

Synthesis and Electrochemical Properties of Pillar[6]quinone

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Keywords: Pillar[6]quinone; Macrocycles; Oxidation; DFT Calculation;

Pillar[n]arenes (n: number of units), macrocyclic *para*-arylene methylene molecules, have attracted attention owing to their symmetrical structures, host-guest properties, and original supramolecular assembly characteristics.¹ Similarly, their quinone counterparts, pillar[n]quinones (P[Q]_n), are also fascinating macrocycles containing electron-deficient quinone units. A hexagonal molecule, pillar[6]quinone (P[Q]₆), is expected to form densely packed structures and is a candidate for organic active material but the synthesis of P[Q]₆ still remains a challenge. We previously reported that the anodic oxidation (1.0 V vs. SCE) of 1,4-dihydroxypillar[6]arene (P[HQ]₆) in methanol gave hexagonal cylinder structures on electrode surfaces which were composed of partially oxidized P[HQ]_{6-m}[Q]_m (composed of both hydroquinone and benzoquinone units) aggregating via quinhydrone formation.²

In this work, we successfully synthesized P[Q]₆ for the first time by oxidation of its hydroquinone precursor P[HQ]₆. Electrochemical oxidation (1.2 V vs. SCE) of P[HQ]₆ in methanol gave the similar hexagonal cylindrical crystal of P[Q]₆ evidenced by single crystal X-ray diffraction, NMR and HRMS analyses.³ In addition, we also found that scalable synthesis of P[Q]₆ was succeeded by chemical oxidation of P[HQ]₆ with phenyliodine(III)bis(trifluoroacetate) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Furthermore, the electrochemical properties and electron-transfer behavior of P[Q]₆ were revealed by various voltammetric studies.

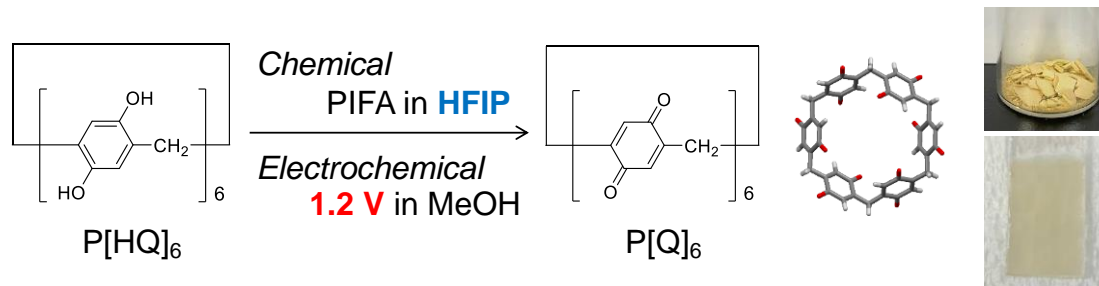


Fig.1 Chemical and electrochemical synthesis of pillar[6]quinone.

References

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