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(n = 8, 10, 12; m = 12, 14, 16)

Scheme S1. The synthesis route for asymmetric zwitterionic dimeric surfactants.



Scheme S2. The synthesis route for counterion coupled gemini surfactants.



(n = 8, 10, 12)

Scheme S3. The synthesis route for anionic dimeric surfactants.



Fig. S1 Variation of equivalent deviation of cmc ( $\Delta$ cmc/cmc<sub>id</sub>) with the stoichiometric mole fraction ( $\alpha$ ) of zwitterionic dimerics (a), cocogems (b) and anionic geminis (c) for the surfactant – IMP mixed systems.



С



f

<u>300</u>

280



1.5

1.0

0.5

0.0

200

240

Wavelength (nm)

220

260

280



h

∎\_**q** 300

1.5

1.0

0.5

0.0

200

220

240

Wavelength (nm)

260







q



Fig S2: The UV-vis spectra of Sudan III in pure components (a-l) and in IMP-surfactant mixtures at  $\alpha = 0.075$  (for zwitterioinc dimerics, m-q); (for cocogems, r-t) and  $\alpha = 0.0075$  (for anionic dimerics, u-w), just after preparation (**a**), 3 (**•**), 7 (**△**), 15 (**V**) and 30 (**⊲**) days. The y-axis scale is for plot denoted as (**a**). The other plots have been shifted vertically by 0.25, 0.5, 0.75 and 1, respectively. A is for IMP,