Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information of

Structural factors of amphiphilic calix[6]biscrowns affecting their vesicle-nanotube transitions in self-assembly

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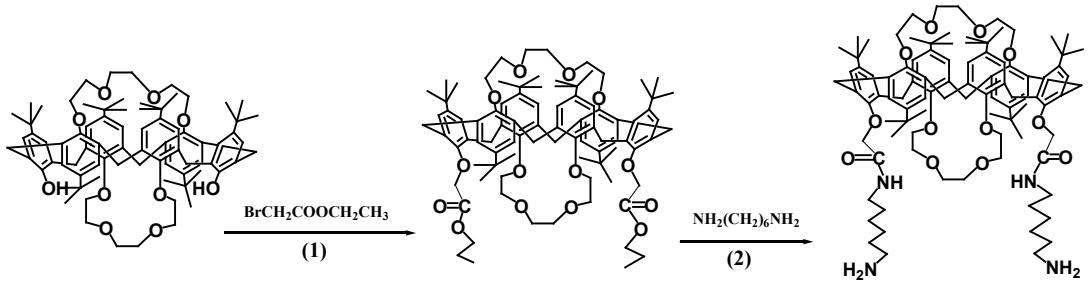
Synthesis and Characterization

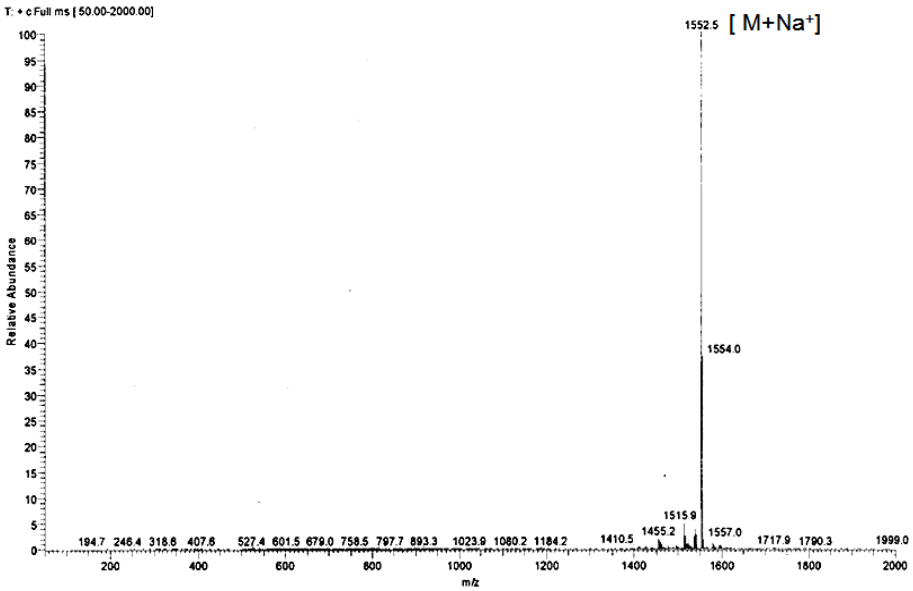
Scheme S1 The synthetic route of terminal amino calix[6]biscrowns (CamA6)



Reagents and reaction:

Calix[6]biscrowns was synthesized according to the reference.[1] (1) K_2CO_3/acetonitrile, reflux, 24 h; (2) $NH_2(CH_2)_6NH_2$ as the solvent and the reagent, room temperature, 24 h.

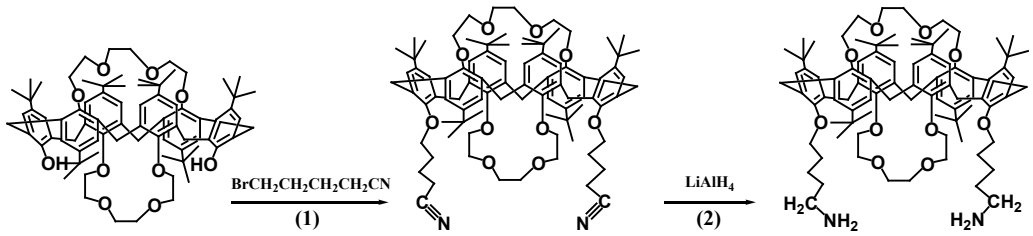
MALDI-TOF Result of CamA6: [M+Na^+] m/z = 1552.5.



^{1}H NMR (500 MHz, $CDCl_3$):

1.14 (18 H, s, C(CH_3)$_3$), 1.23 (34 H, m, C(CH_3)$_3$ and CH_2), 1.40 (18 H, s, C(CH_3)$_3$), 1.44 (4 H, br, NH_2), 2.46 (2 H, t, OCH_2CH_2), 2.53-2.81 (6 H, m, OCH_2CH_2), 2.81-3.69 (26 H, m, OCH_2CH_2, ArCH_2Ar and CONHCH_2), 3.88-4.48 (12 H, m, OCH_2CH_2 and ArCH_2Ar), 4.66 (2 H, ArCH_2Ar), 6.78 (2 H, s, Ar*H*), 6.85 (2 H, m, CON*H*), 7.06 (2 H, s, Ar*H*), 7.10 (2 H, s, Ar*H*), 7.11 (2 H, s, Ar*H*), 7.25 (2 H, s, Ar*H*), 7.30 (2 H, s, Ar*H*);

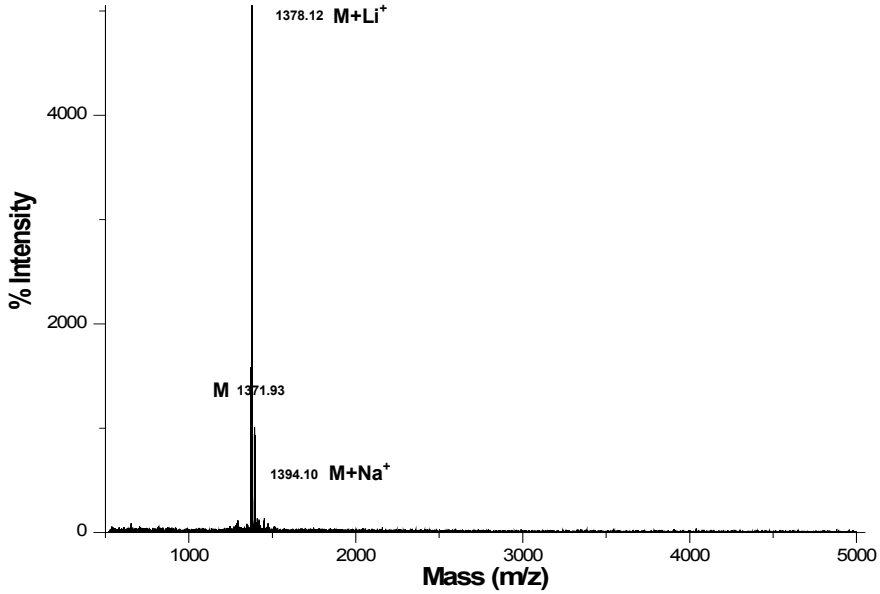
Scheme S2 The synthesis route of terminal amino calix[6]biscrowns (CA5)



Reagents and reaction:

calix[6]biscrowns was synthesized according to the reference. (1) K_2CO_3/acetonitrile, reflux, 24 h; (2) dried tetrahydrofuran (THF) as the solvent, $LiAlH_4$ solution in tetrahydrofuran reflux, 24 h.

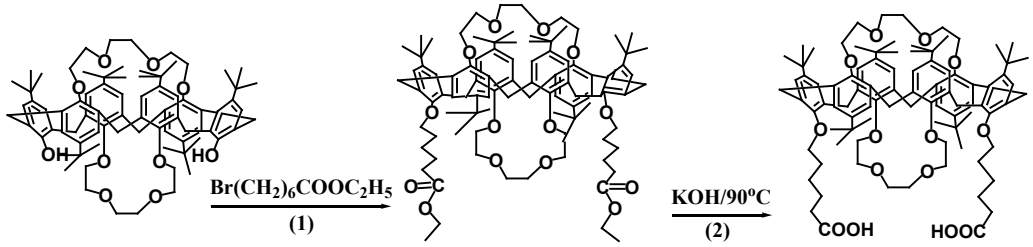
MALDI-TOF Result of CA5: [M] *m*/*z* = 1371.9; [M+Li^+] *m*/*z* =1378.1; [M+Na^+] *m*/*z* = 1394.1;



^{1}H NMR (500 MHz, $CDCl_3$):

1.13-1.16 (54 H, s, C*(CH*$_3$*)*$_3$), 1.2-1.7 (6H, m, C*H*$_2$C*H*$_2$C*H*$_2$), 2.89 (2H, m, CH$_2$N*H*$_2$), 3.56 (24H, m, OC*H*$_2$CH$_2$), 3.62(12H, s, ArC*H*$_2$Ar), 3.93 (2H, m, ArOC*H*$_2$), 4.68 D_2O, 7.35 (6 H, m, Ar*H*), 7.65 (6 H, m, Ar*H*);

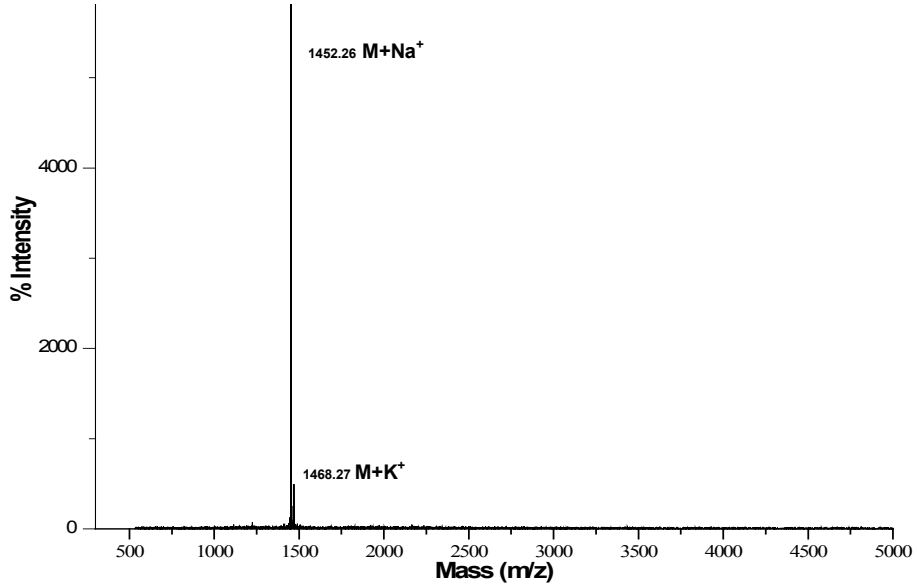
Scheme S3 The synthesized route of terminal carboxyl calix[6]biscrowns (Cca5)



Reagents and reaction:

calix[6]biscrowns was synthesized according to the reference. (1) K_2CO_3/acetonitrile, reflux, 24 h; (2) KOH/Ethanol, reflux, 12 h

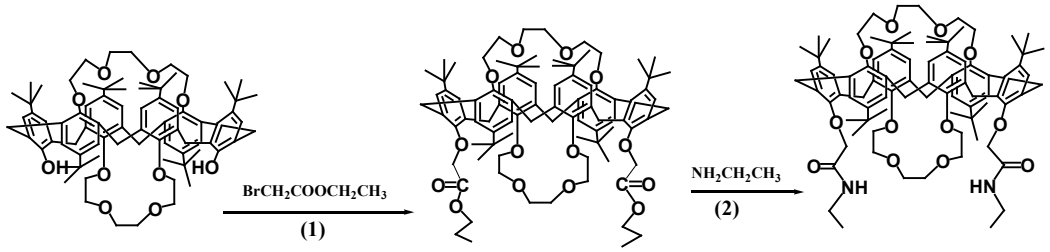
MALDI-TOF Result of Cca5: $[M+Na^+]$ m/z = 1452.2; $[M+K^+]$ m/z = 1468.3;



^{1}H NMR (500 MHz, $CDCl_3$):

0.80-0.87 (7 H, s, C(CH_3)$_3$), 1.04-1.07 (4 H, s, C(CH_3)$_3$), 1.13-1.15 (4 H, s, C(CH_3)$_3$), 1.10 (6 H, s, C(CH_3)$_3$), 1.18 (6 H, s, C(CH_3)$_3$), 1.33 (6 H, s, C(CH_3)$_3$), 1.23-1.29 (9 H, s, C(CH_3)$_3$), 1.37-1.50 (12 H, s, C(CH_3)$_3$), 2.07(6H, m, OCH_2CH_2), 2.14(6H, m, OCH_2CH_2), 2.98(H, m, OCH_2CH_2), 3.16(12H, s, ArCH_2Ar), 3.33(H_2O), 3.42(8H, s, OCH_2CH_2), 4.38 (8H, s, ArOCH_2), 4.14(8H, s, ArOCH_2CH_2), 4.0 (4H, m, ArOCH_2CH_2), 6.56 (2 H, s, ArH), 6.88 (2 H, s, ArH), 7.05 (2 H, s, ArH), 7.14 (2 H, s, ArH), 7.16 (2 H, s, ArH), 7.28 (2 H, s, ArH);

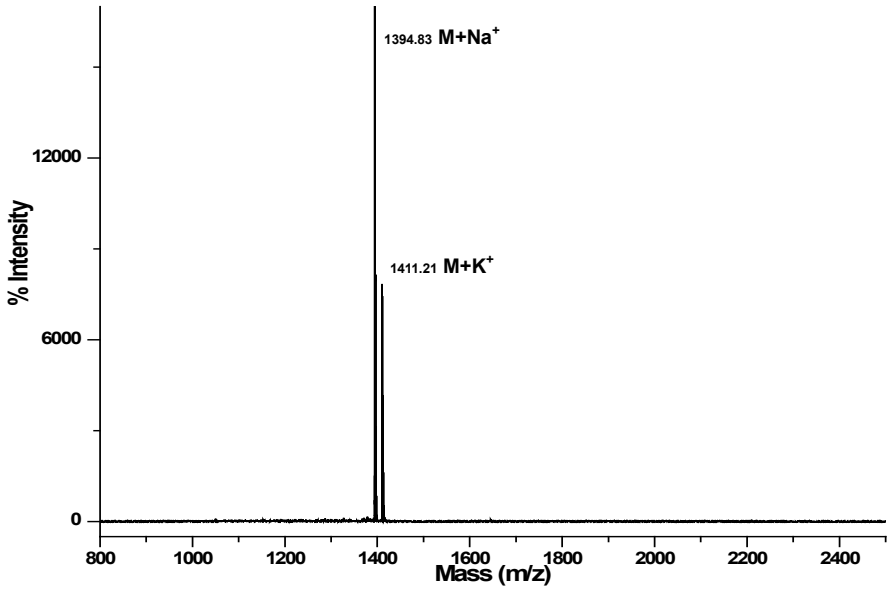
Scheme S4 The synthesized route of terminal methyl calix[6]biscrowns (Cam2)



Reagents and reaction:

Calix[6]biscrowns was synthesized according to the reference.[1] (1) K_2CO_3/acetonitrile, reflux, 24 h; (2) $NH_2CH_2CH_3$ as the solvent and the reagent, room temperature, 24 h.

MALDI-TOF Result of Cam2: [M+Na^+] m/z = 1394.83; [M+K^+] m/z = 1411.21;



^{1}H NMR (500 MHz, $CDCl_3$):

1.17 (18 H, C(CH_3)$_3$), 1.26 (19 H, C(CH_3)$_3$), 1.43 (16 H, C(CH_3)$_3$), 1.61 (7 H, C(CH_3)$_3$), 2.46 (2 H, t, OCH_2CH_2), 2.69 (2H, OCH_2CH_2), 3.01-3.22 (6 H, m, OCH_2CH_2), 3.35-3.62 (18 H, m, OCH_2CH_2 and ArCH_2Ar), 4.00-4.46 (14 H, m, OCH_2CH_2 and ArCH_2Ar), 4.69 (2 H, ArCH_2Ar), 6.81 (2 H, s, Ar*H*), 6.85 (2 H, m, CON*H*), 7.08 (2 H, s, Ar*H*), 7.12 (2 H, s, Ar*H*), 7.16 (2 H, s, Ar*H*), 7.29 (2 H, s, Ar*H*), 7.34 (2 H, s, Ar*H*);

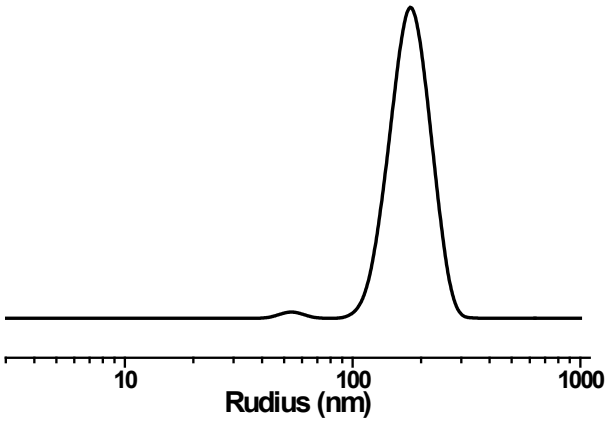


Figure S1 The DLS data of **CamA6** in water/ethanol 1:1

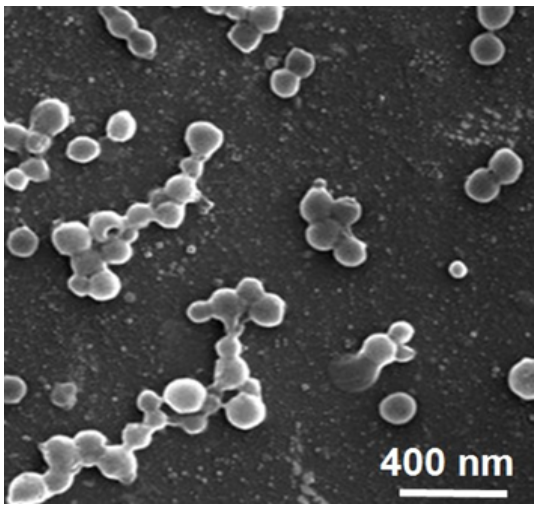


Figure S2 The SEM image of the aggregates of **CA5** in water/ethanol 1:1

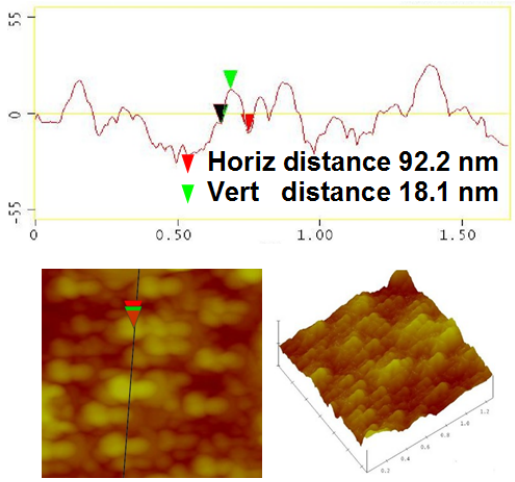


Figure S3 The AFM data of **CA5** in water/ethanol 3:1

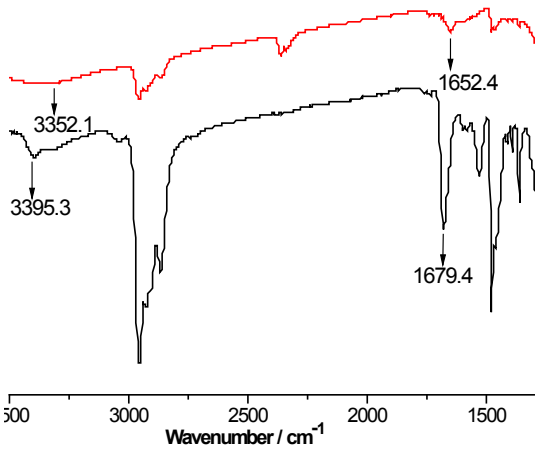


Figure S4 FT-IR spectra of the virgin sample of **CamA6** (black curve) and nanotubes aggregates (red curve); the data was collected from the fresh membrane of **CamA6** (the virgin sample of **CamA6** in pure ethanol solution and the aggregate in water/ethanol (*v*:*v*=3:1) were dropped onto the calcium fluoride crystal platelets and then evaporated quickly).

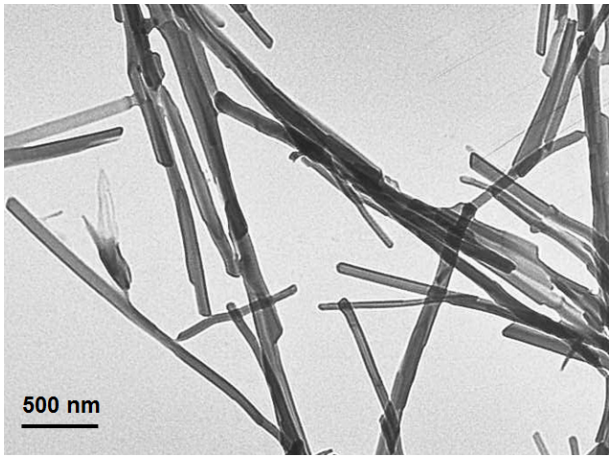


Figure S5 The TEM image of **Cam2** self-assembly in mixed solution (water:/ethanol= 3:1)

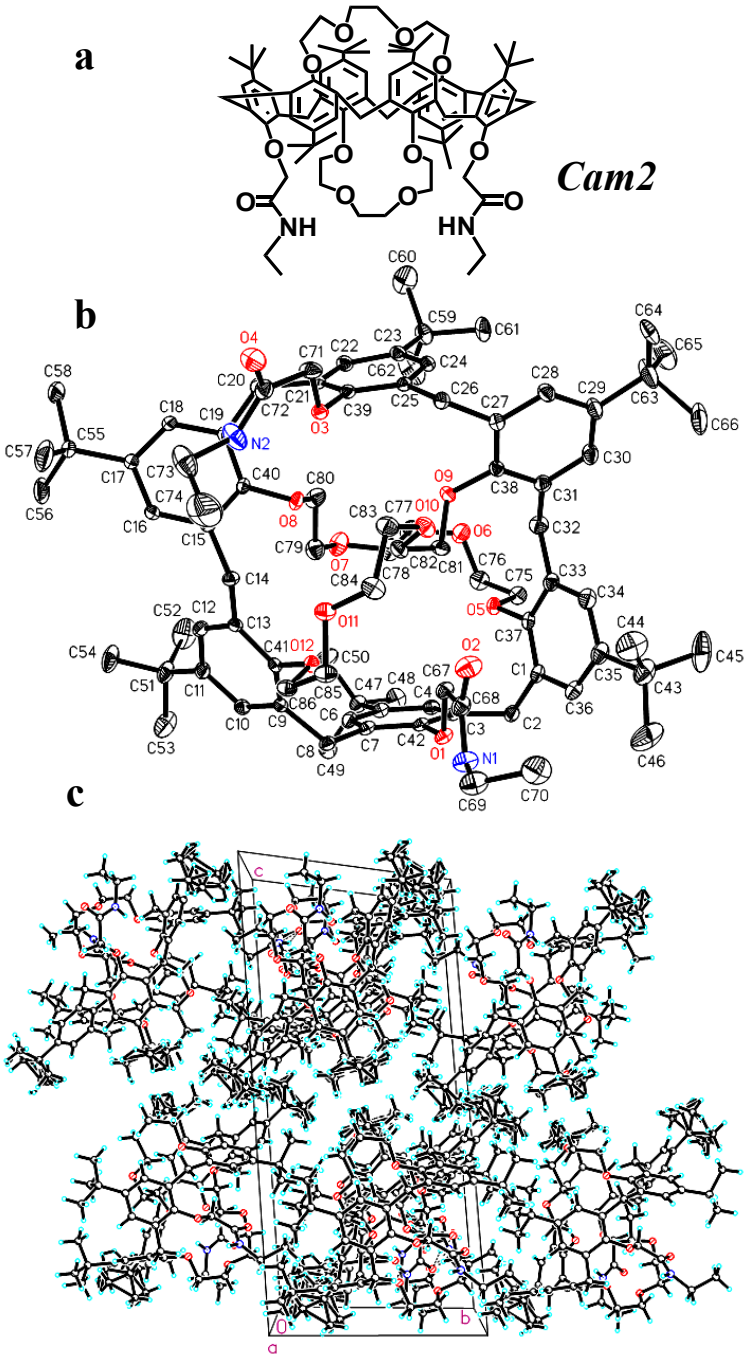


Figure S6. a) The chemical structure of **Cam2**. b) The X-ray single crystal diffraction of **Cam2** and c) the packing model.

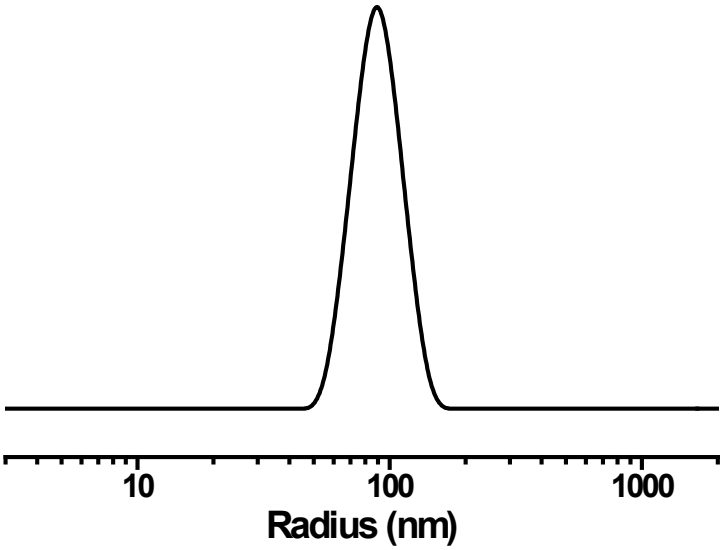


Figure S7. The DLS data of the aggregates of **Cca5** in water/ethanol 1:2

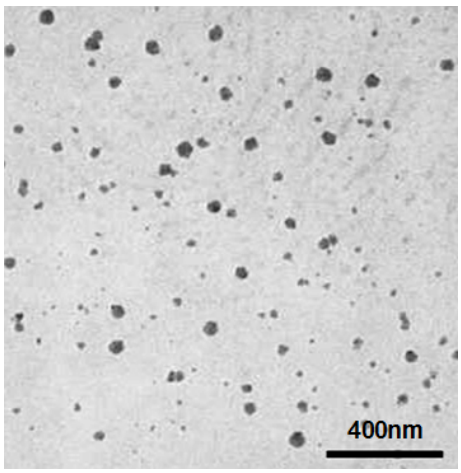


Figure S8. The TEM image of the aggregates of **Cca5** in water/ethanol 3:1

Table S1. The crystal data and structure refinement for Cam2 (dm1076)

Identification code	dm1076
Empirical formula	C86 H118 N2 O12
Formula weight	1371.82
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	
a = 13.0708(13) A	alpha = 93.1610(10) deg.
b = 13.4331(13) A	beta = 98.2840(10) deg.

c = 26.062(3) A	gamma = 117.9160(10) deg.
Volume	3961.8(7) A^3
Z, Calculated density	2, 1.150 Mg/m^3
Absorption coefficient	0.075 mm^{-1}
F(000)	1488
Crystal size	0.359 x 0.312x 0.167 mm
Theta range for data collection	1.59 to 25.50 deg.
Limiting indices	-15<=h<=15, -16<=k<=16, -29<=l<=31
Reflections collected / unique	25451 / 14423 [R(int) = 0.0193]
Completeness to theta = 25.50	97.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6396
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14423 / 130 / 1020
Goodness-of-fit on F2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1791
R indices (all data)	R1 = 0.0752, wR2 = 0.2039
Largest diff. peak and hole	0.698 and -0.369 $e.A^{-3}$

References:

1 a) B. Guan, M. Jiang, X. Yang, Q. Liang and Y. Chen, *Soft Matter* 2008, 4, 1393-1395; b) B. Guan, S. L. Gong, X. J. Wu, Z. G. Li and Y. Y. Chen, *J. Incl. Phenom. Macro. Chem.,* 2006, 54, 81-84.