

Supporting Information

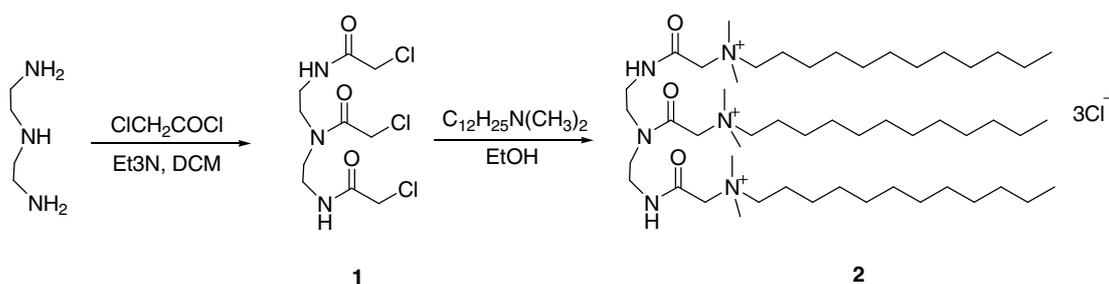
Highly-Ordered Selective Self-Assembly of Trimeric Cationic Surfactant on Mica Surface

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Synthesis of Trimeric Cationic Surfactant DTAD. Compound DTAD was synthesized according to Scheme 1 and characterized by ^1H NMR, ^{13}C NMR, the mass spectrum, and elemental analysis.

SCHEME 1.



Tris(chloroacetyl)diethyltriamine(1). The solution of chloroacetyl chloride (1.5 mL, 14 mmol) in dichloromethane (20mL) was slowly dropped into the solution of diethyltriamine (5.6 mL, 70 mmol) and triethylamine (9.9 mL, 70 mmol) in dichloromethane (100mL) under cooling with an ice bath. The mixture was stirred at

room temperature for 2 h. Methanol was added to the mixture, then the solvent and unreacted substrates were evaporated off under reduced pressure at room temperature. This was purified by filtering through a silica gel column with ethyl acetate/ethanol 20 : 1 and crude product was obtained as a yellow solid, which was recrystallized from ethanol yielding 1.43 g (31%) of white needles: $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta=7.23$ (br, 2H), 4.24 (s, 2H), 4.17 (s, 2H), 4.13 (s, 2H), 3.63-3.70 (m, 8H). MS-ESI(m/z): calcd, 332; found $(\text{M}+\text{H})^+$, 331 (100), 333 (97), 335 (32).¹

Tri(Dodecyldimethylammonioacetoxy)diethyltriamine, trichloride (DTAD) (2).

The mixture of compound **1** (1g, 3 mmol), dodecyldimethylamine (2.9 mL, 11 mmol) and ethanol (50 mL) was heated to 40°C for 72 h. This was concentrated and washed by petroleum ether to remove unreacted dodecyldimethylamine. Then crystallization from acetone/ethanol gave pure compound **2** as a white solid (1.49 g, 51% yield). $^1\text{H NMR}$ (D_2O , c= 4 mM, 400 MHz): $\delta= 4.40$ (s, 2H), 4.08 (s, 2H), 3.97 (s, 2H), 3.62 (m, 2H), 3.59 (m, 4H), 3.49-3.30 (m, 8H), 3.22 (s, 6H), 3.16 (s, 12H), 1.61-1.68 (br, 6H), 1.22 (s, 6H), 1.15 (s, 48H), 0.74 (br, 9H). $^{13}\text{C NMR}$ (D_2O , 100 MHz): $\delta=164.7$, 164.3, 164.1, 63.3, 63.1, 61.5, 61.4, 60.4, 53.1, 53.0, 46.2, 45.6, 37.2, 36.7, 32.0, 30.0, 29.9, 29.8, 29.7, 29.5, 29.0, 28.9, 28.9, 26.3, 26.2, 26.1, 22.6, 22.4, 13.8, 13.8, 13.8. MS-ESI(m/z): calcd, 972; found 288 ($[\text{M}-3\text{Cl}]^{3+}/3$, 100), 451 ($[\text{M}-2\text{Cl}]^{2+}/2$, 66), 936 ($[\text{M}-\text{Cl}]^+$, 4). Anal. Calcd for $\text{C}_{52}\text{H}_{109}\text{C}_{13}\text{N}_6\text{O}_3\cdot 2\text{H}_2\text{O}$: C, 61.91; H, 11.29; N, 8.33. Found: C, 61.81; H, 11.10; N, 7.95.

Surface Tension Measurement. The surface tension of the DTAD solutions was

measured by the drop volume method at 25.00 ± 0.5 °C (Figure 1). The critical micelle concentration of DTAD is 0.29 mM.

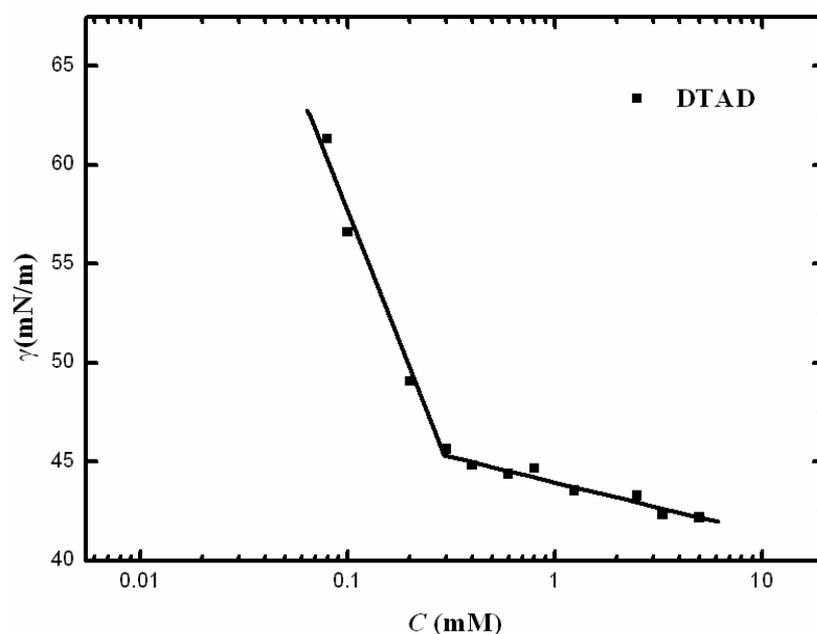


Figure 1. The variation of the surface tension of the DTAD solutions with the concentration at 25.00 ± 0.05 °C.

Atomic Force Microscope (AFM). A Multimode Nanoscope IIIa AFM (Digital Instruments, CA) was used for morphology capturing. For the morphology measurements, the solution of DTAD was dropped onto the freshly cleaved mica substrates and left to equilibrate for 15 min. Then they were dried under a nitrogen flow. All provide morphology images were recorded using a tapping mode with silicon cantilever tips (Park Scientific, CA). They are shown in height mode without any image processing except flattening. Analysis of the AFM images was carried out using the Nanoscope III software, version 5.12r2.

X-Ray Diffraction (XRD). In order to gain information on the thickness of bilayer aggregate of DTAD, cast film of aqueous dispersions (10 mM) of DTAD were examined by X-ray diffraction (Figure 2). The value of d is 2.69 nm.

Cast films for the XRD study were prepared by dispersing the solutions of DTAD onto silicon wafers and then air-dried at room temperature. Finally the wafers were kept under vacuum for 15 min. Reflection XRD studies were carried out with an X-ray diffractometer (Rigaku model D/MAX2500). The X-ray beam was generated with a Cu anode at 40 kV and 200 mA, and the wavelength of the $K\alpha$ beam was 1.5406 Å. The X-ray beam was directed to the edge of film, and the scanning 2θ was recorded from 1 to 20°, using a step width of 0.02°

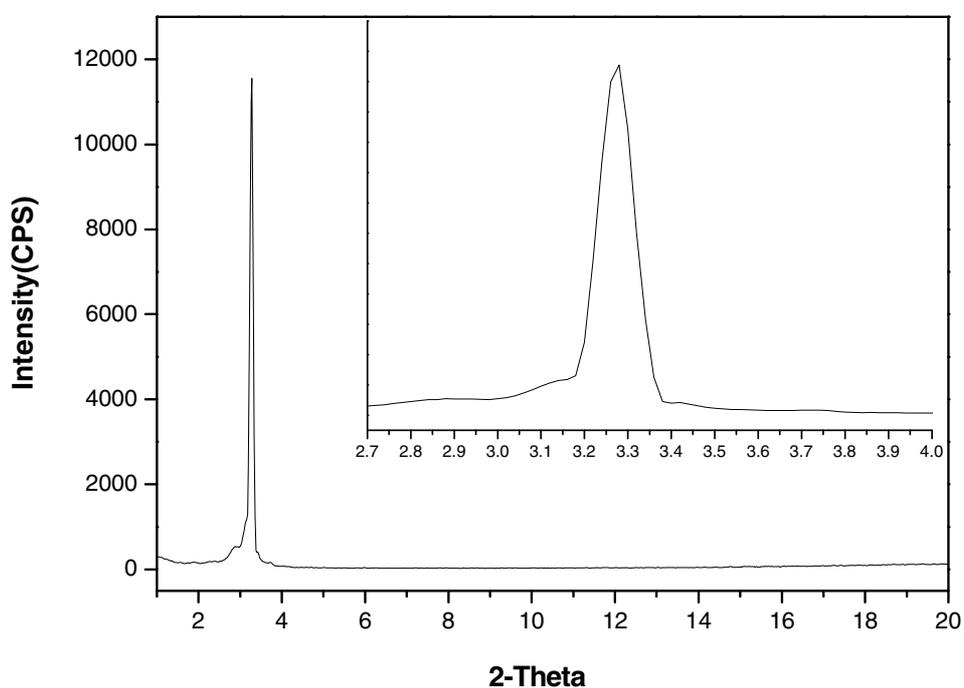


Figure 2. Experimental XRD pattern of DTAD.

X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectroscopy data were obtained by X-ray photoelectron spectroscopy (VGESCALAB MKII spectrometer) with an AlK α monochromatic X-ray source. The base pressure was about 3×10^{-9} mbar. The binding energy scales were referenced to 284.8 eV as determined by the location of the maximum peaks in the C 1s spectra of hydrocarbon (CH_x), associated with adventitious contamination. Each spectrum was curve-fitted using the Xpspeak95 version 3.1 software. In the curve fitting, the widths (FWHM) of Gaussian peaks were maintained constant for all components in a particular spectrum.

References

- (1) Valiyaveetil, V. S., Fngbersen, J. F. J., Verboom, W., Reinhoudt, D. N. *Angew. Chem.* **1993**, *105*, 942-944.