



Self-assembling of supramolecular adducts by sulfonato-calix[4]arene and pyridinium gemini guests in neutral aqueous solution



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ABSTRACT

The formation of self-assembled structures triggered by pyridinium-based gemini guests in the presence of a sulfonato-calix[4]arene receptor has been thoroughly examined via isothermal titration calorimetry (ITC) in neutral aqueous solution. Data confirm the existence of a 1:1 host–guest complex, in which the guest is strongly bound to the host cavity, and the formation of a 2:1 capsular-like adduct. The splitting of the ΔG° term into the enthalpic and entropic contributions allowed to highlight the often opposing forces driving the encapsulation process which strongly depend on the size and shape of the gemini guest.

1. Introduction

All biological processes take place in water and involve reversible and weak non-covalent interactions between molecular species spanning from simple inorganic salts to several organic compounds. Naturally occurring receptors have inspired the design of water-soluble artificial receptors that simulate natural systems in their ability to bind a given substrate [1–4]. To this end, different receptors, such as cyclodextrins, cucurbiturils, resorcinarenes and calixarenes have been designed and their binding features extensively examined [5]. Recently, reversible encapsulation processes involving confined molecules [6–8] have been exploited to isolate species in small spaces for the stabilization [9,10] and transport of biologically relevant compounds [11] or the development of uncommon reaction pathways [12–15]. Molecular assemblies and containers formed by calixarene receptors, capable to recognize and suitably accommodate target guests, are systems of current interest. These ligands have an intrinsic bowl shape which makes them versatile building blocks for the formation of capsular-like adducts in solution [16].

We have shown that negatively charged gemini guests trigger the self-assembling of homodimeric capsules in the presence of a cationic calixarene receptor in aqueous solution at physiological pH [17,18]. These water-soluble architectures may form thanks to concerted hydrophobic and electrostatic interactions between the positively charged host and the aromatic and dianionic guests. Gemini guests interact with the calixarene by inserting their aromatic moieties into the lipophilic

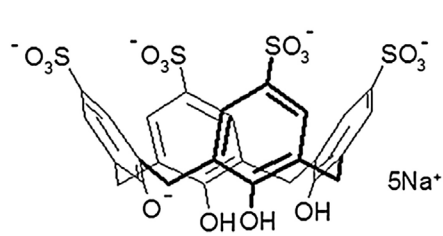
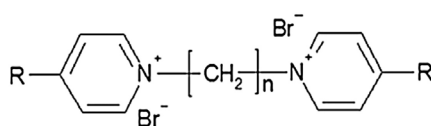
cavity of the host while placing their polar sulfonate groups at the charged upper rim of the calixarene [19–21]. The intriguing and versatile features of these host–guest systems have inspired new paths and strategies for the design of increasingly efficient capsules in such a competitive solvent [22,23].

We have recently reported on the formation of supramolecular capsular adducts in neutral aqueous solution through the recognition/inclusion of pyridinium-based gemini guests by the anionic *p*-sulfonato-calix[4]arene [24]. This receptor belongs to the prominent family of water-soluble calixarene derivatives which were first reported by Shinkai et al. [25]. Sulfonatocalix[n]arenes (SCnAs) have earned increasingly attention in supramolecular chemistry as they benefit from several advantageous features. They are easily prepared with good yields and are enough soluble in water to enhance the forces (e.g. hydrophobic and π -stacking interactions) driving guest inclusion into the host cavity that are more effective in aqueous than in organic media. The sulfonate groups at the upper rim provide synergistic anchoring points which enable SCnAs to display large binding ability and molecular selectivity towards a variety of organic cations. Finally, SCnAs are biocompatible and thus suitable for diverse biological and pharmaceutical applications [26,27]. Owing to their preorganized conical structures and the binding properties of their cavities, SCnAs have been employed for enzyme mimicking, molecular recognition, ion sensing, crystal engineering, catalysis, enzyme assays as well as several scopes in biological/medicinal chemistry [28,29].

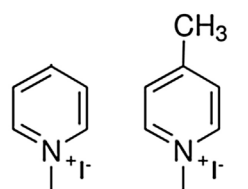
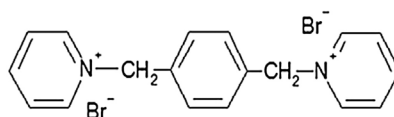
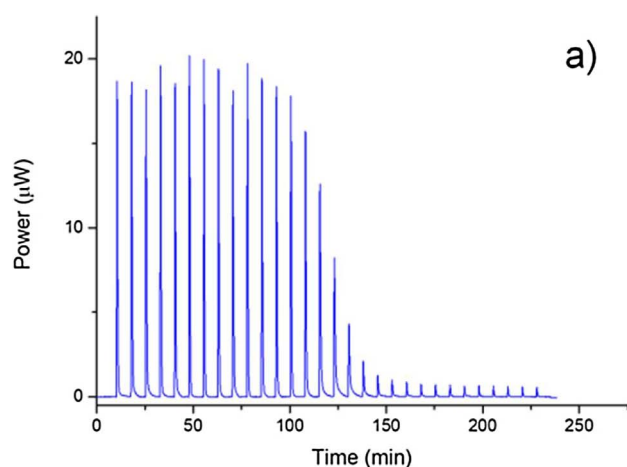
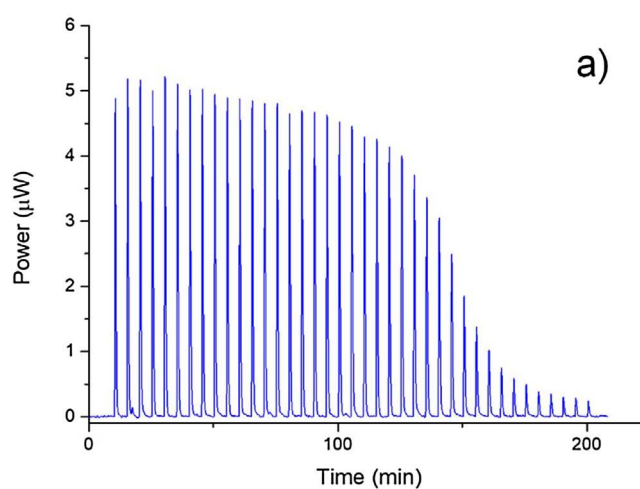
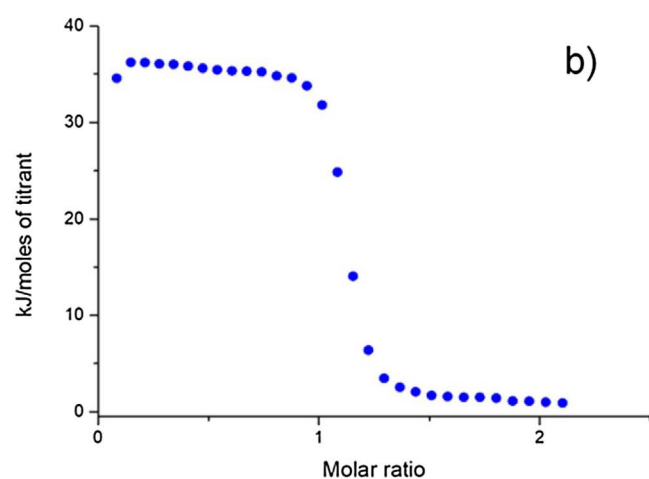
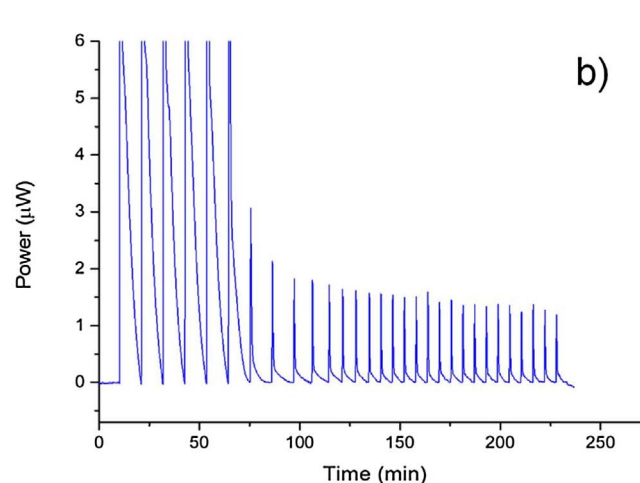
The molecular recognition properties of the *p*-sulfonato-calix[4]

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**C4TS****BPCn**

R=H; n=2, 4, 6, 8, 10

BPicC4R=CH₃; n=4**NMPy** **NMPic****BPX****Scheme 1.** Host and guests investigated.**a)****a)****b)****b)****Fig. 1.** a) Isothermal calorimetric titration of 3 mM **C4TS** into 0.3 mM **BPC6** at 25 °C in buffered aqueous solution (pH 6.9, phosphate buffer); b) integrated heat data.

arene **C4TS** with the cationic gemini guests shown in [Scheme 1](#) were initially investigated by ¹H and DOSY NMR spectroscopy. Two species were found to form in neutral aqueous solution: the 1:1 host-guest complex and the capsular-like assembly in which two hosts surround

Fig. 2. Isothermal calorimetric titrations at 25 °C in buffered aqueous solution (pH 6.9, phosphate buffer) of a) 1 mM **C4TS** into 0.08 mM **BPC6** (final H/G = 1.7); b) 10 mM **C4TS** into 0.5 mM **BPC6** (final H/G = 6; under these conditions, the HG complex is fully formed in the calorimetric vessel after 5–6 injections; however, these points will not be included in the data refinement and this experiment will deal just with the formation of the H₂G species.).

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