

# A Study on Synthesis, Structure, and Spectroscopic and Electrochemical Properties of Bromo- and Ethynyl-Substituted Pyromellitic Diimide-Based Macrocycles

ハリム, エムディ エルシャド

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氏 名 : エムディ エルシャド ハリム

論 文 名 : A Study on Synthesis, Structure, and Spectroscopic and Electrochemical Properties  
of Bromo- and Ethynyl-Substituted Pyromellitic Diimide-Based Macrocycles(臭素及びエチニル置換ピロメリット酸ジイミド基盤マクロサイクル類の合成、構造、  
並びにスペクトル及び電気化学的性質に関する研究)

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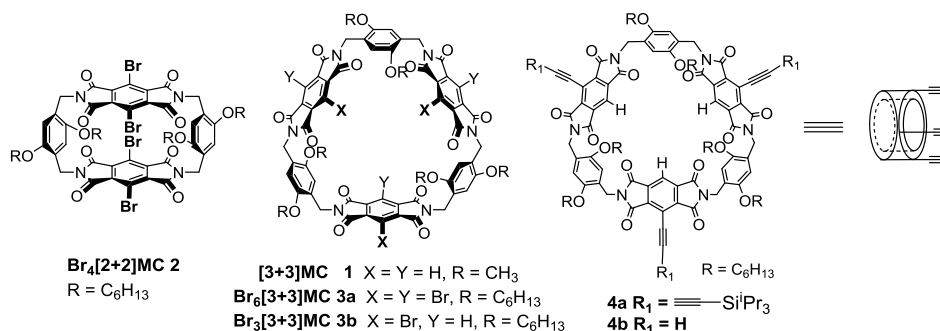
## 論 文 内 容 の 要 旨

Macrocycles with their interesting structures and properties are promising candidates to construct supramolecular structures. Till now there exist very few reports in the literature on the covalently linked nanotubes based on macrocycles, presumably due to difficulties in synthesizing suitably functionalized macrocycles and the formation of nanotubes by their connection. We have been interested in incorporating macrocyclic motif into the nanotube framework. As the component of macrocycles, we have chosen the pyromellitic diimide moiety with electron-accepting properties. We previously reported that the pyromellitic diimide-based [3+3]macrocycle ([3+3]MC) **1** has an electron-deficient cavity in which the electron-rich [2.2]paracyclophane is included inside the cavity *via* a charge transfer CT interaction.

As the next step toward the synthesis of molecular tubes, we designed a method to synthesize functionalized macrocycles as the key synthetic precursors to nanotubes. We first chose the bromo-substituted [3+3]MCs as the target molecules since the halogen atoms can be converted into various functional groups. In this thesis, we report the synthesis of bromo-substituted [3+3]MCs and Br<sub>4</sub>[2+2]MC **2** and their properties based on the UV/Vis spectra and redox properties.

Br<sub>3</sub>[3+3]MC **3b** has become available in gram-quantities by the direct cyclodehydration of the bromo-substituted pyromellitic acid with the diamine in acetic acid at 100 °C. In these reactions, the [3+3]MC is almost exclusively formed and purification of the [3+3]MCs is quite easy. However, an application of this reaction for the synthesis of Br<sub>6</sub>[3+3]MC **3a** resulted in a lower yield, and the conventional cyclization of the dianhydride and the diamine in THF, followed by dehydration with Ac<sub>2</sub>O and NaOAc exclusively provided Br<sub>4</sub>[2+2]MC **2** but in low yield.

Br<sub>4</sub>[2+2]MC **2** and Br<sub>6</sub>[3+3]MC **3a** show similar absorption spectra to each other, while the intensities of the absorption bands of **3a** are higher than the corresponding bands of **2**. The cyclic voltammetric data suggest that the introduction of the bromine atoms into the pyromellitic diimide moieties of the macrocycle



stabilizes the anion radical and dianion species of the macrocycles  $\text{Br}_4[2+2]\text{MC}$  **2** includes a toluene molecule inside the electron-deficient cavity, which was revealed by a single crystal X-ray analysis.

$\text{Br}_3[3+3]\text{MCs}$  **3b** is a suitable precursor for the synthesis of functionalized macrocycles. We set the ethynyl-substituted  $[3+3]\text{MCs}$  as the next target molecules since the ethynyl group is a useful precursor for the Glaser coupling. In fact, the Sonogashira coupling of the  $\text{Br}_3[3+3]\text{MC}$  **3b** with triisopropylsilylacetylene afforded the macrocycle **4** in good yield. The UV/Vis spectrum of the macrocycle **4** showed significant red shift of the absorption band compared to the parent macrocycle. In addition, the radical anion and dianion species of the ethynyl-substituted macrocycle are greatly stabilized as suggested by the cyclic voltametry measurements, because of the delocalization of the electrons over the ethynyl groups. We have now examined the dimer formation of the  $[3+3]\text{macrocycle}$  **4** by the Glaser type coupling.