

## FOCUS REVIEW

# Unique properties of amphiphilic POSS and their applications

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Our recent studies on advanced materials based on polyhedral oligomeric silsesquioxane (POSS) functionalized with polar substituents are reviewed. First, the effects on the thermal properties of ion pairs after tethering to POSS are demonstrated. A decrease in the melting temperature and an increase in the decomposition temperature of the ion pairs were simultaneously achieved after POSS was modified with these ion pairs. The effects of the structural features of POSS on the thermal properties of ionic pairs in such compounds are explained. Next, selective encapsulation of bioactive molecules using POSS-core dendrimers is described. The binding affinity of bio-active molecules was enhanced through the formation of hydrogen bonds with POSS-core dendrimers, and this enhancement was achieved by utilizing the amphiphilic properties of POSS-core dendrimers. The system design concept and the results are explained. Finally, we introduce the unique optical properties that can be induced in dyes through encapsulation in POSS-core dendrimers, with a focus on the influence of the POSS core on the molecular rotation of the dye in the excited state.

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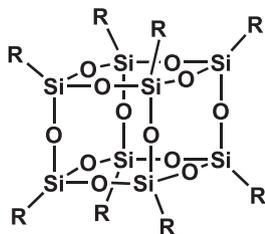
**Keywords:** dendrimer; encapsulation; fluorescence; ionic liquid; POSS

## INTRODUCTION

A typical polyhedral oligomeric silsesquioxane (POSS) molecule has a cubic rigid ( $T_8$ ) structure represented by the formula  $R_8Si_8O_{12}$ . The central inorganic core ( $Si_8O_{12}$ ) is functionalized with organic substituents (R) at each of the eight vertices (Figure 1). POSS possesses a symmetrical cubic structure. Because of such structural features, POSS is expected to have distinctly different characteristics from those of planar molecules. Based on these characteristics, a large number of high-performance materials have been developed.<sup>1–14</sup> Because the molecular shapes and conformations of POSS vary depending on its substituents,<sup>2</sup> POSS has been effectively used as a building block at the molecular scale to construct functional nanomaterials. Furthermore, water-soluble POSS derivatives have been synthesized and recently applied as bio-functional materials, such as sensors or probes to monitor biological events, through their unique properties that are observed only in water.<sup>15–24</sup> In this review, advanced functional materials made from POSS derivatives modified with polar substituents are introduced. We mainly present our recent findings on the intriguing substances that originated from these amphiphilic POSS derivatives. First, the thermal properties of POSS and POSS salts are explained. In particular, the curious thermodynamics of POSS-based ionic liquids (ILs) are demonstrated. In the following three chapters, we illustrate the peculiar behaviors of POSS materials with polar substituents. In addition, we describe selective encapsulation of biomolecules by POSS-core dendrimers and the influence of the POSS core on the excited states of the encapsulated dyes.

## REINFORCEMENT OF THERMAL AND MECHANICAL PROPERTIES OF PLASTICS BY POSS

Closed silica cubes show a high thermal and chemical stability. For example, it has been reported that POSS can enhance the thermal and mechanical properties of a polymer if it is introduced into a polymer with high compatibility.<sup>25,26</sup> For example, the simple incorporation of POSS into polymer chains, with or without covalent bonds, can improve the thermal stability of the polymer to pyrolysis.<sup>27</sup> Polyimide aerogels can be reinforced more effectively by crosslinking with POSS derivatives than by crosslinking with polymers.<sup>28</sup> In a previous report from our group, well-dispersed polymer composites were prepared with various types of polymers and POSS fillers, and it was demonstrated that the POSS fillers can contribute to enhancing the thermal stability of the polymer matrices.<sup>29</sup> From a thermogravimetric analysis to compare  $T_{d20}$  values, which are defined as the decomposition temperature that results in a 20% (w/w) weight loss, the  $T_{d20}$  values of polystyrene (PS) composites containing 5 wt % octyl- and octadecyl-POSS were significantly increased comparing the PS film without POSS fillers ( $\Delta T_{d20} = +24.5$  and  $+28.6$  °C, respectively). The  $T_{d20}$  value of the poly(methyl methacrylate) increased markedly by  $+67.4$  °C by adding phenyl-POSS. The thermal stabilities of PS and ethylene-(vinyl acetate) copolymer films were also enhanced by adding 5 wt% phenyl-POSS ( $\Delta T_{d20} = +20.4$  and  $+17.7$  °C). By using other POSS fillers, such as octyl- and octadecyl-POSS, the  $T_{d20}$  values of PS composites were greatly enhanced ( $\Delta T_{d20} = +24.5$  and  $+28.6$  °C, respectively).



**Figure 1** Chemical structure of POSS.

In addition, we observed a large reinforcement of the mechanical properties of conventional polymers by simply mixing as a POSS filler, as shown by dynamic mechanical analysis. For instance, the addition of 5 wt% phenyl-, octyl- and octadecyl-POSS increased the storage moduli of poly(methyl methacrylate) by 37%, 30% and 34%, respectively. The moduli of the PS composites were enhanced by 65 and 59% by adding 5 wt% phenyl- and octyl-POSS, respectively. The suppression of molecular motions of the polymer chains by POSS could be responsible for the enhancements of the thermal and mechanical properties.

### THE UNIQUE THERMAL PROPERTIES OF ION PAIRS ASSEMBLED ONTO POSS

Three-dimensional polymeric materials have gained attention because of the different properties that can originate from their structural features. Room temperature ILs, which possess a melting temperature below 25 °C, have been obtained using POSS as a polyanion (Figure 2).<sup>30</sup> It has been found that connecting ion pairs to POSS can greatly improve the thermal stability and decrease the melting temperatures of the ion pairs. However, the contribution of the POSS core to the thermodynamics in these cases is unclear. Thereby, we attempted to assess whether the cubic structure of POSS or the rigidity of its silica cage had the largest effect on the thermal properties of the ion pairs. The results and plausible mechanisms from our recent study<sup>31</sup> are described here.

A series of POSS molecules with variable numbers of ion pairs was prepared via acid–base neutralization using POSS-(COOH)<sub>8</sub> and (Bmim)OH (Figure 2a).<sup>30,31</sup> The stoichiometry between POSS and the ion pairs was adjusted by changing the feeding ratios. We named these salts POSS-Im<sub>n</sub> (where *n* is the number of imidazolium cations tethered to the POSS core). Each product was colorless and transparent (Figure 2b). All samples containing the POSS moiety yielded single peaks at –66 p.p.m. in <sup>29</sup>Si nuclear magnetic resonance spectra, and these peaks were assigned to the T<sub>8</sub> POSS structure (Figure 2c). The integration areas under the peaks in the <sup>1</sup>H nuclear magnetic resonance spectrum corresponded to the desired ratios and to the number of imidazolium cations. The samples were stored in a glove box in an argon atmosphere, and the water abundance was kept below 1.5 wt%, as determined by a Karl Fischer moisture titrator. Further characterization data indicated that all products were sufficiently pure for the analyses. We also prepared the ion pair Arm-Im, which was composed of the side chain of the POSS salts, for comparison purposes to evaluate the effects of connection to POSS.

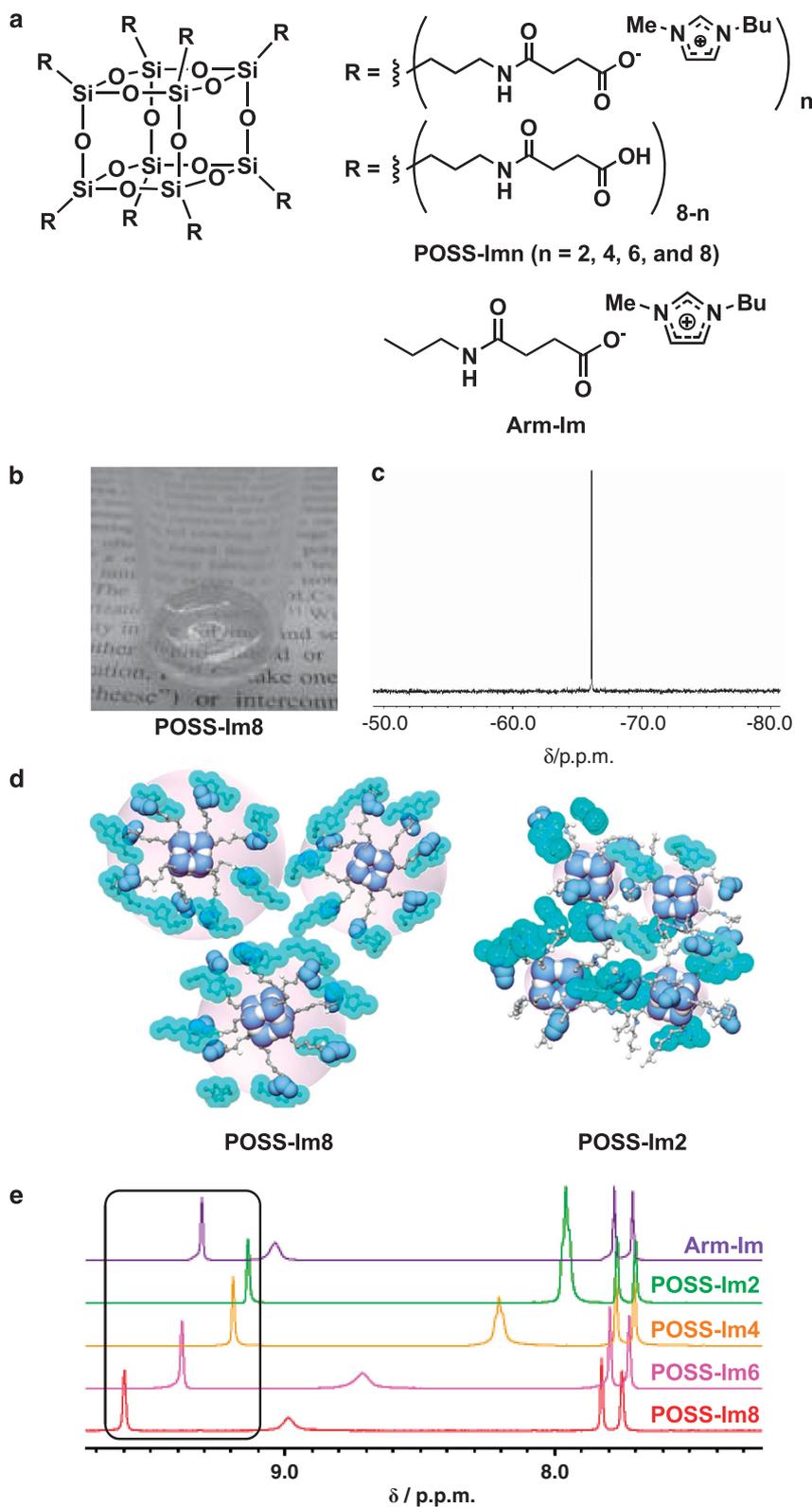
The thermal stability of the synthetic compounds against pyrolysis was evaluated by thermogravimetric analysis (Table 1). We observed two weight losses in all samples. Because similar molecular weights were obtained after the first weight loss, this step was assigned to the degradation of the carboxyl groups. Therefore, the *T*<sub>d</sub> value represents the influence on the thermal stability of the carboxyl groups after introducing (Bmim<sup>+</sup>) to POSS. The *T*<sub>d</sub> values of POSS-Im<sub>6</sub> and

POSS-Im<sub>8</sub> were higher than those of Arm-Im and POSS-(COOH)<sub>8</sub>. In contrast, POSS-Im<sub>2</sub> and POSS-Im<sub>4</sub> showed lower *T*<sub>d</sub> values than Arm-Im and POSS-(COOH)<sub>8</sub>. These results indicated that the large number of ion pairs tethered to POSS is essential for inducing the characteristic changes in thermal stability observed in POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub>. In addition, the presence of POSS makes only a minor contribution to the increase in thermal stability because POSS-Im<sub>2</sub> and POSS-Im<sub>4</sub> showed lower *T*<sub>d</sub> values than Arm-Im. These results imply that the structural features of POSS could contribute more than its rigidity to enhancing the thermal stabilities of POSS-based ILs.<sup>29</sup>

To determine the melting temperatures (*T*<sub>m</sub>s), differential scanning calorimetry measurements were executed (Table 1). The endothermic peaks assigned to the melting process were observed below 100 °C for all POSS-containing compounds except POSS-Im<sub>2</sub>. Therefore, POSS-Im<sub>4</sub>, POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub> can be categorized as ILs. Notably, POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub> melted below 25 °C. Thus, they can be classified as a room temperature ILs. Significant tendencies were obtained from the comparison. The *T*<sub>m</sub> values of POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub> were 19 and 23 °C lower than that of Arm-Im, respectively. In contrast, the *T*<sub>m</sub> values of POSS-Im<sub>2</sub> and POSS-Im<sub>4</sub> were not below 100 °C. Therefore, a large number of ion pairs is necessary to decrease the *T*<sub>m</sub>s of POSS-tethered ion compounds. Similar to the data from thermogravimetric analysis, when a large number of ion pairs accumulate on POSS, the POSS-based molecules have thermal properties that are characteristic of ILs.

To explain the thermodynamics of the melting process of POSS with tethered ion pairs, the fusion enthalpies and entropies ( $\Delta H_{\text{fus}}$  and  $\Delta S_{\text{fus}}$ ) per single imidazolium molecule were calculated from the areas of the endothermic peaks observed in the differential scanning calorimetry profiles (Table 1). The differences in the thermodynamics between POSS-Im<sub>4</sub> and POSS-Im<sub>6</sub> are also presented in Table 1. POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub> had lower  $\Delta H_{\text{fus}}$  values than did Arm-Im. In contrast, POSS-Im<sub>2</sub> and POSS-Im<sub>4</sub> had larger values of  $\Delta H_{\text{fus}}$  than did Arm-Im. These results can be explained by the cubic structure of POSS, as shown in the proposed models in Figure 2d. After tethering to the cubic core, the distal ion pairs are expected to be isolated and distributed in a star-shape. These structures disrupt the aggregation of ion pairs. Thus, the interaction between the POSS molecules could be reduced in POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub>. The smaller values of  $\Delta S_{\text{fus}}$  for POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub> than that of Arm-Im can also be explained by the contribution of the structural features of POSS to the thermal properties. The star-shaped distribution of the ion pairs usually increases the symmetry of the molecules, leading to high thermal stability.<sup>32</sup> In summary, when a large number of ion pairs accumulate on POSS, a star-shaped structure should be induced. This structure results in POSS molecules with larger exclusion volumes and a greater symmetry, both of which could reduce the intermolecular interactions between individual POSS molecules. Hence, the melting temperatures of these POSS-based substances decrease. During the melting process, the symmetric conformation of the POSS-IL molecules could be the main contributor to their thermal behavior. Thus, linking ion pairs to POSS can simultaneously lower the melting temperature and enhance the thermal stability of the compound.

The introduction of the POSS core into ILs can present another beneficial property. The chemical shifts of the peak assigned to the 2-position of imidazolium were compared in the <sup>1</sup>H nuclear magnetic resonance spectra with POSS-Im<sub>n</sub> (*n* = 2, 4, 6 and 8) and Arm-Im (Figure 2e). It has been reported that the strength of the ability to solubilize cellulose of imidazolium-based ILs can be evaluated from the degree of the downfield shift of this peak.<sup>33</sup> From our data, the peak positions in POSS-Im<sub>6</sub> and POSS-Im<sub>8</sub> showed a larger



**Figure 2** (a) Chemical structures of the ionic pairs. (b) Appearance and (c)  $^{29}\text{Si}$  nuclear magnetic resonance (NMR) spectrum of POSS-Im8 at 25 °C. (d) Proposed conformations of the POSS-based ionic compounds. (e)  $^1\text{H}$  NMR spectra of the ionic compounds in dimethyl sulfoxide at 25 °C.

downfield shift than those in Arm-Im, indicating that the strength of the hydrogen bonds was significantly increased by tethering to POSS. The POSS-based molecular design could therefore be feasible for

developing good solvents to dissolve cellulose. Further application of the enhancement of hydrogen bonding strength is demonstrated in the next section.

## HYDROPHOBIC SPACES CREATED BY POSS IN AQUEOUS SOLUTIONS

The closed cubic silica structure has extremely low polarity.<sup>34</sup> Therefore, most hydrocarbon-substituted POSS derivatives are soluble in weakly polar organic solvents, such as chloroform, tetrahydrofuran and sometimes hexane. In contrast, by introducing polar functional groups at the vertices, POSS becomes soluble in polar solvents, such as water and methanol.<sup>35–37</sup> In particular, the core of the POSS dendrimers has a crucial role in these properties as a result of its large overall shape and the groove between the dendrons even with the small number of repeating units in the dendrons.<sup>38</sup> Notably, the hydrophobic spaces around the silica cube are maintained in these polar solvents.<sup>39–44</sup> In other words, POSS shows amphiphilicity, which originates from the weak polarity of the closed silica cage in water. The hydrophobicity of POSS can work as a driving force to make a strong interaction with hydrophobic molecules, leading to their encapsulation inside POSS-based materials in aqueous media. For example, we synthesized a series of POSS network polymers with different crosslinking ratios.<sup>42</sup> In particular, POSS polymers

containing disulfide linkers encapsulated hydrophobic molecules in aqueous solutions (Figure 3a).<sup>43</sup> In contrast, under reducing conditions, we demonstrated that dye-loaded network polymers released encapsulated molecules (Figure 3b). Finally, we were able to detect the increase of the emission intensity from the sample containing the intercellular concentration of reduced glutathione (Figure 3c).

The encapsulation of guest molecules was also observed in dendrimers.<sup>44</sup> We assumed that the core of the dendrimers had a crucial role in creating the hydrophobic spaces because of the overall shape and the groove between the dendrons. Based on this idea, we evaluated the encapsulating ability of POSS-core dendrimers and compared it with that of polyamidoamine dendrimers, which possess the same dendrons but a different core (Figure 4). The amount of encapsulated guest molecule inside each dendrimer was evaluated with various types of aromatic molecules and dyes. Consequently, it was found that POSS-core dendrimers captured more guest molecules without a loss of affinity compared with polyamidoamine dendrimers.<sup>44</sup> These results were applied to prevent the fluorescence photobleaching of dyes<sup>44</sup> and to convert the photon energy to higher energy levels than those of the incident light in aqueous media.<sup>45</sup> Thus, POSS can work as a scaffold to construct molecular assemblies in water and can form the basis of biomimetics.

**Table 1** Thermodynamic parameters of the ionic compounds determined from the DSC and TGA curves

Salt	$T_d$ (°C)	$T_m$ (°C)	$T_m$ (°C) <sup>a</sup>	$T_g$ (°C) <sup>a</sup>	$\Delta H_{fus}$ (kJ mol <sup>-1</sup> )	$\Delta S_{fus}$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>b</sup>
Arm-Im	202	49	48	-40	15	47
POSS-Im8	234	45	23	-52	6.8	21
POSS-Im6	233	44	19	-55	11	35
POSS-Im4	188	59	ND	ND	39	120
POSS-Im2	165	142	ND	ND	41	99

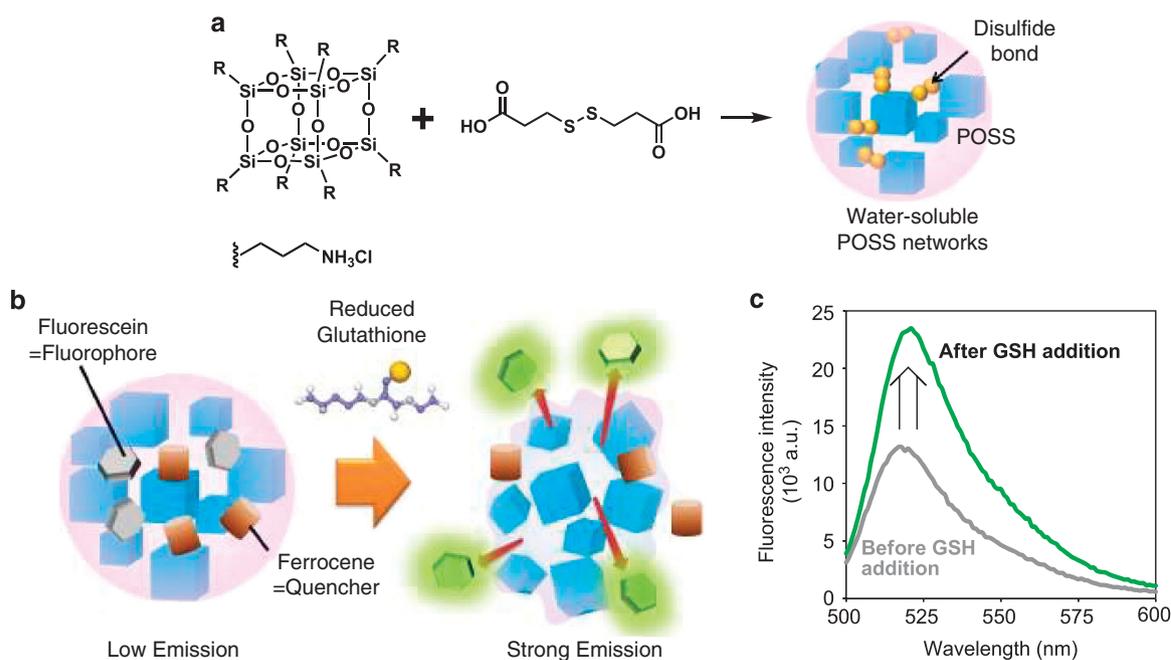
Abbreviations: DSC, differential scanning calorimetry; ND, not determined; POSS, polyhedral oligomeric silsesquioxane; TGA, thermogravimetric analysis.

<sup>a</sup>Determined from the second heating curves.

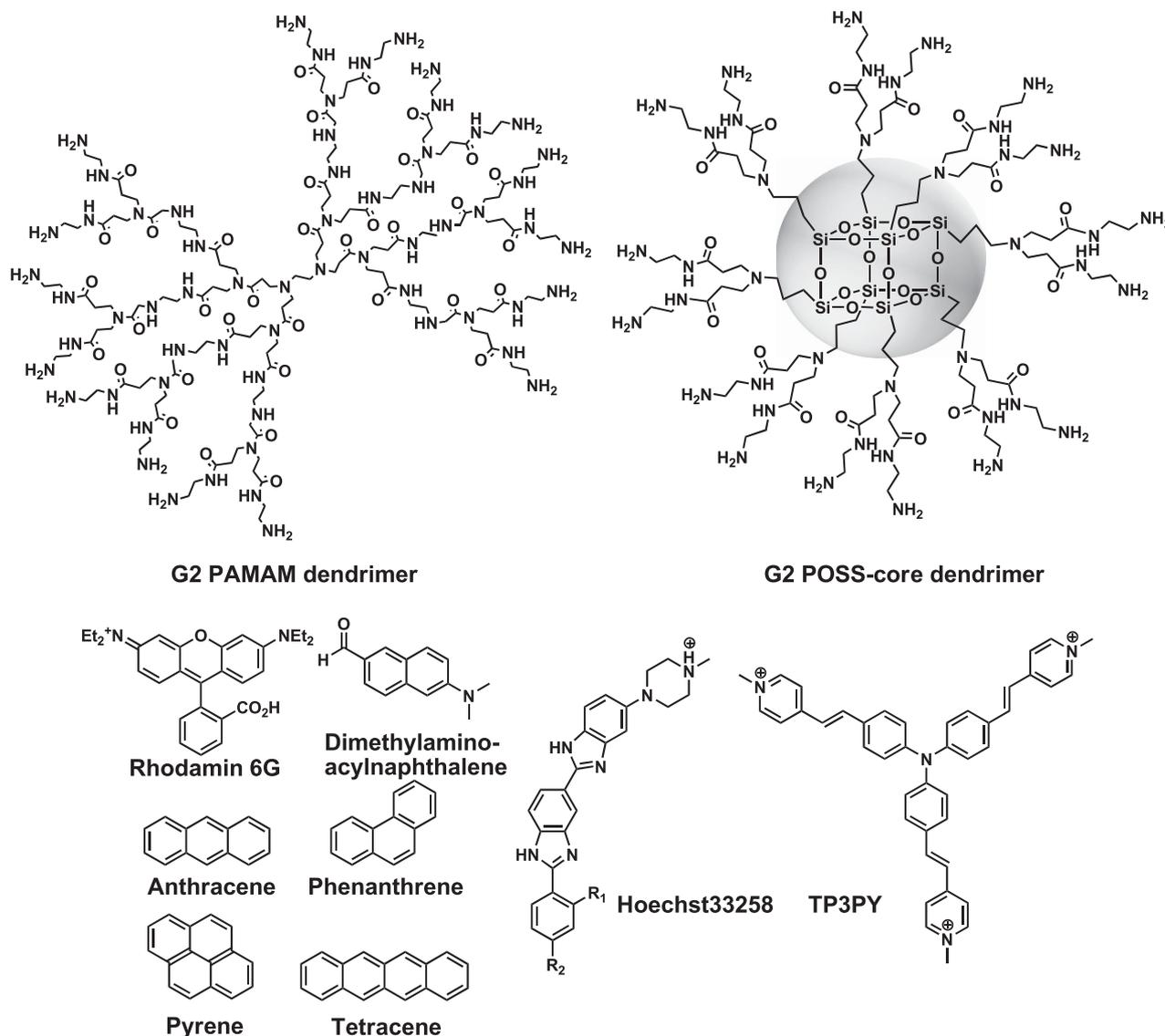
<sup>b</sup>Calculated from the following relation:  $\Delta S_{fus} = \Delta H_{fus}/T_m$ .

## DESIGN TO SELECTIVELY ENCAPSULATE BIOACTIVE MOLECULES INTO POSS-CORE DENDRIMERS

We have explained the superior encapsulation ability of water-soluble POSS-core dendrimers.<sup>44</sup> In water, POSS-core dendrimers can take up a globular conformation and can create distinct hydrophobic spaces around the POSS core. Consequently, larger amounts of the hydrophobic guest molecules can be sustained inside the dendrimers than in the same generation of the polyamidoamine dendrimer, which has similar dendrons.<sup>44</sup> Then, we proceeded to realize the selective encapsulation by POSS-core dendrimers.<sup>46</sup>



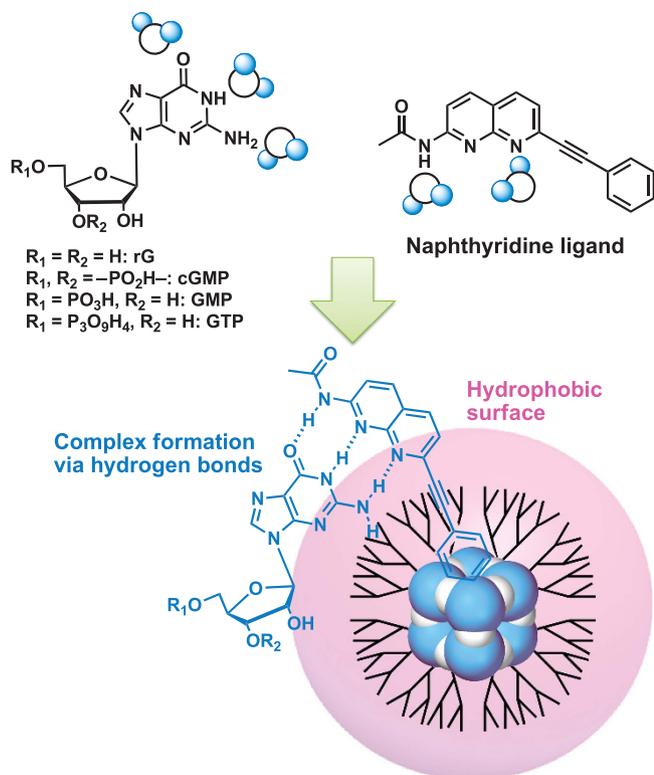
**Figure 3** (a) Creation of strong hydrophobic spaces inside the water-soluble POSS network polymers with disulfide bonds. (b) Schematic illustration of the detection of glutathione. The encapsulated fluorophores (fluorescein) and quenchers (ferrocene) are released by adding glutathione. Subsequently, the fluorescence emission is recovered. (c) Increasing the fluorescence emission of the disulfide bond-containing POSS network polymers by adding glutathione.



**Figure 4** Chemical structures of the dendrimers and the guest molecules encapsulated in the POSS-core dendrimer.

Molecular assemblies via hydrogen bonds have been used to construct pre-programmed architectures. To achieve stable complexation and precise recognition, a new series of ligand molecules has been explored.<sup>47,48</sup> In biological fields, hydrogen-bond-mediated molecular recognition is often used to capture target substances. For example, in the active pocket of RNA polymerases, nucleoside triphosphates are recognized with template sequences that are based on hydrogen-bond patterns.<sup>49</sup> Accordingly, mRNAs can be produced with high fidelity. Complexation with the complementary nucleosides is below the level of detection in water in the absence of enzymes, because the hydration at the binding sites via hydrogen bonds crucially inhibits complexation in water. The hydrophobic environments inside the enzymes can enhance the stability of the complex by isolating it from water molecules. In the POSS-IL study, we observed that the hydrogen bond strength was significantly enhanced in POSS-Im6 and POSS-Im8.<sup>31</sup> Inspired by these results, we sought to apply the hydrophobic space created inside POSS-core dendrimers as a scaffold to enhance complex stability via hydrogen bonds.<sup>46</sup>

The strategy for selective encapsulation in POSS-core dendrimers is illustrated in Figure 5. We expected that the POSS core could provide hydrophobic spaces inside the dendrimer, leading to the enhancement of hydrogen bonding. We designed the ligand molecule with a 1,8-naphthyridine moiety; this ligand can form a complex with guanine via hydrogen bonds.<sup>50,51</sup> In the bulk water, the ligand is not observed to form a complex with guanine nucleotides. Subtle changes in the optical properties of the naphthyridine ligand are expected to occur on binding. However, the complexation, with hydrogen bond formation, is expected to be enhanced in POSS-core dendrimers because of the distinct hydrophobicity of the POSS core. In particular, as in fluorescence sensors for guanosine moieties in previous studies,<sup>52,53</sup> the fluorescence emission can be quenched via electron transfer through the hydrogen bonds. In other words, the decrease in the emission represents formation of a complex between the naphthyridine ligand and the guanosine nucleotides. Therefore, quantitative data such as the binding constants can be evaluated from the changes in the optical properties induced by the complexation via hydrogen bonds.<sup>54,55</sup>

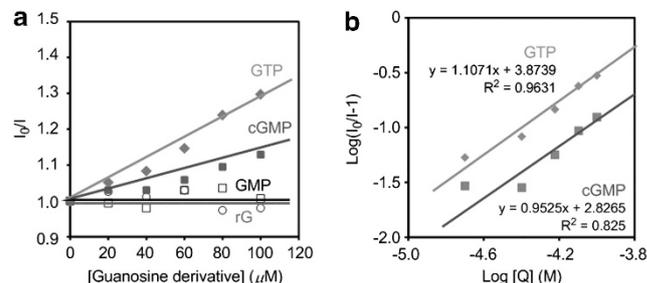


**Figure 5** Chemical structures of guanosine nucleotides and the naphthyridine ligand and a model of complexation enhancement via hydrogen bonds at the hydrophobic surface created by POSS.

We examined the changes in the fluorescence intensity elicited by the naphthyridine ligand by titration of a series of guanosine nucleotides (Figure 6a).<sup>46</sup> Fluorescence emission with a peak at 380 nm was observed when the ligand was added to aqueous solution. The addition of guanosine triphosphate (GTP) caused a significant decrease in emission from the ligand. Less quenching was observed when cyclic guanosine monophosphate (cGMP) was titrated into the solution. These data suggest that complex formation should occur with GTP or cGMP. In contrast, only slight changes in the emission intensity were observed in the presence of rG and GMP. These results indicate that the interaction between GTP and the ligand can be enhanced by the G2 POSS-core dendrimer.

To examine the influence of the existence of the POSS core, we measured the fluorescence emission by the same procedure but used the G2 polyamidoamine dendrimer, which possesses an ethylene diamine core instead of a POSS core. Following the addition of guanosine nucleotides, including GTP, the fluorescence emissions from the ligand were only slightly different. These results indicate that the POSS core is responsible for enhancing the complex formation between the naphthyridine ligand and GTP. As expected, the hydrophobic space around the POSS core reduced the hydration of the naphthyridine ligand, enhancing the affinity of the complex through hydrogen bonding. Moreover, the fluorescence measurements were also monitored in the presence of adenosine triphosphate, and it was revealed that the emission was unchanged. This result indicates that the triphosphate group has slightly influence on the emission property of the naphthyridine ligand.

Plots to evaluate the binding constants according to the degree of emission quenching are shown in Figure 6b. The binding constants were determined ( $K_{A,GTP} = 7500 \text{ M}^{-1}$ ,  $K_{A,cGMP} = 670 \text{ M}^{-1}$ ). It was



**Figure 6** (a) Stern-Volmer plots in the presence of the naphthyridine ligand by adding various types of guanosine nucleotides. (b) The plots to determine the binding constants between the naphthyridine ligand and the guanosine nucleotides. The slopes represent the number of binding guanosine nucleotides. The y intercepts represent the  $\log K_A$  values. The lines were prepared with the least-squares method.  $R^2$  is the determination coefficient. A full color version of this figure is available at *Polymer Journal* online.

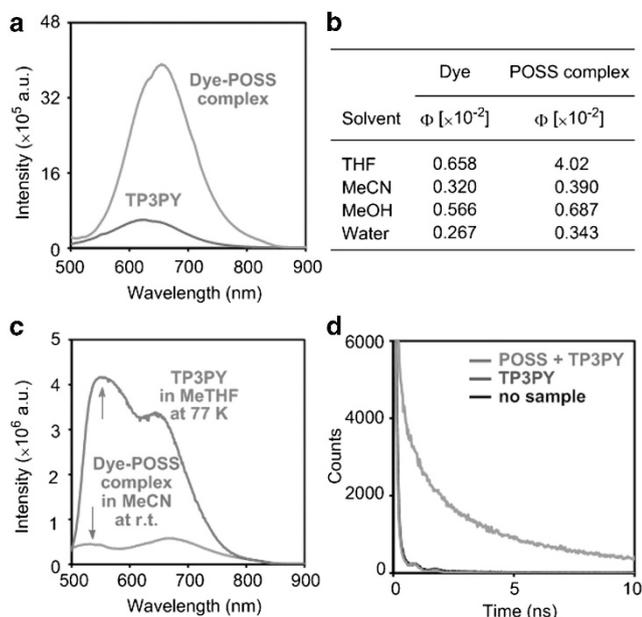
found that POSS can enhance the binding affinity of GTP  $\sim 10$  times more than that of cGMP. These results suggest that the naphthyridine ligand can selectively recognize GTP in the POSS-core dendrimer. From these data, we conclude that encapsulation in dendrimers can be made selective. Furthermore, in this system, the POSS-core dendrimer and the ligand molecules simply interact via non-covalent bonds. Therefore, the target guest molecules could be tuned by replacing the ligand units.

#### FREEZING EFFECT OF MOLECULAR MOTION IN POSS-CORE DENDRIMERS

The encapsulation ability of POSS-cores was introduced in the previous section. This ability arises from the amphiphilicity of POSS-core dendrimers, as a result of the hydrophobic POSS core and the polar dendrons. Next, we describe research on the unique optical properties of dyes encapsulated in POSS-core dendrimers. We have found that encapsulation at room temperature induced photochemical properties detectable only in the frozen glassy matrix of 2-methyltetrahydrofuran at  $-196^\circ\text{C}$  without complexation.<sup>56,57</sup> Suppression of the molecular rotation of dyes has a role in expressing these optical characteristics. The details are explained below.

We prepared and encapsulated trisvinyl-pyridinium triphenylamine (TP3PY, Figure 4)<sup>56</sup> in POSS-core dendrimers, and we examined a series of properties of these dendrimer complexes. First, to confirm the encapsulation and to assess the stability of the complexes in solution, we measured the absorption of the supernatants obtained from the solutions, which contained TP3PY with various concentrations of POSS-core dendrimer after storage under ambient conditions. The supernatant of pure TP3PY had a lower absorption with a peak at 474 nm after 3 days compared with those in the presence of POSS-core dendrimer. In contrast, the absorption from the supernatant decreased in a manner that corresponded to the increase in the concentration of the POSS-core dendrimer. The decreases in the absorption were completely suppressed in the presence of 10 equivalents of the POSS-core dendrimer. These data suggest that 10 equivalents of the POSS-core dendrimer is necessary to maintain the solution state of TP3PY. The branching of TP3PY and its larger size than the POSS-core dendrimer might result in the requirement of an excess of dendrimer to stabilize TP3PY's solution state.

The optical properties of TP3PY in the presence or absence of the POSS-core dendrimer were investigated in various solvents. Representative spectra in tetrahydrofuran are shown in Figure 7a.



**Figure 7** (a) Representative emission spectra of TP3PY in the presence (green line) or absence (red line) of the POSS-core dendrimer at 25 °C in tetrahydrofuran (THF) with excitation at 474 nm. (b) The changes in the fluorescence quantum yields of TP3PY in various solvents after encapsulation in the POSS-core dendrimer. (c) Emission spectra of TP3PY at 77 K in 2-methyltetrahydrofuran with excitation at 474 nm. The arrows indicate the peak tops of the emission band from the localized excitation states. (d) Fluorescence decay curves of TP3PY at 550 nm in phosphate-buffered saline. All measurements were monitored at 25 °C with excitation at 375 nm. A full color version of this figure is available at *Polymer Journal* online.

Clear enhancements of quantum yields were observed by encapsulation in each solvent (Figure 7b). The quantum yield of the emission of TP3PY was enhanced sixfold in the presence of POSS-core dendrimer than that of TP3PY in tetrahydrofuran. Notably, in water and acetonitrile, new emission bands were observed (Figure 7c). From these data, it is proposed that the POSS-core dendrimer has a key role in increasing the emission intensity of TP3PY.

To clarify the mechanism of increasing the quantum yields by encapsulating in POSS-core dendrimers, a series of measurements was performed. According to the solvatochromic shift of the emission from TP3PY, a Lippert–Mataga plot was made.<sup>58</sup> A linear relationship between the solvent polarity and the Stokes shift was obtained. The emission band of TP3PY with a peak at 650 nm was assigned as the induced charge transfer band. Moreover, the transition dipole moment ( $\Delta\mu$ ) was calculated as 11.80 D from the slope of the fitted line. This data indicates that the emission of TP3PY at 650 nm should be assigned as a twisted intramolecular charge transfer band.<sup>59</sup> A new emission peak at 550 nm, assigned as the localized excitation band, was observed at  $-196$  °C in 2-methyltetrahydrofuran, resulting in the emission with two peaks (Figure 7c). These data also suggest that the emission of TP3PY originates from the twisted intramolecular charge transfer band. From the data, it can be said that the POSS-core dendrimer has an ability to suppress the motions of the encapsulated molecules even in excited states. We measured the fluorescence life times of TP3PY (Figure 7d). As expected, the new emission with the peak at 550 nm had a long life time. The data indicated that the emission from the localized excitation band appeared after the encapsulation. The twisting at the excited state was inhibited by encapsulation in POSS-core dendrimers at room temperature.

These results illustrate that the nonirradiation decay caused by molecular tumbling should be efficiently suppressed by encapsulation in POSS-core dendrimers; therefore, the emission of TP3PY can be increased. Optical probes with longer life times are favorable for improving the signal-to-noise ratio as the signal emission can be gathered after decaying the self-emission from the sample. Encapsulation in POSS-core dendrimers should be feasible for developing practical fluorescence probes.

## CONCLUSION

The cubic silica of POSS has attracted attention as a building block for nanomaterial construction. The modified POSS derivatives with functional groups showed various types of interesting properties. As we illustrate in this review, POSS can generate special environments as a result of its structural features. Currently, there are few applications of these special environments that arise from the intrinsic characteristics of POSS, such as its amphiphilicity. However, the environments have the potential to extend the applicability and versatility of POSS for the construction of advanced materials not only in materials science but also in biochemistry. We all can expect to receive new nanomaterials based on the special distinct spaces created by POSS.

- 1 Kuo, S. & Chang, F. POSS related polymer nanocomposites. *Prog. Polym. Sci.* **36**, 1649–1696 (2011).
- 2 Laine, R. M. Nanobuilding blocks based on the  $[\text{OSiO}_{1.5}]_x$  ( $x=6, 8, 10$ ) octasilsesquioxanes. *J. Mater. Chem.* **15**, 3725–3744 (2005).
- 3 Fina, A., Monticelli, O. & Camino, G. POSS-based hybrids by melt/reactive blending. *J. Mater. Chem.* **20**, 9297–9305 (2010).
- 4 Cordes, D. B., Lickiss, P. D. & Rataboul, F. Recent Developments in the Chemistry of cubic polyhedral oligosilsesquioxanes. *Chem. Rev.* **110**, 2081–2173 (2010).
- 5 Gnanasekaran, D., Madhavan, K. & Reddy, B. S. R. Developments of polyhedral oligomeric silsesquioxanes (POSS), POSS nanocomposites and their applications: a review. *J. Sci. Ind. Res.* **68**, 437–464 (2009).
- 6 Madbouly, S. A. & Otaigbe, J. U. Recent advances in synthesis, characterization and rheological properties of polyurethanes and POSS/polyurethane nanocomposites dispersions and films. *Prog. Polym. Sci.* **34**, 1283–1332 (2009).
- 7 Chattopadhyay, D. K. & Webster, D. C. Thermal stability and flame retardancy of polyurethanes. *Prog. Polym. Sci.* **34**, 1068–1133 (2009).
- 8 Lickiss, P. D. & Rataboul, F. Fully condensed polyhedral oligosilsesquioxanes (POSS): from synthesis to application. *Adv. Organomet. Chem.* **57**, 1–116 (2008).
- 9 Lichtenhan, J. D. Polyhedral oligomeric silsesquioxanes: building blocks for silsesquioxane-based polymers and hybrid materials. *Comment. Inorg. Chem.* **17**, 115–130 (1995).
- 10 Pieliuchowski, K., Njuguna, J., Janowski, B. & Pieliuchowski, J. Polyhedral oligomeric silsesquioxanes (POSS)-containing nanohybrid polymers. *Adv. Polym. Sci.* **201**, 225–296 (2006).
- 11 Joshi, M. & Butola, B. S. Polymeric nanocomposites-polyhedral oligomeric silsesquioxanes (POSS) as hybrid nanofiller. *J. Macromol. Sci. Polym. Rev.* **C44**, 389–410 (2004).
- 12 Phillips, S. H., Haddad, T. S. & Tomczak, S. J. Developments in nanoscience: polyhedral oligomeric silsesquioxane (POSS)-polymers. *Curr. Opin. Solid St. M.* **8**, 21–29 (2004).
- 13 Li, G., Wang, L., Ni, H. & Pittman, Jr. C. U. Polyhedral oligomeric silsesquioxane (POSS) polymers and copolymers: a review. *J. Inorg. Organomet. Polym.* **11**, 123–154 (2002).
- 14 Schwab, J. J. & Lichtenhan, J. D. Polyhedral oligomeric silsesquioxane (POSS)-based polymers. *Appl. Organomet. Chem.* **12**, 707–713 (1998).
- 15 Wu, J. & Mather, P. T. POSS polymers: physical properties and biomaterials applications. *Polym. Rev.* **49**, 25–63 (2009).
- 16 Ghanbari, H., Cousins, B. G. & Seifalian, A. M. A nanocage for nanomedicine: polyhedral oligomeric silsesquioxane (POSS). *Macromol. Rapid Commun.* **32**, 1032–1046 (2011).
- 17 Tanaka, K. & Chujo, Y. Advanced functional materials based on polyhedral oligomeric silsesquioxane (POSS). *J. Mater. Chem.* **22**, 1733–1746 (2012).
- 18 Naka, K., Fujita, M., Tanaka, K. & Chujo, Y. Water-soluble anionic POSS-core dendrimer: synthesis and copper(II) complexes in aqueous solution. *Langmuir* **23**, 9057–9063 (2007).
- 19 Tanaka, K., Kitamura, N., Naka, K. & Chujo, Y. Multi-modal  $^{19}\text{F}$  NMR probe using perfluorinated cubic silsesquioxane-coated silica nanoparticles for monitoring enzymatic activity. *Chem. Commun.* **44**, 6176–6178 (2008).
- 20 Tanaka, K., Inafuku, K. & Chujo, Y. Ratiometric multimodal chemosensors based on cubic silsesquioxanes for monitoring solvent polarity. *Bioorg. Med. Chem.* **16**, 10029–10033 (2008).

- 21 Tanaka, K., Kitamura, N., Takahashi, Y. & Chujo, Y. Reversible signal regulation system of  $^{19}\text{F}$  NMR by redox reactions using a metal complex as a switching module. *Bioorg. Med. Chem.* **17**, 3818–3823 (2009).
- 22 Tanaka, K., Kitamura, N., Naka, K., Morita, M., Inubushi, T., Chujo, M., Nagao, M. & Chujo, Y. Improving proton relaxivity of dendritic MRI contrast agents by rigid silsesquioxane core. *Polym. J.* **41**, 287–292 (2009).
- 23 Tanaka, K., Kitamura, N. & Chujo, Y. Bi-Modal quantitative monitoring for enzymatic activity with simultaneous signal increases in  $^{19}\text{F}$  NMR and fluorescence using silica nanoparticle-based molecular probes. *Bioconjugate Chem.* **22**, 1484–1490 (2011).
- 24 Tanaka, K., Kitamura, N. & Chujo, Y. Heavy metal-free  $^{19}\text{F}$  NMR probes for quantitative measurements of glutathione reductase activity using silica nanoparticles as a signal quencher. *Bioorg. Med. Chem.* **20**, 96–100 (2012).
- 25 Kim, K. M., Ouchi, Y. & Chujo, Y. Synthesis of organic-inorganic star-shaped polyoxazolones using octafunctional silsesquioxane as an initiator. *Polym. Bull.* **49**, 341–348 (2003).
- 26 Kim, K. M., Keum, D. K. & Chujo, Y. Organic-inorganic polymer hybrids using polyoxazolone initiated by functionalized silsesquioxane. *Macromolecules* **36**, 867–875 (2003).
- 27 Dasari, A., Yu, Z. -Z., Mai, Y. -W., Cai, G. & Song, H. Roles of graphite oxide, clay and POSS during the combustion of polyamide 6. *Polymer* **50**, 1577–1587 (2009).
- 28 Guo, H., Meador, M. A., McCorkle, L., Quade, D. J., Guo, J., Hamilton, B., Cakmak, M. & Sprowl, G. Polyimide aerogels cross-linked through amine functionalized polyoligomeric silsesquioxane. *ACS Appl. Mater. Interfaces* **3**, 546–552 (2011).
- 29 Tanaka, K., Adachi, S. & Chujo, Y. Structure-property relationship of octa-substituted POSS in thermal and mechanical reinforcements of conventional polymers. *J. Polym. Sci. Part A: Polym. Chem.* **47**, 5690–5697 (2009).
- 30 Tanaka, K., Ishiguro, F. & Chujo, Y. POSS ionic liquid. *J. Am. Chem. Soc.* **132**, 17649–17651 (2010).
- 31 Tanaka, K., Ishiguro, F. & Chujo, Y. Thermodynamic study of POSS-based ionic liquids with various numbers of ion pairs. *Polym. J.* **43**, 708–713 (2011).
- 32 Asuncion, M. Z., Ronchi, M., Abu-Seir, H. & Laine, R. M. Synthesis, functionalization and properties of incompletely condensed “half cube” silsesquioxanes as a potential route to nanoscale Janus particles. *C. R. Chimie* **13**, 270–281 (2010).
- 33 Xu, A., Wang, J. & Wang, H. Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems. *Green Chem.* **12**, 268–275 (2010).
- 34 Tanaka, K., Adachi, S. & Chujo, Y. Side-chain effect of octa-substituted POSS fillers on refraction in polymer composites. *J. Polym. Sci. Part A: Polym. Chem.* **48**, 5712–5717 (2010).
- 35 Feher, F. J. & Wyndham, K. D. Amine and ester-substituted silsesquioxanes: synthesis, characterization and use as a core for starburst dendrimers. *Chem. Commun.* 323–324 (1998).
- 36 Feher, F. J., Wyndham, K. D., Soulivong, D. & Nguyen, F. Syntheses of highly functionalized cube-octameric polyhedral oligosilsesquioxanes ( $\text{R}_8\text{Si}_8\text{O}_{12}$ ). *J. Chem. Soc. Dalton Trans.* 1491–1497 (1999).
- 37 Gravel, M. C., Zhang, C., Dinderman, M. & Laine, R. M. Octa(3-chloroammoniumpropyl) octasilsesquioxane. *Appl. Organometal. Chem.* **13**, 329–336 (1999).
- 38 Zhang, X., Haxton, K. J., Ropartz, L., Cole-Hamilton, D. J. & Morris, R. E. Synthesis and computer modelling of hydroxy-derivatised carboxilane dendrimers based on polyhedral silsesquioxane cores. *J. Chem. Soc. Dalton Trans.* 3261–3268 (2001).
- 39 Ma, L., Geng, H., Song, J., Li, J., Chen, G. & Li, Q. Hierarchical self-assembly of polyhedral oligomeric silsesquioxane end-capped stimuli-responsive polymer: from single micelle to complex micelle. *J. Phys. Chem. B.* **115**, 10586–10591 (2011).
- 40 Zhang, W., Li, Y., Li, X., Dong, X., Yu, X., Wang, C., Wesdemiotis, C., Quirk, R. P. & Cheng, S. Z. D. Synthesis of shape amphiphiles based on functional polyhedral oligomeric silsesquioxane end-capped poly(L-lactide) with diverse head surface chemistry. *Macromolecules* **44**, 2589–2596 (2011).
- 41 Yu, X., Zhong, S., Li, X., Tu, Y., Yang, S., Van Horn, R. M., Ni, C., Pochan, D. J., Quirk, R. P., Wesdemiotis, C., Zhang, W. B. & Cheng, S. Z. A giant surfactant of polystyrene-(carboxylic acid-functionalized polyhedral oligomeric silsesquioxane) amphiphile with highly stretched polystyrene tails in micellar assemblies. *J. Am. Chem. Soc.* **132**, 16741–16744 (2010).
- 42 Tanaka, K., Inafuku, K., Adachi, S. & Chujo, Y. Tuning of properties of POSS-condensed water-soluble network polymers by modulating the cross-linking ratio between POSS. *Macromolecules* **42**, 3489–3492 (2009).
- 43 Tanaka, K., Ohashi, W., Kitamura, N. & Chujo, Y. Reductive glutathione-responsive molecular release using water-soluble POSS network polymers. *Bull. Chem. Soc. Jpn* **84**, 612–616 (2011).
- 44 Tanaka, K., Inafuku, K., Naka, K. & Chujo, Y. Enhancement of entrapping ability of dendrimers by a cubic silsesquioxane core. *Org. Biomol. Chem.* **6**, 3899–3901 (2008).
- 45 Tanaka, K., Inafuku, K. & Chujo, Y. Environment-responsive upconversion based on dendrimer-supported efficient triplet-triplet annihilation in aqueous media. *Chem. Commun.* **46**, 4378–4380 (2010).
- 46 Tanaka, K., Murakami, M., Jeon, J. -H. & Chujo, Y. Enhancement of affinity in molecular recognition via hydrogen bonds by POSS-core dendrimer and its application for selective complex formation between guanosine triphosphate and 1,8-naphthyridine derivatives. *Org. Biomol. Chem.* **10**, 90–95 (2012).
- 47 Blight, B. A., Hunter, C. A., Leigh, D. A., McNab, H. & Thomson, P. I. An AAAA-DDDD quadruple hydrogen-bond array. *Nat. Chem.* **3**, 244–248 (2011).
- 48 Dohno, C., Kohyama, I., Hong, C. & Nakatani, K. Naphthyridine tetramer with a preorganized structure for 1:1 binding to a CCG/CGG sequence. *Nucleic Acids Res.* **40**, 2771–2781 (2012).
- 49 Westover, K. D., Bushnell, D. A. & Kornberg, R. D. Structural basis of transcription: nucleotide selection by rotation in the RNA polymerase II active center. *Cell* **119**, 481–489 (2004).
- 50 Nakatani, K., Hagihara, S., Goto, Y., Kobori, A., Hagihara, M., Hayashi, G., Kyo, M., Nomura, M., Mishima, M. & Kojima, C. Small-molecule ligand induces nucleotide flipping in (CAG) $_n$  trinucleotide repeats. *Nat. Chem. Biol.* **1**, 39–43 (2005).
- 51 Peng, T., Dohno, C. & Nakatani, K. Mismatch binding ligands function as molecular glue of DNA. *Angew. Chem. Int. Ed.* **45**, 5623–5626 (2006).
- 52 Fang, J. M., Selvi, S., Liao, J. H., Slanina, Z., Chen, C. T. & Chou, P. T. Fluorescent and circular dichroic detection of monosaccharides by molecular sensors: bis[(pyrrolyl)ethynyl]naphthyridine and bis[(indolyl)ethynyl]naphthyridine. *J. Am. Chem. Soc.* **126**, 3559–3566 (2004).
- 53 Sato, Y., Nishizawa, S., Yoshimoto, K., Seino, T., Ichizawa, T., Morita, K. & Teramae, N. Influence of substituent modifications on the binding of 2-amino-1,8-naphthyridines to cytosine opposite an AP site in DNA duplexes: thermodynamic characterization. *Nucleic Acids Res.* **37**, 1411–1422 (2009).
- 54 Lu, S. H., Selvi, S. & Fang, J. M. Ethynyl-linked (pyreno)pyrrole-naphthyridine and aniline-naphthyridine molecules as fluorescent sensors of guanine via multiple hydrogen bondings. *J. Org. Chem.* **72**, 117–122 (2007).
- 55 Cywinski, P. J., Moro, A. J., Ritschel, T., Hildebrandt, N. & Löhmansröben, H. G. Sensitive and selective fluorescence detection of guanosine nucleotides by nanoparticles conjugated with a naphthyridine receptor. *Anal. Bioanal. Chem.* **399**, 1215–1222 (2011).
- 56 Tanaka, K., Jeon, J. -H., Inafuku, K. & Chujo, Y. Enhancements of optical properties of dyes for bioprobes by freezing effect of molecular motion using POSS-core dendrimers. *Bioorg. Med. Chem.* **20**, 915–919 (2012).
- 57 Allain, C., Schmidt, F., Lartia, R., Bordeau, G., Fiorini-Debuisschert, C., Charra, F., Tauc, P. & Teulade-Fichou, M.-P. Vinyl-pyridinium triphenylamines: novel far-red emitters with high photostability and two-photon absorption properties for staining DNA. *ChemBioChem.* **8**, 424–433 (2007).
- 58 Valeur, B. *Molecular Fluorescence* (Wiley-VCH, Weinheim, Germany, 2002).
- 59 Okamoto, A., Tanaka, K., Nishiza, K. & Saito, I. Monitoring DNA structures by dual fluorescence of pyrene derivatives. *J. Am. Chem. Soc.* **127**, 13128–13129 (2005).



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