Title: Giant Surfactants based on POSS(s)-Tethered Macrocycle

Precision Synthesis of Macrocyclic Giant Surfactants Tethered with Two Different Polyhedral Oligomeric Silsesquioxanes at Distinct Ring Locations via Four Consecutive "Click" Reactions

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Fig. S1 ¹³C NMR spectra of (a) DIBO-(VPOSS)-DIBO, (b) VPOSS-cPS, and (c) APOSS-cPS.



Fig. S2 UV spectra of (a) DIBO-(VPOSS)-DIBO (black curve), (b) N₃-PS-N₃ (red curve), and (c) VPOSS-cPS (blue curve).



Fig. S3 FTIR spectra of (a) N₃-PS-N₃ (black curve), (b) VPOSS-cPS (red curve), and (c) APOSS-cPS(blue curve).



Fig. S4 UV spectra of (a) DIBO-(VPOSS)-DIBO (black curve), (b) VPOSS-cPS-alkyne (red curve), and (c) VPOSS-cPS-ACPOSS (blue curve).



Fig. S5 FTIR spectra of (a) Alkyne-(PS-N₃)₂ (black curve), (b) VPOSS-cPS-alkyne (red curve), (c) VPOSS-cPS-ACPOSS (blue curve), (d) VPOSS-cPS-FPOSS (magenta curve), and (e) APOSS-cPS-FPOSS (olive curve).



Fig. S6 ¹³C NMR spectra of (a) VPOSS-cPS-alkyne, (b) VPOSS-cPS-ACPOSS, (c) VPOSS-cPS-FPOSS, and (d) APOSS-cPS-FPOSS.



Scheme S1. Synthetic Approach for ACPOSS-N₃: (i) ethylene glycol, DPTS, DIPC, dry CH₂Cl₂, 0 °C, 68%; (ii) ACPOSS-COOH, DPTS, DIPC, dry CH₂Cl₂, 0 °C, 72%.



Fig. S7 ¹H NMR spectrum (a) and MALDI-TOF mass spectrum (b) of ACPOSS-N₃.