Supporting Information

Viscoelastic lyotropic liquid crystals formed in a bio-based trimeric surfactant system Danping Wang,¹ Lin Feng, Binglei Song,^{*,1} Xiaomei Pei,¹ Zhenggang Cui,¹ and Danhua Xie^{*,2} ¹Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical & Materials Engineering, Jiangnan University, Wuxi, Jiangsu 214122, China ²Fujian Provincial Key Laboratory of Featured Materials in Biochemical Industry; Fujian Province University Key Laboratory of Green Energy and Environment Catalysis, College of Chemistry and Materials, Ningde Normal University, Ningde, Fujian 352100, China

1. Synthesis

The detailed synthetic process, the schematic of which is shown in Fig. 2, is described as follows.

1.1 Synthesis of compound **1.** Phloroglucinol (3.5 g, 0.028 mol), 1,4-dibromobutane (33.7 g, 0.16 mol), anhydrous potassium carbonate (16 g, 0.12 mol) and 40 mL N,N-dimethylformamide (DMF) were added into an single-necked flask. The mixture was stirred at 25 °C for 12 h. After the reaction was completed, the DMF was removed under reduced pressure. The residue was diluted with CHCl₃ and was washed with water, saturated sodium chloride solution and water in sequence. After dried with anhydrous Na₂SO₄, the solvent was removed under reduced pressure. The residue due ther/ethyl acetate (50:1) as the eluent. Compound **2** was obtained as an oily liquid. Yield: 71.5%.

1.2 Synthesis of compound **2.** Dehydroabietic acid (82.6 g, 0.275 mol) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were added into a three-necked flask. Thionyl chloride (50 g, 0.412 mol) was added dropwise at 50 °C. Acidic gas was generated during this process, and it was adsorbed with a saturated NaOH solution. After the addition, the mixture was stirred at 72 °C for 1 h. After cooling, the reaction mixture was evaporated under reduced pressure to remove the excessive thionyl chloride. The obtained dehydroabietic chloride (80 g, 0.25 mol) was dissolved into CH_2Cl_2 and added dropwise into the mixture of 3-dimethylaminopropyl amine (28.2 g, 0.196 mol) and excessive trimethylamine (125.6 g, 1.241 mol) at -5 °C. After the addition, the reaction

^{*} E-mail:ccfsbl@jiangnan.edu.cn; danhuaxie@ndnu.edu.cn

was continued for another 1.5 h. The resulted mixture was then washed with alkaline water three times and extracted with CH_2Cl_2 two times. The extractions were combined and dried using anhydrous Na_2SO_4 . The remaining solvent in the extracts were removed under reduced pressure. The residue was purified on a silica gel column (300-400 mesh) using petroleum ether/ethyl acetate (1:1) as the eluent. Compound **2** was obtained as yellow, viscous liquid. Yield: 80.0%.

1.3 Synthesis of compound tri-R-4-Phe. Compound **1** (9.0 g, 0.017 mol), compound **2** (23.1 g, 0.06 mol) and 50 mL anhydrous ethanol were added into an single-necked flask equipped with a reflux condenser. The mixture was stirred at 80 °C for 72 h. After cooling, the ethanol was removed under reduced pressure. The residue was first washed with ethyl acetate and then recrystallized with ethanol and ethyl acetate three times. The final product was obtained as a white solid after being dried under vacuum at 55 °C. Yield: 54.8%.





Fig. S1¹H NMR spectrum of tri-R-4-Phe (DMSO)



¹H NMR (400 MHz, DMSO) δ 7.76 (t, 3H, N19-1H, N46-1H, N78-1H), 7.15 (d, 3H, C38-1H, C65-1H, C93-1H), 6.96 (d, 3H, C37-1H, C66-1H, C92-1H), 6.81 (s, 3H, C35-1H, C68-1H, C90-1H), 6.13 (s, 3H, C1-1H, C3-1H, C5-1H), 3.95 (s, 6H, C10-2H, C15-2H, C20-2H), 3.35 (t, 6H, C13-2H, C18-2H, C23-2H), 3.28 – 3.20 (m, 6H, C43-2H, C50-2H, C75-2H), 3.14 (d, 6H, C45-2H, C52-2H, C77-2H), 3.03 (s, 18H, C100-3H, C101-3H, C102-3H, C103-3H, C104-3H, C105-3H), 2.84 – 2.65 (m, 9H, C32-2H, C39-1H, C63-2H, C71-1H, C87-2H, C96-1H), 2.27 (d, 3H, C28-1H, C57-1H, C82-1H), 2.03 (d, 3H, C26-1H, C59-1H, C80-1H), 1.90 – 1.54 (m, 30H, C11-2H, C12-2H, C29-2H, C30-2H, C44-2H, C16-2H, C17-2H, C55-2H, C56-2H, C51-2H, C21-2H, C22-2H, C83-2H, C84-2H, C76-2H), 1.49 – 1.28 (m, 9H, C28-1H, C31-2H, C57-1H, C64-2H, C82-1H, C86-2H), 1.17 (s, 9H, C48-3H, C69-3H, C95-3H), 1.15 (s, 9H, C48-3H, C69-3H, C95-3H), 1.13 (d, 18H, C40-3H, C41-3H, C72-3H, C73-3H, C97-3H, C98-3H).



HRMS (ESI) m/z calcd for $C_{93}H_{147}N_6O_6^{3+}$ (M+H)⁺: 481.7133, found 481.7132.

2 The surface activity of aqueous tri-R-4-Phe solutions



Fig. S2 Variations in the equilibrium surface tension (\Box) and intensity of the Nile red fluorescence (\circ) at 625 nm with the tri-R-4-Phe concentration (25 °C)

Tuble Di Dulluce delivity purumeters for the ter 100 at 25	Table S	51 Surface	activity	parameters	for	tri-R-	4-Phe	at 25	°C
---	---------	------------	----------	------------	-----	--------	-------	-------	----

	$C_{20}/$	cmc/	$\gamma_{\rm cmc}/$
	$mmol \cdot L^{-1}$	$\operatorname{mmol} \cdot \operatorname{L}^{-1}$	$mN \cdot m^{-1}$
tri-R-4-Phe	0.07	$0.12^{a}(0.15^{b})$	44.70

a: cmc determined by the surface tension method;

b: cmc determined by the fluorescence probe method;

3. The POM texture observations of tri-R-4-Phe/C $_{12}EO_3$ /water systems



(a)

(b)







(g)

Fig. S3 POM texture observations of 7 samples with different surfactant proportions(a: tri-R-4-Phe=1.5%, $C_{12}EO_3=20\%$, water=78.5%; b: tri-R-4-Phe=5.0%, $C_{12}EO_3=20\%$, water=75.0%; c: tri-R-4-Phe=8.0%, $C_{12}EO_3=20\%$, water=72.0%; d: tri-R-4-Phe=5.0%, $C_{12}EO_3=25\%$, water=70.0%; e: tri-R-4-Phe=5.0%, $C_{12}EO_3=33\%$, water=62.0%; f: tri-R-4-Phe=3.0%, $C_{12}EO_3=40\%$, water=57.0%; g: tri-R-4-Phe=3.0%, $C_{12}EO_3=51\%$, water=46.0%)

4. The Rheological properties of tri-R-4-Phe/C₁₂EO₃/water systems



Fig. S4 Shear stress (σ) plotted as a function of shear rate for tri-R-4-Phe/C₁₂EO₃/water systems with different formulations at 25 °C



Fig. S5 Steady shear viscosity (η) plotted as a function of shear stress for tri-R-4-Phe /C₁₂EO₃/water systems with different formulations at 25 °C



Fig. S6 The molecular structure of R-3-N



Fig.S7 Steady shear viscosity (η) plotted as a function of shear rate for R-3-N/C₁₂EO₃/water systems with different formulations at 25 °C