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Ab initio study of the binding strength of POSS-cation complexes

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Abstract

Polyhedral oligomeric silsesquioxane (POSS) is a cage-shaped molecule comprised of alternating silicon and oxygen atoms that have found increasing use as filler in polymer nanocomposites. The presence of four oxygen atoms on each face of the POSS cage suggests that the molecule forms a stable complex with a cationic atom or molecule. Although experimental evidence exists for gas-phase binding, the lack of an estimate of this binding strength makes it difficult to predict if complex formation is feasible in condensed systems. This paper presents an ab initio DFT study of the binding strength of POSS-cation complexes based on cation type, POSS cage functionalization, and the presence of a counterion. The binding strength of an unfunctionalized (i.e. with H-terminated corners) POSS molecule with a Li^+ ion is found to be ~ 80 kT at room temperature in vacuo. In a poly(styrene) solvent, the polarity of the medium is estimated to affect little this binding energy. Cyclohexyl ligand substitution is found to increase the binding strength by an additional 30 kT. In the presence of a tightly bound counterion (Cl^-), the binding energy drops to the still substantial value of ~ 20 kT. POSS is found also to bind cationic surfactants (through study of the model $^+NH_3CH_3$) at ~ 25 kT, suggesting a possible new route to POSS modification to hinder agglomeration. This study supports the conclusion that POSS-cation complex formation is feasible in the presence of polymer.

Keywords: Computational material science; Polymer electrolytes; Polymer nanocomposites

1. Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a 'cage-shaped' molecule comprised of a silicon and oxygen core (Fig. 1a) of chemical formula $R_8Si_8O_{12}$. The R groups can be short oligomeric units or long polymer chains, and are varied to affect POSS solubility/dispersion in polymer matrices [1].

Among its applications, POSS has emerged as viable filler in high-performance nanocomposites [2]. POSS-polymer nanocomposites show increased toughness vs. the unfilled polymer [3]. In addition, POSS-PEO based polymer electrolytes have been developed [4], with the POSS molecule acting as an inhibitor to PEO crystallization.

The four oxygen atoms on a single 'face' of the POSS cage structurally resembles a crown ether molecule (Fig. 1b), and introduces the possibility that the POSS molecule, like crown ether, may contain an electron rich site that attracts and binds cations [5]. The first motivation to investigate these binding phenomena is obvious: to study the role of POSS in POSS-PEO polymer electrolytes. The second, less obvious, motivation is to introduce the possibility of reducing POSS agglomeration through the introduction of electrostatically bound surfactants.

In both cases, an estimate of the magnitude of this binding strength is important to establish the feasibility of POSS-cation complex formation within polymeric media. If the binding energies are more than a few kT, one expects POSS-cation binding to persist with little regard to the surrounding environment.

The existence of POSS-metal ion complexes is not in question. Baker et al. generated POSS/Na^+ ions in the gas phase through electrospray ionization (ESI) and matrix-assisted laser adsorption/ionization (MALDI) [6,7]. A molecular mechanics study by the same group predicted conformations in which the attached Na^+ ion resides just outside a face of the POSS cage, attached by electrostatic interactions with the four nearest oxygen atoms. They did

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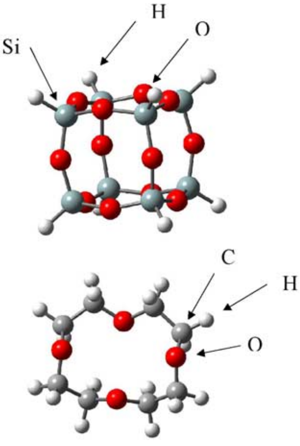

Fig. 1. Structural similarity of the POSS molecule to crown ether. (a) POSS (b) Crown ether.

not, however, present an estimate of the strength of this binding.

This paper comprises a feasibility study of POSS binding to Li^+ and other cations through the use of ab initio quantum chemical calculations, with particular focus on the questions:

(1) Is a POSS-cation complex strongly energetically favorable, and what is the magnitude of the binding strength of their interaction?
(2) Is the presence of such complexes identifiable by IR?
(3) Can cations be passed among POSS molecules?

2. Methodology

This paper employs the GAUSSIAN98™ program, using both the semi-empirical UFF potential and DFT. Initial geometries were generated by molecular mechanics optimization with the UFF potential. The initial structure was further optimized via DFT calculations using the BLYP functional and the 6-311g(d) basis set. The 6-311g(d) basis set was chosen because it generated energies within ~5 kT of those obtained with larger basis sets (Table 1) that are significantly more computationally intensive to use. Binding energies in vacuo were defined as $E = -[E(\text{POSS-cation complex}) - E(\text{POSS}) - E(Li^+)]$. All energies are reported as multiples of kT at room temperature (298 K).

Table 1
Energy convergence with respect to basis set

Basis set	Binding energy (kT)
3-21g	137
6-311g	100
6-311g (d)	85
6311g (d,p)	85
6-311g+(d)	79
6-311g+(d,p)	79
6-311g+(2d,p)	78

Geometry optimization of the POSS-cation complex requires an initial guess of the cation location with respect to the POSS molecule. Multiple trial cation positions were studied, including the interior of the cage. For the case of unsubstituted POSS and Li^+, the minimum energy conformation finds the lithium ion located outside the cage, equidistant from the four oxygen atoms that define a single face (Fig. 2). Baker et al. predicted a similar cation location for POSS-Na^+ through AMBER force field MD [7]. Therefore, subsequent calculations involving different cations or substituted POSS molecules used an initial cation position consistent with these findings.

When simulating corner ligand-substituted POSS with $R = C_6H_5$ (e.g. Fig. 5), the R group (excluding the first carbon attached to Si) was modeled using the UFF force field, and the total energy computed via the ONIOM method.

The calculations that follow are presented without regard to entropic contributions to the free energy. In general, these entropy contributions will tend to decrease the Li^+ preference to bind to the POSS molecule, but are expected to be on the order of a few kT. Therefore, binding is expected if the energetic preference for the bound state is more than a few kT.

3. Results and discussion

The effect of basis set size on binding energy calculations was first investigated on the unsubstituted (corner ligand = H atom) POSS molecule and a single Li^+. As shown in Table 1, the binding energy in the limit of the very large basis set 6-311g+(2d,p) converges to ~78 kT. Subsequent calculations used the 6-311g(d) basis set, since it provides accuracy of ±5 kT at far less computational cost.

Clearly, BLYP-DFT predicts a significant POSS-Li^+ binding energy. Whether such an affinity is expected to persist within a polymer matrix, depends upon the predicted polymer–cation interaction. For example, poly(ethylene oxide) is quite effective at binding Li^+, due to the documented ability of PEO to donate five or six

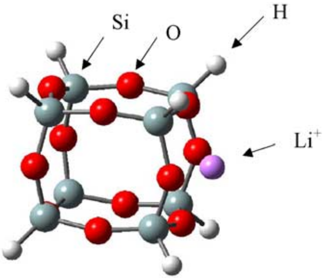

Fig. 2. Minimum energy configuration of POSS-Li^+ complex. The presence of cationic Li^+ distorts the natural POSS cage shape, pulling the adjacent O atoms closer together.

coordinating oxygens to each ion. Johansson et al., using quantum chemical calculations, estimate the PEO-Li^+ binding strength at ~250 kT [8]. In such a system, one expects negligible POSS-Li^+ complex formation at low POSS volume fractions.

By contrast, polystyrene (PS) is a relatively non-polar polymer. To estimate the presence of a PS solvent on the POSS-Li^+ binding energy, the Onsager reaction field model was used [9]. Molecular volume calculations of POSS and POSS-Li^+ provided recommended a_0 values of 5.82 and 5.20 Å, respectively. An Onsager calculation using the PS dielectric constant $\varepsilon = 2.5$ suggests that a PS solvent affects the binding strength (defined as for the case in vacuo) by less than 1 kT.

The minimum energy conformation places the Li^+ outside the POSS cage, equidistant from the four O atoms that define a single face (Fig. 2). A profile of the system energy versus Li^+/POSS face-center distance (defined as the plane created by the four oxygen atoms) provides an energy profile for binding (Fig. 3). Note that Fig. 3 indicates a large (~30 kT) energy barrier to Li^+ migration to the POSS cage center, and that the local minimum inside the cage is disfavored significantly compared to that external to the face.

The strength of the POSS/Li^+ binding significantly distorts the POSS structure, drawing the Li^+-adjacent oxygen atoms closer together than in the unbound state. Oxygen atoms on opposite sides of the same face are separated by 3.88 Å in the unbound state, but for those nearest the Li^+, this value decreases to 3.62 Å.

This deformation of the POSS molecule breaks the symmetry present in the native structure. Fig. 4 shows the estimated IR spectrums for native POSS and the POSS-Li^+ complex, obtained from normal mode analysis. The results indicate the presence of a new peak in the bound state at 1000 cm^{-1}, corresponding to Si–O bond stretching. Fig. 4 was generated by assuming that the calculated IR peaks would be somewhat diffuse. Each peak was assumed to be normally distributed about the calculated value, with a standard deviation of 20 cm^{-1}.

Now that the feasibility of POSS/Li^+ binding has been established, the effects of structural modifications of the POSS or cation are investigated. The results from all systems studied are provided in Table 2 and discussed in turn below.

3.1. Addition of cyclohexyl-side chains

In polymer/POSS systems of interest, the terminal hydrogen atoms are replaced with an organic group to facilitate dispersion in the polymer matrix. One common ligand is the cyclohexyl group. As described in Section 2, this binding energy calculation was performed via the ONIOM method. The results indicate that the presence of the cyclohexyl side chains increases the binding strength from 80 to 110 kT. Baker et al. predicted that styryl and phenylethyl side chain geometries are altered in the presence of a cation, but no such change is found in the cyclohexyl-POSS system. This discrepancy perhaps may be attributed to the fact that the carbon ring in cyclohexyl side group is attached directly to the POSS cage, while styryl and phenylethyl groups contain two intervening carbon atoms.

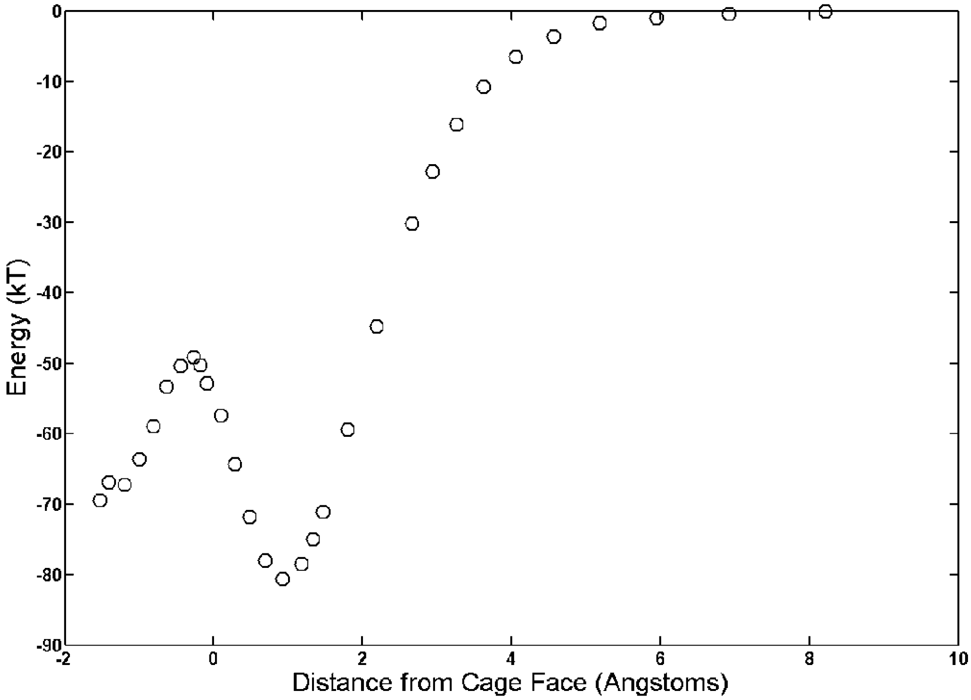

Fig. 3. POSS/Li^+ energy as a function of lithium position. The energy minimum is achieved at a distance ~1 Å from the POSS cage face.

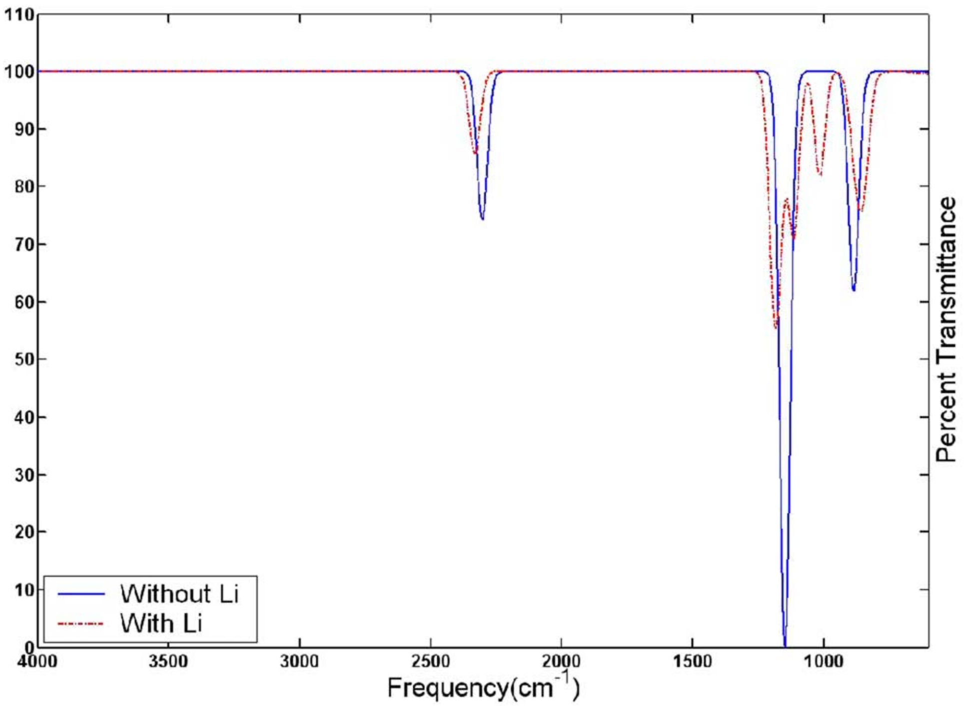

Fig. 4. Predicted IR spectrum of POSS (solid) and POSS/Li$^+$ (dotted). DFT calculations predict the presence of an additional IR peak at ~1000 cm^{-1}.

3.2. Presence of a Cl$^-$ counterion

Since lithium is invariably added to any polymer system as a salt, an anion must be present for each lithium cation. However, depending on the solvating abilities of the polymer matrix, the lithium and corresponding anion may or may not dissociate. POSS association with LiCl in vacuo therefore provides a 'worst case scenario' for binding. Counterion effects are investigated by creating a system of unsubstituted POSS, one Li$^+$, and one Cl$^-$. The initial guess structure is generated by placing Cl$^-$ adjacent to Li$^+$ and outside the POSS cage. The effect of the Cl$^-$ counterion is to reduce the binding energy (defined as $E=[E(\text{POSS})+E(\text{LiCl})-E(\text{POSS/LiCl complex})]$) to ~21 kT, a still significant amount.

3.3. Replace Li$^+$ with $CH_3NH_3^+$

$CH_3NH_3^+$ was chosen as a model ion to represent surfactant molecules. While Li$^+$ binding is of potential interest for applications in polymer electrolytes, the ability of POSS to bind with cations opens another avenue to POSS modification in addition to corner ligand substitution. In particular, association with cationic surfactants might help to impede POSS aggregation, which occurs at volume fractions of more than a few percent and that generally degrades the nanocomposite properties. The binding of energy of $CH_3NH_3^+$ with an unsubstituted POSS molecule was calculated as ~25 kT, suggesting that such modification is possible.

Table 2
Summary of binding energies

POSS terminal group	Cation	Counterion	Predicted binding energy (kT)
H	Li	None	78
C_6H_5	Li	None	120
H	Li	Cl	21
H	CH_3NH_3	None	25

3.4. Feasibility of lithium transfer between two POSS molecules

As a final line of questioning, the facility of cation transfer among POSS molecules is considered. One hypothetical transport mechanism is for the cation to 'jump the gap' between two POSS molecules as they come into close contact (Fig. 5, for cycloyhexyl-POSS).

To test this hypothesis, geometry optimization was performed for a system of two POSS molecules with an intermediate Li$^+$. The initial guess structure contained the two POSS molecules aligned so that the cyclohexyl groups abutted. In the optimized structure, by contrast, the POSS molecules are aligned by 45° to each other, to allow sterically a closer approach of the POSS faces. A series of single energy calculations were then performed in which the position of the Li$^+$ was moved from one POSS molecule to the other while the positions of all other atoms remained constant. The transfer barrier calculated by this method is ~80 kT, implying a very low likelihood of lithium transfer. It should be noted, however, that the method described here does not allow for favorable changes in POSS conformation

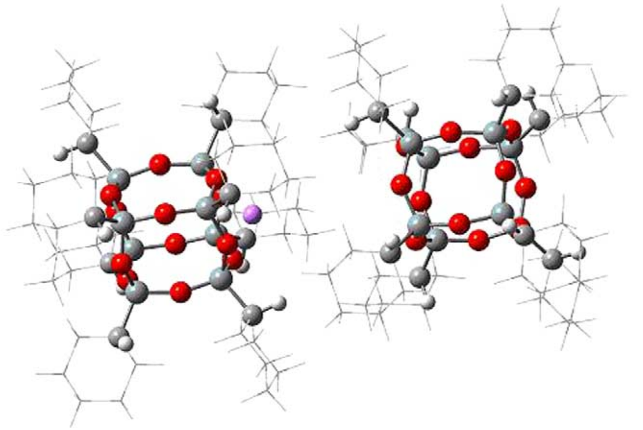

Fig. 5. Structure of two cylohexyl-POSS molecules joined by the attractive force of a single lithium ion as predicted by energy minimization.

during ion transfer that may result in a lower barrier. Further study using a cheaper energy model is needed to investigate these effects.

4. Summary

BLYP-DFT calculations of POSS binding with various cations indicate that the strengths of these associations are substantial. In the case of POSS-Li^+ complex formation, the strength of binding is estimated at room temperature as ~78 kT in vacuo, with little change due to the presence of a polystyrene solvent. Even in unfavorable circumstances (i.e. anion Cl^- remaining tightly bound in vacuo to Li^+), the strength of binding remains ~20 kT. Further, binding (~25 kT in vacuo) was demonstrated for the surfactant-like cation, $CH_3NH_3^+$, indicating a possible mechanism by which to reduce POSS agglomeration in polymer nanocomposites.

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