

Synthesis of Open-Cage Fullerene C₆₀ Derivatives Encapsulating a Hydrogen Peroxide Molecule

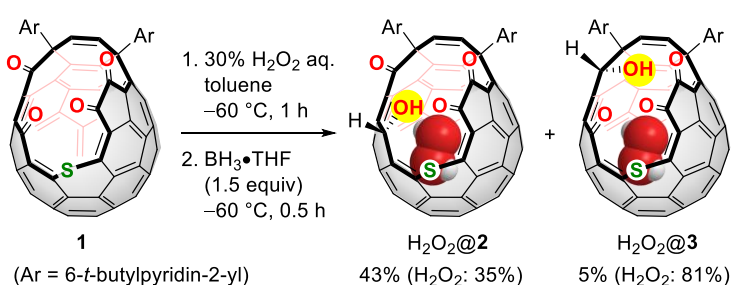
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The use of the cavity in fullerene C₆₀ enables the isolation of a single H₂O molecule which can modulate the properties of the outer sphere by intramolecular interactions with the C₆₀ cage.¹ To establish the stronger interaction between the cage and entrapped species, we studied the encapsulation of an H₂O₂ molecule² which is larger than the H₂O molecule.

As a host molecule, we used **1** which allows an H₂O molecule to be spontaneously encapsulated.³ By subjecting a 30% H₂O₂ aq. to a toluene solution of **1**, followed by the reduction using BH₃•THF at –60 °C,⁴ hydroxylated derivatives **2** and **3** with an

Scheme 1. Synthesis of H₂O₂@**2** and H₂O₂@**3**



OH group at the different positions were obtained in 43 and 5% isolated yields, respectively (Scheme 1). The ¹H NMR spectra (500 MHz, CDCl₃) showed a signal corresponding to an encapsulated H₂O₂ molecule at –4.16 ppm for H₂O₂@**2** and –3.81 ppm for H₂O₂@**3**. We confirmed that the H₂O₂ molecule in **2** escaped with the decreased encapsulation ratio after 6 days at room temperature, while that in **3** did not. These results showed that the position of the OH group affects effective size of the openings and that **3** offers stronger kinetic stabilization for the H₂O₂ against release. The crystallographic analysis showed that the distance of O(OH)•••O(H₂O₂) in H₂O₂@**3** (2.939(5) Å) is obviously shorter than that of H₂O₂@**2** (3.54(2) Å), implying the stronger hydrogen-bonding interaction in the former.

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