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Synthesis of dibenzo-[*b*,*f*][1,5]diazocine-based hosts and their assembly behaviors with C_{60}

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ABSTRACT

Diaryl[*b*,*f*][1,5]diazocine-based macrocycles **5** and **6** with inner cavities have been synthesized via Hay coupling method. Single crystal of **5** shows that it forms a dimeric aggregate via the weak intermolecular interactions between two adjacent rings, which is rarely reported in such macrocycles. Moreover, SEM results reveal that both macrocycles **5** and **6** assemble with C_{60} to form well-ordered fullerene-based nano-rod structures.

Introduction

The design and synthesis of new macrocyclic hosts with inner cavities large enough to assemble with organic guests is always an interesting and exciting research topic in supramolecular chemistry.[1] With the development of various known classes of macrocyclic molecules,[2] hexa-2,4-diyne bridged macrocyclic hosts have attracted great interest since 1980s. Whitlock and his coworkers[3] first designed and synthesized a hexa-2,4-diyne bridged cyclophane **1** (Fig. 1), which is water-soluble, and could form a classical open-faced stacking complex with 2-naphthylmethyltriethylammonium chloride. Breslow' group[4] further developed a three-dimensional hexa-2,4-diyne bridged molecular cage **2** (Fig. 1). In cage **2**, two 1,1,1-tri-phenylethane units were joined together by three diacetylene linkages. Cage **2** could self-adjust its conformation to complex with three benzene molecules. When tri-phenylethane units were replaced by tri-phenyl phosphine oxide units, a new tree-dimensional molecular cage **3** (Fig. 1) was formed.[5] Cage **3** and *p*-nitrophenol could form a complex with the intracavity phosphine oxide as a locus of complexation. Based on the above results, Vögtle' group[6] reported a series of hexa-2,4-diyne bridged concave macrocyclic hosts, and studied their absorption spectra, luminescence properties, and endocavital complexation of small neutral organic guests. More recently, Lauher' group[7] prepared

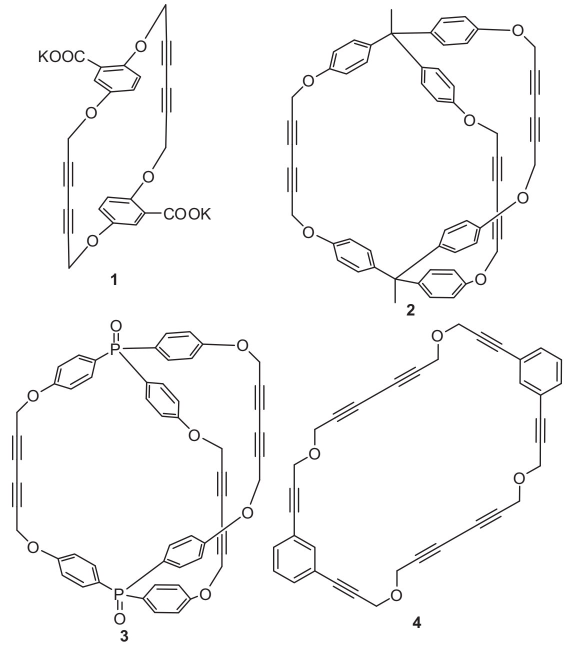

Figure 1. Structures of hexa-2,4-diyne bridged macrocyclic hosts **1**–**4**.

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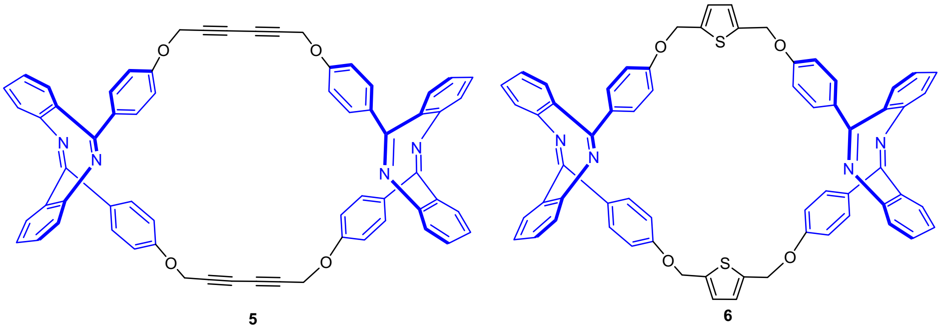
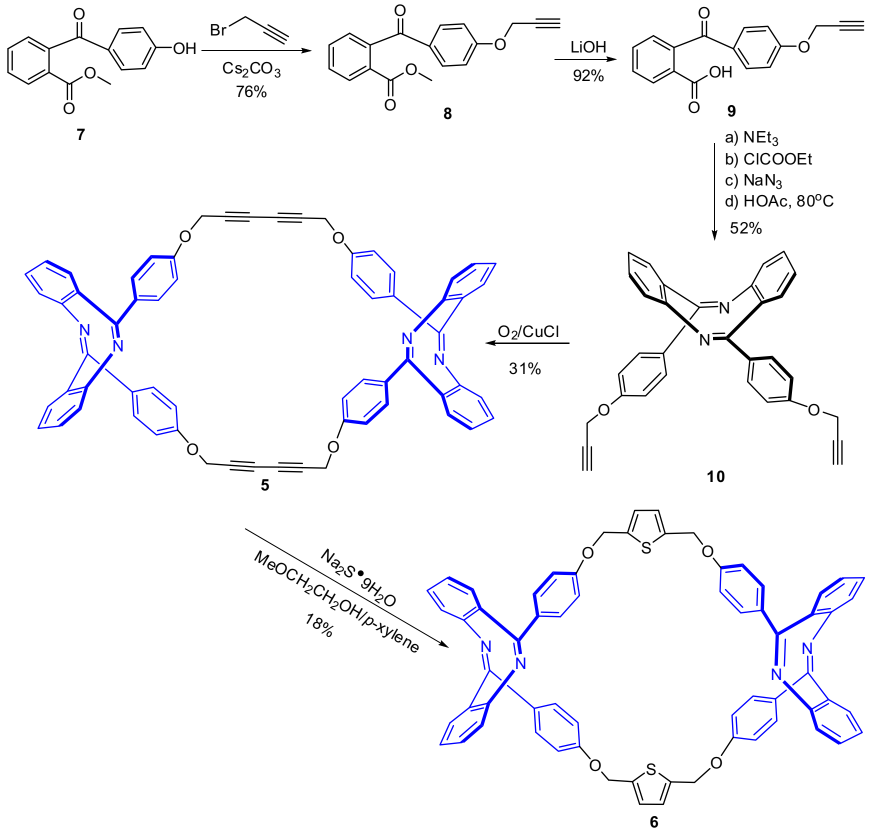


Figure 2. Structures of diaryl[*b*,*f*][1,5]diazocine-based macrocycles **5** and **6**.

another polyether macrocycle **4** with two parallel diacetylene functionalities. This macrocycle could form a stacked column. After slow annealing of a single crystal of **4**, a single-crystal-to-single-crystal polymerization could happen and result in a tubular addition polymer. However, to our knowledge, the synthesis and characterization of hexa-2,4-diyne bridged macrocyclic hosts with larger inner cavities to include bulky guests, such as C_{60}, were rarely reported.[8]

Host molecules which could recognize fullerenes have been intensively investigated in recent years for their roles as separators of specific fullerenes as well as building blocks of well-ordered fullerene-based nanostructures.[9] The design and synthesis of novel macrocycles that could complex with fullerene and its derivatives is still a frontier in this area. Recently, diaryl[*b*,*f*][1,5]diazocine rouses much attention due to its rigid boat conformation which could be switched into planar conformation when being reduced under electrochemical conditions, as reported in the literature.[10] Our group developed a new method for the synthesis of diaryl[*b*,*f*][1,5]diazocine, in which the diazocine synthesis was much faster and more efficient.[11] Diaryl[*b*,*f*][1,5]diazocines might be suitable to construct novel macrocycles due to its rigid boat conformation, which was not reported before. We envisioned that two diazocine units could be joined by two diacetylene linkages to form a new diaryl[*b*,*f*][1,5]diazocine-based macrocycle **5** (Fig. 2), which contained a large inner cavity. Furthermore, inspired by the previous reports,[12] macrocycle **5** could further react with $Na_2S{\cdot}9H_2O$ to afford another new macrocycle **6**. Therefore, herein we report the synthesis of diaryl[*b*,*f*][1,5]diazocine-based hosts **5** and **6** and their assembly behaviors with C_{60}. We found that macrocycle **5** forms a dimeric aggregate via the weak intermolecular interactions between two adjacent rings in single crystal, which is rarely reported in such macrocycles. We also discovered that both macrocycles **5** and **6** could form well-ordered nano-rod structures. To the best of our knowledge, there are no reports on



Scheme 1. Synthetic routes to macrocyclic hosts **5** and **6**.

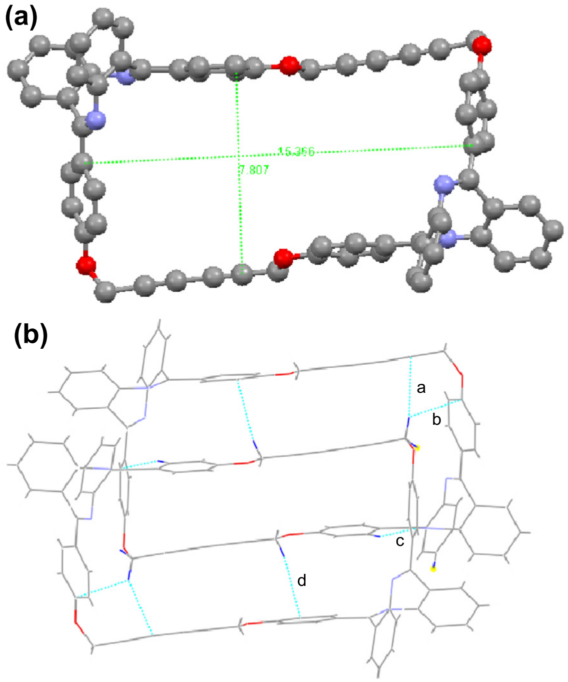


Figure 3. (a) Crystal structure of macrocycle **5** (hydrogen atoms were omitted for clarity), and (b) dimer of **5**.

a macrocycle which could not only self-assemble to form a dimer structure,[13] but also assemble with C_{60} to form a well-ordered nanostructure.

Results and discussion

As shown in Scheme 1, we adopted compound **7** as the starting material for the synthesis, in which the phenol group was used to introduce an progargyl group for future macrocycle formation. Reaction of compound **7** and propargyl bromide afforded compound **8** in 76% yield, which was in turn hydrolyzed to give acid **9** in 92% yield. With acid **9** in hands, we further successfully prepared diaryl[*b*,*f*][1,5]diazocine **10** with two propyne groups in an overall 52% yield using the methodology developed in our laboratory.[11] The dimerization of **10** underwent smoothly to afford macrocyclic **5** in 31% yield using an oxidative coupling method developed by Lauher.[7] Finally, macrocyclic host **6** was obtained in 18% yield as a pale yellow solid by exposing macrocycle **5** to $Na_2S\cdot9H_2O$ in 2-methoxyethanol and *p*-xylene solution. We could not further improve the yield of macrocycle **6**, although various conditions were tried, which may be due to the rigidity of macrocycle **5**. Both hosts **5** and **6** show good solubility in CH_2Cl_2, $CHCl_3$, and toluene. Spectra of ^1H NMR, ^{13}C NMR, and mass spectra confirmed their structures. Especially, ^1H NMR spectra of macrocycle **6** exhibit the proton signals of thiophene units at 6.93 ppm, which suggests the successful conversion of **5** to **6**.

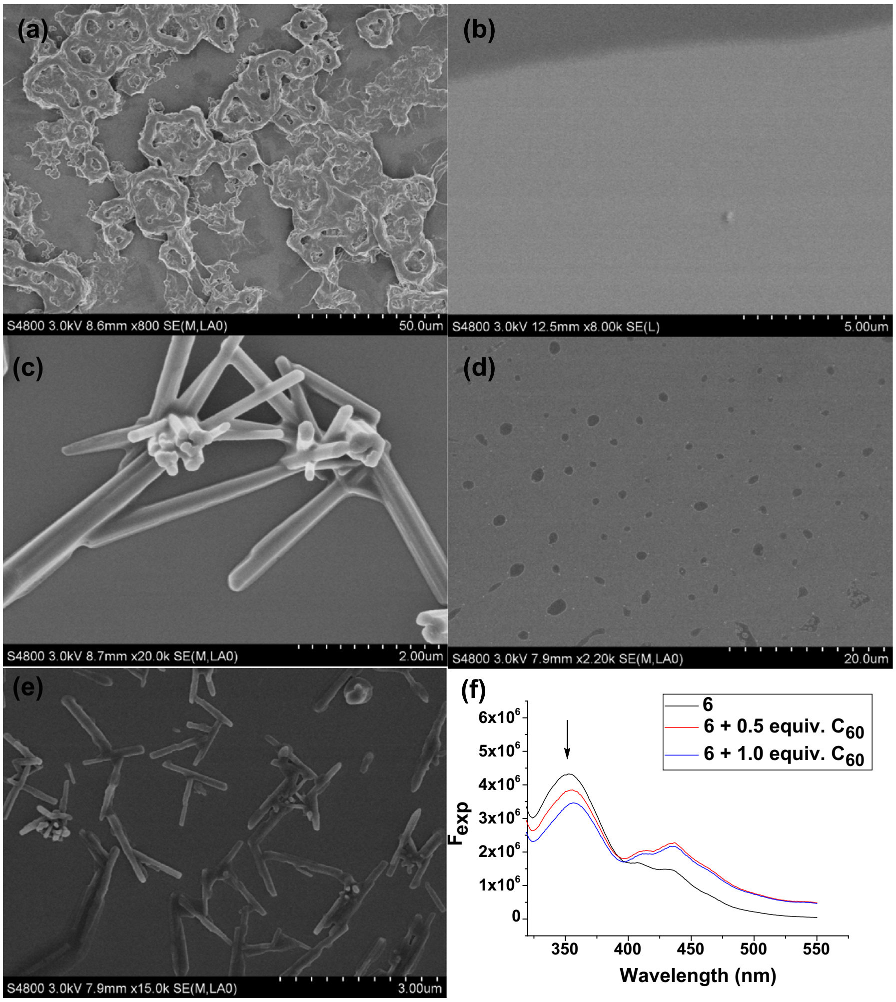


Figure 4. Morphology of C_{60} (2.5×10^{-5} M) (a), **5** (2.5×10^{-5} M) (b), mixture of C_{60} (2.5×10^{-5} M) and **5** (2.5×10^{-5} M) (c), **6** (2.5×10^{-5} M) (d), and mixture of C_{60} (2.5×10^{-5} M) and **6** (2.5×10^{-5} M) (e); the fluorescence spectral changes of **6** (2×10^{-6}M) upon addition of C_{60} ($\lambda_{ex} = 298$ nm) (f).

The single crystal of host **5** obtained from the solution of THF and *n*-hexane provides detailed information of the macrocycle, as shown in Figure 3.[14] The macrocycle nearly adopted a rectangle structure, and contained a cavity of ~15.366 × ~7.907 Å^2 (Fig. 3a). Interestingly, we also found a slipped overlapping of the two adjacent macrocycles, due to the weak noncovalent intermolecular interactions. As shown in Figure 3b, these noncovalent interactions include CH–π interaction (a) with a distance of 2.87 Å between methylene of propyne units and diacetylene units, CH–π interaction (b) with a distance of 2.84 Å between methylene of propyne and one benzene ring of diazocine, π–π interaction (c) with a distance of 3.77 Å between two benzene rings of two adjacent diazocines, and another CH–π interaction (d) with a distance of 2.90 Å between methylene of propyne and one benzene ring of diazocine. This is a new example of dimer based on ring to ring interactions.[12]

We then tried to study the assembly behaviors of hosts **5** and **6** with C_{60}, since the size of the macrocycle falls into a range that could be large enough to host fullerenes. To our surprise, **5** did not show the emission property, which may be due to the formation of dimeric structure resulting in the aggregation-induced quenching effect. Therefore, we could not study the recognition behavior of **5** toward C_{60} via spectrophotometric measurements.[9e] However, scanning electron microscope (SEM) results suggested that macrocycle **5** could assemble with C_{60}. As shown in Figure 4a, the SEM image of C_{60} shows an entangled solid; and that of macrocycle **5** shows the formation a thin film (Fig. 4b). However, when macrocycle **5** (2.5×10^{-5} M) and C_{60} (2.5×10^{-5} M) were mixed together, a nano-rod structure with lengths of several micrometers was observed (Fig. 4c). Some nano-rods even can aggregate to afford bundles. The morphological changes of C_{60} upon addition of macrocycle **5** suggest that macrocycle **5** could assemble with C_{60} to form nano-rods. Similar to macrocycle **5**, SEM image of macrocycle **6** also shows the formation of a thin film (Fig. 4d). Upon the addition of C_{60} to **6**, nano-rod structure with lengths of several micrometers and bundles of nano-rods were also observed (Fig. 4e), suggesting the formation of complex of **6** and C_{60}. The fluorescence spectrum of **6** shows a major emission peak at ~350 nm. When C_{60} was added to the solution of **6**, the fluorescence of **6** was gradually quenched (Fig. 4f), which also means that **6** could recognize toward C_{60}. However, it is difficult to determine the complexation ratio of **6** and C_{60} and the binding constant of **6** toward C_{60} via fluorescence titration experiments, because macrocycle **6**, similar to **5**, still could self-aggregate (even at 10^{-7} M concentration) to induce the quenching effect of fluorescence.[9e] The above experimental results show that both **5** and **6** are good building blocks of well-ordered fullerene-based nanostructures. Although the reason why the nano-rod structure could form is not very clear now, it is certain that the assembly driving force is the formation of complex between macrocycle **5** or **6** and C_{60}. Recently, Iyoda's group reported a macrocyclic pentadecaphenylene-based organogel, which incorporated C_{60} in its cavity to produce a fibrous inclusion.[9e] To our knowledge, other examples of macrocycle which could assemble with C_{60} to form well-ordered nanostructure remain rarely reported.

Conclusion

In summary, we have synthesized diaryl[*b*,*f*][1,5]diazocine-based macrocyles **5** and **6** with inner cavities via Hay coupling method. The single crystal structure of **5** showed that two macrocyclic molecules of **5** could assemble with each other to form an interesting ring-based dimeric structure. Moreover, SEM results suggested that both macrocycles **5** and **6** could assemble with C_{60} to form well-ordered fullerene-based nano-rod structures, which may have potential applications in photoelectric devices. This work showed that diaryl[*b*,*f*][1,5]diazocine is a good building block for macrocycles. Our further work will focus on exploring the applications of the macrocycles in the complexation with other organic guests, which are now underway in our laboratory.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.04.094.

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14. CCDC 967178 contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www. ccdc.cam.ac.uk/data_request/cif.