78 (t, J = 6.6 Hz; 2H; OCH_2CH_2), 1.47–1.31 (m, 6H; $OCH_2CH_2(CH_2)_3$), 0.90 (t, J = 7.1 Hz; 3H; CH_3)

2c: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.41 (dd, J = 6.8 and 2.0 Hz; 2H; 3,5-H in phenyl), 6.83 (dd, J = 6.8 and 2.0 Hz, 2H; 2, 6-H in phenyl), 3.95 (t, J = 6.7 Hz; 2H; OCH_2), 2.99 (s, 1H; C≡C*H*), 1.78 (quin, J = 6.7 Hz, 2H; OCH_2CH_2), 1.25–1.46 (m, 8H; $OCH_2CH_2(CH_2)_4$), 0.89 (t, J = 6.8 Hz; 3H; CH_3).

2d: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 (dd, J = 6.7 and 2.1 Hz; 2H; 3,5-H in phenyl), 6.83 (dd, J = 7.0 and 2.2 Hz; 2H; 2,6-H in phenyl), 3.95 (t, J = 6.6 Hz; 2H; OCH_2), 2.99 (s, 1H; C≡C*H*), 1.78 (quin, J = 7.1 Hz; 2H; OCH_2CH_2), 1.46–1.29 (m, 10H; $O(CH_2)_3(CH_2)_5$), 0.87 (t, J = 6.9 Hz; 3H; CH_3).

Thermal Stability of Complexes 1

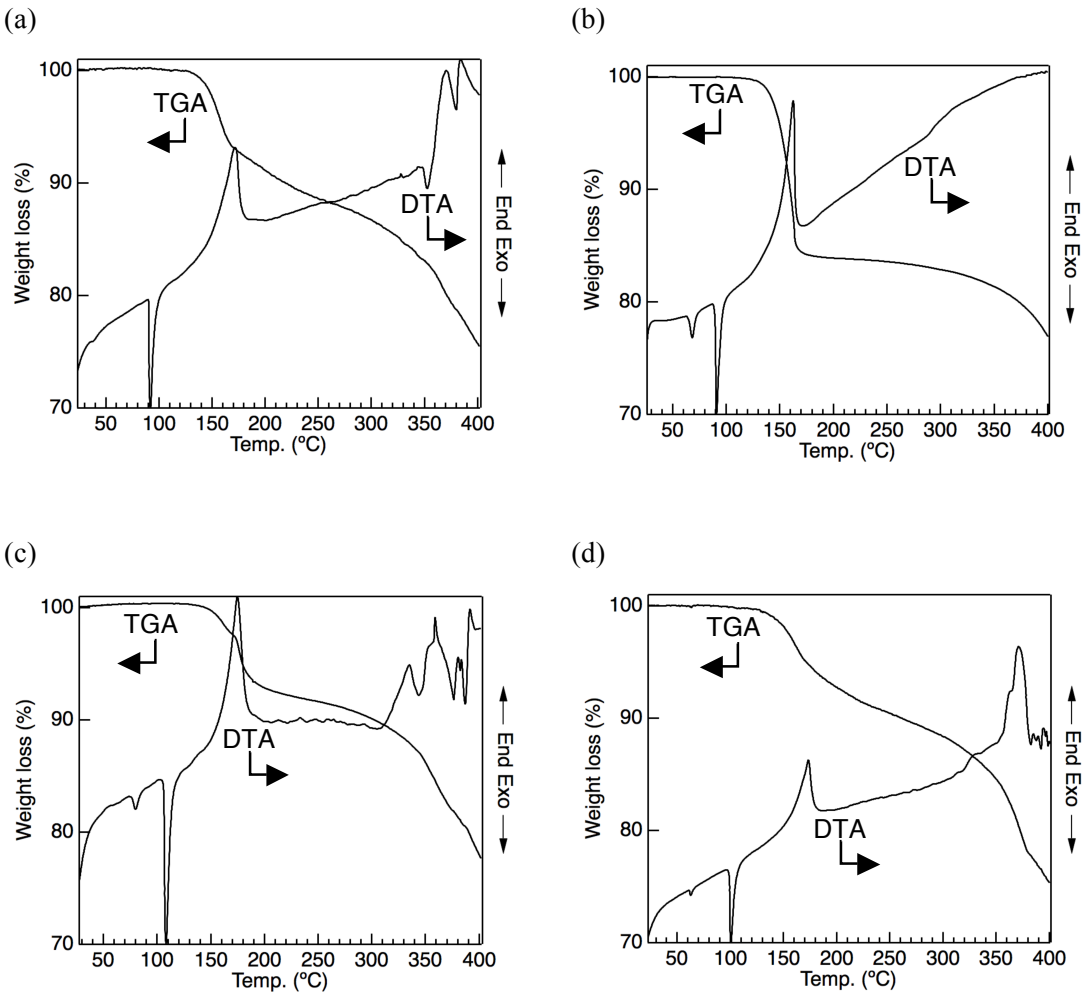


Fig. S1. TG/DTA thermogram of **1a** (a), **1d** (b), **1c** (c), and **1d** (d). Rate = 5 °C/min.

Molecular Structure of Complexes 1 Obtained from Single Crystal X-ray Structural Analysis

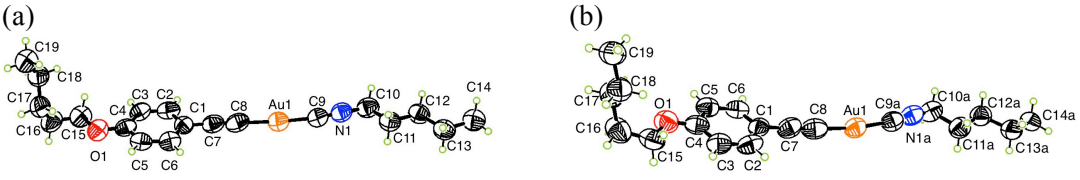


Fig. S2. Crystal structure of **1a:** (a) the major and (b) minor components of the disordered isocyanide ligand (C9≡N1-C10-C11-C12-C13-C14) are shown.

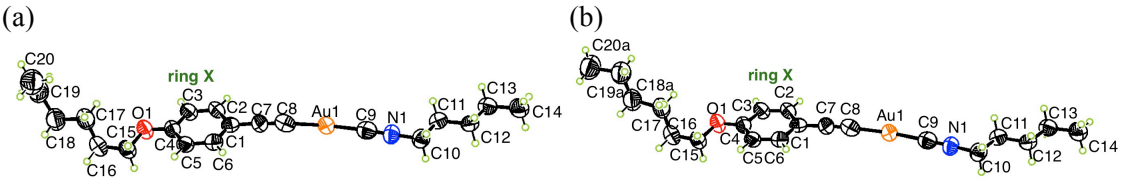


Fig. S3. Crystal structure of **1b:** (a) the major and (b) minor components of the disordered alkoxy chain (C18-C19-C20) are shown.

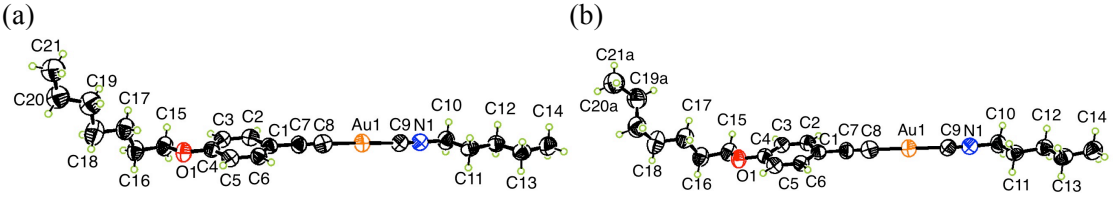


Fig. S4. Crystal structure of **1c:** (a) the major and (b) minor components of the disordered alkoxy chain (C19-C20-C21) are shown.

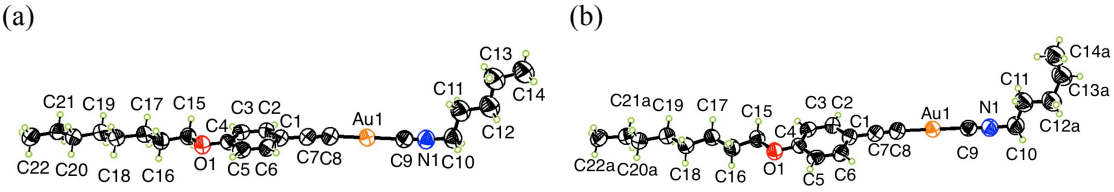


Fig. S5. Crystal structure of **1d:** (a) the major and (b) minor components of the disordered isocyanide ligand (C12-C13-C14) and alkoxy chain (C20-C21-C22) are shown.

Crystal Packing Structure of 1d

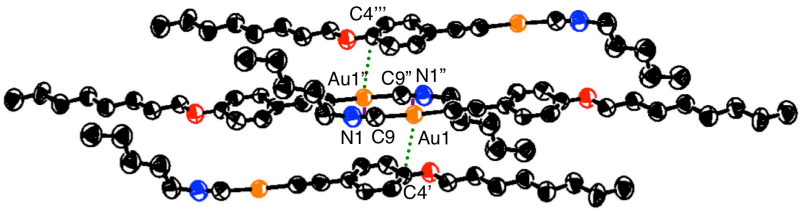


Fig. S6. Crystal packing structure of **1d**. H atoms were omitted for clarity, and only main components of the disordered alkyl chain are shown.
Selected interatomic distance: Au1–Au1'' = 4.837(1) Å, Au1–C4' = Au1''–C4''' = 3.6866(6) Å, Au1–centroid of C9''–N1'' bond = 3.523 Å.

Table S1. Crystal data of complexes **1**.

	1a	**1b**	**1c**	**1d**
Empirical formula	$C_{19}H_{26}AuNO$	$C_{20}H_{28}AuNO$	$C_{21}H_{30}AuNO$	$C_{23}H_{32}AuNO$
Formula weight	481.39	495.4	509.43	523.46
Temperature (K)	293	296	296	296
Color, Habit	colorless, block	colorless, plate	colorless, plate	colorless, plate
Crystal size (mm)	0.10 × 0.10 × 0.10	0.44 × 0.18 × 0.04	0.87 × 0.40 × 0.08	0.64 × 0.22 × 0.05
Crystal system	triclinc	triclinc	triclinc	triclinc
$R[F^2 > 2\sigma(F^2)]$	0.059	0.045	0.037	0.047
w$R(F^2)$	0.174	0.125	0.099	0.132
S	1.14	1.18	1.15	1.01
Space group	*P*-1	*P*-1	*P*-1	*P*-1
Z	2	2	2	2
a (Å)	7.7081 (9)	7.3596 (8)	7.4166 (8)	8.9221 (16)
b (Å)	8.6036 (9)	9.8116 (2)	9.7574 (17)	9.6174 (11)
c (Å)	15.1979 (18)	13.9641 (2)	14.4580 (17)	13.6118 (19)
α (degree)	86.966(6)	89.373 (7)	90.711 (13)	76.298 (10)
β (degree)	80.202 (6)	88.527 (9)	90.313 (11)	77.979 (13)
γ (degree)	69.316 (5)	83.285 (6)	97.749 (11)	87.684 (13)
V (Å^3)	929.14 (19)	1001.06(16)	1036.6 (2)	1109.8 (3)

Thermodynamic Properties of Complexes 1

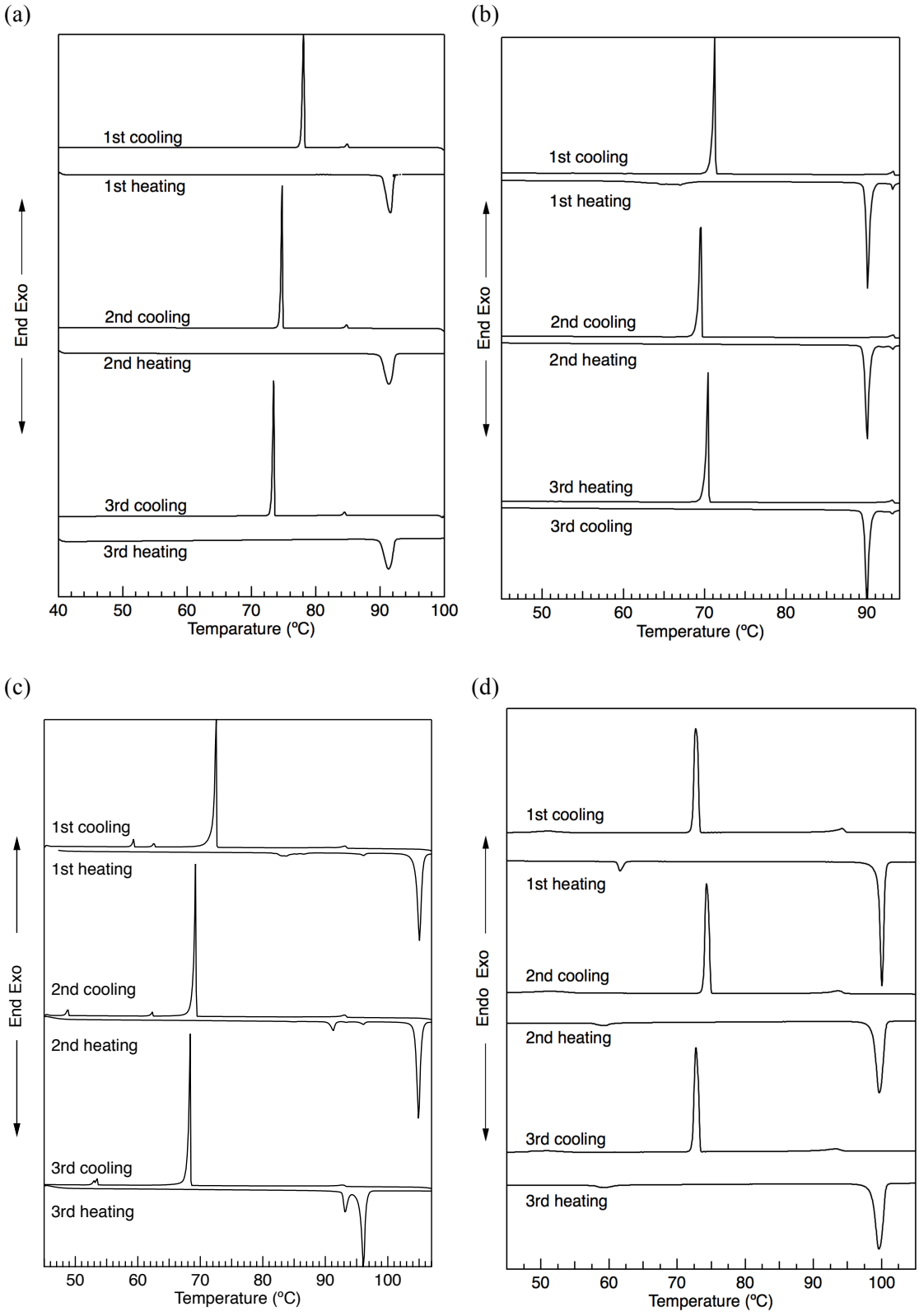


Fig. S7. DSC thermogram of **1a** (a), **1b** (b), **1c** (c) and **1d** (d). Rate = 5 ºC/ min.[2)]

Absorption Spectroscopy of 1

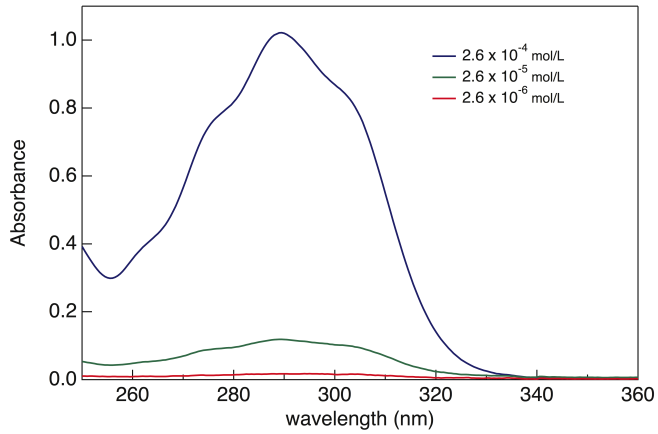


Fig. S8. Concentration dependence of absorption spectrum in **1c** in dichloromethane solution. The concentration of the solution was indicated in the figure. The spectra were measured with quartz cell with 1-mm optical path length.

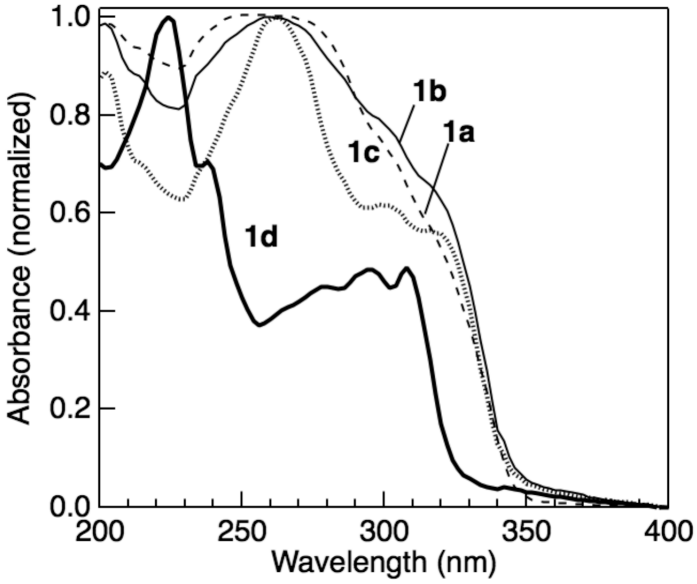


Fig. S9. Normalized UV-Vis absorption spectra of **1** in crystalline phase.

Luminescence Spectroscopy of 1

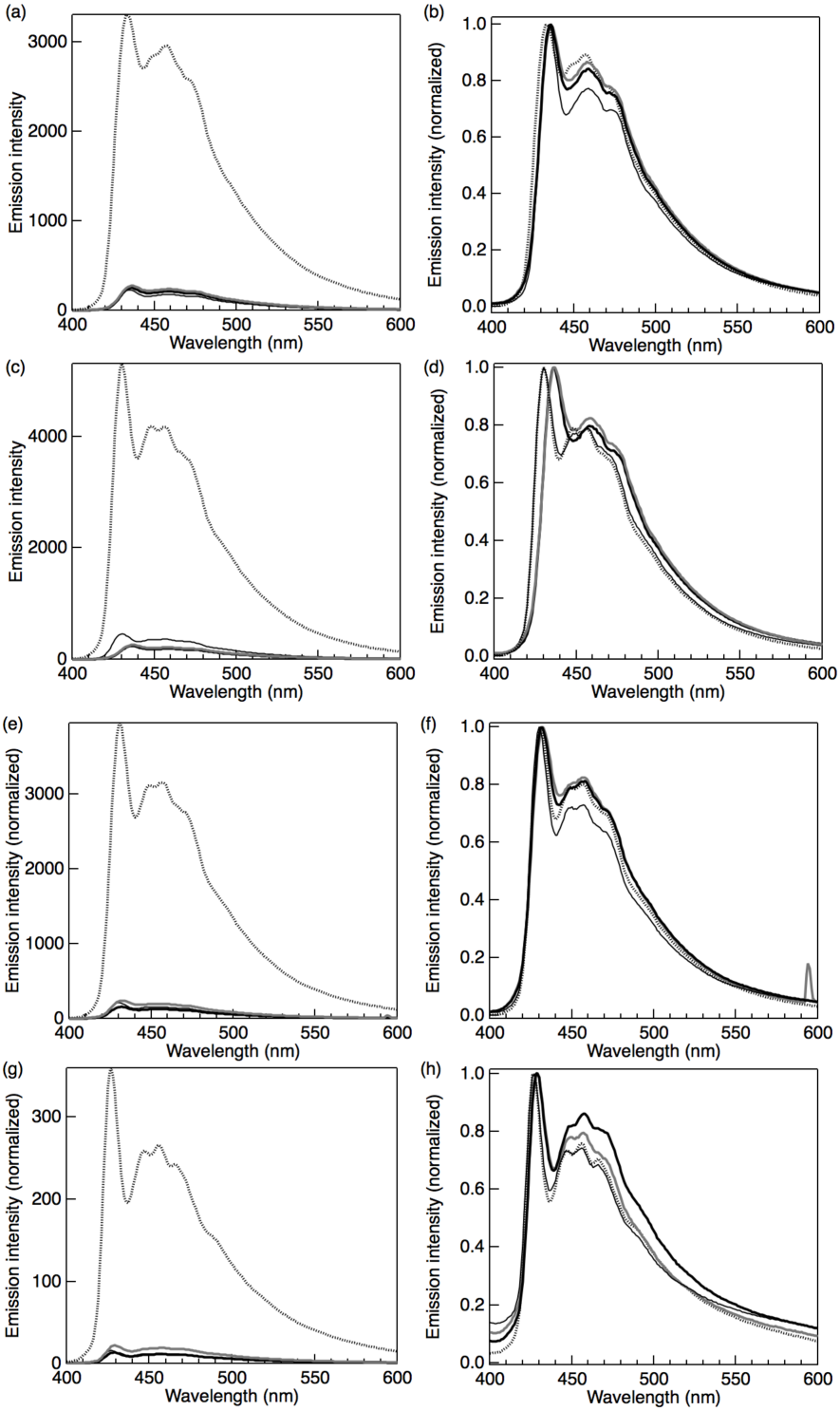


Fig. S10. Emission (right: λ_{ex} = 340 nm) of **1a** (a, b), **1b** (c, d), **1c** (e, f), and **1d** (λ_{ex} = 324 nm, g, h) in crystalline phase (dotted), in LC, and in isotropic phase (gray).

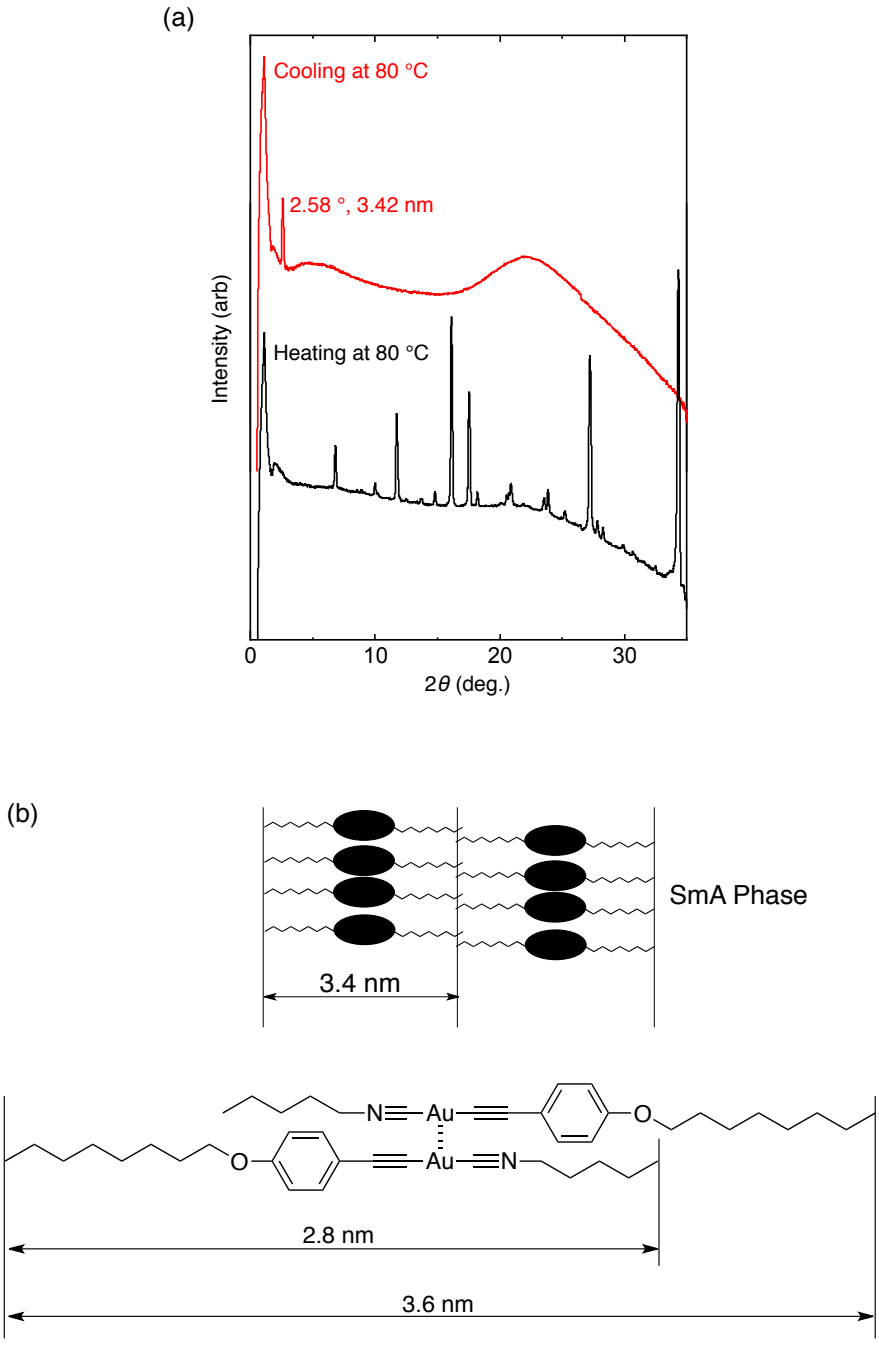


Fig. S11. (a), XRD patterns in **1d** at 80 °C on heating (crystalline phase) and cooling process (smectic liquid-crystalline phase); (b), plausible packing structure of molecules in the smectic phase (top), and molecular length of **1d** (bottom). The molecular length was estimated from the molecular structure obtained by single crystal X-ray analysis.

References and Notes

(1) Vasconcelos, U.B.; Schrader, A.; Vilela, G.D.; Borges, A.C.A.; Merlo, A.A. *Tetrahedron* **2008**, *64*, 4619.

(2) The DSC thermograms of complex **1c** (Fig. S7(c)) is not completely consistent in each scan, because non-negligible thermal decomposition of the complexe took place during the scan cycle.