Supporting Information

Self-assembled mesoscopic surface domains of fluorocarbon-hydrocarbon diblocks can form at zero surface pressure. Tilting of solid-like hydrocarbon moieties compensates for cross-section mismatch with fluorocarbon moieties

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Content:

Sets of experimental and simulated IRRA spectra in the OH and CH_2 stretching vibrational range recorded at different compression states of a *F*8*H*16 monolayer. These spectra were used to determine i) the tilt angle of the *H*16 moiety and ii) the average layer thickness.

30 Ų / molecule	2
Alkyl chain tilt	2
Layer thickness	2
60 Ų / molecule	3
Alkyl chain tilt	3
Layer thickness	3
80 Ų / molecule	4
Alkyl chain tilt	4
Layer thickness	4
100 Ų / molecule	5
Alkyl chain tilt	5
Layer thickness	5

30 Ų/molecule

Alkyl chain tilt a) b) p-pol s-pol 3 experiment simulation 2 0 1 0 -'c -'--lg(*R*/*R*₀) · 10³ $-\log(R/R_{o}) \cdot 10^{3}$ φ/°: 26 -1 30° 34° -2 38 -3 42° 46 62° -4 $\theta = 30^{\circ}$ 66° ψ=90° -5 70° -3 2940 2920 2840 2820 2940 2920 2900 2880 2860 2840 2820 2900 2880 2860 Wavenumber (cm⁻¹) Wavenumber (cm⁻¹)

Figure S1: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 30 Å²/molecule in the range of the antisymmetric and symmetric CH₂ stretching vibrations. The spectra were recorded in a) p-polarization and b) s-polarization at different angles of incidence (φ) of the IR beam. All the spectra were fitted in one global fit with the same parameter. The best fit was achieved with an alkyl block tilt angle θ = 30° and a twist angle ψ = 90°.



Figure S2: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 30 Å²/molecule in the range of the OH stretching vibrations originating from the water subphase. The spectra were recorded in a) p-polarization and b) s-polarization at various angles of incidence (φ) of the IR beam. A layer thickness d = 2.4 nm and an average refractive index n = 1.37 were determined from the fit.



Figure S3: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 60 Å²/molecule in the range of the antisymmetric and symmetric CH₂ stretching vibrations. The spectra were recorded in a) p-polarization and b) s-polarization at different angles of incidence (φ) of the IR beam. All the spectra were fitted in one global fit with the same parameter. The best fit was achieved with an alkyl block tilt angle θ = 30° and a twist angle ψ = 82°.



Layer thickness

Figure S4: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 60 Å²/molecule in the range of the OH stretching vibrations originating from the water subphase. The spectra were recorded in a) p-polarization and b) s-polarization at various angles of incidence (ϕ) of the IR beam. A layer thickness *d* = 1.19 nm and an average refractive index *n* = 1.31 were determined from the fit, from which an actual domain thickness of 2.4 nm was calculated.

80 Ų/molecule



Figure S5: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 80 Å²/molecule in the range of the antisymmetric and symmetric CH₂ stretching vibrations. The spectra were recorded in a) p-polarization and b) s-polarization at different angles of incidence (φ) of the IR beam. All the spectra were fitted in one global fit with the same parameter. The best fit was achieved with an alkyl block tilt angle θ = 31° and a twist angle ψ = 90°.



Figure S6: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 80 Å²/molecule in the range of the OH stretching vibrations originating from the water subphase. The spectra were recorded in a) p-polarization and b) s-polarization at various angles of incidence (ϕ) of the IR beam. A layer thickness *d* = 0.94 nm and an average refractive index *n* = 1.31 were determined from the fit, from which an actual domain thickness of 2.5 nm was calculated.

Layer thickness

100 Å²/molecule Alkyl chain tilt



Figure S7: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 100 Å²/molecule in the range of the antisymmetric and symmetric CH₂ stretching vibrations. The spectra were recorded in a) p-polarization and b) s-polarization at different angles of incidence (φ) of the IR beam. All the spectra were fitted in one global fit with the same parameter. The best fit was achieved with an alkyl block tilt angle θ = 32° and a twist angle ψ = 90°.



Figure S8: Experimental (symbols) and best fitting simulated (lines) IRRA spectra of *F*8*H*16 at 100 Å²/molecule in the range of the OH stretching vibrations originating from the water subphase. The spectra were recorded in a) p-polarization and b) s-polarization at various angles of incidence (ϕ) of the IR beam. A layer thickness *d* = 0.76 nm and a refractive index *n* = 1.31 were determined from the fit, from which an actual domain thickness of 2.5 nm was calculated.