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Supporting Information

Molecular rotors confined at an ordered 2D interface

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1. General

Analytical thin-layer chromatography (TLC) was performed on a glass plate coated with silica gel (230-400 mesh, 0.25 mm thickness) containing a fluorescent indicator (silica gel 60F254, Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral gel, 40-50 μ m, Kanto). IR spectra were recorded on Thermo Scientific Nicolet NEXUS 670 FT-IR and were reported as wavenumbers (v) in cm⁻¹. High resolution ESI-MS spectra were recorded on a Bruker solariX 9.4T spectrometer. Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ on a JEOL JNR-AL300 (300 MHz) spectrometer. UV-Vis absorption spectra were obtained on JASCO V-670. Fluorescent spectra were obtained on JASCO FP-6500.

2. Synthesis

Synthesis of 1



To a solution of 1-dodecanol (1 mL, 4.46 mmol, 1 eq.) and cyanoacetic acid (404 mg, 4.70 mmol, 1.05 eq.) in THF (20 mL), *N*,*N*'-dimethylaminopyridine (DMAP) (567 mg, 4.63 mmol, 1.04 eq.) and *N*,*N*'-dicyclohexylcarbodiimide (DCC) (947 mg, 4.59 mmol, 1.03 eq.) were added and stirred at 60 °C for 22 h. After cooling to room temperature, the mixture was added water and was extracted with EtOAc. The organic layer was washed with brine (2 times), and dried over Na₂SO₄, and then filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography (Hexane:EtOAc = 8:1) to yield **1** as and white solid (943 mg, 83%). ¹H-NMR (300 MHz, CDCl₃) 0.88 (t, 3H, 6.4 Hz), 1.20-1.40 (m, 18H), 1.60-1.70 (m, 2H), 3.44 (s, 2H), 4.20 (t, 2H, 6.7 Hz); ¹³C-NMR (75 MHz, CDCl₃) 13.9, 22.5, 24.5, 25.6, 28.2, 29.0, 29.2, 29.3, 29.4, 29.5, 29.5, 31.8, 67.0, 113.0, 163.0; HRMS (ESI) calcd. for C₁₅H₂₇NNaO₂ [M+Na]⁺ 279.1934, found 279.1934.

Synthesis of CCVJ-C12 (2)



To the THF (5 mL) solution of **1** (246mg, 0.970 mmol, 1 eq.) and 9-julolidinecarboxaldehyde (199 mg, 0.988 mmol, 1.02 eq.), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (250 μ L, 1.68 mmol, 1.73 eq.) was added and stirred for 20 h at room temperature. To the mixture, water was added and extracted with EtOAc and washed with brine (two times), dried over Na₂SO₄, filtered and concentrated. The

crude product was purified by silica gel column chromatography (Hexane:EtOAc = 6:1) to yield **2** as an orange solid (368 mg, 86%). Further purification was possible by recrystallization from hexane. Mp 71.3-71.8°C; FT-IR (KBr, cm⁻¹) 2923, 2854, 2353, 2204, 1710, 1552, 1517, 1447, 1312, 1224, 1152, 1096, 944, 898, 726; ¹H-NMR (300 MHz, CDCl₃) 0.88 (t, 3H, 6.6 Hz), 1.20-1.50 (m, 18H), 1.65-1.75 (m, 2H), 1.90-2.00 (m, 4H), 2.75 (t, 4H, 6.1 Hz), 3.32 (t, 4H, 5.8 Hz), 4.24 (t, 2H, 6.7 Hz), 7.50 (s, 2H), 7.93 (s, 1H); ¹³C-NMR (75 MHz, CDCl₃) 14.0, 21.1, 22.6, 25.8, 27.5, 28.6, 29.2, 29.4, 29.5, 29.5, 29.5, 31.8, 50.1, 65.8, 92.1, 118.0, 118.6, 120.9, 131.7, 147.8, 154.4, 165.0; HRMS (ESI) calcd. for C₂₈H₄₀N₂NaO₂ [M+Na]⁺ 459.2982, found 459.2981.

Synthesis of 31



To the cholesterol (683.4 mg, 1.77 mmol, 1eq), cyanoacetic acid (154 mg, 1.80 mmol. 1.02 eq.), DMAP (241 mg, 1.97 mmol, 1.11 eq.) and DCC (371 mg, 1.80 mmol, 1.02 eq.) was added, dissolved in THF (20 mL) and stirred for 23 h at 60 °C. The reaction mixture was cooled to room temperature and evaporated. The mixture was dissolved in CHCl₃, washed with water, aq. NaHCO₃, and brine, dried over Na₂SO₄. The crude product was purified by silica gel column chromatography (Hexane:EtOAc = 10:1) to yield **3** as an white solid (575 mg, 71%).

Synthesis of CCVJ-Chol (4)



To the THF (10 mL) solution of **3** (501 mg, 1.10 mmol, 1 eq.) and 9-julolidinecarboxaldehyde (223 mg, 1.11 mmol, 1 eq.), DBU (250 μ L, 1.66 mmol, 1.51 eq.) was added and stirred for 22 h at room temperature. To the mixture, water was added and extracted with CHCl₃ (two times), washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography (Hexane:EtOAc = 8.5:1) to yield **4** as an orange clay (230 mg, 31%). FT-IR (KBr, cm⁻¹) 2939, 2353, 2207, 1718, 1532, 1449, 1313, 1227, 1156, 1102, 1008, 955; ¹H-NMR (300

^{1.} W. Schulze, J. Prakt. Chem., 1972, 314, 649. (doi:10.1002/prac.19723140332.1)

MHz, CDCl₃) 0.68 (s, 3H), 0.80-2.10 (m, 44H), 2.39-2.47 (m, 2H), 2.75 (t, 4H, 5.9 Hz), 3.32 (t, 4H, 6.2 Hz), 4.72-4.79 (m, 1H), 5.39-5.41 (m, 1H), 7.50 (s, 2H), 7.92 (s, 1H); ¹³C-NMR (75Hz, CDCl₃) 11.7, 18.6, 19.2, 21.0, 22.4, 22.7, 23.7, 24.2, 27.5, 27.9, 28.1, 29.6, 31.8, 31.8, 35.7, 36.1, 36.5, 36.9, 38.0, 39.4, 39.6, 42.2, 49.9, 50.1, 56.0, 56.6, 75.4, 92.2, 118.1, 118.6, 120.8, 122.7, 122.8, 131.7, 139.8, 147.6, 154.3, 164.3; HRMS (ESI) [M-Na]⁺ 659.4547 (calcd. for C₄₃H₆₀N₂NaO₂, 659.4547).

3. NMR Spectra





Figure S2. ¹³C-NMR spectrum of **1**

0







Figure S4. ¹³C-NMR spectrum of **2**







Figure S6. ¹³C-NMR spectrum of 4

4. Photophysical Properties



b)



Figure S7. UV-vis absorption spectra of (a) CCVJ-C12 (4.99 x 10⁻⁴ M) in CHCl₃ ($\lambda_{max} = 450$ nm) and (b) CCVJ-Chol (5.15 x 10⁻⁴ M) in CHCl₃. $\lambda_{max} = 453$ nm



Figure S8. Excitation spectra of CCVJ-C12 in CHCl₃ $(1.20 \times 10^{-4} \text{ M})$ monitored at 500 nm (a) or 600 nm (b).



Figure S9. Excitation spectra of CCVJ-Chol in $CHCl_3$ (5.15 x 10⁻⁴ M) monitored at 500 nm (a) or 600 nm (b).

Although CCVJ-Chol showed a similar tendency as CCVJ-C12 for benzene and DMSO, due to low solubility, reliable spectra could not be obtained with ethylene glycol, glycerol and their mixtures.



Figure S10. Fluorescence from solid fluorescent rotors. Powder solid: (a) CCVJ-C12, (b) CCVJ-Chol. Excitation wavelength are changed form 260 nm to 470 nm. (c) The cast films of CCVJ-Chol in which the amount was same as (0.62 nm²/molecule) excited at 420 nm. Spectra were obtained from multi channel photo detector (MCPD). No change in the shape of emission spectra was detected.



Figure S11. Fluorescence emissions of CCVJ-C12 (40 µM) in 9% DMSO/H₂O excited at 450 nm.

5. Monolayer Measurements

Since we use freshly prepared ultra-pure water as a subphase at 20 °C, the pH of water should be around pH 7.² Considering the effect of CO₂, it can be ranged between pH 5 to 8. The mechanical energy that can be given to molecules upon compression of the monolayers are much smaller (ca. 1 kcal/mol) than that can affect on bond cleavage reactions (E >> 10 kcal/mol). Ester groups is stable at neutral aqueous conditions. Since the pKa of anilinium is pKa = 2.4³ molecules are not protonated.

^{2.} T. S. Light, Anal. Cham. 1984, 56, 1138-1142.

^{3.} Crampton J. Chem. Res. (S) 1997, 22.

Physical properties of monolayers



Figure S12. Compressibility (*Cs*)-Area (*A*) curves and of compression modulus (*Cs*⁻¹)-Surface pressure (π) curves of CCVJ-C12 (a,c) and CCVJ-Chol (b,d), respectively.

Estimation of Molecular Area

Molecular area of CCVJ-C12 and CCVJ-Chol was estimated from the projection of CPK models by the method similar to the reported one.⁴ Projected image was obtained by using ImageJ (National Institutes of Health, Bethesda, MD) and the area was compared with that of carbon that has an area of 0.091 nm². The projected area of CCVJ-H were estimated to be 0.38 and 0.86 nm² for the top and side view.

^{4.} H. Tachibana, Chem. Edu. J. 2003, 7, 7.



Figure S13. Structures and schematic view of molecular rotors, CCVJ-C12, CCVJ-Chol, and their chromophore CCVJ-H. (a) Estimated molecular area (*A*) for CCVJ-H are shown. Since *A* of cholesterol is known to be 0.4 nm² and liner that of alkyl chain to be 0.2 nm², the projected image of CCVJ-C12 and CCVJ-Chol are overlapped by the chromophore CCVJ-H (A = 0.4 nm²) and their molecular area are both estimated to be 0.4 nm². (b) Selected internal rotations that is possible at compressed state. Rotations around single bonds shown in blue/red arrows may not be inhibited in monolayers when the monolayer is compressed and the parts shown in green are densely packed.



Figure S14. Fluorescent spectra of CCVJ-C12 (a) and CCVJ-Chol (b) without normalizing (without multiplying by area per molecule) upon compression. Corresponding values of area per molecule (nm²/molecule) are shown with coloured lines. ($\lambda_{ex} = 450$ nm)

Brewster angle microscopy (BAM)

BAM observation was performed for CCVJ-C12 and CCVJ-Chol. BAM was employed to directly visualize the film morphology at the air-water interface. The each monolayers on pure water were examined at different surface pressures.



Figure S15. Brewster-angle microscope (BAM) images of (a), (b) CCVJ-C12 and (c), (d) CCVJ-Chol in various pressure.

AFM of LB films



Figure S16. Height profiles of AMF images of LB films of CCVJ-C12 (a,c) and CCVJ-Chol (b,d) before (a,b) and after (c,d) collapse. The cross section of gray lines in AFM images are shown.