

Appendices

Lanthanoid assisted self-assembly of imidazolium cations in organic bi-layers†

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Multi-component solutions containing 1-*n*-ethyl-3-methylimidazolium or 1-*n*-butyl-3-methylimidazolium cations, *p*-sulfonatocalix[4]arene and large mono- or bis-phosphonium cations, as well as lanthanide metal ions, afford self-assembled material incorporating all four components. The calixarenes and phosphonium cations are organized into bi-layers, with the imidazolium cations and gadolinium(m) species incorporated between the bi-layers. The imidazolium cations are confined within essentially 'molecular capsules' based on two calixarenes from adjacent bi-layers, with these cations taking on different orientations, depending on the nature of the phosphonium cation, and whether the metal also binds to sulfonate moieties.

Introduction

Calixarenes are often used in engineering nano-materials, with their cavities able to include small molecules, and are generally referred to as cavitands. For example, the self-assembled solid state material based on *p*-*tert*-butylcalix[4]arene has been used in gas sorption studies, being able to trap gas molecules, including N₂, O₂, CO, CO₂, CF₃Br, CF₄ and CH₄, despite the porosity of the structure.¹ In general terms, calix[*n*]arenes with variable internal cavities, depending on the value of *n*, can be used for confining molecules in the solid state and in solution, depending on the size and shape of the calixarene. This can involve binding large organic molecules through to alkaline earth ions, by simply varying the value of *n* which corresponds to the number of phenolic rings linked together in forming the macrocycles.² Calixarenes can be selectively functionalized at the upper or the lower rim, further adding to their utility, for example, in acting as receptors in molecular recognition, or recognition of Na⁺ and K⁺ ions at the air-water interface.³

Calixarene functionalized at the upper rim with sulfonate groups, *p*-sulfonatocalix[*n*]arenes [*n* = 4, 5, 6 and 8], can act as versatile water soluble amphiphilic macrocyclic receptor molecules. They can bind organic molecules through weak non-covalent interactions, in building complex structures in the solid state, which is well documented.⁴ Moreover, sulfonated calixarenes provide anchoring points for the complexation of organic and inorganic moieties, with lanthanide metal ions, playing an important role in the stability and overall cohesion of the structures through charge balance, hydrogen bonding, bridging, and templating effects.⁵

p-Sulfonatocalix[4]arene, **1**, usually assembles into bi-layer structures with an 'up-down' antiparallel arrangement of the cones in the crystalline material.⁶ The bi-layers are able to confine a diverse range of guest molecules and ions including amino acids and related molecules,⁶ crown ethers and related macrocycles,⁷ viologens,⁸ quinolines,⁹ aquated metal ions, and organic cations including mono- and bis-phosphonium cations.¹⁰ The nature of the included species which can involve coordination, electrostatic, and hydrogen bonding interactions, in turn controls the distance between the bi-layers. The formation of 'molecular capsules'¹¹ is often encountered, with more complex structures possible, based on large spheroidal arrays,¹² nanotubules,¹³ 'Russian dolls' and 'ferris wheels'.¹⁴

We have investigated the complexation of different imidazolium cations, which reside in the cavity of the calixarene, providing a level of predictability on how the cations nestle within the bi-layers. The C₈ chain in 1-*n*-octyl-3-methylimidazolium cation results in the alkyl chain penetrating an adjacent bi-layer, the polar head group residing in the cavity of a calixarene, with gadolinium ions between the bi-layers.¹⁵ In expanding our studies on confining imidazolium cations between bi-layers built of *p*-sulfonatocalix[4]arene, we have explored the outcome of the self-assembly process for shorter alkyl chains, replacing the octyl group by ethyl and butyl, and the results are reported herein. This research was deemed as an important strategy in defining the limits in utilizing the ubiquitous imidazolium cations in constructing multi-component bi-layers. It is noteworthy that such imidazolium cations feature extensively in ionic liquids, with their physical and chemical properties varying according to the length of the alkyl chain, and the nature of the anions.¹⁶ In addition, bis-imidazolium cations have been shown to have each five-membered ring in the cavity of a *p*-sulfonatocalix[4]arene from the same bi-layer or from different bi-layers.¹⁶

Results and discussion

The reaction of a 1 : 1 : 1 ratio of **1** to 1-ethyl-3-methylimidazolium (2 or 3) or 1-butyl-3-methylimidazolium (4 or 5)

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Calixarene C₈-imidazolium interplay as a design strategy for penetrating organic bi-layers†

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1-Octyl-3-methylimidazolium (C₈-mim) cation forms multi-component bi-layers with *p*-sulfonatocalix[4]arene and phosphonium ions, and aquated lanthanide ions, with the imidazolium head group residing in the calixarene cavity and the terminus of the C₈ chain penetrating the adjacent hydrophobic bi-layer which is comprised of calixarenes and phosphonium ions, as part of a porous-like extended structure. Hirshfeld surface analyses reveal the nature of the interactions between the components.

Introduction

A large variety of ionic liquids have been developed with different cations and anions, with a view of exploiting their unique properties such as solubilising power, thermal stability, electrochemical window, etc.¹ The ubiquitous imidazolium-based ionic liquids are available with a diverse range of combination of different alkyl chain lengths on the imidazolium ring, and different counter ions, with the ionic liquids having tuneable properties.^{2–4}

Increasing the alkyl side chain length in 1-alkyl-3-methylimidazolium cations from methyl to butyl gets into the realms of ionic liquids, depending on the nature of the anion. For the series from butyl to octyl, there is an increase in the hydrophobicity of the ionic liquid, along with an increase in viscosity, and a decrease in density and surface tension values due to the formation of Coulombic layers where the ionic head-groups interact with the counter ions, and van der Waals layers are built from the stacking of the alkyl chains.^{5,6} Importantly, as the alkyl side chain of the cation becomes sufficiently long, for ionic liquid water mixtures, micelle like structures are prevalent, ultimately leading to phase separation.^{6,7}

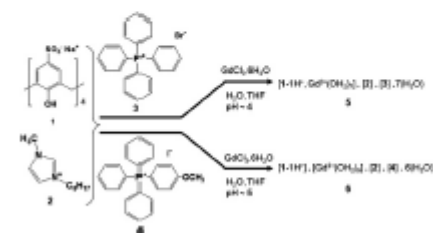
Given the above effect of increasing the alkyl side chain length, we have investigated the self assembly of 1-octyl-3-methylimidazolium (C₈-mim) with symmetrical and unsymmetrical phosphonium cations and *p*-sulfonatocalix[4]arene, **1**. Phosphonium cations and **1**, along with the larger ring size sulfonated calix[6] and [8]arenes, have recently been established in their own right to form discrete crystalline complexes, at least in the presence of aquated lanthanide ions.^{8–14} Also noteworthy is that in

the previous work, a phenyl ring of the phosphonium cation is bound within the cavity of a calixarene.

Herein we demonstrate the versatility of water-soluble sulfonated calix[4]arene in interacting with an imidazolium cation which features in some ionic liquids. This involves establishing host-guest chemistry of the two components in the solid state and how this relates to the interplay of other guest molecules with the same calixarene as reported in other works.^{15–20} Remarkably C₈-mim **2**, forms four component complexes with the calixarene macrocycle **1**, phosphonium cations **3** or **4**, and aquated lanthanide metal ions as an unconventional bi-layer arrangement.²⁰ The selectivity of the charged head group to reside in the cavity of the calixarene as a host-guest component is significant, as is the organic tail of the host-guest complex penetrating the adjacent bi-layer. Hirshfeld surface^{21,22} analysis has also been undertaken for understanding the nature of interplay of the molecules in such complex self assembled systems.

Results and discussion

Complexes **5** and **6** were obtained from water/tetrahydrofuran (THF) by slow evaporation of an equimolar mixture of **1** and **2** and a three-fold excess of aqueous gadolinium(III) chloride, with phosphonium cations, **3** or **4**, as bromide and iodide salts respectively, Scheme 1. Both complexes **5** and **6** crystallise in the



Scheme 1

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Multi-component bi-layers featuring [1-octyl-2,3-dimethylimidazolium \cap *p*-sulfonatocalix[4]arene] supermolecules†

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Multi-component solid state structures containing 1-octyl-2,3-dimethylimidazolium cations, anionic *p*-sulfonatocalix[4]arenes and/or large mono-phosphonium cations, as well as lanthanide metal ions are readily accessible, which have the calixarenes organised into bi-layers with gadolinium(III) coordinated between them. The imidazolium ring is confined in the calixarene cavity, essentially forming "molecular capsules" based on two calixarenes, or with the *n*-octyl chain penetrating the adjacent bi-layer, with the nature of the calixarene-dimethylimidazolium interplay mapped out using Hirshfeld surface analysis. The supermolecules [1-octyl-2,3-dimethylimidazolium \cap *p*-sulfonatocalix[4]arene] are persistent in aqueous solutions (¹H NMR).

Introduction

Imidazolium cations feature in room-temperature ionic liquids as "green solvents", with negligible vapour pressure at room temperature, large liquidus range and a highly solvating capacity in non-coordinating medium, in which a number of organic, inorganic as well as organometallic compounds can be dissolved.^{1–4} Ionic liquids have tunable physicochemical properties depending on the choice of the cation and/or the anion, which typically consist of a bulky, unsymmetric organic cation and smaller organic or inorganic anions.^{3,4} Among the physical properties of ionic liquids, viscosity, density and surface tension are particularly important in the choice of ionic liquid for various applications. Varying the alkyl chain length from ethyl to octyl for a series of 1-alkyl-3-methylimidazolium cations, increases the hydrophobicity and the viscosity of ionic liquids containing such cations, while there is a descending trend in density and surface tension.⁵

In aqueous solutions, ionic liquids have surface active properties similar to surfactants, which leads to self-organisation into micelles or aggregates, depending on the alkyl chain length.⁶ Imidazolium cations with a short chain system can be modeled as polydispersed spherical aggregates, whereas a long chain system can be modeled as a system of regularly sized near-spherical charged micelle.⁷ Addition of a certain amount of water to ionic liquids with long chains results in spontaneous self-organisation into liquid-crystalline ionogels, where segregation of the hydrophilic and hydrophobic

segments takes place, forming regions of confined water, ultimately with the onset of gelation.^{8,9}

We have investigated the complexation of different imidazolium cations with calixarenes in the solid state. The octyl chain in 1-*n*-octyl-3-methylimidazolium cation penetrates an adjacent bi-layer comprised of calixarenes and phosphonium cations, with the polar head group residing in the cavity of a calixarene.⁹ We have also explored the outcome of the self assembly of imidazolium cations with shorter alkyl chains, with ethyl and butyl groups resulting in the formation of bi-layers, with "molecular capsules" comprised of two calixarenes confining an imidazolium cation spanning the bi-layers.¹⁰

In general "molecular capsules" are of interest because of their potential applications in separation technology and sensors.¹¹ Anionic *p*-sulfonatocalix[4]arenes in a bowl-shaped configuration bearing sulfonate groups in the upper rim, can arrange in the solid state, essentially forming "molecular capsules" with various guest molecules confined in the capsule core.¹² The confined guest molecules have inherently weak interactions involving hydrogen bonding and π -stacking, which presumably contributes to the formation and stabilisation of the capsules within the extended structures.¹³ Such calixarenes are also effective in accommodating a wide range of guest molecules in their cavities, including crown ethers,¹⁴ amino acids,¹⁵ nucleic acid bases and derivatives,¹⁶ phenanthroline¹⁷ and viologens.¹⁸ Here the calixarenes are usually arranged into a bi-layer arrangement with varying degrees of complexity.^{16,19}

We now report that the *n*-octyl dimethylimidazolium cation which features in ionic liquids,²⁰ binds to the water soluble sulfonated calix[4]arene, forming complex arrays in the solid state in the presence of large organic phosphonium cations, and lanthanide cations. The use of a long alkyl chain relates to our previous findings for the imidazolium cation devoid of the C-methyl group, where two different assemblies were identified, and when coupled with the results herein, now allows an emerging level of predictability in building complex structures based on these components. The nature of interplay of the molecules in the complex self assembled systems is further analysed and examined using Hirshfeld surface²¹

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Selective Binding of Imidazolium Cations in Building Multi-Component Layers

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Abstract: Addition of 1-alkyl-3-methyl-imidazolium (C_n mim) cations 3–5 to a mixture of bis-phosphonium cation 2 and sodium *p*-sulfonato-calix[4]arene (1) in the presence of lanthanide ions results in the selective binding of an imidazolium cation into the cavity of the calixarene. The result is a multi-layered solid material with an inherently flexible interplay of the components. Incorporating ethyl-, *n*-butyl- or *n*-hexyl-mim cations into the multi-layers

results in significant perturbation of the structure, the most striking effect is the tilting of the plane of the bowl-shaped calixarene relative to the plane of the multi-layer, with tilt angles of 7.2, 28.9 and 65.5°, respectively. The lanthanide ions facilitate complexation,

Keywords: bis-phosphonium cations • calixarenes • host-guest systems • imidazolium cations

but are not incorporated into the structures and, in all cases, the calixarene takes on a 5– charge, with one of the lower-rim phenolic groups deprotonated. ROESY NMR experiments and other ¹H NMR spectroscopy studies establish the formation of 1:1 supermolecules of C_n mim and calixarene, regardless of the ratio of the two components, and indicate that the supermolecules undergo rapid exchange on the NMR spectroscopy timescale.

Introduction

Supramolecular tectons based on organic cavitands have been extensively studied, especially those involving calixarenes and related molecules. These studies have provided a large platform of structural diversity for the formation of multi-component complexes. These include organic molecules of various sizes and shapes, bound through multiple inherently weak interactions.^[1] The smaller ring-size calix[4]- and calix[5]arenes usually adopt the cone-shaped conformation and can bind a wide range of guest molecules in the

cavity, from small solvent molecules like dichloromethane, through to large globular molecules like carboranes and fullerenes.^[2] The self-assembly of these supermolecules can generate infinite networks based on interactions between the organic components and through metal coordination.^[3] In contrast, the larger, readily accessible ring-size calix[6]- and calix[8]arenes can take on a plethora of different conformations (for example, the double-cone conformation) and can also form host-guest and inclusion complexes.^[4]

The water-soluble, small-ring *p*-sulfonated calix[4]arene (1) forms inclusion complexes with the calixarenes arranged in “up-down” antiparallel bilayers when configured in its almost universal cone shape.^[5] More complicated supramolecular architectures are also known, which include helical arrays and icosahedral and cuboctahedral spheroidal arrays comprised of twelve calixarenes. The synthetic strategy for forming such bilayers involves the use of small molecules for inclusion into the calixarene cavity and the extended structure, as well as the use of metal ions, in particular aquated lanthanide ions. Each bilayer has a divergent hydrophilic surface with the cavities of the calixarenes directed away from the bilayer plane.^[6] Alignment of the cavities from one bilayer with the cavities of an adjacent bilayer effectively creates a molecular capsule comprised of two calixarenes. The capsule can contain one common organic molecule, such as a crown ether,^[7] or multiple small molecules,

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Constructing Multicomponent Materials Containing Cavitands, and Phosphonium and Imidazolium Cations

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ABSTRACT: Bis-imidazolium cations, 1,1'-[1,4-phenylenebis(methylene)]bis(3-R-1H-imidazolium-1-yl), (R = methyl or *n*-butyl), form discrete multicomponent complexes in water with various phosphonium cations, anionic *p*-sulfonatocalix[4]arene, and aquated gadolinium(III) ions. The terminal alkyl groups, R, reside in the cavities of the calixarenes, with two calixarenes either adjacent to each other, where they face the same direction and are in the same bilayer arrangement made of calixarenes and phosphonium cations, or where they face opposite directions. Here the calixarenes are similarly part of a bilayer arrangement, or they are part of an extended structure which can be regarded as being built from the assembly of supermolecules or "molecular capsules", [(bis-imidazolium)C(p-sulfonatocalix[4]arene)₂], which are π -stacked through the calixarenes in a head-to-tail fashion. The nature of the product depends on the length of the terminal alkyl group, and the choice of phosphonium cation.

Introduction

Self-assembly involves molecular recognition events with some complementarity of inherently weak interactions, and is a paradigm in building new material. Water-soluble sulfonated calixarenes have been extensively investigated as supramolecular tectons (or building blocks) in crystal engineering, and supramolecular chemistry in general. *p*-Sulfonatocalix[4]arene is the smallest oligomer for these macrocycles and is usually in the cone conformation, where it often assembles in the solid state in the up-down antiparallel bilayer arrangement, simultaneously creating hydrophobic and hydrophilic environments.¹ The bilayer arrangement serves as a platform in the construction of material that mimic the structure and properties of naturally occurring clays.

p-Sulfonatocalix[4]arene can also assemble into more complex arrays, including icosahedral and cuboctahedral arrangements, with the cavities directed away from their surfaces,^{2,3} and "Russian doll" and "ferris wheel" type arrangements.⁴ These arrangements, and the bilayer arrangement, can include metal ions, and organic molecules, with the calixarene being versatile in binding a range of molecules of different sizes and shapes.⁴ The sulfonate groups in *p*-sulfonatocalixarenes in general provide anchoring points for the complexation of organic and inorganic guest molecules, as well as metal ions.⁵ A systematic study on the interplay of Ph_4P^+ with *p*-sulfonatocalix[4]arene using a combinatorial approach generated an extensive library of compounds, depending on the ratio of the ions, pH, and the ionic strength of the solutions.^{6,7} Two major findings have been described: (i) the ability to form pseudopolymorphic phosphonium complexes with one of the phenyl groups of the cation residing in the cavity of the calixarene, and (ii) the arrangement of phenyl embraced phosphonium cations around the calixarene.⁸

Imidazolium cations feature extensively in ionic liquids, which are rapidly gaining prominence through their diversity

of applications in synthesis, materials science, and more.⁹ It is noteworthy that the amphiphilic nature of ionic liquids based on imidazolium cations results in their aggregation which is similar to the behavior of cationic surfactants, and long-chain imidazolium cations can self-organize to form micelles and lyotropic liquid crystals.¹⁰ Related to this is the organization of ionic liquids based on imidazolium cations whereby the anions and cations are arranged alternately.¹¹ Solid-state structures of imidazolium ionic liquids themselves show an interesting interplay of the ions, forming both hydrophilic and hydrophobic channels associated with the arrangement of the alkyl groups.^{10,12}

Recently, the synthesis of ionic liquids based on bis-imidazolium cations was reported.¹³ We have prepared such cations and show herein that they are flexible in building multicomponent ionic solids, in conjunction with *p*-sulfonatocalix[4]arene, and selected phosphonium cations, along with aquated gadolinium(III) ions. Specifically, we have prepared and structurally authenticated complexes containing the designer cations: 1,1'-[1,4-phenylenebis(methylene)]bis(3-methyl-1H-imidazolium-1-yl) (2) and 1,1'-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl) (3) and the phosphonium cations, 4–6, Scheme 1. We show that the terminal groups of the bis-imidazolium cations, 2 and 3, bind in the cavities of two calixarenes which are either facing each other and from adjacent bilayers, or face the same direction in the same bilayer; these type of arrangements are comparable to the inclusion of methyl and benzyl viologens in the *p*-sulfonatocalix[4]arene system.¹⁴

Results and Discussion

The combinations of components, which afforded crystals of complexes I–IV, are summarized in Table 1. The complexes were grown using an equimolar amount of each component with excess of aquated gadolinium(III) ions (typically 3 mol equivalents). In all structures, the terminal parts of the dications reside in the cavities of two calixarenes and are selectively drawn into the space between the phenyl embraced layers of

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***p*-Sulfonatocalix[4]arene–Pyrrolidinium Complexation in Building Multicomponent Layered Arrays**Irene Ling,[†] Yatimah Alias,^{*†} Alexandre N. Sobolev,[‡] and Colin L. Raston^{*†}[†]Chemistry Department, Faculty of Science, University of Malaya, 50608 Kuala Lumpur, Malaysia and[‡]Centre for Strategic Nano-Fabrication, School of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia

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ABSTRACT: *p*-Sulfonatocalix[4]arene and monophosphonium ions, in the presence of *N*-butyl-*N*-methylpyrrolidinium ions and aquated lanthanide ions, assemble into bilayers comprised of calixarenes with the phosphonium cations embedded between them; pyrrolidinium ions reside in the calixarene cavities which are normal to the bilayer plane. Replacing the phosphonium cations with bis-phosphonium ions results in the same interplay of the calixarene and pyrrolidinium cations, but with the formation of a different layered structure, which is now devoid of lanthanide ions, unlike the other bilayers, with all the sulfonate groups of the calixarenes residing in a plane with adjacent calixarenes in alternating directions. In aqueous solutions, a 1:1 supermolecule of the calixarene and pyrrolidinium ion is evident in aqueous solution using ¹H NMR spectroscopy.

Introduction

Host–guest chemistry involving self-assembled molecular containers has potential in various applications, for example, in separation science, receptors, and sensor technology.¹ Cone-shaped calixarene, resorcinarene, and pyrogallolarene can act as receptor molecules with the host–guest supermolecules readily assembling into complex arrays.² This includes the formation of large hydrogen-bonded nanocapsules based on six *C*-methylresorcin[4]arenes and *C*-alkylpyrogallol[4]arenes.³ In the case of calixarenes, the lowest oligomer in the series can assemble into icosahedral and cuboctahedral arrays comprised of 12 such molecules, and continuous structures, depending on the conditions, and the presence of other components.⁴

A variety of different calixarene analogues have been developed, which are effective in molecular and ion encapsulation, and molecular recognition in general.⁵ Water-soluble amphiphilic sulfonated calix[4]arene, **1**, can act as a host for a wide range of guest molecules which then assemble into a diverse array of structures.⁶ Solid-state structures made up of “molecular capsules” based on two *p*-sulfonatocalix[4]arenes are capable of encapsulating a variety of guest molecules such as crown ethers, tetraprotonated cyclam, diprotonated [2,2,2]cryptand, amino acids, and phenanthroline.⁷ In forming “molecular capsules” or otherwise, calix[4] and 5arenes tend to adopt a cone conformation.

We have previously reported on the complexation of imidazolium cations bearing different terminal alkyl groups with *p*-sulfonatocalix[4]arene, where the charged aromatic ring is selectively drawn into the cavity of the calixarene. The solid-state structures can be considered as being based on bilayers built of “molecular capsules” spanning the bilayers,⁸ and when the imidazolium cation has long straight chain alkyl groups, the alkyl chain penetrates the adjacent bilayer.⁹ Herein we investigate the self-assembly involving *N*-butyl-*N*-methylpyrrolidinium, **2**, which like imidazolium cations,

is a common component of ionic liquids. This is with *p*-sulfonatocalix[4]arene, various phosphonium cations, and lanthanide metal ion, Scheme 1. It is noteworthy that the high intrinsic ionic conductivity of ionic liquids containing pyrrolidinium cations is of interest in small electroenergetic (battery component) applications.¹⁰ We find that in all complexes the pyrrolidinium cation has the five-membered heterocyclic residing in the calixarene cavity rather than a phenyl ring of a phosphonium cation.¹¹

Results and Discussion

Colorless crystals of complexes of **I**, **II**, and **III** (Scheme 1) were obtained by slow evaporation from water/tetrahydrofuran (THF) of an equimolar mixture of **1** and **2** with different phosphonium cations, in the presence of a 3-fold excess of aqueous gadolinium(III) chloride. All complexes crystallize in the triclinic space group *P* $\bar{1}$, with each comprised of calixarene anions, pyrrolidinium cations, and phosphonium cations, as well as lanthanide ions (complex **III** excepted) in the ratio 1:1:1:3(0), and included water molecules. In all cases, the pyrrolidinium cations reside in the calixarene cavities with the *N*-butyl chain directed away from the cavity. The *N*-butyl chain is bent in complex **II** which presumably relates to the difference in the mode of coordination of the gadolinium(III) cations, which is manifested in different thicknesses between the calixarene bilayers.

Complex **I**. Complex **I** has one each of the calix[4]arene, pyrrolidinium, benzyltriphenyl phosphonium ions, and a coordinated lanthanide ion, and included water molecules in the asymmetric unit. The conformationally restricted cone-shaped calix[4]arenes, take on a 5– charge (removal of one H-atom on the lower rim) and are arranged back-to-back in bilayers. Each heteroleptic gadolinium(III) metal center is attached to a sulfonate group (Gd–O at 2.437(1) Å) and is coordinated by seven water molecules (Gd–O at 2.355(1)–2.447(1) Å). The water molecules in general are involved in an extensive hydrogen bonding with O...O distances in the range 2.706(2)–2.958(2) Å. Some of the coordinated water molecules are in close proximity to

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Water solubilisation of single-walled carbon nanotubes using *p*-sulfonatocalix[4]arene

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Single-walled carbon nanotubes (SWCNTs) are decorated with nanoparticles of *p*-sulfonatocalix[4]arene which render the nanotubes soluble in water. The nanocomposite was prepared by a solventless grinding method, followed by the addition of water then sonication. The non-covalently modified carbon nanotubes have been characterized using Raman, FTIR spectroscopy, fluorescence spectroscopy, transmission electron microscopy and thermogravimetric analysis.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are rolled-up graphene sheets, which possess remarkable electronic, thermal, optical and mechanical properties.^{1–5} They have been intensely studied for various applications, especially for energy storage, and in nanoelectronics and nanodevices.^{6–9} However, the strong van der Waals attraction between individual hydrophobic nanotubes results in the formation of large bundles, which are insoluble in water. This has limited the applications of SWCNTs, and necessitates the use of intricate processing.^{4,10–13} SWCNTs are also poorly soluble in organic solvents, but this can be overcome using various methods of surface modification. Such methods can also render the SWCNTs soluble in water, which is important in biosensors and drug-delivery systems.⁵ Another method to form solubilised SWCNTs in aqueous media is the introduction of amphiphilic molecules as dispersants, such as surfactants,^{4,13–17} and polymers.^{4,5,18,19} Other methods of enhancing the solubilisation and suspension of SWCNTs in aqueous media include chemical modification at the side walls, defect sites and open ends,⁴ as well as cutting the long entangled CNTs to short lengths.²⁰

Attaching organic hydroxy^{21,22} or amide^{23–24} functional groups to SWCNTs is effective in dispersing them in water through extensive hydrogen-bond formation.²⁴ The incorporation of these functional groups involves a variety of approaches, which includes covalent side-wall coupling reactions, end-group reactions and non-covalent interactions.⁵ Covalent attachment of the organic groups on SWCNTs is most effective using cycloaddition and radical addition reactions.^{19,25–27} A significant disadvantage of covalent functionalisation, however, is the perturbation of the

electronic properties of the SWCNTs, and thus side-wall functionalisation techniques are less favourable compared to non-covalent functionalization.^{19,28,29} Non-covalent attachment of functional groups to SWCNTs involves adsorption of polynuclear aromatic compounds (anthracene,³⁰ pyrene³¹ and porphyrins³² derivatives), synthetic polymers (polystyrene sulfonate and polyvinyl pyrrolidone),¹¹ and adsorption of biomolecules (DNA^{33,34} and peptides^{35,36}). In the non-covalent interaction, aromatic molecules are anchored on the walls of the SWCNT where the hydrophobic part is oriented towards the coplanar surface of the nanotubes via effective π - π stacking while the polar moiety interacts with the solvent regime.^{4,19,27,37} The size of the aromatic moiety as well as the curvature of the nanotube surface determine the strength of the π - π interactions and for molecules containing heteroatoms, the heteroatom- π electron interactions contribute to the interplay of the two components.^{4,38}

Polymers bearing sulfonated organic molecules are effective in encapsulating and solubilising carbon nanotubes in water.^{4,34,38,39} Instead of using a sulfonated polymer we chose a polysulfonated macrocycle, notably *p*-sulfonatocalix[4]arene, to solubilise SWCNT in water. *p*-Sulfonatocalix[4]arene is a cyclic tetramer with hydroxy groups at the lower rim and sulfonate groups at the upper rim. Herein we show that it is effective in solubilising SWCNTs in water, which are surprisingly decorated with nanoparticles of the calixarene on the surface of the nanotubes, rather than the calixarene acting as a surfactant with the molecules assembled over the entire surface.

The non-covalent functionalisation of SWCNT involves *p*-sulfonatocalix[4]arene. This cup-shaped amphiphilic macrocycle is a cyclic tetramer comprised of four phenolic moieties joined by methylene bridges with hydroxy groups at the lower rim and sulfonate groups at the upper rim. Our findings are in direct contrast to a recent report that SWCNTs are insoluble in the presence of *p*-sulfonatocalix[4]arene, and also *p*-phenol sulfonic acid, but not so for the corresponding calix[6] or [8]arene analogues.⁴⁰ Interestingly *p*-sulfonatocalix[4] or [6]arenes modified by alkyl substituents on the phenolic oxygen centre also water-solubilise SWCNTs,⁴¹ as do

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