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Syntheses, crystal structures, and electrochemical properties of multi-ferrocenyl resorcinarenes

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Abstract—Tetraaryl and tetraferrocenyl resorcinarenes **1a**–**1c** have been synthesized by the HCl-catalyzed condensation of resorcinol with aromatic aldehydes or ferrocenecarbaldehyde, which were fully alkylated with ethyl α-chloroacetate to give the activated ethyl resorcinarylacetates **2a**–**2c**. Reaction of **2a**–**2c** with hydrated hydrazine yielded the resorcinarene acylhydrazine derivatives **3a**–**3c**, from which the multi-ferrocenyl functional groups were selectively and efficiently introduced on the upper rim, or on the lower rim, or both on the upper and lower rims of resorcinarenes **4a**–**4c** and calixarenes **4d**–**4f** based upon the condensation reactions of acylhydrazones with ferrocenecarboxaldehyde.

1. Introduction

Calixarenes and resorcinarenes have become popular templates for a number of chemical investigations because it can be produced selectively in large quantities from cheap commercial starting materials and can easily be chemically modified, leading to versatile tail-made receptors.[1–3] In order to design new types of valuable receptor molecules and supramolecular structures, various methods have been developed for complete and selective modification on the upper and lower rims of calixarenes and resorcinarenes.[4–5] Recently, molecular design of calixarenes and resorcinarenes for anion recognition and sensing has become an increasingly important research topics in supramolecular chemistry because selective binding of anions is more demanding than that of cations in view of the high free energies of solvation of anions and that the frequently occurring pH dependency of anion complexation.[6–8] The incorporation of redox-active centers, such as ferrocene into ligands of the calixarene type aimed at the development of molecular sensory devices, which allow electrochemical recognition of trapped guests, has attracted much more attention in the past years. Ferrocene does not directly interact with anions until it is oxidized to ferrocenium, when electrostatic interactions are switched on. Beer and co-workers firstly prepared metallocene amide receptors for binding and sensing anions.[9–10] From then Beer and others reported a lot of works with different strategies for introducing ferrocene[11–22] and other metallocene[23–26] units to the lower and upper rims of calixarenes and resorcinarenes, many of which include an amide hydrogen-bonding group.[27–28] Anions may be recognized in a range of environmental conditions, with some receptors even being active in aqueous solution.[29–31] The tetraferrocenyl resorcinarenes were also obtained from the condensation of resorcinol with ferrocenecarboxaldehyde.[17] In continuation of our studies on molecular design of calixarene acceptors, we are interested in constructing multi-ferrocene functional groups on *p-tert*-butylcalix[*n*]arenes and resorcinarenes. In this paper, we report a selective and efficient procedure to introduce ferrocenes on the upper rim, or on the lower rim, or both on the upper and lower rims of resorcinarenes and calixarenes based upon the condensation reactions of acylhydrazones with ferrocenecarboxaldehyde.

2. Results and discussion

2.1. Synthesis and characterization

Tetraaryl resorcinarenes, which can be easily prepared from the condensation of resorcinol with aromatic aldehydes, have received less attention compared to tetraalkyl resorcinarenes[32–34] because tetraaryl resorcinarenes have less solubility in common solvents and are much difficult for chemical modifications. But rigid aryl groups might create a more stable conformation for resorcinarenes and result in much high selective recognition. Thus resorcinarenes **1a**–**1c** with phenyl, *p*-hydroxyphenyl, and ferrocenyl groups were prepared in high yields from the condensation of

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Keywords: Resorcinarene; Calixarene; Ferrocene; Conformation; Crystal structure.

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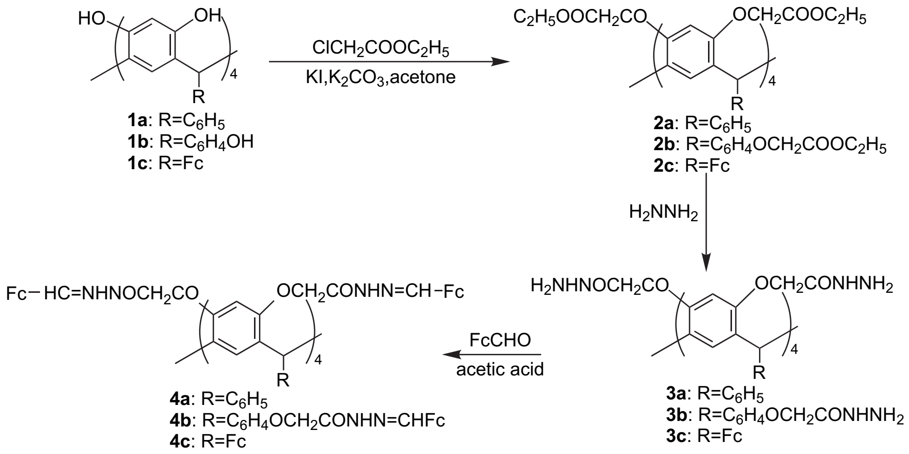

Scheme 1. Synthesis of multi-ferrocenyl resorcinarenes.

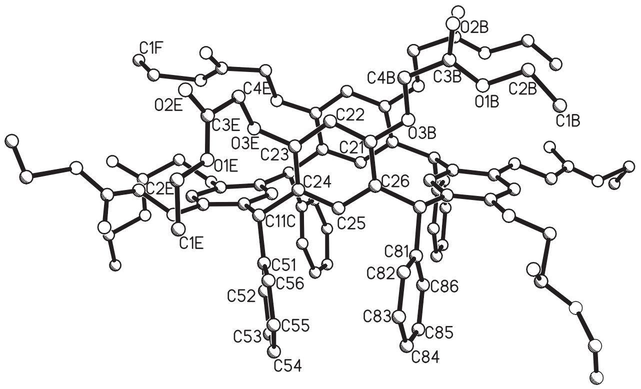

Figure 1. The crystal structure of **2a**.

resorcinol with benzaldehyde, *p*-hydroxybenzaldehyde, and ferrocenecarboxaldehyde according to the published method (Scheme 1).[32–34] Although having very poor solubilities in common solvents, **1a**–**1c** can still be fully O-alkylated with ethyl α-chloroacetate in K_2CO_3/KI/acetone system to give active ester derivatives **2a**–**2c** in 50–70% yield, which make it possible to modify resorcinarene on the upper rim. It must be noticed that there are 8, 12, or 8 active ester groups in **2a**–**2c**, respectively, for the *p*-hydroxyphenyl groups in **1b** would be also alkylated in this procedure. The structures of **2a**–**2c** were characterized by spectroscopic data and fully confirmed by the X-ray single crystal analysis.

The molecular structures are shown in Figures 1–3. The crystal structures give stronger evidence that all hydroxyl groups have been alkylated by ethyl α-chloroacetate to give fully alkylated ethyl calixarylacetate. It can be seen that in **2a**–**2c** the four resorcinol units in the ring were divided into two groups with two resorcinol rings almost perpendicular to the other two resorcinol rings, which show the resorcinarene in boat conformation, with much distorted in a propeller-like manner in **2c**. The stretching directions of two perpendicular resorcinol rings are opposite. One is upper standing and the other is upside down. It is interesting

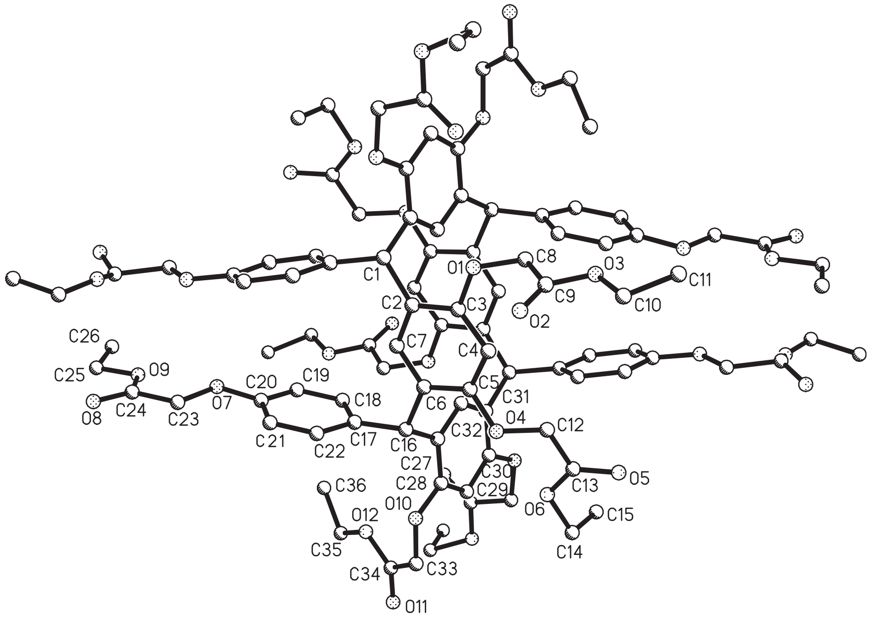

Figure 2. The crystal structure of **2b**.