

Synthesis of new decasubstituted pillar[5]arenes containing glycine fragments and their interactions with Bismarck brown Y

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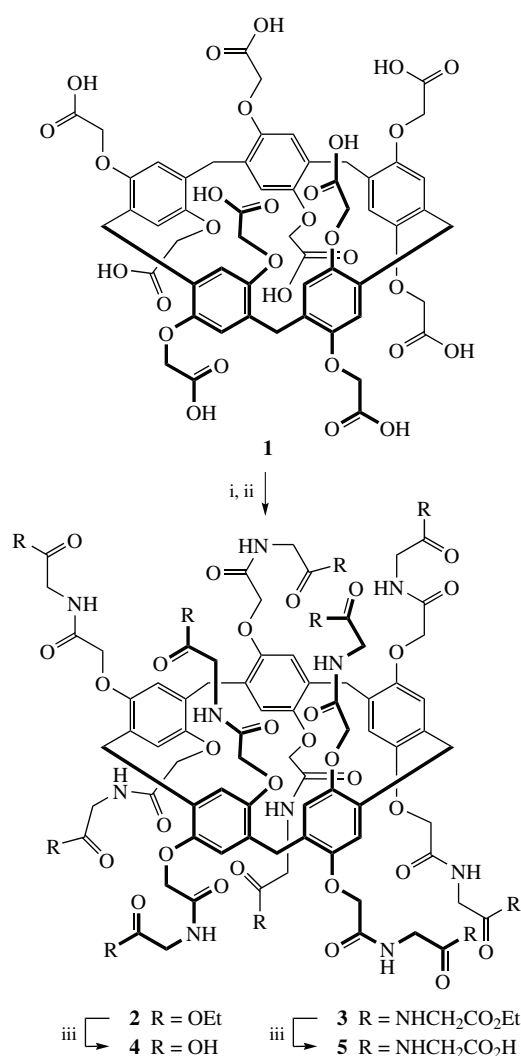
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New water-soluble decasubstituted pillar[5]arenes containing glycine and glycyglycine fragments were synthesized and characterized. The UV, DLS and TEM study showed that interaction of self-associates of the glycyglycine derivatives with Bismarck brown Y produced particles of about 59 nm in size.

Azo dyes have found various applications in science, medicine and technology.^{1–3} Despite the fact that most water-soluble dyes are weakly reactive and non-toxic at low concentrations, they appear to be main source of water pollution, and pose a serious threat to the environment.³ Meanwhile, nanoparticles covalently linked or associated with chromophoric or fluorophoric substances have potential use in sensors, biomimetic systems, as catalysts, selective extractants and drug delivery systems.^{4–10} We have recently proposed¹¹ the use of a new class of macrocycles, pillar[5]arenes, as synthetic blocks for constructing water soluble nanoparticles capable of interacting with azo dyes. The *p*-hydroquinone fragments of these macrocycles are linked to each other by methylene bridges.¹² Pillar[*n*]arenes contain an internal hydrophobic cavity with a diameter comparable to the cavity diameter of corresponding cyclodextrins and cucurbit[*n*]urils.¹³ Pillar[*n*]arenes similarly to cyclodextrins and cucurbit[*n*]urils tend to form host–guest complexes with organic and inorganic ‘guests’. A distinctive feature of pillar[*n*]arene is the presence of free hydroxyl groups that can be variously functionalized.^{14–16}

Previously, self-assembled amphiphilic functionalized pillar[5]arenes^{17,18} and supramolecular polymers^{19–24} based on inclusion complexes consisting of linear (with carbon number ≥ 6) molecule fragments in the cavity of the macrocycle were described in the literature. However, there is no data on the possible formation of self-associates by decafunctionalized pillar[5]arenes. On the other hand, structural proteins elastin and collagen are rich in glycine.²⁵ Collagen fibrils represent a major component in the extracellular matrix and connective tissue providing support for cells.²⁶ Thus, we hypothesize that attachment of glycine and glycyglycine fragments to pillar[5]arenes can promote self-aggregation and affinity to various biomacromolecules.

The starting decaacid **1** was synthesized from commercially available reagents according to the published procedures²⁷ (Scheme 1). It was converted into decachloride by treatment with thionyl chloride in the presence of catalytic amount of DMF.²⁸ Further acylation of glycine and glycyglycine ethyl ester hydrochlorides with this decachloride gave compounds **2** and **3** in 78 and 70% yields, respectively (see Scheme 1). The acylation proceeded in anhydrous dichloromethane in the presence of triethylamine for 48 h.[†]



Scheme 1 Reagents and conditions: i, SOCl₂, reflux; ii, glycine/glycyglycine ester hydrochloride, Et₃N/CH₂Cl₂; iii, LiOH, H₂O/THF, room temperature, then HCl.

of SOCl₂ (10 ml, 0.084 mol) and catalytic amount of DMF. The mixture was refluxed for 18 h and then the excess of SOCl₂ was removed under reduced pressure. The remainder was dried under reduced pressure for 2 h. The obtained residue was dissolved in 10 ml of dichloromethane. The

[†] General procedure for the synthesis of compounds **2** and **3**. 4,8,14,18,23,26,28,31,32,35-Decakis(methoxycarbonyl)pillar[5]arene **1** (0.30 g, 0.252 mmol) was placed into the round-bottom flask followed by addition