



Development of macromolecules and supramolecules based on silicon and arsenic chemistries

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Abstract

Organic–inorganic hybrids are one of the most important tools in materials science. Since the incorporation of abundant elements into single molecules realizes molecular-level hybridization, organic–inorganic hybrid molecules and polymers have attracted increasing attention. In this focus review, the author’s recent works on hybrid materials utilizing silicon and arsenic are overviewed. Among widely used silicon compounds, silsesquioxane ((RSiO_{1.5})_n), adopting a cage structure, is a key structure. Polyhedral oligomeric silsesquioxane (POSS) has been employed for the reinforcement of organic materials, but the author has been working on “single-molecular POSS materials” and “main-chain-type POSS polymers.” In the last half of this review, organoarsenic polymers and supramolecules are introduced. Though experimental studies on organoarsenic compounds have been avoided due to the dangers of conventional synthetic procedures, the author’s practical methods have strongly contributed to the syntheses of functional organoarsenic compounds. The high functionality and usability of organoarsenic compounds are demonstrated.

Introduction

Organic–inorganic hybrid molecules and polymers have increasingly attracted attention in various fields [1, 2]. An abundance of elements provide versatile properties and a breakthrough for the limitations reached with solely organic and inorganic materials. In this focus review, the author’s recent progress on two contrasting elements, i.e., silicon and arsenic, is overviewed. The former has been widely and deeply studied in materials science because of its abundance on the Earth, wide designability, and high performance. On the contrary, the latter has been avoided in experimental research because of the concern of the toxicity of arsenic small molecules. In the first half, the author introduces novel molecular designs for the utilization of cage-silsesquioxanes as the main component of organic–inorganic hybrid materials. Then, game-changing

strategies for the construction of organoarsenic polymers and supramolecules are described.

Cage-silsesquioxane materials

Silicon-based materials have supported our daily life. In particular, siloxane compounds, which contain Si–O–Si species, are absolutely important because they have high durability, good transparency, and structural variation. Siloxane structures are classified into four groups, M (R₃SiO_{0.5}), D (R₂SiO), T (RSiO_{1.5}), and Q (SiO₂) (Fig. 1a). These Si–O bonds form durable frameworks, and the organic substituent R offers stability, solubility, reactivity, and advanced functions of the resultant materials. Silsesquioxanes [3], which are constructed based on T structures, are important components for the development of organic–inorganic hybrids on the molecular level because inorganic three-dimensional networks can be formed with the incorporation of organic substituents. Some silsesquioxane architectures, such as random, ladder [4, 5], and cage types [6–12], are presented in Fig. 1b. Among these T-type materials, the cage-type molecule, polyhedral oligomeric silsesquioxane (POSS), is an attractive building block because of its precisely designed structure. Various types of hybrid molecules and polymers have been developed

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utilizing POSSs. Generally, POSSs are used for to enhance the durability of organic materials. For example, the thermal stability of organic polymers, such as polystyrene and poly(methyl methacrylate) (PMMA), is improved by incorporating POSSs as a side-chain substituent [13], end-functional group [14], or filler [15]. However, despite a number of studies on “POSS-enhanced materials,” those on “single-molecular POSS materials” and “main-chain type POSS polymers” are relatively rare. This is because POSS has a highly symmetric structure, from which arises two challenges: (1) aggregation because of the high crystallinity and (2) the equivalent reactivity of the eight corners. First, the high crystallinity of POSS makes it difficult to fabricate optically transparent films of POSS materials. Even when POSS fillers are added to polymer matrices, they readily cause aggregation to give turbid or phase-separated films at ~10 wt% [15]. Second, it is hard to synthesize POSS monomers for main-chain-type polymers. To obtain the POSS monomers, two reactive sites should be regioselectively introduced in spite of the same reactivity of the eight corners. To this effort, molecular designs to overcome these challenges are described in the following. Additionally, an inchoate work on the electronic properties of POSS is introduced at the end of this section.

Collapse of the symmetry of POSSs

To restrict the crystallinity, the symmetry of POSSs should be reduced. For example, two types of substituents can be introduced to the eight corners of a POSS [16–18]. On the other hand, Naka and coworkers proposed dumbbell- [19, 20] and star-shaped [21, 22] POSSs (Fig. 2). The dumbbell-shaped POSS having trifluoropropyl groups on the corners can be used for the fabrication of thermoplastic optically transparent films [19]. In addition, π -conjugated units sandwiched between two POSSs form transparent films without aggregation-caused quenching [20]. In a further investigation, they reported star-shaped POSSs, in which eight POSSs are substituted at the corners of an octasilicate core. These star-shaped POSSs can effectively reduce crystallinity. In addition, isobutyl-substituted POSSs cannot form transparent films by the dumbbell strategy, but their star-shaped oligomers show success dependent on the linker length [21, 22].

Then, the author has proposed a molecular design that utilizes an incompletely condensed POSS (IC-POSS). An IC-POSS is partially hydrolyzed from the completely condensed POSS (CC-POSS) analogue. T₇-trisilanol, in which one corner of a CC-POSS is hydrolyzed, is a typical IC-POSS [23, 24]. This type of IC-POSS has been traditionally used for synthesizing mono-functional CC-POSSs via condensation with trialkoxysilanes or trichlorosilanes (Fig. 3a), while there were few studies on IC-POSS-based

materials. Meanwhile, the low symmetry of an IC-POSS backbone in comparison with that of a CC-POSS is attractive for practical applications. For a proof of concept, the dispersibility of IC-POSS derivatives in some matrices has been investigated (Fig. 3b).

First, amphiphilic IC-POSSs having poly(ethylene glycol) (PEG) chains have been examined as an emulsifier [25]. The amphiphilic IC-POSSs effectively stabilize emulsions, whereas emulsions with a CC-POSS-analogue are unstable (Fig. 4). It has been confirmed that IC-POSS molecules have a higher dispersibility than do CC-POSSs. It is noteworthy that the melting point of an isobutyl-substituted IC-POSS (−18 °C) is substantially lower than that of its CC-POSS analogue (130 °C), while these POSS derivatives show similar degradation temperatures for 5% weight loss ($T_{d5} = 203$ and 214 °C for the IC-POSS and CC-POSS, respectively). This result indicates that the crystallinity can be reduced without diminishing the thermal stability by exchanging the backbone from CC-POSS to IC-POSS.

Transmission electron microscopy and static light scattering studies have disclosed the self-assembly behaviors of amphiphilic POSSs in water [26]. The CC-POSSs and IC-POSSs form vesicles and micelles, respectively. It is probable that the rigid CC-POSS cores strictly aggregate in the shells because of their high crystallinity, but the amphiphilic IC-POSSs flexibly associate to produce micelles. The size of the micelles can be controlled by the substituents at the corners of the IC-POSSs and the chain length of the PEGs [27].

The high dispersibility of an IC-POSS is suitable for use as a filler in a polymer matrix, as well as water mediate. IC-POSSs having isobutyl, phenyl, and cyclohexyl groups on the corners and hydride, phenyl, vinyl, methyl, ethyl, and cyclohexylethyl groups at the opening moieties were investigated as a filler in PMMA [28]. PMMA films containing 30 wt% of some of the IC-POSS fillers are transparent, while the CC-POSS analogues lead to turbid or phase-separated films, even at 10 wt% concentration (Fig. 5). The high dispersibility of IC-POSS fillers realizes a wide range of properties, such as glass transition temperature, refractive index, and so on. Studies on IC-POSS derivatives have just been launched, and the class of materials is a promising candidate for organic–inorganic hybrids.

Main-chain type POSS polymers

As mentioned above, bifunctional POSS monomers are hard to synthesize. A double-decker-type POSS (DDSQ), which is synthesized by a modification of the cage structure, is a representative POSS monomer (Fig. 6a) [29–31]. Its polymers show a high-thermal stability and a remarkably

Fig. 1 **a** Classification of siloxanes and **b** types of silsesquioxanes

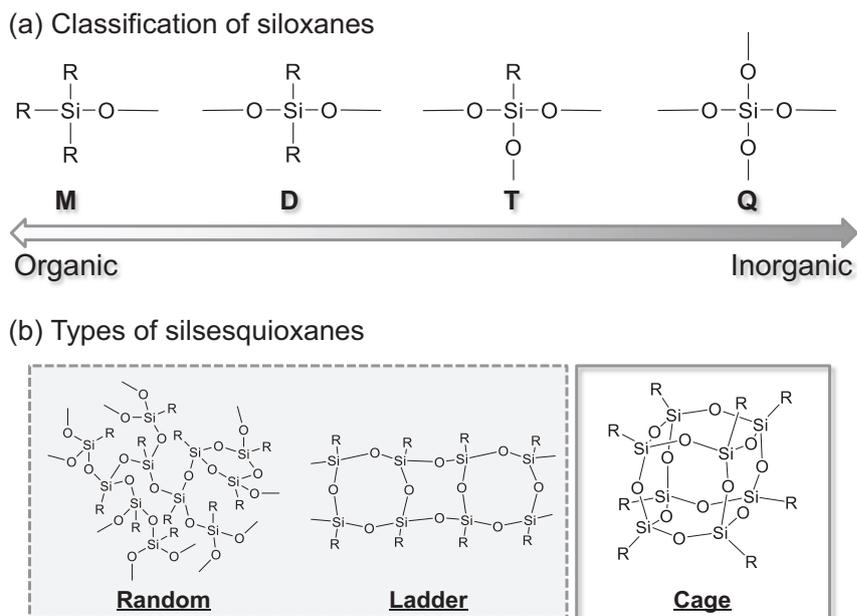
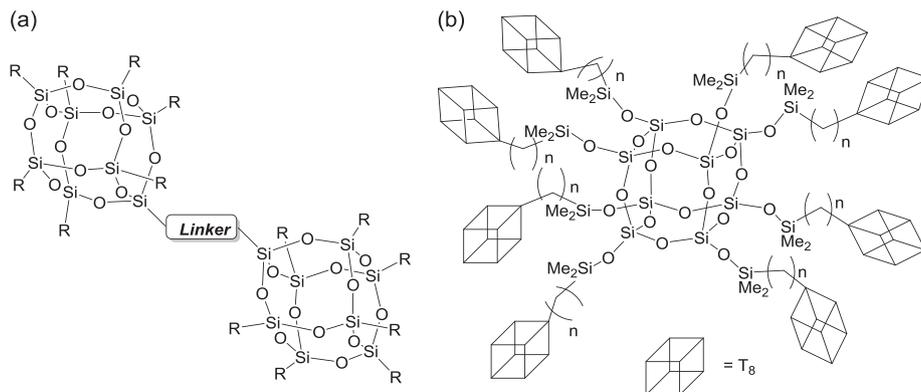


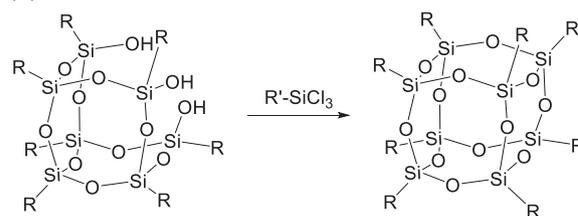
Fig. 2 Chemical structures of **a** dumbbell- and **b** star-shaped POSS derivatives



increased glass transition temperature thanks to the POSS skeleton. Side-opening monomers are also synthesized to produce polyurethanes [32] and polyamides [33] (Fig. 6b). However, the substituents of available cage-modified monomers are limited (DDSQ: phenyl group and side-opening type: isobutyl group), and a further variety of bi-functional POSS monomers is necessary. Naka and co-workers developed the bi-functional T_8 monomer (Fig. 6c) by utilizing the regioselective hydrolysis of (3-aminopropyl) heptaisobutyl POSS and subsequent condensation with triethoxy(3-aminopropyl)silane [34]. Polycondensation of the monomer with pyromellitic dianhydride (PMDA) produces a main-chain-type POSS polyimide. The polyimide shows excellent transparency and thermal stability.

The author then synthesized a POSS polyimide with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and compared the properties with the polyimide synthesized from PMDA [35]. The polyimide with 6FDA shows a higher transparency because of the restriction on

(a) Conventional use



(b) IC-POSS materials

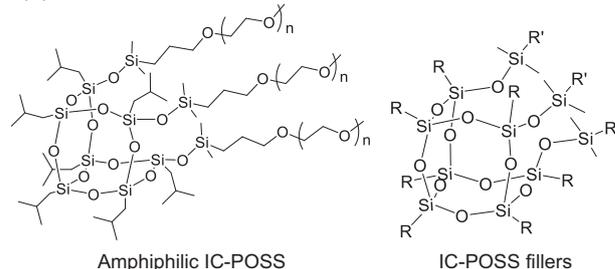


Fig. 3 **a** Conventional use of IC-POSSs for the synthesis of mono-functionalized POSS. **b** Examples of IC-POSS materials

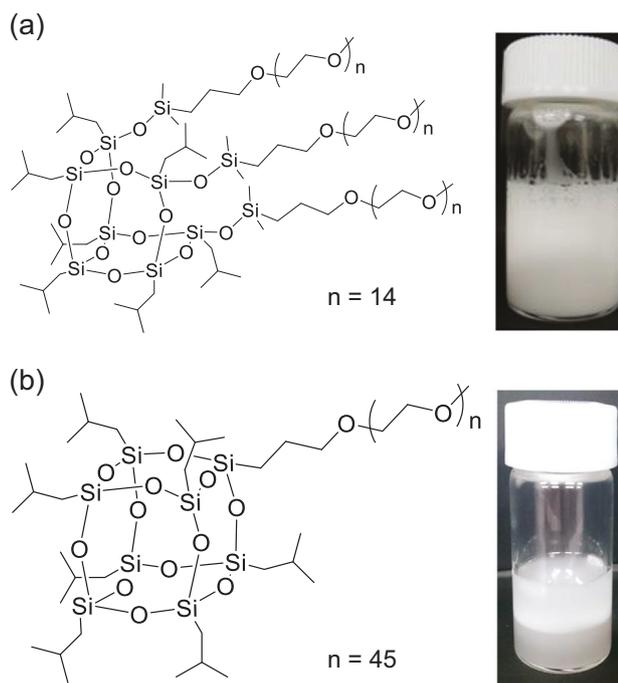


Fig. 4 Chemical structures of amphiphilic POSSs (**a** IC-POSS and **b** CC-POSS) and photographs of mixtures of water and methyl myristate (1:1) 1 h after stirring at 20,000 r.p.m. for 2 min

applicable to the bisvinyl monomer: regioselective hydrolysis and condensation. Hydrosilylation polymerization of the monomer with siloxane monomers having Si–H terminal groups produces polysiloxanes containing POSSs in the main chain. The optical transmittance of the film (35 μm in thickness) is over 98% in the visible region between 780 and 330 nm. Novel monomer design for main-chain-type POSS polymers is currently a popular subject and will continue to be reported.

Study on the electronic properties of POSS

The electronic properties of POSSs remain unexploited. The core of a POSS is composed of Si–O bonds, which have been usually recognized as a nonconjugated unit with π -electrons of organic substituents on the Si atoms. However, some experimental and theoretical studies of POSS imply a contribution of the silsesquioxane core to π -conjugated units directly attached to the Si corners. In 1989, Feher and Budzichowski [36] reported experimental results suggesting an electron-withdrawing behavior of the Si_8O_{12} framework. Then, theoretical studies on aryl-substituted POSSs revealed that the HOMO–LUMO gap can be narrowed by aryl

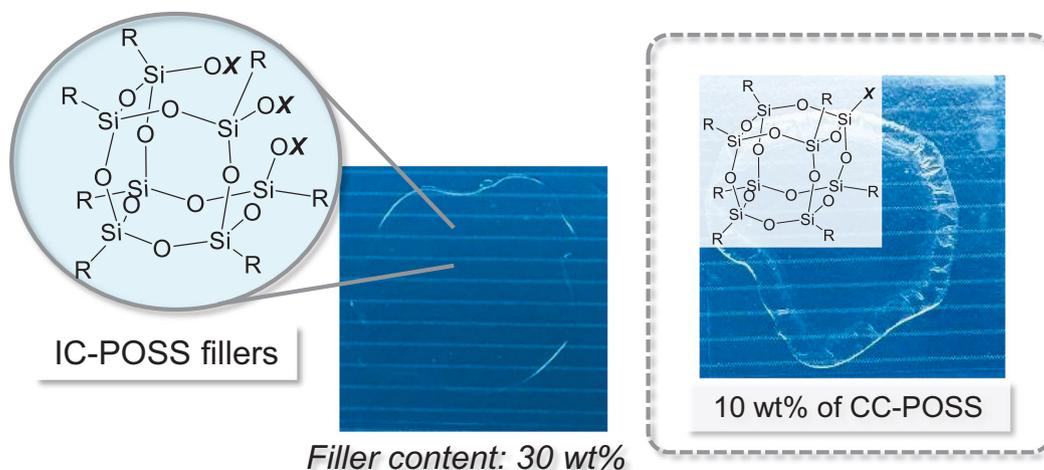


Fig. 5 Photographs of PMMA hybrid films with IC- or CC-POSS fillers

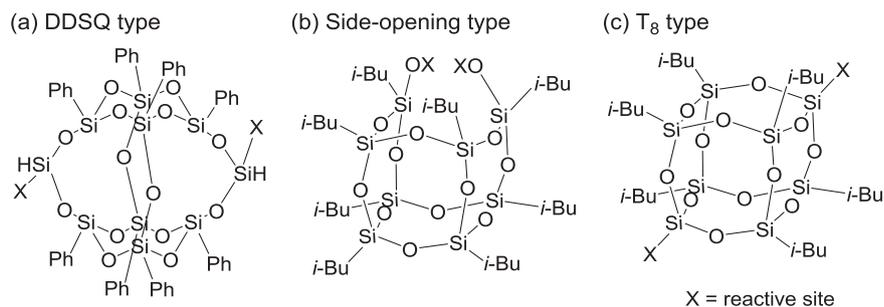
intermolecular charge transfer by the aliphatic structure. It is worth noting that both polymers show no glass transition temperature between room temperature and 400 $^{\circ}\text{C}$, though a lower glass transition temperature is usually observed when using 6FDA. The POSS moiety probably freezes the molecular mobility to significantly increase the glass transition temperature.

As another example of a bifunctional T_8 -type monomer, the author proposed bisvinylhexaisobutyl POSS [32]. The same strategy for bis(3-aminopropyl)hexaisobutyl POSS is

groups [37]. For further investigation on the electronic properties of POSS, experimental knowledge involving aryl-substituted POSSs should be accumulated. To this end, synthetic routes incorporating π -conjugated units with POSS should be investigated.

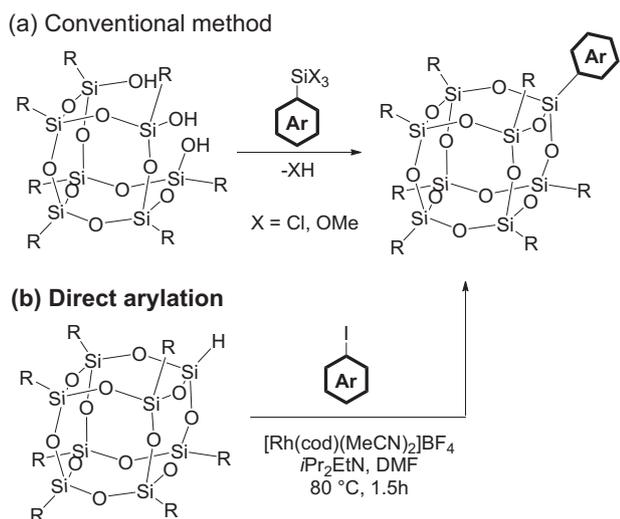
Conventionally, aryl-substituted POSSs have been synthesized by the condensation reaction of trichloro- or trialkoxysilanes having an aryl group with an IC-POSS trisilanol (Scheme 1a). This synthetic route requires highly reactive silane coupling agents, which limit the versatility of

Fig. 6 Chemical structures of bi-functional POSS monomers: **a** DDSQ type, **b** side-opening type, and **c** T₈ type



aryl-substituted POSSs. Meanwhile, Laine's group developed pioneering methods, including the Heck reaction and olefin metathesis of octavinyl POSS leading to octaaryl POSSs [38]. Additionally, they discovered the regioselective synthesis of octa(*p*-iodophenyl) POSS [39, 40]. This precursor is suitable for use in traditional coupling chemistries. The electronic properties of the obtained aryl-substituted POSSs were examined, and the electron-accepting behaviors of POSS cores were studied [40].

Recently, the author has developed the Rh-catalyzed direct arylation of monohydride POSS, which is easily synthesized and stable under ambient conditions [41]. This direct arylation smoothly proceeds with various aryl iodides to give aryl-substituted POSSs (Scheme 1b). An investigation into the electronic properties of the aryl-substituted POSSs revealed that POSS can work as an electron acceptor, but the spherical LUMO located in the cage does not affect the conjugation of the aryl groups. Only the corner to which the aryl group is attached contributes the frontier orbital of the aryl-substituted POSS. To utilize the unique LUMO of POSS, additional studies are under way.



Scheme 1 Synthetic procedures of aryl-substituted POSSs: **a** conventional method, and **b** Rh-catalyzed direct arylation

Arsenic polymers and supramolecules

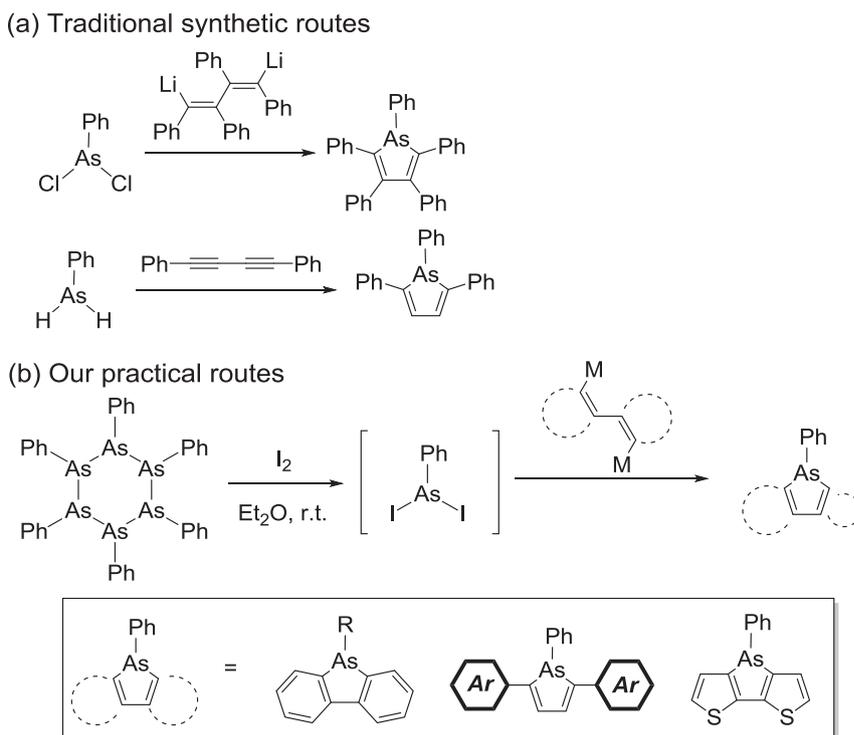
Functional materials based on organoarsenic chemistry remain to be developed. This is mainly because precursors for organoarsenic compounds need volatile and toxic chemicals such as arsenic halides and hydrides. For example, traditional synthetic routes of arsene employ dichlorophenylarsine [42] or phenylarsine [43] (Scheme 2a). Instead of experimental study, functional organoarsenic compounds have recently been examined by theoretical means. These efforts predict that arsene has a low aromaticity, low-lying LUMO, and high-inversion barrier [44–46]. Increasing attention has been given to obtaining experimental proof for these predictions, and thus, practical synthetic routes should be established.

In 2002, Naka and Chujo reported the first synthesis of π -conjugated organoarsenic polymers, poly(vinylene-arsine)s, via alternating radical copolymerization [47]. They also reported a cyclic diarsenic ligand, *cis*-1,4-dihydro-1,4-dimethyl-2,3,5,6-tetrakis(alcoxycarbonyl)-1,4-diarsinine (*cis*-DHDA) [48, 49]. In these pioneering works, cyclooligoarsines are employed as key precursors for developing organoarsenic materials; they are safely and easily prepared from nonvolatile inorganic arsenic precursors [50, 51]. Recently, Naka proposed the in situ generation of diiodoarsine derivatives from cyclooligoarsines [52], and then, the author developed various electrophiles [53] and nucleophiles [54]. The utilization of those reactive species has realized experimental studies in organoarsenic chemistry. In particular, research on the optical and electronic properties of functional organoarsenic compounds [52, 53, 55–59] and on the structure and properties of organoarsenic ligand-based supramolecules [60–63] have remarkably progressed by the author's practical synthetic routes (Scheme 2b). The last half of this review introduces organoarsenic polymers and supramolecules based on this synthetic strategy.

π -conjugated organoarsenic polymers

π -conjugated polymers containing heteroatoms exhibit unique properties that cannot be attained by hydrocarbon

Scheme 2 a Traditional and b the author's practical synthetic routes of arsole derivatives



polymers. Various elements have been incorporated into conjugated systems. In regard to arsenic, the above-mentioned works of Naka and Chujo are the first examples. There were no reports on π -conjugated organoarsenic materials for a decade after the papers on poly(vinylene-arsine)s [51, 64–67]. In 2015, the silence was broken by the author's experimental studies of arsole derivatives based on practical synthetic strategies [52]. Arsole derivatives, e.g., 9-arsafluorenes [52, 53], 2,5-diarylarsoles [55, 56], and dithieno[3,2-*b*:2',3'-*d*]arsoles [57, 58], can be synthesized from in situ generated diiodoarsine species. They possess trivalent arsenic atoms with a high-oxidation resistance in air, while the phosphorus analogues are easily oxidized to pentavalent states. The optical and electronic properties of the arsole derivatives are quite similar to the corresponding phosphole ones; this result is well accorded with the theoretical predictions.

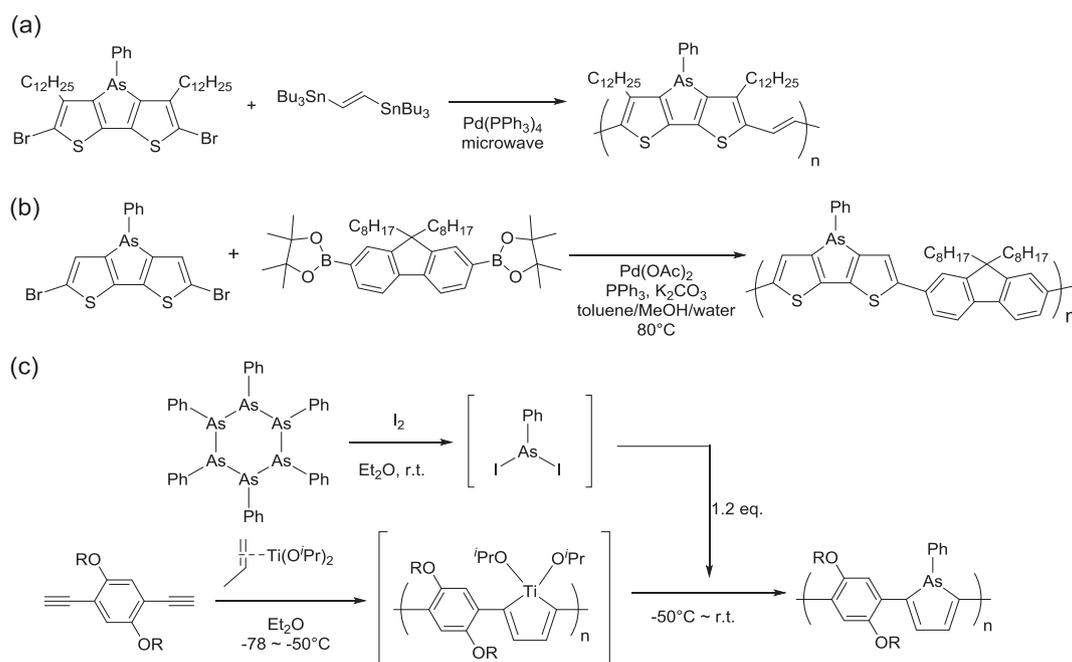
In 2016, Heeney and coworkers reported a dithienoarsole-containing polymer, which is synthesized by a microwave-assisted Stille-polycondensation (Scheme 3a) [67]. They elucidated the conductivity and air stability of the polymer. The author developed a synthesis of dithienoarsole monomers from diiodophenylarsine, and via Suzuki polycondensation, produced a dithienoarsole-containing polymer, as well (Scheme 3b) [60]. Then, it has been disclosed that a reaction between a titanacyclopentadiene polymer, which was developed by Tomita, and diiodophenylarsine yields an arsole-containing polymer (Scheme 3c) [59]. The arsole polymer shows an intense

emission and possesses a high-air stability. Interestingly, the emission color can be tuned by coordination to the arsenic atom. π -conjugated organoarsenic materials will increasingly draw inspiration from these experimental results.

Supramolecules of transition metal complexes with organoarsenic ligands

The arsenic atom has a soft Lewis acidity to form complexes with soft metals [68]. Since trivalent arsenic atoms adopt a trigonal pyramidal structure, and the inversion energy is very high, it can act as a stable stereocenter. Therefore, organoarsenic ligands are a promising candidate to serve as templates to construct supramolecular architectures. Wild and coworkers anticipated the syntheses of optically active organoarsenic oligomers and their helicates [69–72].

The author predicted *cis*-DHDA to be an excellent building block for the construction of supramolecules because of the two arsenic atoms in the rigid backbone [60–63]. Multi-nuclear complexes can be obtained by utilizing *cis*-DHDA. Firstly, the author developed As-stereogenic C_2 -symmetric structures of unsymmetrical *cis*-DHDAs, which are synthesized from cyclooligoarsine and terminal alkynes (Scheme 4) [60]. These chiral *cis*-DHDAs coordinate to copper(I) iodide to form binuclear triple-stranded helicates. Interestingly, the racemic mixtures of the ligands are enantioselectively self-assembled.

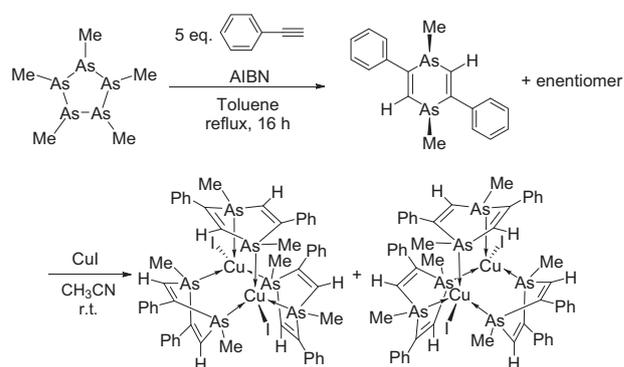


Scheme 3 Syntheses of arsole-containing polymers: **a** microwave-assisted Stille polycondensation, **b** Suzuki–Miyaura polycondensation, and **c** reaction of a titanacyclopentadiene polymer and diiodophenylarsine

The author then focused on the soft Lewis basicity of arsenic atoms. Metal-organic frameworks (MOFs) have attracted substantial attention [73]. Since heterogeneous catalysts are one of their fascinating applications, transition metals should be introduced into the pores. To this end, the ligand sites need to be included in the components of an MOF. However, protecting groups are sometimes necessary to prevent the ligand sites from involvement in the MOF construction [74]. Heteroatoms possessing soft Lewis basicity are promising candidates because their interactions with the hard metal cations that are used as the components of MOFs are relatively weak. In this context, arsenic atoms are suitable as ligand sites in MOFs because of their air stability and Lewis basicity; organophosphorus compounds are also soft Lewis bases [75], but their air sensitivity requires an inert atmosphere for the preparation of MOFs. The author employed a *cis*-DHDA ligand with four carbonate groups as a MOF component [61]. The *cis*-DHDA tetracarboxylate is mixed with copper(II) acetate and 4,4'-bipyridyl under acidic conditions to give single crystals of the MOF (Fig. 7a). As expected, the arsenic atoms with a bare lone pair are introduced in the MOF structure without a protection–deprotection procedure or inert atmosphere (Fig. 7b). This is the first example of the incorporation of trivalent arsenic atoms into an MOF and successfully demonstrates new potential for organoarsenic compounds.

Final remarks

The author's recent works on silicon and arsenic polymers and supramolecules are introduced here. Cage-silsesquioxanes have been widely utilized, but further advancement potentially exists. Precise molecular design will open new avenues to organic-inorganic hybrid materials with excellent functions and performances. Organoarsenic chemistry has just resumed and will be expanded in various fields. Practical synthetic routes will strongly contribute to the progress of experimental studies. Since a deeper understanding of each element directly leads to extending the capability of materials, as described in this



Scheme 4 Syntheses of C_2 -symmetrical *cis*-DHDA and its copper(I) iodide complex

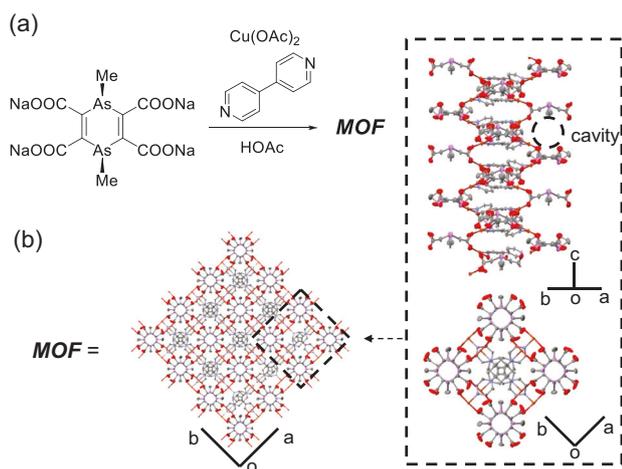


Fig. 7 a Synthesis and b results of X-ray crystallography of the MOF

focus review, the fusion between heteroatom chemistry and materials science continues to be a promising subject for the future.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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