


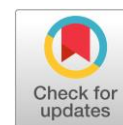


Towards nanomaterials with tubular pores: synthesis and self-assembly of bis-pillar[5]arene

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Abstract

Recently, materials obtained using supramolecular chemistry approaches, and, in particular, spatially preorganized macrocyclic compounds, have attracted close attention of the researchers. Pillar[n]arenes are of special interest due to their tubular spatial structure and macrocyclic cavity. A similar tubular structure is retained in the supramolecular packaging of pillar[5]arene crystals, forming pores. In this study, we developed a block synthetic approach for the preparation of bis-pillar[5]arene containing amide groups. The ability of the synthesized bis-pillar[5]arene to form stable self-associates in solvents of different polarity (CHCl_3 and CH_3OH) was demonstrated by the DLS method. In trichloromethane at concentration of $1 \cdot 10^{-3}$ M, monodisperse associates with average hydrodynamic diameter of 227 nm (PDI = 0.28) are formed; in methanol, stable associates ($1 \cdot 10^{-6}$ M) have an average hydrodynamic diameter of 136 nm (PDI = 0.21). The results obtained can be used to create new supramolecular systems, molecular machines, or capture and detect various organic molecules.

Key findings

- A one-pot synthesis of bis-pillar[5]arene was carried out.
- The spatial structure of the synthesized bis-pillar[5]arene was confirmed by 2D NOESY NMR spectroscopy data.
- In methanol, bis-pillar[5]arene (at $1 \cdot 10^{-6}$ M) formed stable nanostructured associates with an average hydrodynamic diameter of 136 nm.

Keywords

pillar[n]arene
self-assembly
paracyclophanes
bis-pillar[5]arene
amide fragments

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1. Introduction

Supramolecular self-assembly of macrocyclic compounds is one of the most productive tools of supramolecular chemistry [1] for the targeted formation of nanosized catalytic systems [2], smart materials [3], polymers [4], etc. Highly efficient and highly organized natural supramolecular systems, such as chlorophyll, serve as a source of inspiration for the modern researchers. The amazing diversity of nature's molecular building blocks capable of controlled self-assembly promotes spontaneous non-covalent self-organization into higher-order supramolecular architectures with unique properties. Usually the basis of nature-like artificial supramolecular systems are spatially preorganized macrocyclic or rigid framework heterocyclic compounds [5].

Of the special interest to researchers involved in the creation of supramolecular systems is a relatively young class of macrocyclic compounds, first presented in 2008 [6] – pillar[n]arenes. Pillararenes, like well-known classes of macrocyclic compounds such as crown ethers, cyclodextrins, calixarenes, etc., tend to form host-guest complexes [7–9]. Along with this, they have a number of attractive characteristics, such as synthetic availability, a tubular spatial structure that forms an electron-donating cavity, and, as a consequence, the ability to pass extended acyclic fragments of “guests” through the macrocyclic ring [10]. Recent studies show that such tubular porosity is retained in the packing of pillar[5]arene crystals formed during supramolecular self-assembly [11]. Such supramolecular structures can be used to separate complex mixtures of isomers of organic

molecules [12]. However, such a tubular structural motif is practically impossible to preserve in solution. As a rule, pillar[5]arenes described in the literature are solvated individual molecules in solutions [13]. The answer to this problem may be the creation of multimacrocytic systems capable of self-assembly in organic solvents.

Thus, here we present the concept of creating bis-pillar[5]arene containing tertiary amide fragments in their structure, capable of supramolecular self-assembly in organic solvents.

2. Materials and methods

^1H , ^{13}C , and 2D NOESY NMR spectra were obtained on a Bruker Avance-400 spectrometer ($^{13}\text{C}\{^1\text{H}\}$ – 100 MHz and ^1H – 400 MHz). Chemical shifts were determined against the signals of residual protons of deuterated solvent (CDCl_3 , $(\text{CD}_3)_2\text{SO}$). The concentration of sample solutions was 3–5%. Attenuated total internal reflectance IR spectra were recorded with a Spectrum 400 (Perkin Elmer) Fourier spectrometer. The IR spectra from 4000 to 400 cm^{-1} were considered in this analysis. The spectra were measured with 1 cm^{-1} resolution and 64 scans co-addition. Elemental analysis was performed with a Perkin Elmer 2400 Series II instrument.

MALDI spectra were recorded on an Ultraflex III mass spectrometer. *p*-Nitroaniline was used as a matrix. The melting points of the substances were determined on a Boettius heating table. The purity of the compounds was monitored by boiling and melting points, as well as by ^1H NMR spectra. Additional control of the purity of compounds and monitoring of the reaction were carried out by thin-layer chromatography using Silica G, 200 μm plates, UV 254.

4-(Hydroxycarbonylmethoxy)-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (**1**) was synthesized according to the literature method [14]. Mp = 117–119 °C (122 °C [14]). ^1H NMR (CDCl_3 , δ , ppm, J/Hz): 3.51–3.71 (*m*, 27H, $-\text{O}-\text{CH}_3$), 3.75–3.82 (*m*, 10H, $-\text{CH}_2-$), 4.31 (*s*, 2H, $-\text{O}-\text{CH}_2-\text{C}(\text{O})-$), 6.52–6.83 (*m*, 10H, Ar-H). Mass spectrum (MALDI-TOF): calculated $[\text{M}^+]$ m/z = 794.3, found $[\text{M}+\text{Na}]^+$ m/z = 816.9, $[\text{M}+\text{K}]^+$ m/z = 832.9.

2.1. Method for the synthesis of 1,1'-(piperazine-1,4-diyl)bis[4-(carbonylmethoxy)-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene] (**3**)

Monoacid **1** (0.50 g, 0.63 mmol) was placed in a round-bottom flask equipped with a magnetic stirrer and a reflux condenser with a calcium chloride tube; then 10 ml of trichloromethane was added. The reaction mass was cooled to -5 °C, and 5 ml of thionyl chloride (16.8 mmol) was added. The resulting mixture was stirred at -5 °C for 1 h, then refluxed for 1.5 h. After this, the solvent and excess thionyl chloride were removed under reduced pressure, and the residue was dried for two hours under reduced pressure. The resulting dry residue was dissolved in dichloromethane (10 ml). Then

the resulting solution was added over 20 minutes to a mixture of 0.03 g of piperazine (0.31 mmol) and 1 ml of triethylamine (7.2 mmol) in 20 ml of dichloromethane. The mixture was stirred at room temperature under argon atmosphere for 24 h. Then the reaction mixture was washed with 2 M hydrochloric acid solution (2×30 ml) and distilled water (2×30 ml). The organic phase was separated, dried over 3 Å molecular sieves, then the solvent was removed under reduced pressure, and the residue was recrystallized from 2-propanol. The residue obtained was dried under reduced pressure over phosphorus pentoxide.

Yield: 0.21 g (40%), colorless crystals. Mp = 168–170 °C. ^1H NMR ($(\text{CD}_3)_2\text{SO}$, δ , ppm, J/Hz): 3.40–3.80 (*m*, 74H, $-\text{O}-\text{CH}_3$, $-\text{CH}_2-$), 4.15 (*m*, 4H, $-\text{N}(\text{CH}_2\text{CH}_2)_2\text{N}-$), 4.26 (*m*, 4H, $-\text{N}(\text{CH}_2\text{CH}_2)_2\text{N}-$), 4.38 (*s*, 4H, $-\text{O}-\text{CH}_2-\text{C}(\text{O})-$), 6.65–7.18 (*m*, 20H, Ar-H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, δ , ppm): 29.48, 29.53, 29.96, 30.28, 49.38, 49.90, 55.92, 55.99, 56.24, 56.34, 56.41, 56.48, 56.53, 56.63, 65.2, 113.96, 114.05, 114.11, 114.21, 114.36, 114.42, 127.82, 127.53, 128.79, 128.82, 128.91, 128.97, 129.04, 150.22, 150.27, 150.35, 150.41, 150.46, 150.52, 150.61, 166.74. FTIR (v/cm^{-1}): 3017 ($-\text{C}_{\text{Ph}}-\text{H}$), 2933 ($-\text{CH}_2-$), 1656 ($\text{C}(\text{O})\text{N}=\text{}$), 1215 ($\text{C}_{\text{Ph}}-\text{O}-\text{CH}_2-$). Mass spectrum (MALDI-TOF): calculated $[\text{M}^+]$ m/z = 1639.7, found $[\text{M}^+]$ m/z = 1639.5. Elemental analysis. Found (%): C, 70.27; H, 6.47; N, 1.72. $\text{C}_{96}\text{H}_{106}\text{N}_2\text{O}_{22}$. Calculated, %: C, 70.31; H, 6.52; N, 1.71.

2.2. Determination of hydrodynamic particle size by dynamic light scattering (DLS)

The particle sizes and zeta potentials were determined by a Zetasizer Nano ZS at 20 °C. The instrument contains a 4 mW He-Ne laser operating at a wave length of 633 nm and incorporated noninvasive backscatter optics (NIBS). The measurements were performed at the detection angle of 173° and the software automatically determined the measurement position within the quartz cuvette. Chemically pure organic solvents CHCl_3 , DMSO, CH_3OH were used to prepare the solutions. During the experiment, the solutions of pillar[5]arene **3** ($1 \cdot 10^{-3}$ – $1 \cdot 10^{-6}$ M) were kept for 1 h, and then the sizes of the resulting particles were measured. Electrophoretic mobility of different samples was determined using a folded capillary cuvette (Folded Capillary Cell DTS1060, Malvern, U.K.). The experiments were carried out for each solution in triplicate. The results were processed by the DTS program (Dispersion Technology Software 4.20).

3. Results and Discussion

It is known that pillar[5]arenes are capable of forming tubular structures in aggregates or at the phase interface due to supramolecular packaging [11, 12]. It is also known that regioselective functionalization of pillar[5]arenes leads to the formation of supramolecular polymers in solutions and at the interface [15]. All these processes of supramolecular

self-assembly are happening either at high concentrations or in a crystalline structure.

Preserving the tubular pores of nanoaggregates during their supramolecular self-assembly in solution at low concentrations is of interest. Such nanostructured systems can find application as potential adsorbents and nanocatalysts.

Thus, we hypothesized that covalently cross-linked bis-pillar[5]arenes containing amide fragments will promote association processes and the preservation of the tubular supramolecular structure of associates in solution.

The development of approaches to the synthesis of poly-macrocyclic structures containing pillar[5]arene fragments is a complex task, completing which will make it possible to obtain multifunctional nanosized polycyclophanes capable of molecular recognition of various organic and inorganic compounds [16]. Monosubstituted pillar[5]arenes, in addition to their unique spatial structure that allows the formation of supramolecular self-associates, are interesting as precursors for the synthesis of bi- and polymacrocyclic compounds. Despite this, there are practically no data in the literature on the synthesis of multi-pillar[5]arene systems containing amide groups [16].

We chose the block synthesis of multi-pillar[5]arenes as a synthetic approach to obtain such structures. It consisted in combining monosubstituted macrocycles into a single bimacrocyclic system. In this case, there was an interaction between the anchor functions of the linker fragment and the terminal macrocycles. Pillar[5]arene **1** containing a carboxyl group and its corresponding acid chloride **2** were chosen as anchor fragments of terminal macrocycles. As a linker fragment of multi-pillar[5]arenes, we chose piperazine, which is widely used for the preparation of hyper-branched compounds [17] and also has amino groups convenient for functionalization.

To implement the block approach in the synthesis of the target bis-pillar[5]arene containing amide groups, the acylation of piperazine with pillar[5]arene acid chloride **2** in dichloromethane was studied (Scheme 1). Triethylamine was used as a base that binds hydrogen chloride released during the synthesis. The synthesis was carried out within 24 h, the progress of the reaction was monitored by thin layer chromatography. The target bis-pillar[5]arene **3** was isolated by recrystallization from 2-propanol. The relatively low yield of target compound **3** is due to the formation of a mono-substitution by-product observed in the mass

spectrum of the reaction mixture. Varying the reaction conditions (time, temperature, catalysts) did not allow increasing the yield of the product.

Figure 1 shows the MALDI mass spectrum and the ^1H NMR spectrum of bis-pillar[5]arene **3**, in which the protons of methoxy groups and methylene bridges resonate in the form of a multiplet in the region δ 3.4–3.8 ppm. The signals of the piperazine fragment are two multiplets in the region of δ 3.8–3.9 and δ 4.0–4.3 ppm. Signals of oxymethylene protons are observed in the form of singlets at δ 4.4 ppm. The mass spectrum shows the peak at 1639.5 m/z , corresponding to the peak of the molecular ion of bis-pillar[5]arene **3**.

The structure of synthesized macrocycle **3** was confirmed by ^1H , ^{13}C NMR, IR spectroscopy and MALDI mass spectrometry, and the composition was determined using elemental analysis.

The spatial structure of bis-pillar[5]arene **3** was additionally established by 2D NMR ^1H - ^1H NOESY spectroscopy (Figure 2).

The presence of cross-peaks of the nuclear Overhauser effect between the protons of the piperazine and aryl fragments, between the protons of the piperazine and oxymethylene fragments, as well as between the protons of the aryl fragments of macrocyclic units clearly indicates a spatially close arrangement of macrocyclic fragments relative to each other. This fact confirms the expected tubular shape of bis-pillar[5]arene **3**.

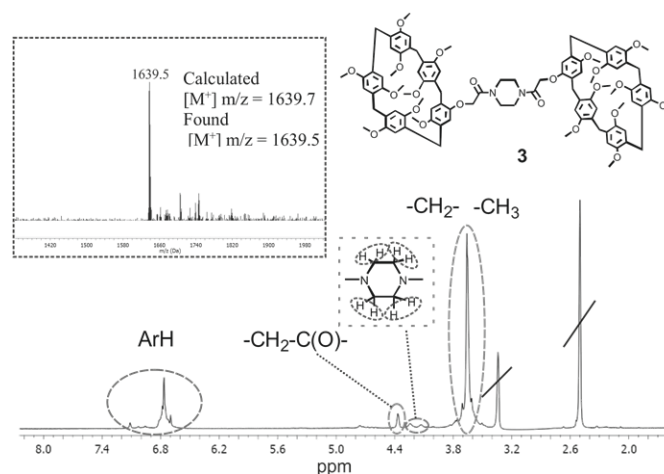
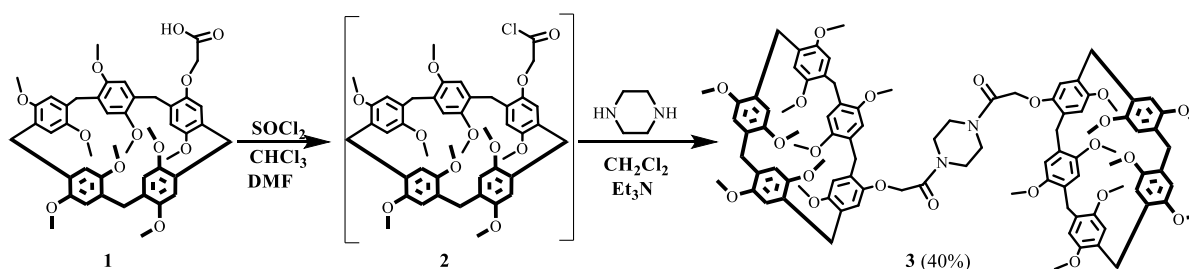


Figure 1 ^1H NMR spectrum of compound **3** ($(\text{CD}_3)_2\text{SO}$, 25 °C, 400 MHz) (the inset shows the MALDI mass spectrum of bis-pillar[5]arene **3**).



Scheme 1 Synthesis of target pillar[5]arene **3**.

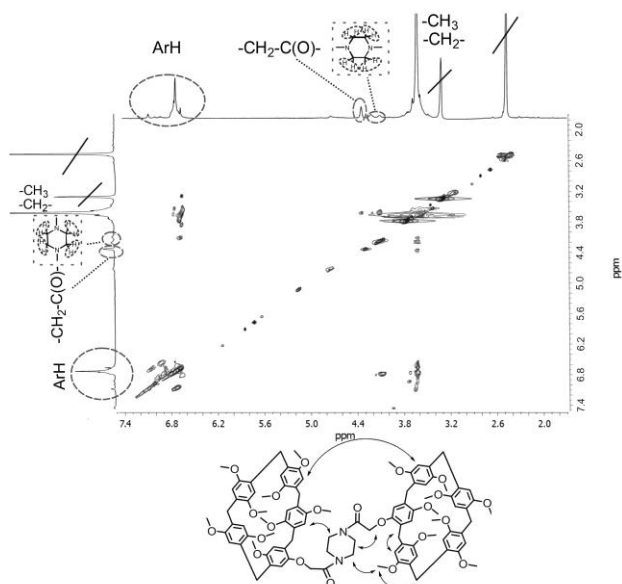


Figure 2 2D ^1H - ^1H NOESY NMR spectrum of compound **3** ($(\text{CD}_3)_2\text{SO}$, 25 $^\circ\text{C}$, 400 MHz).

The presence of amide fragments in the structure of the macrocycle, as a rule, promotes the emergence of self-association processes [18]. It should be noted that in the case of the formation of associates by bis-pillar[5]arene **3**, the tubular shape of the formed pores is obviously retained.

The self-association of bis-pillar[5]arene **3** was studied in trichloromethane and methanol using the dynamic light scattering method (DLS). It was found that bis-pillar[5]arene **3** forms aggregates (Figure 3) in the studied concentration range ($1 \cdot 10^{-3}$ – $1 \cdot 10^{-6}$ M). Thus, at concentration of $1 \cdot 10^{-3}$ M in trichloromethane (Figure 3a), monodisperse associates are formed with average hydrodynamic diameter of 227 nm and polydispersity index (PDI) 0.28. In methanol, a monomodal distribution of associates **3** is observed at a concentration of $1 \cdot 10^{-6}$ M (Figure 3b). The average hydrodynamic diameter was 136 nm (PDI = 0.21). It should be noted that in both cases there is a symbate increase in the hydrodynamic diameter of the particles with increasing concentration of macrocycle **3** (ESI). In this case, in trichloromethane at concentration of $1 \cdot 10^{-3}$ M stable associates with a ζ -potential of 18 mV are formed, and in methanol associates **3** are more stable at a concentration of $1 \cdot 10^{-6}$ M with a ζ -potential of 21 mV. By analogy with the literature data [18], it can be assumed that the increase in the size of aggregates with growth concentration of bis-pillar[5]arene **3** in trichloromethane is associated with the formation of a looser, porous, polymer-like structure.

In methanol, denser and stable nanoassociates **3** are formed at a lower concentration, which is due to the higher polarity of methanol ($\epsilon = 32.63$ [19]) compared to trichloromethane ($\epsilon = 4.64$ [19]) with more pronounced hydrophobic effect of the solvent, leading to the formation of macrocycle nanoparticles [20]. It is known from the literature data [21, 22] that pillar[5]arenes do not form associates in DMSO due to strong solvation of macrocycles.

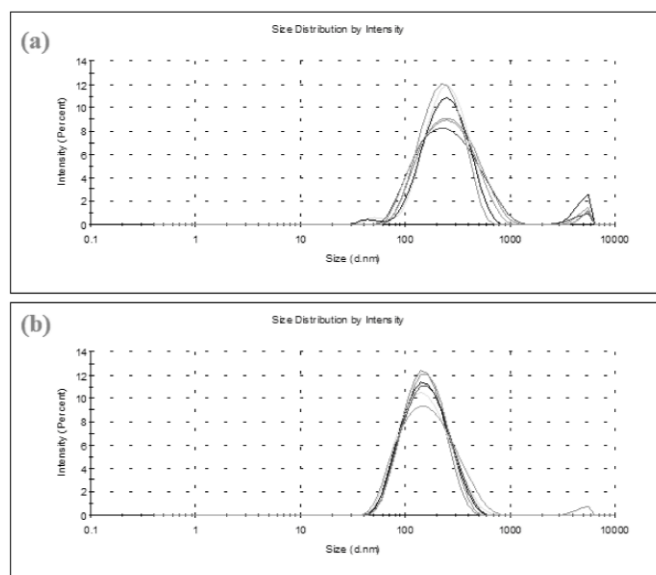


Figure 3 Size distribution of the particles by intensity for bis-pillar[5]arene **3**: in trichloromethane ($1 \cdot 10^{-3}$ M) (a), in methanol ($1 \cdot 10^{-6}$ M) (b).

In this regard, the self-association of bis-pillar[5]arene **3** in aprotic DMSO ($\epsilon = 45$ [19]) was additionally studied, and it was shown that no stable self-associates of macrocycle **3** are formed in the entire studied concentration range.

Thus, a block approach to the synthesis of bis-pillar[5]arene **3**, which contains amide groups and is capable of save a tubular pore shape in protic solvents, was developed. Such nanosized structures containing several fragments of pillar[5]arenes can find application in the creation of materials capable of molecular recognition of target substrates.

4. Limitations

In this study, we developed a block synthetic approach for the preparation of bis-pillar[5]arene containing amide groups. We chose piperazine as a linker fragment of bis-pillar[5]arene. The low yield of target product **3** requires further study of approaches to the synthesis. The optimization of the suggested approach will make it possible to further develop a method for the preparation of multi-pillar[5]arenes containing more than two macrocyclic fragments.

5. Conclusions

Thus, a block synthetic approach to the preparation of bis-pillar[5]arene **3** containing amide groups was developed. The structure of all obtained compounds was confirmed by physicochemical methods, i.e., IR, NMR spectroscopy, and mass spectrometry, and the composition was confirmed by elemental analysis. The spatial structure of the synthesized bis-pillar[5]arene **3** was confirmed by 2D ^1H - ^1H NOESY NMR spectroscopy data. The ability of the synthesized bis-pillar[5]arene **3** to form stable self-associates in solvents of different polarity (CHCl_3 and CH_3OH) was demonstrated by the DLS method. In trichloromethane at a concentration of

$1 \cdot 10^{-3}$ M, monodisperse associates with average hydrodynamic diameter of 227 nm (PDI = 0.28) are formed; in methanol, stable associates of compound **3** ($1 \cdot 10^{-6}$ M) have an average hydrodynamic diameter of 136 nm (PDI = 0.21). So, more stable nanostructured associates are formed in methanol, which can be used to create new supramolecular systems, molecular machines, or capture and detect various organic molecules.

• Supplementary materials

This manuscript contains supplementary materials, which are available on the corresponding online page.

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• Conflict of interest

The authors declare no conflict of interest.

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