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Synthesis of Janus cube containing Si–H moieties

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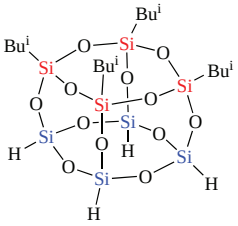
The first representative of the Janus cube with hydrogen substituents was obtained from all-*cis*-[Bu^{i}SiO(OH)]$_4$ by its capping with HSiCl$_3$ followed by gentle hydrolysis causing internal condensation. The compound has an extremely low maximum loss temperature, which is approximately halfway between H$_8$Si$_8$O$_{12}$ and (octaisobutyl)octasilsesquioxane.



New Janus cube
Reactive substituents
Low melting point

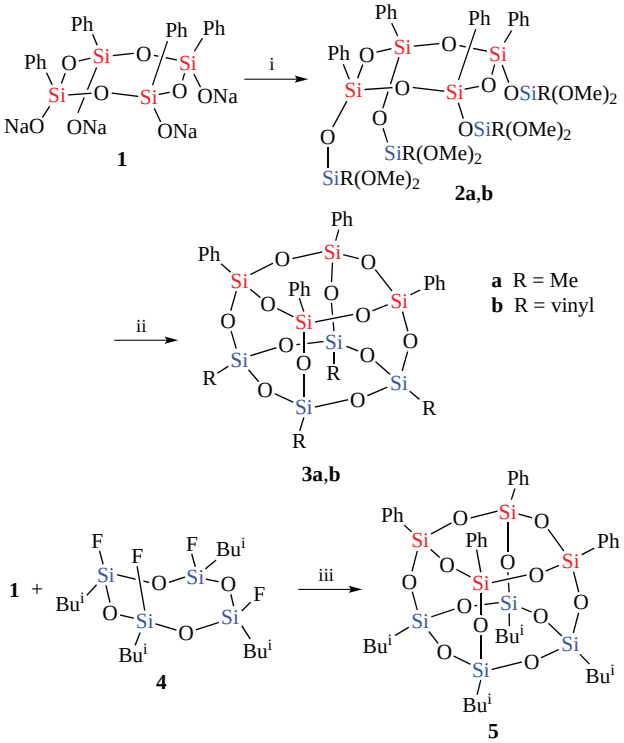
Keywords: siloxanes, octasilsesquioxanes, organosilicon compounds, Janus particle, TG-DTA.

Organic–inorganic composite materials are widely used because of their excellent oil, flame and heat resistance, and good processability.[1] Among them, cubic octasilsesquioxane, an organic–inorganic hybrid molecule with cubic symmetry and eight functionalities, is attractive as a future nanoscale structural unit. A group of compounds consisting solely of the T silicon atoms, such as octasilsesquioxane, possesses properties intermediate between the linear D structure siloxanes and inorganic silica (Q units). Their excellent thermal, electrical, and optical properties make them important materials for industrial applications such as low-k materials, resistant materials, and nano-ink printing materials.[2]

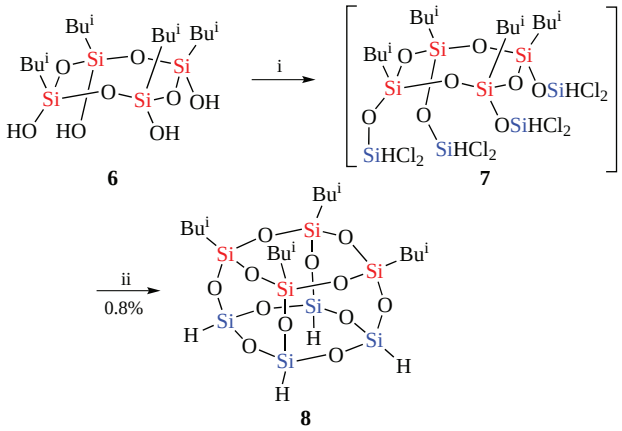
Janus cubes, which have different substituents on the face-to-face side of silsesquioxane, are currently in demand. In 2010, Laine *et al*., starting from cyclic tetrasilanolate **1**, performed intramolecular condensation of dialkoxysilyl groups in the subsequent cyclotetrasiloxanes **2a**,**b** (Scheme 1) thus affording Janus cubes **3a**,**b**.[3] The products were analyzed by FT-IR and MALDI-TOF MS. However, X-ray crystallographic analysis was not performed, so the structures were not ultimately established. In 2016, our group subjected the same tetrasilanolate **1** to the reaction with cyclic tetrakis-fluorosilane **4**, which brought about Janus cube with phenyl and isobutyl groups **5** (see Scheme 1).[4] In that study, the Janus structures were first revealed by X-ray crystallography.

However, in view of the abovementioned results, the diversity of Janus cubes of type **5** thus accessed seems limited inasmuch as phenyl and isobutyl substituents can be hardly modified. Therefore, the search for intermediates with reactive groups suitable for bottom-up modification of Janus cube looks more challenging. The preferred method for this purpose may be the Laine intramolecular condensation. Based on this, Kuroda *et al*. synthesized Janus cubes with alkoxy groups using the hydrolysis of cyclosiloxane with alkoxysilyl groups.[5] In contrast, we focused on Janus cubes with highly reactive Si–H moieties (*cf*. ref. 6). Herein, we report the synthesis of Si–H/Janus cubes by intramolecular condensation and their unique thermal properties.

The initial tetrasilanol **6**, all-*cis*-[Bu^{i}SiO(OH)]$_4$, was synthesized using a previously reported[7] method (Scheme 2). The obtained ethereal solution of compound **6** was reacted with trichlorosilane to afford crude material containing compound **7** (for details, see Online Supplementary Materials). This solution was then added dropwise to an acetone–water mixture at 0 °C under argon, and the reaction mixture was stirred at room temperature for 2 days. Finally, the desired Si–H/Janus cube **8** was isolated by wet column chromatography and recycle-type GPC, however in a very low yield of 0.8% (see Scheme 2, for



Scheme 1 *Reagents and conditions*: i, RSiCl$_3$, MeOH, hexane, room temperature, 24 h; ii, H$_2$O, HCl (ref. 3); iii, CHCl$_3$, reflux, 1 day (ref. 4).



Scheme 2 *Reagents and conditions*: i, $HSiCl_3$, Et_3N, Et_2O, 0 °C, 24 h; ii, H_2O, acetone, 0 °C to room temperature, 2 days.

compound characterization, see Online Supplementary Materials).

Compound **8** was identified by ^1H, ^{13}C, ^{29}Si NMR spectroscopy, mass spectrometry, and elemental analysis. The ^1H NMR spectrum indicated the presence of Bu^i and H groups with an integral intensity ratio of 9 : 1, suggesting that compound **8** contains Bu^i and H groups in a 1 : 1 ratio. The ^{29}Si NMR spectrum displayed only two singlets at δ –67.3 and –84.5 ppm, which corresponded to Bu^i and Si–H substituted silicon, respectively. These chemical shifts were consistent with previously reported ones for octaisobutyloctasilsesquioxane and $H_8Si_8O_{12}$ (δ –67.9[8] and –84.6 ppm,[9] respectively).

Compound **8** exhibited low thermal stability. During simultaneous thermogravimetry (TG)/differential thermal analysis (DTA) under a nitrogen stream, it revealed endothermic properties at 80 °C in DTA (Figure 1). However, no weight change could be observed within the corresponding temperature range, so its melting point should be 80 °C. This result is consistent with the results of melting point measurements. During the TG analysis of **8**, the 5% weight loss temperature was 183 °C. Remarkably, the compound evaporated completely at 250 °C leaving no residue. In general, the heat resistance of cage-type silsesquioxanes is high. However, the thermophysical properties are highly dependent on the substituents on the silicon.[10] The maximum loss temperature (T_{max}) of compound **8** was approximately halfway between those of $H_8Si_8O_{12}$ and octaisobutyloctasilsesquioxane.

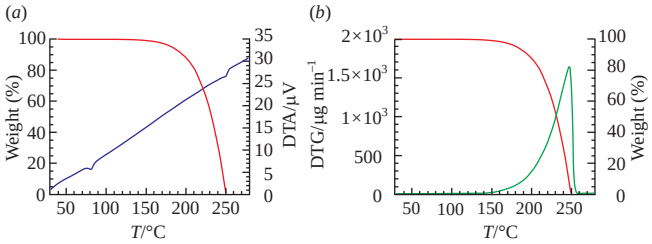


Figure 1 Thermal stability of Si–H/Janus cube **8**: (*a*) TG-DTA curve and (*b*) TG-DTG curve (temperature raising 10 K min^{-1}, under nitrogen).

In conclusion, the novel Si–H/Janus cube was synthesized using intramolecular condensation of O–$SiHCl_2$ moieties. The synthesized compound **8** has a low melting point, and its maximum weight loss rate temperature is halfway between those of $H_8Si_8O_{12}$ and (octaisobutyl)octasilsesquioxane. This investigation of thermophysical properties will serve as a guideline for the design of materials using silsesquioxane in the future.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.010.

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