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Supplementary Information

Controlled Synthesis of Pillar[6]arene-based Hexagonal Cylindrical Structures on an Electrode Surface by Electrochemical Oxidation

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Experimental

General

Cyclic voltammetry (CV) measurements and constant potential electrolysis were carried out using an ALS 6005C Electrochemical Analyzer. Bipolar electrolysis was conducted using a Hokuto Denko HABF-501A as a power supply for driving electrodes. Optical microscope observations were conducted with an Olympus SZX10. 3D laser microscope observation was performed with a Shimadzu SFT-4500. SEM observations were performed using a Shimadzu SS-550. UV-vis spectra were collected using a Shimadzu UV-1800 spectrophotometer. Fourier transform infrared (FT-IR) spectra were measured on a Shimadzu IRTracer-100. Powder X-ray diffraction (PXRD) analysis was performed on a Rigaku SmartLab with CuKα radiation. TEM observation and acquisition of corresponding selected area electron diffraction patterns were performed using a JEM-3100FEF transmission electron microscope (JEOL, Tokyo, Japan) at an acceleration voltage of 300 kV.

Materials

All reagents and chemicals were obtained from commercial sources and used without further purification otherwise noted. 1,4-Dihydroxypillar[6]arene was prepared according to a procedure defined in the literature.[1,2] Indium-tin-oxide (ITO), platinum (Pt), gold (Au) and glassy carbon (GC) plates were purchased from commercial sources.

Preparation of pillar[6]arene cylinder structures by CV and constant potential electrolysis

An electrolytic cell equipped with an ITO plate (10 × 10 mm^2), Pt plate and SCE were used as a working electrode, counter electrode, and a reference electrode, respectively, was filled with 0.1 M Bu_4NPF_6/MeOH (10 mL) and 1 mM 1,4-dihydroxypillar[6]arene. Before electrolysis, Ar bubbling was conducted for the cell. Deposited thin films on an electrode surface were purified by washing with MeCN. In the constant potential electrolysis, 0.3 mg of the product was obtained after passing 100 mC at 1.2 V vs. SCE.

Bipolar electrolysis

The experimental configuration is shown in Fig. 4a, using an ITO plate (10 × 20 mm^2) as a bipolar electrode (BPE) and Pt plates (20 × 20 mm^2) as driving electrodes. 5 mM Bu_4NPF_6/MeOH (20 mL) containing 1 mM 1,4-dihydroxypillar[6]arene was used as an electrolyte. A DC voltage (5 V) was applied between the driving electrodes for 1 min. at room temperature. The potential difference between both poles of the BPE was estimated as 3.2 V with monitoring an electric field transmission efficiency ($\theta = 0.81$) during electrolysis.[3]

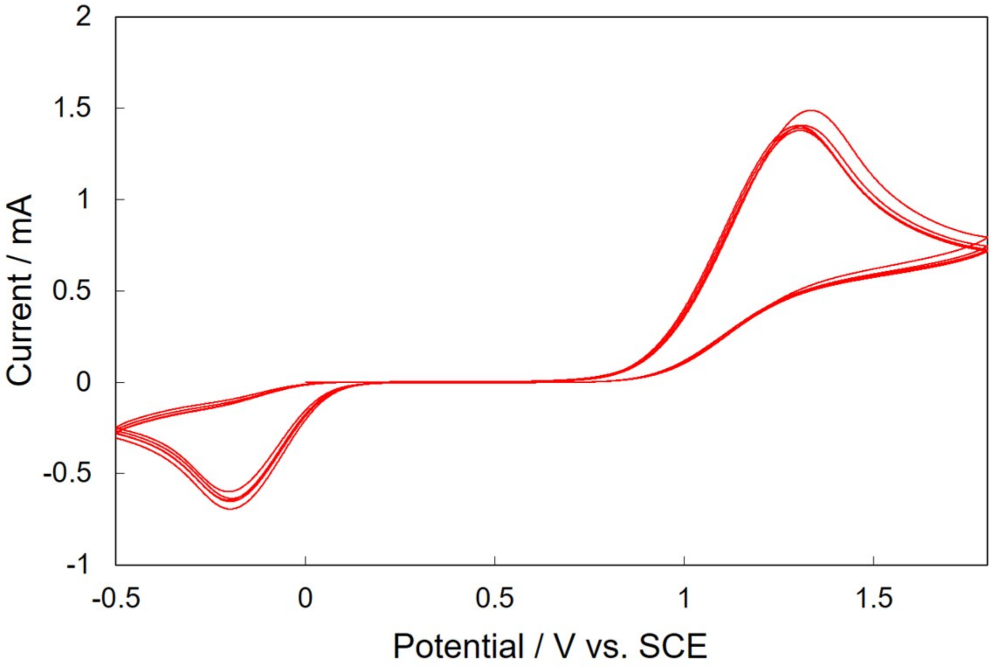

Fig. S1 Cyclic voltamograms of hydroquinone (6 mM) measured in 0.1 M Bu_4NPF_6/MeOH using an ITO glass (10 × 10 mm^2) as a working electrode at a scan rate of 100 mV/s..

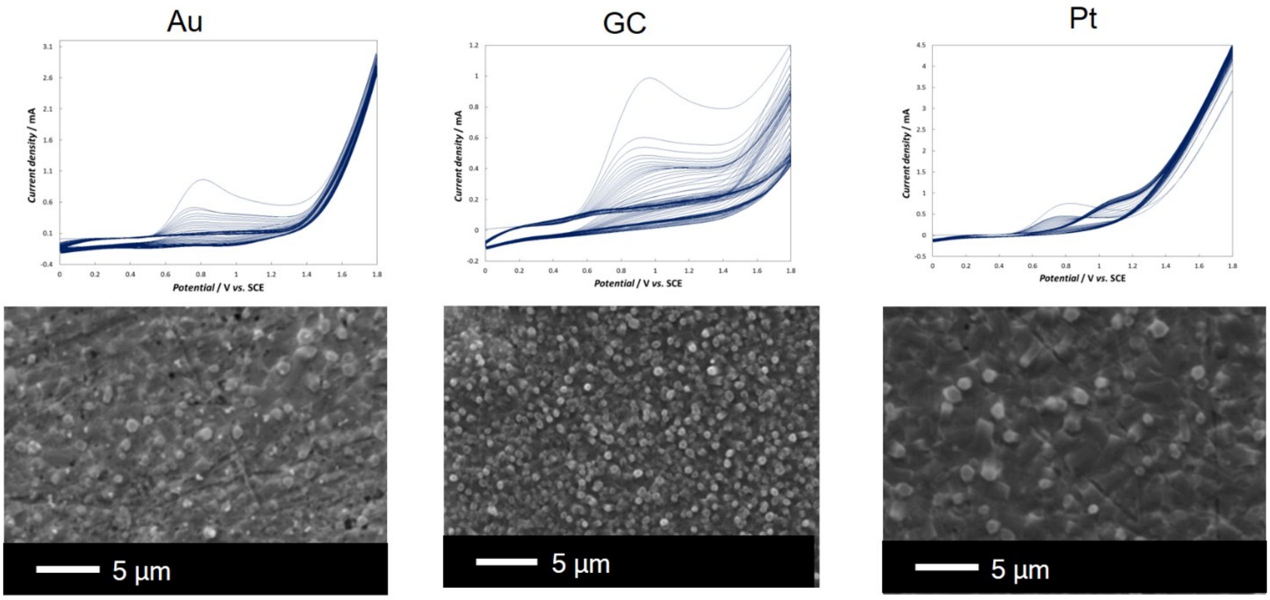

Fig. S2 Cyclic voltammograms of pillar[6]arene (1 mM) measured in 0.1 M Bu_4NPF_6/MeOH using various electrode materials (10 × 10 mm^2) at a scan rate of 100 mV/s, and the SEM images of each electrode surface after electrolysis.

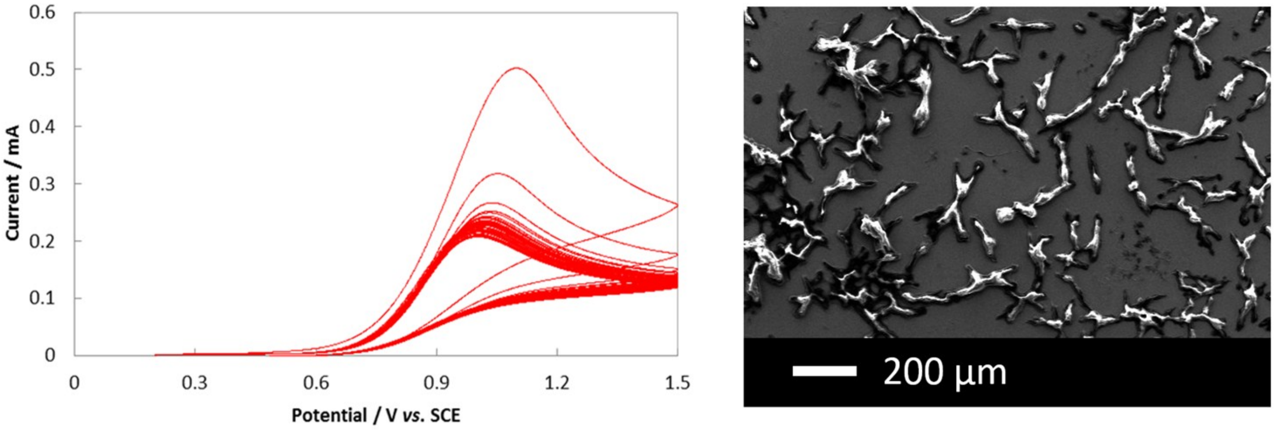

Fig. S3 Cyclic voltammograms of pillar[5]arene (1 mM) measured in 0.1 M Bu_4NPF_6/MeOH using an ITO electrode (10 × 10 mm^2) at a scan rate of 100 mV/s, and the SEM image of the deposition on the electrode.

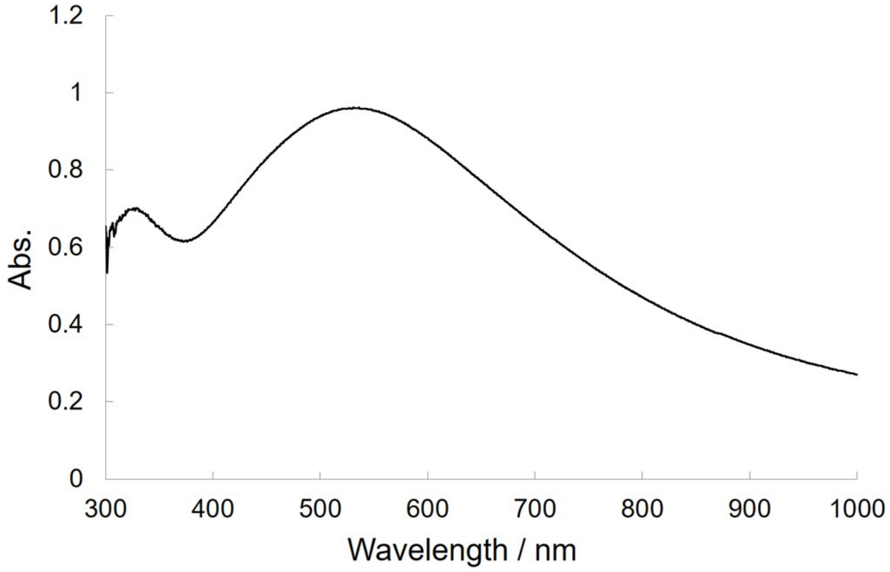

Fig. S4 UV-vis absorption spectrum of the pillar[6]arene CT complex formed on an ITO electrode.

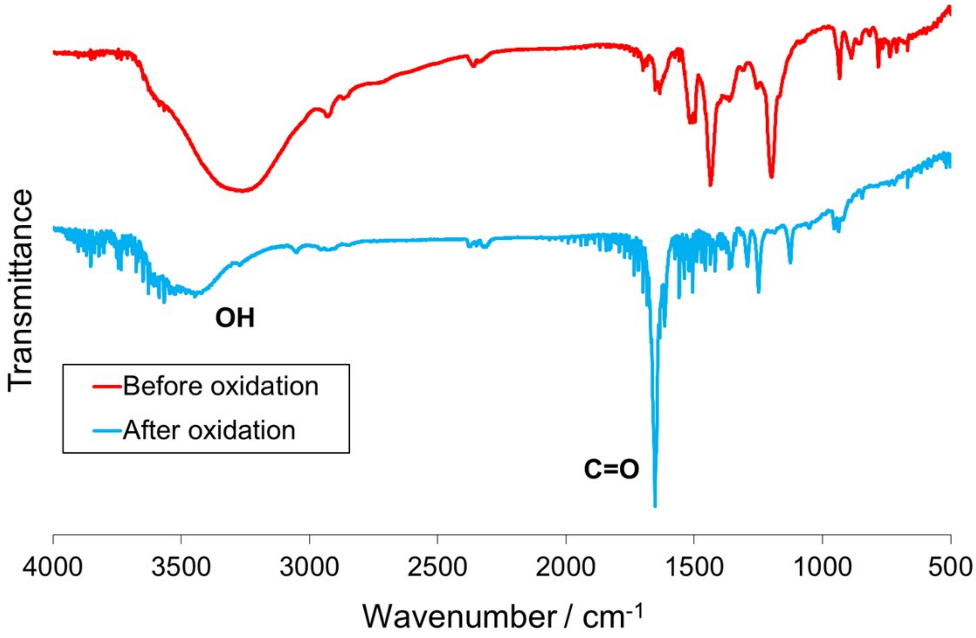

Fig. S5 IR spectra of pillar[6]arene before and after anodic oxidation (KBr).

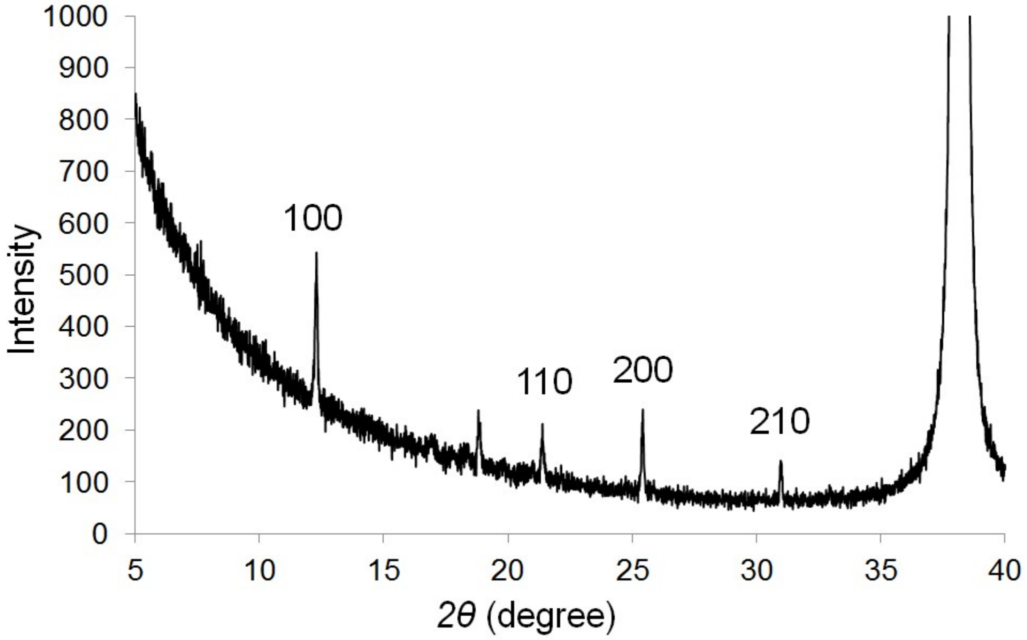

Fig. S6 PXRD pattern of pillar[6]arene CT complex prepared on an Au electrode.

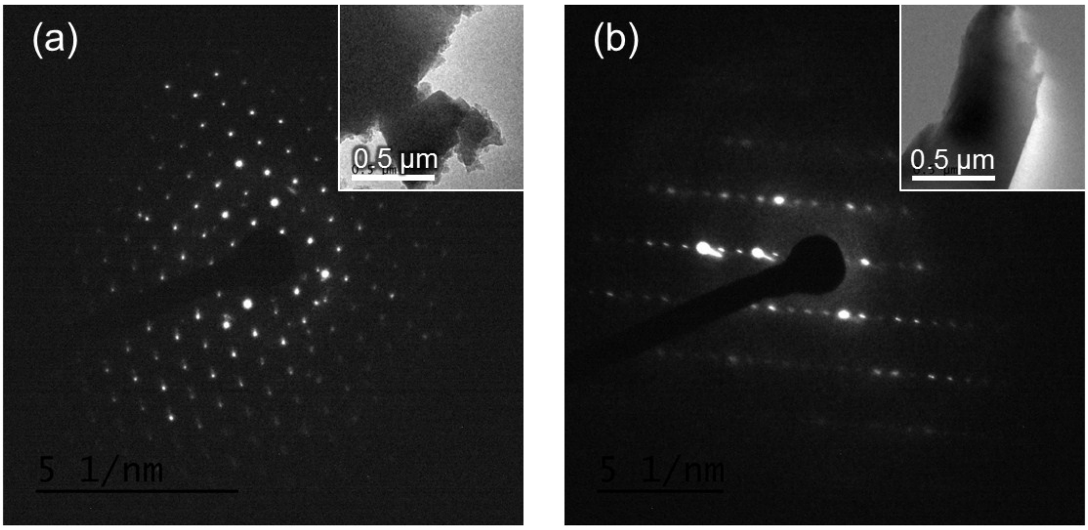

Fig. S7 TEM image (inset) and selected-area electron diffraction patterns of a cylinder from cross section (a) and lateral face (b).

References

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3. Y. Koizumi, N. Shida, M. Ohira, H. Nishiyama, I. Tomita and S. Inagi, *Nat. Commun.*, 2016, **7**, 10404.