

Synthesis and Cooperative Molecular Recognition of Homoditopic Host Molecule with Rebek's Cavitanths

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A resorcinarene-based cavitand possesses a deepened vase-like structure, showing unique molecular recognitions and catalytic properties. We developed ditopic bisresorcinarene **2**, which is composed of two resorcinarenes connected with four aliphatic chains.^[1] Here, we synthesized biscavitand **1** possessing two Rebek's deepened cavitand units (Figure 1a).

In the crystal structure of **1**, two stereoisomerisms were found: one is the clockwise/anticlockwise interconversion of the interannular hydrogen bonding of the amide groups, and the other is the (P)/(M) helical interconversion of the bisresorcinarene unit. The kinetic analysis using EXSY technique revealed that the interconversion of the interannular hydrogen bonds and the helix-helix interconversion occurred independently. To reveal the guest binding behavior of the biscavitand **1**, NMR and ITC experiment were conducted in toluene. The guest binding of biscavitand **1** with **G1** showed strong negative cooperativity with association constants (K_{a1} and K_{a2}) of 440,000 and 10,000 L mol⁻¹, respectively, in toluene (Figure 1b).

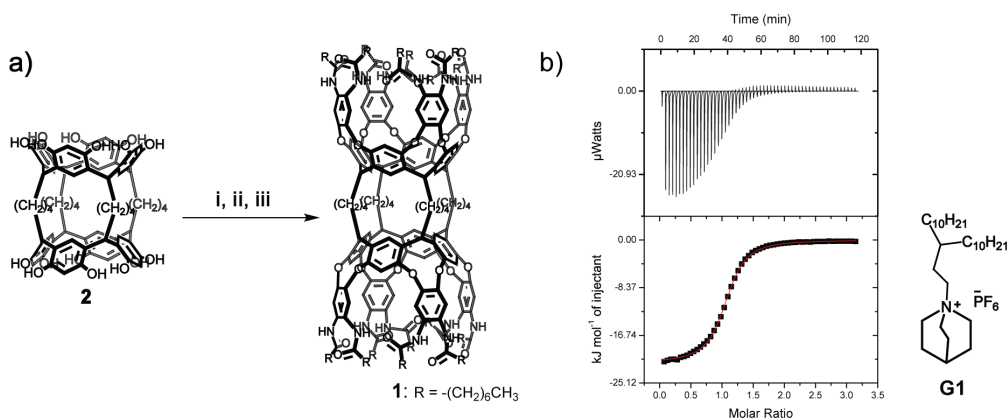


Figure 1. a) Synthesis of biscavitand **1**. Reagents: (i) 1,2-difluoro-4,5-dinitrobenzene, DIPEA, DMF; (ii) Raney-Ni, H₂, DMF/MeOH; (iii) octanoyl chloride, DMAP, pyridine. b) ITC titration experiment of **1** with **G1** in toluene and chemical structure of **G1**.

[1] H. Yamada, T. Ikeda, T. Mizuta, T. Haino, *Org. Lett.*, **2012**, *14*, 4510–4513.; D. Shimoyama, T. Ikeda, R. Sekiya, T. Haino, *J. Org. Chem.*, **2017**, *82*, 13220–13230.; D. Shimoyama, H. Yamada, T. Ikeda, R. Sekiya, T. Haino, *Eur. J. Org. Chem.*, **2016**, 3300–3303.