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## A cationic water-soluble biphen[3]arene: synthesis, host–guest complexation and fabrication of a supra-amphiphile†

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The first cationic water-soluble biphen[3]arene was synthesized and its host–guest complexation with sodium 1-hexanesulfonate was investigated, which was further used to change the aggregation of the amphiphilic guest in water.

Since water provides an environment for life where numerous biochemical processes take place, the development of host–guest systems that operate in water is a desirable but challenging goal for researchers working in the field of molecular recognition.<sup>1</sup> Synthetic water-soluble macrocyclic receptors can be used in mimicry of natural processes such as specific recognition of bioactive molecules (nucleotides, microbial/viral pathogens, antigens) or enzymatic transformation of substrates.<sup>2</sup> While organic-soluble systems have offered insight into the forces involved in binding, particularly those affecting selectivity, they are not responsible for the strong desolvation and entropic benefits experienced in water.<sup>3</sup> The most effective way to increase the solubility of synthetic receptors in water is probably the introduction of various hydrophilic moieties into the cavity portals, which results in the appearance of positive or negative charges or electroneutrality of synthetic receptors.<sup>4</sup>

Numerous efforts have been made to develop novel macrocyclic receptors which are able to selectively and effectively bind various guests because of the extensive applications of host–guest recognition in a wide range of fields, such as chemosensors,<sup>5</sup> molecular machines and nano-devices,<sup>6</sup> artificial transmembrane channels,<sup>7</sup> drug delivery systems,<sup>8</sup> supramolecular polymers<sup>9</sup> and other advanced functional materials.<sup>10</sup> Some classical supramolecular macrocycles, including crown ethers,<sup>11</sup> cyclodextrins,<sup>12</sup> calixarenes,<sup>13</sup> cucurbiturils<sup>14</sup> and pillararenes,<sup>15</sup> have been extensively studied over the past few

decades. Notably, among these active synthetic receptors, cationic macrocyclic molecules bearing characteristic functional groups have recently attracted particular attention because of their efficient complexation with some biologically important anionic guests, suggesting that these types of molecules can be used for the nucleic acid condensation, gene delivery and antimicrobial.<sup>16</sup> For example, Cohen and coworkers reported that decoration of pillararene scaffolds with positively charged quaternary ammonium or imidazolium groups resulted in the effective inhibition of several clinically important Gram-positive pathogens.<sup>16c</sup> Recently, Huang and coworkers employed the size selective host–guest complexation between cationic water soluble pillar[6]arenes modified by trimethylammonium groups on both sides and ATP to potentially inhibit the efflux pump of multidrug resistant cancer cells, resulting in the enhancement of the efficacy of cancer chemotherapy.<sup>16d</sup> Undoubtedly, it can be foreseen that water-soluble cationic macrocyclic molecules will catch increasing attention and find wide applications in future. Therefore, design and development of novel macrocyclic hosts with unique structures and fine host–guest properties become a promising work to enrich the toolbox of supramolecular chemists.

Biphen[*n*]arenes,<sup>17</sup> including biphen[3]arenes and biphen[4]arenes, are a new kind of macrocyclic hosts appeared in the supramolecular world recently, which are firstly reported by Li and coworkers. Their repeating units 4,4'-biphenol or 4,4'-biphenol ether are linked by methylene bridges at the 3- and 3'-positions. Biphenarenes possess different topological structures to calixarenes, cyclotrimeratrylenes, resorcinarenes and pillararenes, which are composed of mono-benzene units. The unique geometries and convenient chemically functionalization of biphenarenes endow them with remarkable abilities to selectively bind different kinds of guests and make them promising candidates for constructing a wide variety of attractive supramolecular systems. In our previous work,<sup>17b</sup> we prepared the anionic water-soluble biphen[3]arene by introducing carboxylate anionic groups on both rims of biphen[3]arene, which could be used in controllable self-assembly and

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controlled release. In this study, we reported the preparation of a cationic water-soluble biphen[3]arene **H** and investigated its host-guest complexation with sodium 1-hexanesulfonate **G1** and two other aromatic anionic guests (**G2**, **G3**). Furthermore, we constructed a supra-amphiphile using **H** and amphiphilic **G** as the building blocks by taking advantage of host-guest chemistry, which was further used to change the aggregation of the amphiphilic guest in water. **G** itself could form small sphere micelles by self-assembly. However, the host-guest complex of **H** with **G** self-assembled into regular nanoparticles in aqueous solution.

Herein, we prepared the first cationic water-soluble biphen[3]arene **H** in a facile method (Scheme 1). With the aim of obtaining **H**, precursor **2** with bromoethoxy groups was prepared through the cyclization of monomer **H** with para-formaldehyde in 1,2-dichloroethane, where boron trifluoride diethyl etherate ( $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ) acted as a catalyst.<sup>4b</sup> Bearing six alkyl bromide terminal groups makes **2** be easily functionalized to generate the derivatives of biphen[3]arene. By treating **2** with excess trimethylamine in methanol, compound **H** containing three trimethylammonium groups on both sides was prepared as a white solid (90% yield). Biphen[3]arene **H** has good solubility in water to give a clear solution. Furthermore, **H** is so moisture-sensitive that it will quickly become soft on exposure to a humidified atmosphere for a short period of time, though it remains solid in a dry environment.

The complexation of **H** with **G** was investigated by  $^1\text{H}$  NMR spectroscopy. Due to the relatively poor solubility of **G** in aqueous solution, sodium 1-hexanesulfonate (**G1**) was used as a model compound. Fig. 1 showed the sequential addition of 1.0 and 2.0 equivalent (eq.) **H** to a solution of **G1** in  $\text{D}_2\text{O}$ . As shown in Fig. 1b and c, the  $^1\text{H}$  NMR spectra of a solution containing **H** and **G1** showed only one set of resonance peaks, indicating fast-exchange complexation between **H** and **G1** on the  $^1\text{H}$  NMR time scale.<sup>16a</sup> In the presence of **H**, the peaks related to protons of **G1** displayed upfield shifts ( $\Delta\delta = -0.31, -0.23, -0.35, -0.30$  and  $-0.23$  ppm for protons  $\text{H}_{1a}, \text{H}_{1b}, \text{H}_{1c}, \text{H}_{1d,1e}$  and  $\text{H}_{1f}$ ,

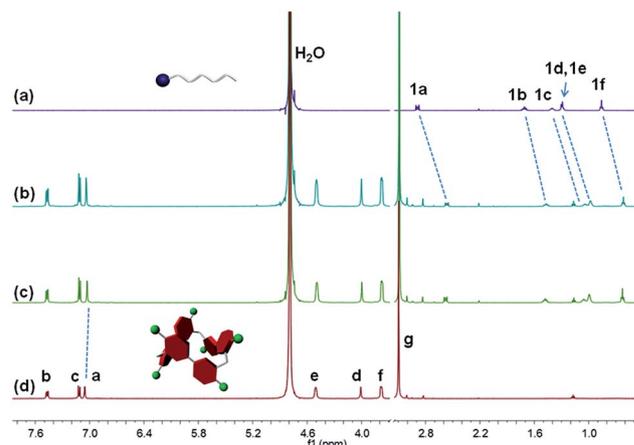
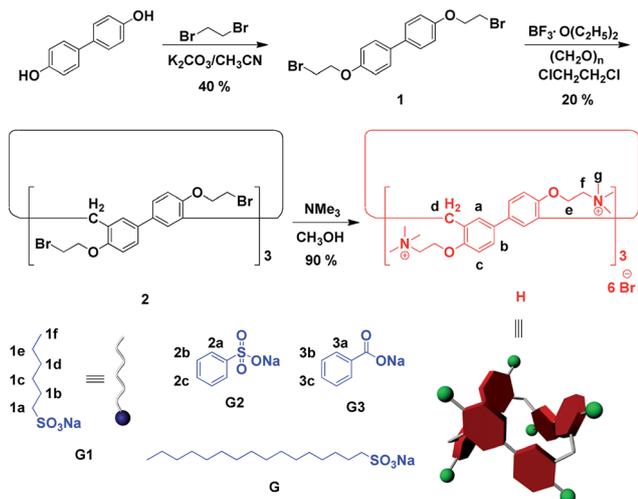


Fig. 1  $^1\text{H}$  NMR spectra (400 MHz,  $\text{D}_2\text{O}$ , 293 K) of (a) 2.00 mM **G1**; (b) 1.00 mM **G1** and 2.00 mM **H**; (c) 2.00 mM **G1** and 2.00 mM **H**; (d) 2.00 mM **H**.

respectively), suggesting the formation of a host-guest complex between **H** and **G1**. In addition, protons on **H** also exhibited slight chemical shift changes. The peak related to the proton  $\text{H}_a$  on the biphenyl rings shifted upfield from 7.06 to 7.03 ppm due to the interactions between **H** and **G1**. These phenomena supported the host-guest complexation between **H** and **G1**.

Moreover, 2D NOESY NMR analysis of an aqueous solution of **H** (10.0 mM) and **G1** (10.0 mM) was performed to investigate the relative spatial positions of this complex (Fig. S10–S12, ESI $^\dagger$ ).<sup>17b</sup> Nuclear overhauser effect (NOE) correlation signals were observed between the aromatic proton  $\text{H}_a$  of **H** and the protons ( $\text{H}_{1c}, \text{H}_{1d,1e}, \text{H}_{1f}$ ) of **G1**. Additionally, correlations between the proton  $\text{H}_d$  or  $\text{H}_e$  of **H** and the protons  $\text{H}_{1b}, \text{H}_{1c-1e}$  or  $\text{H}_{1f}$  of **G1** were also observed. The formation of the complex might be mainly driven by hydrophobic and electrostatic interactions, because the hydrophobic cavity of **H** possessed the ability to hold the hydrophobic alkyl chain of **G1**. Moreover, the cationic trimethylammonium groups of **H** could bind the anionic sulfonate group of **G1** via electrostatic interactions.<sup>4b</sup> Further evidence for the formation of the **H** $\supset$ **G1** complex was confirmed by an electrospray ionization mass spectrometry (ESI-MS) experiment, revealing a peak at  $m/z$  274.3, corresponding to  $[\text{H}\supset\text{G1} - 5\text{Br}]^{5+}$  (Fig. S26, ESI $^\dagger$ ), which demonstrated the formation of a 1 : 1 complex between **H** and **G1**.

In addition to the formation of the host-guest complex with sodium alkyl sulfonate (**G1**), cationic water-soluble biphen[3]arene **H** could complex with other anions, such as sodium benzenesulfonate (**G2**) and sodium benzoate (**G3**) (Scheme 1). In the case of the guest **G2**, upon addition of 1.0 eq. **H**, signals derived from  $\text{H}_{2a-2c}$  of the sulfophenyl group exhibited upfield shifts. At the same time, protons on **H** also displayed chemical shift changes (Fig. S8, ESI $^\dagger$ ). In contrast to **H** $\supset$ **G1**, the **H** $\supset$ **G2** complex did not show NOE correlations between the protons of sulfophenyl group ( $\text{H}_{2a-2c}$ ) and the host's protons (Fig. S13 and S14, ESI $^\dagger$ ), indicating the formation of a non-threaded complex mainly driven by electrostatic interaction.<sup>17c</sup> This is reasonable because the benzyl unit is too bulky to locate in the cavity of **H**.



Scheme 1 Synthetic route to the cationic water-soluble biphen[3]arene **H** and chemical structures of other compounds studied here.

Similar complexation-induced effects were observed for the interaction of **G3** with **H**, which also confirmed the non-interpenetrated geometry (Fig. S9, S15 and S16, ESI†).

To measure the association constant and stoichiometry of the complexation between **H** and **G1**,  $^1\text{H}$  NMR titration experiments were carried out in  $\text{D}_2\text{O}$ .<sup>4b</sup> On the basis of chemical shift changes of  $\text{H}_a$  on **H** (Fig. S17, ESI†), the association constant ( $K_a$ ) for the complex **H**⊃**G1** was calculated to be  $(1.56 \pm 0.07) \times 10^3 \text{ M}^{-1}$  by employing a non-linear curve-fitting method (Fig. S18, ESI†). Moreover, a mole ratio plot for the complexation between **H** and **G1** showed that the stoichiometry of the complex between **H** and **G1** was 1 : 1 (Fig. S19, ESI†), in good agreement with the result obtained from ESI-MS. Compared with **H**⊃**G1**, the  $K_a$  values for **H**⊃**G2** and **H**⊃**G3** were decreased to be  $(5.92 \pm 0.01) \times 10^2 \text{ M}^{-1}$  and  $(6.22 \pm 0.02) \times 10^2 \text{ M}^{-1}$ , respectively (Fig. S20–S25, ESI†), due to the inadequate complexation arising from the bulky size of **G2** and **G3**.

After the establishment of this new host–guest recognition motif in aqueous solution, we further applied it to fabricate a supra-amphiphile<sup>4b</sup> and investigated its self-assembly in water. **G** itself is an amphiphilic molecule which contains a hydrophobic alkyl chain and a hydrophilic sodium sulfonate head. By using the concentration-dependent conductivity measurements, the critical aggregation concentration (CAC) value of **G** was evaluated to be  $1.24 \times 10^{-5} \text{ M}$  (Fig. S27, ESI†). However, the CAC of **G** in the presence of **H** was decreased to be about  $1.69 \times 10^{-6} \text{ M}$  (Fig. S28, ESI†). The CAC value of **G** decreased by a factor of *ca.* 7.3 was ascribed to the formation of a stable host–guest complex between **H** and **G**.<sup>19</sup> Transmission electron microscopy (TEM) and dynamic light scattering (DLS) experiments assisted in the visualization of the self-assembly sizes and morphologies of **G** and **H**⊃**G**. As shown in Fig. 2a, **G** itself self-assembled in water to form small solid spheres with an average diameter of about 4 nm when the concentration was higher than its CAC value. The diameter is near to the length of two **G** molecules, confirming the formation of micelles. The average size of micelles formed by **G** was detected by DLS with a value of  $\sim 3 \text{ nm}$  (Fig. S29, ESI†). Interestingly, in the presence

of **H**, a supra-amphiphile was formed on the basis of the novel host–guest recognition motif, resulting in the formation of regular nanoparticles with a diameter of  $\sim 18 \text{ nm}$ , drastically different from the smaller micelles formed by **G** alone (Fig. 2b and c). The DLS result showed that the average diameter of the aggregates formed from **H**⊃**G** was  $\sim 19 \text{ nm}$  (Fig. S30, ESI†), in agreement with the corresponding value obtained from the TEM images. Zeta potential experiment was also conducted to evaluate the potential changes before and after binding of the aggregated species (Fig. S31 and S32, ESI†). **G** self-assembled in water to form micelles with a zeta potential of  $-4.88 \text{ mV}$ . Upon addition of **H**, the zeta potential of the aggregates formed by **H**⊃**G** increased to  $+12.1 \text{ mV}$ . It is reasonable that spherical aggregates are negatively charged self-assembled from **G** alone, while the aggregates formed by **H**⊃**G** become positive by introducing cationic host. The self-assembly process might be that **H** bonds **G** to form a host–guest complex in aqueous solution resulting from the balance of electrostatic interaction (Fig. 2d). Cationic macrocyclic host **H** is embedded into the layer of micelle assembled from **G** due to the host–guest interaction, resulting in charge imbalance of the micelle surface. The adjacent micelles gather together to create stable charge balance states and form large self-assembled aggregates.

Additionally, the optimal molar ratio between **H** and **G** for constructing supramolecular aggregates was studied *via* fluorescence spectroscopy by pyrene ( $1.00 \mu\text{M}$ ) as a probe.<sup>15b</sup> The fluorescent intensity at 359 nm vs. the concentration of **H** added in the presence of **G** ( $80.0 \mu\text{M}$ ) was shown in Fig. S33 (ESI†). Upon gradual addition of **H**, the fluorescent intensity of pyrene at 359 nm underwent a sharp decrease until the minimum was reached at a **H**/**G** ratio of 0.168. Then an inverse increase was observed upon further addition of **H**. The initially rapid decrease of the fluorescent intensity of pyrene indicated the formation of a higher-order complex between **H** and **G** with a tendency toward supra-amphiphilic aggregation, which was then disassembled upon further addition of excess **H** to gradually afford a simple 1 : 1 complex.<sup>8b</sup> The inflection was observed at the **H**/**G** molar ratio of 0.168, which meant that the optimal molar ratio between **H** and **G** for the supra-amphiphilic assembly was approximately 1 : 6 related to the neutral state. The formation of larger aggregates was attributed to the charge balance of the host–guest system.

In conclusion, we have successfully prepared the first cationic water-soluble biphen[3]arene **H** bearing three trimethylammonium moieties on both sides. The presence of six positive charges makes it possible to act as an anion receptor. Mainly driven by hydrophobic and electrostatic interactions, this cationic water-soluble biphen[3]arene could bind sodium 1-hexanesulfonate to form a host–guest complex with the association constant of  $(1.56 \pm 0.07) \times 10^3 \text{ M}^{-1}$ . In addition, we used this novel recognition motif to construct a supra-amphiphile by using **H** and amphiphilic **G** as the building blocks, which was further used to change the aggregation of the amphiphilic guest in water. In contrast to the small sphere micelles formed by amphiphilic molecule **G**, the host–guest complex between **H** and **G** self-assembled into regular nanoparticles in water. This new recognition motif based on the

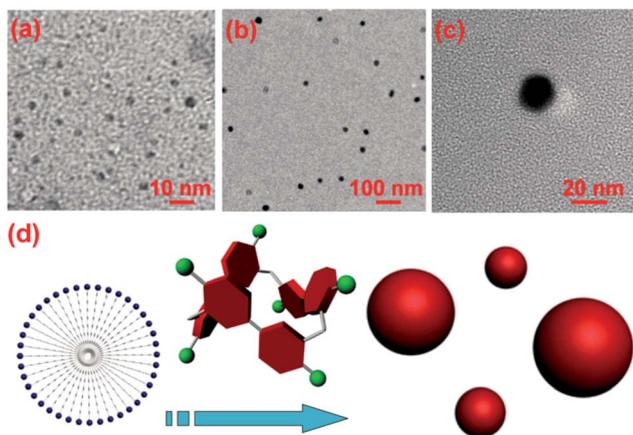


Fig. 2 TEM images: (a) **G** ( $5.00 \times 10^{-4} \text{ M}$ ); (b) **H**⊃**G**, (c) enlarged image of **H**⊃**G** ( $3.33 \times 10^{-4} \text{ M}$ ). (d) Illustration of the formation of the aggregates.

cationic water-soluble biphen[3]arene absolutely will be helpful for the fabrication of biphenarenes-based functional architectures and definitely bring about many prospective substantial applications, such as chemo-sensors, molecular machines, supramolecular polymers, drug delivery systems and controlled release.

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