Supplementary Materials for

Fluorinated Polymer Surfactants Bearing Alternating Peptide Skeleton Prepared by Three-Component Polycondensation

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General methods:

Materials. Compound 1 was prepared according to the literature. Trifluoromethanesulfonic acid (TfOH, Kanto chemicals), isobutyaldehyde (TCI), benzaldehyde (Kanto), biphenyl-4-carboxaldehyde (TCI), 1H,1H-heptafluorobutylamine (TCI), 1H,1H-pentadecafluoroctylamine (Wako), i-propylalcohol (Taiyo), chloroform (Kanto), and hexane (Kanto) were used as obtained. PANAM dendrimer generation 4 (core type: ethylenediamine, sigma-aldrich) MeOH solution was used as obtained for the DOSY measurement.

Measurements. $^1$H NMR (400 MHz), $^{13}$C NMR (100 MHz), and $^{19}$F NMR (376 MHz) spectra were recorded on a Bruker AVANCE II 400 spectrometer using CDCl$_3$, DMSO-$d_6$, and CD$_3$OD as the solvent. $^1$H- and $^{13}$C NMR spectra were calibrated using residual undeuterated solvent and tetramethyilsilane as the internal standard, while $^{19}$F spectra were calibrated using CF$_3$COOH as a standard. DOSY measurements were carried out using 3.0 mg of compound in 600 μL of CDCl$_3$ to estimate the diffusion coefficients. DOSY spectra were recorded on a Bruker AVANCE II 400 spectrometer. All experiments were run without spinning to avoid convection. The standard Bruker pulse program, ledbpgp2s, employing simulated echo and longitudinal eddy delay with bipolar gradients and two spoil gradients, was utilized. The obtained DOSY spectra were processed by Topspin 3.2 software. Diffusion dimension was generated using the inversion of Laplace transform driven by the CONTIN method. Diffusion coefficients of a chosen narrow chemical shift in the spectra of the compounds were extracted by using Dynamics center software (ver. 2.4.8, Bruker). FT-IR spectra using a KBr pellet were measured using a Thermo Fischer Scientific Nexus 870 spectrometer. FT-IR spectra via an attenuated total reflection (ATR) method were measured using a Perkin Elmer spectrum 100 spectrometer. SEC analyses were carried out using a chromatographic system consisting of a Shimadzu LC-20AT pump with a Shimadzu SPD-20A (UV detector) equipped with two consecutive linear polystyrene gel columns (Tosoh TSKgel GMH$	imes$5-H and TSKgel G3000H$	imes$10) at room temperature according to polystyrene standards using DMF as an eluent (flow rate: 1.0 mL/min). Differential scanning calorimetry analyses (DSC) were carried out on DSC7020 EXSTAR (Seiko Instruments Inc.) for P1, P2, P3, and P6 and DSC-60 plus (Shimadzu Co. Ltd.) for P4 and P5 under N$_2$ atmosphere (flow rate: 150 mL/min). Thermogravimetric analyses (TGA) were carried out on TG/DTA 7300 EXSTAR (Seiko Instruments Inc.) under N$_2$ atmosphere (flow rate: 50 mL/min). The surface tensions of the surfactant solutions were determined by the Wilhelmy plate method at 25 °C using a DY-500 surface tension meter (Kyowa Kaimen Kagaku Co. Ltd.), the accuracy of which was intermittently checked with ultrapure water. The Pt plate was cleaned by flaming, and glassware was rinsed sequentially with ultrapure water and organic solvents. The size distribution of the assemblies of the P6 solution was measured with a DLS instrument (DLS-7000, Otsuka Electronics Co. Ltd.) using an Ar laser with a wavelength of 488 nm as the source at 75 mW.
at 25 °C. The time-dependent correlation function of the scattered light intensity was measured at a scattering angle of 90°. The size distributions were determined using the software provided with the instrument. The critical micelle concentration of P6 was determined by UV spectra using a UV-3600 Plus UV-VIS-NIR spectrophotometer (Shimadzu Co. Ltd, Japan).

**Synthetic procedures to give alternating peptides**

**Synthesis of P1**

To a mixture of 1H,1H-heptafluorobutylamine (1.07 mL, 8.00 mmol) in i-PrOH (4.0 mL) was added TfOH (708 μL, 8.00 mmol) at 0 °C, which was followed by the addition of 1 (985 mg, 8.00 mmol). After the dissolution of 1, isobutylaldehyde (730 μL, 8.00 mmol) was added to the mixture at the same temperature. The mixture was warmed to room temperature, stirred for 4 d, and concentrated in vacuo. The resulting crude was further stirred for 2.5 d at room temperature and diluted with CHCl3. The reaction was quenched by the addition of water. The products were extracted with CHCl3. The combined organic layer was dried over MgSO4, filtered, and concentrated in vacuo. The crude was diluted with a small amount of CHCl3 and the solution was reprecipitated in hexane to give hexane-insoluble part (P1, 2.30 g, 85%) as a pale yellow oil and hexane-soluble part (534 mg, 18%) as a pale yellow oil: Mw 7,400 Da (estimated by DOSY); Mw/Mn 1.5 (estimated by SEC on the basis of polystyrene standards); Tg −23.6 °C; Td5 203.6 °C; Td10 221.9 °C; 1H NMR (400 MHz, 293 K, CDCl3) δ 7.63 (brd, NH), 7.40 (brd, NH), 6.97 (brd, NH), 4.16–3.94 (m, 3H, CH, CH2), 3.33–3.10 (m, 2H, CH2), 2.16 (brd, 1H, CH), 1.03–0.90 (m, 6H, CH3) ppm; 13C NMR (100 MHz, 293 K, CDCl3) δ 174.8, 174.0, 172.2, 169.9, 116.0 (m), 68.3, 68.2, 47.9 (td, JCF = 22, 7.1 Hz), 43.0, 41.0, 38.7 (t, JCF = 22 Hz), 31.6, 31.5, 19.3, 17.4 ppm; 19F NMR (376 MHz, 293 K, CDCl3) δ −81.37, −81.29, −81.41, −81.45, −81.48, −81.72, −81.74, −81.77, −117.73, −117.89, −120.00, −128.47, −128.54, −128.72 ppm; IR (KBr) ν 3315, 3086, 2969, 2939, 2880, 2615, 2536, 1733, 1655, 1538, 1471, 1394, 1376, 1354, 1222, 1119, 1030, 994, 958, 914, 787, 759, 739, 668, 639 cm−1.

**Synthesis of P2**

To a mixture of 1H,1H-heptafluorobutylamine (1.07 mL, 8.00 mmol) in i-PrOH (4.0 mL) was added TfOH (708 μL, 8.00 mmol) at 0 °C, which was followed by the addition of 1 (985 mg, 8.00 mmol). After the dissolution of 1, benzaldehyde (816 μL, 8.00 mmol) was added to the mixture at the same temperature. The mixture was warmed to room temperature, stirred for 4 d, and concentrated in vacuo. The resulting crude was further stirred for 2.5 d at room temperature and diluted with CHCl3. The reaction was quenched by the addition of water. The products were extracted with CHCl3. The combined organic layer was dried over MgSO4, filtered, and concentrated in vacuo. The crude was diluted with a small amount of CHCl3 and the solution was reprecipitated in hexane to give hexane-insoluble part (P2, 2.45 g, 82%) as an orange oil and hexane-soluble part (510 mg, 17%) as an orange oil: Mw 7,300 Da (estimated by DOSY); Mw/Mn 1.8 (estimated by SEC on the basis of polystyrene standards); Tg −23.6 °C; Td5 203.6 °C; Td10 221.9 °C; 1H NMR (400 MHz, 293 K, CDCl3) δ 7.63 (brd, NH), 7.40 (brd, NH), 6.97 (brd, NH), 4.16–3.94 (m, 3H, CH, CH2), 3.33–3.10 (m, 2H, CH2), 2.16 (brd, 1H, CH), 1.03–0.90 (m, 6H, CH3) ppm; 13C NMR (100 MHz, 293 K, CDCl3) δ 174.8, 174.0, 172.2, 169.9, 116.0 (m), 68.3, 68.2, 47.9 (td, JCF = 22, 7.1 Hz), 43.0, 41.0, 38.7 (t, JCF = 22 Hz), 31.6, 31.5, 19.3, 17.4 ppm; 19F NMR (376 MHz, 293 K, CDCl3) δ −81.37, −81.29, −81.41, −81.45, −81.48, −81.72, −81.74, −81.77, −117.73, −117.89, −120.00, −128.47, −128.54, −128.72 ppm; IR (KBr) ν 3315, 3086, 2969, 2939, 2880, 2615, 2536, 1733, 1655, 1538, 1471, 1394, 1376, 1354, 1222, 1119, 1030, 994, 958, 914, 787, 759, 739, 668, 639 cm−1.
standards); $T_g$ = −13.3 °C; $T_d5$ = 217.2 °C; $T_d10$ = 246.5 °C; $^{1}$H NMR (400 MHz, 293 K, CDCl$_3$) δ 7.49 (brd, NH), 7.37 (brd, Ar, 5H), 6.73 (brd, NH), 4.40 (s, CH), 4.39 (s, CH), 4.13–3.85 (m, CH$_2$), 3.36–3.16 (m, CH$_3$) ppm; $^{13}$C NMR (100 MHz, 293 K, CDCl$_3$) δ 172.8, 172.3, 172.0, 169.6, 137.3, 137.2, 129.2, 129.1, 128.9, 128.3, 127.5, 127.4, 119.0 (m), 116.1 (m), 66.4, 66.3, 46.5 (td, $J_{CF} = 22.5$, 13 Hz), 42.9, 41.2, 38.6 (t, $J_{CF} = 23.5$ Hz) ppm; $^{19}$F NMR (376 MHz, 293 K, CDCl$_3$) δ −81.31, −81.33, −81.35, −81.38, −81.40, −81.69, −81.71, −81.74, −117.51, −120.09, −128.32, −128.41, −128.73 ppm; IR (KBr) ν 3310, 3071, 3032, 2941, 1655, 1528, 1498, 1455, 1422, 1393, 1354, 1221, 1174, 1118, 1058, 1030, 1003, 989, 960, 916, 739, 756, 668, 653 cm$^{-1}$.

**Synthesis of P3**

To a mixture of 1H,1H-heptafluorobutylamine (1.07 mL, 8.00 mmol) in $i$-PrOH (4.0 mL) was added TfOH (708 μL, 8.00 mmol) at 0 °C, which was followed by the addition of 1 (985 mg, 8.00 mmol). After the dissolution of 1, biphenyl-4-carboxaldehyde (1.46 mg, 8.00 mmol) was added to the mixture at the same temperature. The mixture was warmed to room temperature, stirred for 4 d, and concentrated in vacuo. The resulting crude was further stirred for 2.5 d at room temperature and diluted with CHCl$_3$. The reaction was quenched by the addition of water. The products were extracted with CHCl$_3$. The combined organic layer was dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude was diluted with a small amount of CHCl$_3$ and the solution was reprecipitated in hexane to give hexane-insoluble part (P3, 2.25 g, 63%) as a yellow solid and hexane-soluble part (1.39 g, 38%) as a yellow solid: $M_w$ 7,100 Da (estimated by DOSY); $M_w/M_n$ 1.5 (estimated by SEC on the basis of polystyrene standards); $T_g$ 31.4 °C; $T_d5$ 234.6 °C; $T_d10$ 264.0 °C; $^{1}$H NMR (400 MHz, 293 K, CDCl$_3$) δ 7.47–7.33 (m, Ar, NH), 6.65 (brd, NH), 4.45 (s, CH), 4.44 (s, CH), 4.20–3.89 (m, CH$_2$), 3.39–3.23 (m, CH$_3$) ppm; $^{13}$C NMR (100 MHz, 293 K, CDCl$_3$) δ 172.8, 172.3, 169.5, 141.9, 141.8, 140.2, 136.1, 135.9, 128.8, 127.94, 127.89, 127.79, 127.65, 127.61, 127.07, 127.01, 126.95, 66.0, 46.5 (t, $J_{CF} = 20.5$ Hz), 43.0, 41.2, 38.6 (t, $J_{CF} = 25$ Hz) ppm; $^{19}$F NMR (376 MHz, 293 K, CDCl$_3$) δ −81.29, −81.31, −81.34, −81.36, −81.38, −81.71, −81.73, −81.76, −117.45, −120.05, −128.32, −128.41, −128.73 ppm; IR (KBr) ν 3319, 3070, 3032, 2941, 1655, 1528, 1455, 1422, 1393, 1354, 1221, 1174, 1118, 1058, 1030, 1003, 989, 960, 916, 739, 756, 668, 653 cm$^{-1}$.

**Synthesis of P4**

To a mixture of 1H,1H-pentadecafluoroctylamine (1.07 mL, 8.00 mmol) in $i$-PrOH (4.0 mL) was added TfOH (708 μL, 8.00 mmol) at 0 °C, which was followed by the addition of 1 (985 mg, 8.00 mmol). After the dissolution of 1, isobutylaldehyde (228 μL, 2.50 mmol) was added to the mixture at the same temperature. The mixture was warmed to room temperature, stirred for 4 d, and concentrated in vacuo. The resulting crude was further stirred for 3 d at room temperature and diluted with CHCl$_3$. The reaction was quenched by the addition of water. The products were extracted with CHCl$_3$. The
combined organic layer was dried over MgSO₄, filtered, and concentrated in vacuo. The crude was diluted with a small amount of CHCl₃ and the solution was reprecipitated in hexane to give hexane-insoluble part (P₄, 583 mg, 43%) as a white solid and hexane-soluble part (848 mg, 63%) as a white solid: \( M_w \) 7,600 Da (estimated by DOSY); \( M_w/M_n \) 1.2 (estimated by SEC on the basis of polystyrene standards); \( T_g \) −1.3 °C; \( T_d5 \) 217.3 °C; \( T_d10 \) 236.5 °C; \(^1\)H NMR (400 MHz, 293 K, CDCl₃) \( \delta \) ppm; \(^{13}\)C NMR (100 MHz, 293 K, CD₃OD) \( \delta \) 177.0, 171.8, 70.03, 69.99, 42.97, 32.84, 19.83, 18.83, 18.73 ppm; \(^{19}\)F NMR (376 MHz, 293 K, CDCl₃) \( \delta \) −81.58, −81.60, −81.64, −81.67, −81.69, −81.73, −81.75, −117.06, −122.59, −122.90, −123.67, −124.16, −124.25, −127.04 ppm; IR (KBr) \( \nu \) 3319, 2988, 1692, 1653, 1525, 1204, 1148, 1104, 1020, 790, 701, 668, 567, 531 cm⁻¹.

**Synthesis of P₅**

To a mixture of 1H,1H-pentadecafluorooctylamine (582 \( \mu \)L, 2.50 mmol) in \( \gamma \)-PrOH (1.25 mL) was added TfOH (221 \( \mu \)L, 2.50 mmol) at 0 °C, which was followed by the addition of 1 (308 mg, 2.50 mmol). After the dissolution of 1, benzaldehyde (255 \( \mu \)L, 2.50 mmol) was added to the mixture at the same temperature. The mixture was warmed to room temperature, stirred for 4 d, and concentrated in vacuo. The resulting crude was further stirred for 3 d at room temperature and diluted with CHCl₃. The reaction was quenched by the addition of water. The products were extracted with CHCl₃. The combined organic layer was dried over MgSO₄, filtered, and concentrated in vacuo. The crude was diluted with a small amount of CHCl₃ and the solution was reprecipitated in hexane to give hexane-insoluble part (P₅, 956 mg, 67%) as a yellow solid and hexane-soluble part (651 mg, 45%) as a yellow solid: \( M_w \) 7,400 Da (estimated by DOSY); \( M_w/M_n \) 1.3 (estimated by SEC on the basis of polystyrene standards); \( T_g \) 0.7 °C; \( T_d5 \) 231.7 °C; \( T_d10 \) 254.9 °C; \(^1\)H NMR (400 MHz, 293 K, CDCl₃) \( \delta \) ppm; \(^{13}\)C NMR (100 MHz, 293 K, CD₃OD) \( \delta \) 175.0, 172.8, 171.9, 139.5, 139.4, 130.5, 130.3, 129.8, 129.7, 129.41, 129.35, 128.9, 127.8, 67.5, 45.3, 43.2, 41.9 ppm; \(^{19}\)F NMR (376 MHz, 293 K, CDCl₃) \( \delta \) −81.51, −81.54, −81.59, −81.62, −81.65, −81.67, −116.50, −119.08, −122.62, −122.94, −123.65, −124.06, −124.36, −127.04 ppm; IR (KBr) \( \nu \) 3315, 2960, 1651, 1524, 1143, 1053, 1020, 884, 736, 700, 665, 567, 531 cm⁻¹.

**Synthesis of P₆**

To a mixture of 1H,1H-pentadecafluorooctylamine (582 \( \mu \)L, 2.50 mmol) in \( \gamma \)-PrOH (1.25 mL) was added TfOH (221 \( \mu \)L, 2.50 mmol) at 0 °C, which was followed by the addition of 1 (308 mg, 2.50 mmol). After the dissolution of 1, biphenyl-4-carboxaldehyde (456 mg, 2.50 mmol) was added to the mixture at the same temperature. The mixture was warmed to room temperature, stirred for 4 d, and concentrated in vacuo. The resulting crude was further stirred for 3 d at room temperature and diluted with CHCl₃. The reaction was quenched by the addition of water. The products were extracted with CHCl₃. The combined organic layer was dried over MgSO₄, filtered, and concentrated in vacuo. The
crude was diluted with a small amount of CHCl$_3$ and the solution was reprecipitated in hexane to give hexane-insoluble part (P6, 1.04 g, 64%) as a white solid and hexane-soluble part (0.95 mg, 41%) as a white solid: $M_w$ 8,800 Da (estimated by DOSY); $M_w/M_n$ 1.2 (estimated by SEC on the basis of polystyrene standards); $T_g$ 45.5 °C; $T_{d5}$ 199.8 °C; $T_{d10}$ 235.4 °C; $^1$H NMR (400 MHz, 293 K, CDCl$_3$) $\delta$ 7.46–7.32 (m, Ar, NH), 6.80 (brd, NH), 4.46 (s, CH), 4.45 (s, CH), 4.19–3.88 (m, CH$_2$), 3.39–3.24 (m, CH$_2$) ppm; $^{13}$C NMR (100 MHz, 293 K, CDCl$_3$) $\delta$ 172.8, 172.3, 172.2, 169.5, 141.9, 141.8, 140.2, 140.1, 136.1, 136.0, 128.8, 128.0, 127.9, 127.8, 127.79, 127.65, 127.61, 127.0, 66.1, 46.8 (t, $J_{CF} = 22.5$ Hz), 43.1, 41.2 ppm; $^{19}$F NMR (376 MHz, 293 K, CDCl$_3$) $\delta$ –81.44, –81.55, –81.58, –81.61, –81.64, –116.51, –119.18, –122.57, –122.86, –123.63, –123.92, –124.37, –127.03 ppm; IR (KBr) $\nu$ 3318, 3033, 1662, 1533, 1488, 1413, 1217, 1146, 1009, 882, 837, 808, 763, 735, 721, 699, 661, 565 cm$^{-1}$. 
$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, DOSY, and IR spectra

Figure S1. $^1$H NMR spectrum of P1 (400 MHz, CDCl$_3$, 298 K).

Figure S2. $^{13}$C NMR spectrum of P1 (100 MHz, CDCl$_3$, 298 K).

Figure S3. $^{19}$F NMR spectrum of P1 (376 MHz, CDCl$_3$, 298 K).
Figure S4. DOSY correlations of P1 (400 MHz, CDCl₃, 298 K).

Figure S5. IR spectrum of P1 (KBr).
Figure S6. $^1$H NMR spectrum of P2 (400 MHz, CDCl$_3$, 298 K).

Figure S7. $^{13}$C NMR spectrum of P2 (100 MHz, CDCl$_3$, 298 K).

Figure S8. $^{19}$F NMR spectrum of P2 (376 MHz, CDCl$_3$, 298 K).
Figure S9. DOSY correlations of P2 (400 MHz, CDCl₃, 298 K).

Figure S10. IR spectrum of P2 (KBr).
Figure S11. $^1$H NMR spectrum of P3 (400 MHz, CDCl$_3$, 298 K).

Figure S12. $^{13}$C NMR spectrum of P3 (100 MHz, CDCl$_3$, 298 K).

Figure S13. $^{19}$F NMR spectrum of P3 (376 MHz, CDCl$_3$, 298 K).
Figure S14. DOSY correlations of P3 (400 MHz, CDCl₃, 298 K).

Figure S15. IR spectrum of P3 (KBr).
Figure S16. $^1$H NMR spectrum of P4 (400 MHz, CDCl$_3$, 298 K).

Figure S17. $^{13}$C NMR spectrum of P4 (100 MHz, CD$_2$OD, 298 K).

Figure S18. $^{19}$F NMR spectrum of P4 (376 MHz, CDCl$_3$, 298 K).
Figure S19. DOSY correlations of P4 (400 MHz, CDCl₃, 298 K).

Figure S20. IR spectrum of P4 (KBr).
Figure S21. $^1$H NMR spectrum of P5 (400 MHz, CDCl$_3$, 298 K).

Figure S22. $^{13}$C NMR spectrum of P5 (100 MHz, CD$_3$OD, 298 K).

Figure S23. $^{19}$F NMR spectrum of P5 (376 MHz, CDCl$_3$, 298 K).
**Figure S24.** DOSY correlations of P5 (400 MHz, CDCl₃, 298 K).

**Figure S25.** IR spectrum of P5 (KBr).
Figure S26. $^1$H NMR spectrum of P6 (400 MHz, CDCl$_3$, 298 K).

Figure S27. $^{13}$C NMR spectrum of P6 (100 MHz, CDCl$_3$, 298 K).

Figure S28. $^{19}$F NMR spectrum of P6 (376 MHz, CDCl$_3$, 298 K).
Figure S29. DOSY correlations of P6 (400 MHz, CDCl₃, 298 K).

Figure S30. IR spectrum of P6 (KBr).
Figure S31. Calibration curve in CDCl$_3$ for $M_w$ prediction using imine A (MW: 175.23, log D: $-8.55$), unit model B (MW: 376.45, log D: $-8.70$), and PAMAM dendrimer (MW: 14214.17, log D: $-9.15$) as standards. Imine A and unit model B were prepared according to the literature.$^{1a}$
Figure S32. DSC profile of P1.

Figure S33. DSC profile of P2.
Figure S34. DSC profile of P3.

Figure S35. DSC profile of P4.
Figure S36. DSC profile of P5.

Figure S37. DSC profile of P6.
Comparison of IR spectra of cotton gauze before and after modification.

**Figure S38.** IR spectrum of modified gauze (ATR).
UV spectra of P6

**Figure S39.** UV spectra of P6 at various concentrations (CHCl₃, room temperatures).

**Figure S40.** Normalized absorbance of P6 at 337, 340, 350, and 360 nm as a function of concentration (wt%).
Figure S41. TGA profile of P1.

Figure S42. TGA profile of P2.
**Figure S43.** TGA profile of P3.

**Figure S44.** TGA profile of P4.
Figure S45. TGA profile of P5.

Figure S46. TGA profile of P6.

References