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POLIMERY

Recent achievements and applications of silsesquioxane-based hybrid materials – an overview

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Abstract: Based on a literature review from the last 3 years, potential applications of hybrid materials based on silsesquioxanes in engineering, catalysis, biomedicine, and drug delivery systems are presented. Methods of synthesis of such materials are also discussed, considering publications from previous years. Silsesquioxanes are characterized by a defined stable three-dimensional structure consisting of an inorganic core (Si-O-Si) and organic substituents. The rigid core and multifunctionality of substituents make silsesquioxanes ideal candidates for use in the synthesis of innovative materials in the areas of chemistry and biomedicine.

Keywords: Polyhedral oligomeric silsesquioxane, water purification, catalytic systems, biomedicine, drug nano-carriers, chemotherapy, porous materials.

Najnowsze osiągnięcia i zastosowania materiałów hybrydowych na bazie silseskwioksanów

Streszczenie: Na podstawie przeglądu literaturowego z ostatnich 3 lat przedstawiono potencjalne zastosowania materiałów hybrydowych na bazie silseskwioksanów w inżynierii, katalizie, biomedycynie i systemach podawania leków. Omówiono również metody syntezy tego typu materiałów, biorąc pod uwagę publikacje z wcześniejszych lat. Silseskwioksany charakteryzują się zdefiniowaną stabilną trójwymiarowa strukturą składającą się z nieorganicznego rdzenia (Si-O-Si) oraz organicznych podstawników. Sztywny rdzeń i wielofunkcyjność podstawników czynią silseskwioksany idealnymi kandydatami do stosowania w syntezie innowacyjnych materiałów w obszarach chemii i biomedycyny.

Słowa kluczowe: poliedryczny oligomeryczny silseskwioksan, oczyszczanie wody, systemy katalityczne, biomedycyna, nanonośniki leków, chemioterapia, materiały porowate.

The pioneering reports on the synthesis of polyhedral oligomeric silsesquioxanes (POSS) *via* hydrolysis of trifunctional silanes – phenyltrichlorosilane [1] and methyltrichlorosilane [2] appeared as early as 1946. The research-areas related to structures involving Si-O bonds have for many years been dominated by both silica and silicone oils, rubbers, and resins [3]. The new opening for studies on silsesquioxanes, due to significant progress

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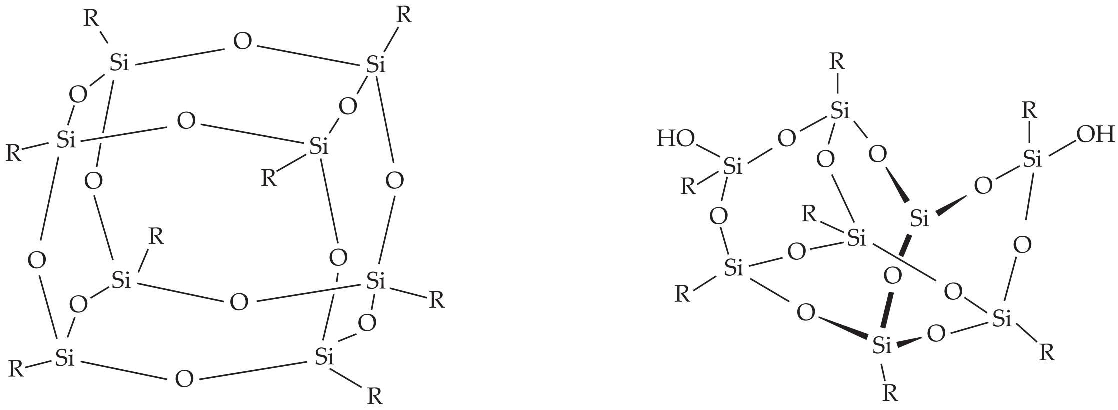

Fig. 1. Examples of fully and partly condensed T_8 type silsesquioxanes (R-organic group)

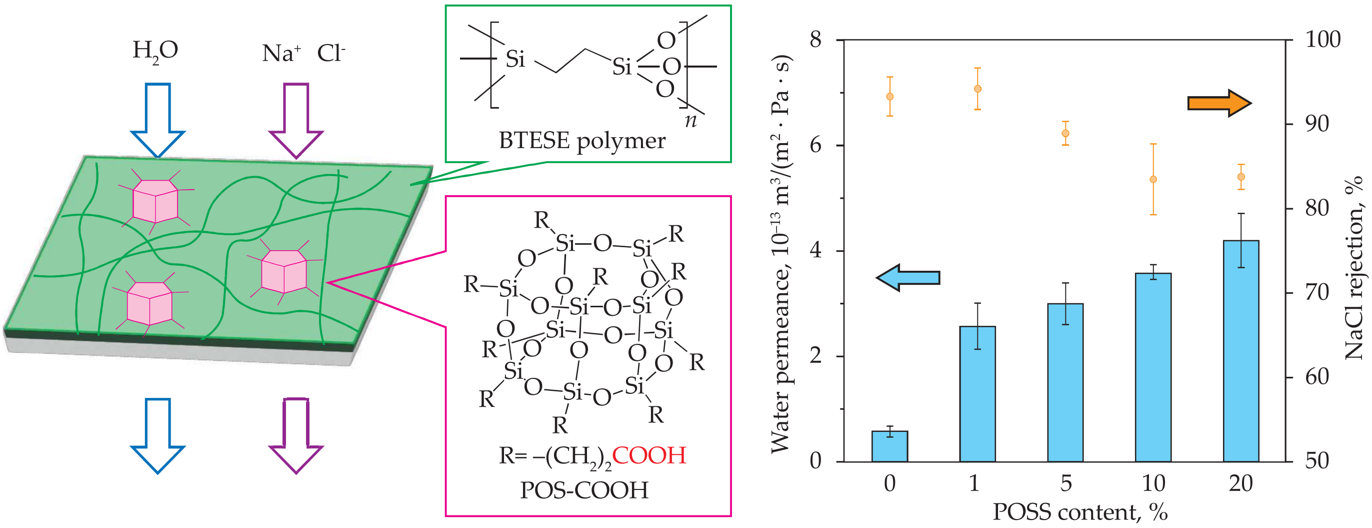

Fig. 2. Membrane's components, including T_{10}-type POSS, and their water separation properties. Reprinted from [9]

in analytical techniques, dates back to the seventies of the last century [4] and was later summarised in extensive reviews [5–7]. Over the last 10–15 years, the interest in studies on silsesquioxanes has grown dramatically due to potential applications in such areas as e.g. materials, energy, catalysis and biomedicine [8]. This class of hybrid materials of 3D are considered the smallest (1–3 nm) soluble particles of silica having basic chemical structure (fully condensed cages) of $(RSiO_{1.5})_n$ (=T_n), where n = 6, 8, 10 and R corresponds to hydrogen or an organic group. Several partially condensed structures have been described, and practical application was also considered (Fig. 1).

In the present review, the abbreviation POSS will be used for these unique structures, having sizes of 1–3 nm [5]. POSS structures present good solubility, non-toxicity, as well as thermal, mechanical, and chemical resistance as well as ability to be modified in the periphery bearing organic or hydrogen. Thus, they form a useful class of well-defined compounds for the generation of novel high-performance organic-inorganic hybrid systems [8].

SILSESQUIOXANES AND RELATED BRANCHED SILOXANE SYSTEMS FOR WATER PURIFICATION

A potentially important application of materials including hydrophilic silsesquioxane was described presenting an effective system of reverse osmosis membranes in water desalination (Fig. 2) [9].

Carboxyl functionalised T_n-type (n = 8, 10, and 12) polyhedral oligomeric silsesquioxanes (POSS-COOH) were used as hydrophillic nanofiller additive for composite organosilicon membranes matrix, based on polymer obtained from 1,2-bis(triethoxysilyl)ethane (BTESE) [10]. The carboxyl-modified silsesquioxanes were used as a mixture of 8, 10 and 12 oligomeric systems (Fig. 3). The increased contents of POSS-COOH from 1 to 20% led to increased water permeance but at the same time salt rejection decreased as a result of increased hydrophilicity. The optimum properties of the membrane were obtained with the BTESE polymer matrix containing 1% of POSS-COOH.

The same research group [11] studied membranes made by hydrolytic polycondensation of BTESE and 3-glycidy-

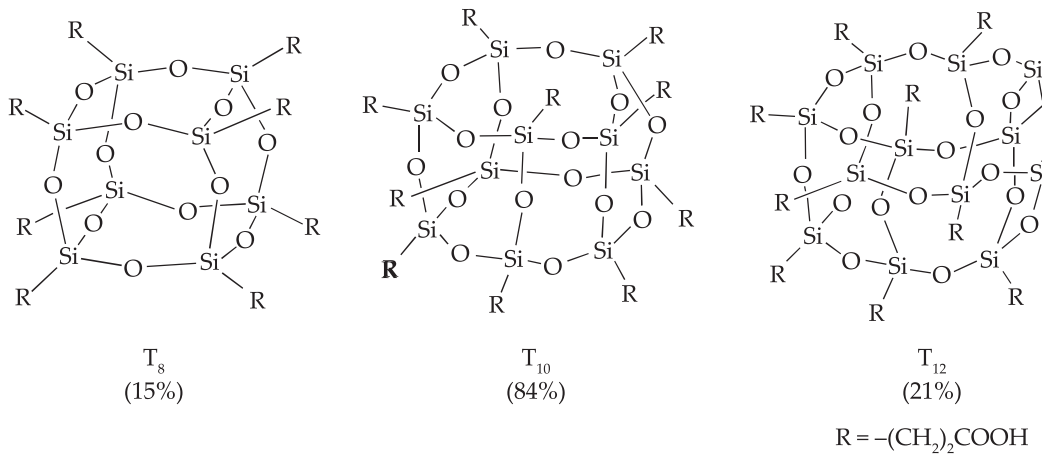

Fig. 3. Structures of POSS-COOH hybrid containing 8, 10, and 12 silicon atoms in the silsesquioxane core. Reprinted from [9]

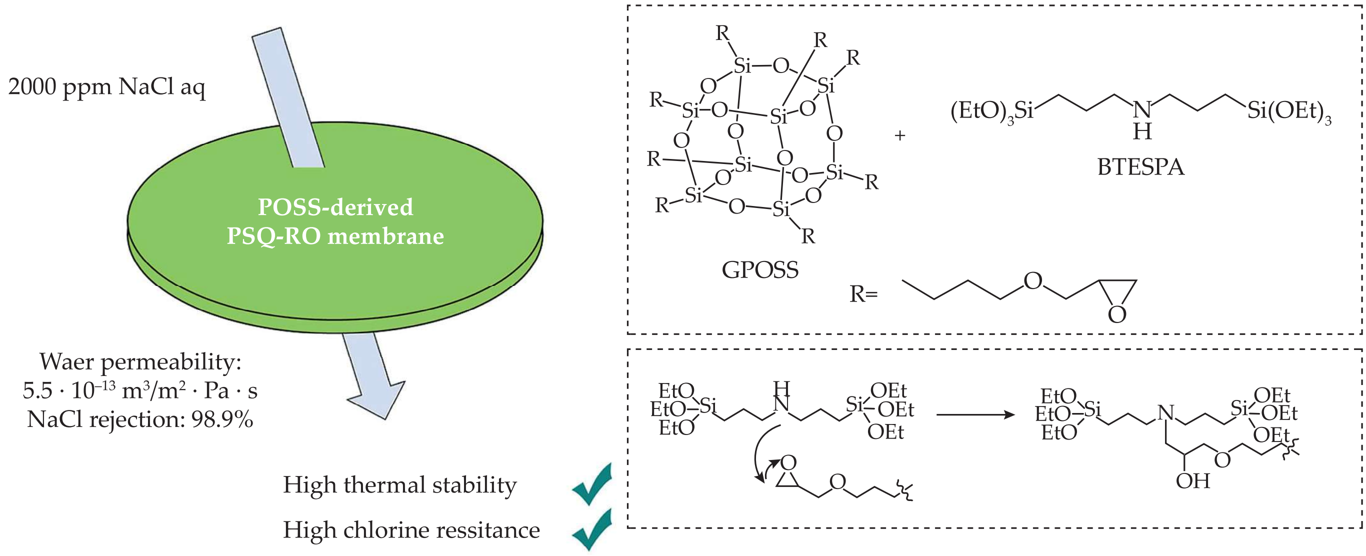

Fig. 4. Effectiveness of BTESE/GPOSS. Reprinted from [11]

loxypropyl-POSS (GPOSS) (Fig.4). It was found that such a system was superior compared to the one with T$_8$-type POSS-COOH.

A comprehensive study of four different POSS nanomaterials for nanofiltration membranes with enhanced permeability have been presented [12]. The following T$_8$-type POSS structures were analysed: octylamine POSS, methoxypolyethylene glycol POSS and a partly open cage of trisilanol isobutyl POSS on a support layer prepared from polyethersulfone (15 wt%), polyethylene glycol (21 wt%) and dimethylacetamide (64 wt%). The active nanofiltration layer was prepared from piperazine (PIP) and trimesoyl chloride (TMC) *via* interfacial polymerization (Fig. 5) [13]. The best results were obtained for a system involving octylamine POSS activated by trimethylamine in rejection of Na_2SO_4 (98%) compared e.g. to NaCl (40%).

The effectiveness of mono-component membrane, obtained from organo-bridged trialkoxysilanes i.e. 2,5-bis[2-(triethoxysilyl)vinyl]pyrazine (BTES-VPz) (Fig. 6) was studied and compared to earlier described ones prepared from 1,4-[2-(triethoxysilyl)vinyl]ben-

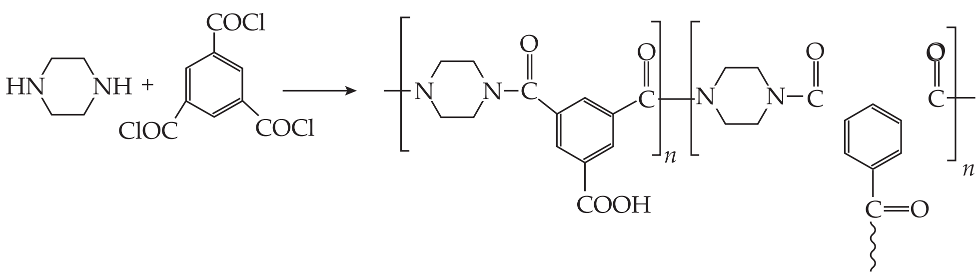

Fig. 5. Interfacial polymerization of piperazine and trimesoyl chloride. Reprinted from [13]

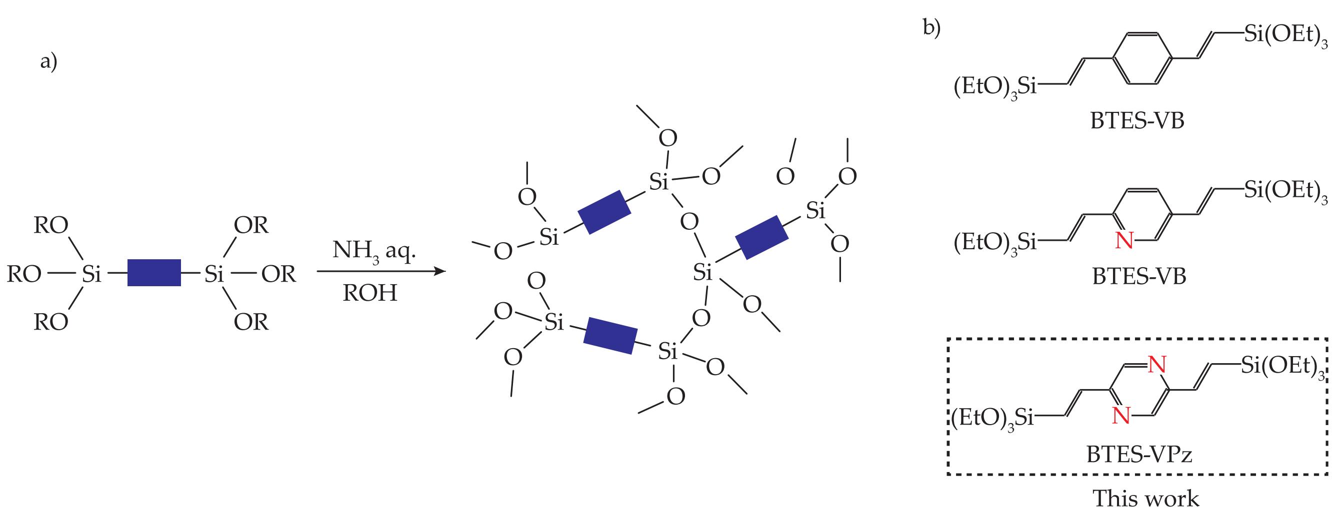

Fig. 6. Formulas of: a) polycondensation of organo-bridged trialkoxysilanes, b) structure of divinylarene-bridged trialkoxysilanes. Reprinted from [14]

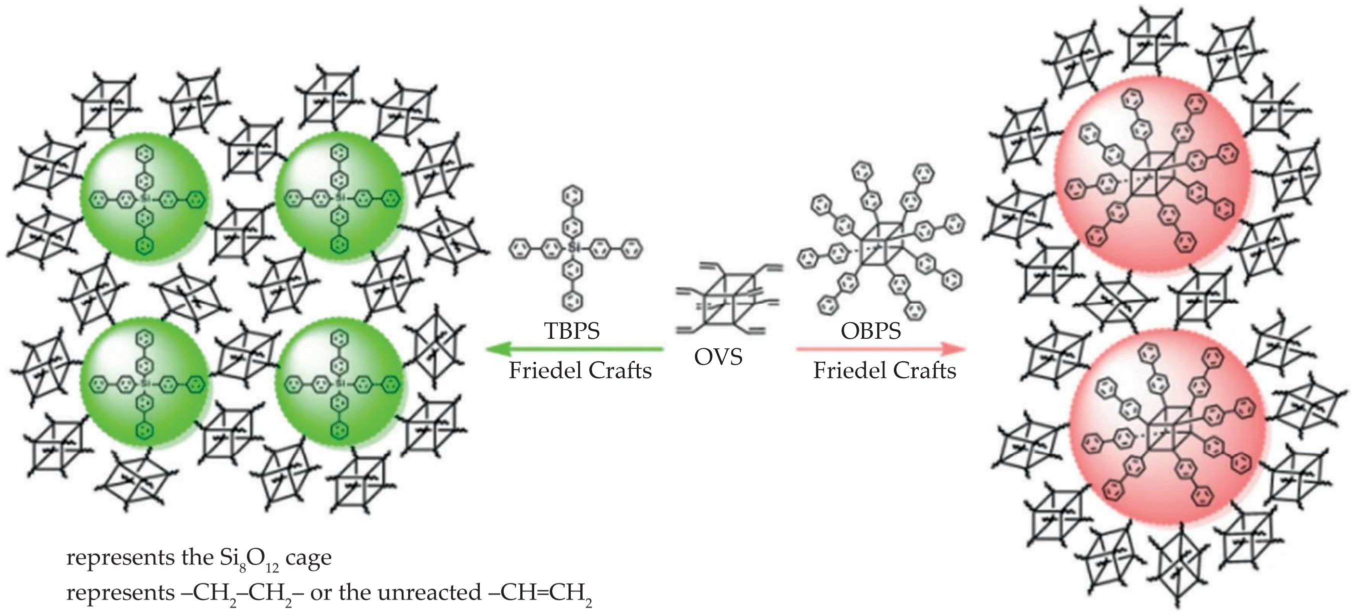

Fig. 7. Synthetic pathways to silsesquioxane containing water purification polymers. Reprinted from [16]

T a b l e 1. Effect of POSS and related branched siloxane systems on water desalination

Pristine polymer	Silsesquioxane	Water permeance*	Salt rejection	Ref.
Polycondensed BTESE	POSS-COOH	500% increase	95% (NaCl)	[9]
PIP + TMC on PES	POSS- NH_2	20% increase	95% (Na_2SO_4)	[12]
	POSS-APB	8% decrease	71% (Na_2SO_4)	
	POSS-PEG	10% increase	98% (Na_2SO_4)	
	POSS-TSB	170% increase	76% (Na_2SO_4)	
Polycondensed BTESE	GPOSS	170% increase	98.9% (NaCl)	[11]
Polycondensed BTES	-	-	97% (NaCl)	[14]
PIP + TMC on PES	OVS	170% increase	97% (Na_2SO_4) 90% ($MgSO_4$) 30% (NaCl) 27% ($MgCl_2$)	[17]

*Relative to pristine polymer

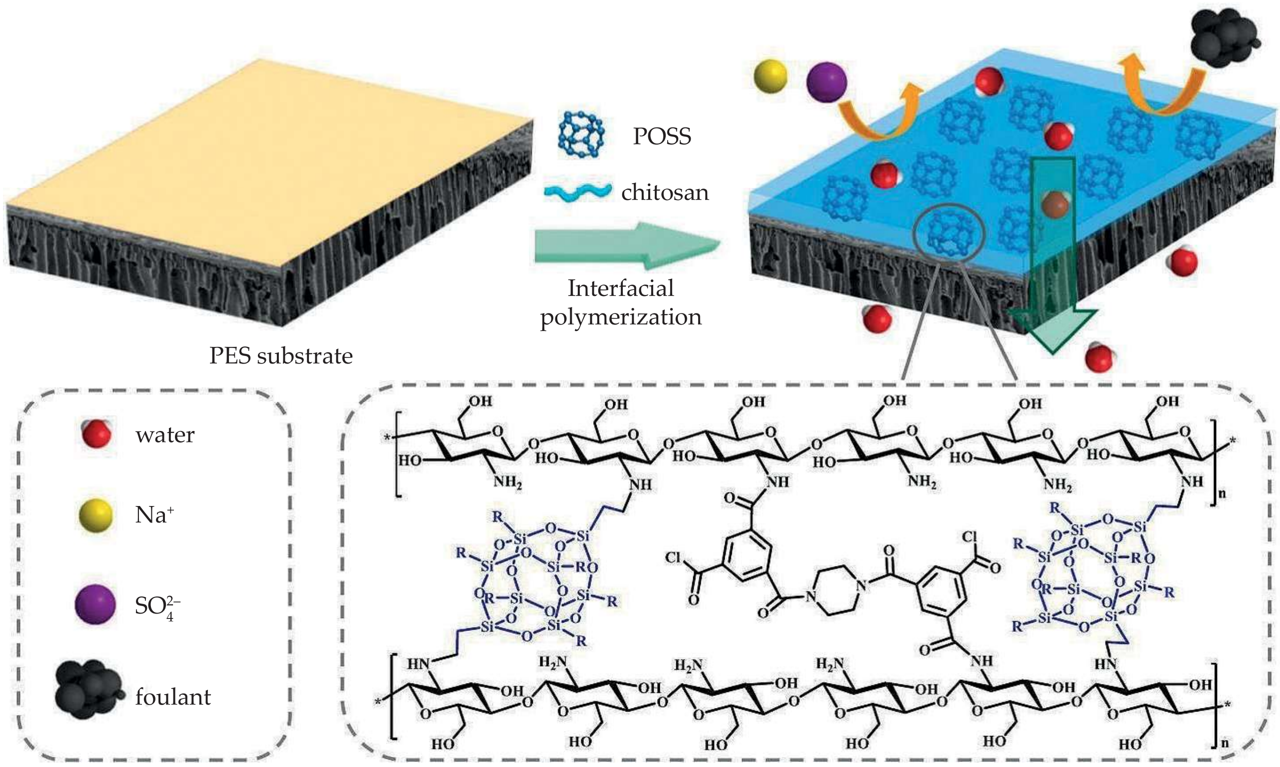

Fig. 8. Preparation of membranes with chitosan/POSS. Reprinted from [17]

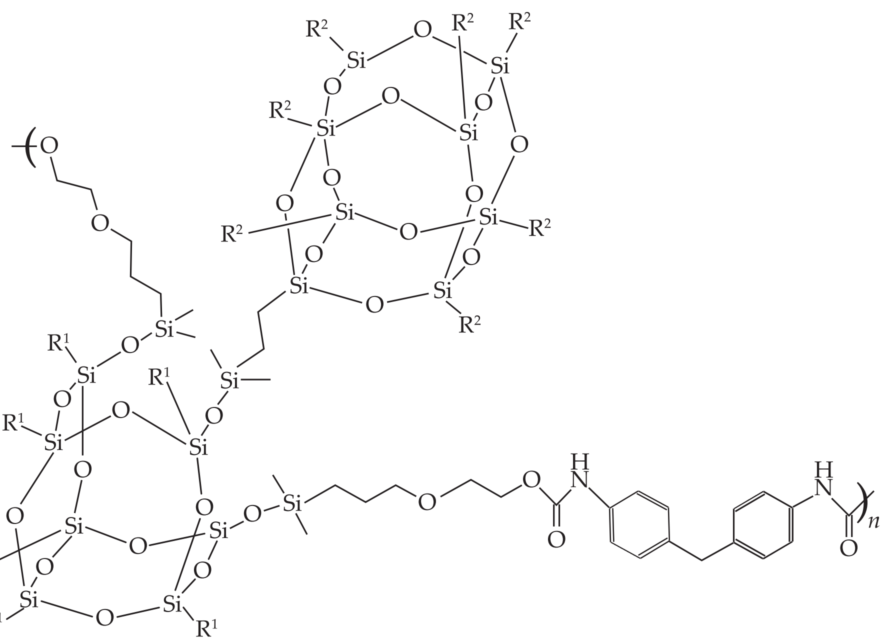

Fig. 9. Structure of polymers containing POSS in main and side chains. Reprinted from [18]

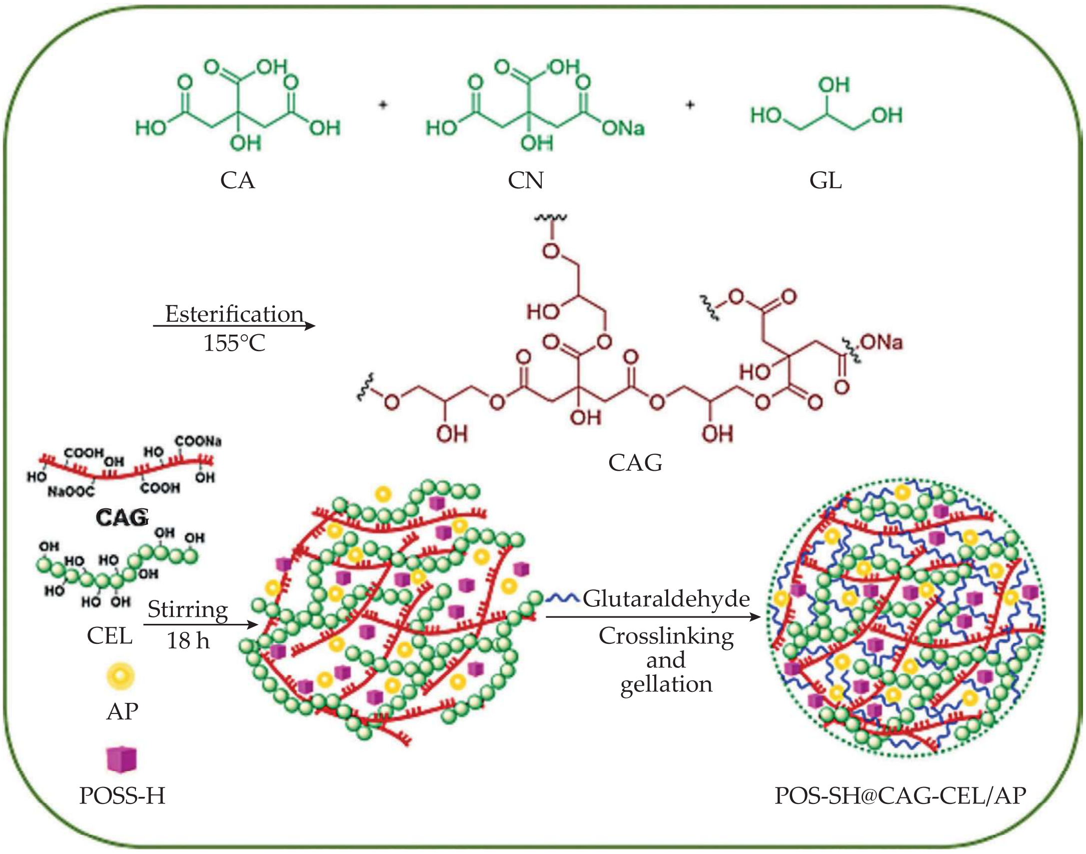

Fig. 10. Preparation of the hydrogel for thallium adsorption. Reprinted from [19]

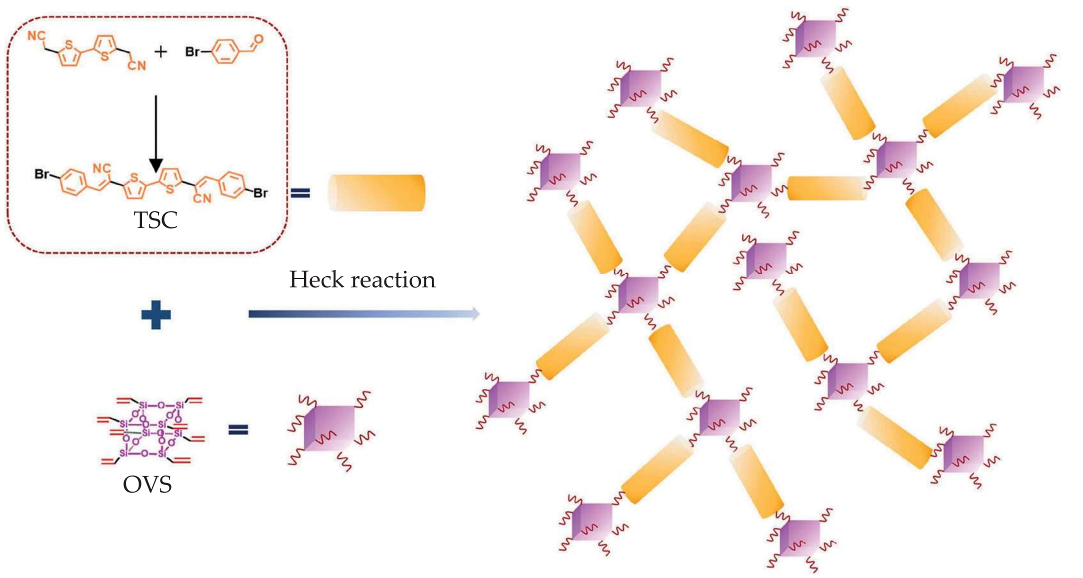

Fig. 11. Schematic preparation of PTSC. Reprinted from [20]

zene (BTES-VB) and 2,5-[2-(triethoxysilyl)vinyl]pyridine (BTES-VP) [14, 15]. Amongst these three membranes demonstrate the highest water permeation of 2.1 x 10^{-13} m^3/($m^2 \cdot Pa \cdot s$) and NaCl rejection of 97% was found for BTES-VPz. The properties were ascribed to the water affinity of nitrogen.

Two groups of porous polymer membranes were synthesised *via* Friedel-Crafts alkylation of terabiphenylsilane (TBPS) and octabiphenylsilsesquioxane (OBPS) with octavinylsislsesquioxanes (OVS) (Fig. 7) [16]. These turned out as efficient adsorption systems for the removal of toxic, bulky organic dyes, such as rhodamine B, Congo red, and crystal violet (2230 mg/g) and Pb^{2+} salts (300 mg/g). It has also been shown that the polymers can be regenerated and reused.

Hybrid membranes of crosslinked chitosan and octavinyl-POSS (OVS) [17] on the polyamide layer (Fig. 8) [12]. Combining chitosan and POSS leads to a system with optimum hydrophilicity, pore size and electronegativity of such the type of membrane having large poten-

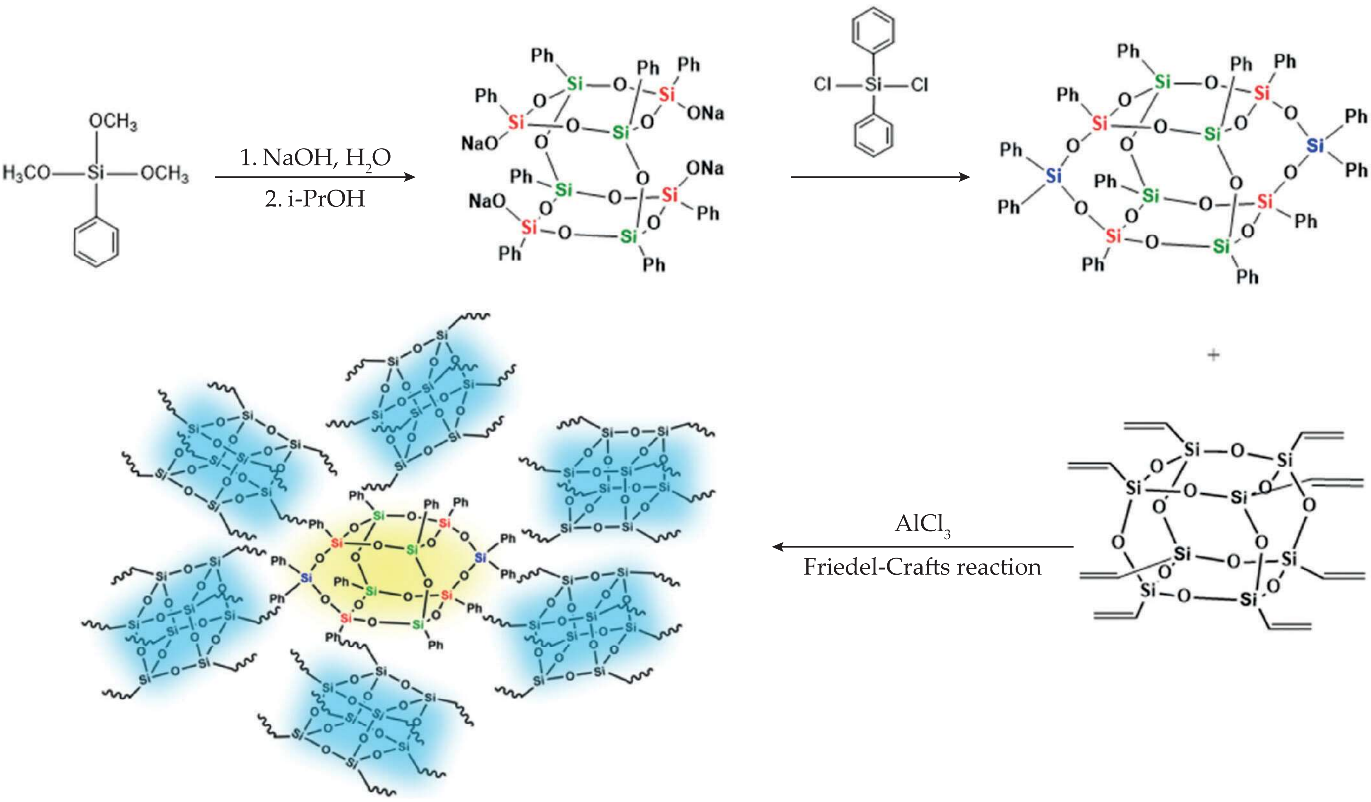

Fig. 12. Preparation of siloxane-based porous polymers incorporating double-decker and cage silsesquioxanes. Reprinted from [21]

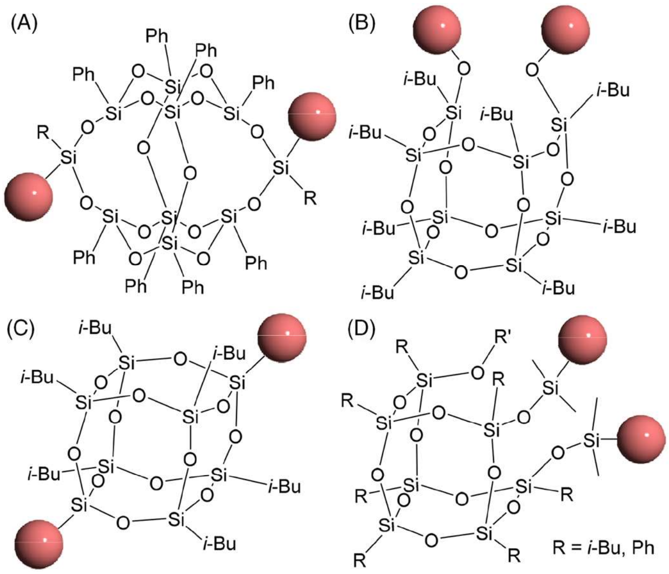

Fig. 13. Double-decker and side-open silsesquioxanes incorporated into siloxane polymers as main and side moieties. Reprinted from [22]

tial in water purification and desalination. The extent of salt rejection follows the order $Na_2SO_4 > MgSO_4 > NaCl > MgCl_2$ in agreement with higher repulsion by negatively charged membrane against divalent anions. The highest rejection was found for Na_2SO_4 reaching over 97%.

In summary, one can reach the conclusion that the addition of POSS nanoparticles increases the water affinity of the membrane or hydrogel structure, improves the rejection of salts as well as heavy metals, and limits the pore size of active layers. Thus, POSS containing systems appear to have a considerable potential for efficient water purification and desalination.

MATERIALS CHEMISTRY AND CATALYSIS

Novel polyurethanes with built-in open and closed cage silsesquioxanes in the main and side chain, respectively, were synthesized and thermal, and mechanical properties of such the materials were evaluated [18]. The POSS cages had isobutyl and phenyl side substituents (Fig. 9) that highly affected glass transition, melting point, and film hardness. The systems involving phenyl substituents exhibited increased T_g.

Cage and double-decker type silsesquioxanes (the latter comprised of two "decks" of silsesquioxanes stacked on top of one another) based distinctive porous materials are claimed as effective systems for the removal of environmental pollutants. It has been well proven that materials incorporating cage silsesquioxanes possess increased thermal stability and additionally allow synthesis of novel materials having designed functions Recently a rather exotic composite hydrogel was described made of cellulose (CEL), biodegradable polymer (CAG), synthesised by esterification of citric acid (CA) with glycerol (GL), T_8-type 3-mercaptopropyl substituted silsesquioxane (POSS-SH) and apple peel (AP) (Fig. 10) as an efficient composite for removal of thallium (1) from water [19]. It offered an adsorption capacity of 350 mg/g, being eco-friendly, reusable, and thermally stable.

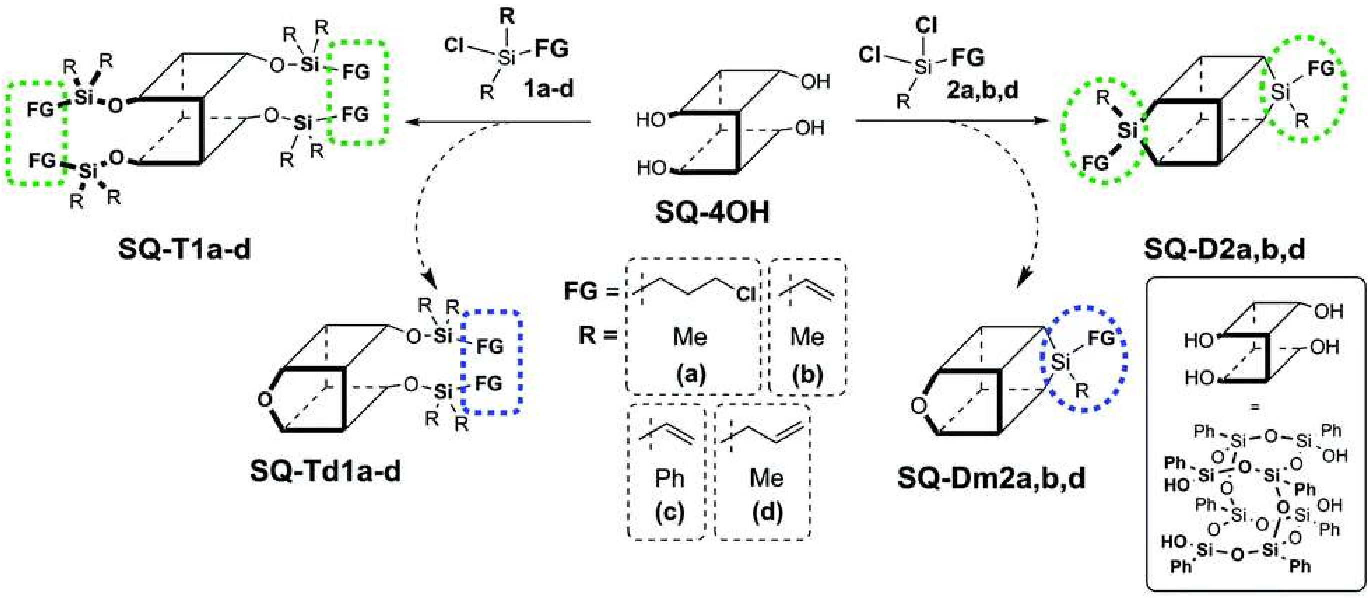

Fig. 14. Preparation of tetra-di- and mono-substituted double-decker silsesquioxanes (DDSQs). Reprinted from [23]

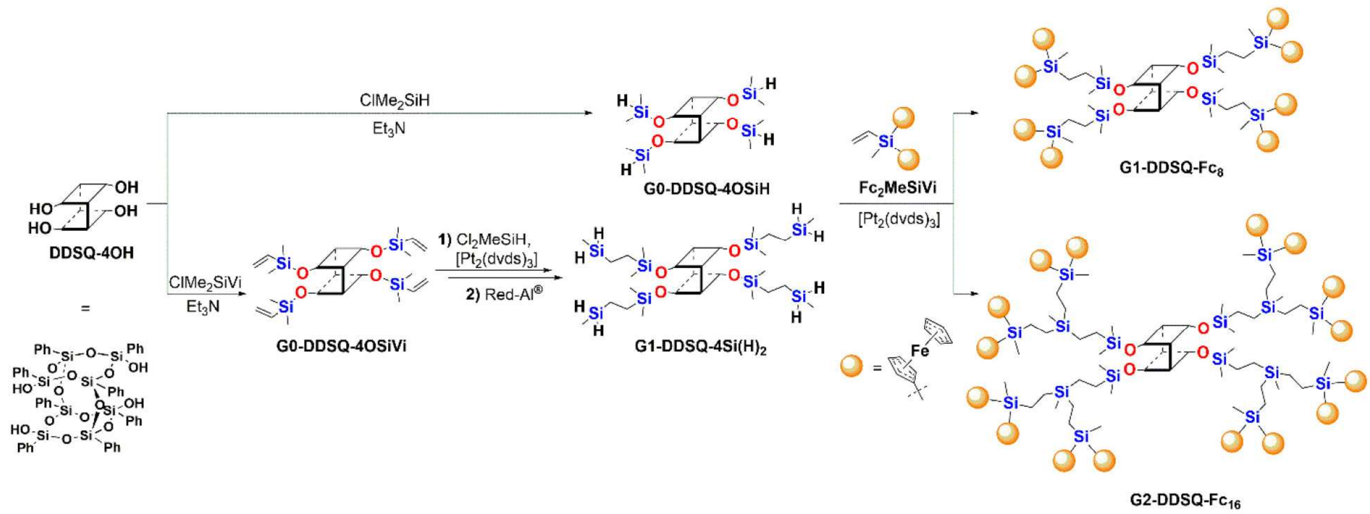

Fig. 15. Synthetic pathway to ferrocene dendrimers with silsesquioxane core. Reprinted from [24]

A novel fluorescent porous hybrid polymer incorporating silsesquioxane moieties, made by Heck reaction of octavinylsilsesquioxanes with dibromo-distyryl-bithiphens bearing CN substituents (PTSC), was described (Fig. 11) [20]. It was found to be an efficient material for the adsorption, detection, and recovery of Au(III) ions from waste water once a hybrid aerogel was prepared by PTSC blending with soft chitosan.

Three types of hybrid porous polymeric materials were described as having different molar ratios of octavinylsilsesquioxanes and phenyl substituted double-decker silsesquioxanes i.e., 1.5:1, 4.5:1and 7.5:1 (Fig. 12). These polymers show good stability, high specific areas, pore volumes and adsorption of pesticides, especially imidacloprid. The best results were obtained for the material with the highest contents of octavinylsilsesquioxanes []21.

The effect of cage structure on the properties of silsesquioxane polymers was carefully studied based on monomers with phenyl substituents (Fig. 13).

These materials with double-decker and side-open cage structures in the main chain have shown negligible influence of cage and linker structure on their optical properties but thermal properties were affected mainly. The results can have an important impact on the future design of silsesquioxane hybrid polymers for intended applications [22].

A number of novel double decker systems has been described, made by hydrolytic condensation reaction of SQ-4OH with chlorosilanes (Fig. 14).

The use of an open system with four reactive OH silsesquioxane groups allows the generation of a series of new materials. However, the mmolar scale and often low yield resulting in multi-step syntheses have to be overcome for any practical application [23]. They became a starting point for the synthesis of metallodendrimers having double-decker silsesquioxane core and ferrocenyl substituents in the outer sphere (Fig. 14) [24]. The electrochemical properties make them a novel potential material as electroactive films.

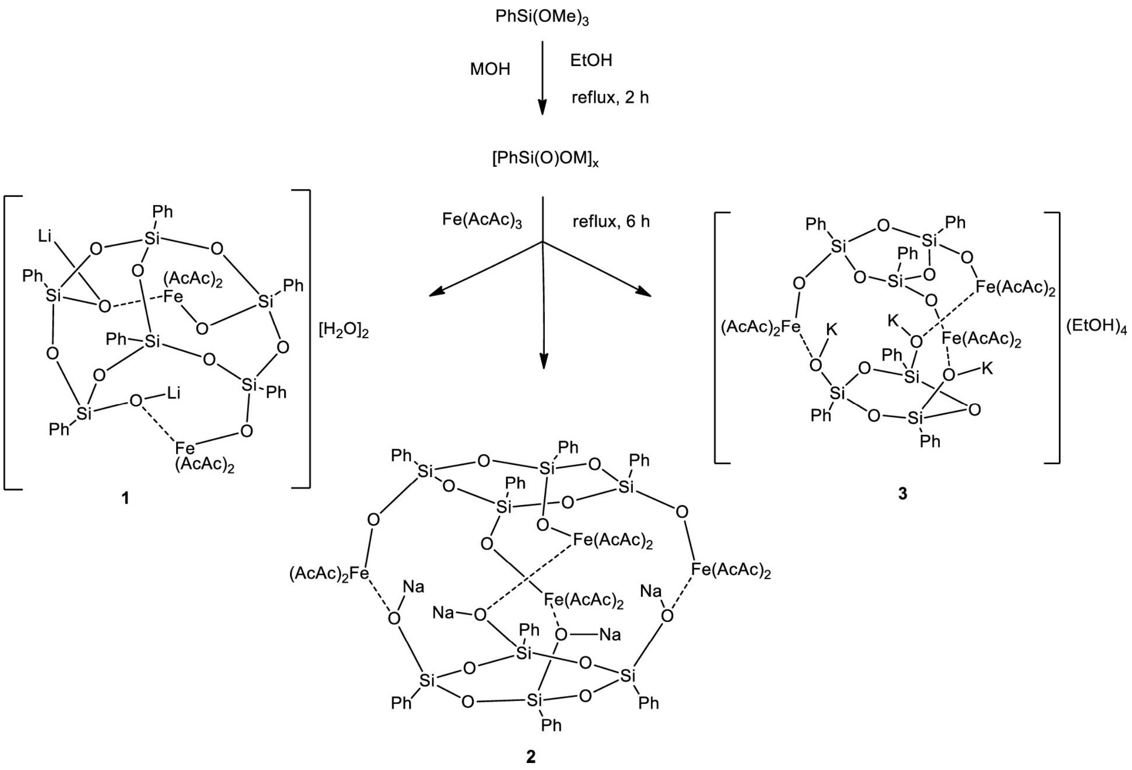

Fig. 16. Fe(III) coordination entities with phenylsilsesquioxnes. Reprinted from [26]

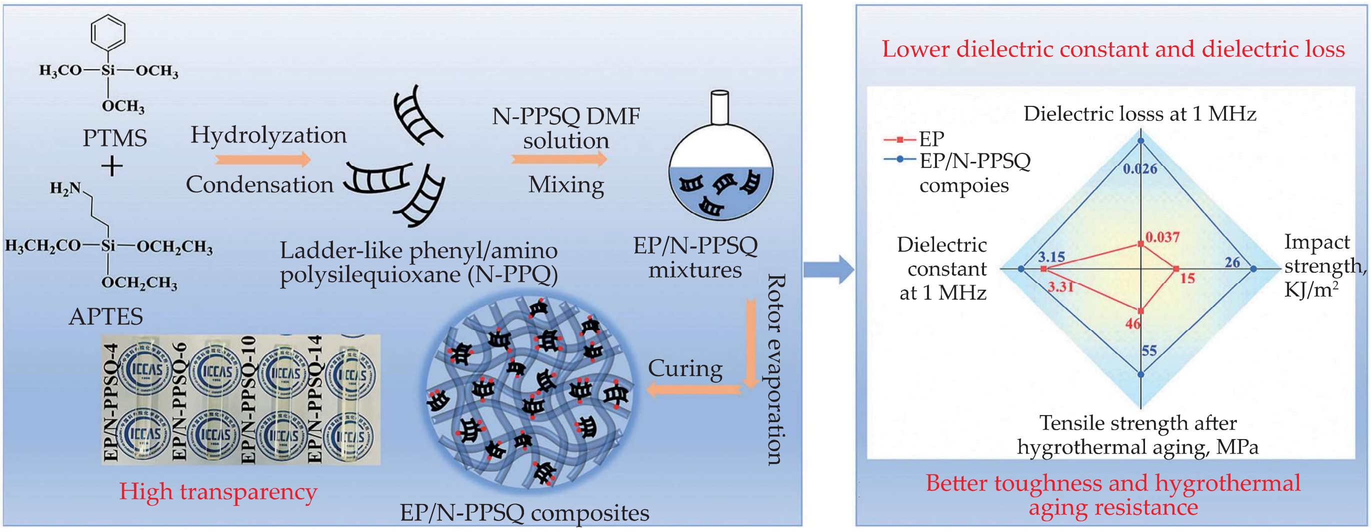

Fig. 17. Preparation and properties of ladder silsesquioxanes composites. Reprinted from [29]

The research on metallasilsesquioxanes is intensively carried out by A. N. Bilyachenko group [25]. Recently, Fe(III)-based phenylsilsesquioxane/acetylacetonate coordination entities (Fig. 16) were found to present high activity in the oxidation of inert alkanes with peroxides (55% yield) and in the cycloaddition of CO_2 with epoxides (58–96%) [26].

Similarly, hexa-copper phenylsilsesquioxane/acetate coordination entities were described as catalysts in the oxidation of alkanes, though with a rather limited yield of 30% [27]. While the three new luminescent cage-like lanthanide silsesquioxanes (Tb^{3+}, Tb^{3+}/Eu^{3+} and Gd^{3+}) are expected to be efficient optical temperature sensors [28].

Recently novel composites of epoxy resins with ladder-like polysilsesquioxane containing phenyl and amino groups (N-PPSQ) *via* a facile co-condensation process for EP modification were described. Such a system offers excellent mechanical and dielectric properties. The detailed effects of N-PPSQ incorporation on the mechanical, dielectric, hydrothermal aging, and optical properties of EP substrate were thoroughly investigated (Fig. 17) [29].

A novel structure *via* facile synthesis of POSS-stoppered rotaxanes were presented. They exhibited stability in the solution at elevated temperature and under acidic conditions that can lead to their potential application in the

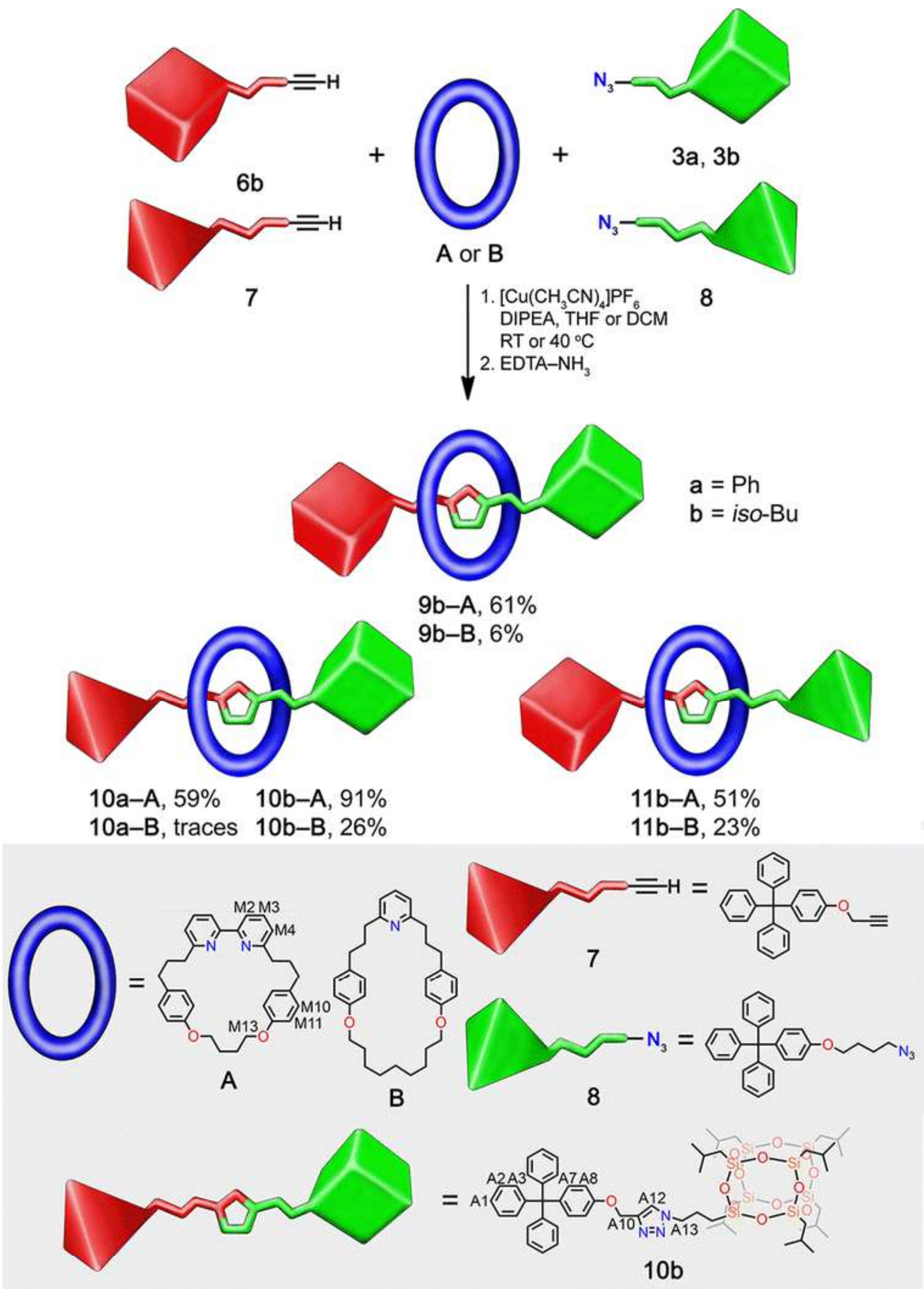

Fig. 18. The CuAAC active-template approach exploited to construct rotaxanes incorporating cage-like silsesquioxane stoppers. A- bipyridine, B- pyri-dineincorporating macrocycles 3a/b/8; azide functionalised stoppers; 6b/7 alkyne functionalised stoppers. Reprinted from [30]

formation of MIMs (mechanically interlocked materials) and catalysis (Fig. 18) [30].

POSS COMPOSITES IN GENERAL HEALTHCARE

The application of silsequioxanes in dentistry is probably the oldest area of research going back to the beginning of the 21-st century [31]. It is also being continued recently, concentrating on preparing novel dental composites with improved mechanical properties and lowered shrinkage on polymerisation. Composites of hydroxyapatite (HA) with heptaisobutyltri(methacryloxypropyl)dimethylsiloxy)heptasilsesquioxane (HIB-Met) as a filler modifying the surface of HA that might also

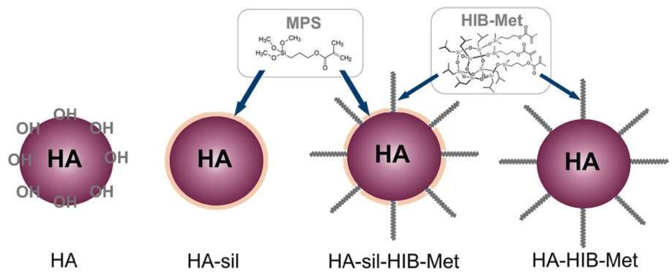

Fig. 19. Preparation scheme of the composites. Reprinted from [32]

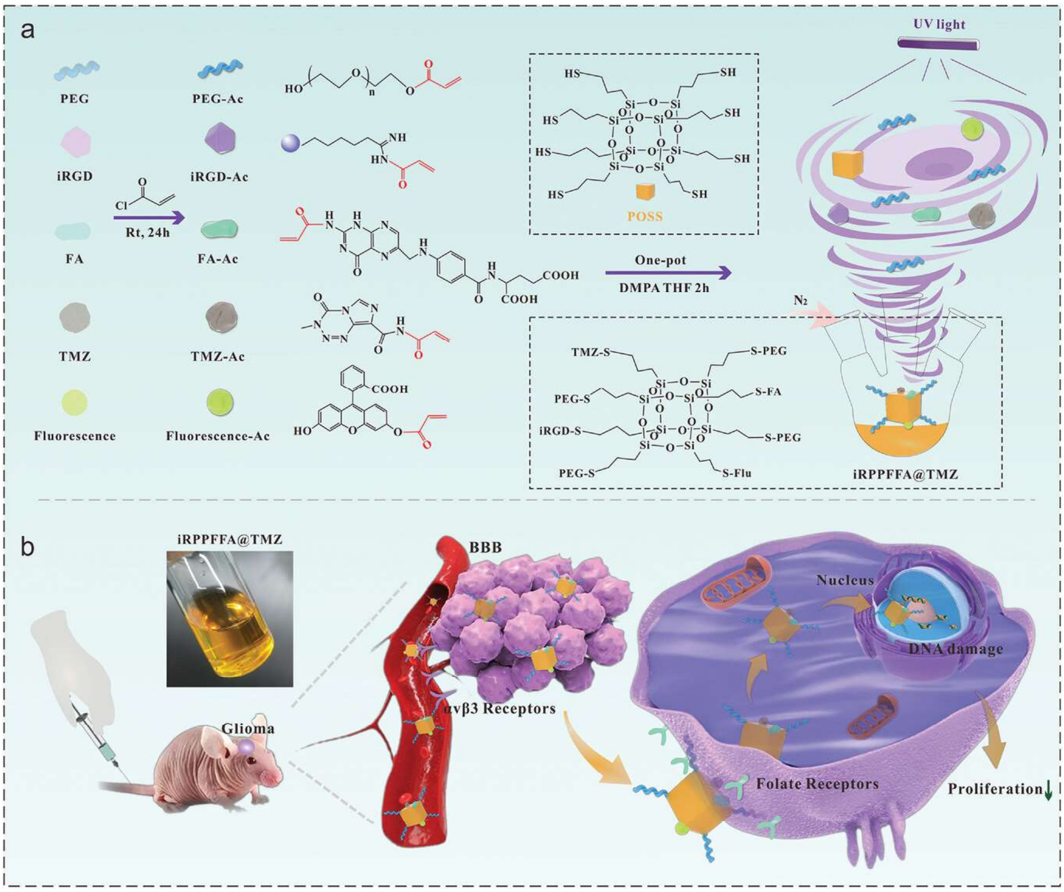

Fig. 20. Schematic preparation of POSS modified nanoparticles and mechanism of orthotopic GBM chemotherapy. Reprinted from [36]

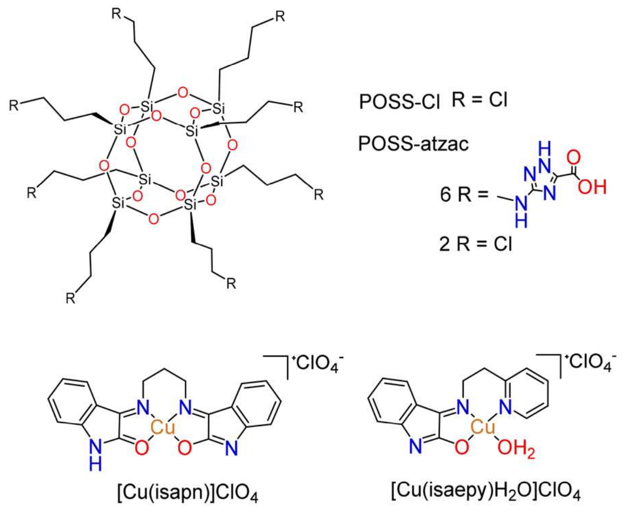

Fig. 21. Structure of modified POSS nano-carrier and copper drugs. Reprinted from [37]

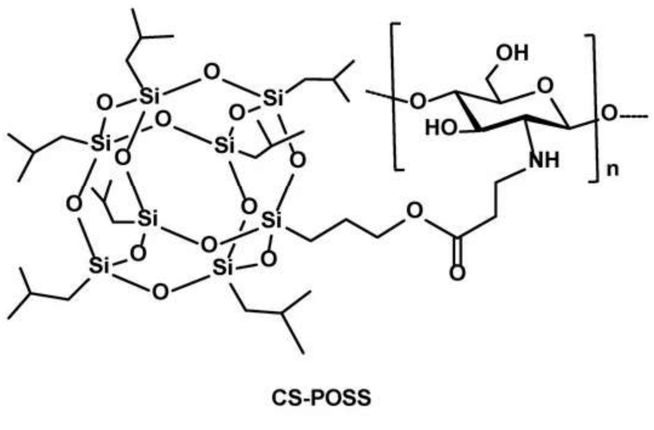

Fig. 22. Structure of chitosan-POSS hybrid. Reprinted from [38]

be silanized with methacryloxypropyltrimethoxysilane (MPS) before mixing with the filler. (Fig. 19) [32].

It was found that hydrophobization of the HA surface by HIB-Met resulted in enhanced mass stability of the obtained composites on incubation in aqueous environments. Surface modification of quartz fibres for restorative dentistry composites with methacrylate-POSS has also been recently reported [33]. Such a system has proven to exhibit improved physic-mechanical properties with stronger interfacial bonding of dental composites.

A T_8-type POSS structure is considered an ideal drug carrier in which physical and chemical properties can be adjusted by functionalisation of R substituents. The most often synthesised conjugates are equipped with e.g., $(CH_2)_3SH$- moieties "POSS(SH)" [34] or so-called "POSS(OH)$_{32}$" [35]. Thus, POSS(SH) was modified with

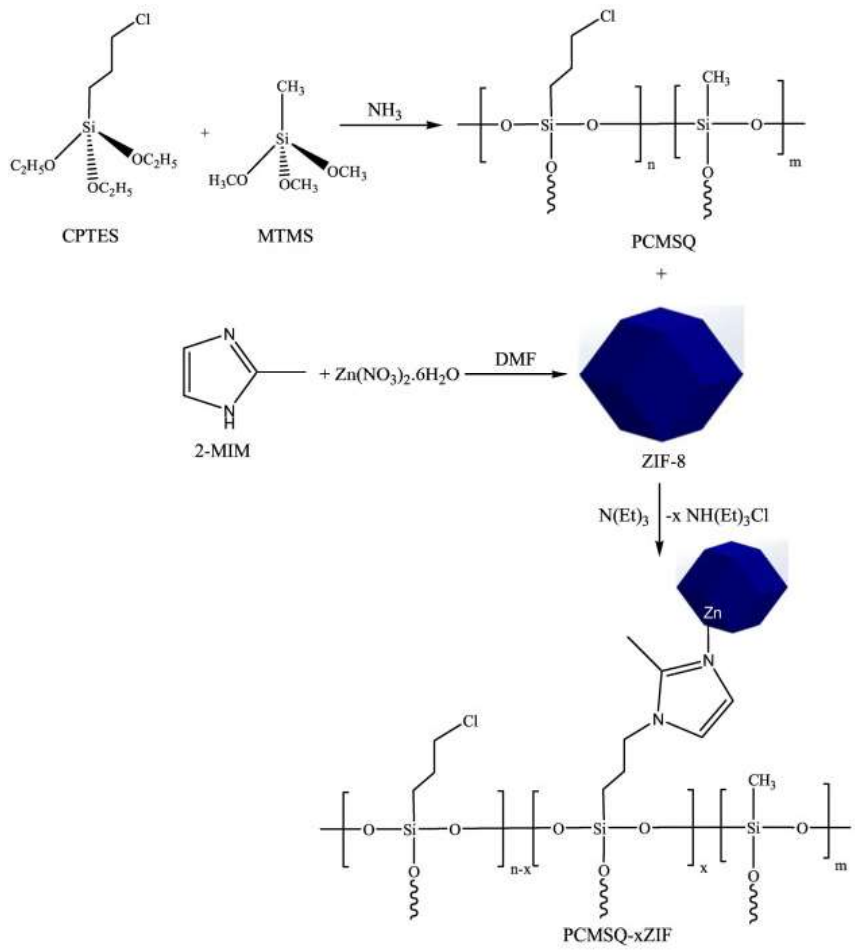

Fig. 23. Synthesis of PCMSQ-xZIF (x = 0.05 and 0.1). Reprinted from [41]

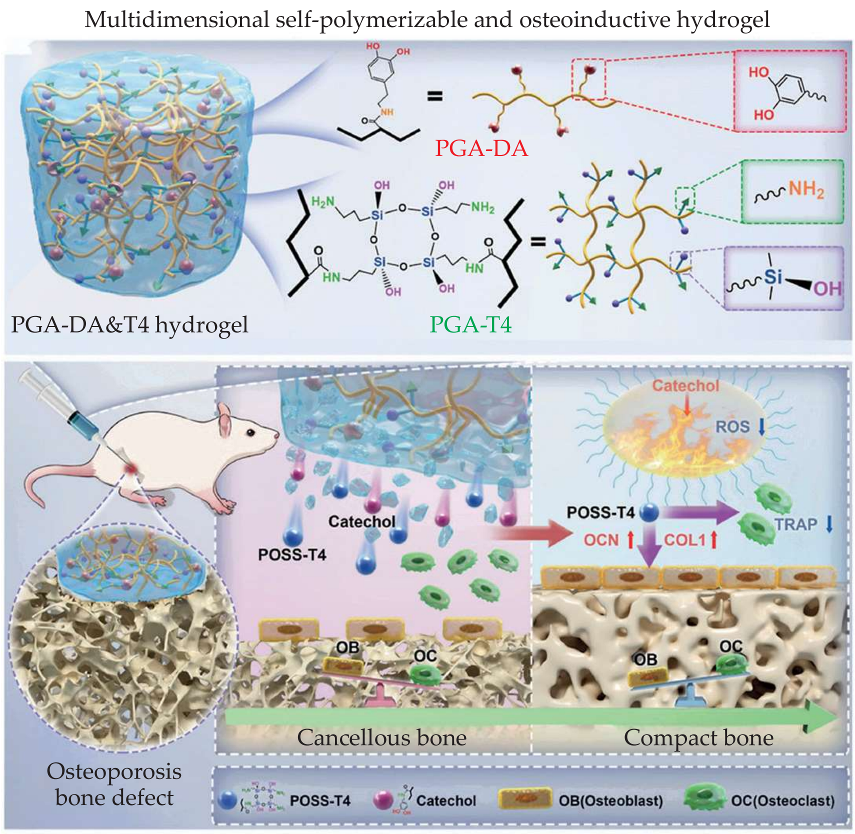

Fig. 24. Preparation and activity of the hybrid of poly(γ-glutamic acid)/dopamine/hydrophilic sisesquioxane. Reprinted from [42]

gold (sized less than 100 nm) nanoparticles crosslinking POSS *via* thiol linkage. Such the material was found biocompatible with two cell lines (C2C12 and L929) and, in the authors' opinion, can be used as a drug delivery vehicle in cancer therapy [34]. POSS(SH)-based multifunctional nanoparticles were prepared *via* photoinitiated one pot method (Fig. 20). Such the drug delivery platform for temozolomide (TMZ) and cyclic peptide CCGRDKGPDC (iRGD) was found to be effective in BBB penetration and showed high tumour killing-effects inhibiting glioblastoma (GBM) cells in mice [36].

A novel anticancer drug delivery system was described using hexa-triazole-substituted POSS (Fig. 21) as a nanocarrier for copper(II) metallodrugs against melanoma cell lines SK-MEL-147 and SK-MEL-05. Such systems have proven to exhibit increased cytotoxicity and better selectivity. IC_{50} decreased from >100 to 0.66 μM for $[Cu(isapn)]^+$ (isapn= *N*,*N'*[bis-(3,3'-indolin-2-one)]-1,3-diiminopropane) and the relevant decrease for $[Cu(isaepy)]^+$ (isaepy=N-[*bis*-(3-indolin-2-one)]-2-iminoethylpyridine) was from 38 to 1.76 μM against SK-MEL-147 melanoma cells. While *in vivo* studies have shown that total DNA fragmentation was reached at concentration of 25 μM/mL for both copper systems [37].

Chitosan-POSS hybrid nanomaterials were synthesised, using acryloxypropylheptaisobutyl-POSS *via* Michael addition reaction [38].

Such conjugates were evaluated for potential antibacterial effects in healthcare-associated infections. It was found that apart from physical, chemical, and rheological properties, drug release and biocompatibility make such hydrogels promising materials in the fabrication of medical and surgical devices [39]. A related research was devoted to the preparation of highly porous foams and biological response to systems made of poly-methyl-siloxane and polymethyl-phenyl-silsesquioxane *via* a ceramic route with such fillers as Na_2O, CaO, and P_2O_5 [40].

The foam composites of poly-chloropropylmethylsilsesquioxane (PCMSQ) equipped with zeolite imidazolate framework (ZIF-8) were prepared and analysed for their loading capacity of acyclovir, and tetracycline. They have shown strong antibacterial effect towards *S. Aureus* and *E. Coli* [41].

An organic/inorganic hybrid material composed of poly(γ-glutamic acid), hydrophilic silsesquioxane and dopamine was developed as a promising hydrogel for osteoporotic bone regeneration (Fig. 24). It presents highly elastic and superior mechanical properties as well as strong osteoblastic bioactivity. Thus, it shows important potential in the area of osteoporosis therapy [42].

3D-printed polylactic acid/polymethyl silsesquioxane scaffold was developed and coated with ethylcellulose/vitamin E microparticles using the electrospray method. MTT test performed with fibroblast cells proved the biocompatibility of the scaffold. Being non-toxic it may have good potential as a wound dressing material [43].

CONCLUSIONS

In this brief review, we have highlighted the very recent progress in the research on the applied side of organic-inorganic hybrid systems – polyhedral oligomeric silsesquioxanes (POSS). A wide spectrum of potential applications includes dentistry, drug nanocarriers, catalytic systems and water purification. This is due to the extraordinary properties of these nanomaterials, which are rigid, non-toxic, and thermally stable. Most of the reviews do not focus on the synthesis and structures, while it seems important to show the interested potential reader what features are generated by tuning the organic outer sphere of POSS, leading to the development of valuable properties.

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Authors contribution

K.P. – conceptualization, writing-original draft, writing-review and editing; J.K. – writing-original draft, writing-review and editing; W.A.S. – conceptualization, supervision, writing-original draft, writing-review and editing, visualization.

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Conflict of interest

The authors declare no conflict of interest.

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