

Self-assembly supramolecular structure through complementary multiple hydrogen bonding of heteronucleobase-multifunctionalized polyhedral oligomeric silsesquioxane (POSS) complexes†

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Received 21st September 2011, Accepted 11th November 2011

DOI: 10.1039/c1jm14699h

In this study, we synthesized octakis(vinylbenzylthymine-siloxy)silsesquioxane (OBT-POSS), *via* hydrosilylation with octakis(dimethylsiloxy)-silsesquioxane ($Q_8M_8^H$) and vinyl benzylthymine (VBT). The synthesis of octakis((vinylbenzyltriazolyl) methyladenine-siloxy)silsesquioxane (OBA-POSS) was prepared by click chemistry from octa-azido functionalized POSS (OVBN₃-POSS) with propynyl-adenine (PA). The self-assembly lamellae structure based on a supramolecular network through the OBA-POSS/OBT-POSS complex was observed. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopic analyses revealed the presence of multiple hydrogen bonding between the adenine and thymine groups of OBA-POSS/OBT-POSS complex. Because of its strong reversible intermolecular multiple hydrogen bonding, this is a successful example of a POSS-based polymer-like supramolecular material at room temperature with high thermal properties (such as $T_g \sim 100$ °C).

Introduction

Complementary multiple hydrogen bonding interactions in molecular design have recently received significant attention because of the tendency to form new supramolecular structures that show thermoreversible characteristics.^{1,2} Self-assembled polymers are usually formed through covalent bonds in traditional polymer chemistry, including bonds connecting monomer units and attaching functional groups to the polymer backbone. Recently, highly directional and sufficiently strong non-covalent bond pairs have substituted these conventional covalent bonds.^{3–5} The approach toward the preparation of supramolecular polymers is for strong hydrogen bonding between small molecules or oligomers to be exploited for the self-assembly of extended linear chains.^{6–22} Under suitable experimental conditions, such small molecules or oligomer assembly can display polymeric-like rheological or mechanical properties, because of their supramolecular structure.²³ It is well-known that complementary multiple hydrogen bonding arrays play a fundamental role in complex biological systems (*e.g.* DNA duplexes). The self-assembly of pairs of DNA strands is mediated by intermolecular hydrogen bonding between complementary purine [adenine (A) and guanine (G)] and pyrimidine [thymine (T) and cytosine (C)] bases attached to a phosphate sugar backbone: G binds

selectively to C and A binds selectively to T.²⁴ Taking this cue from nature, we wondered whether we could enhance thermal and mechanical properties of these materials by preparing synthetic nucleotides based on oligomer supramolecular networks, which is still a challenging subject.

Recently, researchers have developed a novel class of organic/inorganic hybrid materials based on polyhedral oligomeric silsesquioxane (POSS) nanoparticles.^{25–34} POSS is an inorganic Si_8O_{12} core, which can be functionalized by attaching seven inert organic hydrocarbon groups and a unique functional group or eight functional groups that are capable of polymerization or cross-linking.^{35–38} Through appropriate design of the structure, these POSS derivatives can be tailored for specific applications, such as polymer light emitting diodes,^{39,40} liquid crystals,⁴¹ photoresists,⁴² low dielectric constant materials^{43,44} and self-assembly structures.^{45,46} Jeoung *et al.* and Carroll *et al.* used a POSS derivative with one diaminopyridine arm which was able to self-assemble through thymine-functionalized monolayers on a gold surface or polystyrene matrix.^{47,48} Cheng *et al.* reported eight diaminopyridine arms of POSS, which are able to self-assemble forming a physically crosslinked polymer-like structure through self-quadruple hydrogen bonding interactions between the arms.⁴⁹

In this study, two new star-like supramolecular POSS-based materials have been synthesized; first the star octuply-thymine functionalized POSS (octakis(vinylbenzylthymine-siloxy) silsesquioxane, OBT-POSS) was produced *via* hydrosilylation of octakis(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) with vinyl benzylthymine (VBT), as shown in Scheme 1. Then, the star

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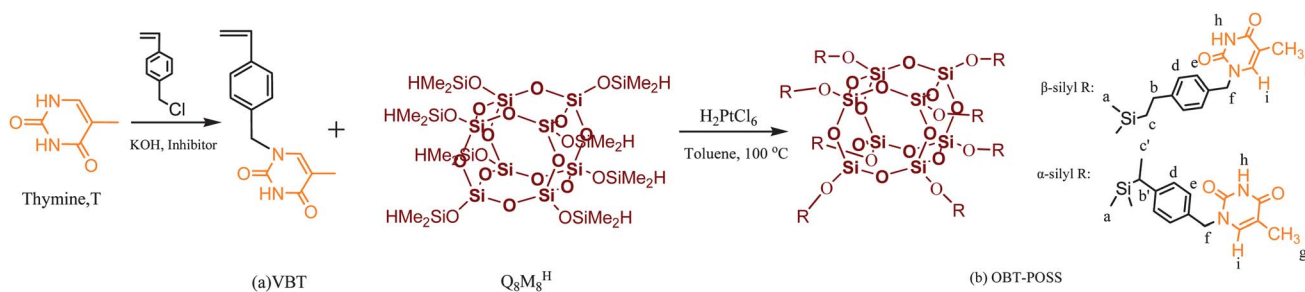
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1jm14699h

octuply-adenine functionalized POSS (octakis((vinylbenzyl triazolyl) methyl adenine-siloxy)silsesquioxane, OBA-POSS) was synthesized from octuply-azido functionalized POSS (OVBN₃-POSS) with propynyl-adenine (PA) *via* a click reaction as shown in Scheme 2. These self-assembled supramolecular structures and multiple hydrogen bonding interactions of OBA-POSS/OBT-POSS complexes were characterized using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), and transmission electron microscopy (TEM) analytical methods. Additionally, the supramolecular POSS network with film-formation ability and mechanical properties was produced by mixing OBT-POSS with OBA-POSS as a result of multiple hydrogen bonding interactions between complementary thymine-adenine multifunctional groups.

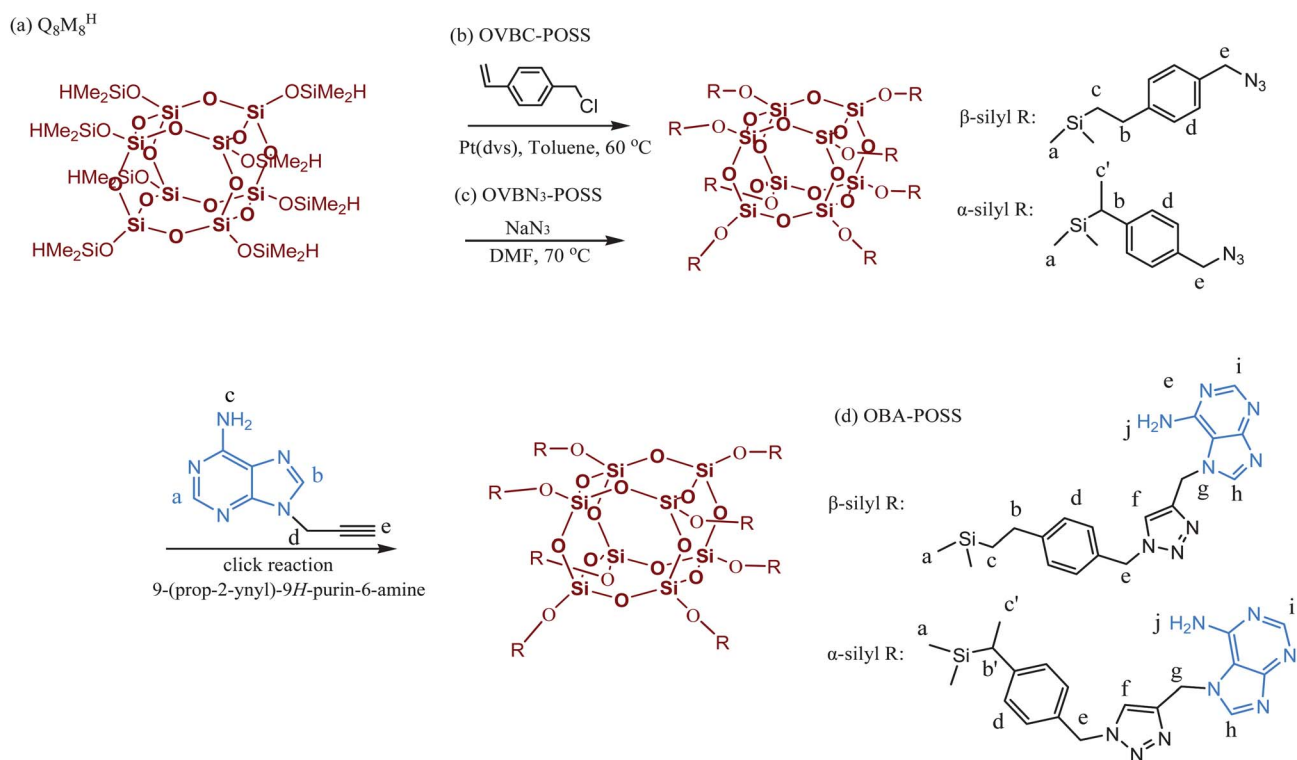
Experimental

Materials

Octakis(dimethylsiloxy)silsesquioxane (Q₈M₈^H) containing eight hydrosilane groups was obtained from Hybrid Plastics. Thymine, adenine, sodium azide (NaN₃), copper(i) bromide (CuBr, 98%), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 99%), were purchased from Aldrich Chemical Company. Vinylbenzyl chloride was purchased from Acros Organics (Germany) and was distilled prior to use. Dimethylformamide (DMF) was distilled from CaH₂ under vacuum prior to use. Sodium hydride in oil (57–63%) was purchased from Alfa. Propargyl bromide was purchased from Tokyo Kasei Kogyo Co., Japan. All other chemicals were of reagent grade and used as received without any purification. 1-(4-vinylbenzyl)



Scheme 1 The synthesis of VBT (a), and hydrosilylation with Q₈M₈^H to form OBT-POSS (b).



Scheme 2 The reaction scheme of hydrosilylation of VBC with Q₈M₈^H (a) to give OVBC-POSS (b), azide substitution to form OVBN₃-POSS (c) and click reaction with propynyl adenine to form OBA-POSS (d).

thymine (VBT) was prepared using a procedure described elsewhere.⁵⁰

Synthesis of OBT-POSS

OBT-POSS was synthesized based on the procedure shown in the Scheme 1. $Q_8M_8^H$ (1 g, 0.98 mmol) and VBT (2 g, 7.95 mmol) in toluene solution (50 mL) was heated at 100 °C under argon while the catalyst H_2PtCl_6 (0.05 mL, 0.13 mmol) was added using a syringe.⁵¹ After stirring for 4 h, the H_2PtCl_6 catalyst was removed using activated charcoal. The solvent was removed by rotary evaporation and a white powder of OBT-POSS was formed. 1H NMR ($CDCl_3$): δ 11.31 (s, 1H), δ 7.60 (s, 1H), δ 7.20 (d, 2H), 7.00 (d, 2H), 4.70 (s, 2H), 2.87 (t, 2H), 2.51 (q, 1H), 1.70 (s, 1H), 1.05 (d, 3H), 0.75 (t, 2H), 0.05 (m, 6H) ppm. ^{29}Si NMR ($CDCl_3$): δ 15.59, -109.0 ppm. GPC: ($M_n = 3400$ g mol⁻¹, Figure S1).†

Synthesis of propynyl-adenine

Propynyl-adenine (PA) was prepared using adenine (1 g, 0.02 mol) and sodium hydride in DMF (30 mL) solution while stirring at ambient temperature. After 1 h, 1.5 g (0.03 mol) of propargyl bromide was added and the mixture was stirred at room temperature for 24 h. The combined filtrates were evaporated to dry under vacuum. A column chromatographic method (EA : hexane) was applied for the separation of PA. 1H NMR ($CDCl_3$): δ 2.54 (t, 1H, $C\equiv C-H$), 5.02 (d, 2H, $CH_2C\equiv C$), 5.66 (br, 2H, NH_2), 8.03 (s, 1H), 8.41 (s, 1H). FTIR (KBr, cm^{-1}): 3369, 3272, 3249 (N-H str.), 3140 (alkyne C-H str.), 2931, 2875 (aliphatic C-H str.), 2110 ($C\equiv C$ str.), 1693 ($C=N$ str.), 1610 (N-H def.).

Synthesis of OVBN₃-POSS

OVBN₃-POSS was synthesized *via* the reaction between OVBC-POSS and sodium azide (NaN_3), as shown in Scheme 2.^{52,53} The OVBC-POSS was prepared using $Q_8M_8^H$ (1 g, 0.98 mmol) and vinyl benzyl chloride (1.20 g, 7.86 mmol) in toluene (50 mL). The solution was heated at 60 °C under argon and then Pt(dvs) (0.07 mL, 0.13 mmol) was added using a syringe. After stirring for 4 h, the Pt(dvs) catalyst was removed using activated charcoal. Solvent removal by rotary evaporation gave a viscous liquid. We used GPC data and ^{29}Si NMR spectrometer to determine the chemical structure of OVBC-POSS (Figure S1, and S2).† In a typical experiment synthesizing OVBN₃-POSS, OVBC-POSS (1 g, 0.45 mmol), NaN_3 (1.01 g, 15.4 mmol) and anhydrous DMF (50 mL) were added to a flask. The reaction was maintained at 120 °C for 48 h. The solutions were concentrated and the residues were dissolved in THF and the sodium salts were removed using a neutral alumina column. The yellowish viscous liquid was obtained after drying in a vacuum oven overnight at room temperature.

Synthesis of OBA-POSS *via* click reaction

PA (0.62 g, 3.61 mmol), OVBN₃-POSS (1 g, 0.44 mmol) and CuBr (3.5 mg, 0.025 mmol) were dissolved in DMF (20 mL) in a flask equipped with a magnetic stirring bar. After a short freeze-thaw-pump cycle, PMDETA (5.2 mL, 0.025 mmol) was added and the reaction mixture was carefully degassed by three

freeze-thaw-pump cycles, then stirred at ambient temperature for 24 h. After removing all the solvents at reduced pressure, the residues were dissolved in DMSO and passed through a neutral alumina column to remove copper catalysts. All chemical reactions of synthesizing OBA-POSS are summarized in Scheme 2. 1H NMR (DMSO): δ 5.37 (s, 2H), 7.91 (s, 2H, NH_2), 8.10 (s, 1H), 8.15 (s, 1H) ppm. FTIR (KBr, cm^{-1}): 3369, 3272, 3249 (N-H str.), 2931, 2875 (aliphatic C-H str.), 1089 (Si-O-Si), 1693 ($C=N$ str.), 1610 (N-H def.).

Preparation of supramolecular OBT-POSS/OBA-POSS complexes

Mixtures of OBT-POSS and OBA-POSS with different ratios were prepared by solution-blending. DMF solutions containing 5 wt% of the polymer mixture were stirred over night; the solvent was then removed by evaporation at 50 °C for 2 days under vacuum.

Characterization

1H and ^{13}C NMR spectra were examined with a Varian Unity Inova 500 FT NMR spectrometer operating at 500 MHz using $CDCl_3$ and DMSO as solvents. The glass transition temperatures of the blend films were determined by DSC using a TA Q-20 instrument. The scan rate was 20 °C min⁻¹ in the range of 30–220 °C; the temperature was then held at 220 °C for 1 min to ensure complete removal of the residual solvent. The T_g measurements were performed in the DSC sample cell after the sample (5–10 mg) had been cooled rapidly to -50 °C from the melt in the first scan. The glass transition temperature was defined as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines. FTIR spectra of the polymer blend films were examined using the conventional KBr disk method. A DMF solution containing the blend was cast onto a KBr disk and dried under conditions similar to those used in the bulk preparation. The film used in this study was sufficiently thin to obey the Beer-Lambert law. FTIR spectra were examined using a Bruker Tensor 27 FT-IR spectrophotometer; 32 scans were collected at a spectral resolution of 1 cm^{-1} . TEM images were taken using a Hitachi H-7500 transmission electron microscope operated at an accelerating voltage of 100 kV. Ultrathin sections of the TEM samples (*ca.* 70 nm thickness) were prepared using a Leica Ultracut UCT microtome equipped with a diamond knife.

Results and discussion

Synthesis and characterization of OBT-POSS

OBT-POSS was synthesized through the hydrosilylation of vinylbenzyl thymine with octakis(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$), as shown in Scheme 1 and the reaction was characterized using 1H NMR, ^{13}C NMR, ^{29}Si NMR, and FTIR analytical methods. For VBT, two doublets and the quartet resonance proton resonance peaks from the vinyl group ($1H_b$, $1H_a$ and $2H_c$) in the VBT are located at 5.26, 5.77 and 6.98 ppm with a relative molar ratio of 1 : 1 : 1, corresponding to *iso*-, *trans*- and substituted vinyl protons. The resonances of methyl in

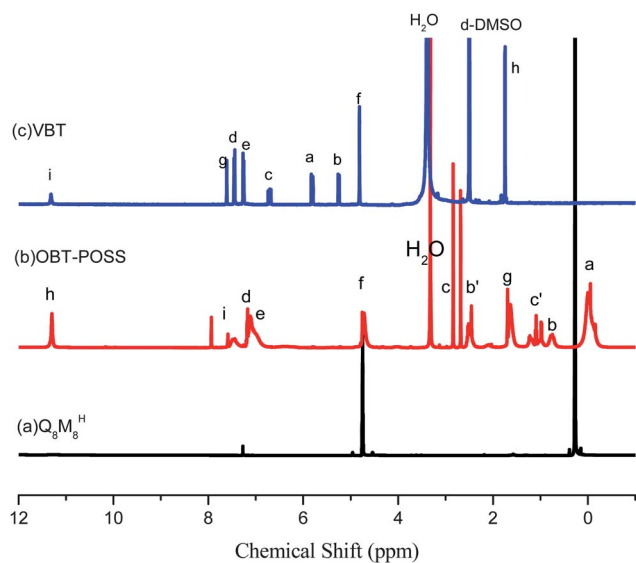


Fig. 1 ^1H NMR spectra of (a) $\text{Q}_8\text{M}_8\text{H}$ in CDCl_3 , (b) OBT-POSS and (c) VBT in d -DMSO.

thymine (H_h), and benzyl CH_2 (H_f) at a molar ratio of 3 : 2 are observed at $\delta = 1.80$ and 4.87 ppm, respectively. The NH in the thymine group is located 11.30 ppm and all other peaks are assigned in Fig. 1c. The peaks for the vinyl group of VBT (*ca.* 5.3, 5.8, and 6.7 ppm) in Fig. 1c and Si-H protons (4.7 ppm) in Fig. 1a disappeared in the spectrum of OBT-POSS in Fig. 1b, supporting the complete hydrosilylation reaction. The spectrum in Fig. 1b indicates that the vinyl groups of VBT underwent hydrosilylation of the Si-H bonds of $\text{Q}_8\text{M}_8\text{H}$ in both the α and β configurations, *i.e.*, a mixture of these two orientations exists. We observed the ratios of β to α linkages (1.98 : 1) for OBT-POSS, according to the integration of the signals for the protons marked *b* (2H, β -side groups) and *b'* (1H, α -side groups). Fig. 2 displays the corresponding ^{13}C NMR spectra of the VBT and OBT-POSS. The vinyl group of VBT at 114.3 and 135.9 ppm disappeared in OBT-POSS, also indicating the complete reaction of hydrosilylation. All other peaks are also assigned in Fig. 2.

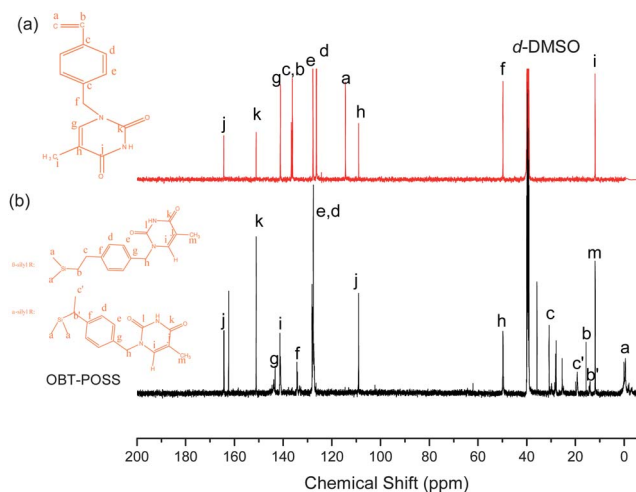


Fig. 2 ^{13}C NMR spectra of (a) VBT and (b) OBT-POSS in d -DMSO.

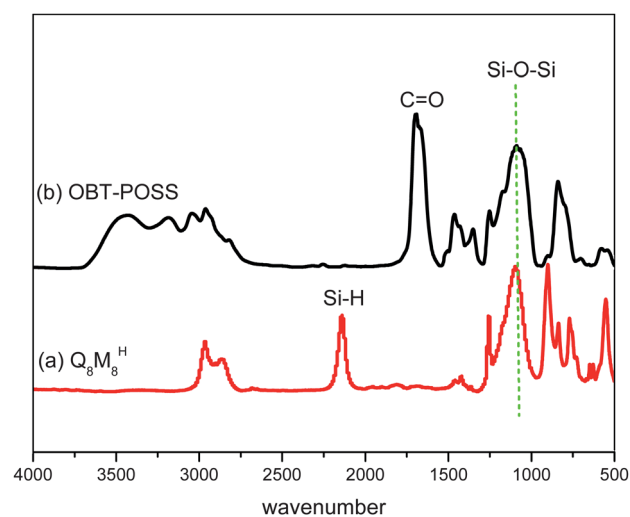


Fig. 3 FTIR spectra of (a) $\text{Q}_8\text{M}_8\text{H}$, and (b) OBT-POSS.

The ^{29}Si NMR spectra of $\text{Q}_8\text{M}_8\text{H}$ and OBT-POSS [Figure S3],[†] show two peaks at -1.4 and -107.1 ppm and two peaks at 15.7 and -109.23 ppm, respectively. The downfield shift from -1.4 to 15.7 ppm confirms that the hydrosilylation occurred to completion under the reaction conditions. Fig. 3 presents the FTIR spectra of $\text{Q}_8\text{M}_8\text{H}$ and OBT-POSS. The strong absorption peak at *ca.* 1100 cm^{-1} represents the vibrations of the siloxane Si-O-Si groups and is a general feature of POSS derivatives. The characteristic stretching vibration of the Si-H groups appears as a signal at 2200 cm^{-1} [Fig. 3a]. In the FTIR spectrum of OBT-POSS, we attribute the band at 1694 and 1674 cm^{-1} to the free and hydrogen-bonded C=O bond of thymine groups, respectively.

The absence of a stretching vibration band at 2200 cm^{-1} indicates that the hydrosilylation occurred to completion. Thus, the ^1H NMR, ^{13}C NMR, ^{29}Si NMR and FTIR spectra are consistent with the formation of OBT-POSS.

Synthesis and characterization of OBA-POSS

We initially attempted to synthesize the star octuply-adenine functionalized POSS (OBA-POSS) based on the OBT-POSS

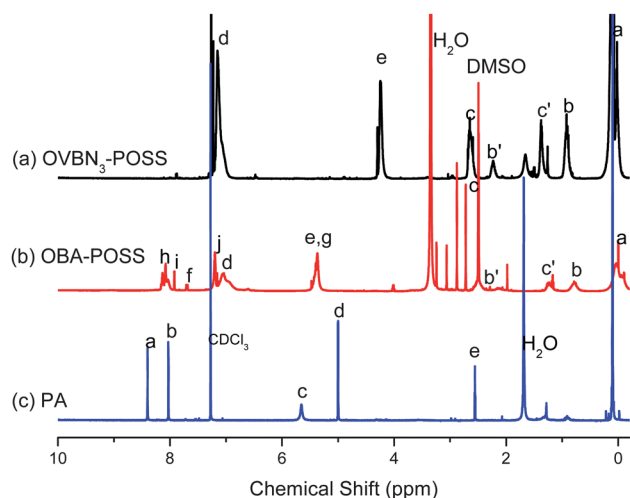


Fig. 4 ^1H NMR spectra of (a) $\text{OVBN}_3\text{-POSS}$ in CDCl_3 , (b) OBA-POSS in d -DMSO and (c) propynyl adenine (PA) in CDCl_3 .

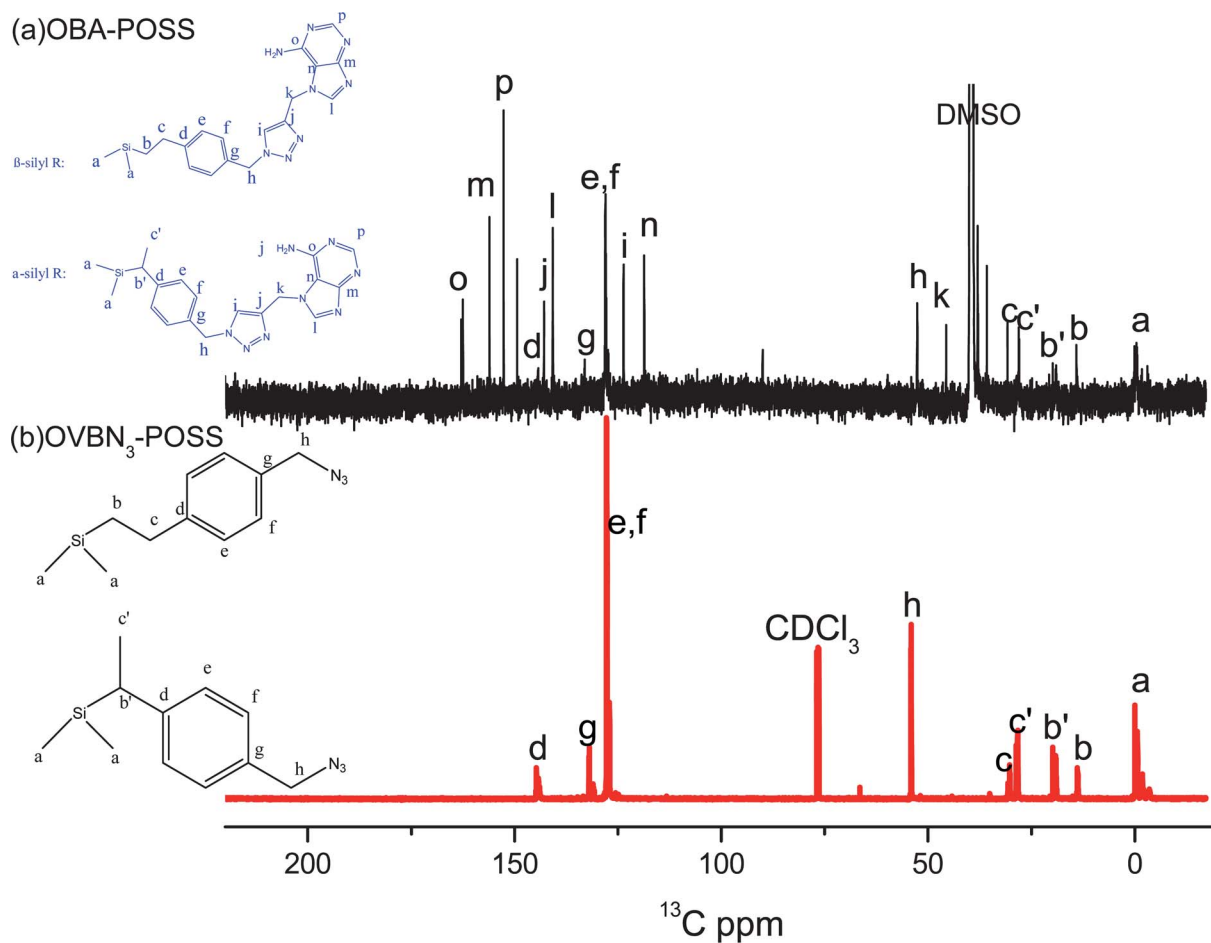


Fig. 5 ^{13}C NMR spectra of (a) OBA-POSS in *d*-DMSO and (b) OVBN₃-POSS in CDCl₃.

concept through the hydrosilylation of vinylbenzyl adenine with Q₈M₈^H. Unfortunately, the reaction did not continue to completion even after 2 days at 60 °C. ¹H NMR and FTIR analyses, revealed that most of the vinyl and Si-H groups remained unreacted. It is well-known that the hydrosilylation is hampered by severe side reactions under highly polar functional groups, such as adenine groups in this case.⁵⁴

As a result, another potential star octuply-adenine functionalized POSS was synthesized *via* the click reaction of OVBN₃-POSS with propynyl-adenine (PA) as shown in Scheme 2. Fig. 4 shows the ¹H NMR spectra of OVBN₃-POSS, OBA-POSS, and PA. The resonance of the benzyl CH₂ connected to the azide atoms at 4.31 ppm of OVBN₃-POSS is shown in Fig. 4a. This peak significantly shifted down field from 4.31 to 5.38 ppm of OBA-POSS, as shown in Fig. 4b. The observation that no traces of resonance existed at 4.31 ppm suggested that the click reaction occurred to completion under the reaction conditions. In addition, the singlet at 2.55 ppm corresponding to the C≡C-H disappeared and the singlet at 5.00 ppm corresponding to C≡C=CH₂ of PA, also shifted downfield to 5.38 ppm. These observations suggested that the click reaction occurred to completion under the reaction conditions. Fig. 5 displays the corresponding ¹³C NMR spectra of OVBN₃-POSS and OBA-POSS. The benzyl carbon (C-h) peak appeared at 53.0 ppm and shifted to 52.6 ppm after the click reaction with PA. The peaks at

123.6 ppm and 143.2 ppm are the carbons of the triazole structures resulting from the click reaction of OBA-POSS. The methyl and methylene carbons of OVBN₃-POSS remained in OBA-POSS at 0.2 ppm and 19.8 ppm, respectively. All other carbon

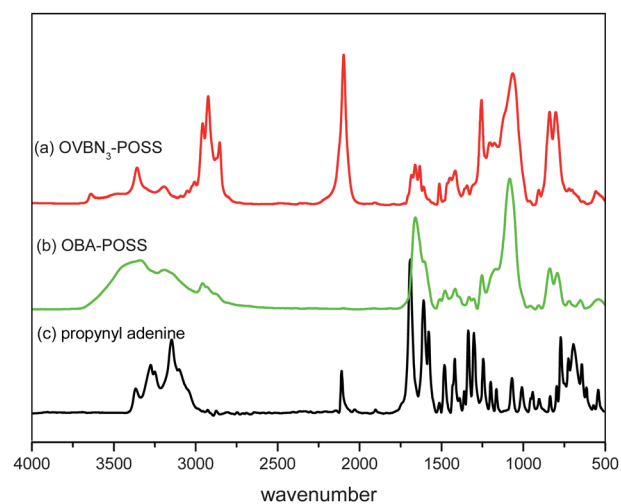


Fig. 6 FTIR spectra of (a) OVBN₃-POSS (b) OBA-POSS and (c) propargyl-adenine.

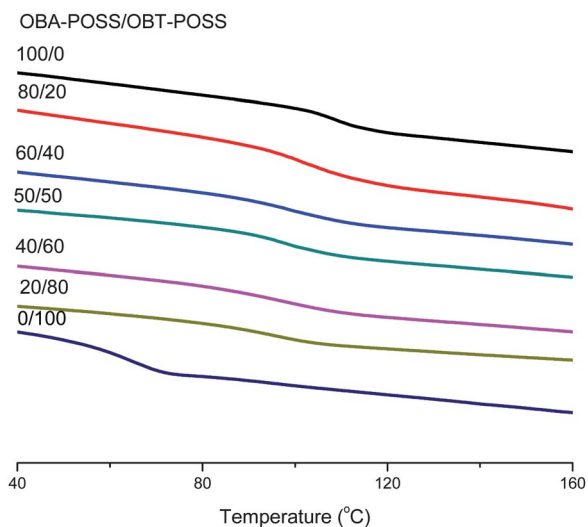


Fig. 7 DSC thermograms of OBA-POSS/OBT-POSS mixtures.

signals for OBA-POSS are assigned in Fig. 5a. The complete disappearance of the characteristic azide and acetylene groups could be confirmed by FTIR analysis as shown in Fig. 6. The peak at 2100 cm^{-1} , corresponding to the azide absorbance of $\text{OVBN}_3\text{-POSS}$ and the peak at 2110 cm^{-1} , corresponding to the acetylene absorbance of PA, were completely disappeared in OBA-POSS and the Si–O–Si (siloxane) group absorption band of POSS, which appears at 1100 cm^{-1} in OBA-POSS copolymers. It indicated that all the azide and acetylene functionalities participated in the click reaction. All results based on $^1\text{H NMR}$, $^{13}\text{C NMR}$, and FTIR analyses specified that the synthesis of OBA-POSS was successful.

Thermal properties of supramolecular OBT-POSS/OBA-POSS complexes

The glass transition temperature is an important physical property reflecting a change in intermolecular interactions. DSC

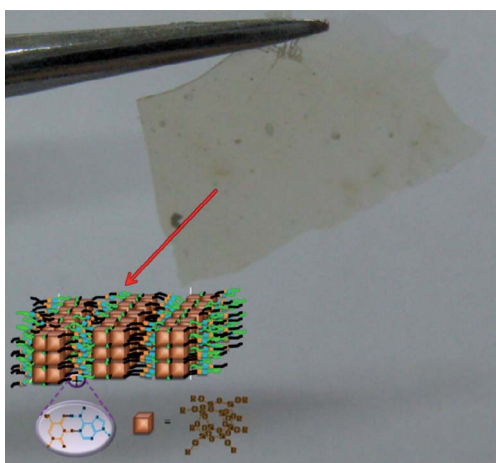


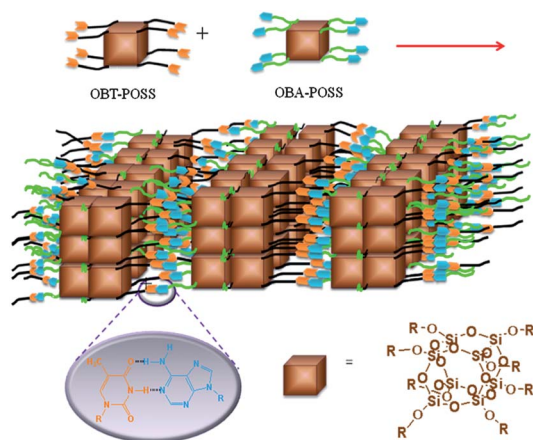
Fig. 8 Supramolecules films prepared with a mixture of OBA-POSS/OBT-POSS (60 : 40).

analyses of OBT-POSS/OBA-POSS complexes provided further insight into the behavior of the hydrogen-bonding supramolecules. Fig. 7 displays DSC thermograms of OBT-POSS/OBA-POSS complexes, where the OBT-POSS and OBA-POSS components contain various contents of adenine and thymine, respectively. Interestingly, pure OBT-POSS and OBA-POSS show the glass transition temperature at $65\text{ }^\circ\text{C}$ and $110\text{ }^\circ\text{C}$, respectively during the second heating scan. Comparing octakis [dimethyl(phenethyl)siloxy] silsesquioxane (OS-POSS) ($T_g = -51\text{ }^\circ\text{C}$) with octakis[dimethyl (4-acetoxy phenethyl)siloxy] silsesquioxane (OA-POSS) ($T_g = -14\text{ }^\circ\text{C}$), and octakis[dimethyl (4-hydroxyphenethyl)siloxy]silsesquioxane (OP-POSS) ($T_g = 18\text{ }^\circ\text{C}$),⁵⁵ significant increases in T_g were observed because of the strong self-complementary multiple hydrogen bonding interaction existing in OBT-POSS and OBA-POSS.

In addition, these binary mixtures of OBT-POSS and OBA-POSS exhibit only one glass transition temperature, revealing that they are completely miscible. Moreover, the glass transition temperatures were located at close temperatures to those of different various contents of OBA-POSS, suggesting that the OBT-POSS and OBA-POSS take complex shapes.⁵⁶

Compared with the value of glass transition temperature of pure OBT-POSS at $65\text{ }^\circ\text{C}$; when OBA-POSS was incorporated into the OBT-POSS at OBA-POSS/OBT-POSS ratio of 60 : 40, the value of glass transition temperatures increased by $30\text{ }^\circ\text{C}$ relative to that of pure OBT-POSS.

The value of T_g shifted higher upon increasing the adenine content in the component through strong multiple hydrogen bonding interactions between the A and T units. We considered this ratio as being the optimal for the preparation of polymeric membrane films. These hydrogen-bonded supramolecular thin films with a non-covalently bonded 3D network (Fig. 8) were brittle at room temperature and broke into pieces under an external force load. We are planning to produce better supramolecules incorporating more covalent bonding sites and more-flexible oligomer chains in the near future. The supramolecular structure of OBT-POSS/OBA-POSS complexes can be described by hydrogen bond-induced physical crosslinking, as shown in Scheme 3.



Scheme 3 The possible supramolecular OBA-POSS/OBT-POSS complexes.

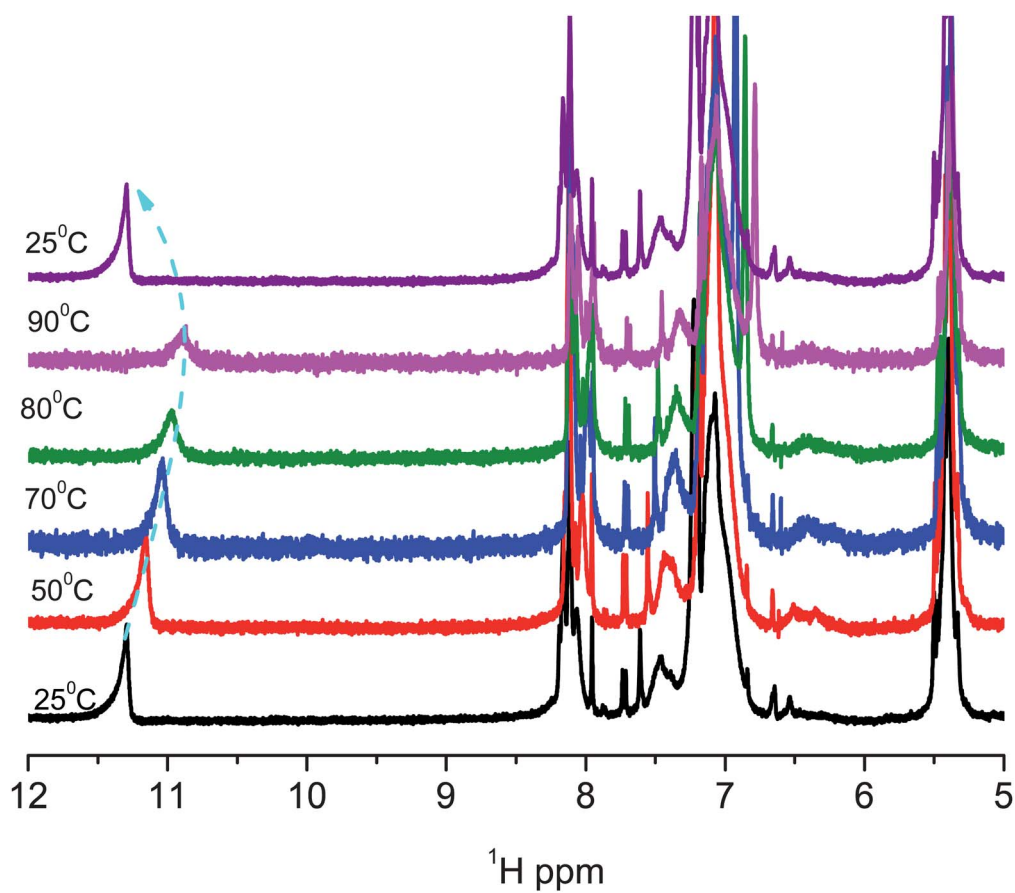


Fig. 9 ^1H NMR spectra N-H chemical shift of OBA-POSS/OBT-POSS (60 : 40) at different temperatures.

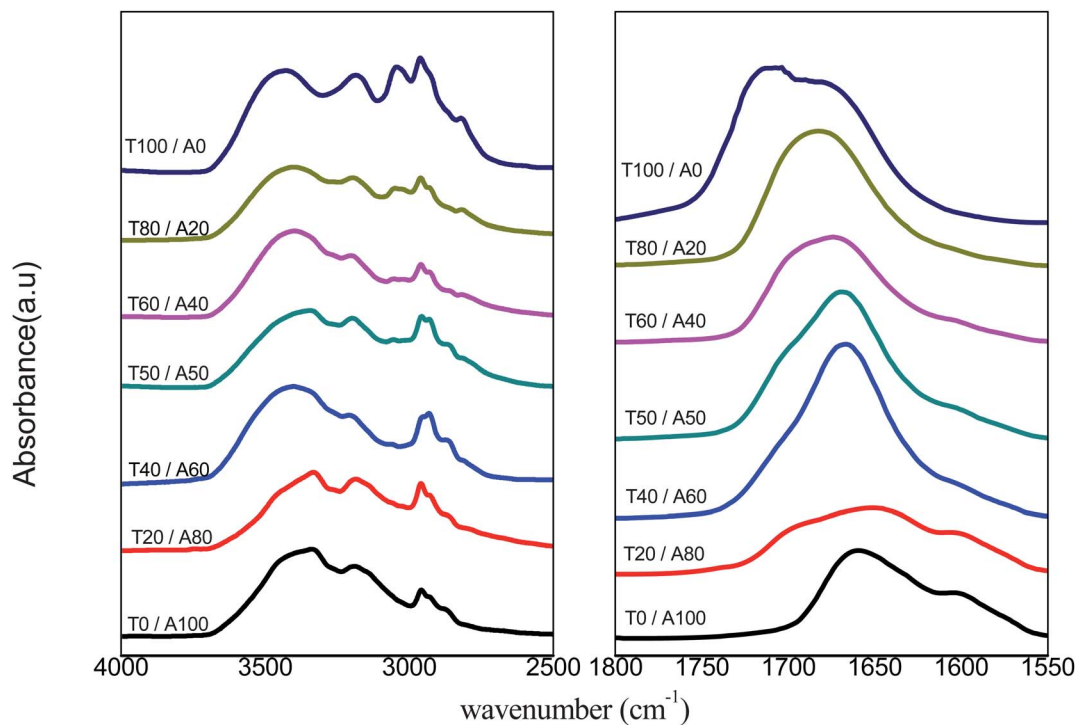


Fig. 10 FTIR spectra of different OBA-POSS/OBT-POSS mixtures at (a) 4000–2500 cm^{-1} and (b) 1800–1550 cm^{-1} .

Complementary multiple hydrogen bonding interaction and reversibility analyses of supramolecular OBT-POSS/OBA-POSS complexes

Figure S4 displays ^1H NMR spectra of OBT-POSS/OBA-POSS mixtures at various ratios in d_6 -DMSO solution.[†] The addition of OBA-POSS to the OBT-POSS solution led to a highfield shift of the signal (N–H) of the thymine group, which initially appeared at 11.31 ppm to 11.23 ppm (40 wt% OBA-POSS), indicating that multiple intermolecular hydrogen bonding occurred between the T and A groups. In our previous study,⁵⁰ the inter-association equilibrium constant ($K_a = 534 \text{ M}^{-1}$) between T and A groups from two low-molecular-weight model compounds mixtures, 9-hexadecyladenine (AC-16) and 9-hexadecylthymine (TC-16), was calculated using the results of ^1H NMR spectroscopic titration in CDCl_3 at room temperature, based on the method that had been developed by Benesi and Hildebrand.⁵⁷ In this study, pure OBT-POSS and OBA-POSS dissolve only in highly-polar solvents, such as DMF and DMSO, therefore, the chemical shift or inter-association equilibrium constant would be smaller than in CDCl_3 solution.

The reversibility of supramolecular formation was also investigated using variable-temperature ^1H NMR spectroscopy

in d_6 -DMSO because the ability to form or break the hydrogen bonding by external stimuli is interesting in these materials. The temperature dependence of the N–H proton chemical shift of the OBA-POSS/OBT-POSS (60 : 40) complex in d_6 -DMSO is shown in Fig. 9. As the temperature is raised from 25 to 90 °C, we can see that the N–H resonance of the thymine group shifts systematically to the upfield region, from 11.3 to 10.8 ppm. However, as soon as the sample is cooled to ambient temperature, the N–H resonance of the thymine group returns to its original position at 11.3 ppm, suggesting that the gradual decrease in the intensity of the N–H resonance with increasing temperature can be attributed to the gradual dissociation of complementary hydrogen bonds,⁵⁸ and the supramolecular complexes are provided with thermoreversible character. Thus, these results show that the octa-functionalized OBT-POSS and OBA-POSS by A–T recognition formed a network with a reversible structure.

Infrared spectroscopy is also a highly effective method of investigating the multiple hydrogen bonding interactions of supramolecules. It can be used as a tool to study, both qualitatively and quantitatively through the formation of multiple hydrogen bonds. Confirmation of multiple hydrogen bond formation between OBT-POSS and OBA-POSS was readily obtained using FTIR spectroscopy in Fig. 10. It is clear that the characteristic peaks of the thymine groups of OBT-POSS at 1688 and 1651 cm^{-1} correspond to the free and hydrogen-bonded C=O group, respectively. The characteristic peak of the adenine groups of OBA-POSS were at 1657 cm^{-1} (bonded NH_2 scissor plus ring stretching), and 1600 cm^{-1} (ring stretching plus bonded NH_2 scissor) and the Si–O–Si peak of POSS assigned at 1089 cm^{-1} . Fig. 10a, FTIR spectra at room temperatures, shows a number of broad absorption bands in the 3200–3600 cm^{-1} region: the N–H stretching region of the OBT-POSS and OBA-POSS where the band at 3450 cm^{-1} corresponds to free NH stretching, and the absorptions shifted to 3362 cm^{-1} are attributed to A interacting with the T units.⁵⁹ In addition, a peak appeared at 3200 cm^{-1} that corresponded to the NH group in T interacting with the A group.⁶⁰ Fig. 10b shows FTIR spectra (1500–1800 cm^{-1}) as mentioned above, the signal of the free and hydrogen bonded C=O groups of OBT-POSS appearing at 1688 cm^{-1} and 1651 cm^{-1} belong to the thymine groups. The characteristic peaks of adenine groups of OBA-POSS were at 1657 cm^{-1} and 1600 cm^{-1} corresponding to the hydrogen bonded and free pyridine ring stretching groups. We observed three major peaks by analyzing these spectra using the second derivative technique, representing the free C=O groups (1690–1700 cm^{-1}); multiple hydrogen bonding groups between A and T units (1655–1665 cm^{-1}); and free pyridine ring stretching group (1600–1610 cm^{-1}). Here, we combined the multiple hydrogen bonding interaction of C=O group of thymine with that of the NH_2 group of adenine units (*ca.* 1655–1665 cm^{-1}), the pyridine group of adenine groups interacting with the NH group of the thymine groups (*ca.* 1655–1665 cm^{-1}), and the self-complementary multiple hydrogen bonding between T–T (1651 cm^{-1}) and A–A units (1657 cm^{-1}). All these four absorption peaks are combined as multiple hydrogen bonding interactions in OBA-POSS/OBT-POSS complexes because in many bands it was difficult to calculate the quantitative area fraction of each peak. Additionally, we only focused on the fractions of free thymine and adenine groups in

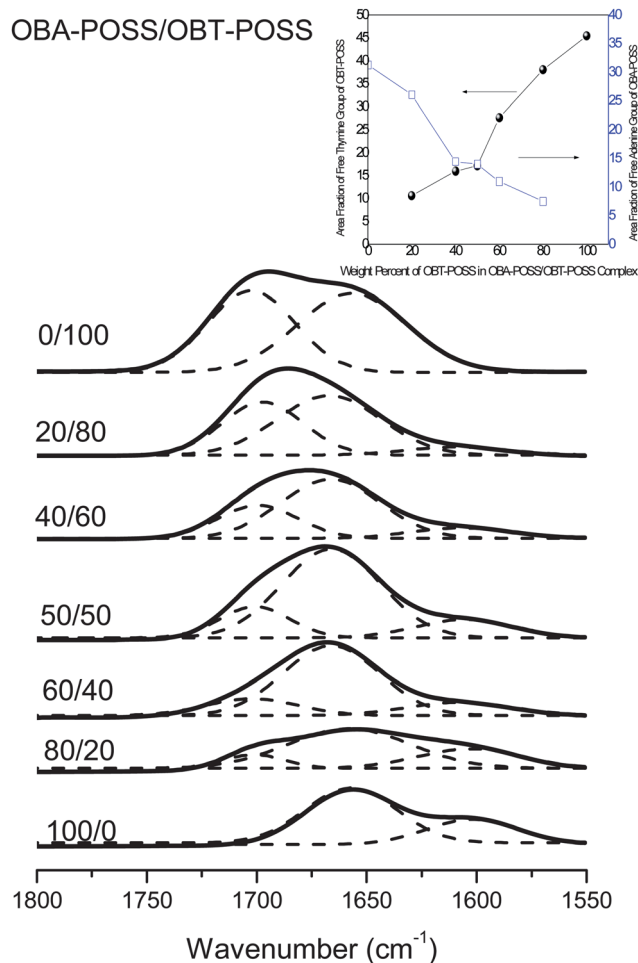


Fig. 11 Curve fitting of the signals in the FTIR spectra of the OBA-POSS/OBT-POSS mixtures.

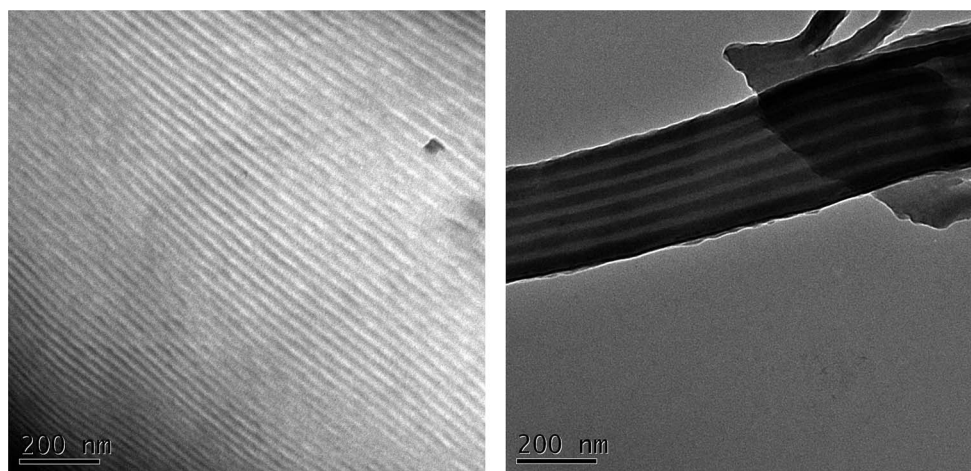


Fig. 12 Transmission electron microscopy images of OBA-POSS/OBT-POSS (60 : 40) mixture.

OBT-POSS/OBA-POSS complex. For deconvolution, we fitted a series of Gaussian distributions to quantify the fraction of each of the peaks as shown in Fig. 11. The fractions of free C=O of the thymine group in OBT-POSS clearly decreased with the increasing OBA-POSS content. Similarly, the free adenine group in OBA-POSS also decreased with the increase in OBT-POSS content, indicating the existence of multiple hydrogen bonding interactions between the A and T groups.

Transmission electron microscopy of OBT-POSS/OBA-POSS structures

Transmission electron microscopy examination of a sample of a OBA-POSS/OBT-POSS (60 : 40) mixture, as shown in Fig. 12, prepared by evaporation of a DMF solution, revealed the presence of a self-assembling alternating lamellae structure and long-range order pattern with a lamellar period of *ca.* 30–40 nm. The dark regions are attributed to the POSS-rich layers because the silicone elements of POSS have a higher mass contrast than organic carbon or nitrogen functional groups of adenine and thymine.⁴⁴ We are not able to provide a definite supramolecular structure at this stage, but it is clear that the following structure is responsible for the surprising aggregation stability.⁶¹ It is reasonable to assume that the complementary units form the multiple hydrogen bonded pairs in OBA-POSS/OBT-POSS. The entirely different behaviors of the pure compound and 60 : 40 of mixtures of OBA-POSS and OBT-POSS may be attributed to the spontaneous association of the complementary components into a polycondensation based on multiple hydrogen bonding interactions. This process may be described as the self-assembly supramolecular polymer based on molecular recognition between complementary components as shown in Scheme 3. It is important to point out the structural analogy between our self-assembly structure and microphase separation of the block copolymer in the bulk state.⁶² This self-assembly lamellae structure of OBA-POSS/OBT-POSS complex is similar to the microphase separation of the block copolymer in the bulk state. The lamellae assembly through molecular recognition and three-dimensional growth by molecular stacking are common in both systems. This would lead to the design and the synthesis of a wide

range of self-assembling supramolecular structures with specified internal organization.

Conclusions

Well-defined star like adenine and thymine functionalized POSS was synthesized through the combination of click reaction in the presence of multifunctional azide-POSS and hydrosilylation. Incorporating these multiple hydrogen bonding units results in the formation of new supramolecular structures. FTIR and NMR spectroscopy provided clearly positive evidence for the formation of intermolecular multiple hydrogen bonds between OBT-POSS and OBA-POSS units. Meanwhile, DSC analysis with high T_g behavior revealed that the OBA-POSS/OBT-POSS complex possesses strong intermolecular multiple hydrogen bonding interactions as a result of self-complementary interactions, which provides a potential route towards production of supramolecular thin films.

Acknowledgements

This work was supported financially by the National Science Council, Taiwan, Republic of China, under Contract No. NSC 100-2221-E-110-029-MY3 and NSC 100-2628-E-110-001.

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