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Communication

Synthesis and characterization of bis-[1]rotaxanes *via* salen-bridged bis-pillar[5]arenes

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The series of salen-bridged bis-pillar[1]arenes were conveniently prepared by condensation reaction of 5,5′-methylenebis(2-hydroxybenzaldehyde) or 5,5′-(propane-2,2-diyl)bis(2-hydroxybenzaldehyde) with mono-amido-functionalized pillar[5]arenes containing different terminal aminoalkyl groups in refluxing ethanol. The ^{1}H NMR and 2D-NOESY spectra indicated that the salen-bridged bis-pillar[5]arenes with longer alkylene linker (n = 3, 4, 6) formed the fascinating bis-[1]rotaxanes, while the salen-bridged bis-pillar[5]arenes with short hydrazine and ethylenediamino linker (n = 0, 2) predominately existed in free form. The single crystal structure of the bis-pillar[5]arene ambiguously indicated that two propylenediamino linker inserted in to two cavities of pillar[5]arene to form a novel bis-[1]rotaxanes.

In recent years, pillararenes have become the most attractive supramolecular hosts after crown ethers, cyclodextrins, calixarenes, and cucurbiturils [1,2]. Pillararene have a longer unique tubular cavity with the substituents on ring point to two opposite directions [3,4]. The unique tubular structure of pillararene has been demonstrated to be novel useful supramolecular hosts and applied in the construction of new supramolecular polymers, molecular devices, artificial transmembrane channels, as well as chemical and physical responsive materials [5–9]. Therefore, the most easily prepared pillar[5]arene has been widely used as wheel component in constructing interlocked assemblies including various pillararene-based pseudorotaxanes with diverse functions [10–17]. In this respect, the mono-functionalized pillar[5]arenes showed to be the one of the most versatile candidates for assembly of pseudo[1]rotaxanes and pseudo[1]rotaxanes [18–23]. For this purpose, various longer chain axels and larger functionalized stoppers have been introduced into pillar[5]arenes [24–29]. Our group also prepared various functionalized mono-functionalized pillar[5]arene Schiff base, thiourea, pyridylimine and polyamide derivatives and found that these functionalized pillar[5]arene derivatives with longer side chains tending to form stable pesudo[1]rotaxane and [1]rotaxane both in solution and in solid state [30–36]. In order to further exploit the potential applications of functionalized pillar[5]arene on the construction of [1]rotaxanes and catananes, we initialized the project on assembly of functionalized bis-[1]rotaxanes and tris-[1]rotaxanes. We have successfully developed efficient synthetic protocols for construction of unique bis-[1]rotaxanes by employing dithiourea or diamide as the bridging linker [37,38]. Very recently, Wang and Meguellati also synthesized self-included pillar[5]arene-based bis-[1]rotaxanes by using longer alkylene bis-triazole bridge [39]. Herein, we wish to report the convenient synthesis of salen-bridged bispillar[5]arene derivatives by the condensation reaction of mono-amido-functionalized pillar[5]arenes with 5,5′-methylenebis(2-hydroxybenzaldehyde) or 5,5′-(propane-2,2-diyl)bis(2-hydroxybenzaldehyde) and construction of the fascinating bis[1]rotaxanes.

The synthetic route for the desired salen-bridged bis-pillar[5]arenes was illustrated in Scheme 1. The amido-functionalized pillar[5]arenes $\mathbf{2^n}$ (n = 0, 2, 3, 4, 6) were prepared from ammonolysis reaction of ethyl pillar[5]arene-oxyacetate with diaminoalkanes according to our previously reported synthetic method [30]. The condensation of 5,5′-methylenebis(2-hydroxybenzaldehyde) **1** and amido-functionalized pillar[5]arenes $\mathbf{2^n}$ (n = 0, 2, 3, 4, 6) was carried out in refluxing ethanol for 12 h. The desired salen-bridged bis-pillar[5]arenes $\mathbf{3^n a}$ (n = 0, 2, 3, 4, 6; R = H) were easily obtained in moderate yields (Scheme 1). Under same reaction conditions, when 5,5′-(propane-2,2-diyl)bis(2-hydroxybenzaldehyde) was used in the reaction, the corresponding salen-bridged bis-pillar[5]arenes $\mathbf{3^n b}$ (n = 0, 2, 3, 4, 6; R = CH_3) were also prepared in moderate yields. The structures of the obtained ten salen-bridged bis-pillar[5]arenes $\mathbf{3^n a}$-$\mathbf{3^n b}$ were fully characterized by IR, HRMS, ^{1}H and ^{13}C NMR spectroscopes.

^{1}H NMR spectra is the convenient evidence for elucidation the chemical structures for the interlocked molecules. ^{1}H NMR spectra of the bis-pillar[5]arenes $\mathbf{3^0 a}$ and $\mathbf{3^2 a}$ showed that there are no

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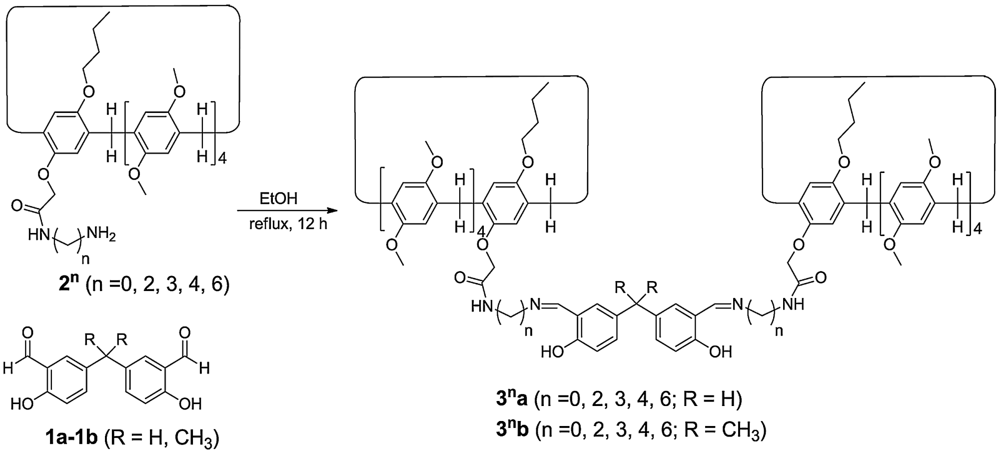
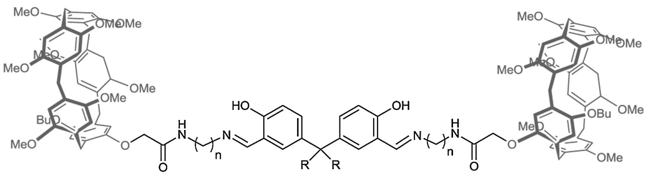
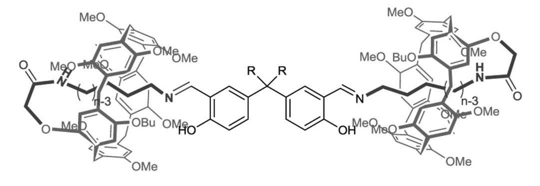


Scheme 1. Synthesis of salen-bridged bis-pillar[5]arenes 3^na-3^nb.

signals at very high magnetic field (Fig. 1), which suggested that the bridged hydrazinyl and ethylenediamino chain did not insert in the cavity of two pillar[5]arene. Therefore, the two scaffolds of pillar[5]arenes were connected by the shorter bridged diimido chain from outside bis-pillar[5]arenes $\mathbf{3^0a}$ and $\mathbf{3^2a}$ (Scheme 2). ^{1}H NMR spectra of bis-pillar[5]arene $\mathbf{3^3a}$ clearly showed one broad peak at -0.10 ppm and two mixed peaks at (-1.69) – (-1.87) ppm. The characteristic signals of bridged Schiff base were stilly observed in normal magnetic field, which strongly indicated the two propylenediamino linker threading into the cavity of the pillar [5]arene to form the novel bis-[1]rotaxanes (Scheme 2). The ^{1}H NMR spectra of bis-pillar[5]arene $\mathbf{3^4a}$ also displayed a mixed peak at 0.52–0.44 ppm, a broad peak at -0.97 ppm and a mixed peak at (-1.86) – (-1.93) ppm. Similarly, the ^{1}H NMR spectra of the bis-pillar[5]arene $\mathbf{3^6a}$ displayed four peaks at 0.04 ppm, (-0.79) – (-0.87) ppm, -1.80 ppm and -2.30 ppm, respectively. Therefore, the butylenediamino and hexylenediamino linker actually existed in the cavity of pillar[5]arene to form the bis-[1]rotaxanes. The ^{1}H NMR spectra of the bis-pillar[5]arenes $\mathbf{3^nb}$ (n = 0, 2, 3, 4, 6) also showed similar absorption patterns. That is, there are no signals at high magnetic field in the compounds $\mathbf{3^0b}$ and $\mathbf{3^2b}$, while several signals at high magnetic field were observed in compounds $\mathbf{3^3b}$-$\mathbf{3^6b}$ with propylenediamino, butylenediamino and hexylenediamino linkers. It should be pointed out that the salen scaffold could not inserted into the cavity of the pillar[5]arene due to its larger volume of the disubstituted benzenes. On the basis of these results, we could get a conclusion that bis-pillar[5]arenes with short hydrazine and ethylenediamino linkers exist in the free form due to stronger repulsion of two molecular pillar[5]arene, and bis-pillar[5]arenes with longer alkylenediamino linkers predominately form the unique bis-[1]rotaxanes (Scheme 2). It should be pointed out that this conclusion is agreed with our previously prepared pillar[5]arene mono-Schiff bases, in which longer than propylenediamino linker could form [1]rotaxanes [30].



Free form: 3^na, 3^nb (n = 0, 2; R = H, CH$_3$)



bis-[1]rotaxane: 3^na, 3^nb (n = 3, 4, 6; R = H, CH$_3$)

Scheme 2. Formation of free form and bis-[1]rotaxanes.

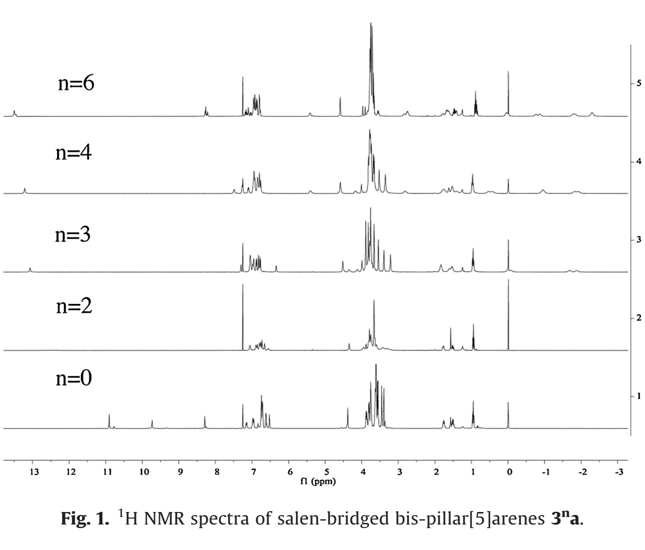


Fig. 1. ^{1}H NMR spectra of salen-bridged bis-pillar[5]arenes $\mathbf{3^na}$.

In order to confirm the formation of unique bis-[1]rotaxanes, NOESY spectra of the compounds $\mathbf{3^4a}$ (Fig. 2), $\mathbf{3^6a}$ (Fig. 3), $\mathbf{3^4b}$ and $\mathbf{3^6b}$ (Figs. S1 and S2 in Supporting information) were recorded. From the Fig. 2, the correlations between the protons of Ha$_4$, Hb$_4$, Hc$_4$ in bridged butylene group to the protons of Hd$_4$, He$_4$, Hf$_4$, Hg$_4$ in methoxy and phenyl group were clearly observed. In the Fig. 3, The protons of Ha$_3$, Hb$_3$, Hc$_3$, Hd$_3$ in hexylene group were similarly correlated with protons He$_3$, Hf$_3$, Hg$_3$, Hh$_3$ in ring of pillar[5]arene. The similar correlation pattern were also observed in the NOESY spectra of $\mathbf{3^4b}$ and $\mathbf{3^6b}$ (Figs. S1 and S2). These results unambiguously indicated that the bis-[1]rotaxanes were formed in these salen-bridged bis-pillar[5]arenes. It has been known that the ω-aminoalkylamido chain was inserted into the cavity to form a pseudo[1]rotaxanes in starting amido-functionalized pillar[5] arenes $\mathbf{2^n}$ (n = 2, 3, 4, 6). In the formation of salen-bridged bis-pillararenes, the shorter ethylenediamino chain was forced to thread out of the cavity because the repulsion of two scaffolds of pillar[5]arenes. The longer than propylenediamino chains retained in the cavity of form the bis-[1]rotaxanes. Therefore, the length of the alkyleneadiamino chains controlled the formation of bis-[1]rotaxanes.

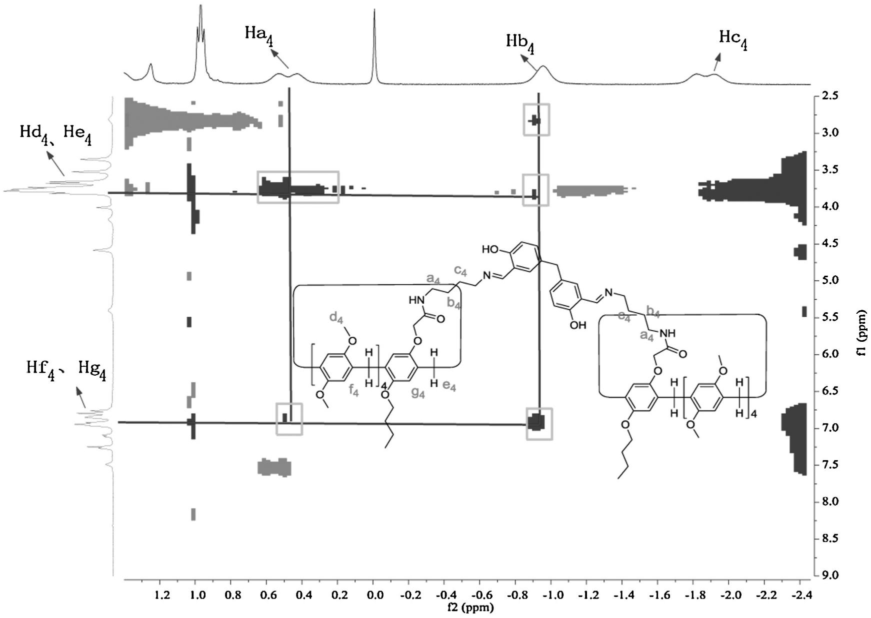


Fig. 2. The NOESY spectra of the compound **3^4a**.

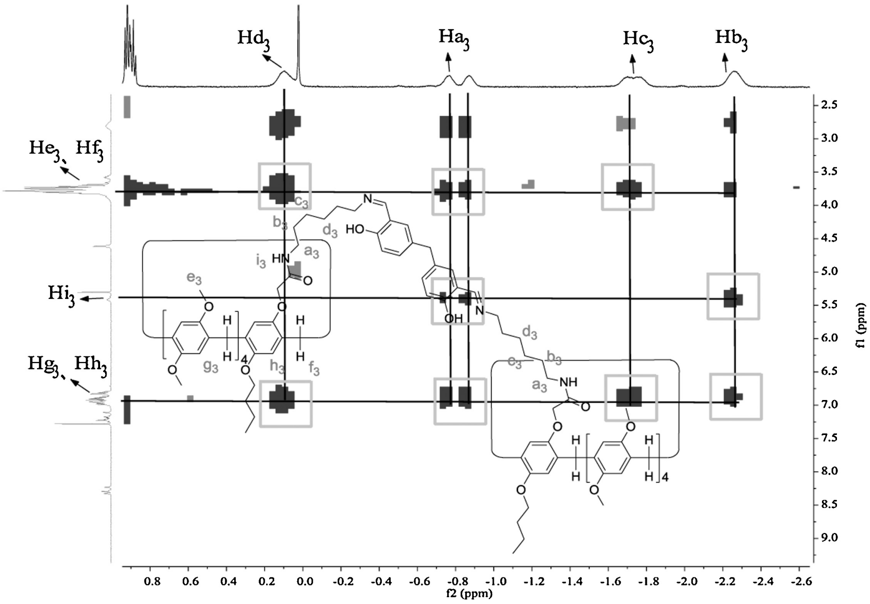


Fig. 3. The NOESY spectra of the compound **3^6a**.

The single crystal structure of the compound **3^3b** was successfully determined by X-ray diffraction method (Fig. 4). Single crystal data for compounds **3^3b** (CCDC 1940468) has been deposited at the Cambridge Crystallographic Data Center. The suitable single crystal of the compound **3^3b** was obtained from the slow crystallization of the compound **3^3b** in a mixture of chloroform and ethanol for more than one week. From the Fig. 4, it can be seen that the two propylenediamino units actually threaded into both cavities of the two pillar[5]arenes and were connected by the salen-bridge. Thus, the unique bis-[1]rotaxanes were really formed. It is also seen that the middle bis-phenol bridge exist in jagged arrangement, which made two scaffolds of pillar[5]arenes in very close manner. Therefore, the

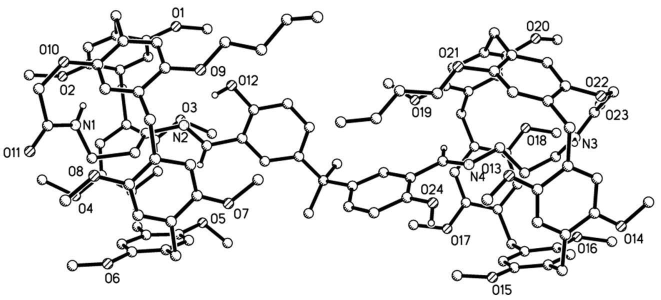


Fig. 4. Single crystal structure of the bis-pillar[2]arene **3^3b**.

propylenediamino units is obviously the most short linker for the formation of bis-[1]rotaxanes.

In summary, we have successfully synthesized series of salen-bridged bis-pillar[1]arenes by condensation reaction of 5,5′-methylenebis(2-hydroxybenzaldehyde) or 5,5′-(propane-2,2-diyl) bis(2-hydroxybenzaldehyde) with mono-amido-functionalized pillar[5]arenes containing different terminal aminoalkyl groups. The analysis of ^{1}H NMR, 2D-NOESY spectra and determination of single crystal structure clearly indicated that the salen-bridged bis-pillar[5]arenes with longer alkylene linker (n = 3, 4, 6) formed the fascinating bis-[1]rotaxanes, while the salen-bridged bispillar[5]arenes with short hydrazine and ethylenediamino linker (n = 0, 2) predominately existed in free form. Therefore, the present work not only provided new novel bis-[1]rotaxane systems based on excellent performance of pillar[5]arenes, but also gave efficient methodology for construction more complicated supramolecular architectures.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2019.09.014.

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