Electronic Supplementary Material (ESI) for ChemComm.

A new amphiphilic pillar[5]arene: synthesis, controllable self-assembly in water and application in white-light-emitting system

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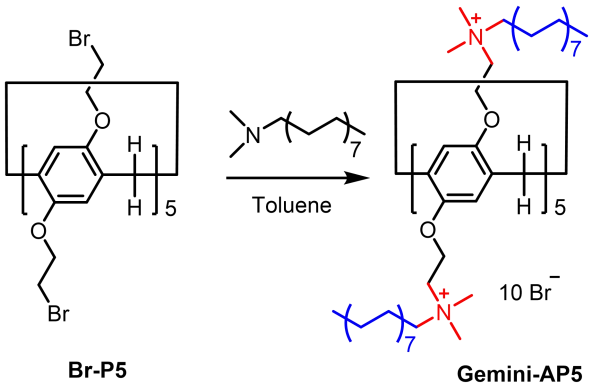
Supporting information

1. Materials and methods

N,N-Dimethylhexadecan-1-amine, boron trifluoride etherate, triformol, adenosine triphosphate and tetraphenylporphyrin were reagent grade and used as received. **BrP5** was synthesied according the reported reference.[S1] Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. ^{13}C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometry at 100 MHz. Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. The SEM samples were prepared on clean Si substrates. Each sample solution was deposited onto a Si substrate, placed in a refrigerator for 30 min, and freeze-dried in a freeze-drying machine at –20 °C under reduced pressure. Fluorescence spectra were recorded on a Hitachi F-7000 Fluorescence Spectrophotometer. Confocal images were acquired using an Olympus FLUOVIEW FV1000 confocal laser scanning unit mounted on an IX81 fixed stage upright microscope. **Transmission Electron Microscopy (TEM) Studies:** The self-assembly behavior of the system was studied using TEM. The solutions of the samples were first made in water. These samples were prepared by drop-coating the solutions onto a carbon-coated copper grid. TEM experiments were performed on a JEM-1200EX instrument with an accelerating voltage of 80 kV. **Dynamic Light Scatting Experiments:** The mean diameter of the assemblies of **Gemini-AP5** were measured by DLS experiments on a Nano-ZS ZEN3600 instrument at 25 °C. The scattering intensity was measured at an angle of 175°. An average of three successive measurements was noted for each sample. **Surface Tension Investigation:** Aqueous solutions of **Gemini-AP5, RD-AP5** and **Mono-AP6** at different concentrations were first prepared and the surface activity of the solutions was investigated by a Jzhy1-180 surface tension meter at 25 °C.

2. Synthesis of ***Gemini-AP5***

Scheme S1. *Synthetic route to* ***Gemini-AP5***



Br-P5 (1.62 g, 1.00 mmol) was added to a solution of *N,N*-Dimethylhexadecan-1-amine (2.70 g, 10.0 mmol) in dry toluene (50 mL). The mixture was stirred at 100 °C for 24 hours under nitrogen atmosphere. Then the solvent was evaporated and the residue was purified by recrastal in CH_3CH_2OH to give **Gemini-AP5** as a white solid (3.0 g, 75%). The proton NMR spectrum of **Gemini-AP5** is shown in Fig. S1. ^{1}H NMR (400 MHz, DMSO-d_6, 293K) δ (ppm): 7.02 (s, 10H), 4.37 (s, 20H), 4.16 (s, 10H), 3.81 (s, 40H), 3.30 (s, 60H), 1.75 (s, 20H), 1,24 (s, 280H) 0.86 (t, J = 6 Hz, 30H). The ^{13}C NMR spectrum of **Gemini-AP5** is shown in Fig. S2. ^{13}C NMR (100 MHz, DMSO-d_6, 293K) δ (ppm): 127.03, 123.94, 115.95, 79.76, 79.43, 79.10, 31.81, 29.63, 29.56, 29.24, 22.60, 14.40. LR-ESI-MS is shown in Fig. S3: m/z 639.2 [**M** − 6Br]$^{6+}$; 782.3 [**M** − 5Br]$^{5+}$; 1007.1 [**M** − 4 Br + 2 H_2O]$^{4+}$.

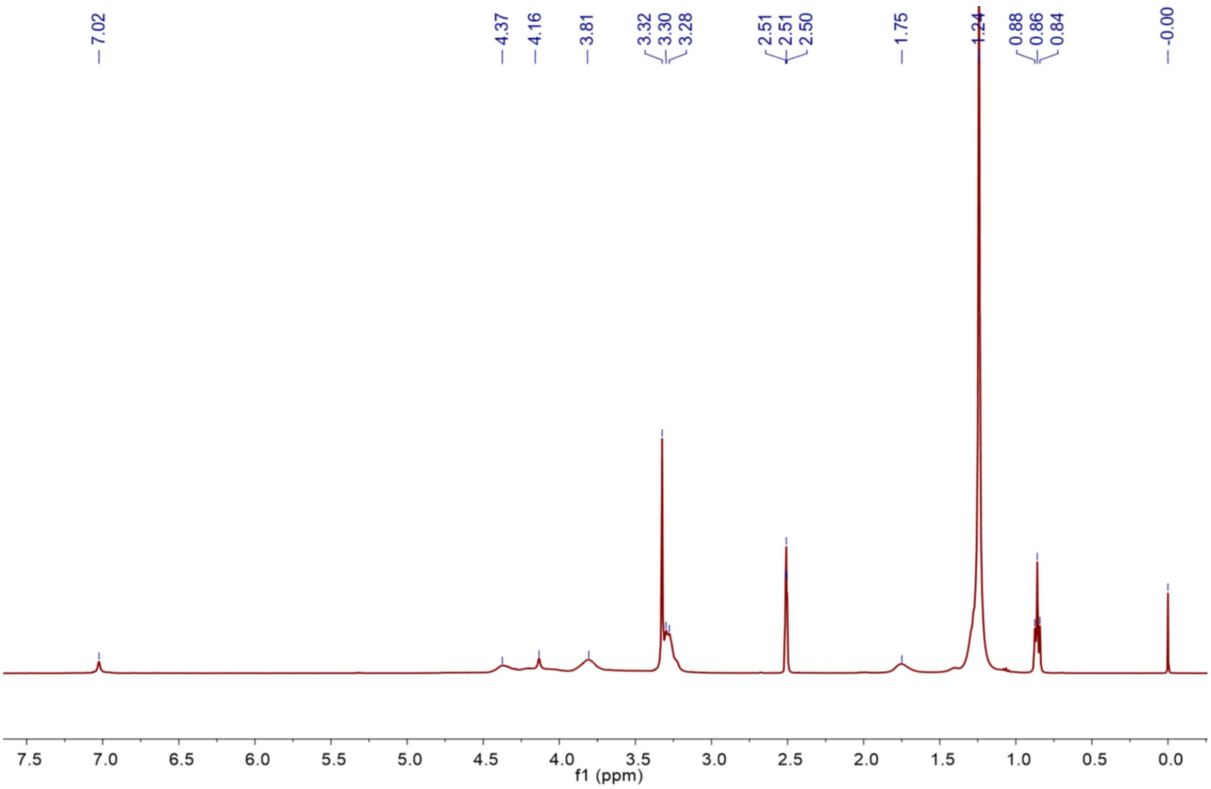


Figure S1. ^{1}H NMR spectrum (400 MHz, DMSO, 293 K) of **Gemini-AP5**.

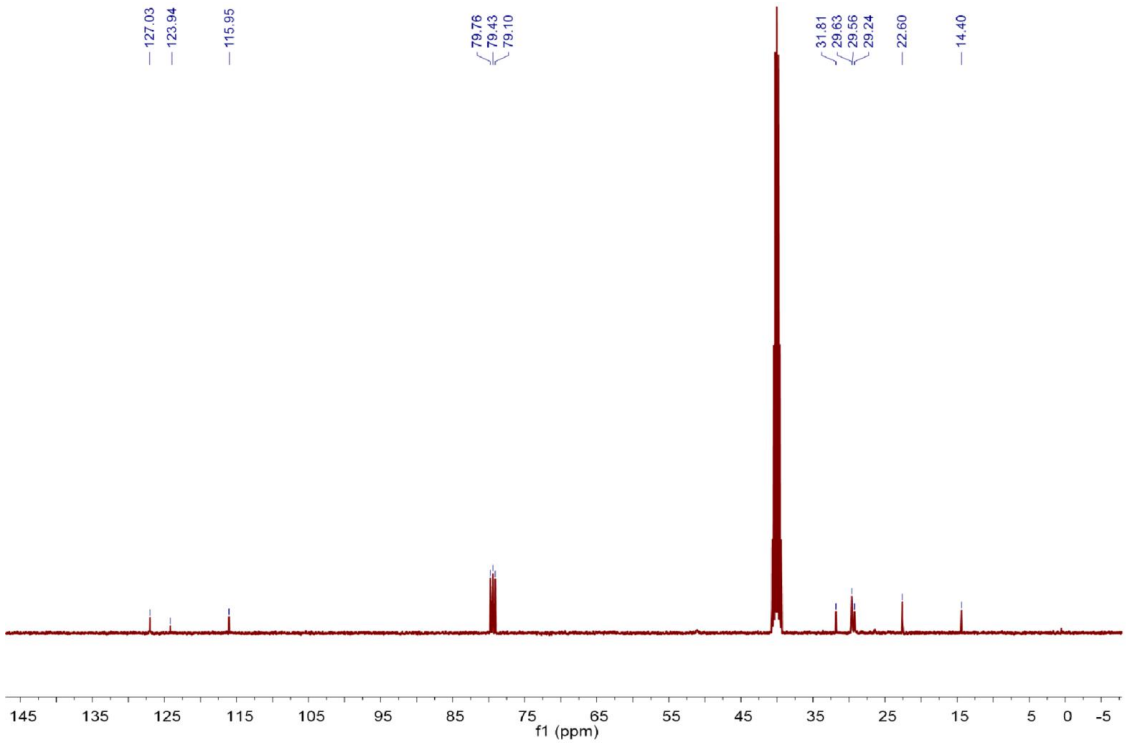


Figure S2. ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 293 K) of **Gemini-AP5** .

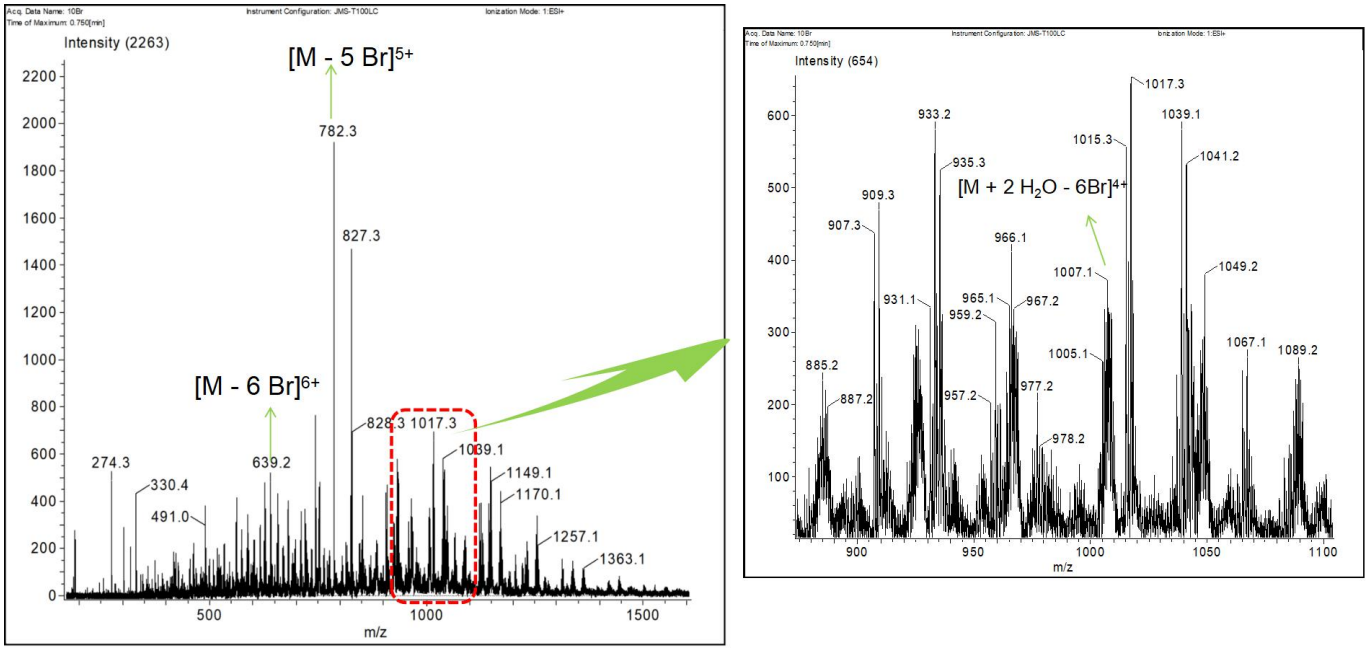


Figure S3. Electrospray ionization mass spectrum of **Gemini-AP5**.

3. Self-assembly of Gemini-AP5 in water

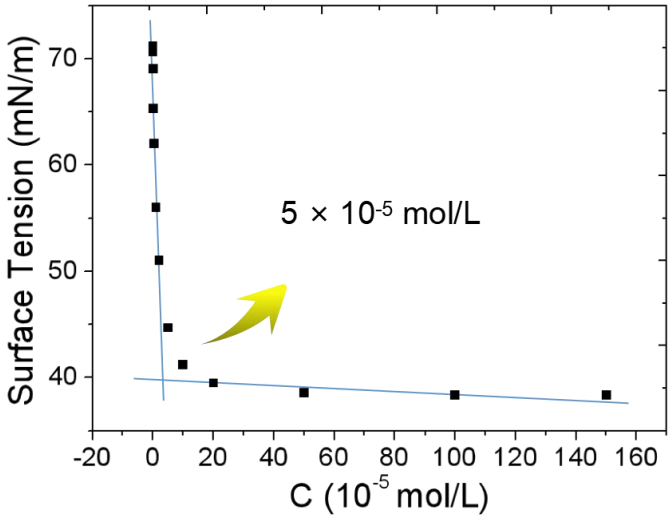


Figure S4. *J-C* curves of **Gemini-AP5,** from this curve we found that the CAC value of **Gemini-AP5** is about 5×10^{-5} mol/L.

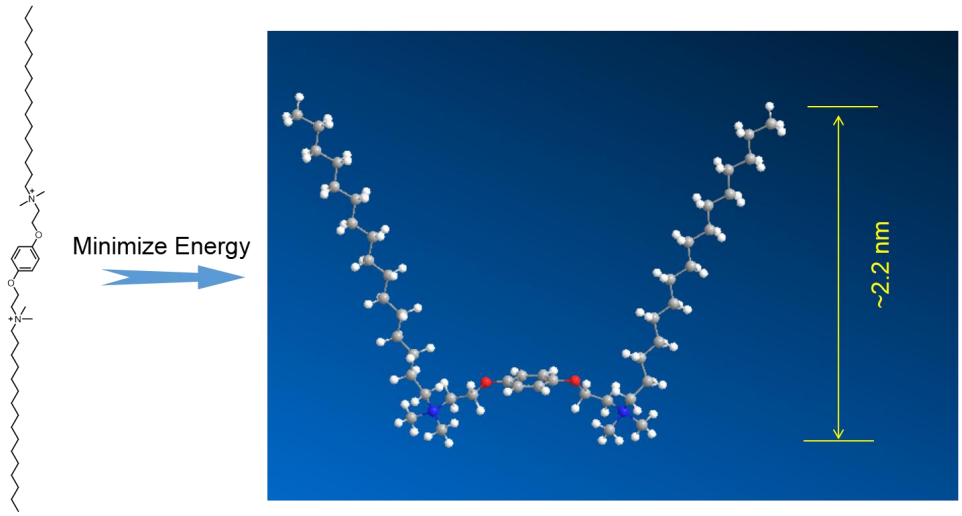


Figure S5. Minimize energy model of the model structure calculated by Chem. 3D (MM2 minimize energy).

4. ATP induced morphology transformation

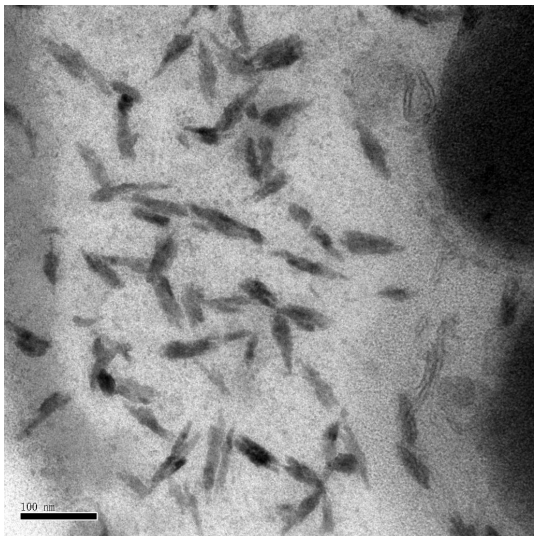


Figure S6. TEM image of **Gemini-AP5&ATP** after addition of HCl.

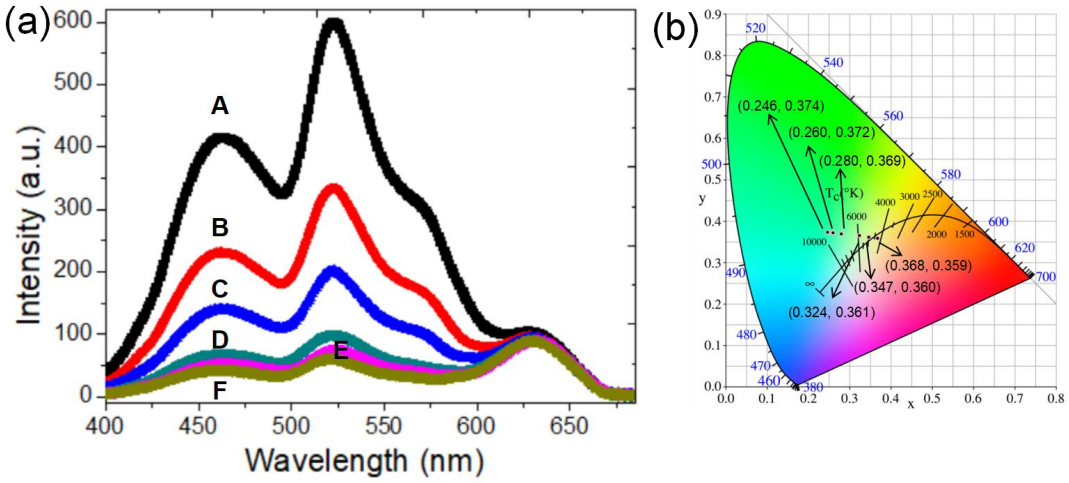


Figure S7. (a) Fluorescence spectra of **Gemini-AP5&TPP-CTPE-FL** ([**Gemini-AP5**] = 1.00×10^{-4} mol/L, [**TPP**] = 1 mg/mL, [C] = [**CTPE**] = [**FL**], A: [C] = 1.00×10^{-6} mol/L, B: [C] = 7.00×10^{-7} mol/L; C: [C] = 3.00×10^{-7} mol/L; D: [C] = 1.00×10^{-7} mol/L; E: [C] = 6.00×10^{-8} mol/L; F: [C] = 6.00×10^{-8} mol/L). (b) CIE chromaticity coordinate of **Gemini-AP5&TPP-CTPE-FL** according to the spectra recorded in (a).

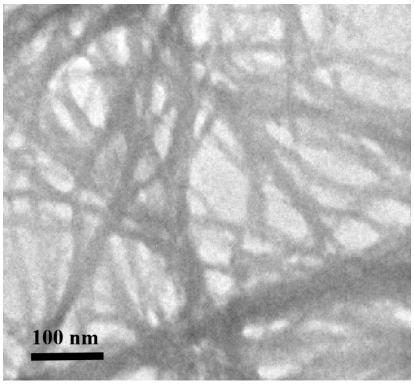


Figure S8. TEM image of **Gemini-AP5** and **GTP** co-self-assembly in water.

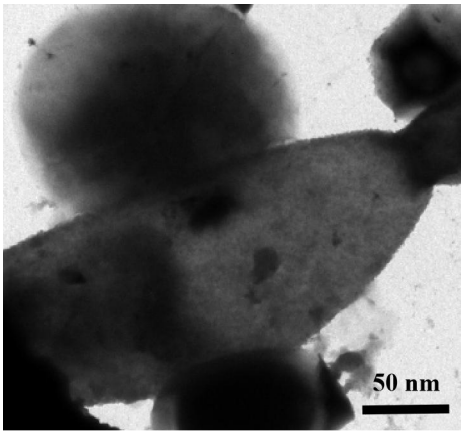


Figure S9. TEM image of several vesicles fused together.

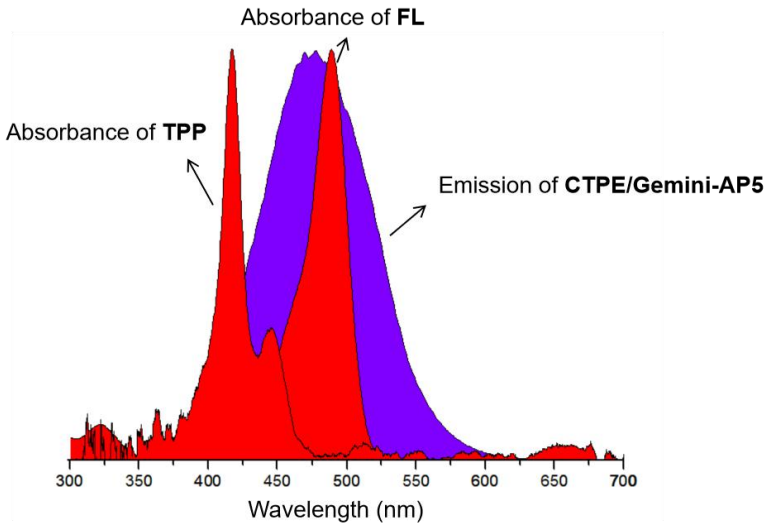


Figure S10. Normalized emission spectrum of **CTPE-Gemini-AP5**, absorption spectrum of **TPP** and absorption spectrum of **FL**.

The fluorescence quantum yields were determined using the following formula:[S2]

$\varphi_i = \varphi_s (n^2/n_s^2)(I_i/I_s)[(1-10^{-As(\lambda_{exc})})/(1-10^{-Ai(\lambda_{exc})})]$

where φ is fluorescence quantum yield, A is the absorbance at the excitation wavelength, I the area under the fluorescence spectra, and n is the refractive index of the solvent in which the sample was collected. The subscripts "i" and "S" refer to the sample of interest and the standard, respectively. Coumarin 153 in EtOH (φ = 0.546) was used as a standard. The quantum yield was thus estimated to be 13.2% for this system.

5. References

S1. a) Y. Ma, X. Ji, F. Xiang, X. Chi, C. Han, J. He, Z. Abliz, W. Chen, F. Huang, *Chem. Commun.,* **2011**, *47*, 12340; b) Y. Yao, J. Li, J. Dai, X. Chi, M. Xue, *RSC Adv.* **2014**, *4*, 9039.

S2.W.-C. Geng, Y.-C. Liu, Y.Y. Wang, Z. Xu, Z. Zhang, C.-B. Yang and D.S. Guo, *Chem. Commun.*, **2017**, *53*, 392.