Supporting Information

Mechanical Control of Enantioselectivity of Amino Acid Recognition by Cholesterol-Armed Cyclen Monolayer at the Air-Water Interface

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1. Materials.

Water used for the subphase was distilled using an Autostill WG220 (Yamato) and deionized using a Milli-Q Lab (Millipore). Its specific resistance was greater than 18 MΩ cm. Spectroscopic grade chloroform (Kanto Chem.) was used as the spreading solvent. Amino acids were purchased from Wako Chemical Co. or Peptide Institute. Synthesis of the cholesterol-armed cyclen NaCl complex **1** was described previously.[1]

2. Measurements.

The π-A isotherms were measured at 20.0 ^{o}C using an FSD-300 computer-controlled film balance (USI System, Fukuoka). Compression was commenced at a rate of 0.2 mm s^{-1} ~10 min after spreading. Fluctuation of the subphase temperature was within ±0.2 ^{o}C. LB films were prepared using the vertical dipping method with up-stroke and down-stroke motions of 5 mm min^{-1} from the pure water and aqueous amino acid subphases. Monolayers were transferred onto gold-deposited glass slides at different surface pressures of 10, 20, and 30 mN m^{-1}. Infrared spectra of the LB film on a gold-deposited glass were obtained using an FT-IR spectrometer (Nicolet NEXUS 670FT-IR) equipped with an MCT detector (for RAS, reflection absorption spectroscopy). All data were collected by the RAS method at a spectral resolution of 4 cm^{-1}.

3. Binding constants

Binding constants (*K*) were determined in the surface pressure range from 1 to 40 mN m^{-1} using a Langmuir type equation under the assumption that an increase in the molecular area values of the π-*A* isotherms is proportional to the adsorption amount of amino acids. Surface pressures above 40 mN m^{-1} were avoided because of the possibility of a monolayer collapse.

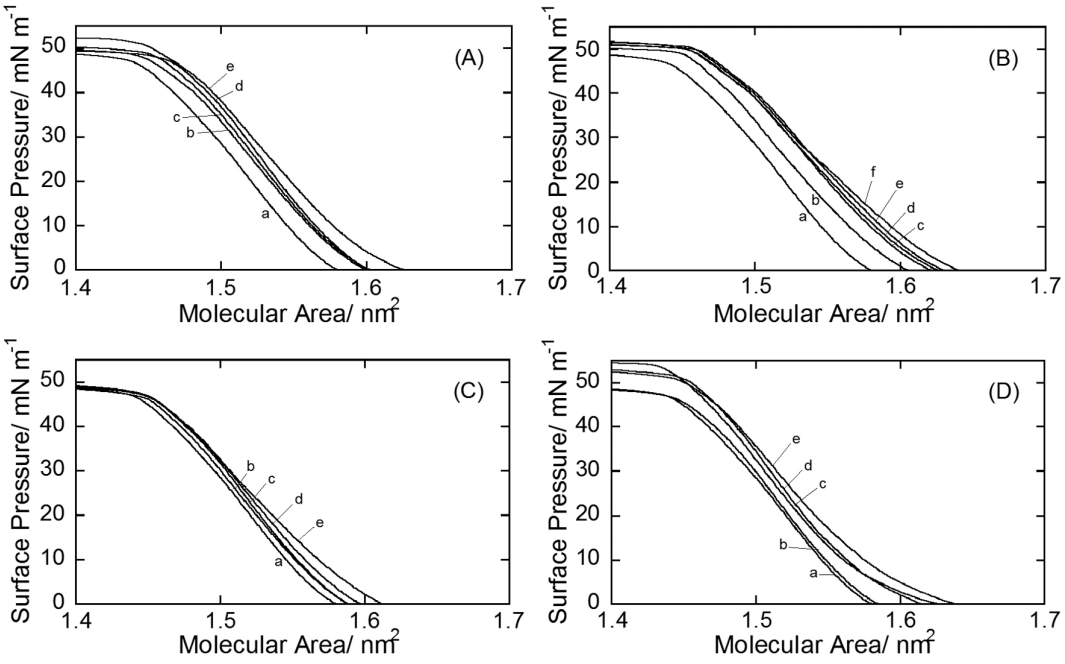

Figure 1SI. π-*A* Isotherms of the cholesterol-armed cyclen NaCl complex monolayer at 20.0 ± 0.2 ^{o}C: (A) a, on pure water; b, on 1.5 mM L-leucine; c, on 2 mM L-leucine; d, on 2.5 mM L-leucine; e, on 5 mM L-leucine: (B) a, on pure water; b, on 0.5 mM D-leucine; c, on 1 mM D-leucine; d, on 1.5 mM D-leucine; e, on 2 mM D-leucine; f, on 3 mM D-leucine: (C) a, on pure water; b, on 1 mM L-valine; c, on 1.5 mM L-valine; d, on 3 mM L-valine; e, on 5 mM L-valine: (D) a, on pure water; b, on 1 mM D-valine; c, on 2 mM D-valine; d, on 4 mM D-valine; e, on 10 mM D-valine.

Table 1SI. Binding constants (K) of enantiomeric leucine and valine to the cholesterol-armed cyclen NaCl complex monolayer.

Surface Pressure [mN m^{-1}]	$K_{L\text{-}Leu}$ [M^{-1}]	$K_{D\text{-}Leu}$ [M^{-1}]	$K_{D\text{-}Leu}/K_{L\text{-}Leu}$	$K_{L\text{-}Val}$ [M^{-1}]	$K_{D\text{-}Val}$ [M^{-1}]	$K_{D\text{-}Val}/K_{L\text{-}Val}$
1	85.2	1063	12.47	—	—	—
6	156.3	957.4	6.127	23.0	191.9	8.338
11	179.3	934.5	5.211	29.6	144.9	4.886
16	214.4	959.4	4.475	76.1	115.6	1.518
21	231.7	1015	4.381	143.6	164.6	1.146
26	301.9	1190	3.943	336.5	198.3	0.589
31	384.7	1453	3.776	712.5	289.9	0.407
36	428.5	1565	3.653	788.0	364.5	0.463
40	425.1	1729	4.066	814.2	410.1	0.504

4. FT-IR-RAS spectra

The peak at 1461-1480 cm^{-1} (black), derived from the monolayer **1**, was used as a reference peak for peak intensities. In the region of 1300-1800 cm^{-1}, each peak is distinguished by different colors. The color code is as follows: 1406-1409 cm^{-1} (ν_{COO^-}), purple; 1510-1527 cm^{-1} (δ_{NH3^+}), red; 1546-1584 cm^{-1} (ν_{COO^-}), brown; 1606-1612 cm^{-1} (δ_{NH3^+}), green; 1731-1741 cm^{-1} (overlapping $\nu_{C=O(ester)}$ and $\nu_{C=O(carboxylic\ acid)}$), blue.

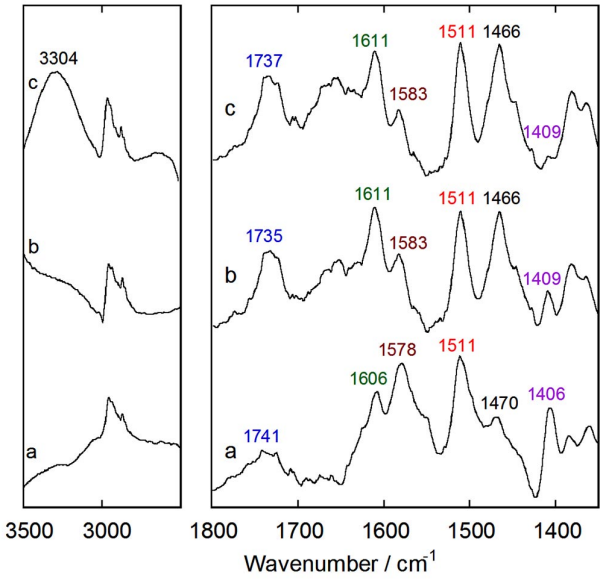

Figure 2SI. FT-IR-RAS spectra (1300-1800 and 2500-3500 cm^{-1}) of LB films (10 layers) of cholesterol-armed cyclen NaCl complex **1**: a monolayer transferred from 3 mM aqueous L-leucine at surface pressure of a, 10 mN m^{-1}; b, 20 mN m^{-1}; c, 30 mN m^{-1}.

References

1. Shinoda, S.; Okazaki, T.; Nishimura, T.; Hori, K.; Tsukube, H. *Chem. Commun.* **2001**, 976-977.