

Tailoring Low-Polarity Ionic Liquids Using Polyhedral Oligomeric Silsesquioxane (POSS) for Advanced Polymer Hybrids

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Keywords: POSS; ionic liquid; polarity

Abstract

Polyhedral oligomeric silsesquioxane (POSS) can create hydrophobic spaces in various media including water-soluble networks and dendrimers. In particular, since the development of POSS ionic liquids (ILs), much effort has been devoted to investigating their thermal properties. In this manuscript, we report that POSS can create hydrophobic spaces in ILs. In comparison with a series of POSS ILs and ion pairs, we investigated the effects of the POSS core on the microenvironment around dyes in ILs by evaluating normalized polarity and Kamlet–Taft parameters with several types of solvatochromic dyes as probes. Consequently, it was revealed that POSS ILs should have low polarity where POSS could play a critical role in enhancing intermolecular interactions from the directly-connected anion to other species including cations and dyes. In terms of applications, it was found that low-polarity POSS ILs have high compatibility with conventional conjugated polymers, which can be used for fabricating highly-efficient luminescent ionic-liquid hybrid films owing to the isolation of each polymer chain by POSS even under ionic environments.

1. Introduction

Room-temperature ionic liquids (ILs) have attracted tremendous attention in various fields including synthetic chemistry, engineering and nanoscience.^[1,2] Owing to their unique physical properties such as high polarity, negligible vapor pressure, and wide thermal tolerance window, ILs have the potential to be used as an alternative to conventional organic solvents. Furthermore, ILs make a great contribution in the field of polymer chemistry. High-polar ILs can be used as reaction media for polymeric materials such as natural polymers including cellulose, chitin, and chitosan by disrupting their strong hydrogen bonding networks.^[3] Moreover, the low volatility of ILs can also be used as recyclable green solvents to synthesize functional polymers with reversible deactivation radical polymerization.^[4] Polymerized ionic liquids are called as poly(ionic liquids) or polymerized ionic liquids (PILs). PILs are regarded as subfamilies such as polyelectrolytes and ionomers and had high potential to be applied for ionic conductive materials.^[5] Recently, IL-polymer composites have attracted much attention as a new platform for multifunctional applications, such as responsive and sensitive sensors, actuators, environment, batteries, fuel cells, and biomedical applications.^[6–9] In order to expand the potential of ILs to create advanced polymer hybrids, it is of great significance to modulate the fundamental physicochemical properties. Therefore, many researchers have investigated the polarity of ILs.^[10–15]

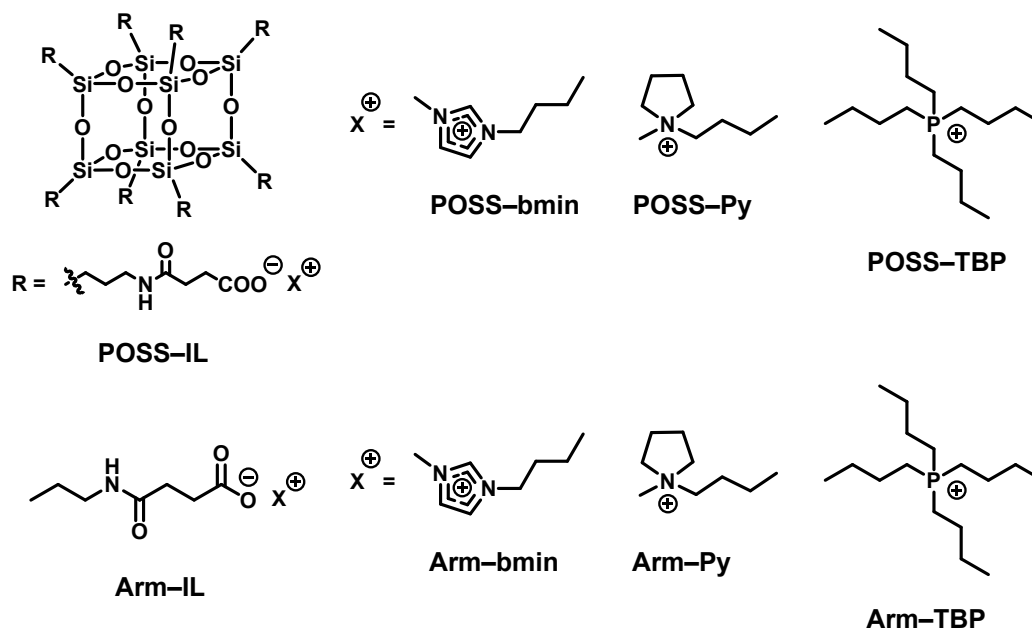
Polyhedral oligomeric silsesquioxane (POSS) has a siliceous cubic structure with eight organic functional groups at each vertex. Because of its chemical component, POSS is regarded as an organic–inorganic hybrid molecule.^[16–36] By simply mixing POSS with various media, we can readily obtain hybrids even with the organic materials which have been difficult to hybridize by conventional methods, such as polyurethane,^[37] soft materials^[38–46] and conjugated polymers^[47–51]. In addition, we have applied POSS for fabricating hybrid-type ILs and have previously reported unique thermal properties of POSS ionic liquids (POSS ILs) composed of the modified POSS having eight

carboxylates and imidazolium cations.^[52,53] By isolating ion pairs through the POSS core, the lowering effect on the melting temperature was observed without losing the thermal stability, resulting in production of the room-temperature IL (Figure 1a, **POSS–bmin**).^[54] Additionally, the POSS-based ionic liquid crystal was also obtained.^[55] Furthermore, based on the high thermal stability of POSS ILs, applications such as electrolytes of dye-sensitized solar cells have been accomplished.^[56,57] Meanwhile, very little information still has been reported on the polarity of POSS ILs. In the polar solvents such as water, POSS has been shown to be able to create hydrophobic pockets around the cubic silica core. As a result, various hydrophobic molecules, such as dyes^[58–60], drugs^[61,62], nucleic acids^[63,64], fatty acids^[65], surfactants^[66] and even nanoplastics^[67] were captured in POSS-containing hydrophilic polymers under aqueous conditions. Furthermore, the cubic core of the POSS can work as a basis for a three-dimensional symmetric whole structure, and the lower polarity region could be created around the core in the resulting POSS ILs compared to conventional ILs. Taking these results into consideration, it is presumable that a unique space with quite a different property from the charge-filled atmosphere might appear around the POSS core in ILs.

Herein, we present the results of our systematic study on the polarity of POSS ILs by exploring the normalized polarity (E^N_T) and Kamlet–Taft parameters (α , β , and π^*). By combining several types of solvatochromic dyes (Figure 1b), we investigated the effects of the POSS core on the microenvironment around the dyes in ILs. By changing the counter cations, we also evaluated to enhance the hydrophobic regions in POSS ILs (Figure 1a). Finally, we found that the POSS IL can have high compatibility with conventional conjugated polymers. The homogeneous films with ILs were able to be obtained only with the POSS IL. The effects of the POSS core were confirmed by comparison with those of model compounds (Arm ILs) (Figure 1a). To the best of our knowledge, this is the first example to clearly demonstrate that POSS can create a hydrophobic microenvironment even in ILs and can be applied as a scaffold for the

development of conjugated polymer–IL hybrids.

(a)



(b)

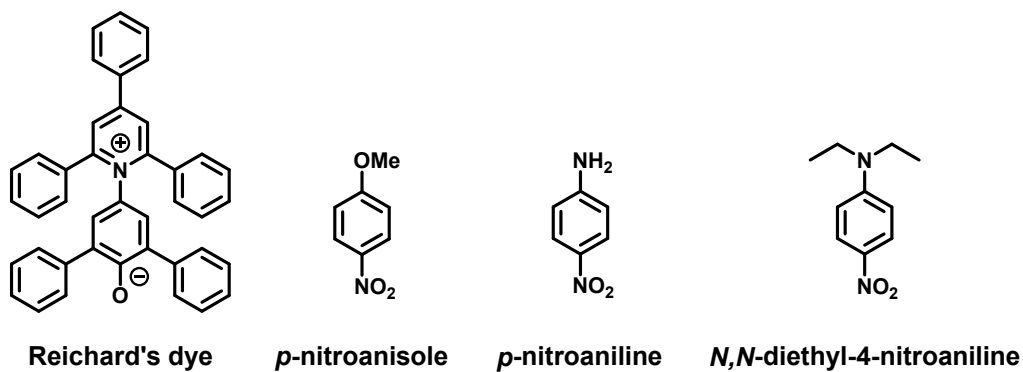


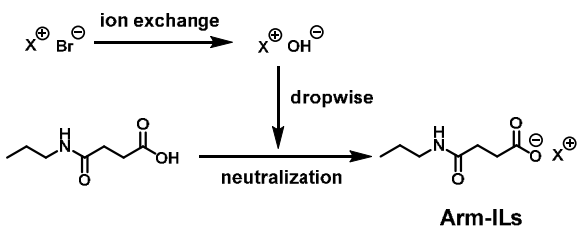
Figure 1. Chemical structures of (a) POSS and Arm ionic liquids (**POSS-IL** and **Arm-IL** (control)), (b) solvatochromic dyes used in this study.

2. Results and discussion

2-1. General procedure for the preparation of the ILs

Exactly the same equivalent of bromide anion of 1-butyl-3-methylimidazolium bromide (**bminBr**), tetrabutylphosphonium bromide (**TBPBr**), and 1-butyl-1-methylpyrrolidinium bromide (**PyBr**) to the carboxyl groups was converted into hydroxyl anion by anion exchange resin (Amberlite–IRA400) in water, and neutralized with each carboxyl compound suspended in H₂O (Scheme 1). The residual Br anion was titrated with AgNO₃ under a nitric acid condition to confirm that it was 0. The aqueous solution was concentrated with a rotary evaporator and residual liquid was freeze-dehydrated to give a white solid. The solid was dried *in vacuo* and stored under N₂ atmosphere. They were characterized by ¹H, ¹³C, and ²⁹Si NMR methods (Chart S1–S15) and determined to be pure enough for further experiments. All **ILs** were confirmed to be amorphous at room temperature by powder X-ray diffraction analysis (Figures S1–S8) and to possess a glass transition temperature below 0 °C (Figures S9–S12 and Table S1).

Samples for spectroscopic studies were prepared as follows; appropriate aliquots of solvatochromic probe stock CH₂Cl₂ solutions were added to **POSS–COOH** or **Arm–COOH** and evaporated. An appropriate amount of counter cations (Scheme 1, **XOH**) suspended in H₂O was then added to synthesize ILs. The prepared ILs were then freeze-dehydrated and spectroscopic experiments were performed under N₂ atmosphere. The spectroscopic experiments were conducted several times and the reproducible results were adopted. Considering the reliability of the parameters and the significant digits in the experimental accuracy, the parameters are given to two decimal places. All dyes were diluted to appropriate absorbance, and all spectra are listed in the Supporting Information (Figures S13–S47 and Tables S2–S9).



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2-2. The E^N_T scale

For molecular solvents, the relative dielectric permittivity, ϵ_s , usually denoted as the static dielectric constant, is a key parameter for the quantitative evaluation of solvent polarity. However, for ion pairs consisting of three-dimensional steric components, conventional ϵ_s measurements are assumed to be inappropriate because ϵ_s would reflect only low density values due to volume effects. Therefore, previous studies on the polarity of ILs have relied on spectroscopic techniques.^[13,68] The most prominent polarity scale is based on the solvatochromic shift of the low-frequency band in the light absorption spectrum of Reichardt's zwitter-ionic dye betaine-30.^[69,70] This shift can be expressed in terms of a normalized polarity parameter, E^N_T , which is set at one for water and zero for tetramethylsilane. E^N_T values for ILs have been compiled by Reichardt. Kamlet and Taft have also developed a system based on comparing the effects on the UV-vis absorption spectra of sets of closely related dyes that were selected to probe particular solvent properties to describe scales of hydrogen bond acidity (α), hydrogen bond basicity (β) and dipolarity/polarizability effects (π^*).^[71-75] Thus, in this study, we discuss the solvent polarity of ILs based on E^N_T values.

First, the E^N_T values of ILs were evaluated. The E^N_T value was calculated by equations (1) and (2). The term $\lambda_{\max}$ is the maximum absorption wavelength of Reichardt's dye. All spectra were recorded at 25 °C, and further details are shown in the Supporting Information.

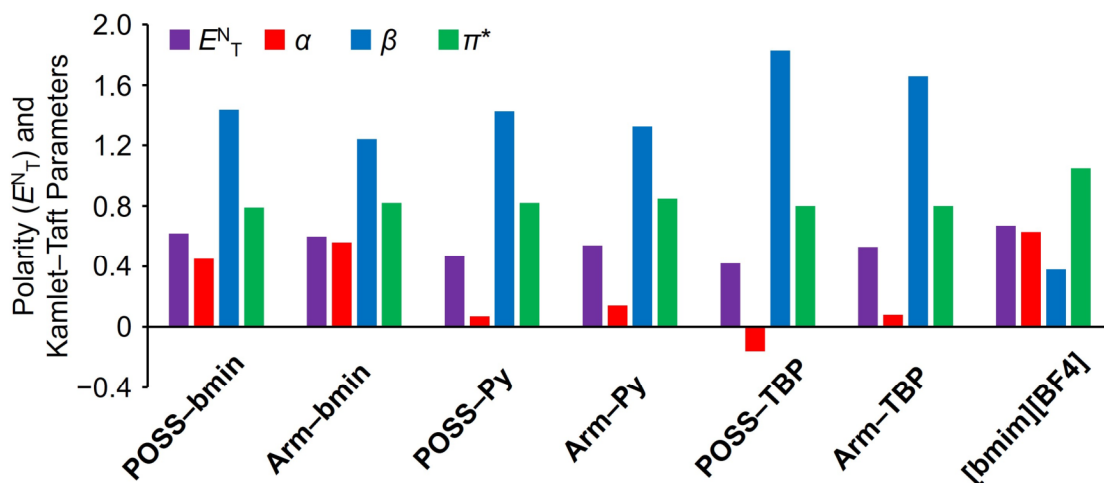
$$E_T(30) = \frac{28\,591}{\lambda_{\max}(\text{nm})} \quad (1)$$

$$E^N_T = \frac{E_T(30)(\text{solvent}) - E_T(30)(\text{TMS})}{E_T(30)(\text{water}) - E_T(30)(\text{TMS})} = \frac{E_T(30)(\text{solvent}) - 30.7}{32.4} \quad (2)$$

Table 1. Polarity (E_T^N) and Kamlet–Taft parameters for ILs

Solvent	E_T^N	α	β	π^*
POSS–bmin	0.62	0.45	1.44	0.79
Arm–bmin	0.60	0.56	1.24	0.82
POSS–Py	0.47	0.07	1.43	0.82
Arm–Py	0.54	0.14	1.33	0.85
POSS–TBP	0.42	−0.16	1.83	0.80
Arm–TBP	0.53	0.08	1.66	0.80
[bmim][BF₄] ^a	0.67	0.63	0.38	1.05

^a The parameter was cited from ref. 11. **[bmim][BF₄]**: 3-butyl-1-methylimidazolium tetrafluoroborate

**Figure 2.** Polarity (E_T^N) and Kamlet–Taft parameters for ILs.

Since the E_T^N is regarded as a general scale for the solvating ability of conventional molecular solvents and is the most commodity parameter to estimate the polarity of ILs as mentioned above.^[13,14] The lower E_T^N value represents lower solvent polarity. From the summary of the measurements as shown in Table 1 and Figure 2, almost the same E_T^N values were obtained from **POSS–bmin** and **Arm–bmin**. According to the previous study,

it was found that the alternation of the anion species should have little influence on the E^N_T values with the series of 1,3-dialkylimidazolium-based ionic liquids, and these ionic liquids exhibit E^N_T values between *ca.* 0.5 and 0.7.^[69] Considering this information, it is revealed from our study that **POSS-bmin** and **Arm-bmin** should have almost the same polarity not only as each other but also as conventional ILs, such as **[bmim][BF₄]** (Table 1).^[11]

In contrast, comparing the E^N_T values between **POSS-Py** and **Arm-Py** or **POSS-TBP** and **Arm-TBP**, it was clearly shown that POSS ILs should have lower polarity. The E^N_T values of pyrroldinium-based and phosphonium-based ILs strongly depend on the nature of anion.^[69] Therefore, it is likely that the difference between POSS ILs and Arm ILs came from the difference of the anion structure. Notably, the E^N_T value of **POSS-TBP** was 0.42, which is the lowest value among non-fluorine substituted ionic liquids. According to the previous studies on the extremely-low polarity of the POSS core,^[58–67] it is proposed that the hydrophobic pockets around the silica cube might play a critical role in the E^N_T value of POSS ILs.

To obtain deep insight into the lower polarity of POSS ILs, more detailed analyses were performed on the E^N_T value. Although Reichardt's dye is neither a hydrogen bond donor nor a Lewis acid, this molecule is capable of forming interactions with the microenvironment through van der Waals interactions and hydrogen bond acceptability. This complexity of interactions can be solved by splitting it into multiple parameters. One of the most commonly used multiparametric equation is the Kamlet–Abboud–Taft (KAT) equation (3), which includes distinct parameters for the solvent's dipolarity/polarizability (π^*), hydrogen-bond donor ability (α), and hydrogen-bond accepting ability (β), which are called Kamlet–Taft parameters.^[70–72,75,76]

$$E_T(30) = [E_T(30)]_0 + a\alpha + b\beta + s(\pi^* + d\delta) \quad (3)$$

In the equation (3), δ represents a polarizability correction term depending on whether the solvent is aromatic ($\delta = 1.0$), polyhalogenated aliphatic ($\delta = 0.5$), or neither of the two ($\delta = 0.0$). $[E_T(30)]_0$ corresponds to the gas-phase value, and a, b, s and d are solvent-independent coefficients indicative of the susceptibility of Reichardt's dye to the solvent properties α , β , and π^* . Hence, from this point of view, Kamlet–Taft parameters were evaluated in order to investigate the origin of the difference between E^N_T values of POSS ILs and Arm ILs (Table 1).

2-3. π^* values

The π^* value represents the effects of dipolarity and polarizability of the solvent. The differential stabilization of the more polar excited state with respect to the ground state of the dye is evaluated. Therefore, π^* is derived from the change in the energy of the local electric field generated by the ionic liquid. From the comparison with POSS ILs and Arm ILs, it was shown that the π^* values were almost the same and relatively larger than those of non-aqueous molecular solvents, suggesting that the local electric field generated by the ion pairs should be hardly affected by the POSS core. Furthermore, since the ion pairs in POSS ILs are arranged around the silica cubic core, dye–solvent interactions occur away from the POSS core and are less likely to be affected by POSS. Hence, the effect of the POSS core is originated from other factors represented by α or β values.

2-4. β values

The β value means hydrogen-bond basicity of the solvent and is mainly concerned with the nature of anion in ion pairs. The most impressive point is that POSS ILs exhibited larger β values than Arm ILs, meaning that the POSS core should play a significant role in the enhancement of hydrogen bonds between anion and dye molecules. This tendency was able to be supported by the data from the ^1H NMR spectra of **POSS–bmin** and **Arm–bmin** (Figure 3). Accordingly, the chemical shifts of the signal peak from the 2-position

proton of 1-methyl-3-butylimidazolium cation in POSS ILs showed a larger downfield shift than those of Arm ILs. It has been reported that there is a good correlation between the width of the downfield shift of this peak and the β value calculated from the UV-vis absorption spectrum of 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-di-one dye.^[77] Although there are large structural differences between POSS and Arm ILs, a good correlation between their β values and ^1H NMR chemical shifts was observed. This fact means that it is expected to broaden the applicability of the evaluation method. These data suggest that in POSS ILs, the strength of hydrogen bonds between cations and anions should be enhanced more than in Arm ILs. This fact is consistent with the previous studies where the hydrophobic pockets around the POSS core and the suppression of molecular tumbling can contribute to enhancing complexation through hydrogen bonding.^[58–67] Similarly to these results, the interaction between cations and anions is reinforced by the POSS core in POSS ILs. As a result, large β values can be observed from POSS ILs.

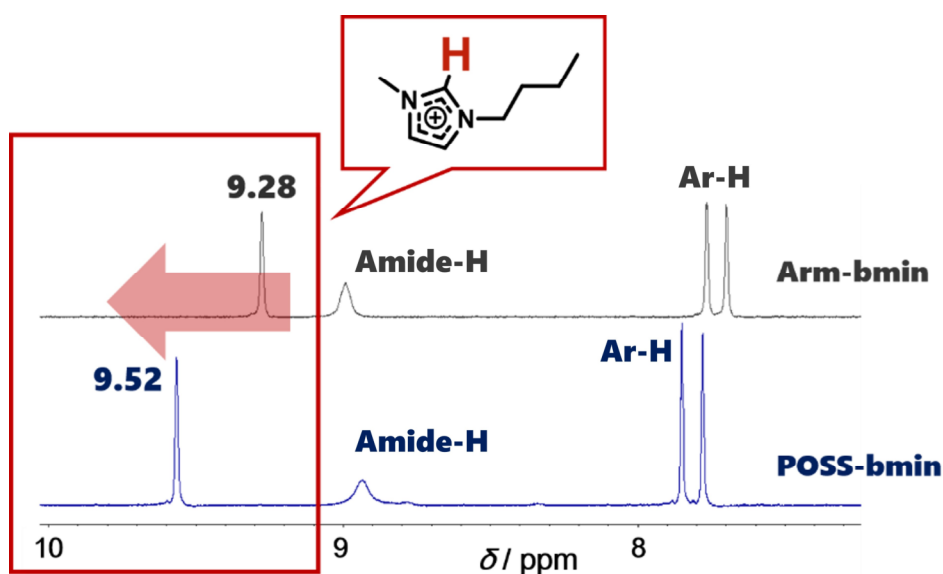


Figure 3. ^1H NMR spectra of POSS-bmin and Arm-bmin.

2-5. α values

The α value represents hydrogen-bond acidity of the solvent and is basically dominated by the nature of cation. Interestingly, in contrast to the fact that ionic liquids based on the same cations usually exhibit almost the same values,^[11] POSS ILs exhibited lower α values than Arm ILs in all counter cations. It is said that there is a competition between the anion and the probe dye solute for the cation.^[11] Therefore, it is presumable that the interaction between dye and cation represented by the α value might be lowered by the strong cation–anion interaction in the POSS-connected ion pair.

From the above data, a scenario is proposed according to the lower α and higher β values observed in POSS ILs (Figure 4). In conventional ILs, the cation–anion interactions are weakened by introducing bulky substituents or delocalized π systems to the ions to lower the melting point. On the other hand, in POSS ILs, the steric structure of the POSS core should play an important role in lowering the melting temperature by isolating the ion pairs without weakening the Coulombic interaction between ions.^[54] Moreover, the hydrophobic space around POSS can greatly enhance the intermolecular interactions in directly-connected ion pairs. As a result, significant differences in the parameters should be observed. These data with Reichardt's dye suggest a high hydrogen-bond accepting ability because of an unshielded phenolate anion. Therefore, the contribution of α to KAT equation is much more significant than β .^[70] In summary, it is revealed from our findings that the low E^N_T values of POSS ILs should be originated from the effect of enhanced cation–anion interactions represented by lower α values.

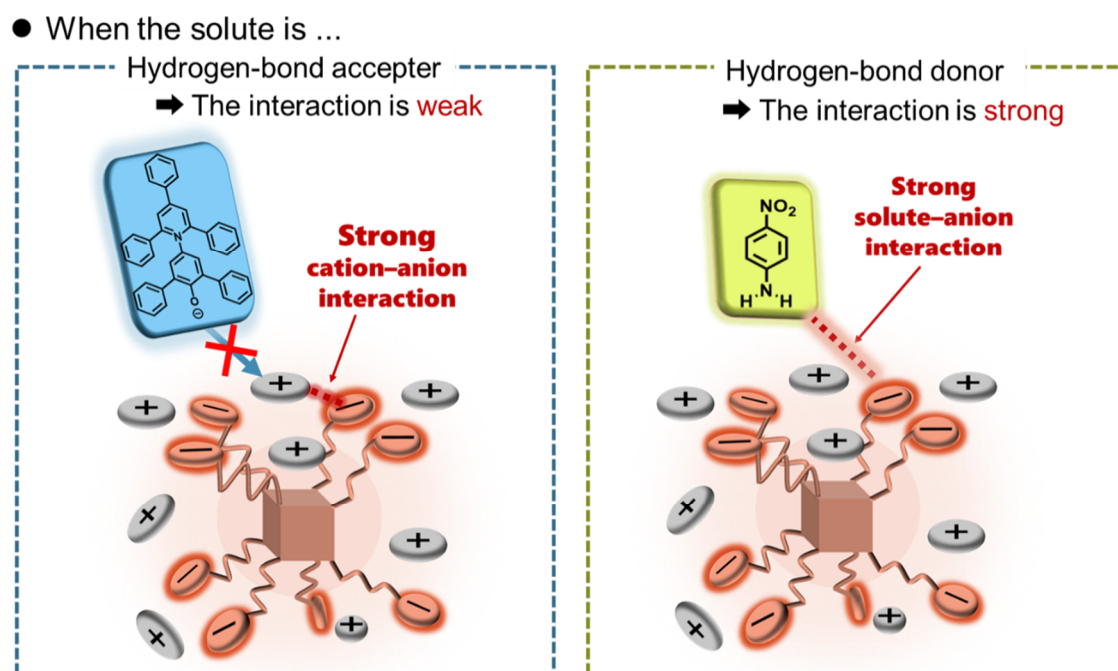


Figure 4. Plausible mechanism of low α and high β of POSS–ILs.

2-6. Compatibility with π -conjugated polymers

ILs which have high compatibility and subsequent dispersion ability for π -conjugated polymers are a versatile material for realizing advanced devices such as light-emitting electrochemical cells (LECs).^[78,79] LECs have a single-layered structure consisting of simple blends with light-emitting π -conjugated polymers (or small organic molecules) and electrolytes, such as ILs. The most critical problem in developing LECs is the incompatibility of polymers and electrolytes. The required properties of electrolytes for LECs are: (1) a low E^{N}_{T} value and (2) no fluorine substituent. In this point of view, we presumed that POSS ILs should be a promising candidate to meet these demands. Therefore, to evaluate the applicability of POSS ILs as a matrix, we evaluated the dispersion ability of the synthesized ILs for conventional π -conjugated polymers. As a combination of the ILs and π -conjugated polymers, it was reported that the polyfluorene (PF) with side chains composed of imidazolium ionic liquid components showed strong intercalation with reduced graphene oxide.^[80] In this previous study, the π -conjugated polymer and imidazolium ionic liquid components were directly connected by covalent bonds, and no emission property was evaluated. Therefore, there is much room to investigate IL-conjugated polymer hybrid materials.

Poly(3-hexhyl)thiophene (P3HT) was used as a π -conjugated polymer, and **POSS-TBP** was selected as an ionic liquid among POSS ILs because **POSS-TBP** exhibited the lowest E^{N}_{T} value. **Arm-TBP** was also used for comparison. The hybrid films were prepared by the same method for comparison. The detailed sample preparation method and SEM images of the films are shown in the Supporting Information. To check the compatibility of the ILs with P3HT, field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray analysis (EDX) measurements were carried out (Figures 5 and 6). Accordingly, we observed that the hybrid film of P3HT and **Arm-TBP** showed a phase-separated structure composed of polymer-rich domains and ionic liquid-rich domains. About 500 nm P3HT nanoparticles accumulated in the **Arm-TBP** matrix,

forming 5–10 μm domains. In contrast, the hybrid film of P3HT and **POSS–TBP** showed a flat and homogeneous surface without any phase separation. These observations indicate the better compatibility of **POSS–TBP** with P3HT than that of **Arm–TBP**. As shown in the hybrid film with P3HT and **Arm–TBP**, little compatibility between ionic species and hydrophobic polymer chains was observed. This is supported by the report that the polymer solubility in ILs is dominated by hydrogen bonding interactions.^[81] Considering these results, it is likely that POSS ILs can encapsulate π -conjugated polymers into hydrophobic pockets around the POSS which should be created by lower polar ionic side chains and the bulky POSS core. Furthermore, the bulky POSS can separate the polymer chains and suppress the aggregation of the π -conjugated polymers. Owing to these effects, the π -conjugated polymers can form homogeneous states even in the IL matrix.

Optical properties of polymers in ILs were examined (Figure 7). From UV–vis absorption spectra, it was found that the hybrid film of P3HT and **Arm–TBP** exhibited a lower energy absorption band. It is suggested that the absorption spectrum of P3HT is composed of two contributions; (i) a lower energy component which is generated from crystalline regions formed by weakly interacting H-aggregates and (ii) a higher energy component associated with more disordered chains located in majority in the amorphous regions of the film.^[82,83] These results suggest that polymer chains should aggregate at the molecular and nano level in **Arm–TBP**, while well dispersion should be induced in **POSS–TBP**. By isolating each polymer chain in **POSS–TBP**, the intrinsic electronic structure of P3HT can be preserved.

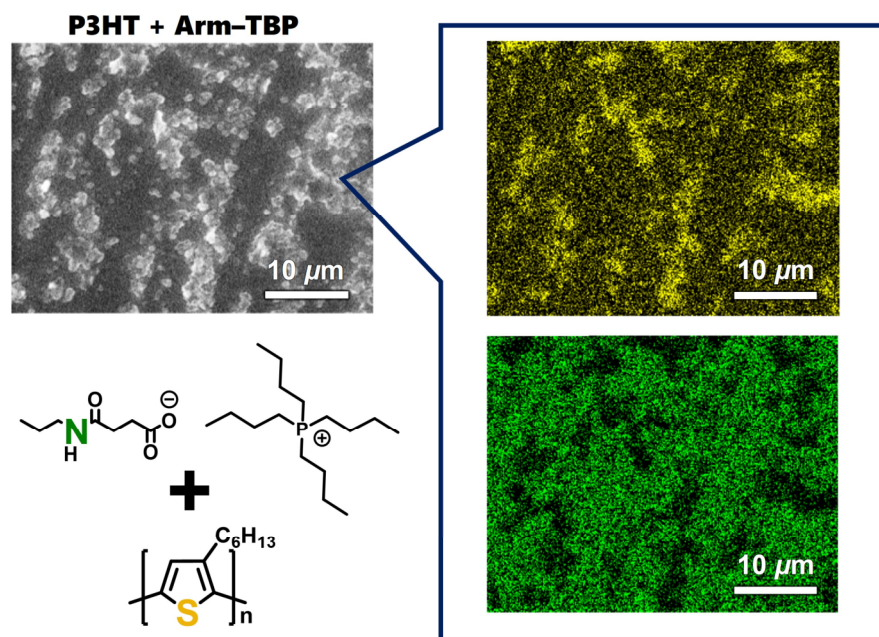


Figure 5. SEM (left) and EDX (right) images of composite film of P3HT and **Arm-TBP**. Yellow represents the sulfur atoms of P3HT and green represents the nitrogen atom of **Arm-TBP**.

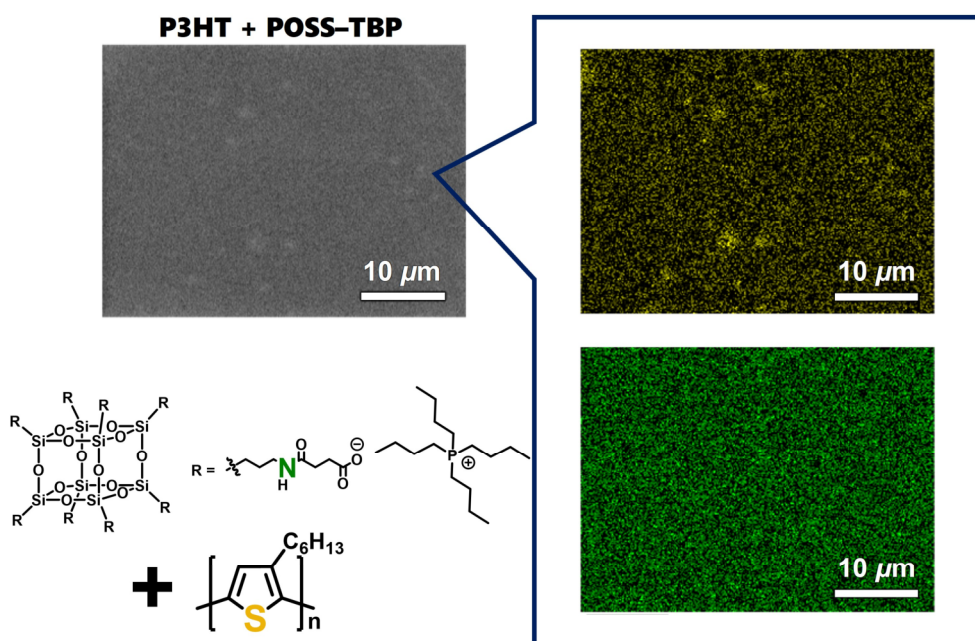


Figure 6. SEM (left) and EDX (right) images of composite film of P3HT and **POSS-TBP**. Yellow represents the sulfur atoms of P3HT and green represents the nitrogen atom of **POSS-TBP**.

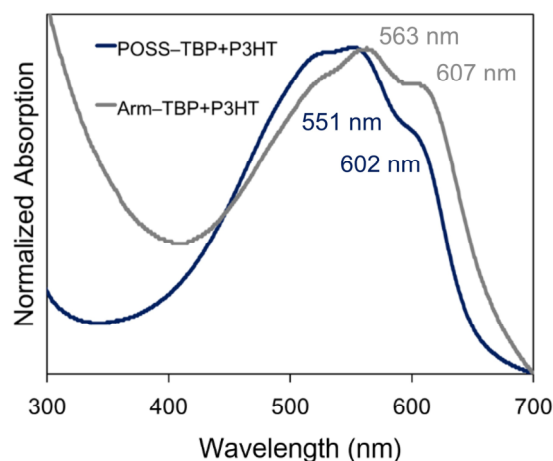


Figure 7. Absorption spectra of composite films of P3HT and **ILs**.

Finally, we prepared hybrid films with PF which is well known as a luminescent polymer. Through the same protocol, we prepared the hybrid films with **POSS-TBP** and **Arm-TBP**. The detailed sample preparation method is shown in the Supporting Information. As we expected, the homogeneous film was obtained only by using **POSS-TBP** according to the SEM observations (Figure S52), although 5–10 μm domains of PF were observed in the hybrid film of PF and **Arm-TBP**. The homogeneous dispersion of PF in the IL matrix was also supported by the fact that the absorption band of the hybrid film with **POSS-TBP** was sharper than that of the hybrid film with **Arm-TBP** (Figure 8). Moreover, it should be emphasized that a larger emission efficiency (Φ_{PL}) was detected from the sample containing **POSS-TBP**. Aggregation-caused quenching should be suppressed by disturbing the formation of aggregates in the hydrophobic pockets in POSS ILs.

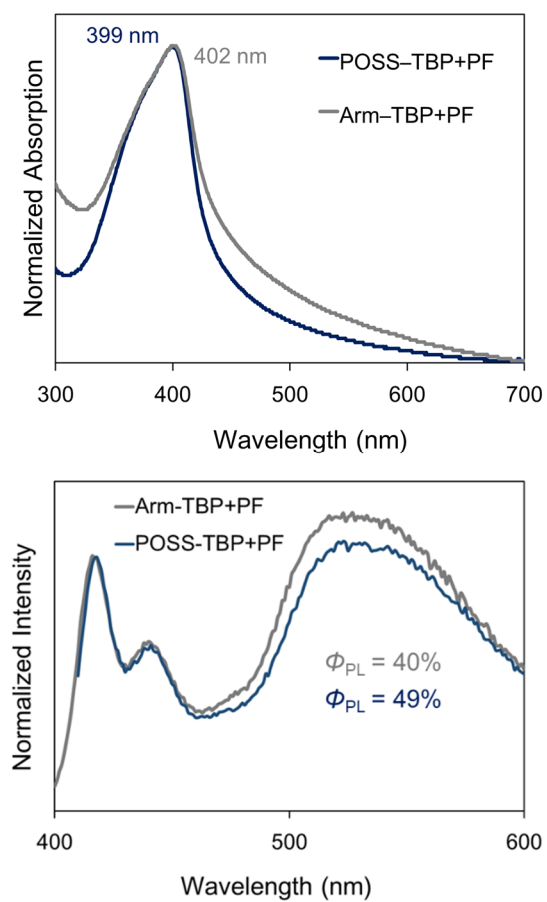


Figure 8. Absorption and photoluminescence spectra of composite films of PF and ILs, excited at maximum absorption wavelengths.

3. Conclusion

We have carried out the systematic study of the polarity of ionic liquids based on POSS IL by a spectroscopic method and compared them to investigate the effect of POSS. POSS ILs possessed low normalized polarity (E^N_T) compared with Arm ILs. Kamlet–Taft parameters were also determined, and POSS ILs showed low hydrogen-bond donating ability (α) and high hydrogen-bond accepting ability (β). This property is attributed to the strong cation–anion interaction of multivalent anions in POSS ILs. Finally, the potential application of POSS ILs as solvents for poorly soluble π -conjugated polymers were demonstrated. **POSS–TBP** and **Arm–TBP** were mixed with P3HT and PF, and **POSS–TBP** exhibited much better compatibility with both π -conjugated polymers. This is the first report to clearly demonstrate that POSS provides a venue for changing the physical properties of ion pairs. These results highlight the potential applications of POSS ILs that have been difficult to realize with conventional high-polar ILs, such as the preparation of ionic-liquid luminescent hybrid films with low-polar light-emitting π -conjugated polymers, and indicate a strategy for developing high-performance ILs and functional materials based on POSS.

Acknowledgement

This work was partially supported by the Iketani Science and Technology Foundation and JSPS KAKENHI Grant Numbers 24K01570 (for K.T.).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

4. References

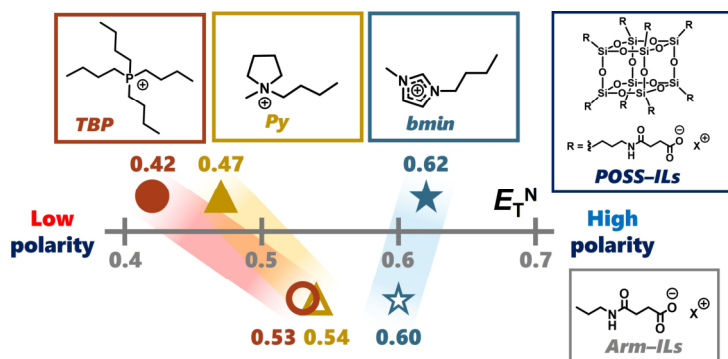
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The effects of the POSS core on the microenvironment around dyes in ionic liquids (ILs) were investigated through normalized polarity (E_T^N) and Kamlet–Taft parameters with several types of solvatochromic dyes as a probe. Consequently, it was revealed that POSS core should provide a low-polar environment even in ILs. Additionally, POSS could play a critical role in enhancing intermolecular interactions from the directly-connected anion to other species including cations and dyes. Furthermore, we obtained the hybrid films containing POSS IL and conventional conjugated polymers, and confirmed that each polymer chain can be isolated even under ionic environments owing to POSS.