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基于柱[5]芳烃主客体包结构筑分子响应型超分子水凝胶

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摘要 主客体相互作用是在水溶液中与大环主体分子形成稳定的包结物的理想驱动力. 以功能化的苯并咪唑衍生物为客体(**M**), 水溶性柱[5]芳烃为主体构建了一种分子响应型超分子水凝胶. 通过 ^{1}H NMR, 2D NOESY 和扫描电子显微镜(SEM)研究了水凝胶的成凝胶机理. 有趣的是, 主客体包结作用、柱[5]芳烃间有序的“外腔”π-π 相互作用和分层堆积对于获得超分子水凝胶是必不可少的, 非共价键相互作用的动态可逆性使凝胶体系对温度变化/化学刺激产生响应. 此外, 加入竞争性客体己二腈(ADN)/百草枯(PQ)后, 柱[5]芳烃基水凝胶可转化为溶胶. 因此, 该超分子水凝胶可以选择性识别有机分子.

关键词 超分子水凝胶; 水溶性柱[5]芳烃; 竞争包结; 分子识别; 自组装

Molecule-Responsive Supramolecular Hydrogel Constructed from Pillar[5]arene Based on Host-Guest System

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Abstract The host-guest interaction was qualified as an ideal drive force to form stable inclusion complexes with macrocyclic host molecules in aqueous solution. Herein, a multi-responsive supramolecular hydrogel was constructed based on a functionalized benzimidazole derivative guest (**M**) with soluble pillar[5]arene as a host group. The mechanism of hydrogel formation was explored by the ^{1}H NMR, 2D NOESY and scanning electron microscope (SEM) in depth study. Interestingly, host-guest inclusion, the ordered “exo-wall” π-π interaction and hierarchical stacking of pillar[5]arene was indispensable to obtain the supramolecular hydrogel, which endowed the gel system with response to temperature change/chemical stimuli. Upon addition of competitive guests adiponitrile (ADN)/paraquat (PQ), pillar[5]arene-based hydrogel could be converted into sol. Herein, the organic molecules could be selectively recognized by the hydrogel.

Keywords supramolecular hydrogel; soluble pillar[5]arene; competitive inclusion; molecular recognition; self assembly

1 Introduction

Supramolecular hydrogels have caused numerous interests in plethora fields due to their extensive applications.[1,2] Taking advantage of far-ranging tunable functional groups and delicate non-covalent interactions, supramolecular hydrogels are facile to disassemble and reassemble under the stimulation of external environments, which endows them with remarkable stimuli-responsive abilities.[3~6] Supramolecular hydrogels constructed by hydrogen bonding or host-guest interactions showed excellent thermal responsiveness. Simultaneously, stimuli-responsive supramolecular hydrogels can be utilized in chemo/biosensors, self-healing materials, *etc*.[7~9] Moreover, when multiple responsive functional moieties or non-covalent interactions are involved, the application can

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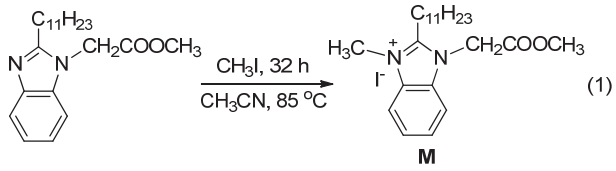
be achieved simultaneously or sequentially by different stimuli.[10~12] Stimulus-responsive properties have been widely used in the construction of functional materials through host-guest interaction. Recently, many stimulus-responsive systems have been developed to fabricate smart materials,[13,14] among which responsive hydrogels that can reversibly switch between free-flowing liquid and free-standing gel states have aroused increasing interest due to their applications in molecule sensors.

Host-guest interaction, a kind of fascinating noncovalent driving force, is susceptive to be destroyed by environmental changes so that they can provide supramolecular systems with stimuli-responsive properties.[15~17] For example, Qiu *et al*.[18] reported multi-responsive supramolecular gels based on charge transfer interactions in 2018. Chen *et al*.[19,20] reported supramolecular nanoplatforms via cyclodextrin host-guest recognition for synergistic gene-photodynamic therapy in 2018. Since the host-guest interactions between pillar[*n*]arenes and cationic guests (such as imidazolium, ammonium and pyridinium salts) are high-selective and reliable.[21,22] It's convincing to explore the application of pillar[*n*]arene-based host-guest chemistry in the field of molecular recognition.[23] Much interest in using macrocycles with intrinsic cavities as desirable hosts for the specific recognition of small molecular targets has been aroused. Pillar[*n*]arene, as a new family of macrocyclic host molecules, was first reported by Ogoshi *et al*.[24] in 2008. Pillar[*n*]arenes have various supramolecular assembly driving forces including C—H···π, π-π, cation-π, hydrophobic/hydrophilic interaction,[25,26] *etc*. Meanwhile, pillar[*n*]arenes[27,28] are endowed with considerable capacity for binding various guest molecules and constructing diverse supramolecular systems. Moreover, the incorporation of variable functional groups is well established for pillar[*n*]arenes,[30] which renders them ideal candidates for gel material. So far, researches about pillar[*n*]arenes are mainly concerned about the pillar[*n*]arene monomers, which are lack of linkages with different molecules each other and behave a monotonous way. So, it is still a challenge to construct supramolecular systems by host-guest interactions bearing pillar[*n*]arenes.[31,32] Particularly, multi-responsive supramolecular hydrogels based on small molecules and pillar[5]arenes has been less reported.[33,34] It aroused our interest whether small molecules and pillar[5]arene could form supramolecular hydrogel.

In recent years, recognition and detection of toxic molecules and organic molecularls have gained paramount importance in biological, chemical and environmental applications. Among the various molecules, adiponitrile is considered to be toxic molecules for human health, natural environment and pollution to water bodies. Besides, paraquat (PQ), which is also called *N*,*N*′-dimethyl-4,4′-bipyridinium salt,[35] has high toxicity. As one of the non-selective, high-efficiency and quick-acting herbicides, it possesses considerable risks to human health and environmental protection.[36] Therefore, sensitive, selective, and technically effective methods for detection of adiponitrile and PQ are still needed.

On the basis of the above phenomena, two-component supramolecular host-guest hydrogel (named **SH-BP5**) based on benzimidazole derivative (**M**) and pillar[5]arene (**BP5**) was prepared. The hydrogel could form stable 3D supramolecular aggregation-induced emission (AIE) hydrogel through the host-guest interactions, C—H···π, "exo-wall" π-π interactions[37~39] and hierarchical assembly. Benzimidazole derivative (**M**) with alkyl chain as the hydrophobic guest was synthesized by employing the following strategy (Eq. 1). Next, soluble pillar[5]arene (**BP5**) with strong hydrophilicity was introduced as host molecule. Finally, AIE hydrogel **SH-BP5** was obtained via host-guest interaction. Interestingly, by rationally introducing competitive molecules adiponitrile (ADN)/paraquat (PQ) into the hydrogel **SH-BP5**, the disassembly of **SH-BP5** could be obtained, meanwhile, the gel state was collapsed. Recognition of specific organic pollutant molecules was achieved.



(1)

2 Results and discussion

2.1 Synthesis of compound M

Compound **M** was synthesized using the method described in our previous article (Eq. 1).[40] In this experiment, we found that **M** could not only form a gel with cyclodextrin, but also form a supramolecular hydrogel with the pillar[5]arene through the host-guest interaction.

2.2 AIE of hydrogel SH-BP5

Hydrogel **SH-BP5** showed an aggregation-induced fluorescence emission (AIE)[41~43] in pure water with the reduction of temperature. The destruction of hydrogen bonds at elevated temperature also induced the sol-gel phase transition, which indicated that **SH-BP5** has thermo-stimuli-response. Such a performance is highly beneficial for potential applications in fluorescence soft materials.

2.3 Host-guest complex between M and BP5

In order to explore the self-assembly mechanism between **M** and **BP5**, ^{1}H NMR, 2D NOESY and X-ray diffraction (XRD) had been performed. First, ^{1}H NMR titration was utilized to confirm the host-guest complexation between **BP5** and **M** molecule. As shown in Figure 1c, upon addition of 0.5 equiv. of **BP5**, H-1, H-2, CH_2 (H-6), CH_3 (H-7) signals on **BP5** and H_h, H_e, $H_{i\text{-}l}$ protons on **M** showed downfield shifts, respectively. This downfield shifts could be attributed to the dissociation of **M** and the C—H···O hydrogen bonding interactions existed between

M and **BP5**. Meanwhile, multiple C—H···π interactions between C—H (H_{i-l}) moieties of **M** and the π-electron-rich pillar[5]arene cavity were formed. To test if **M** could be efficiently released from the **SH-BP5** complex by competitive replacement with ADN, ^{1}H NMR experiment was conducted to characterize the process of competitive binding. In Figure 1d, with the addition of 0.5 equiv. of ADN to **SH-BP5**, the protons H_h, H_e, H_{i-l}, on **M** gradually shifted upfield, which suggested that **M** was released from the **SH-BP5** complex and ADN occupied the cavity of **BP5**. Simultaneously, the hydrogel was destroyed due to the change of C—H···π interactions. In addition, the assignment and correlation of the protons were further validated by the 2D NOESY spectra of **BP5** and **M**. As shown in Figure 2, the cross peaks A/A' represented the correlations between the signal of protons H-2 on aromatic protons and Hg, Hf on **M**, which implied that the aromatics moieties were included in the **BP5** cavity.

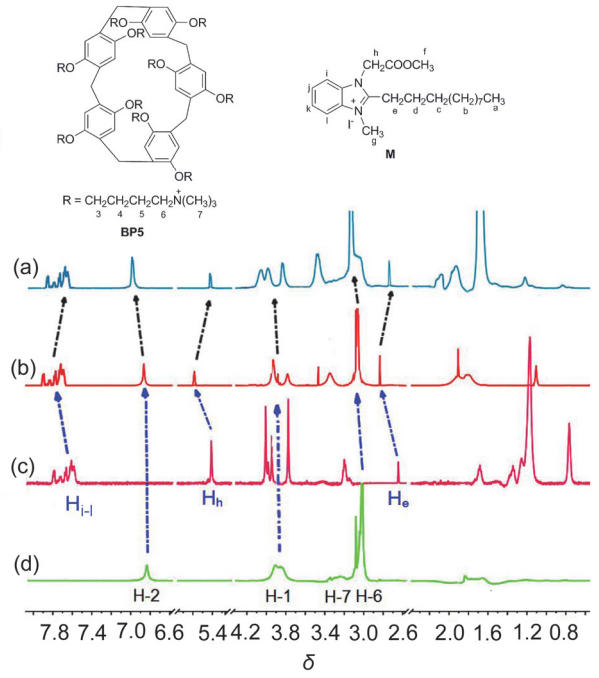


Figure 1 ^{1}H NMR spectra (600 MHz, D_2O, 298 K) of (a) **BP5** solution (6.0×10^{-6} mol•L^{-1}), (b) **M** solution (1.2×10^{-5} mol•L^{-1}), (c) **M** and **BP5** mixed solution (**M** ∶ **BP5**, 1 ∶ 0.5 in molar ratio) and (d) upon the addition of 0.5 equiv. of ADN into (c)

To further certify possible host-guest interaction mechanism, the XRD experiments were carried out. For **M**, there was a sharp peak at 25.52° and the corresponding *d* value was 0.352 nm, indicating the existing of π-π stacking. The peak at $2\theta=30.1°$ corresponding to the *d*-spacing value of 0.296 nm indicated the existence of hydrogen bond in solid state. What's more, the *d* value of 1.401 nm at $2\theta=6.3°$ was less than twice the length of the theoretical alkyl chain of **M** molecules, which was due to the combination of two **M** molecules through hydrophobic interaction in each unit of the arrays. After the formation of **SH-BP5**, the peak at $2\theta=6.3°$ on **SH-BP5** was disappeared. Meanwhile, the *d*-spacing of 0.308 nm at $2\theta=29.98°$ suggested that π-π stacking existed in **SH-BP5**.

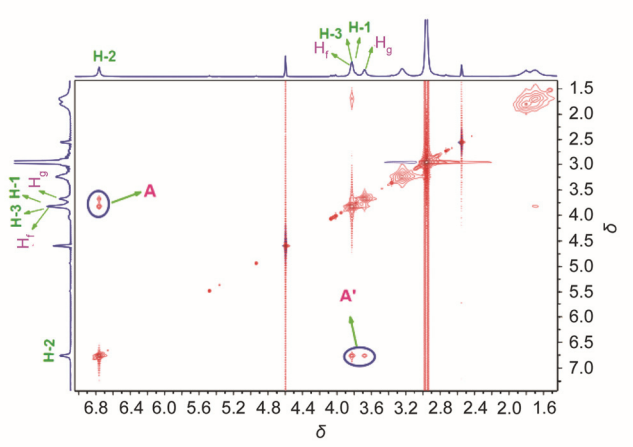


Figure 2 2D NOESY spectrum of **M** and **BP5** (**M**/**BP5**, 1: 0.5 in molar ratio) mixed solutions in D_2O

2.4 Molecular recognition characteristics of SH-BP5 for ADN/PQ

It is well known that pillar[*n*]arenes can form complex with positively charged guests. Pillar[5]arene shows very strong binding affinities with the competitive guest adiponitrile/paraquat (ADN/PQ), so it is envisioned that hydrogel **SH-BP5** could be disassembled by addition of a competitive guest. The competitive guest ADN/PQ was added to **SH-BP5**, and the obtained solution could not form hydrogel by heating or cooling because ADN/PQ has stronger competitive binding with pillar[5]arene than **M**, resulting in the destruction of the gel state (Figure 3). In terestingly, as shown in Figure 4, several kinds of organic molecules were added into the hydrogel **SH-BP5**, respectively, only the addition of ADN gave **SH-BP5** obvious gel-sol transition. The results indicated that the hydrogel **SH-BP5** can selectively recognize ADN. Meanwhile, the SEM image (Figure 5) also showed that the network structure of hydrogel **SH-BP5** was destroyed and turned into a well-regulated bulk structure of **SH-BP5-ADN**.

According to the above experimental results and the structural parameters of **BP5** reported in the literatures,[44] the possible inclusion modes between **BP5** and **M** were presented in Scheme 1. The aromatic moieties of **M** penetrated into the cavity of **BP5** by host-guest interactions and inclusion interactions. Thus, a stable hydrogel **SH-BP5** was formed. However, when ADN/PQ was added into **SH-BP5**, **SH-BP5** was disrupted because of competitive interaction between **M** and ADN/PQ (Scheme 1). Supramolecular hydrogel **SH-BP5** exhibited a peak at *m*/*z*= 422.3913, corresponding to **BP5**+**M**, indicating that the complexation reaction between **BP5** and **M** was 1 ∶ 1 stoichiometry.

3 Conclusions

In conclusion, host-guest interactions have become one of practical and popular interactions in the construction of

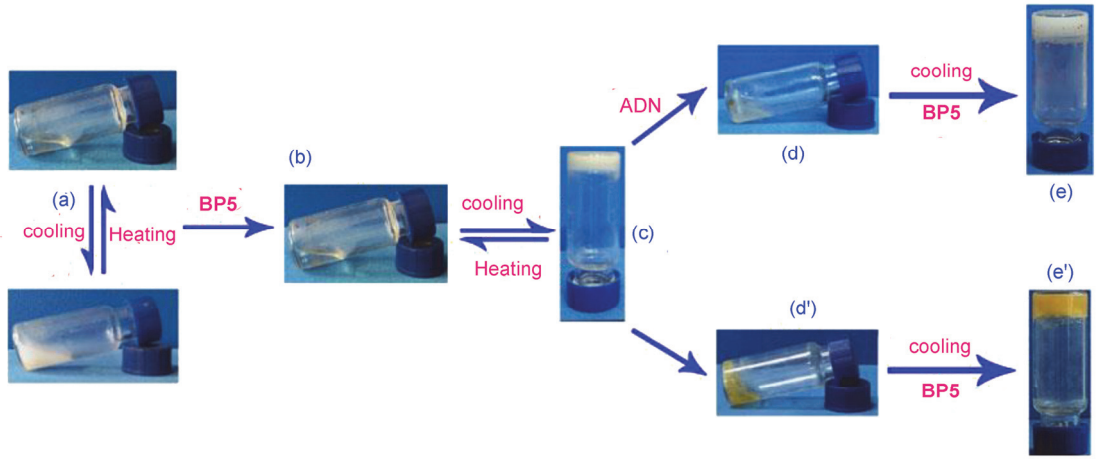


Figure 3 Formation process and chemical stimuli-response of supramolecular hydrogel **SH-BP5** (λ_{ex}=340 nm)
(a) **M** solution (8.0×10^{-6} mol•L^{-1}), (b) **M** (8.0×10^{-6} mol•L^{-1}) and **BP5** (4.0×10^{-6} mol•L^{-1}) hot sol, (c) **SH-BP5** hydrogel (w=2.0%, **M**∶**BP5**, 1∶0.5 in molar ratio), (d) after adding of ADN (1.6×10^{-5} mol•L^{-1}) into hydrogel **SH-BP5** (c), (d') after adding of **PQ** (1.6×10^{-5} mol•L^{-1}) into hydrogel **SH-BP5** (c), (e) and (e') after adding of **BP5** (4.0×10^{-6} mol•L^{-1}) into (d) and (d') hydrogel recovered again

Figure 4 Responsive properties of organic solvents for the hydrogel **SH-BP5** (w=2.0%, λ_{ex}=340 nm, **M**/**BP5**, 1∶0.5 in molar ratio)

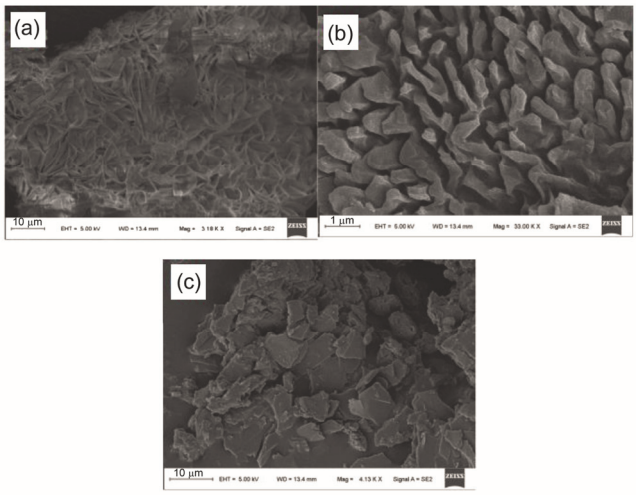


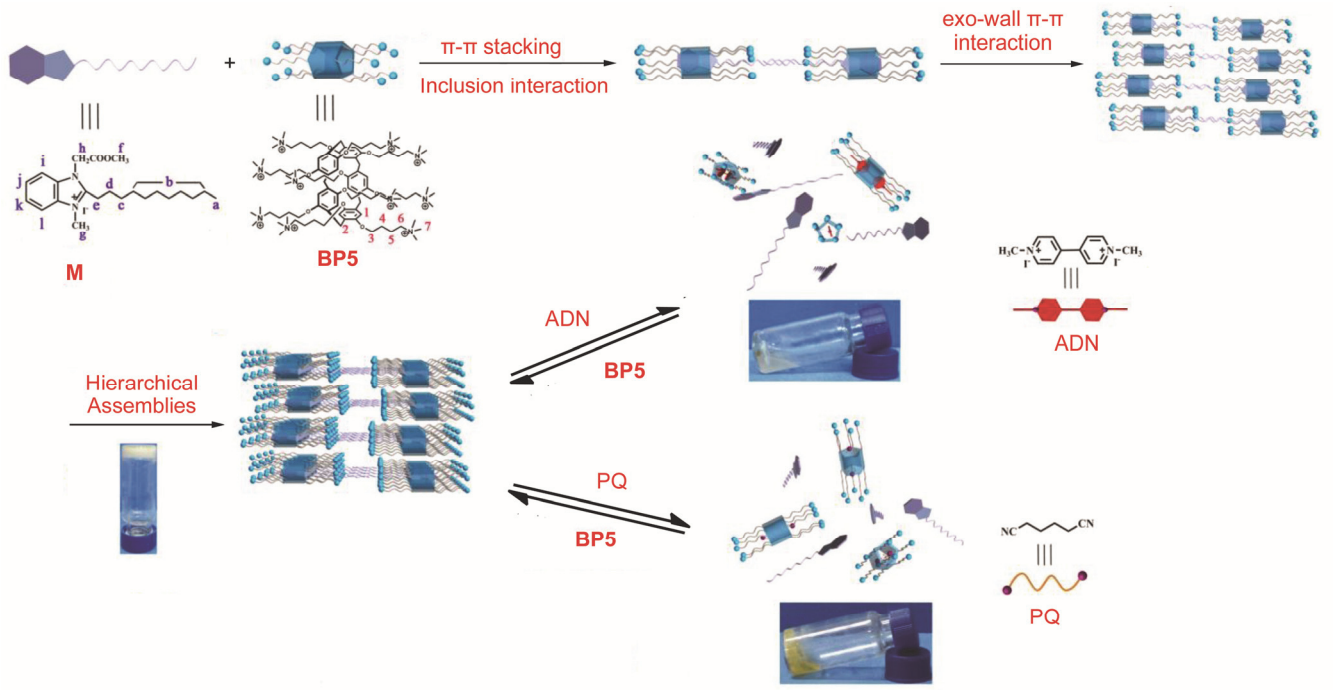
Figure 5 SEM images of the xerogels of (a) **SH-BP5**, (b) **SH-BP5-AND** and (c) **SH-BP5-PQ**

supramolecular hydrogels. Supramolecular hydrogel **SH-BP5** based on the benzimidazole **M** and pillar[5]arene **BP5** was successfully developed. Salient features of **SH-BP5** included the thermal-responsive nature and the reversible chemical-stimuli-responsive behavior. On the basis of the competition of host-guest interactions, the 3D network hydrogel could be transformed to sol by addition of competitive guest molecules (ADN/PQ). This was mainly due to the effectively disassembled process which was destructed the "exo-wall" π-π interactions and host-guest interactions of **SH-BP5**. More importantly, with addition of enough **BP5** to the disassembled sol and the gel state was recovered again. The reason why **M** could be released from its host-guest complex was the higher binding affinity of ADN/PQ with pillar[5]arene than that of **M** molecule. These phenomena showed that the **SH-BP5** has excellent molecular recognition behavior.

4 Experimental section

4.1 Synthesis and characterization of guest M

N-Methoxycarbonylmethyl-2-undecyl-1*H*-benzimidazole (1.03 g, 3.0 mmol) was added into 50 mL of acetonitrile, and stirred at room temperature for 15 min. Then iodomethane 1.27 g, 9.0 mmol) was slowly dripped into the solution. The mixture was stirred under reflux at 85 ℃ for 32 h under nitrogen atmosphere. Then the solution was evaporated under vacuum. The residue was collected, recrystallized with acetone/water and t.en dried in vacuum. 0.78 g of white powder compound **M** (73% yield) was obtained. m.p. 108～110 ℃; ^{1}H NMR (600 MHz, D_2O) δ: 7.89～7.68 (m, 4H), 5.50 (s, 2H), 4.10 (s, 3H), 3.86 (s, 3H), 2.73 (s, 2H), 1.76～1.79 (m, 2H), 1.43～1.45 (m, 2H), 1.25～1.27 (m, 14H), 0.85 (t, J=12 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 168.65, 154.27, 153.96, 131.58, 133.95, 131.17, 126.83, 113.72, 112.63, 50.38, 110.61, 40.39, 31.81, 31.57, 29.63, 26.17, 20.78, 14.06; HRMS (ESI) calcd for $C_{22}H_{35}N_2O_2$ (**M**−I)$^+$ 359.5320, found 359.2949.



Scheme 1 (a) Chemical structures of **M**, **BP5**, ADN and PQ, (b) proposed assembly mechanisms of supramolecular hydrogel **SH-BP5** and (c) disassembly of **SH-BP5** with competitive guest ADN/PQ and the gel state destroyed after addition of guest molecules

4.2 Preparation of hydrogel SH-BP5

First, the gelator (**M**), pillar[5]arene (**BP5**) and pure water were put in a reagent bottle (1.0 mL) and then heated until the solids were dissolved completely. After the solution was cooled to room temperature, the hydrogel **SH-BP5** could be obtained, respectively, and the corresponding critical gel concentration was about 2.0 mg• mL^{-1}. The pillar[5]arene was synthesized using a method described in our lab previously.[45,46]

4.3 General procedure for ^{1}H NMR experiments

For ^{1}H NMR titrations, the host molecule (**BP5**) and 1 equiv. of guest (**M**) stock solutions were prepared in deuterium water. Aliquots of the two solutions were mixed directly in NMR tubes.

Supporting Information ^{1}H NMR, ^{13}C NMR and ESI-MS spectra of **M**; ^{1}H NMR spectrum of **BP5** and ESI-MS spectrum of the complex between **BP5** and **M**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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