Electronic Supplementary Material (ESI) for Soft Matter.

Non-dependence of Dodecamer Structures on Alkyl Chain Length in Platonic Micelles

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Table of Contents

General considerations

Materials and Synthesis. All chemical reagents were purchased from Tokyo Chemical Industry Co. and Sigma-Aldrich Co., which were used without further purification. The chemical reactions for the synthesis of quaternary amines bearing calix[4]arene-based amphiphiles was carried out under nitrogen atmosphere. The progress of the reactions was monitored using thin layer chromatography (TLC), and detected using ultraviolet (UV; 254 nm) irradiation. Nuclear magnetic resonance spectra were recorded with a 500 MHz Bruker spectrometer using methanol-d4 as solvents.

Synthesis procedures of primary amines bearing calixarene-based amphiphiles

Synthesis of primary amines bearing calixarene lipid with butyl tails (PACaL4). PACaL4 was synthesized using same procedure as that reported before.[1] *N*-Boc-propargylamine (0.194 g, 1.25 mmol), copper(II) sulfate pentahydrate (10.2 mg, 37.4 μmol), and sodium ascorbate (39.5 mg, 0.199 mmol) were dissolved in dry DMF (10 mL), and then a solution of azide bearing calix[4]arene derivative (0.218 g, 0.249 mmol) in dry DMF (5 mL) was added to the mixture. The reaction mixture was stirred for 48 h at 90 °C. The mixture was cooled to room temperature, and then concentrated at reduced pressure. The crude product was purified by reversed phase silica gel column chromatography (water), which afforded a brown solid (0.356 g, 0.239 mmol, 96%). The solution of the purified compound (0.356 g, 0.239 mmol) was treated with 4N HCl/EtOAc solution for 1h. The solvent was evaporated, and the residue was washed with CH_2Cl_2 and EtOAc. III was obtained as a light yellow solid (0.260 mg, 100%). ^{1}H NMR (500 MHz, methanol-d4): δ (ppm) = 8.05 (s, 4H), 6.69 (s, 8H), 5.36 (s, 8H), 4.43 (d, J = 13.0 Hz, 4H), 4.26 (s, 8H), 3.85 (t, J = 8.00 Hz, 8H), 3.13 (d, J = 13.0 Hz, 4H), 1.88 (m, 8H), 1.47 (m, 8H), 0.998 (t, J = 7.5 Hz, 12H). ESI–MS (M^{2+}/2): calcd for $C_{60}H_{82}N_{16}O_4$ 545.3, found 545.5.

Synthesis of primary amines bearing calixarene lipid with pentyl tails (PACaL5). PACaL5 was synthesized using a similar procedure described for QACaL4. Yield: 0.424 g, 0.369 mmol, 95%. ^{1}H NMR (500 MHz, methanol-d4): δ (ppm) = 8.08 (s, 4H), 6.70 (s, 8H), 5.36 (s, 8H), 4.42 (d, J = 13.0 Hz, 4H), 4.28 (s, 8H), 3.86 (t, J = 8.00 Hz, 8H), 3.13 (d, J = 13.0 Hz, 4H), 1.91 (m, 8H), 1.41 (m, 16H), 0.95 (t, J = 7.5 Hz, 12H). ESI–MS (M^{2+}/2): calcd for $C_{64}H_{90}N_{16}O_4$ 573.4, found 573.5.

Synthesis of primary amines bearing calixarene lipid with heptyl tails (PACaL7). PACaL7 was synthesized

using a similar procedure described for PACaL4. Yield: 0.670 g, 0.0.533 mmol, 90%. ^{1}H NMR (500 MHz, methanol-d4): δ (ppm) = 8.03 (s, 4H), 6.67 (s, 8H), 5.32 (s, 8H), 4.42 (d, J = 13.0 Hz, 4H), 4.28 (s, 8H), 3.86 (t, J = 8.00 Hz, 8H), 3.13 (d, J = 13.0 Hz, 4H), 1.87 (m, 8H), 1.30 (m, 24H), 0.95 (t, J = 7.5 Hz, 12H). ESI–MS (M^{2+}/2): calcd for $C_{72}H_{106}N_{16}O_4$ 629.4, found 629.5.

Synthesis of primary amines bearing calixarene lipid with octyl tails (PACaL8). PACaL8 was synthesized using a similar procedure described for PACaL4. Yield: 0.300 g, 0.236 mmol, 93%. ^{1}H NMR (500 MHz, methanol-d4): δ (ppm) = 8.07 (s, 4H), 6.69 (s, 8H), 5.35 (s, 8H), 4.41 (d, J = 13.0 Hz, 4H), 4.27 (s, 8H), 3.85 (t, J = 8.00 Hz, 8H), 3.14 (d, J = 13.0 Hz, 4H), 1.91 (m, 8H), 1.35 (m, 32H), 0.901 (t, J = 7.5 Hz, 12H). ESI–MS (M^{2+}/2): calcd for $C_{76}H_{114}N_{16}O_4$ 657.5, found 657.6.

Characterization of micellar structures with small angle scattering and analytical ultracentrifugation measurements

Small angle X-ray scattering (SAXS) measurements. The powder of PACaL*n* was dissolved in 50 mM aqueous NaCl to be required concentration. The prepared samples were left for at least one day to equilibrate at room temperature. Small angle X-ray scattering (SAXS) measurements were carried out at the BL-40B2 beamline of the SPring-8 facility, Hyōgo Prefecture, Japan. A 30 × 30 cm imaging plate (Rigaku R-AXIS VII) detector was placed 1 m from the sample. The wavelength of the incident beam (λ) was adjusted to 0.10 nm. This setup provided a q range of 0.20−4 nm^{-1}, where q is the magnitude of the scattering vector, defined as $q = 4\pi \sin\theta/\lambda$, with a scattering angle of 2θ. The X-ray transmittance of the samples was determined by using ion chambers located in front of and behind the sample. The detailed experimental procedures are reported elsewhere.[1] The absolute SAXS intensities were recorded using the absolute scattering intensities of water.[2, 3]

The micellar SAXS profiles were fitted to core-shell spheres or cylinders by using the following expression [4]:

$$I(q) = \left\{ 3V_{\mathrm{C}}(\rho_{\mathrm{C}} - \rho_{S}) \frac{j_1(qR_{\mathrm{C}})}{qR_{\mathrm{C}}} + 3V_{\mathrm{S}}\rho_{\mathrm{S}} \frac{j_1(qR_{\mathrm{S}})}{qR_{\mathrm{S}}} \right\}^2 \quad (1)$$

$$I(q) = \frac{L\pi}{q} \left\{ S_{\mathrm{C}}(\rho_{\mathrm{C}} - \rho_{\mathrm{S}}) \frac{J_1(qR_{\mathrm{C}})}{qR_{\mathrm{C}}} + S_{\mathrm{S}}(\rho_{\mathrm{S}} - \rho_{\mathrm{Sol}}) \frac{J_1(qR_{\mathrm{S}})}{qR_{\mathrm{S}}} \right\}^2 \quad (2)$$

Here, R_{c} and R_{s} are the outer radii of the core and micelle (core + shell), and ρ_{c}, ρ_{s}, and ρ_{sol} are the electron

density of the core, the shell, and the solvent, respectively. J_1 and j_1 are the first Bessel function and second spherical Bessel function, respectively. V_c and V_s are the particle volume of the core and micelle (core + shell), respectively. S_C and S_S are the cross-sectional areas of the core and micelle (core + shell), respectively. For the fitting in SAXS, we took the size distribution described by the Gaussian function into account.

$$P(R) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{(R-R_0)^2}{2\sigma^2}\right]$$

The R_0 and σ are the average radius of the micelle and the standard deviation of micelle size, respectively. The SAXS profiles in the low q region follow the Guinier relation given by the following equation [4]:

$$I(q) = I(0)\exp(-q^2 R_g^{\,2}/3) \tag{3}$$

where $I(0)$ is the forward scattering intensity at $q = 0$. $I(0)$ and the gyration radius (R_g) are determined from the intercept and the slope of the ln($I(q)$) vs. q^2 plot (Guinier plot). Due to inter-particle interference, the $I(0)$ and R_g values depend on the sample concentration. In order to remove the concentration effects, the SAXS intensities recorded at different concentrations were extrapolated to zero concentration.

Determination of micellar molar mass by SAXS. The molar mass of the micelles can be given by the following equation [4]:

$$M_w = I(0)\{N_A c(\Delta\rho\bar{\upsilon})^2\} \tag{4}$$

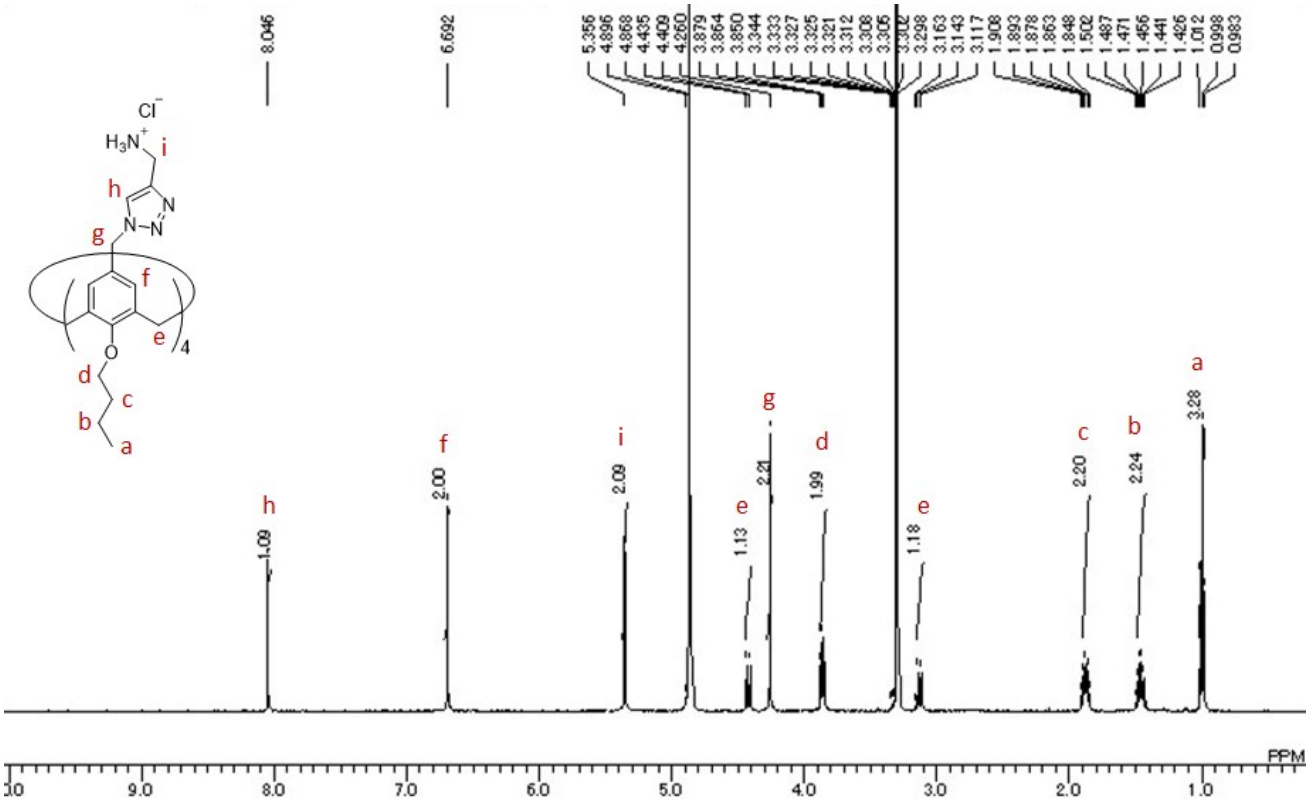
Where M_w is weight averaged molecular weight, c is the concentration of lipids, N_A is Avogadro's number, and $\Delta\rho$ is the scattering length difference, which can be calculated from the electron number and the molecular weight of the lipid and the solvent. The term $\bar{\upsilon}$ indicates the specific volume of micelles in the solution, which can be determined by the density of the micellar solutions and the solvent (Figure S2).

Multi-angle light scattering coupled with asymmetric flow field flow fractionation (AF4-MALS) measurements. PACaL*n* (10 mg mL^{-1}) was prepared in 50 mM aqueous NaCl. Aliquots (30 μL) of the sample solution were injected into an Eclipse 3+ separation system (Wyatt Technology Europe GmbH, Dernbach, Germany) for asymmetrical flow field flow fractionation (AF4) at 25°C. The output from AF4 was then passed sequentially through a Dawn Heleos II multiangle light-scattering (MALS) detector (Wyatt

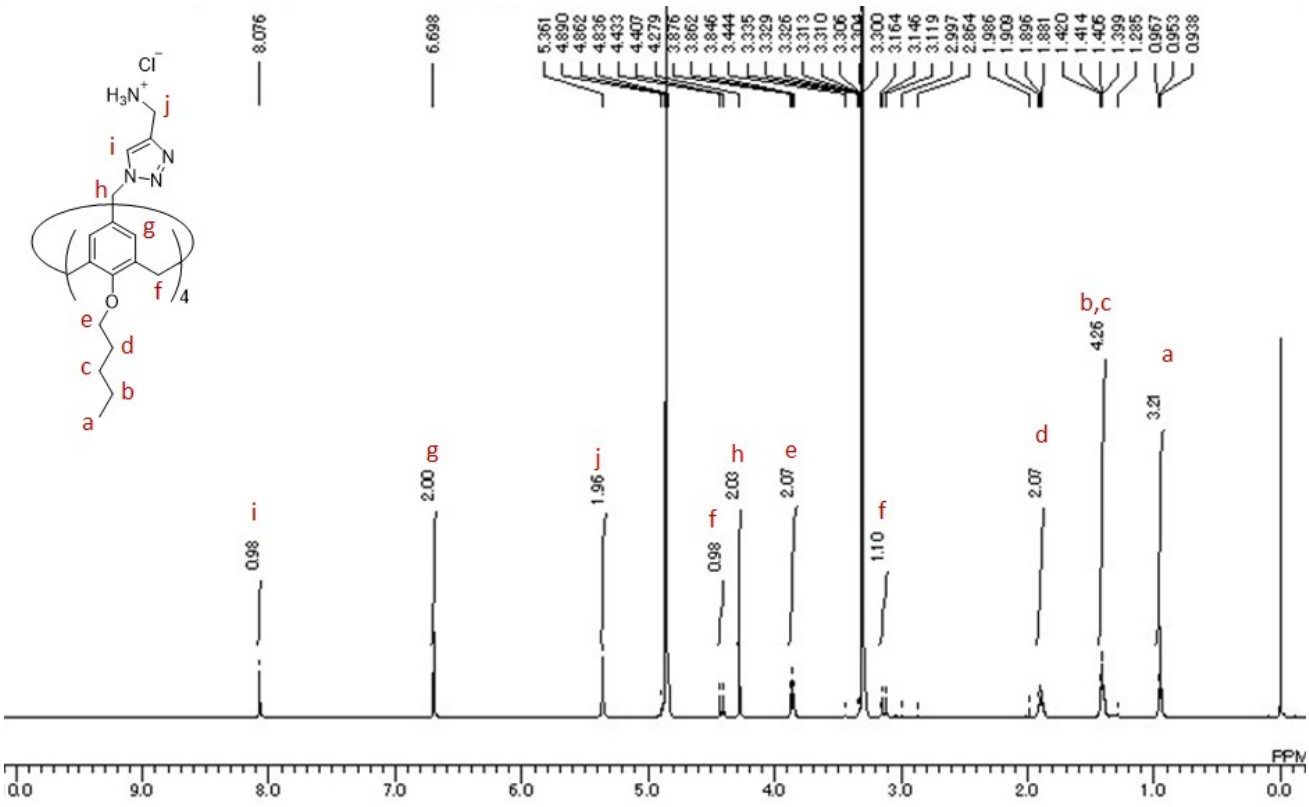
Technology), UV detector, and an Optilab rEX DSP differential refractive index (RI) detector (Wyatt Technology), operating at a wavelength of 658 nm. A Wyatt channel (Eclipse 3 channel LC) attached to a membrane (polyether sulfone membrane; 1 kDa LC) at the bottom of the channel was used for the measurements. The cross-flow and channel-flow rates were fixed at 4.0 and 1.0 mL min^{-1}, respectively. Detailed experimental procedures are reported elsewhere.[4] The specific refractive index increments ($\partial n/\partial c$) and the extinction coefficients (ε at 270 nm) of the micelles in aqueous solution were determined using a DRM-1021 differential refractometer (Otsuka Electronics, Osaka) and a Jasco V-630 spectrometer, respectively (see Figure S2).

Analytical ultracentrifugation (AUC). Analytical ultracentrifugation of PACaL*n* micelles was performed using a Beckman Optima XL-1 ultracentrifuge at 25 °C. The samples were dissolved in 50 mM aqueous NaCl to be required concentration. The reference cell was filled with the NaCl solution while the sample cell was filled with the micelle solutions. The rotor speeds were set at 3.0×10^4 rpm. From analyzing the Rayleigh fringe, the apparent weight average molecular weight $M_{w,App}$ and Q (= $M_{w,App}/M_{z,App}$) were determined at each sample concentration, providing the M_w and Q for the samples by extrapolating the concentration to zero. [4]

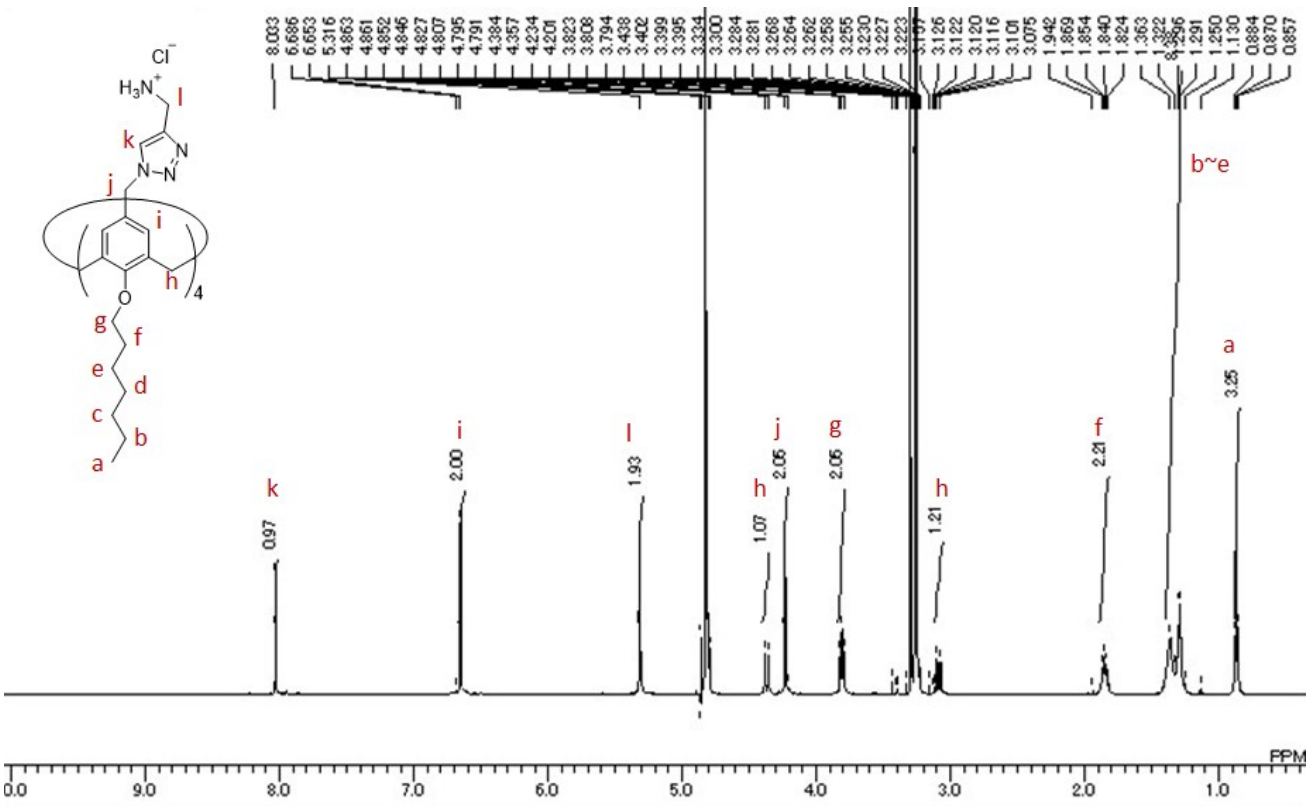
NMR spectra



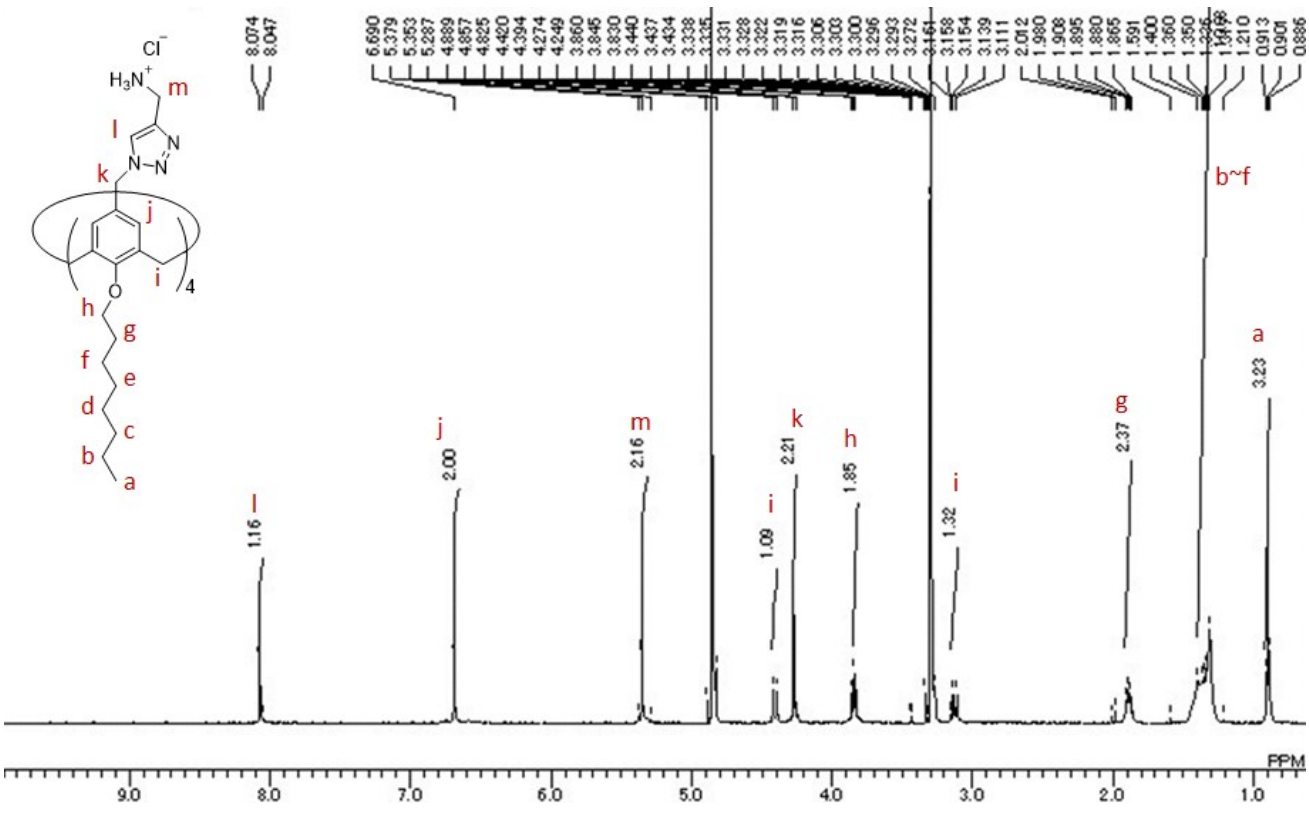
[1]H-NMR spectrum of compound PACaL4.



[1]H-NMR spectrum of compound PACaL5.



^{1}H-NMR spectrum of compound PACaL7.



^{1}H-NMR spectrum of compound PACaL8.

Figure S1

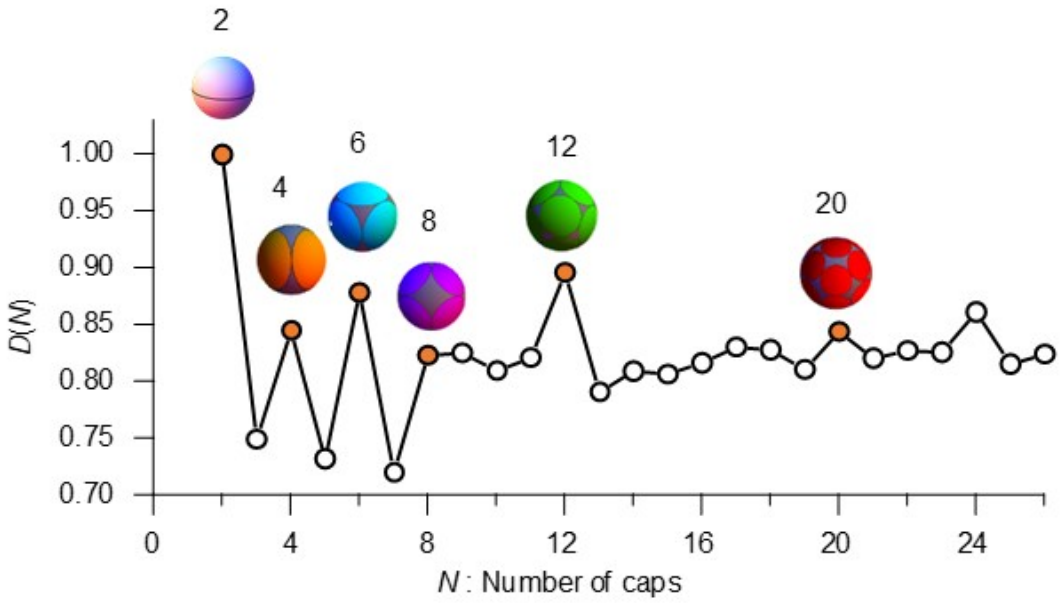


Figure S1. $D(N)$ for N ranging from 2 to 26. Certain numbers produce a local maximum and are identical to the number of the vertices of Platonic solids.

Figure S2

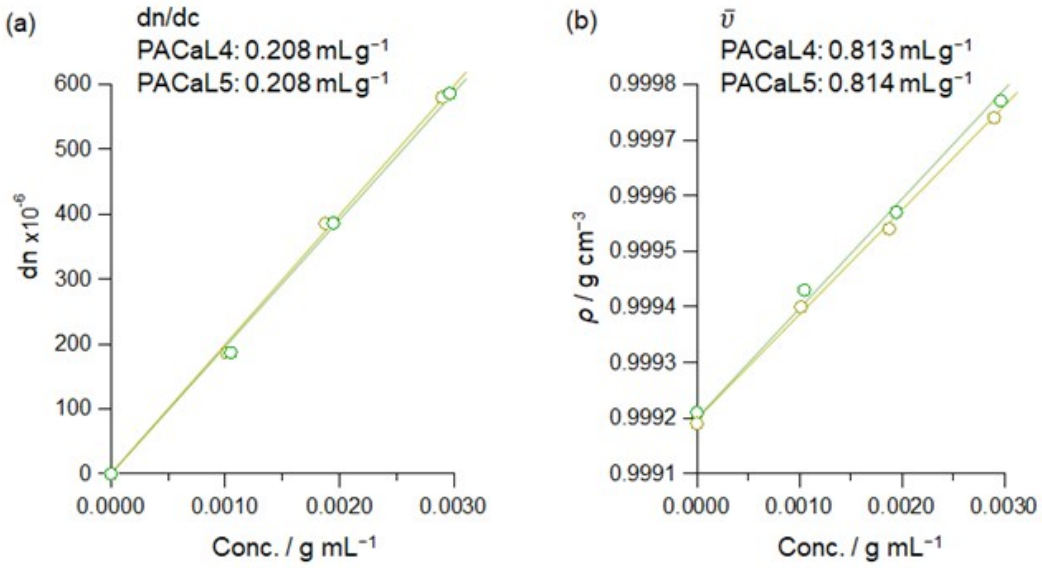


Figure S2. (a) Concentration dependence of refractive index increment and density increment for PACaL*n* micelles (yellow: PACaL4, green: PACaL5) in 50 mM aqueous NaCl (pH = 3.0).

Figure S3

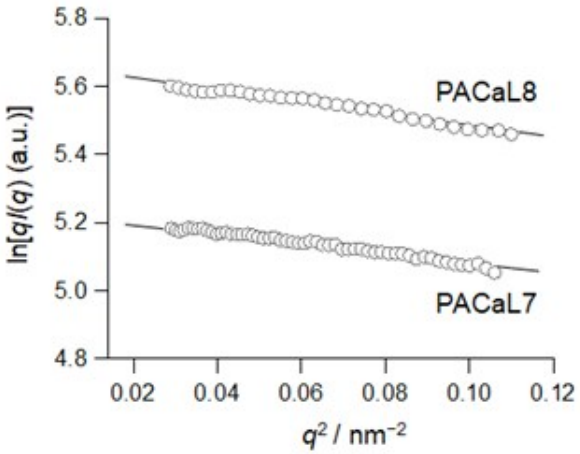


Figure S3. The cross-sectional Guinier plot for PACaL7 and 8 providing the cross-sectional radius.

Figure S4

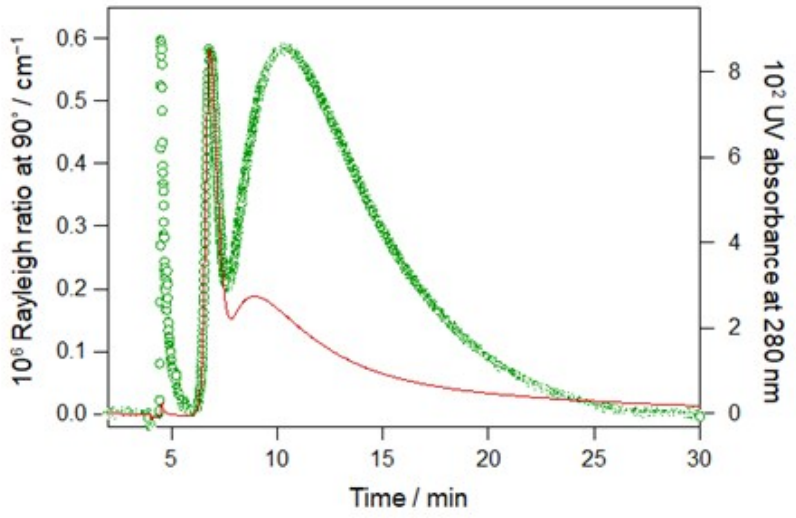


Figure S4. AF4-MALS fractograms of PACaL6 micelles in 50 mM NaCl aqueous solutions (pH = 3.0). The green points and red lines are the Rayleigh ratio at 90° and UV absorbance at 280 nm.

Figure S5

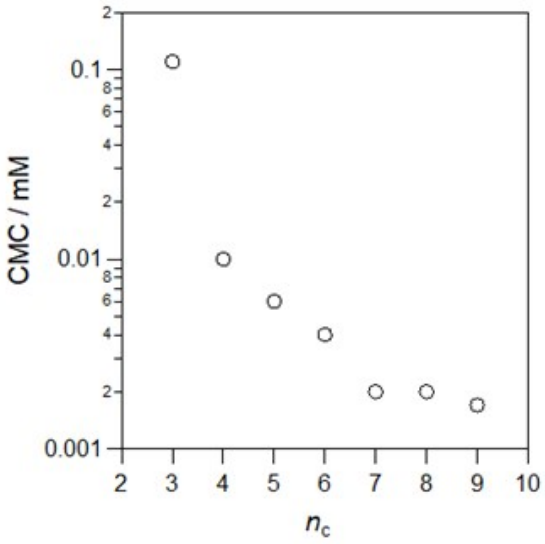


Figure S5. Alkyl chain dependence of critical micelle concetration (CMC) .

Figure S6

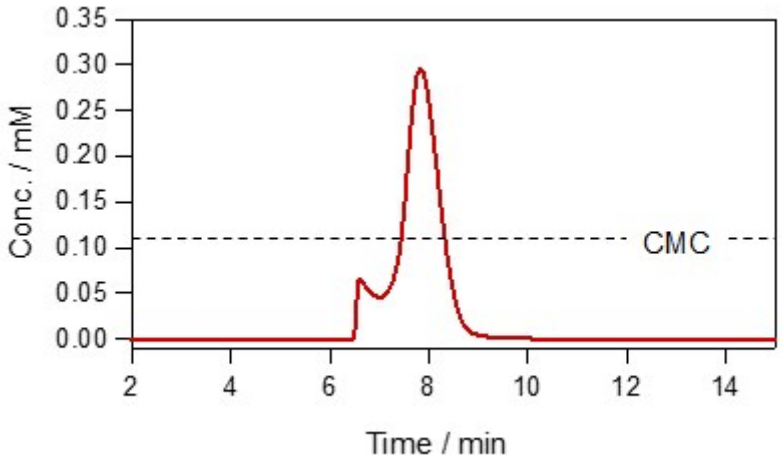


Figure S6. The concentration profile determined by UV absorbance in AF4-MALS fractograms of PACaL3 micelles in 50 mM NaCl aqueous solutions (pH = 3.0).

References

1. S. Fujii, Y. Sanada, T. Nishimura, I. Akiba, K. Sakurai, N. Yagi and E. Mylonas, *Langmuir*, 2012, **28**, 3092-3101.
2. L.A. Feigin, D.I. Svergun, George W. Taylor, Structure analysis by small-angle X-Ray and neutron scattering, Plenum Press, New York, 1987.
3. D. Orthaber, A. Bergmann and O. Glatter, *Journal of Applied Crystallography*, 2000, **33**, 218-225.
4. S. Fujii, J. H. Lee, R. Takahashi and K. Sakurai, *Langmuir*, 2018, **34**, 5072-5078.