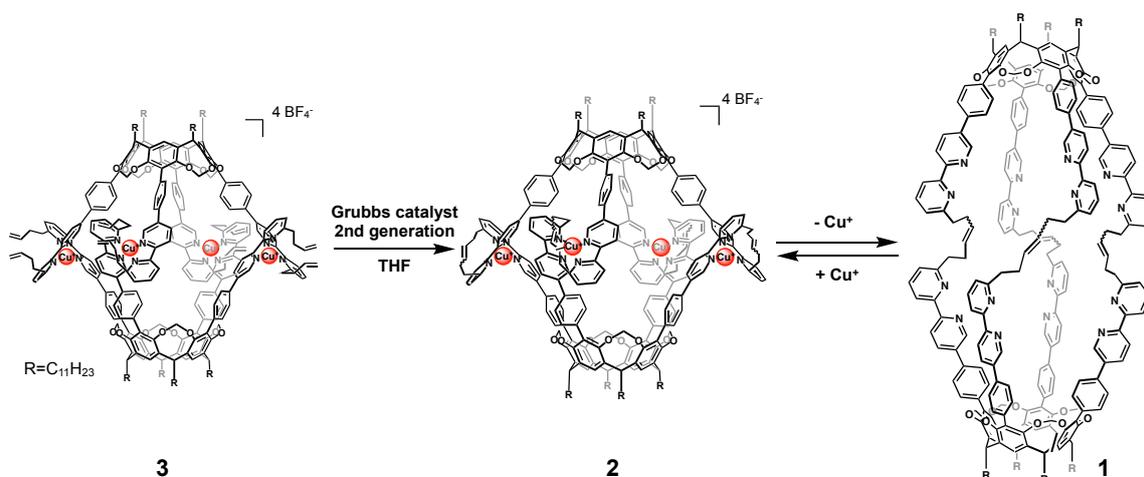


1C2b

Synthesis and Molecular Recognition of Size-regulable
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Covalently-linked capsules such as carcerands and hemi-carcerands are of great interest due to unique molecular recognitions within their nanometric cavities. There are limited examples of covalently-linked capsules that demonstrate tunable molecular recognitions by changing their size and dimension of their internal cavities by external stimuli.



Scheme 1. Synthesis of capsule 1, 2, and 3.

The coordination capsule **3** were subjected to ring-closing olefin metathesis to result in the covalently-linked capsule **2**. Removal of copper ions of capsule **2** gave rise to capsule **1** that retains its capsular structure (Scheme 1). DOSY experiments and molecular mechanics calculations estimated the internal space of capsule **1** that is larger than that of capsule **2**.

Guest encapsulation of capsule **1** and **2** was investigated using NMR spectroscopy. 4,4'-Diacetoxybiphenyl (**4**) was selectively encapsulated within capsule **2** over **1**. The large molecular dimension of **6** permitted it sitting within the cavity of **1**. When a mixture of guests **4**, **5** and **6** was placed in a solution of **1**, **6** was selectively captured. The addition of copper ions released the bound guest **6** to bring the host-guest complex of **4**⊂**2**. The addition of ethylenediamine released the coordinated copper ions to result in **6**⊂**1** (Fig. 1).

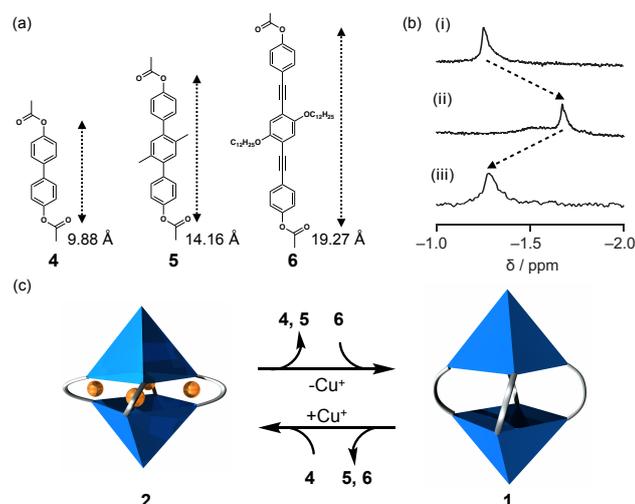


Fig. 1. (a) Molecular structure of guest **4**, **5**, and **6**. (b) ¹H NMR spectra (500 MHz, chloroform-*d*₁, 223 K) of (i) a mixture of capsule **1** (0.2 mM) and guest **4-6** (4.0 mM, each), (ii) upon the addition of 4 eq of [Cu(NCCH₃)₂]BF₄ into the solution, and (iii) upon addition of 32 eq of ethylenediamine into the previous solution. (c) Schematic representation of the guest switching property.