

## Supporting Information

for

*Enzyme-responsive supramolecular polymer by complexation  
of bis(p-sulfonatocalixarenes) with suberyl dicholine-based  
pseudorotaxane*

Dong-Sheng Guo, Tian-Xing Zhang, Yi-Xuan Wang, Yu Liu \*

*Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry,*

*Nankai University, Tianjin, 300071, P. R. China*

*E-mail: yuliu@nankai.edu.cn Fax: (+86)22-2350-3625*

## Table of Contents

---

### Experimental Section

<b>Materials</b>	S3
<b>Measurements</b>	S5
NMR measurements	S5
Dynamic light-scattering (DLS) measurements	S9
The diffusion ordered spectroscopy (DOSY) measurements	S12
Transmission Electron Microscopy (TEM) measurements	S13
Mass spectroscopy measurements	S14
<b>References</b>	S17

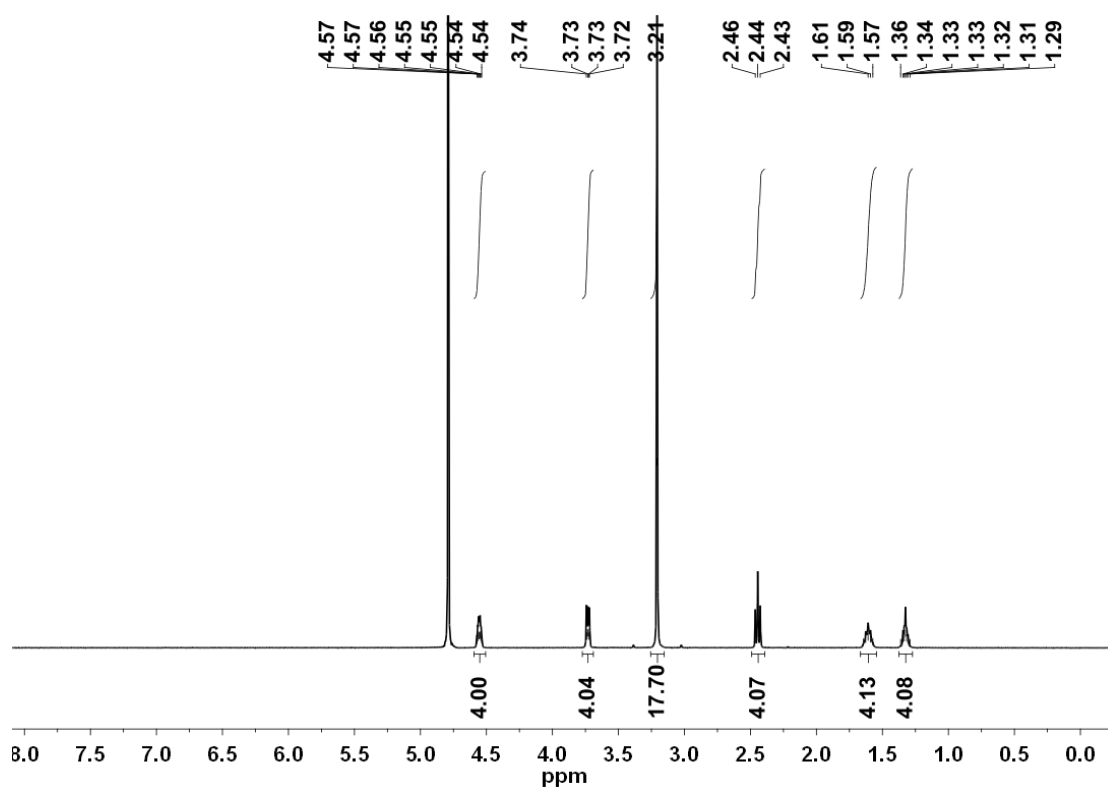
---

## Experimental Section

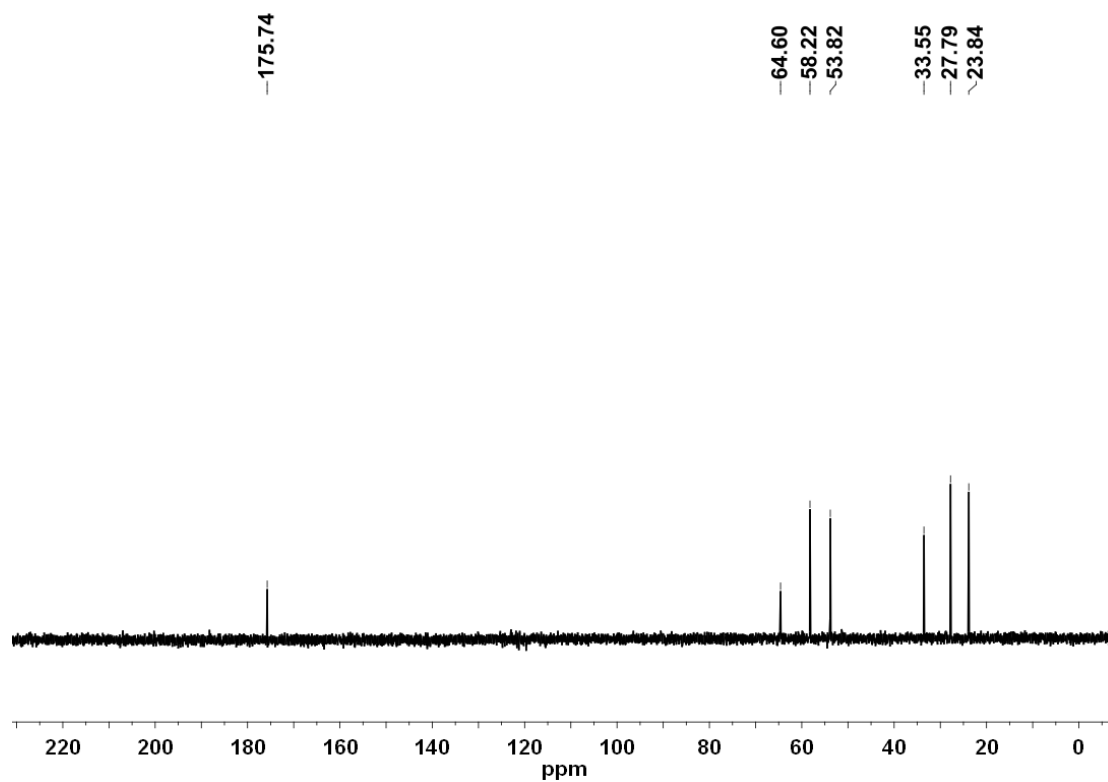
### Materials:

*Bis(p-sulfonatocalix[4]arene) octasodium (bisSC4A·8Na<sup>+</sup>)* was synthesized and purified referring to the literature process.<sup>[1]</sup> Dimethyl suberate and 30% sodium methoxide were purchased from Alfa Aesar, and N,N-dimethylethanolamine was from Aladdin. All other materials and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted.

**Preparation of suberyl dicholine diiodide (DiCh):**<sup>[2]</sup> A mixture of dimethyl suberate (2.99 mL, 15 mmol), N,N-dimethylethanolamine (3.02 mL, 30 mmol) and 30% sodium methoxide (0.3 g, 2 mmol) was refluxed for 1 h. N,N-dimethylethanolamine (3.02 mL, 30 mmol) and 30% sodium methoxide (0.3 g, 2 mmol) were added dropwise to the mixture. After being heated for 5 h to evaporate the side product methanol, the excess N,N-dimethylethanolamine was removed under reduced pressure and the residue was treated with 30 mL toluene and acetic acid (2 mmol) in 20 mL ice water. The organic layer was separated, washed with the saturated brine, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure to yield the brown oil (3.70 g). To a solution of the brown oil (3.70 g) in dry acetone (30 mL) was added iodomethane (2.91 mL, 47 mmol). The mixture was refluxed for 48 h. After being cooled to room temperature, the precipitate was filtered off and washed with acetone. Recrystallization from acetonitrile yielded a white solid (5.76 g, 64%): mp 155–156 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 4.57–4.54 (m, 4H), 3.74–3.72 (m, 4H), 3.21 (s, 18H), 2.44 (t, J = 7.5 Hz, 4H), 1.64–1.57 (m, 4H), 1.36–1.29 (m, 4H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O) δ 175.74, 64.60, 58.22, 53.82, 33.55, 27.79, 23.84; QFT-ESI-MS (m/z): 173.1406 ([*(M-2I)/2*]<sup>2+</sup>).



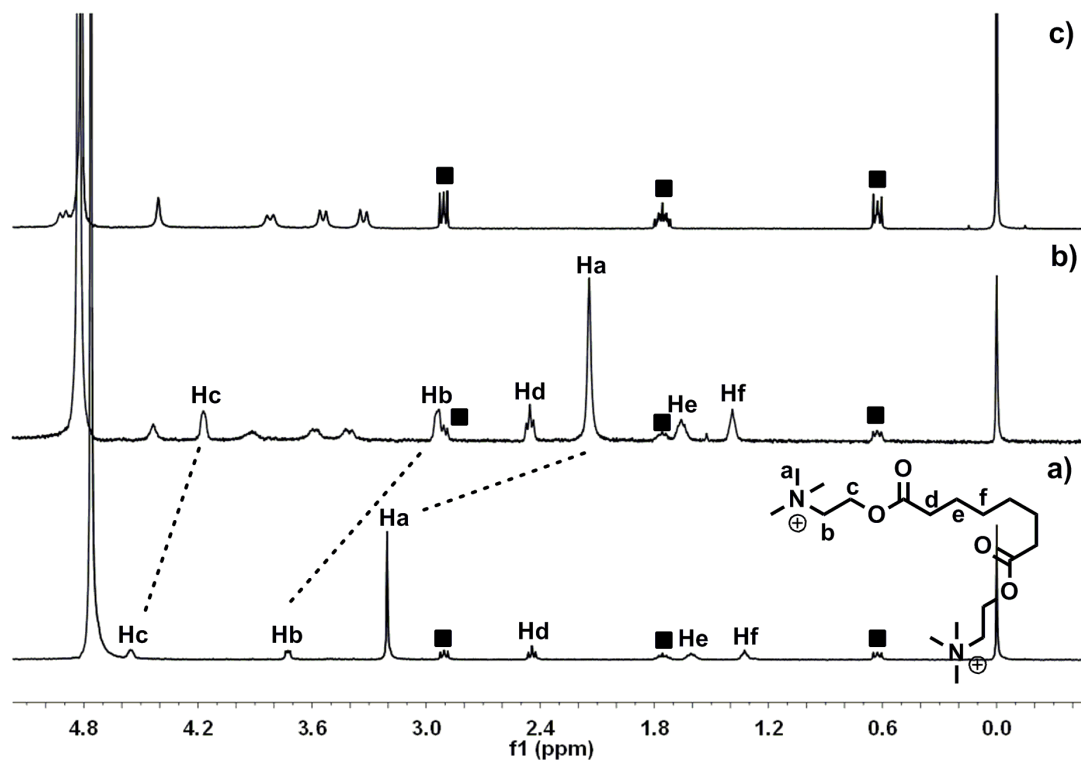
**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, 298 K) of DiCh.



**Figure S2.** <sup>13</sup>C NMR spectrum (100 MHz, D<sub>2</sub>O, 298 K) of DiCh.

### Measurements:

**NMR measurements.**  $^1\text{H}$  NMR spectra were recorded on Bruker spectrometer in  $\text{D}_2\text{O}$  at 298 K, using 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an external reference.



**Figure S3.**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{D}_2\text{O}$ , 298 K) of a) DiCh, b) 1 mM bisSC4A with 1 equiv DiCh, c) bisSC4A. “■” represents the proton of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), which was added as an external reference.

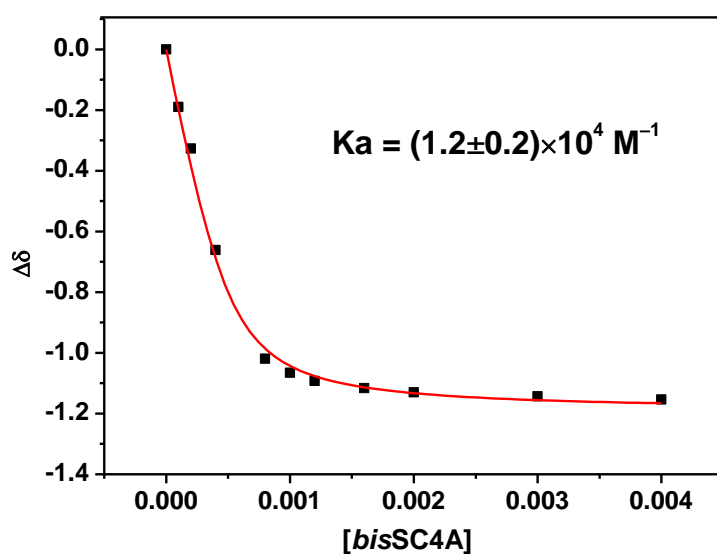
### Determination of the association constants.

For the present host-guest system, chemical exchange is fast on the NMR time scale. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of DiCh guest and varying concentrations of

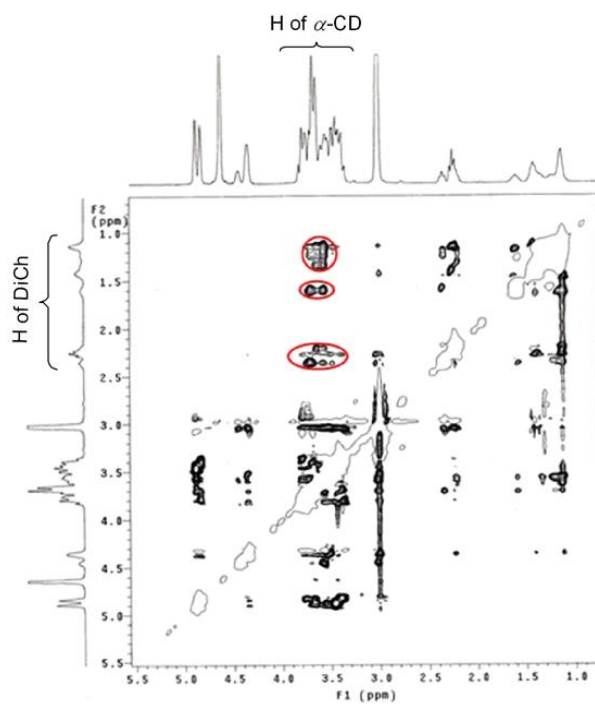
calixarene host. Using the nonlinear curve-fitting method, the association constant was obtained for the host-guest combination from the following equation by the isodesmic or equal-K model:<sup>[3]</sup>

$$\Delta\delta = (\Delta\delta_{\infty}/[G]_0) (0.5[H]_0 + 0.5([G]_0 + 1/K_a) - (0.5 ([H]_0^2 + (2[H]_0(1/K_a - [G]_0) + (1/K_a + [G]_0)^2)^{0.5}))$$

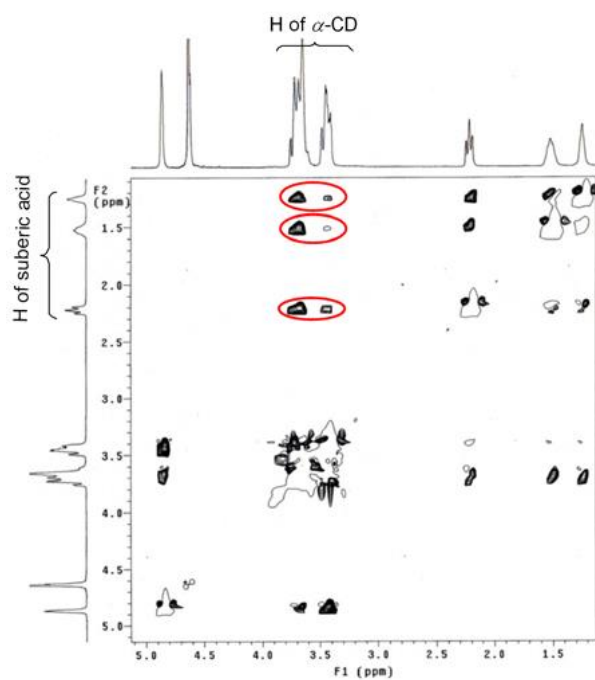
Where  $\Delta\delta$  is the chemical shift change of  $H_a$  on DiCh guest at  $[H]_0$ ,  $\Delta\delta_{\infty}$  is the chemical shift change of  $H_a$  when the guest is completely complexed,  $[G]_0$  is the fixed initial concentration of the DiCh guest, and  $[H]_0$  is the initial concentration of calixarene host.



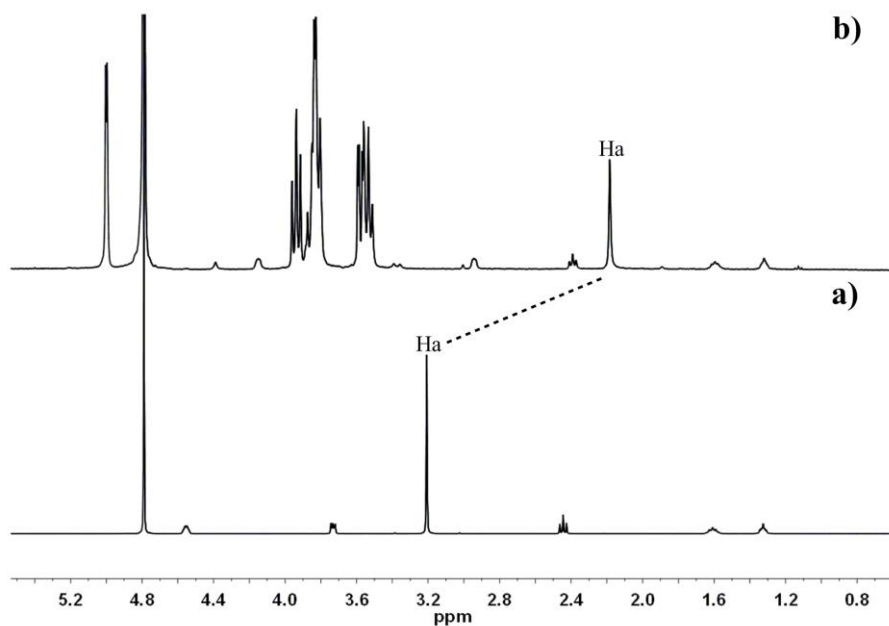
**Figure S4.**  $^1\text{H}$  NMR spectral changes of quaternary ammonium of DiCh upon addition of *bisSC4A* in  $\text{D}_2\text{O}$  at 298 K ( $[\text{DiCh}] = 1.0$  mM,  $[\text{bisSC4A}] = 0, 0.1, 0.2, 0.4, 0.8, 1.0, 1.2, 1.6, 2.0, 3.0, 4.0$  mM). The nonlinear least-squares analysis of the differential chemical shifts ( $\Delta\delta$ ) to calculate the association constant ( $K_a$ ) for DiCh@*bisSC4A*.



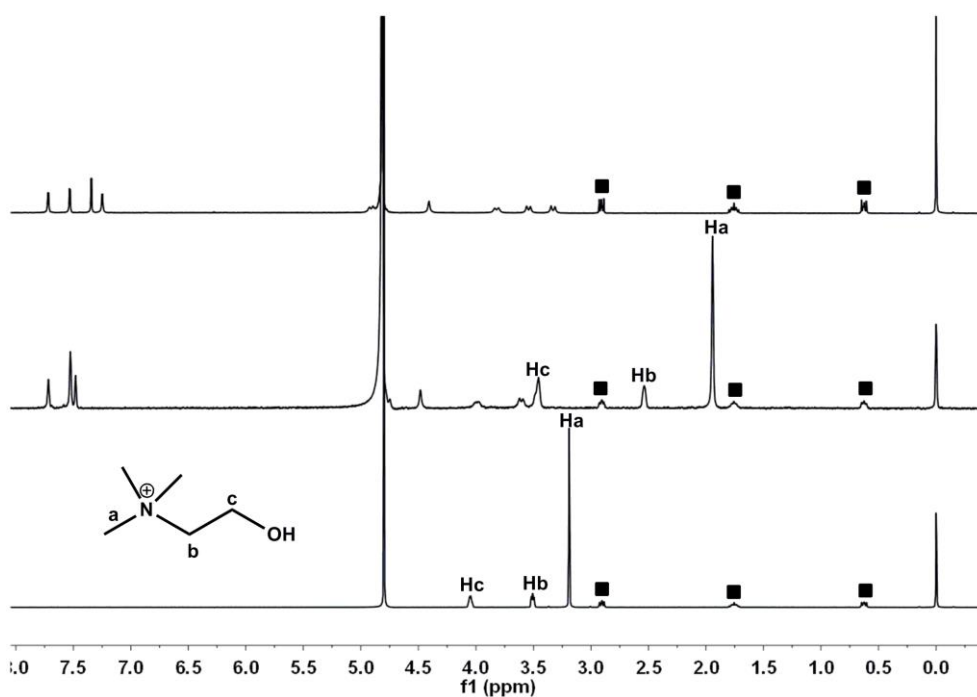
**Figure S5.** ROESY spectrum (300 MHz, D<sub>2</sub>O, 298 K) of DiCh (10 mM) with 100 mM  $\alpha$ -CD with a mixing time of 250 ms.



**Figure S6.** ROESY spectrum (300 MHz, D<sub>2</sub>O, 298 K) of suberic acid (3 mM) with 10 mM  $\alpha$ -CD with a mixing time of 250 ms.



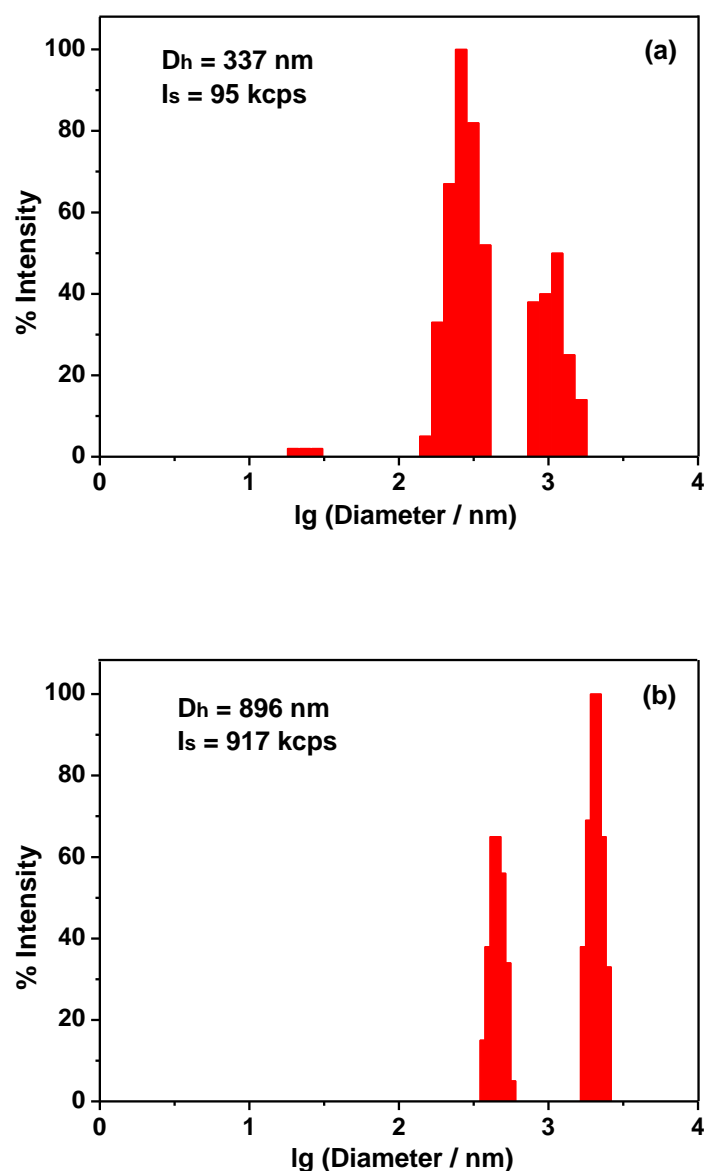
**Figure S7.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{D}_2\text{O}$ , 298 K) of a) DiCh, b) 1 mM DiCh with 1 equiv *bis*SC4A and 10 equiv  $\alpha$ -CD.



**Figure S8.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{D}_2\text{O}$ , 298 K) of a) choline chloride, b) 1 mM *bis*SC4A with 2 equiv choline chloride, c) *bis*SC4A. “■” represents the proton of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), which was added as an external reference.

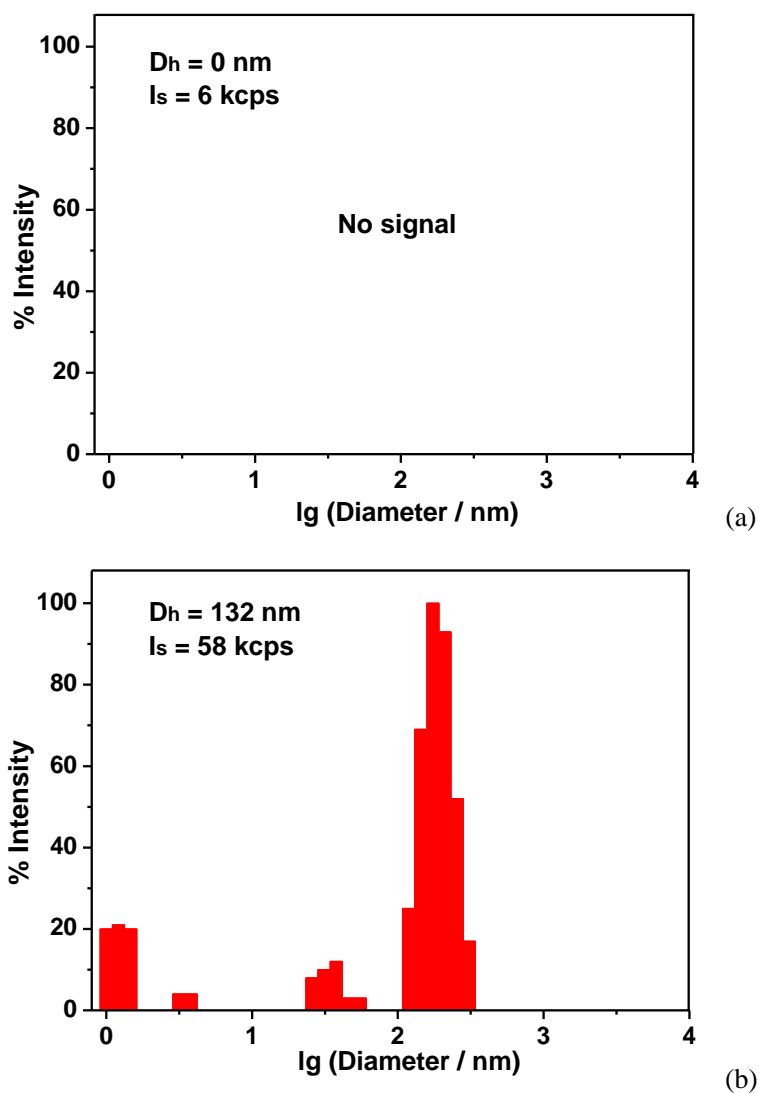


**Dynamic light-scattering (DLS) measurements.** The samples were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 532 nm at 298 K. All DLS measurements were performed at a scattering angle of 90°. The sample solutions were prepared by filtering each component solution (1.5 mL in total volume) respectively through a 220 or 450 nm syringe filter into a clean scintillation vial at the different concentrations.

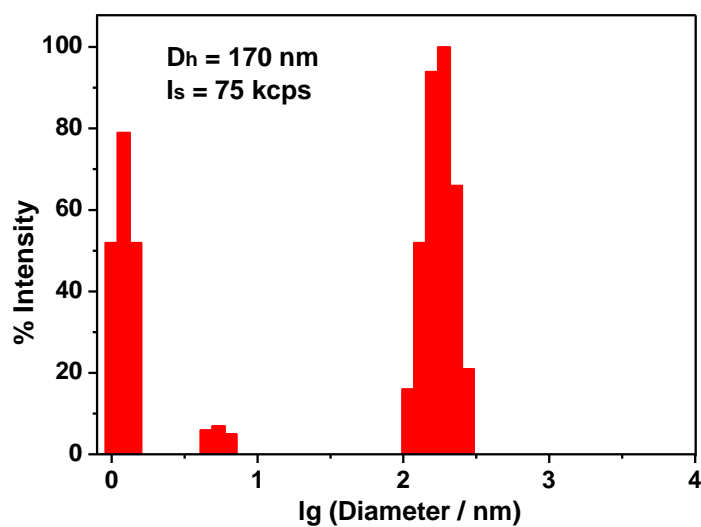


**Figure S9.** Hydrodynamic diameter distribution of 1 mM DiCh with 1 equiv *bisSC4A* (a), with 1 equiv *bisSC4A* and 10 equiv  $\alpha$ -CD (b).  $D_h$  and  $I_s$  represents the averaged

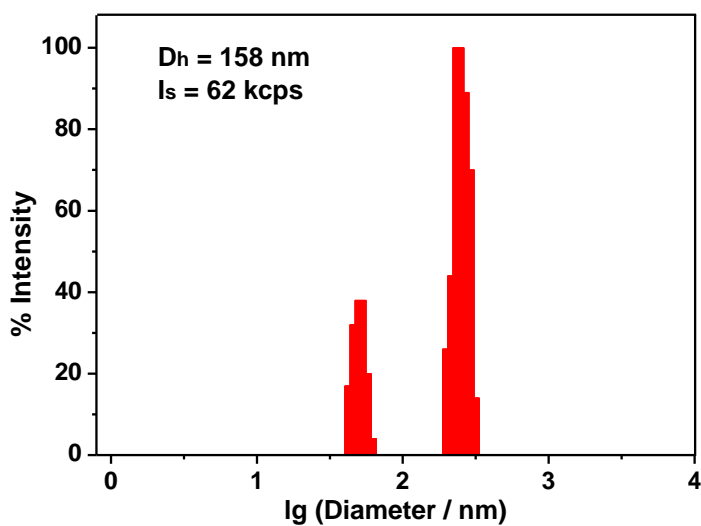
hydrodynamic diameter and the scattering intensity, respectively.



**Figure S10.** (a) Hydrodynamic diameter distribution of 1 mM DiCh with 1 equiv *bisSC4A* after incubation with 10 U/mL BChE for 24 h at 303 K. (b) Hydrodynamic diameter distribution of 1 mM DiCh with 1 equiv *bisSC4A* and 10 equiv  $\alpha$ -CD after incubation with 10 U/mL BChE for 24 h at 303 K.



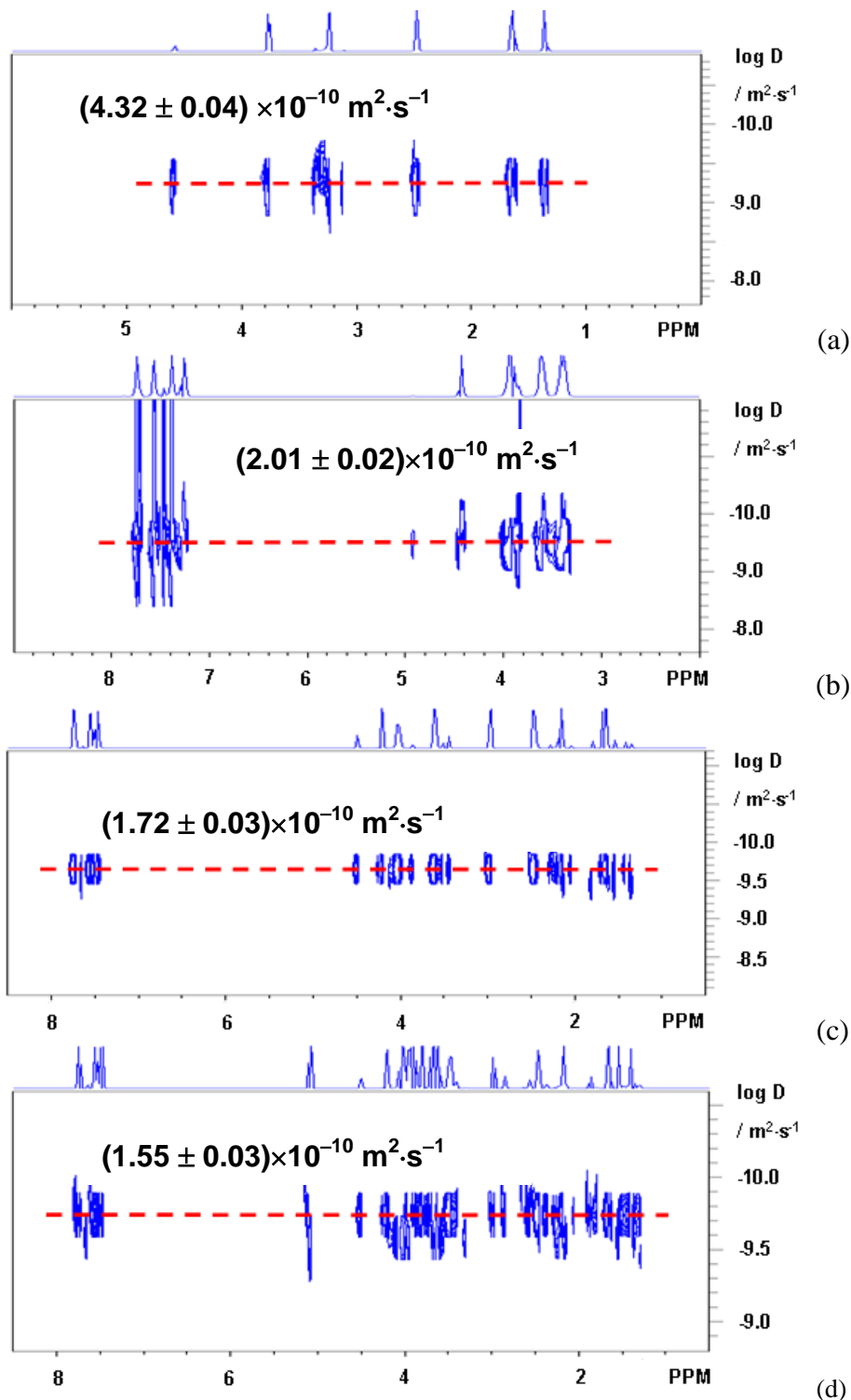
(a)



(b)

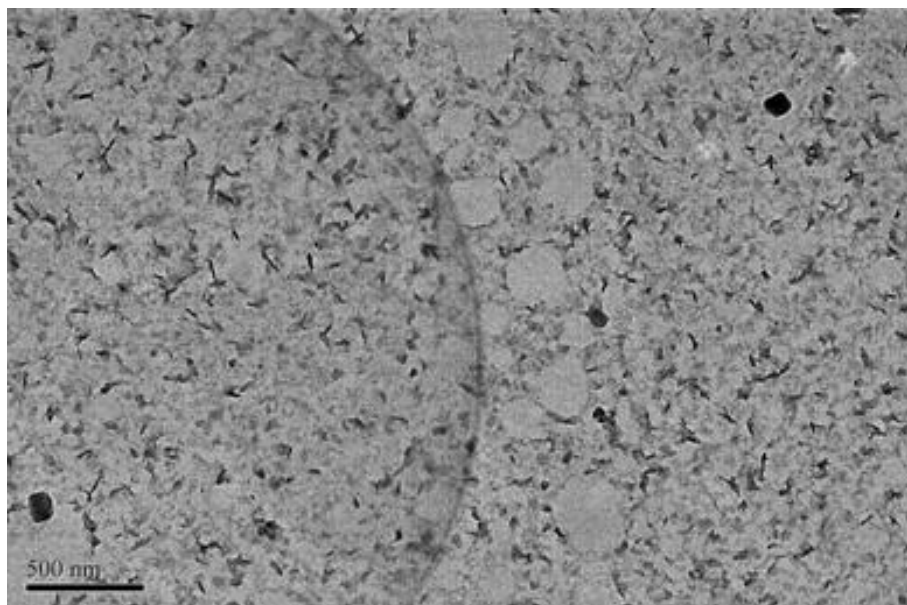
**Figure S11.** (a) Hydrodynamic diameter distribution of 10 mM  $\alpha$ -CD. (b) Hydrodynamic diameter distribution of 1 mM suberic acid with 10 equiv  $\alpha$ -CD.

**The diffusion ordered spectroscopy (DOSY) measurements.** DOSY experiments were performed on a Bruker DPX 600 MHz spectrometer. When the systems had different assemblies, we chose the larger one.

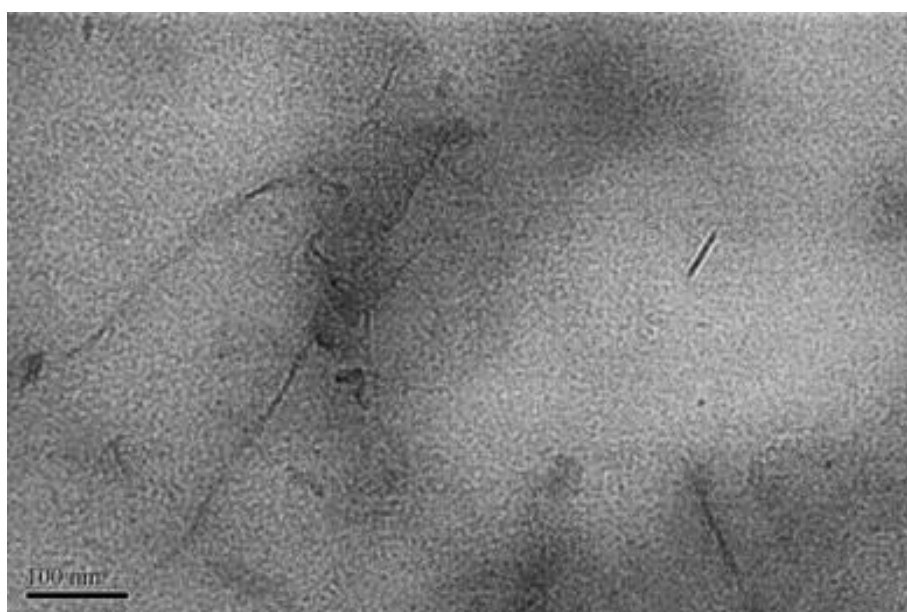


**Figure S12.** DOSY NMR spectrum (600 MHz,  $\text{D}_2\text{O}$ , 298 K) of 20 mM DiCh (a), 20 mM *bis*SC4A (b), 20 mM DiCh@*bis*SC4A (c), 20 mM DiCh@ $\alpha$ -CD/*bis*SC4A (d).

**Transmission Electron Microscopy (TEM) measurements.**  $1.0 \times 10^{-5}$  M (calculated from the repeat units) sample solutions were dropped onto a copper grid. The grid was then air-dried. The samples were examined by a high-resolution TEM (Tecnai G2 F20 high-resolution TEM) operating at an accelerating voltage of 200 kV.



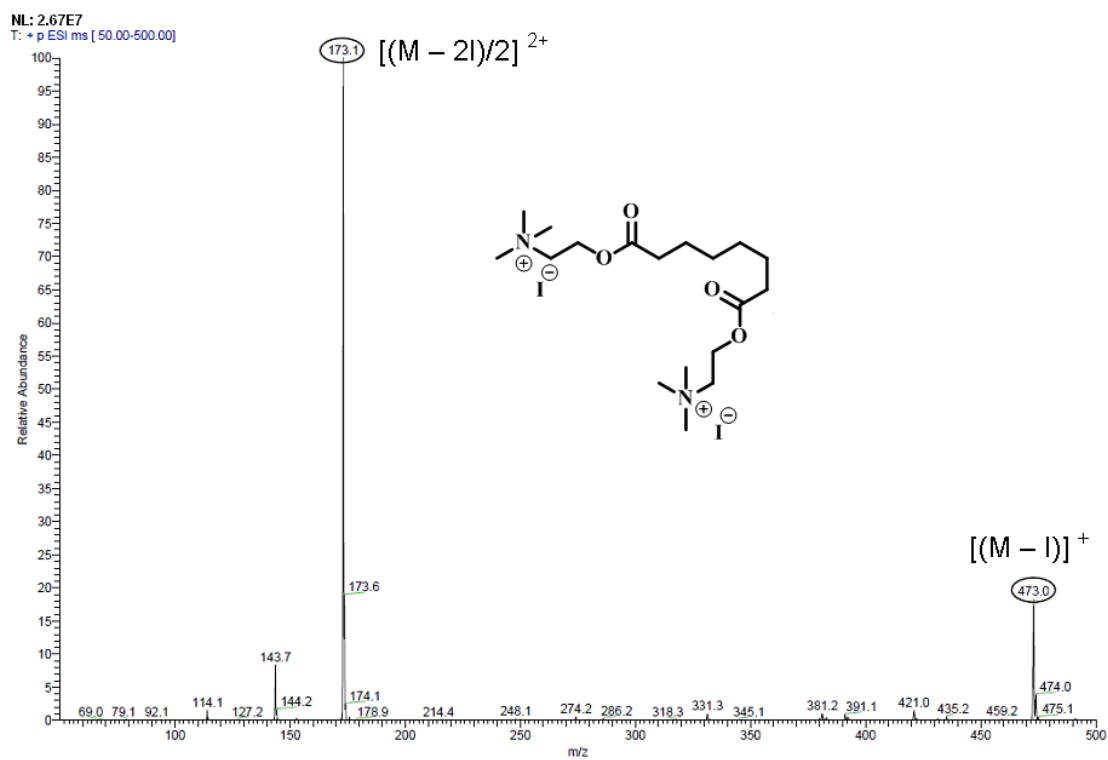
(a)



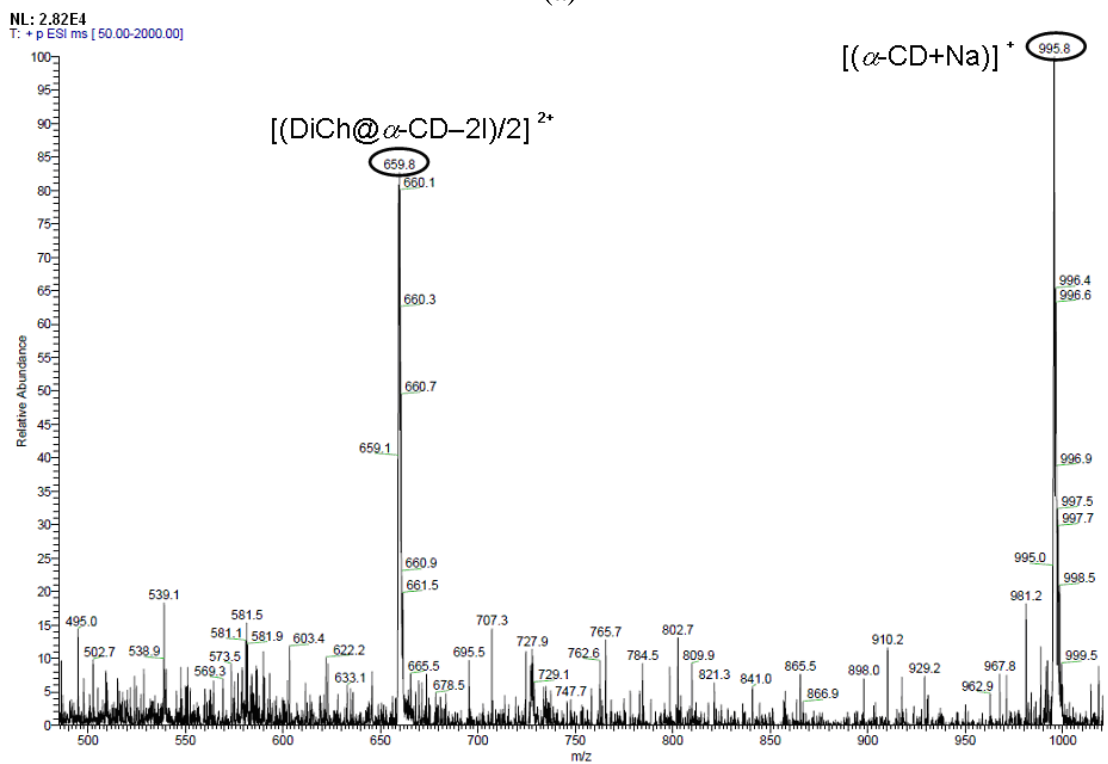
(b)

**Figure S13.** TEM images of the linear supramolecular DiCh@*bis*SC4A (scale bar = 500 nm) (a) and DiCh@ $\alpha$ -CD/*bis*SC4A (scale bar = 100 nm) (b) at different magnification.

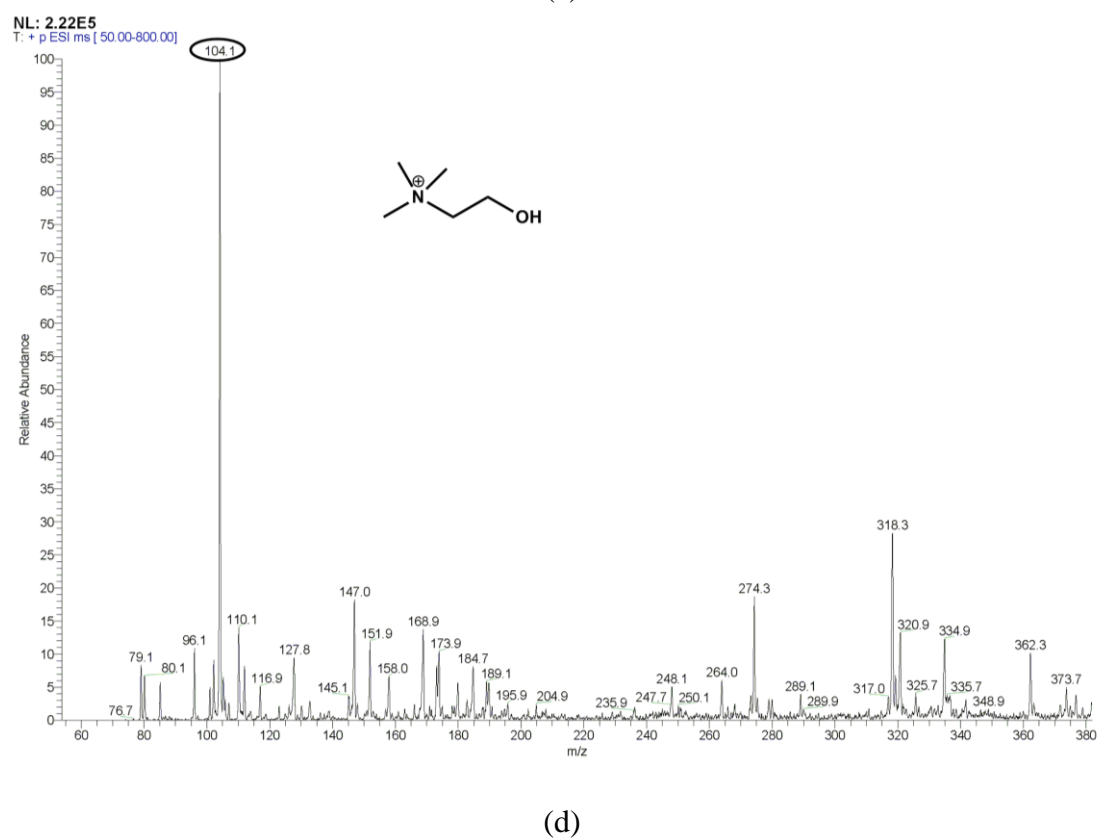
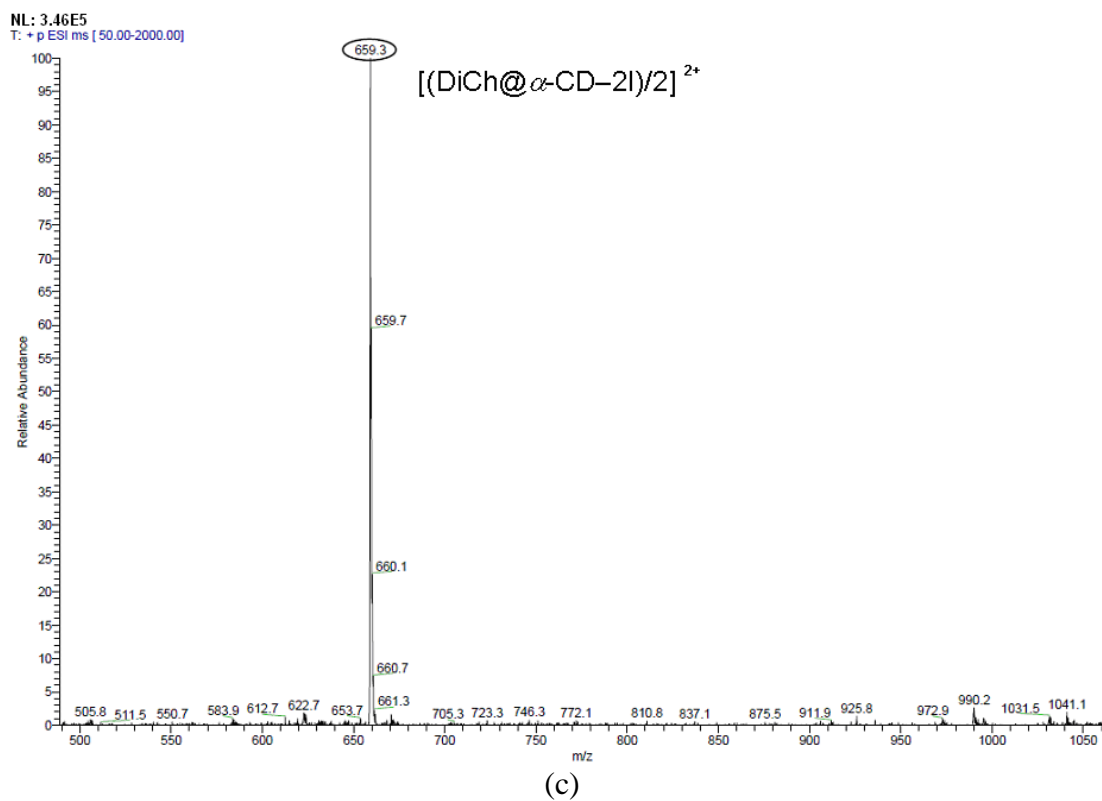
**Mass spectroscopy measurements.** Mass spectra were recorded by IonSpec QFT-ESI MS (Termo-Finnigan LCQ-Advantage).

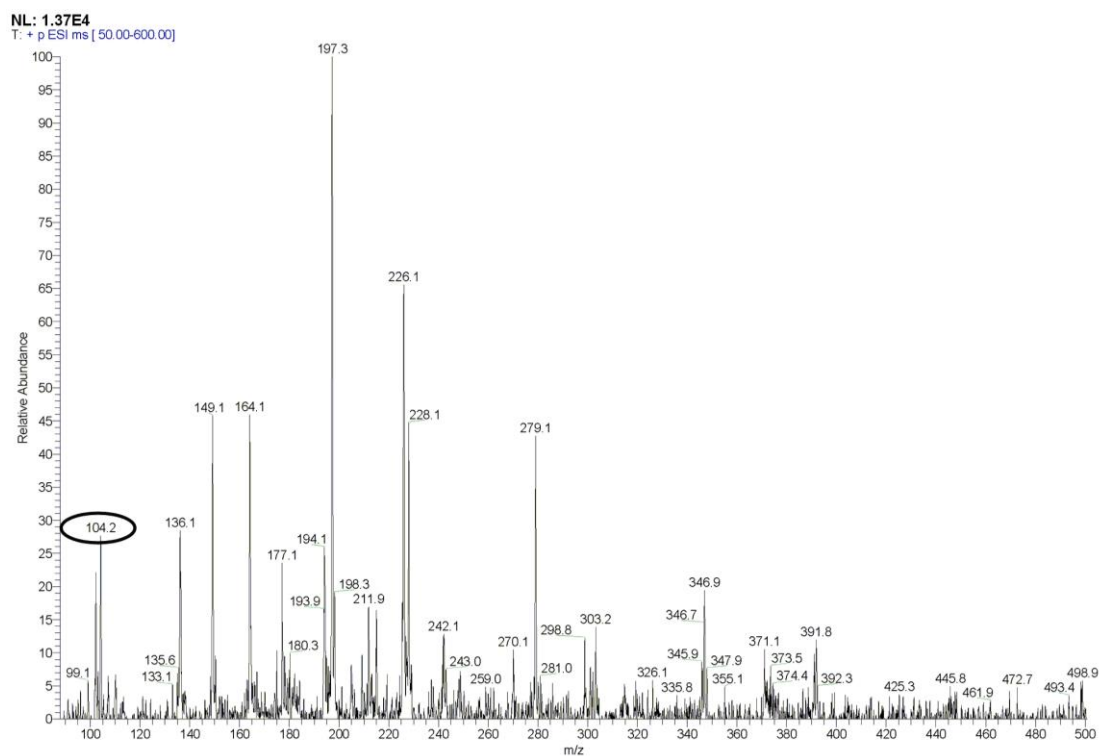


(a)

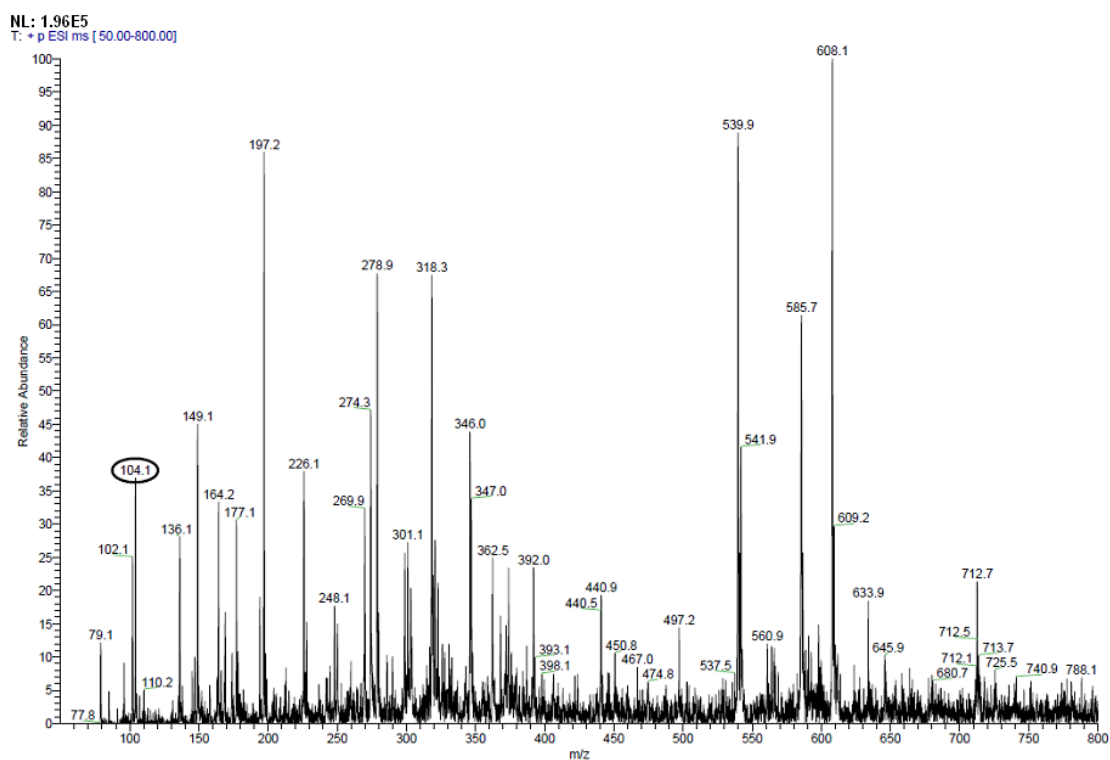


(b)





(e)



(f)

**Figure S14.** ESI-MS of a solution containing DiCh (a), a solution containing DiCh with 1 equiv *bis*SC4A and 10 equiv  $\alpha$ -CD (b), a solution containing DiCh with 1



equiv  $\alpha$ -CD (c), a solution containing 1 mM DiCh after incubation with 10 U/mL BChE for 24 h at 303 K (d), a solution containing 1 mM DiCh with 1 equiv. *bis*SC4A after incubation with 10 U/mL BChE for 24 h at 303 K (e), and a solution containing 1 mM DiCh with 1 equiv *bis*SC4A and 10 equiv  $\alpha$ -CD after incubation with 10 U/mL BChE for 24 h at 303 K (f).

## References

- 
- [1] D.-S. Guo, S. Chen, H. Qian, H. Q. Zhang, Y. Liu, *Chem. Commun.*, 2010, **46**, 2620–2622.
- [2] A. Shimomura, J. B. Cohen., *J. Chem. Soc., Trans.*, 1922, **121**, 2051–2059.
- [3] (a) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang, H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1807–1816; (b) C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu, X. Jia *Chem. Commun.*, **2010**, *46*, 9016–9018; (c) Z. Chen, A. Lohr, C. R. Saha-Möller, F. Würthner, *Chem. Soc. Rev.*, **2009**, *38*, 564–584; (d) Y. Liu, K.-R. Wang, D.-S. Guo, B.-P. Jiang, *Adv. Funct. Mater.*, **2009**, *19*, 2230–2235.