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Novel fullerene receptors based on calixarene–porphyrin conjugates

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Abstract—Several different synthetic approaches enabling a direct covalent connection between the *meso*-position of porphyrin and the upper rim of calix[4]arene have been studied. The best results were obtained via condensation of an excess of pyrrole and *p*-methylbenzaldehyde with calix[4]arene-5,17-dialdehyde under $BF_3{\cdot}Et_2O$ catalysis in $CHCl_3$. Subsequent oxidation of the intermediate porphyrinogen gave the corresponding bis-porphyrin–calixarene conjugate in 15% overall yield. The ^1H NMR complexation study revealed the pronounced selectivity of the bis-porphyrin derivative towards C_{70} fullerene.

Calix[4]arenes and their relatives[1] are frequently used as molecular scaffolds in the design of elaborate supramolecular systems, including a variety of functional receptors. Among various hosts for fullerene recognition, calix[*n*]arenes have played an important role since the pioneering work of Shinkai's and Atwood's groups.[2] There are numerous examples[3] demonstrating that spherical fullerenes are attracted by a shape-complementary cavity of calixarenes to form complexes both in solution and in the solid state. Recent studies have shown that the curved π surfaces of C_{60} or C_{70} fullerenes can interact with the (metallo)porphyrin moieties by attractive π–π interactions.[4] Consequently, various multiporphyrin systems and extensive studies of porphyrin/fullerene interactions have been reported.[5]

In our previous study we showed that the combination of porphyrin and calixarene motifs within one molecule leads to novel receptors with many interesting complexation properties.[6] As we have reported recently, calix[4]arene or thiacalix[4]arene–porphyrin conjugates with porphyrin units preorganised in the distal positions, behave as molecular tweezers[7] that can pick up fullerenes in solution. Despite the fact that the connection between the porphyrin and calixarene units was constructed via relatively mobile spacers, the receptors exhibited pronounced selectivity towards fullerene C_{70}. In this context, we expected that mounting the tetraarylporphyrin moiety directly to the upper rim of calix[4]arene would lead to more preorganised structures, and hence, to higher selectivity of fullerene complexation. In this letter we report on the synthesis and binding properties of such compounds—calix[4]arenes bearing porphyrins directly connected via the *meso*-positions.

Calix[4]arenes with porphyrin moieties directly connected via the *meso* position to the upper rim are not easily accessible and only a few examples of these types of structures can be found in the literature.[6a,8] The synthesis of the target compound **5** is depicted in Scheme 1. The starting dialdehyde **1** was obtained via formylation of 25,27-dipropoxycalix[4]arene with dichloromethyl methyl ether[9] in a high yield, which was then used for the mixed aldehyde condensation[10] with *p*-tolualdehyde and pyrrole (route I). The stoichiometric ratio of the reactants (**1**:*p*-tolualdehyde:pyrrole = 1:6:8) under $BF_3{\cdot}Et_2O$ catalysis gave the target bis-porphyrin derivative **5** in a very low yield (0.4%). Surprisingly, under these conditions the mono-substituted calixarene **4a** bearing one unreacted formyl group was isolated (in addition to tetra-*p*-tolylporphyrin) as the main product (14%).[11]

As the use of excess pyrrole did not lead to good results, we turned our attention to the application of more preorganised starting compounds. Thus, *p*-tolualdehyde was transformed into the corresponding dipyrromethane **2** and used for the condensation (route II). Although the number of molecules needed for condensation is much lower than that in route I (7 vs 15), this

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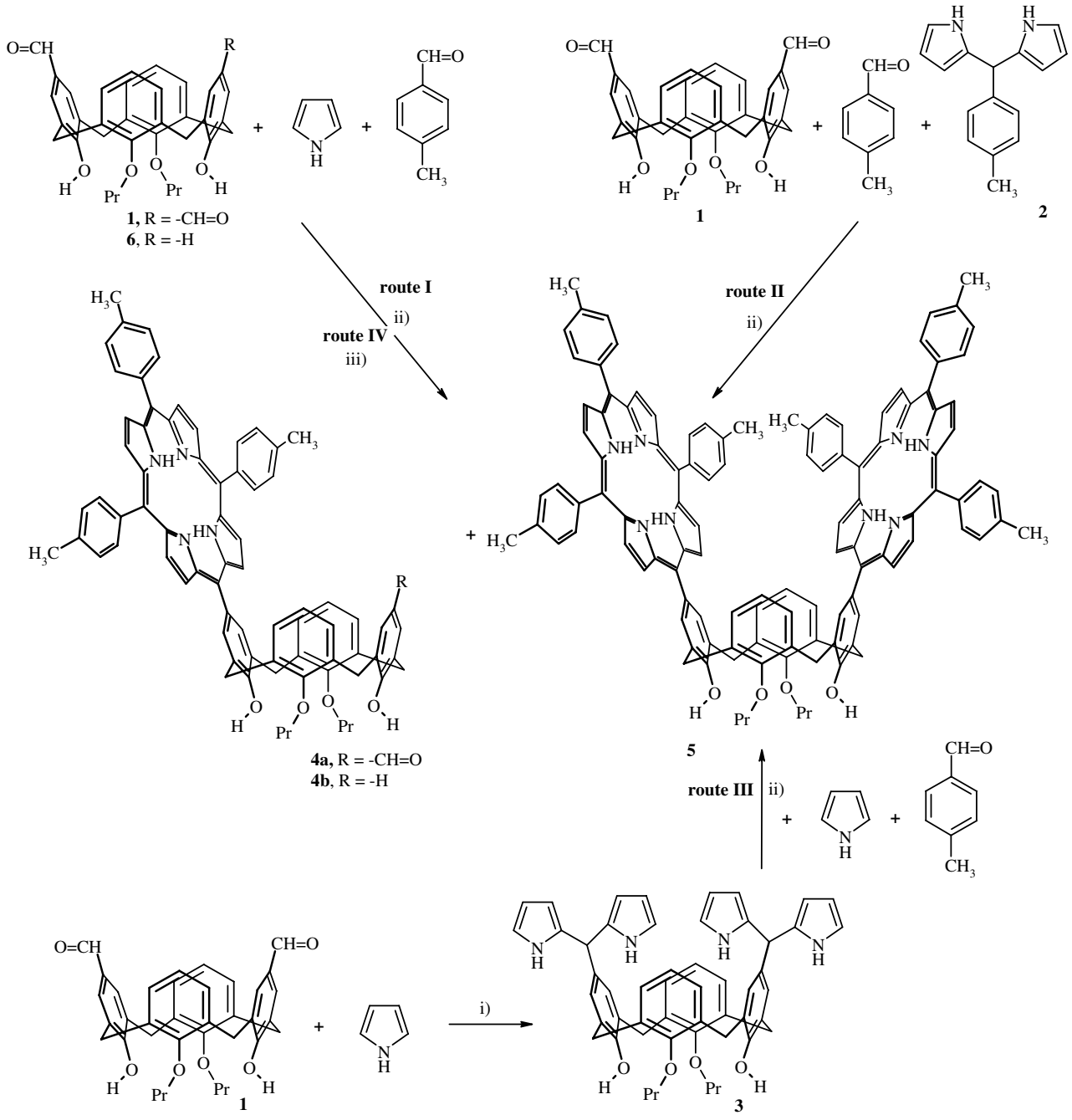

Scheme 1. Reagents and conditions: (i) Excess pyrrole, rt/3 h (85%); (ii) (a) $CHCl_3$, cat. $BF_3{\cdot}Et_2O$, rt/7 h, (b) DDQ, rt (0.4–15%); (iii) CH_3CH_2COOH, reflux (0.1%).

strategy gave only a slightly better result—compound **5** was isolated in 1% yield. In route III, calix[4]arene dialdehyde **1** was reacted with excess pyrrole to give the bis-dipyrromethane derivative **3** in 85% yield.[12,13] Unfortunately, condensation of **3** with pyrrole and *p*-tolualdehyde and subsequent oxidation of the intermediate porphyrinogen with DDQ gave the target compound **5** in only 3% yield. The next method used for porphyrin synthesis involved route IV, where a mixture of **1**, pyrrole and *p*-tolualdehyde was stirred under reflux in propionic acid in the presence of air. This procedure led to a complicated reaction mixture from which derivative **5** was isolated in a very low yield (0.1%) via repeated preparative TLC. As all attempts to obtain compound **5** in an acceptable yield failed, we decided to return to route I and further optimise the reaction conditions. After many trials and errors, we found that the condensation of dialdehyde **1**, pyrrole and *p*-tolualdehyde in a ratio of 1:86:88 ($CHCl_3/BF_3{\cdot}Et_2O$ catalysis) gave bis-porphyrin **5** in 15% yield.[14] To gain a deeper insight into the mechanism of fullerene complexation, a model compound **4b** having only one porphyrin unit on the upper rim was prepared. Compound **4b** was obtained via route IV from the corresponding monoaldehyde **6** in 10% yield.[15]

The UV–vis absorption spectra of **5**, shown in Figure 1, are similar to those obtained for 5,10,15,20-tetraphenylporphyrin (**TPP**). In our opinion, a small red