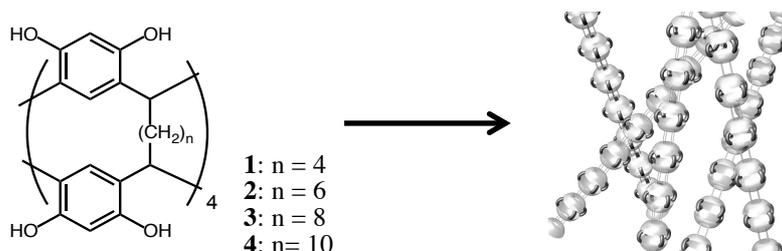


# Synthesis and Supramolecular Polymerization of Rim-to-Rim Connected Biscalix[4]resorcinarene Bridged by Alkyl Chains

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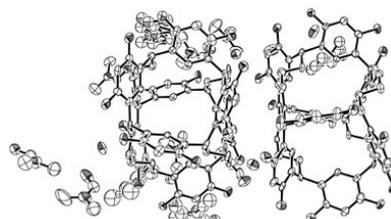
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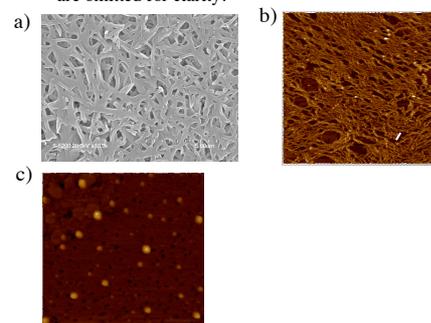
The homoditopic nature of rim-to-rim connected bisresorcinarenes **1–4** is potentially useful for the successful synthesis of supramolecular polymers. Originally, Kudo, Nishikubo, and co-workers discovered rim-to-rim connected bisresorcinarene **1**<sup>1</sup> during the synthesis of a double-cyclic ladder type oligomer, named “noria.”<sup>2</sup> In this session, we will present the modified synthetic method for rim-to-rim connected bisresorcinarenes **1–4**.<sup>3</sup> For example, the macrocyclization reactions of resorcinol with dialdehydes and dimethoxyacetals were carried out in acidic ethanol at 80 °C for three days. When 1,8-octandial reacted with resorcinol, the bisresorcinarene **2** was obtained in 27% yield. By contrast, the reaction of 1,8-octandiacetal and resorcinol under the same conditions gave obviously improved yield of bisresorcinarene **2** (62%).

The crystal structure of **1** confirms that the lower rims of the two resorcinarene moieties are connected by the four alkyl chains (Fig. 1). One resorcinarene core is slightly twisted toward the other, resulting in a  $D_4$ -symmetric helical conformation. The *P* and *M* conformations combine into a racemic pair.

Figure 2 shows the SEM and AFM images of the cast films of **2** prepared from its ethanol solution. In the presence of toluene, the supramolecular polymerization of **2** was observed (Fig. 2a,b). By contrast, a film prepared in the presence of DMF contained particle-like aggregates (Fig. 2c), suggesting that the competitive hydrogen bonding of the DMF molecules to the phenolic hydroxyl groups most likely disrupted the dimeric structures.



**Figure 1.** Molecular structure of **1**. View along *a*-axis. Ellipsoids are shown at 50%. Hydrogen atoms are omitted for clarity.



**Figure 2.** (a) SEM and (b, c) AFM images of cast films prepared from ethanol solutions of **2** in the presence of: (a, b) toluene, (c) dimethylformamide. (b)  $9.0 \times 9.0 \mu\text{m}^2$ , (c)  $5.0 \times 5.0 \mu\text{m}^2$ .

## Reference

- 1) H. Kudo, T. Nishikubo, *Jpn. Kokai Tokkyo Koho*, **2008**, JP 280269 A.
- 2) H. Kudo, R. Hayashi, K. Mitani, T. Yokozawa, N. Kasuga, T. Nishikubo, *Angew. Chem. Int. Ed.* **2006**, *45*, 7948-7952.
- 3) H. Yamada, T. Ikeda, T. Mizuta, T. Haino, *Org. Lett.* **2012**, *14*, 4510-4513.