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) K₂CO₃/acetonitrile, reflux, 24 h; (2) NH₂(CH₂)₆NH₂ as the solvent and the reagent, room temperature, 24 h.

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

¹H NMR (500 MHz, CDCl₃):
1.14 (18 H, s, C(CH₃)₃), 1.23 (34 H, m, C(CH₃)₃ and CH₂), 1.40 (18 H, s, C(CH₃)₃), 1.44 (4 H, br, NH₂), 2.46 (2 H, t, OCH₂CH₂), 2.53-2.81 (6 H, m, OCH₂CH₂), 2.81-3.69 (26 H, m, OCH₂CH₂, ArCH₂Ar and CONHC(CH₂)), 3.88-4.48 (12 H, m, OCH₂CH₂ and ArCH₂Ar), 4.66 (2 H, ArCH₂Ar), 6.78 (2 H, s, ArH), 6.85 (2 H, m, CONH), 7.06 (2 H, s, ArH), 7.10 (2 H, s, ArH), 7.11 (2 H, s, ArH), 7.25 (2 H, s, ArH), 7.30 (2 H, s, ArH);
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) K₂CO₃/acetonitrile, reflux, 24 h; (2) dried tetrahydrofuran (THF) as the solvent, LiAlH₄ 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;

¹H NMR (500 MHz, CDCl₃):
1.13-1.16 (54 H, s, C(CH₃)₃), 1.2-1.7 (6H, m, CH₂CH₂CH₂), 2.89 (2H, m, CH₂NH₂), 3.56 (24H, m, OCH₂CH₂), 3.62(12H, s, ArCH₂Ar), 3.93 (2H, m, ArOCH₂), 4.68 D₂O, 7.35 (6 H, m, ArH), 7.65 (6 H, m, ArH);
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$_2$CO$_3$/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$_2$CH$_2$), 2.14(6H, m, OCH$_2$CH$_2$), 2.98(H, m, OCH$_2$CH$_2$), 3.16(12H, s, ArCH$_2$Ar), 3.33(H$_2$O), 3.42(8H, s, OCH$_2$CH$_2$), 4.38 (8H, s, ArOCH$_2$), 4.14(8H, s, ArOCH$_2$CH$_2$), 4.0 (4H, m, ArOCH$_2$CH$_2$), 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]biscrows (Cam2)

Reagents and reaction:
Calix[6]biscrows was synthesized according to the reference.\(^1\) (1) \(\text{K}_2\text{CO}_3/\text{acetonitrile}, \text{reflux}, 24\) h; (2) \(\text{NH}_2\text{CH}_2\text{CH}_3\) as the solvent and the reagent, room temperature, 24 h.

MALDI-TOF Result of Cam2: \([\text{M+Na}^+]\) m/z = 1394.83; \([\text{M+K}^+]\) m/z = 1411.21;

\(^1\text{H}\) 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\(_2\)CH\(_2\)), 2.69 (2H, OCH\(_2\)CH\(_2\)), 3.01-3.22 (6 H, m, OCH\(_2\)CH\(_2\)), 3.35-3.62 (18 H, m, OCH\(_2\)CH\(_2\) and ArCH\(_2\)Ar), 4.00-4.46 (14 H, m, OCH\(_2\)CH\(_2\) and ArCH\(_2\)Ar), 4.69 (2 H, ArCH\(_2\)Ar), 6.81 (2 H, s, ArH), 6.85 (2 H, m, CONH\(_2\)), 7.08 (2 H, s, ArH), 7.12 (2 H, s, ArH), 7.16 (2 H, s, ArH), 7.29 (2 H, s, ArH), 7.34 (2 H, s, ArH);
**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)

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<th>Value</th>
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<tr>
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<tr>
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<td>Wavelength</td>
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<tr>
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<tr>
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<tr>
<td>beta</td>
<td>98.2840(10) deg.</td>
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</tbody>
</table>
**c** = 26.062(3) Å  
**gamma** = 117.9160(10) deg.

**Volume**  
3961.8(7) Å³

**Z, Calculated density**  
2,  1.150 Mg/m³

**Absorption coefficient**  
0.075 mm⁻¹

F(000)  
1488

**Crystal size**  
0.359 x 0.312 x 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 F²

**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 eÅ⁻³

References: