Electronic Supplementary Information

Cholesterol-Aided Construction of Distinct Self-Organized Materials from Luminescent Gold(I)-Isocyanide Complex Exhibiting Mechanochromic Luminescence

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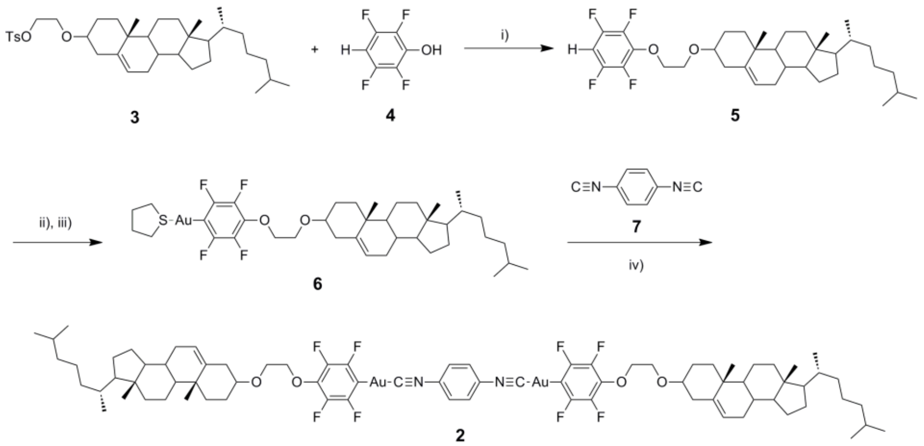
Materials and Methods

Column chromatography was performed using 63–210 μm silica gel. All other commercially available reagents and solvents were of reagent grade and used without further purification. The solvents for the preparation of the aggregates were all spectral grade and used without further purification. ^{1}H NMR spectra were recorded on a JEOL LA400 or a BRUKER-DPX 300 spectrometer and chemical shifts are reported in ppm (δ) with the signal of TMS as internal standard. High-resolution mass spectrum was recorded on JEOL JMS-T100LP at the Center for Instrumental Analysis, Hokkaido University. Fluorescence spectra were recorded on a JASCO FP6600 spectrofluorometer, respectively. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Samples for the IR measurements were carefully sandwiched with KBr plates to avoid mechano-induced phase change. The absence of the phase change was confirmed by checking the emission colors of the samples. Circular dichroism spectra were recorded on a JASCO J840 spectropolarimeter. Powder X-ray diffraction analysis was carried out with a Rigaku Rint-2200 X-ray diffractometer with monochromated CuKa radiation. All X-ray diffraction experiments were performed at room temperature. Scanning electron microscopic images were acquired by using JEOL JSM-6330F field emission scanning electron microscopy. Samples were drop-cast on silicon substrate, dried in vacuo for 12 h, and sputtered with Os using Meiwafosis Neoc Pure Osmium Coater before observation.

Synthesis and characterization

Gold(I)-isocyanide complex **2** were synthesized according to Scheme S1. Synthesis of compounds **3**[S1] and **7**[S2] were reported previously.



Scheme S1. i) K_2CO_3, DMF, 65 °C, 4 h; ii) *t*-BuLi, THF, −78 °C to −30 °C, 12 h; iii) chloro gold(I)(tetrahydrothiophene), room temperature; iv) CH_2Cl_2, 5 h.

Synthesis of 5: Compound **3** (0.59 g, 1.0 mmol), 2,3,5,6-tetrafluorophenol (**4**, 0.17 g, 1.0 mmol) and K_2CO_3 (1.54 g, 10 mmol) were mixed in dry DMF (15 mL) and the solution was refluxed for 6h at 65 °C. The resultant mixture was diluted with $CHCl_3$, and washed with H_2O and brine. The combined organic layer was dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: $CHCl_3$) to give **5** as a white solid (0.45 g, 0.78 mmol, 78 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.67 (s, 3H), 0.85-2.35 (m, 41H), 3.06-3.24 (m, 1H), 3.80 (t, 2H, J = 9 Hz), 4.36 (t, 2H, J = 9 Hz), 5.34-5.36 (d, 1H), 6.70-6.82 (m, 1H).

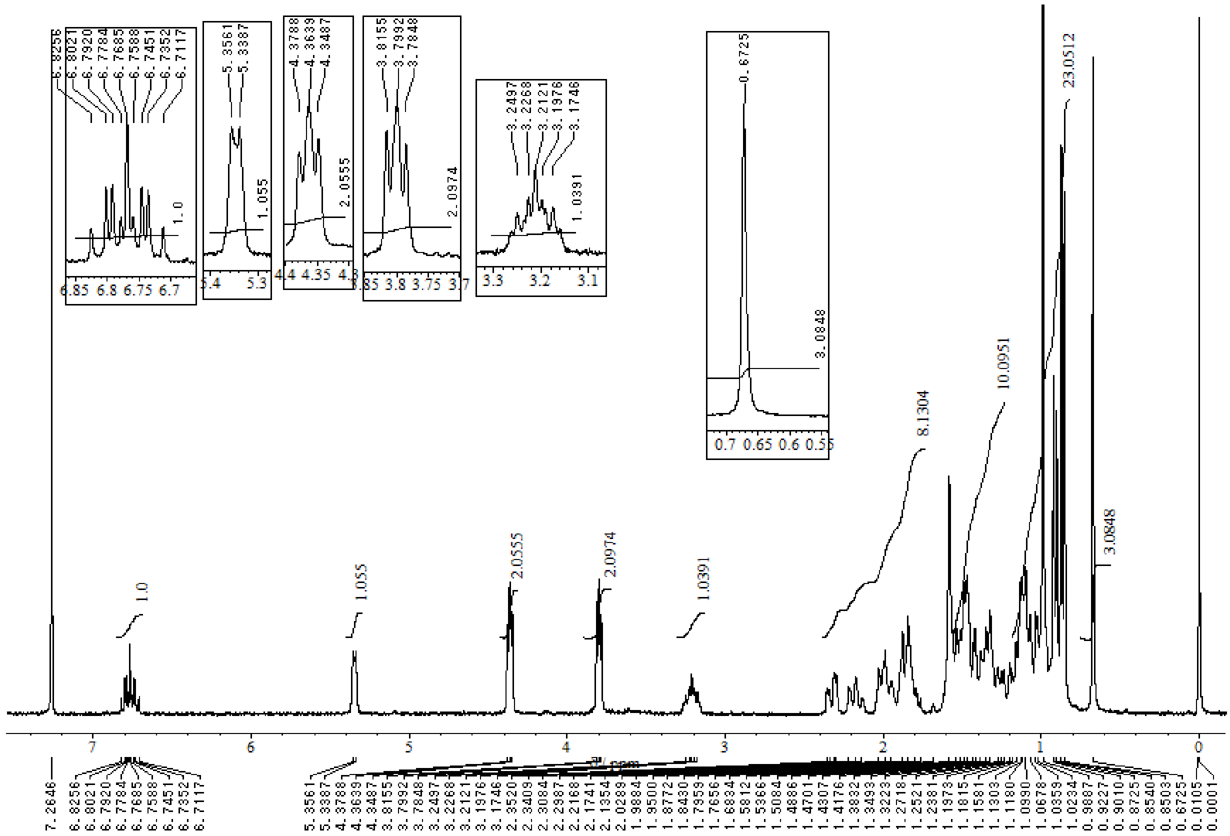


Chart S1. ^{1}H NMR spectrum of **5** in $CDCl_3$.

Synthesis of 2: To a THF (20 mL) solution of **5** (0.45 g, 0.78 mmol), *t*-BuLi (1.72 M in pentane, 1.1 mL, 1.9 mmol) was added dropwise at −78 °C under N_2 atmosphere. The mixture was stirred for 0.5 h at −78 °C and for 12 h at −30 °C, and cooled again to −78 °C. To this solution, chlorogold(I)(tetrahydrothiophene) (250 mg, 0.78 mmol) was added in portions. The reaction mixture was allowed to warm to room temperature and added by a few drops of water. After addition of Na_2SO_4, the mixture was passed through a Florisil column (ID: 20 mm; length: 100-mm) and the elution was evaporated under reduced pressure with a rotary evaporator to give dark purple liquid of crude **6**. The crude mixture of **6** was dissolved in CH_2Cl_2 (20 mL), and then **7** (50 mg, 0.39 mmol) was added to the solution. After stirred for 5 h at room temperature, the mixture was washed with water, and combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: toluene→$CHCl_3$) to give **2** as a white solid (290 mg, 0.17 mmol, 44 % yield). This compound was decomposed upon heating over 150 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 0.68 (s, 6H), 0.86-2.38 (m, 82H), 3.20-3.27 (m, 2H), 3.79 (t, 4H, J = 9.6 Hz), 4.29 (t, 4H, J = 9.6 Hz), 5.36 (d, 2H), 7.77 (s, 4H). MS (ESI): *m/z* calcd for $C_{78}H_{103}O_4N_2Au_2F_8$ 1677.71157 [MH^+], found 1677.71711.

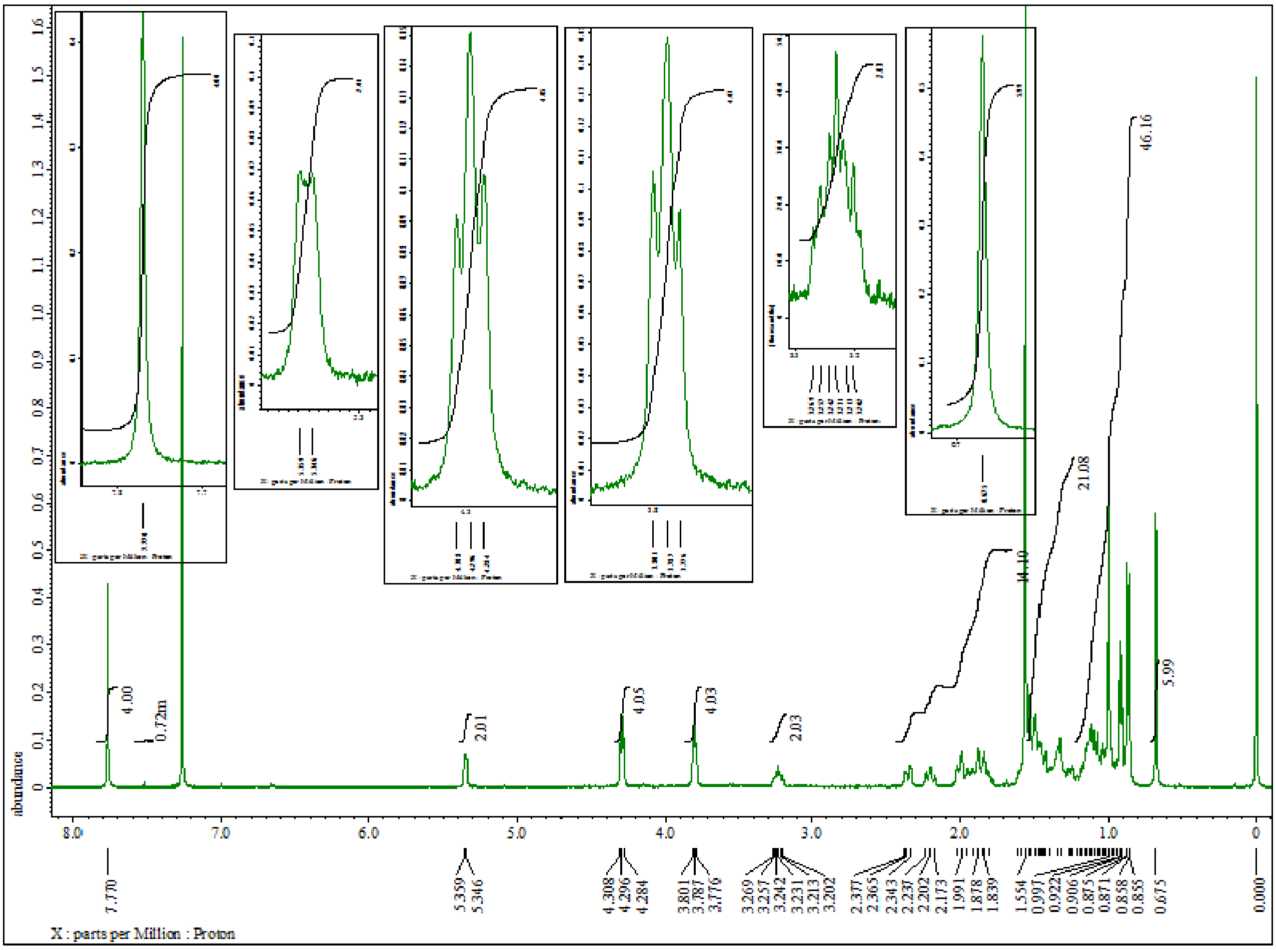


Chart S2. ^{1}H NMR spectrum of **2** in $CDCl_3$.

Supplementary Figures

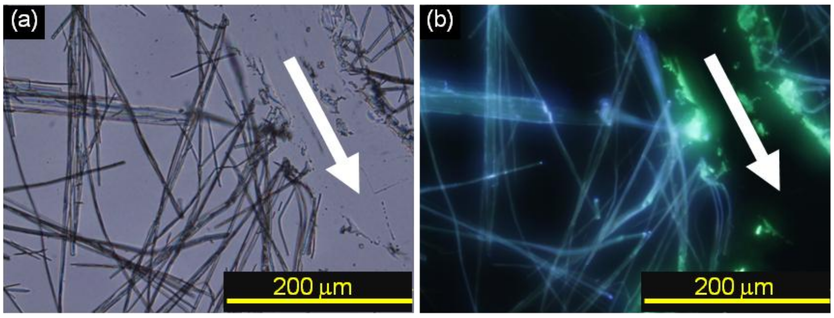


Fig. S1 (a) Optical microscopy (OM) and (b) fluorescence optical microscopy (FLOM) images of fibrous microstructures of **2** upon grinding with spatula along to the white arrow.

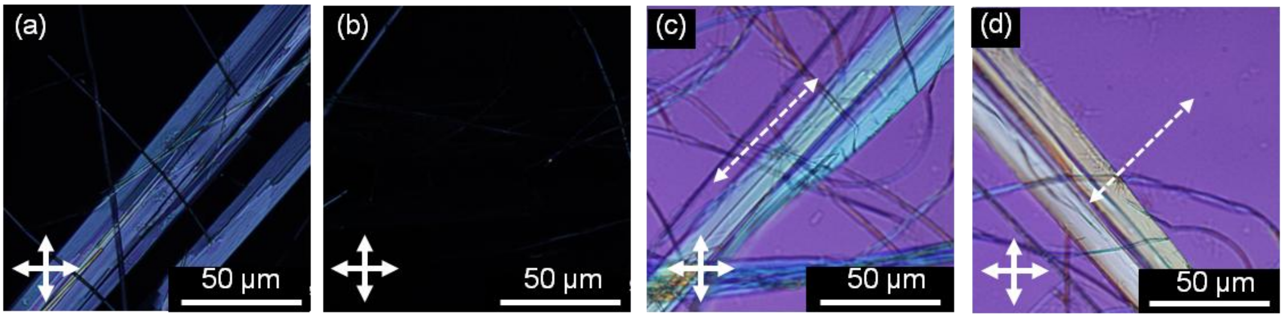


Fig. S2 (a,b) POM images of a microbelt of **2** oriented (a) 45° and (b) parallel to the polarizer. (c,d) POM images of a microbelt oriented (c) parallel and (d) perpendicular to the slow axis (dotted arrows) of a 530-nm retardation plate.

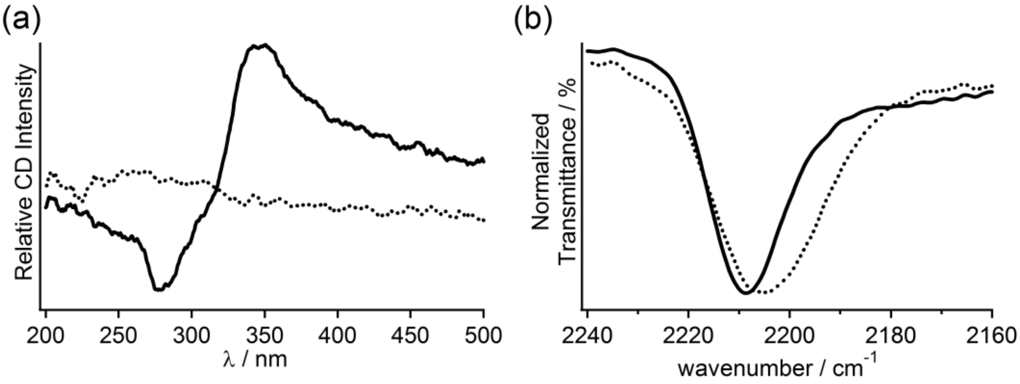


Fig. S3 (a) CD and (b) IR spectra of unground (solid line) and ground (dotted line) powder of **2**.

Supporting References

[S1] A. Bajaj, P. Kondiah, S. Bhattacharya, *J. Med. Chem.*, 2007, **50**, 2432–2442.

[S2] A. Efraty, I. Feinstein, L. Wackerle, A. Goldman, *J. Org. Chem.*, 1980, **45**, 4059–4061.