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Synthesis of Crown Ether-tethered b-Cyclodextrin and Fabrication of Its Self-assembled Monolayer on Gold Surface

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Abstract: A novel β-cyclodextrin derivative **6** bearing a crown ether moiety has been synthesized by a convenient method in 9.4% yield. Its self-assembled monolayer (SAM) was fabricated on the gold surface, which was characterized by using surface-enhanced Raman spectra.

Keywords: Cyclodextrin derivative, crown ether, self-assembled monolayer.

A number of cyclodextrin (CD) derivatives and crown ethers have been designed and synthesized in order to examine their molecular/ions recognition mechanics and control molecular assembly and self-assembly. However, CD derivatives linked by crown ether have rarely been synthesized and their molecular assembly has not been extensively investigated[1]. In the present communication, we report the synthesis of 4', 5'-dimercap -tomethylene-benzo-15-crown-5 tethered β-cyclodextrin and its self-assembled monolay-er (SAM) was fabricated on the gold surface.

The crown ether modified β-CD **6** was synthesized according to **Scheme 1**. In this synthetic route, 4', 5'-bis(bromomethyl)-benzo-15-crown-5 **2**[2] and thiourea were stirred for 24 h in EtOH at 50°C, then the mixture was hydrolyzed with aqueous NaOH (10%). After acidification, it is extracted with ether. Finally, the crude product was recrystallized from cyclohexane to give pure sample **3**. Moreover, **3** and the mono-[6-*O*-(*p*-toluenesulfonyl)]-β-CD **5**[3] was stirred in DMF for 10 days under N_2 at 70°C. After evaporation of DMF, the residue was dissolved in hot water, then poured into acetone with vigorous stirring. The brown precipitate formed was purified by the column of Sephadex G-25 with the elution of water two times to give pure **6** in 9.4% yield. These samples are confirmed by elemental analysis and spectroscopic data[4].

The Au-foil was immersed in a solution of **6** (0.1 mol/L) at room temperature for 24 h, then washed with water. The SAM was obtained. In the surface-enhanced Raman spectra of the SAM, the characteristic frequency of S-C at 713 cm^{-1} was shown, but the characteristic vibration of S-H at 2574 cm^{-1} does not exist[5]. Meanwhile, the vibration of the modified CD **6** can be observed at 2890, 1577, 1488, 1291, 1002 cm^{-1}. These results indicate the formation of the SAM on the gold surface.

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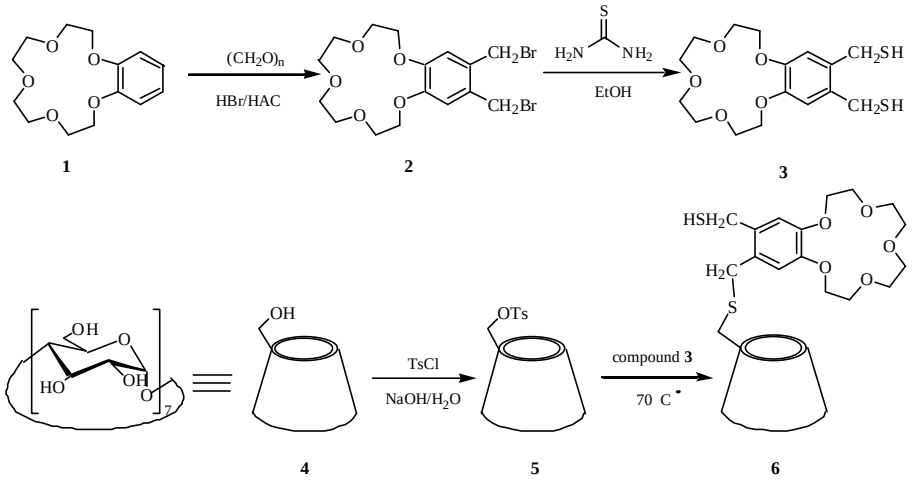
Scheme 1



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References and Notes

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4. **3**: mp 108-110°C, ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 6.77 (s, 2H, ArH), 4.12 (t, 4H, $CH_2OArOCH_2$, J=4Hz), 3.88 (t, 4H, J=4Hz, $ArCH_2S$-*2), 3.75 (m, 12H, $CH_2CH_2OCH_2CH_2$ & OCH_2*2), 1.83 (t, 2H, J=6Hz, SH*2); **6**: ^{1}H NMR (300MHz, D_2O, δ ppm): 6.5-7.2 (m, 2H, ArH), 4.83 (s, 7H, C_1-H), 2.7-3.9 (m, 58H, C_2~C_6 -H and H on crown ether moiety). FT-IR (KBr), ν=3297, 2928, 2879, 2504, 1599, 1504, 1453, 1405, 1360, 1291, 1250, 1152, 1078, 1032, 940, 853 cm^{-1}. Anal. Calcd. for $C_{58}H_{92}O_{39}S_2 \cdot 2H_2O$, C, 46.03; H, 6.39; S, 4.24. Found: C, 45.88; H, 6.40; S, 4.48.
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