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Synthesis of bromo- and iodo-substituted pyromellitic diimide-based [2+2]- and [3+3]macrocycles, and their absorption spectra and electrochemical and inclusion properties[#]

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ABSTRACT

New pyromellitic diimide-based tetrabromo[2+2]macrocycle ([2+2]MC) **2**, tribromo- and hexabromo[3+3]MCs **3a** and **3b**, as well as triiodo[3+3]MC **3c** were synthesized as structural units of covalently bound nanotubes, and their absorption spectra and redox properties, as well as inclusion phenomena of the [2+2]MC **2** were reported. Tetrabromo[2+2]MC **2** forms a 1:1 inclusion complex with toluene, whose structure was revealed by X-ray structural analysis.

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,[2] presumably due to difficulties in synthesizing suitably functionalized macrocycles and the formation of nanotubes by their connection. We are 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[1a] since this moiety has four connecting sites; two nitrogen atoms for the construction of the macrocycles, and the carbon atoms at the *para*-positions of the benzene ring of the diimide moiety for the connection of the macrocycles (Figure 1). We previously reported that the pyromellitic diimide-based [3+3]macrocycle ([3+3]MC)[3] **1a** has an electron-deficient cavity in which the electron-rich [2.2.2]paracyclophane is included inside the cavity *via* a charge transfer (CT) interaction.[1a]

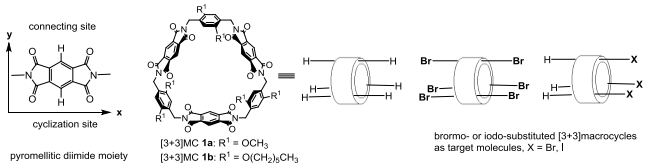

Figure 1. Pyromellitic diimide moiety as a component of the macrocycles, parent [3+3]macrocycles **1a** and **1b**, and the bromo- and iodo-substituted [3+3]macrocycles as target molecules.

In our continuing effort toward the synthesis of molecular tubes, we designed a method to synthesize functionalized macrocycles as the key synthetic precursors to nanotubes.[1a] We first chose the bromo- and iodo-substituted [3+3]MCs as the target molecules since the halogen atoms can be converted into various functional groups. We now report the synthesis of bromo- and iodo-substituted [3+3]MCs and tetrabromo-[2+2]MC and their properties based on the UV/Vis spectra and redox properties. The structure of the host-guest complex between Br_4[2+2]MC **2** and toluene was revealed by an X-ray crystallographic analysis.

We previously reported the first synthesis of the parent [3+3]MC **1a** by the cyclodehydration between pyromellitic dianhydride and 1,4-bis(aminomethyl)-2,5-dimethoxybenzene **4** in NMP at 150 °C.[1a] This reaction

See Ref. 1.

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