

マンデル酸を利用したキラルなレゾルシンアレーン超分子カプセルの合成

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Synthesis of Chiral Resorcinarene-Based Supramolecular Capsule by the Use of Mandelic Acid (¹School of Science, Hiroshima University, ²International Institute for Sustainability with Knotted Chiral Meta Matter (WPI-SKCM²), Hiroshima University, ³Graduate School of Advanced Science and Engineering, Hiroshima University) ○Senri Miyagi¹, Yudai Ono², Takeharu Haino^{2,3}

Our group reported the synthesis of a supramolecular capsule **2** formed by the self-assembly of a resorcinarene-based cavitaand **1** possessing four bipyridine arms with Cu(I). Capsule **2** exists as a racemic mixture of (*P*)- and (*M*)-forms. These enantiomers are in equilibrium in solution containing CH₃CN. When chiral guest molecules are bound to **2**, the chiral cavity recognizes the guest chirality to lead to diastereoselective complexation, thereby forming a one-handed helical structure. We investigated the conditions for chiral induction of **2** using mandelic acid as a chiral additive. CD spectra of **2** showed that (*R*)- and (*S*)-mandelic acid induced the (*P*)- and (*M*)-forms, respectively. When 16 equivalents of (*R*)-mandelic acid were added to the reaction mixture of **1** and Cu(I) in dichloroethane–acetonitrile, the (*P*)-form of **2** was preferentially formed with an enantiomeric excess of 83%.

Keywords : resorcinarene; circular dichroism; host-guest chemistry

当研究室は、4つのビピリジンアームをもつキャビタンド分子**1**と一価の銅イオンを用いたカプセル分子**2**の合成について報告している(Figure 1a)¹。**2**は、右巻き(*P*)と左巻き(*M*)のらせん構造をもち、配位性溶媒であるアセトニトリルを含む溶液中で平衡状態にある(Figure 1b)。**2**は包接空間にキラルなゲスト分子を取り込むと、ジアステレオ選択的な錯形成を起こし、片巻きのらせん構造を選択的に形成する。本研究では、キラルな有機酸であるマンデル酸を用いた光学活性カプセル分子**2**の新しい調製方法を見出した。*(R)*-マンデル酸を16当量添加し、**1**の自己集合を行ったところ、83%eeの光学純度でキラルなカプセル分子**2**が得られた(Figure 1c)。*(R)*-マンデル酸は**2**を(*P*)-体、(*S*)-マンデル酸は(*M*)-体に誘導することがわかった。

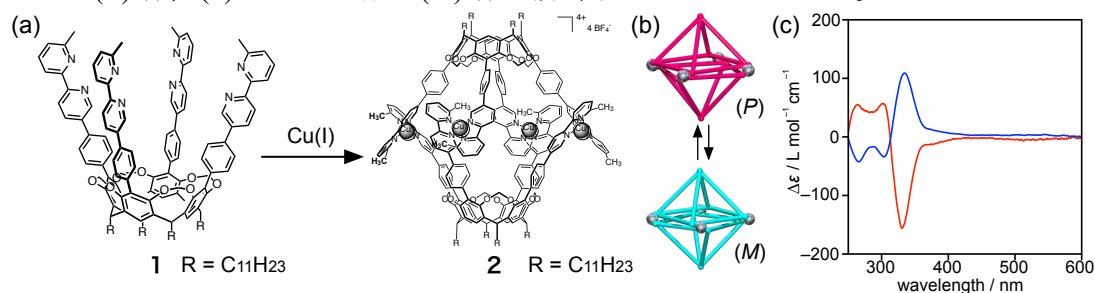


Figure 1. (a) Molecular structure and synthesis of **2**. (b) Illustration of (*P*)-(*M*) interconversion of **2**. (c) CD spectra of **2** prepared using (*R*)-mandelic acid (red curve) and (*S*)-mandelic acid (blue curve).

1) T. Imamura, T. Machara, R. Sekiya, T. Haino, *Chem. Eur. J.*, **2016**, 22, 3250-3254.