Multi-component bi-layers featuring [1-octyl-2,3-dimethylimidazolium ∩ 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 ∩ p-sulfonatocalix[4]arene] are persistent in aqueous solutions (^{1}H 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-methyl-imidazolium 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.[6,8]

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[4,5]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] phenanthroline[17] and viologens.[18] Here the calixarenes are usually arranged into a bi-layer arrangement with varying degrees of complexity.[14,19]

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 surface[21]

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analysis, and imidazolium cation–calixarene association in solution is investigated using ^{1}H NMR spectroscopy.

Results and discussion

Slow evaporation of equimolar mixtures of **1** and **2** and phosphonium salts, **3** or **4**, in the presence of a three-fold excess of aqueous gadolinium(III) in water–tetrahydrofuran (THF), Scheme 1, afforded complexes **I** and **II**, Fig. 1. In both cases, the n-octyl dimethylimidazolium cation is selectively drawn into the calixarene cavity primarily through the *N*-methyl group. Both structures have a bi-layer arrangement of calixarenes, with one arranged back-to-back and the other in an offset back-to-back manner, with and without incorporation of phosphonium cations, but the interplay of the bi-layers is distinctly different. Complex **I** can be considered as being built of "molecular capsules" with the imidazolium cation encapsulated by two calixarenes with the alkyl chain bent. In contrast, complex **II** has the essentially straight long alkyl chain of the imidazolium cation penetrating the next calixarene bi-layer.

Complex I

Complex **I** crystallises in the monoclinic space group $P2_1/m$, ($Z = 2$), with the asymmetric unit comprising of a p-sulfonato-calix[4]arene with an aquated gadolinium(III) cation, one n-octyl dimethylimidazolium cation distributed between two positions, and one phosphonium cation [(3-methoxyphenyl)-triphenylphosphonium], along with half-populated disorder including water molecules. The calixarenes form "molecular capsules" over inversion centres, although electrical neutrality requires one of them to take on a 4− charge and the other a 5− charge. Thus one proton has been removed from the lower rim of one of the calixarenes making up the walls of the "capsules". The homoleptic gadolinium(III) metal ions are located on a mirror plane with one forming a secondary coordination sphere with eight disordered water molecules while the other has nine water molecules. The metal ion interacts with the calixarene through hydrogen bonding in
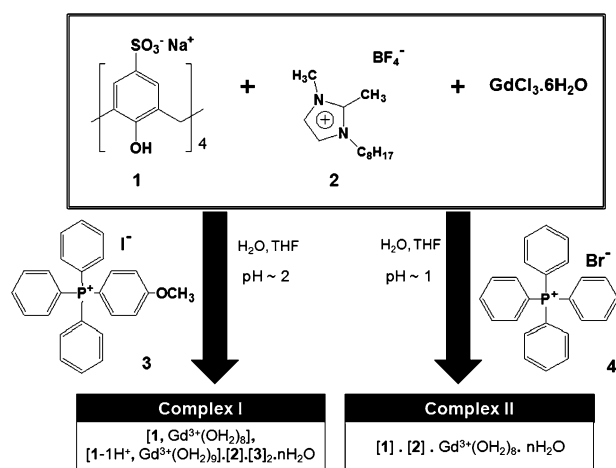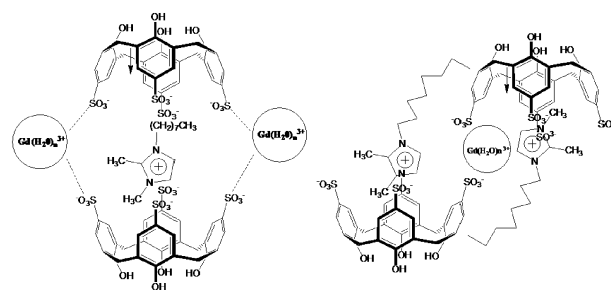
Fig. 1 Different arrangements of the n-octyl dimethylimidazolium cation within the "molecular capsule" (left) and the bi-layer (right), for complexes **I** and **II**, respectively.

the equator of "molecular capsules", as judged by the close proximity of the O-atom of the sulfonate group to the aquated gadolinium cations, the closest O$\cdots$O distances being 2.529(1) to 2.883(2) Å. The disordered water molecules are involved in extended hydrogen bonding with O$\cdots$O distances in the range 2.622(8) to 3.061(6) Å.

In the extended structure, the "molecular capsules" are embedded into the usual bi-layer arrangement, Fig. 2, with each "capsule" shrouding one disordered imidazolium cation over two sites with equal population. The imidazolium charged head group is positioned within the calixarene cavity, with the calixarene pinching around the guest. The angles of all four phenolic rings with the basal plane of the four methylene bridges at the lower rim of the calixarene are 51.11(1)°, 63.55(5), 45.18(6)°, and 63.06(4)°. The encapsulated imidazolium cations have multiple interactions with the walls of the capsules, namely weak hydrogen bonding and C–H$\cdots\pi$ interactions, Fig. 3. The charged head group of the dimethyl-imidazolium cation is involved in: (i) C$\cdots\pi$ (centroid) inter-actions from the methyl group to the phenyl ring of the calixarene with a C$\cdots$ring centroid distance of 3.61 Å, and (ii) hydrogen bonding to the calixarene sulfonate groups, with C–H$\cdots$O distances ranging from 2.51 to 2.78 Å (corresponding C$\cdots$O distances are 3.28 to 3.64 Å). The long aliphatic chain is distorted and resides in the calixarene cavity, with (i) C–H$\cdots$O close contacts ranging from 2.30 to 2.81 Å (corresponding C$\cdots$O distances are 3.21 to 3.79 Å), and (ii) C–H$\cdots\pi$ (centroid) interactions to the phenyl ring of the calixarene, with distances ranging from 2.64 to 2.74 Å (corresponding C$\cdots$O distances are 3.56 to 3.63 Å).

The bi-layer contains calixarenes and phosphonium cations which are in the common phenyl embrace arrangement in a grid network, filling the interstices between the interfaces of the calixarene hydroxyl groups with an overall bi-layer thickness of 13.0 Å, Fig. 2. This type of arrangement has been reported with a similar combination of calixarenes and phosphonium cations, Fig. 4.[22] The phosphonium cations have C$\cdots\pi$ close contacts at 3.64 Å involving the interaction between the calixarene methylene bridge and the phenyl ring of the phosphonium cation. The H-atoms on the phosphonium cations are also involved in weak hydrogen bonding with O-atoms of the calixarene molecules, for both the sulfonate and hydroxyl groups, with short contacts from 2.60 to 2.70 Å and 2.86 Å (corresponding C$\cdots$O distances are 3.44 to 3.45 Å and 3.72 Å), respectively. The "molecular capsules" are

Scheme 1 Synthesis of the two complexes based on four different components: **1** as the calixarene, **2** as the imidazolium cation, **3** or **4** as phosphonium cations, and aquated gadolinium(III).
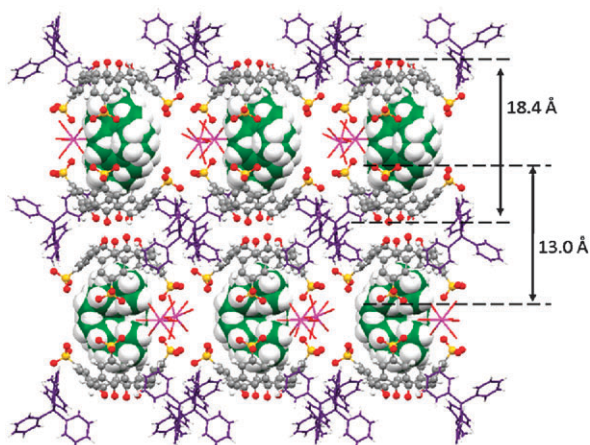
Fig. 2 Projection of complex **1** along the *a*-axis showing the arrangement of n-octyl dimethylimidazolium cations (green) encapsulated in the "capsules" of calixarenes.
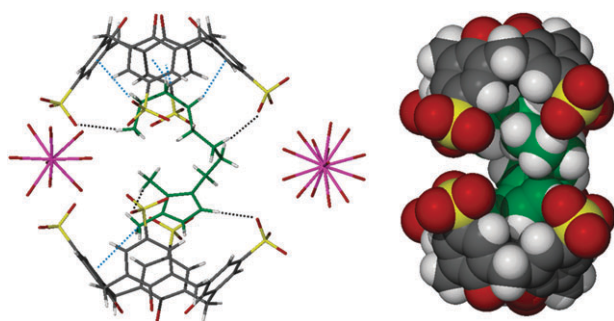

Fig. 3 Arrangement of n-octyl dimethylimidazolium cation in the "molecular capsule" in complex **I**, showing nearest contacts (left) and the corresponding space filling (right). The disordered parts of the imidazolium cation are omitted for clarity.

approximately 18.4 Å in length along the principle axis, Fig. 2. Interestingly *p*-sulfonated calix[5]arene can form bi-layer structures in the presence of gadolinium(III), with a similar "molecular capsule" arrangement, incorporating pyridine N-oxide.[23]

Complex II

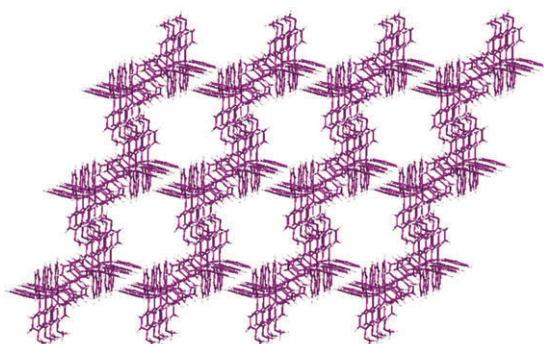Complex **II** crystallises in the triclinic space group $P\bar{1}$, ($Z = 2$), with the asymmetric unit comprised of one calix[4]arene, one imidazolium cation and one gadolinium(III) cation, which has a secondary coordination sphere through hydrogen bonding with the calixarenes and water molecules. The homoleptic metal ion is coordinated by eight water molecules, and has close contacts with the sulfonate groups of the calixarene through extensive hydrogen bonding, the Gd–O···O distances ranging from 2.684(2) Å to 2.840(1) Å. The crystalline water molecules in the extended structure are involved in a hydrogen bonding network with O···O distances in the range of 2.687(2) to 2.902(2) Å.

In complex **II**, the large phosphonium cations are absent in the structure which is reflected in a significant difference in the distance between the bi-layers, with a more compact inter layer, 14.7 Å thick, and bi-layer, 9.67 Å thick, Fig. 5. In our previous structure based on n-octyl imidazolium,[9] the bi-layer thickness is much larger, which relates to the incorporation of the positively charged phosphonium cations within the bi-layers. The n-octyl dimethylimidazolium cation in the present study fits tightly in the calixarene cavity in the pinched cone configuration (the angles between the plane of all four phenyl rings of the calixarene with respect to the basal plane consisting of four methylene bridges are 73.02(4)°, 37.33(4)°, 71.61(4)°, and 42.14(4)°), Fig. 5, with the long alkyl chains in contact with a neighbouring calixarene molecule, and penetrating the adjacent bi-layer. The flexibility of the n-octyl is demonstrated with the alkyl chain being slightly twisted in being accommodated into the tightly packed bi-layer.

The n-octyl dimethylimidazolium ring resides in the calixarene cavity, through (i) C···π interactions of the methyl groups and the phenyl rings of the calixarene, with close distances ranging from 3.32 to 3.33 Å, and (ii) C–H···O interactions between H-atoms of the cation and calixarene sulfonate groups, with C–H···O distances ranging from 2.64 to 2.72 Å (corresponding C···O distances are 3.19 to 3.32 Å). Multiple close contacts involving the n-octyl chain and neighbouring calixarene are evident with the octyl chain penetrating the next bi-layer, in between calixarenes, with (i) C–H···O contacts at 2.74 and 2.93 Å (corresponding C···O distances are 3.46 and 3.90 Å) for adjacent sulfonate groups, and (ii) C–H···H–C contacts ranging from 2.49 to 2.58 Å (corresponding C···C distances are 3.95 to 4.35 Å) for H-atoms on the calixarene molecules. The terminal C-atom of the octyl chain nestles close to a methylene bridge of a calixarene in the next bi-layer at 4.18 Å (corresponding H···H distance 3.49 Å).
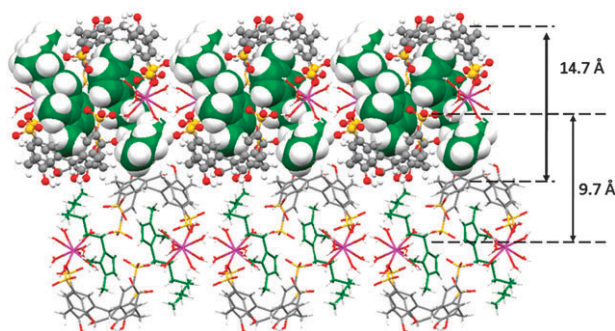

Fig. 4 Stick representation of embedded phosphonium molecules projected along the *b*-axis in complex **I**.

Fig. 5 Projection of the extended structure in complex **II** along the *a*-axis, with some space filling of the imidazolium cations (green).

Hirshfeld surface analysis

Visualisation of close intermolecular interactions between the molecules in the solid state was undertaken using Hirshfeld surface analysis. The parameter d_{norm} is of particular interest, as it displays a surface with a red-white-blue colour scheme; bright red spots for contacts shorter than the sum of their van der Waals radii, while blue regions are devoid of close contacts.[24] Fig. 6(a) and (c) show the Hirshfeld surfaces for both the calixarene anion and dimethylimidazolium cation for complex **II**. The Hirshfeld surface analysis was not undertaken for complex **I** because of the disorder fragment associated with the dimethylimidazolium cation.

The red regions with yellow arrows pointing identify the closest contacts associated with H···C interactions (*i.e.* C–H···π) between dimethylimidazolium cation and calixarene. In the fingerprint plots, the area circled in yellow corresponds to the C–H···π interactions with $d_e + d_i = 2.5$ Å, and the wing at the upper left of the plot, Fig. 6(d), highlights the characteristic C–H···π donor interactions involving the H-atom of imidazolium cation pointing towards the calixarene phenyl rings (centroids), making up 16% of the Hirshfeld surface. Three distinct spikes in the fingerprint plot Fig. 6(b) are evident, resulting from the weak hydrogen bonding interactions and are identified as red regions (green arrows) in Fig. 6(a) and 6(c). The spike (circled in green), results from close C–H···O contacts, principally from the dimethylimidazolium H-atoms in close proximity to the calixarene sulfonate groups, making up 26% of the Hirshfeld surface. The outermost spikes in the same plot (circled in red) represent O···H hydrogen bonding interactions, with the lower spike being the acceptor spike (O-atoms from the calixarene interacting with H-atoms from water molecules), and the upper spike is the donor spike (H-atoms from calixarene interacting with O-atoms from water molecules).
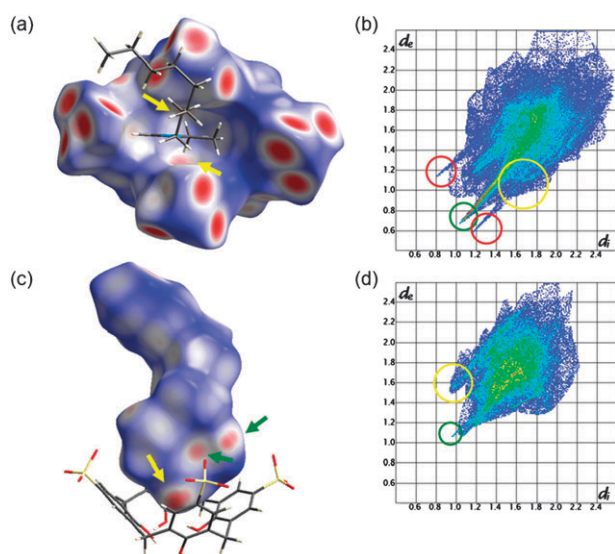
The fingerprint plots are similar in shape to other published crystal structures of n-octyl dimethylimidazolium, but there are differences between the structures.[9] These relate to the arrangement of n-octyl methylimidazolium molecules in the cavity of calixarenes, and the shorter, closer C–H···π and C–H···O interactions, noting the imidazolium ring in the present study has a C-methyl substitution.

Solution studies

The interplay of the n-octyl dimethylimidazolium cation and *p*-sulfonatocalix[4]arene was examined using ¹H-NMR at 25 °C in D_2O, for a 1:1 mixture of the two species, Fig. 7. This shows that the two components indeed form supermolecules in solution, [1-octyl-2,3-dimethylimidazolium ∩ *p*-sulfonatocalix[4]arene], rather than the interplay of the two components in the solid state being associated with crystal packing. We note that the imidazolium BF_4^- salt has limited solubility in water for greater than a 1:1 mixture with the calixarene, and determining a binding constant was not possible as the system is likely to be complicated by complex micelle formation. In this context it is noteworthy that in the ionic liquid–water system, the imidazolium based ionic liquids with long alkyl chains on the imidazolium ring can initiate phase separation.[3]

As to the formation of supermolecules, the upfield chemical shifts experienced by the *N*-methyl (Hγ), the closest carbon atom of n-octyl (Hβ), and the unique H-atom (Hδ), as well as for the aromatic protons of the five-membered ring protons (Hα₁ and Hα₂) is consistent with the dimethylimidazolium five-membered ring residing in the cavity of the macrocycle. The protons of the hydrophobic aliphatic chain of the cation have minimum chemical shifts. Thus the NMR results confirm the formation of a supermolecule of calixarene and dimethylimidazolium, [1-octyl-2,3-dimethylimidazolium ∩ *p*-sulfonatocalix[4]arene], rather than a "capsule" with both the head group and the long alkyl chain in its confines, and thus a shielding effect of the calixarenes. Rapid exchange on the NMR time scale with respect to the imidazolium head group residing in the calixarene cavity is evident as there are changes in chemical shifts with a change in ratio of the two

Fig. 6 Hirshfeld surfaces for (a) calixarene and (c) dimethylimidazolium molecules for complex **II**, showing all close contacts of dimethylimidazolium cation and calixarene, with their respective fingerprint plots ((b) and (d)).
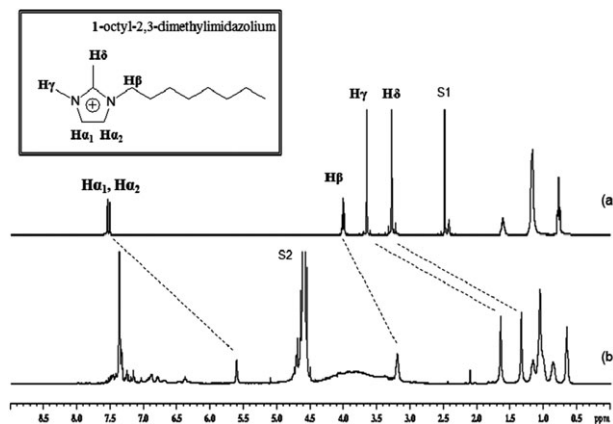

Fig. 7 ¹H-NMR spectrum for (a) n-octyl dimethylimidazolium and (b) n-octyl dimethylimidazolium in *p*-sulfonatocalix[4]arene (1:1), measured in DMSO (S1) and D_2O (S2).

components, and the calixarene is conformational mobile with the appearance of a broad peak for the methyl protons, at 3.85 ppm. Competition experiments between the imidazolium cation and a phenyl ring of the phosphonium cation residing in the calixarene cavity was not possible due to limited solubility of the phosphonium salts in water.

Conclusions

Supramolecular assemblies incorporating n-octyl dimethyl-imidazolium cations in a *p*-sulfonated calix[4]arene system afforded two novel structures which depend on the nature of the phosphonium cations. The interplay of the n-octyl dimethylimidazolium cation five-membered ring is rather similar for both complexes, notably with the methyl terminal alkyl chain residing in the calixarene cavity. The calixarenes are organised into the common bi-layers, linked by the gadolinium(III) metal centre with either the dimethylimidazolium cation confined in the calixarene cavity, or the terminal n-octyl chain penetrates into the adjacent bi-layer. A remarkable finding is the incorporation of phosphonium cations into the bi-layer itself, by adding a simple substituent on the *para*-position of one of the phenyl rings in a tetraphenyl phosphonium cation. The consequence of incorporating a C-methyl group on the imidazolium cation offers additional weak hydrogen bonding interactions between the H-atoms and the O-atoms of the calixarene sulfonate groups.

Having studied the host–guest chemistry of *p*-sulfonated calix[4]arene with a series of imidazolium cations,[9,10,22] a level of predicting the nature of the structures is now possible with the preferential binding of the calixarene towards smaller charged molecules of imidazolium cations rather than phenyl rings of large organic cations.[25] The formation of bi-layers is ubiquitous, but controlling the inclusion of phosphonium cations within the bi-layers is a challenge.

Experimental

p-Sulfonatocalix[4]arene sodium salt,[26] and 1-octyl-2,3-dimethylimidazolium[20] tetrafluoroborate salt were synthesised according to the literature procedures. [Ph₃PPhOMe]I and [Ph₄P]Br were purchased from Sigma Aldrich. A hot solution of GdCl₃·6H₂O in water (0.5 mL) was added to a hot solution of phosphonium salt with *p*-sulfonatocalix[4]arene in a mixture of THF and water (1 : 1, 2 mL). The resulting solutions were left to cool and then allowed to slowly evaporate with crystals formed after several days. All NMR spectra were collected on a Varian 400 MHz spectrometer using D_2O at 25 °C. The chemical shift changes of all the proton signals of the dimethyl-imidazolium were analysed.

Crystallography†

All data were measured from single crystals using Oxford Diffraction Xcalibur and Gemini CCD diffractometers at $T = 100(2)$ K with monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). Data corrected for Lorentz and polarization effects, absorption correction applied using multiple symmetry equivalent reflections. The structures were solved by direct method and refined on F^2 using the SHELX-97 crystallographic package[27] and X-seed interface.[28] A full matrix least-squares refinement procedure was used, minimizing $w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. Agreement factors ($R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and GooF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ are cited where n is the number of reflections and p is the total number of parameters refined. Non-hydrogen non-disordered atoms were refined anisotropically. The positions of hydrogen atoms were partly localized from difference Fourier synthesis, partly calculated and their atomic parameters were constrained to the bonded atoms during the refinement with C_{Ph}–H $= 0.95$ Å, C_{Me}–H $= 0.98$ Å, and 0.99 Å in CH_2.

Crystal/refinement details for complex I

$C_{28}H_{20}O_{16}S_4^{4-}$, $C_{28}H_{19}O_{16}S_4^{5-}$, $2(C_{25}H_{22}OP^+)$, $GdO_8H_{16}^{3+}$, $GdO_9H_{18}^{3+}$, $C_{13}H_{25}N^+$, $14(H_2O)$, $C_{119}H_{170}Gd_2N_2O_{65}P_2S_8$, $M = 3301.49$, colourless rod, $0.36 \times 0.16 \times 0.15$ mm³, $a = 14.2968(2)$, $b = 36.8876(3)$, $c = 14.6319(2)$ Å, $\beta = 110.886(1)°$, $V = 7209.45(15)$ Å³, $Z = 2$, $D_c = 1.521$ g cm⁻³, $\mu = 1.146$ mm⁻¹, $F_{000} = 3408$, $2\theta_{max} = 64.8°$, 182 632 reflections collected, 24 970 unique ($R_{int} = 0.0812$). Final GooF $= 1.002$, $|\Delta\rho_{max}| = 3.3(2)$ e Å⁻³, $R_1 = 0.0909$, $wR_2 = 0.2241$, R indices based on 16 522 reflections with $I > 2\sigma(I)$, 871 parameters, 33 restraints.

Crystal/refinement details for complex II

$C_{28}H_{20}O_{16}S^{4-}$, $C_{13}H_{25}N^+$, $Gd(OH_2)_8^{3+}$, $5(H_2O)$, $C_{41}H_{71}GdN_2O_{29}S_4$, $M = 1341.49$, colourless prism, $0.41 \times 0.34 \times 0.14$ mm³, $a = 13.2450(2)$, $b = 14.6552(3)$, $c = 15.3003(3)$ Å, $\alpha = 103.867(2)$, $\beta = 100.692(1)$, $\gamma = 98.878(1)°$, $V = 2771.10(9)$ Å³, $Z = 2$, $D_c = 1.608$ g cm⁻³, $\mu = 1.438$ mm⁻¹. $F_{000} = 1382$, $2\theta_{max} = 74.5°$, 63 423 reflections collected, 27 437 unique ($R_{int} = 0.0249$). Final GooF $= 1.005$, $|\Delta\rho_{max}| = 3.4(1)$ e Å⁻³, $R_1 = 0.0323$, $wR_2 = 0.0819$, R indices based on 22 954 reflections with $I > 2\sigma(I)$, 701 parameters, 0 restraints.

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