Supplementary Material (ESI) for Chemical Communications

Supplementary Information

for

Stable Supramolecular Helical Structure of C_6-Symmetric Hydrogen-Bonded Hexakis(phenylethynyl)benzene Derivatives with Amino Acid Pendant Groups and Their Unique Fluorescence Properties

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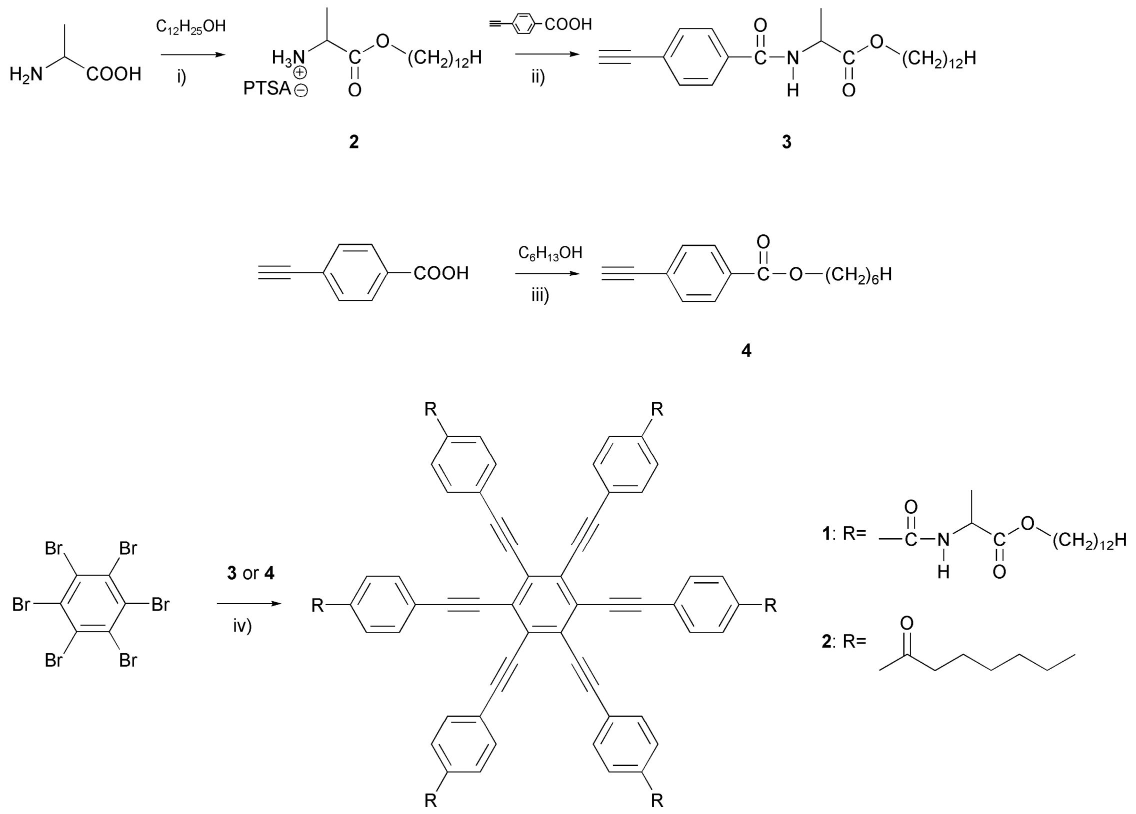
1. Instruments and Materials

Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-A400 (400, 100 MHz) or a JEOL ECA-600 (600, 150 MHz) in $CDCl_3$. Chemical shifts of ^{1}H and ^{13}C are reported in δ values referred respectively to tetramethylsilane and $CDCl_3$ as internal standards. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University. Optical rotations were measured in a 5-cm cell using an Otsuka Electronics PM-201A polarimeter. IR spectra were recorded with a Jasco FT-IR-460 Plus / IRT-30 spectrophotometer. UV-visible absorption (UV-vis) and circular dichroism (CD) spectra were measured using a Hitachi U-4000S spectrophotometer and a Jasco J-820P spectropolarimeter, respectively. The temperature was controlled with a Komatsu Electronics SPR-7 for UV-vis spectral measurements and a Jasco PTC-423L apparatus for CD spectral measurements. Fluorescence (FL) spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. The temperature was controlled with a Komatsu Electronics CTE32 apparatus.

Materials. Unless otherwise noted, reagents were commercially available and used without purification. Dehydrated chloroform ($CHCl_3$), L-alanine and D-alanine were purchased from Wako Pure Chemical Industries, Ltd. 1-dodecanol, 1-hexanol and triethylamine (TEA) were obtained from Kishida Chemical Co., Ltd. TEA was distilled over calcium hydride. Ethyl 4-iodobenzoate, (trimethylsilyl)acetylene, hexabromobenzene, bis(triphenylphosphine)palladium dichloride ($Pd(PPh_3)_2Cl_2$), copper(I) iodide (CuI), triphenylphosphine (PPh_3), *p*-toluenesulfonic acid monohydrate (PTSA), *N*,*N'*-Dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole monohydrate (HOBt) were from Tokyo Chemical Industry Co., Ltd. Silica gel used for column chromatography was Silica gel C-200 from Wako. 4-Ethynylbenzoic acid was prepared according to a previously reported method.[1] The new compounds were prepared by the synthesis outlined in Scheme 1.



Scheme 1 Synthesis of the hexakis(phenylethynyl)benzene derivatives: i) PTSA, toluene; ii) HOBt, DCC, TEA, $CHCl_3$; iii) $SOCl_2$; iv) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, TEA.

D-Alanine Dodecyl Ester *p*-Toluenesulfonate (D-**2**). A mixture of D-alanine (3.20 g, 35.9 mmol), 1-dodecanol (7.64 g, 41.0 mmol) and PTSA (7.51 g, 39.5 mmol) in toluene (30 mL) was refluxed overnight using Dean–Stark trap. After the evaporation of the solvent, the residue was washed with diethyl ether. After filtration, the white solid was recrystallized from *n*-hexane. Yield 8.31 g (54 %). ^{1}H NMR (400 MHz, rt): δ 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.23-1.32 (m, 18H, CH_2), 1.45 (d, *J* = 7.2 Hz, 3H, C*CH_3), 1.51-1.55 (m, 2H, $OCH_2C\underline{H_2}$), 2.35 (s, 3H, PTSA-), 3.95-4.09 (m, 3H, C*H and OCH_2), 7.14 (d, *J* = 8.4 Hz, 2H, PTSA-), 7.75 (d, *J* = 8.4 Hz, 2H, PTSA-), 8.19 (s, 3H, NH_3+).

L-Alanine Dodecyl Ester *p*-Toluenesulfonate (L-**2**). The other enantiomer L-**2** was also obtained in the same way as that described for D-**2** (60 % yield). ^{1}H NMR (400 MHz, rt): δ 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.22-1.31 (m, 18H, CH_2), 1.44 (d, *J* = 7.2 Hz, 3H, C*CH_3), 1.50-1.54 (m, 2H, $OCH_2C\underline{H}_2$), 2.34 (s, 3H, PTSA-), 3.96-4.07 (m, 3H, C*H and OCH_2), 7.13 (d, *J* = 8.4 Hz, 2H, PTSA-), 7.75 (d, *J* = 7.6 Hz, 2H, PTSA-), 8.15 (s, 3H, NH_3+).

4-Ethynylbenzoyl-D-Alanine Dodecyl Ester (D-**3**).[2] After HOBt (1.79 g, 11.7 mmol) and DCC (2.41 g, 11.7 mmol) were added to a dispersion solution of 4-ethynylbenzoic acid (1.62 g, 11.1 mmol) and D-**2** (5.01 g, 11.7 mmol) in dehydrated $CHCl_3$ (35 mL) at ambient temperature (20 - 25 ˚C), TEA (1.7 ml) was added to the mixture. The solution was stirred at ambient temperature (20 - 25 ˚C) for 3 days. After filtration, the solvent was removed under reduced pressure. The residue was recrystallized from *n*-hexane. The crude product was purified by silica gel chromatography with $CHCl_3$ as the eluent and then recrystallized from *n*-hexane to give a white crystalline solid (2.30 g, 54 %). Mp 72.7-74.0 °C. ^{1}H NMR (400 MHz, rt): δ 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.26-1.37 (m, 18H, CH_2), 1.53 (d, *J* = 7.2 Hz, 3H, C*CH_3), 1.63-1.70 (m, 2H, $OCH_2C\underline{H}_2$), 3.20 (s, 1H, ≡CH), 4.13-4.23 (m, 2H, OCH_2), 4.74-4.81 (m, 1H, C*H), 6.76 (d, *J* = 6.8 Hz, 1H, NH), 7.56 (d, *J* = 8.8 Hz, 2H, aromatic protons), 7.76 (d, *J* = 8.4 Hz, 2H, aromatic protons). ^{13}C NMR (100 MHz, rt): δ 14.11, 18.76, 22.68, 25.79, 28.51, 29.17, 29.33, 29.48, 29.54, 29.61, 31.89, 48.64, 65.88, 79.55, 82.71, 125.57, 126.99, 132.29, 133.95, 165.86, 173.22. Anal. Calcd (%) for $C_{24}H_{35}NO_3$: C, 74.77; H, 9.15; N, 3.63. Found: C, 74.64; H, 9.35; N, 3.43. $[\alpha]_D^{rt}$ -36.0° (*c* 1.00 in $CHCl_3$).

4-Ethynylbenzoyl-L-Alanine Dodecyl Ester (L-**3**). The other enantiomer L-**3** was also obtained in the same way as that described for D-**3** (59 % yield). Mp 72.1-73.9 °C. ^{1}H

NMR (400 MHz, rt): δ 0.88 (t, *J* = 7.0 Hz, 3H, CH_3), 1.26-1.36 (m, 18H, CH_2), 1.53 (d, *J* = 7.2 Hz, 3H, C^*CH_3), 1.63-1.70 (m, 2H, $OCH_2C\underline{H}_2$), 3.20 (s, 1H, ≡CH), 4.13-4.23 (m, 2H, OCH_2), 4.74-4.81 (m, 1H, C*H), 6.76 (d, *J* = 6.8 Hz, 1H, NH), 7.56 (d, *J* = 8.4 Hz, 2H, aromatic protons), 7.77 (d, *J* = 8.4 Hz, 2H, aromatic protons). Anal. Calcd (%) for $C_{24}H_{35}NO_3$: C, 74.77; H, 9.15; N, 3.63. Found: C, 74.86; H, 9.10; N, 3.60. $[\alpha]_D^{rt}$ +36.2° (*c* 1.00, $CHCl_3$).

Hexakis[4-((*R*)-1-(dodecyloxycarbonyl)ethylcarbamoyl)phenylethynyl]benzene (D-**1**).[3] A mixture of D-**3** (1.98 g, 5.14 mmol), hexabromobenzene (289 mg, 0.524 mmol), $Pd(PPh_3)_2Cl_2$ (66 mg, 0.094 mmol), CuI (66 mg, 0.35 mmol) and PPh_3 (133 mg, 0.507 mmol) in TEA (40 mL) was refluxed under nitrogen. After 8 days, hexabromobenzene (140 mg, 0.254 mmol) was added to the reaction mixture and the stirring under reflux was continued for another 8 days. After cooling to room temperature, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$ (100 ml) and then the dark brown solution was washed twice with 0.2 N HCl (100 ml), three times with brine (250 ml), dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was thoroughly washed with dichloromethane, ethyl acetate and acetone. A residual yellow solid was dried and then dissolved in a small amount of $CHCl_3$. An orange brown viscous solid (629 mg, 34 %) was obtained by casting from this solution. Decomp. Temp. approximately 250 °C. IR (cast film from a *n*-dodecane solution, cm^{-1}): 3255 (amide A), 2923, 2853, 2197w (C≡C), 1749 (C=O ester), 1633 (amide I), 1534 (amide II), 1458, 1346, 1330, 1274, 1203, 1173 (C(=O)-O-C). ^1H NMR (600 MHz, 40 °C, 100.0 mg ml^{-1}): δ 0.88 (t, *J* = 6.9 Hz, 3H, CH_3), 1.27-1.40 (m, 18H, CH_2), 1.63 (d, *J* = 7.6 Hz, 3H, C^*CH_3), 1.68-1.74 (m, 2H, $OCH_2C\underline{H}_2$), 4.14-4.26 (m, 2H, OCH_2), 4.71-4.76 (m, 1H, C*H), 7.00 (br, 2H, aromatic protons), 7.25 (br, 2H, aromatic protons), 7.76 (br, 1H, NH). ^{13}C NMR (150 MHz, 40 °C, 100.0 mg ml^{-1}): δ 14.08, 17.67, 22.71, 26.03, 28.79, 29.40, 29.44, 29.68, 29.71, 29.75, 31.97, 49.10, 65.48, 89.74 (C≡C), 98.84 (C≡C), 126.21, 127.30,[4] 131.36, 134.28, 167.61, 172.96. Anal. Calcd (%) for $C_{150}H_{204}N_6O_{18}$: C, 75.72; H, 8.64; N, 3.53. Found: C, 75.93; H, 8.87; N, 3.40. $[\alpha]_D^{rt}$ +4.2° (*c* 1.00, CHCl$_3$).

Hexakis[4-((*S*)-1-(dodecyloxycarbonyl)ethylcarbamoyl)phenylethynyl]benzene (L-**1**). The other enantiomer L-**1** was also obtained in the same way as that described for D-**1** (42 % yield). Decomp. Temp. approximately 250 °C. IR (cast film from a *n*-dodecane solution, cm^{-1}): 3257 (amide A), 2923, 2853, 2197w (C≡C), 1750 (C=O ester), 1633 (amide I), 1535 (amide II), 1459, 1346, 1330, 1274, 1203, 1172 (C(=O)-O-C). ^{1}H NMR (600 MHz, 40 °C, 100.0 mg ml^{-1}): δ 0.88 (t, J = 6.9 Hz, 3H, CH$_3$), 1.27-1.40 (m, 18H, CH$_2$), 1.63 (d, J = 6.9 Hz, 3H, C*CH$_3$), 1.69-1.73 (m, 2H, $OCH_2C\underline{H}_2$), 4.14-4.26 (m, 2H, OCH$_2$), 4.71-4.76 (m, 1H, C*H), 7.00 (br, 2H, aromatic protons), 7.25 (br, 2H, aromatic protons), 7.74 (br, 1H, NH). ^{13}C NMR (150 MHz, 40 °C, 100.0 mg ml^{-1}): δ 14.09, 17.67, 22.71, 26.03, 28.79, 29.40, 29.44, 29.68, 29.71, 29.75, 31.97, 49.10, 65.48, 89.73 (C≡C), 98.83 (C≡C), 126.21, 127.30,[4] 131.36, 134.29, 167.60, 172.95. Anal. Calcd (%) for $C_{150}H_{204}N_6O_{18}$: C, 75.72; H, 8.64; N, 3.53. Found: C, 75.74; H, 8.58; N, 3.49. $[\alpha]_D^{rt}$ -4.4° (*c* 1.00, CHCl$_3$).

4-Ethynylbenzoic Acid Hexyl Ester (**4**).[5] To a stirred solution of 4-ethynylbenzoic acid (1.38 g, 9.44 mmol) in 1-hexanol (12.28 g, 120.2 mmol) was added thionyl chloride (3.67 g, 31.1 mmol) dropwise at room temperature. After the reaction mixture was refluxed for 27 hours, 1-hexanol and thionyl chloride were distilled out under reduced pressure. The residue was recrystallized from acetone to give a brown crystalline solid

(0.99 g, 45 %). Mp 48.1-49.4 °C. ^{1}H NMR (400 MHz, rt): δ 0.90 (t, *J* = 6.8 Hz, 3H, CH_3), 1.26-1.44 (m, 6H, CH_2), 1.73-1.80 (m, 2H, $OCH_2C\underline{H}_2$), 3.22 (s, 1H, ≡CH), 4.31 (t, *J* = 6.6 Hz, 2H, OCH_2), 7.55 (d, *J* = 8.0 Hz, 2H, aromatic protons), 8.00 (d, *J* = 8.4 Hz, 2H, aromatic protons). ^{13}C NMR (100 MHz, rt): δ 13.99, 22.53, 25.67, 28.62, 31.43, 65.37, 79.92, 82.83, 126.57, 129.39, 130.50, 132.02, 165.97.

Hexakis[4-(hexyloxycarbonyl)phenylethynyl]benzene (**2**). The ester compound **2** was also obtained in the same way as that described for D-**1** except for the purification. After the crude product was exhaustively washed with acetone, the residue was purified by silica gel chromatography with $CHCl_3$ as the eluent to give a yellow powder in 30 % yields. Decomp. Temp. approximately 300 °C. ^{1}H NMR (400 MHz, rt, 10.0 mg ml^{-1}): δ 0.92 (t, *J* = 6.8 Hz, 3H, CH_3), 1.25-1.47 (m, 6H, CH_2), 1.77-1.82 (m, 2H, $OCH_2C\underline{H}_2$), 4.34 (t, *J* = 6.6 Hz, 2H, OCH_2), 7.63 (d, *J* = 7.8 Hz, 2H, aromatic protons), 8.03 (d, *J* = 7.8 Hz, 2H, aromatic protons). ^{13}C NMR (100 MHz, rt, 10.0 mg ml^{-1}): δ 14.02, 22.54, 25.69, 28.64, 31.46, 65.53, 89.22 (C≡C), 99.22 (C≡C), 127.02, 127.74, 129.70, 130.81, 131.56, 165.83. Anal. Calcd (%) for $C_{96}H_{102}O_{12}$: C, 79.64; H, 7.10. Found: C, 79.93; H, 7.18.

2. UV-Vis, CD and FL Measurements (Figures 2 - 4 and S1 - S3)

Solutions (4.20×10^{-5} M) of hexakis(phenyletynyl)benzene derivatives were prepared in 100-mL flasks equipped with stopcocks, and UV-vis and CD spectra were measured in a 1-mm cell. Aliquots (5.0 ml) of the solutions were transferred to 50-mL flasks equipped with stopcocks and diluted, and then UV-vis and CD spectra of the solutions (4.20×10^{-6} M) were measured in a 1-cm cell. The more diluted solutions (4.20×10^{-7} M) were prepared in the same method as that described for the 4.20×10^{-6}

M solutions, and then UV-vis, CD and FL spectra of the 4.20×10^{-7} M solutions were measured in a 1-cm cell. Fluorescence quantum yields were determined relative to 9,10-diphenylanthracene ($\phi = 0.84$ in benzene).[6] In addition, the 4.20×10^{-4} M solutions of L-**1** and D-**1** in *n*-dodecane and 1,1,2,2-tetrachloroethane (TCE) were prepared in 50-mL flasks equipped with stopcocks, and UV-vis and CD spectra were measured in a 0.1-mm cell, and IR spectra were measured in a 1-mm cell.

3. References and Notes

S1. (a) E. Yashima, T. Matsushima and Y. Okamoto, *J. Am. Chem. Soc.*, 1997, **119**, 6345-6359; (b) M. A. Saito, K. Maeda, H. Onouchi and E. Yashima, *Macromolecule*s, 2000, **33**, 4616-4618.

S2. K. Okoshi, K. Sakajiri, J. Kumaki and E. Yashima, *Macromolecules*, 2005, **38**, 4061-4064.

S3. K. Praefcke, B. Kohne and D. Singer, *Angew. Chem. Int. Ed.*, 1990, **29**, 177-179.

S4. Two signals are overlapped.

S5. B. D. Hosangadi and R. H. Dave, *Tetrahedron Lett.*, 1996, **37**, 6375-6378.

S6. (a) W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235; (b) J. V. Morris, M. A. Mahaney and J. R. Huber, *J. Phys. Chem.*, 1976, **80**, 969-974.

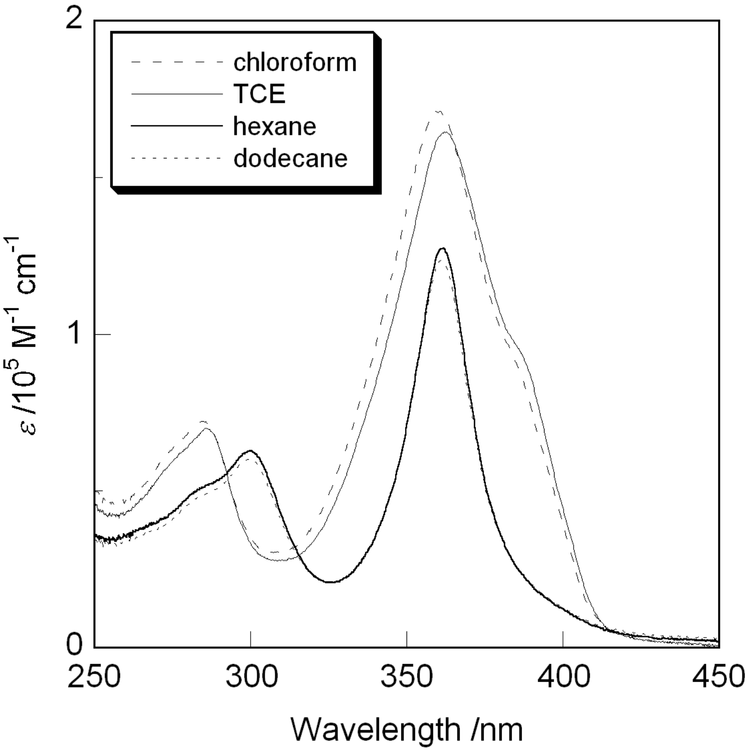


Fig. S1 UV-vis spectra of L-**1** in chloroform, 1,1,2,2-tetrachloroethane (TCE), *n*-hexane and *n*-dodecane (4.2×10^{-5} M) at 25 °C.

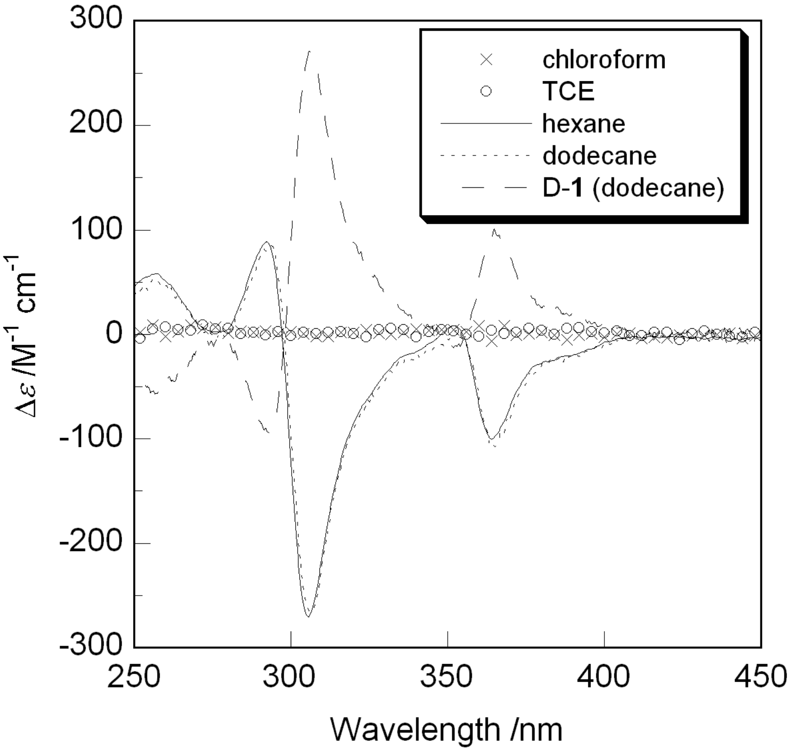


Fig. S2 CD spectra of L-**1** in chloroform, 1,1,2,2-tetrachloroethane (TCE), *n*-hexane and *n*-dodecane solutions (4.2 × 10^{-5} M) at 25 °C. CD spectrum of D-**1** in *n*-dodecane (4.2 × 10^{-5} M) at 25 °C is also shown.

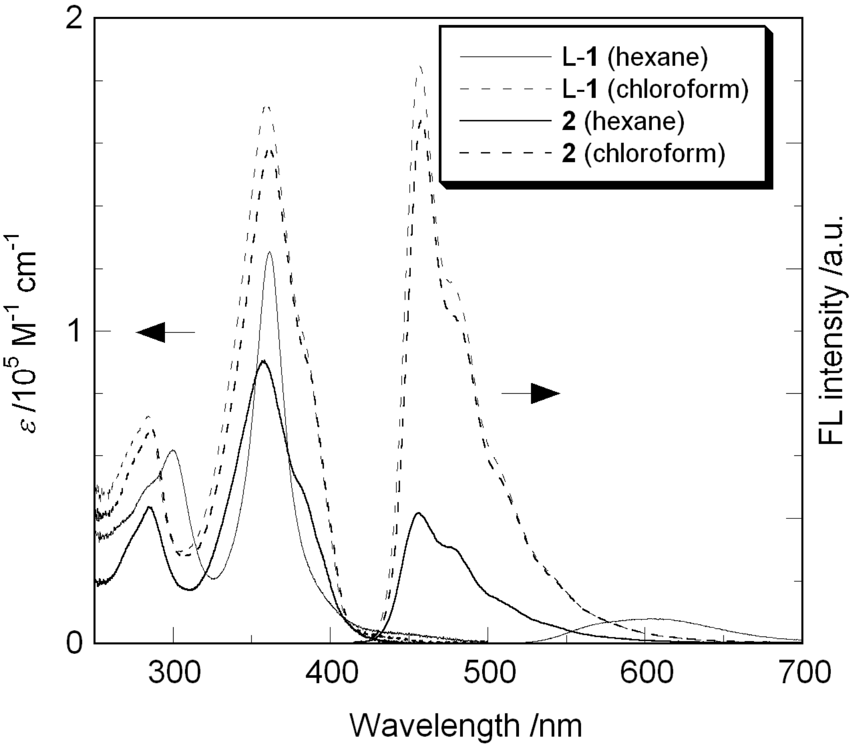


Fig. S3 UV-vis (4.2 × 10^{-6} M) and FL (4.2 × 10^{-7} M) spectra of L-**1** and **2** in chloroform and *n*-hexane (4.2 × 10^{-7} M) at 25 °C. FL spectra ($\lambda_{ex.}$ = 360 nm) were normalized using the absorption values at 360 nm.