Supramolecular Chemistry

DOI: 10.1002/anie.200603841

Well-Designed Supramolecular Clusters Comprising Triphenylmethylamine and Various Sulfonic Acids**

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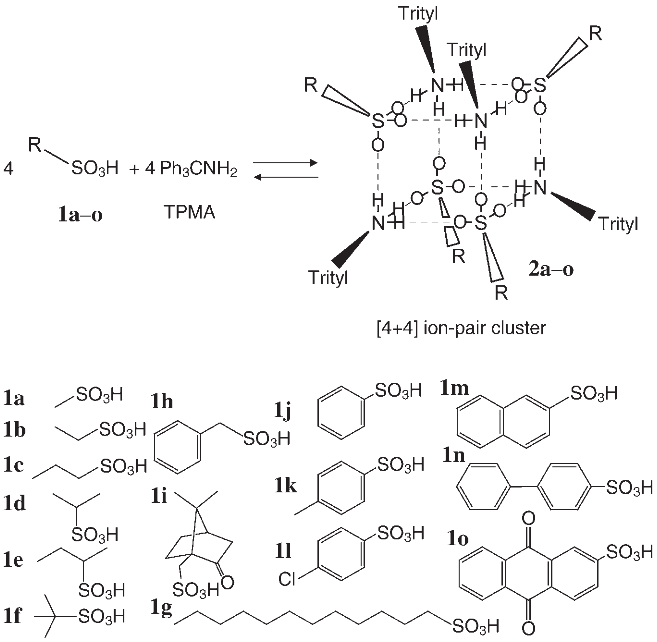
Organic nanoparticles have attracted considerable research interest in molecular biology and life sciences[1] as well as nanotechnology and materials science[2] because of their unique properties. However, the preparation of nanoparticles with a uniform size has remained an important area of study. Organic synthesis is a reliable method for preparing monodisperse particles; silsesquioxane derivatives and dendrimers are useful starting molecules in this area.[3,4] Furthermore, we can prepare homogeneously sized particles more efficiently and in greater amounts by borrowing techniques from supramolecular chemistry.

Numerous well-defined supramolecular capsules and clusters have been obtained by self-assembling through noncovalent bonds.[5,6] With respect to supramolecular clusters, we and other research groups have studied [4+4]-type clusters,[7] which consist of eight organic components of two types connected through hydrogen bonds. Cubic assemblies held together with hydrogen bonds have been proposed to be present, experimentally and theoretically, in ice cubes,[8] and these clusters have been observed in certain combinations of mineral acids and ammonium ions.[9]

However, organic clusters, which should be useful in nanoscience, are rare. All of those known to date contain organic ammonium ions as a key functional moiety, whereas the counteranions vary: carboxylate;[7a–c] thiolate;[7d] phosphonothioate.[7e] We recently described the self-assembly of four ammonium and four triphenylacetate ions into a [4+4] ion-pair cluster through a cubic network of hydrogen bonds.[7a] However, these clusters are obtained only in a few combinations of amines and triphenylacetate.

Herein, we describe—as a result of research from a different angle—that [4+4] ion-pair clusters composed of triphenylmethylammonium and sulfonate ions can be obtained easily and efficiently in the solid state and in solution with many different sulfonic acid derivatives. The universality of sulfonate-containing clusters, as observed in these experiments, contributes to their potential utility. These novel clusters have inherent shapes and sizes that are controlled by the substituent on the sulfonic acid. Their preparation is based on the specificity of the combination of the ammonium and sulfonate ions; this system is potentially useful for synthesizing organic nanoparticles.

Triphenylmethylamine (TPMA) and monosulfonic acids **1** were used to provide the respective cations and anions (Scheme 1) by mixing TPMA with a molar equivalent of the monosulfonic acid in THF. Single crystals suitable for analysis by X-ray diffraction were recrystallized from 1-propanol, 1-butanol, and acetonitrile. We also confirmed the presence of these clusters in solution by ^{1}H NMR spectroscopy and mass spectrometry.



Scheme 1. Fabrication of the [4+4] ion-pair clusters **2a–o** from TPMA and the sulfonic acids **1a–o**.

A crystallographic study revealed that four molecules of sterically hindered TPMA and four molecules of benzenesulfonic acid, **1j**, assemble into a [4+4] ion-pair cluster, **2j**, through a cubic hydrogen-bonded network,[10] and that the binary components are located alternately at the apex of the

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[**] This work was supported by a Grant-in-Aid for Scientific Research in the Priority Areas "Super-Hierarchical Structures (466)" (no. 18039025) and "Molecular Nano Dynamics (432)" (no. 17034039) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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cube as shown in Figure 1 a. The ammonium and the sulfonate ions are held together by hydrogen bonds (Figure 1 b). The hydrogen-bonded network is closed and can be considered zero-dimensional. A total of twelve phenyl groups, present in the four triphenylmethyl groups (trityl groups), cover the hydrophilic core (Figure 1 c) and form a barrier. Within the core, eight central atoms, four nitrogen and four sulfur atoms, form a cube (Figure 1 d). This characteristic structure, similar to a reverse micelle, contributes to the high solubility of the ammonium–sulfonate salt in nonpolar solvents such as chloroform, benzene, and ethyl acetate.

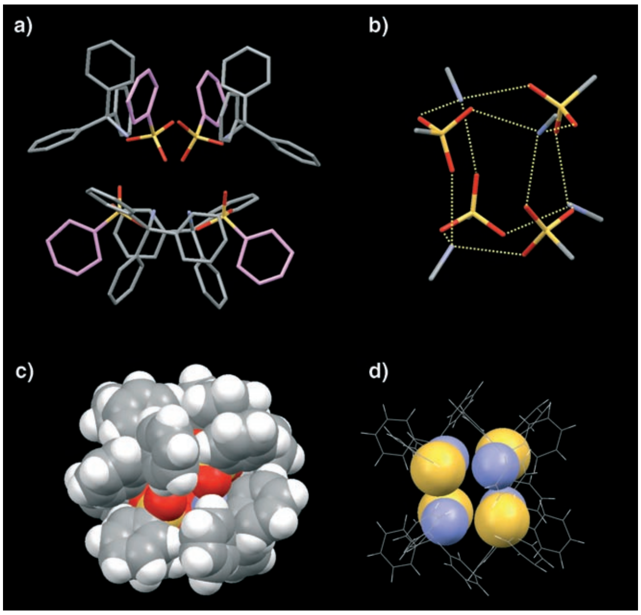

Figure 1. a) X-ray crystal structure of the supramolecular cluster **2j**. b) Network of hydrogen bonds (yellow dashed lines) within the cluster. c) Space-filling representation of the cluster. d) The central elements within the cluster. C gray (benzene rings of **1j** purple in (a)), H white (omitted in (a) and (b)), N blue, O red, S yellow.

From a topological viewpoint, the primary ammonium ion is a tridentate hydrogen-bond donor and the sulfonate ion is a tridentate hydrogen-bond acceptor (Figure 1 b). The directions of the hydrogen bonds reflect the geometry around the central atom, tetrahedral, which is the same for each donor; therefore, the complementary pairs topologically assemble into a cubic hydrogen-bonded cluster without strain. A pair consisting of primary ammonium and sulfonate ions is a very effective combination. Moreover, the bulky trityl groups, with a shape similar to that of a three-leaf clover, play an important role in the formation and stabilization of the cluster **2j**. Hence, hydrophobic phenyl tiles are formed, which leave no space on the surface; the hydrophobic shell protects the cubic core from polar solvents, thus strengthening the association. In contrast, salts of smaller primary amines and sulfonic acids form ladders or sheets of hydrogen-bonded networks, but not a cube. Amines with smaller substituents have no ability to form a hydrophobic barrier to protect the hydrogen-bonded core. Hence, bulky substituents such as trityl groups are essential for the fabrication of cubic clusters.

We extended the range of ammonium–sulfonic acid clusters by using various other sulfonic acid derivatives, as shown in Scheme 1, bottom. As out of more than 100 ammonium–carboxylate combinations, only 14 yielded [4+4] ion-pair clusters, we were astonished to find that all the sulfonic acids we used formed clusters. The results are summarized in Table 1.

Table 1: Sizes of the substituents on the sulfonic acids **1a–o** and of the clusters **2a–o**.

Cluster	Sulfonic acid	Substituent volume [Å^3][a]	Cluster size [Å][b]
2a	methanesulfonic acid	28.6	17.7
2b	ethanesulfonic acid	45.5	18.1
2c	propanesulfonic acid	62.4	disordered
2d	2-propanesulfonic acid	62.4	18.0
2e	2-butanesulfonic acid	79.3	18.1
2f	3-butanesulfonic acid	79.2	18.8
2h	phenylmethanesulfonic acid	100.6	19.3
2i	(±)-10-camphorsulfonic acid	162.7	19.1
2j	benzenesulfonic acid	83.8	18.1
2k	*p*-toluenesulfonic acid	101.6	19.6
2l	4-chlorobenzenesulfonic acid	126.3	19.9
2m	2-naphthalenesulfonic acid	127.9	21.8
2n	4-biphenylsulfonic acid	154.7	23.2
2o	2-anthraquinonesulfonic acid	185.5	27.4

[a] Obtained by AM1 semiempirical calculations by using the SPARTAN'04 program. [b] The largest distance between any two atoms in each of the supramolecular clusters **2a–o**; cluster **2g** was omitted because its crystal structure was not determined.

A small cluster is formed from methanesulfonic acid, **1a**,[10] whereas a large planar cluster is formed from 2-anthraquinonesulfonic acid, **1o**.[10] The space groups of clusters **2a**, **2j**, and **2o** were $P2_1/a$, $I\bar{4}c2$, and $C2/c$, respectively. From a crystallographic point of view, it is interesting that the clusters can be fabricated in spite of the different space groups. Cluster size increases with increasing bulkiness of the substituent on the sulfonic acid. The largest distances between any two atoms found in clusters **2a**, **2j**, and **2o** were 17.7 Å, 18.1 Å, and 27.4 Å, respectively. The shapes of the clusters were also investigated. A methyl group is much smaller than a trityl group and **2a** took the form of a truncated tetrahedron (Figure 2 a); in contrast, a phenyl group is less bulky than a trityl group but has nearly the same molecular length and the cluster of **2j** is spherical (Figure 2 b). Anthraquinonyl is longer and broader than trityl, and **2o** is a tetrahedron

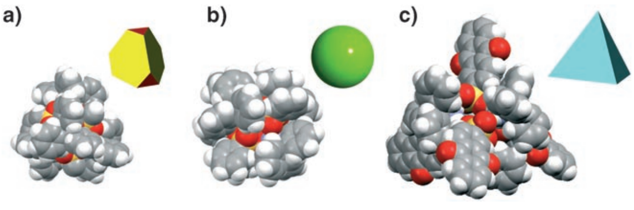

Figure 2. Space-filling representations and schematic representations of the characteristic shapes of the supramolecular clusters a) **2a**, b) **2j**, and c) **2o**. C gray, H white, N blue, O red, S yellow.

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(Figure 2c). Anthraquinonyl groups, as found in **2o**, are well-known as pigment platforms; because organic pigments are expected to have useful functions in photonic and optoelectronic materials, such clusters may find applications in functional organic materials. Additionally, bulkier functional sulfonic acids may be used in conjunction with a bulky amine such as benzhydrylamine and many combinations of amines and sulfonic acids form clusters.

Clusters of the [4+4] type are commonly noted in organometallic supramolecular structures and have been reported by many groups.[11] In hydrogen-bonded architectures, however, this type of cluster is rare. The wide range and robustness of the TPMA–sulfonate system may be attributed to the acidity of sulfonic acid in addition to the topology of the hydrogen-bonded network and the steric effect of the substituents. Its high acidity gives sulfonic acid preference over other hydrogen-bond acceptors and solvent molecules, and the cubic hydrogen-bonded networks are thus tightly held together.

In a set of experiments discussed below, we confirmed the presence of [4+4] ion-pair clusters in solution by directly measuring their supramolecular weights. Although we did not detect the actual weight of **2j** by mass spectrometry (FAB, MALDI-TOF, or ESI) as the ion-pair cluster had no charge, a significant peak attributed to its sodium adduct was observed in the ESI spectrum, with a parent peak at m/z 1691.6 ($[M+\mathrm{Na}]^+$). The same result was observed for the cluster of *p*-toluenesulfonic acid, **2k**.

Evidence supporting the presence of **2j** in solution was also obtained by monitoring the changes in the ^{1}H NMR chemical shifts of the *ortho-* and *para*-CH protons of benzenesulfonic acid, **1j**, on addition of aliquots of TPMA (Figure 3). Below a TPMA:**1j** ratio of 1:1, the addition of TMPA results in the resonance signal of the *ortho*-CH protons moving upfield from $\delta = 7.9$ to 7.4 ppm, while the signal of the *para*-CH protons at $\delta = 7.4$ ppm moves only slightly. The chemical shift of the *ortho*-CH protons was saturated at a ratio of 1:1 (Figure 3). Obviously, the trityl group of TPMA causes a large upfield chemical shift for the *ortho*-CH protons arising from ring-current effects, although this effect is small for the *para*-CH proton. Moreover, when the concentration of **2j** was raised from 1 mM to 50 mM, the signal of the *ortho*-CH protons shifted upfield significantly. Thus, use of ^{1}H NMR spectroscopy has established a tight association between TPMA and **1j** at equimolar ratio in a nonpolar solvent. These measurements strongly suggest that a combination of TPMA and **1j** yields a [4+4] ion-pair cluster in solution, which corresponds to the cluster obtained in the crystalline state. Other ammonium sulfonates may also form clusters in the same manner.

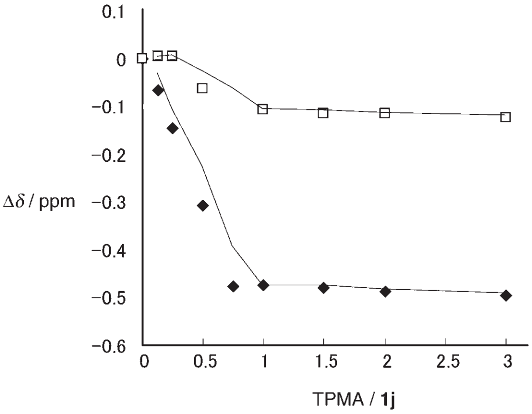

Figure 3. Changes in the chemical shifts of the *ortho*-CH protons (◆) and *para*-CH proton (□) of **1j** as a function of the TPMA/**1j** ratio in $CDCl_3$/MeOD at 25 °C.

In summary, we have demonstrated an efficient and robust fabrication of [4+4] ion-pair clusters consisting of four TPMA and four sulfonic acid components in the solid state and in solution. Surprisingly, a wide range of sulfonic acids yielded clusters. The efficiency of formation and the robustness of the clusters are due to three factors: the topology of the hydrogen-bonded network; the steric effect of the substituents; the acidity of the sulfonic acids. To the best of our knowledge, this is the first report of a system for preparing convenient and adaptable supramolecular clusters with inherent shapes and sizes. In addition, this cubic network is promising as a supramolecular synthon that may lead to the construction of higher-order architectures. Because of their nanoscale sizes, these clusters may also have potential as quantum dots. To create novel compounds for applications in materials and life science, the screening of sulfonic acids that contain functional motifs, such as organic dyes, fluorophores, and organic semiconductors, is currently underway in our laboratory.

Experimental Section

Single-crystal X-ray diffraction data were collected on a Rigaku RAXIS-RAPID imaging-plate diffractometer with graphite-monochromated $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.54187$ Å). Mass spectra of the clusters were obtained by using a BioTOF II instrument (Bruker Daltonics, Billerica, MA). The Supporting Information provides the mass spectrum of the supramolecular cluster composed of TPMA and benzenesulfonic acid (**1j**). The ^{1}H NMR spectroscopic investigation was performed on a JEOL JNM-ECP400 FT-NMR system (400 MHz).

Received: September 19, 2006
Revised: December 7, 2006
Published online: February 13, 2007

Keywords: cage compounds · cluster compounds · hydrogen bonds · nanostructures · supramolecular chemistry

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