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REVIEW

Permethylated Silicon: A Structural Motif with a Critical Role in Shaping the Properties of Organic–Inorganic Compounds

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Abstract

The distinctive features of Si–O and Si–C bonds make the integration of silicon-organic moieties into organic structures significantly influence the architecture and properties of the resulting hybrid materials often confering conformational flexibility, hydrophobicity, surface activity, self-assembly capacity and dual character (amorphous–crystalline, flexible–rigid, mesomorphic). As a result, silicon-based structural units show considerable potential in the design of functional compounds and materials, relevant for fields such as sensor technology, optoelectronics, catalysis, energy storage and even biomedical applications. In the context of recent advances in the synthesis and functionalization of organosilicon compounds, widely reported in the specialized literature, a series of derivatives have been obtained by chemical coupling of siloxane or silane (as a bridge or tail) moieties with triazole, thiadiazole and other functionalized aromatic moieties. Some of these compounds, but also simpler α,ω-bifunctional disiloxanes, have been investigated as ligands for metal ions, leading to the formation of coordination compounds with different dimensionalities (from 0D to 3D), which can outline a distinct class in coordination chemistry. In this paper, such recently obtained representative organosilicon compounds and their metal-containing derivatives are reviewed, highlighting their defining structural and behavioral features. Although the silicon-based moiety is often perceived as chemically inert in these systems, it plays an essential role in controlling the structural and functional properties of the resulting assemblies.

Keywords Organic-inorganic Compounds · Organosilicons · Siloxane Bond · Coordination Compounds · Polymers · Dual State

1 Introduction

Despite the limited interest aroused in the scientific community by the initial discovery of organosilicon compounds, continued research has revealed their remarkable properties and versatility. In response to the challenges of emerging technologies, rapid advances in silicon chemistry have led to the creation of materials that meet stringent requirements in various fields, from computer science to aerospace, significantly influencing technological progress throughout the 20th and early 21st centuries [1]. A special place among silicon-containing compounds is occupied by organosiloxane derivatives, due to the unique properties arising from the electronic structure of the siloxane bond and organic groups attached to silicon atoms. In fact, systematic research on silicon-based compounds began with the development of polymer chemistry, when polydimethylsiloxanes (PDMS) were first synthesized. They are formed by alternating dimethylated silicon and oxygen atoms in chains of different lengths, with Si–OH or $Si(CH_3)_3$ groups at the ends. In a disiloxane bond, as in hexamethyldisiloxane, for example (Fig. 1), a pair of non-participating electrons from the oxygen enters into conjugation with the *d* orbitals of the silicon, on one side of the molecule, while the other pair will also enter into conjugation with the Si–C antibonding orbital, σ*Si–C, leading to a decrease in the interatomic distance, which gives the greatest stability to these bonds [2–7]. The longer Si–C bond (1.87–1.90 Å) confers flexibility to the attached organic groups, which can rotate almost freely creating a

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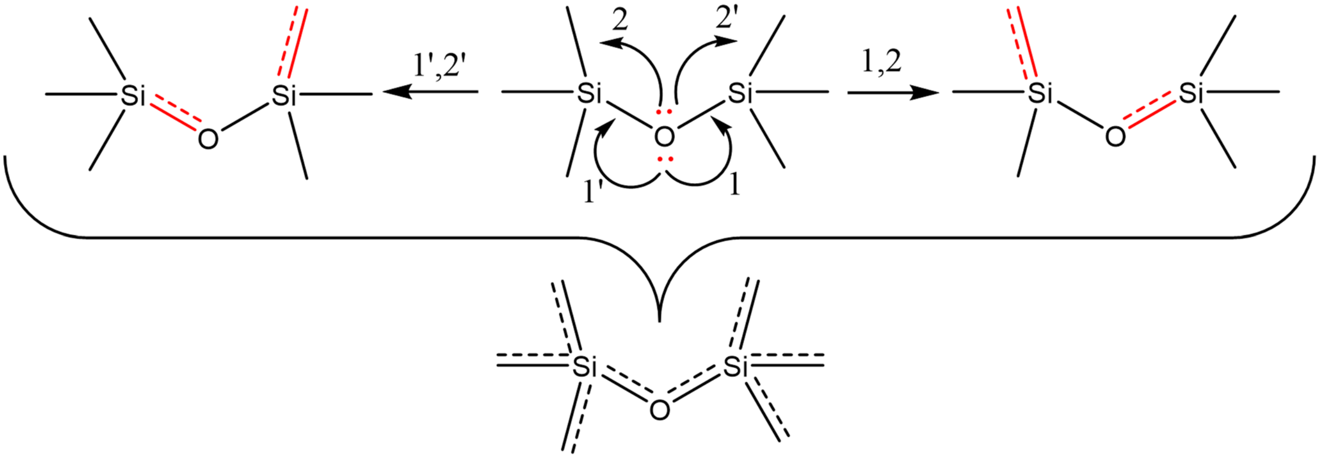

Fig. 1 Electron distribution in the siloxane bond illustrated for hexamethyldisiloxane [7]

hydrophobic shield around the silicon backbone, reducing polar interactions and conferring unique properties such as low viscosity and surface energy, high gas permeability and lipophilicity, tendencies potentiated by strongly nonpolar methyl groups as in the case of PDMS [8]. All of these make PDMS among the most studied and used inorganic polymers, being the basis of most technical silicone products including oils, greases, coatings, resins, elastomers.

The wide variety of functional groups that can be attached and the reaction conditions supported by silicon allow for a wide range of compounds and properties to be obtained [9–11]. Silicon is also found in a wide range of low molecular weight organosilicon compounds (reagents, proligands, surfactants, coatings, etc.) but also in coordination compounds, although much less often. The introduction of a silicon atom into an organic compound can significantly modify the physicochemical properties [11, 12], such as lipophilicity and metabolic processes. This has led to the concept of isosteric carbon-silicon exchange, known as the "carbon-silicon switch", with unusual effects leading to the discovery of new functional molecules including the emergence of sila-drugs with modified pharmacological properties [13–16].

Coordination chemistry of silicon has attracted significant attention due to its diverse properties and potential applications in fields such as supramolecular chemistry, catalysis, medicinal chemistry, and materials technology. A wide range of sophisticated coordination complexes of silicon with low-valent silicon in silylene or disilene have been developed [17], as well as hypervalent (penta-/hexa-coordinate) forms [18–25]. New synthetic methodologies, structural elucidations, bond analyses, and potential applications in catalysis and chemical transformations have been explored [26]. The evolution of X-type silyl ligands coordinated to transition metals, featuring unique sigma-donating abilities of interest for catalysis, has been recently reviewed [27]. In contrast to the simple arylsiloxides and siloxides containing bulky substituents discussed previously [28–33], coordination compounds of the siloxane group also deserve attention. However, due to the negative hyperconjugation of the type $n_o \rightarrow \sigma_{Si-C}$, Si–O–Si exhibits low basicity [6], under these conditions oxygen requires highly electrophilic Lewis acids, such as BF_3 and BCl_3 [34], or perfluorinated aluminates [2]. Substitution with electron-donating groups increases the probability of dative bond formation but may lead to hydrolytic instability. Although progress has been made in activating the siloxane bond to improve coordination capacity, serious limitations still exist [2, 35].

2 Multifunctional Proligands Containing Passive Silane/Siloxane Units

A strategy to benefit from the behavioral peculiarities that the siloxane bond can induce through its unique electronic structure (resonance character [35], covalent-ionic and partially double bond, and implicitly the variable bond angle, depending on the nature of the substituents on the silicon atoms, would be to incorporate it as a chemically passive fragment in the structure of compounds bearing common coordination groups (-COOH, –CN, –C =N–, $–NH_2$, -pyridyl, etc.). This approach, although apparently simple, is quite original, with relatively few reports in the literature [28, 36] (Fig. 2). Studies by other authors [37–39] have shown, for example, that the longer Si–C bond length in a Si-centered tetrahedral ligand uniquely influences the structure of the resulting metal–organic frameworks (MOFs) (Fig. 2a). Thus, in the case of tetrakis-4-carboxyphenylsilane [38], it was found that the coordination efficiency increases, increasing the nuclearity compared to the carbon-centered analogue, while in the case of tetrakis(4-tetrazolylphenyl) methane [40] (Fig. 2b) it was found that the orientation of the

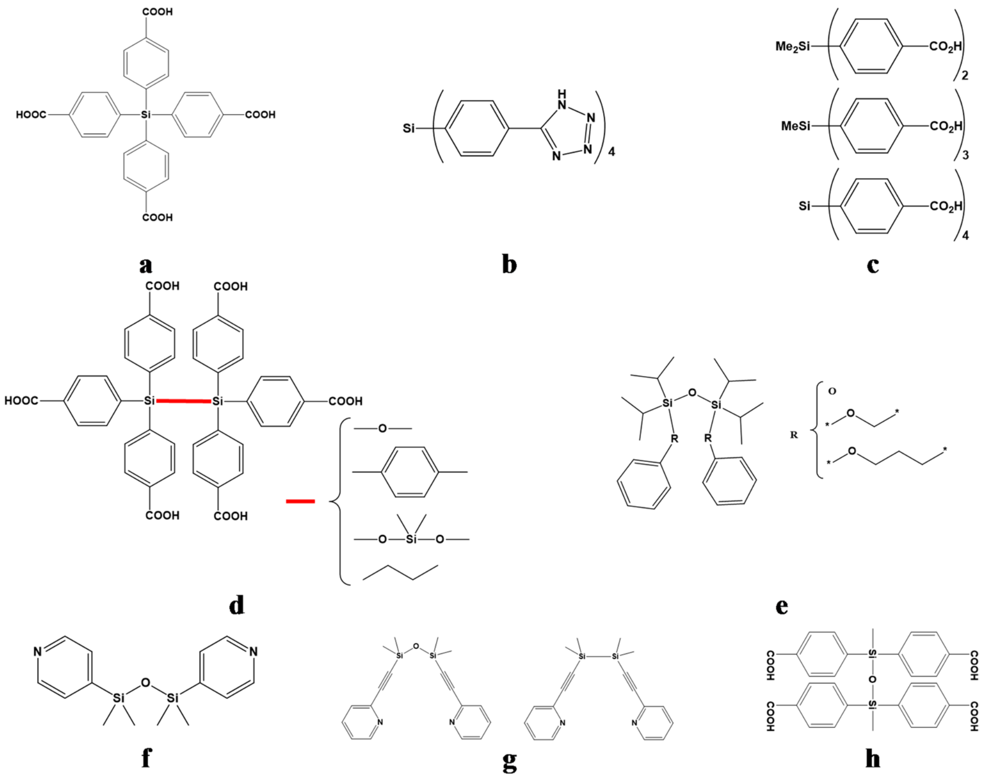

Fig. 2 Examples of organic-inorganic compounds containing silane/siloxane units: **a** [37–39]; **b** [40]; **c** [41]; **d** [39, 41–44]; **e** [28]; **f** [45]; **g** [46]; **h** [47]

metal-based nodes is affected, leading to an increase in the unit cell volume and the free space accessible to the solvent. In addition, tetrahedral centers have a greater potential to generate new three-dimensional (3D) structural motifs compared to a planar connector, and the use of silicon instead of carbon presents several advantages, including a simple synthesis of the connector [41] (Fig. 2c). More recently, a series of metal-organic networks of "light metal" (Li^+ and Na^+) were reported to have been prepared using silicon-centered connectors of the type $Me_xSi(p\text{-}C_6H_4CO_2H)_{4-x}$ (x = 2, 1, 0) (Fig. 2c) [41]. In 2017, White's group reported the first connected 3D MOF structure incorporating a disiloxane-based linker, namely a disiloxane hexacarboxylic acid [42]. Expanding the range of MOFs with this ligand has led to unique topologies [42]. Extended versions of it by inserting ethylene [39], phenylene [43] or dimethylsiloxane [44] units are considered of interest for the synthesis of MOFs with significantly lower metal loadings than their isoreticular analogues, which could lead to materials with higher gravimetric storage capacities [43]. In addition, in the case of the trisiloxane linker, due to its high flexibility, it could adjust its backbone geometry so as to expand or contract to optimize binding to metal nodes in MOFs or lead to dynamic MOFs that can "breathe" [44] (Fig. 2d).

Another type of reported siloxane-spaced ligands consists of alkylpyridine units attached telechelically via silylether bonds to the tetra(*iso*-propyl)disiloxane unit. This type of ligand is capable of forming a variety of coordination structures with metals, depending on the anion used, but which have been shown to be non-porous [28] (Fig. 2e). 1,3-Bis(pyridyl)tetramethyldisiloxane (Fig. 2f) [45] or bis(pyridylethynyl) spaced with tetramethyldisiloxane or tetramethylsilane (Fig. 2g) [46] have also been prepared and used as ligands, especially for silver, and interesting structural aspects have been observed. However, the effect of the presence of the silicon-containing moiety in the coordination compounds on their properties is very little addressed, the relevant being the claim of hydrophobicity and water stability of MOFs formed with a tetracarboxylic acid with a methyl-substituted siloxane core (Fig. 2h) [47].

The relatively poor bibliographic representation could be attributed to the difficulties of synthesis when harsh conditions are required (i.e., strong ionic environments) and characterization (high flexibility could prevent the assembly and stabilization of the compounds into highly ordered structures suitable for analysis) or the occurrence of phase separation due to the polarity difference. However, the effects obtained and the application prospects of these compounds would justify efforts to overcome these obstacles.

In addition to the flexibility, offered to the electron-donating groups in adopting coordination geometries, the contrasting coexistence of flexible, hydrophobic siloxane moieties with the polar, rigid coordination blocks, can induce significant differences in properties, compared to fully silicone or fully organic analogues. Such derivatives generally exhibit dual characteristics or properties that lie on the border between those of their respective classes, including: flexible versus rigid, amorphous versus crystalline, hydrophobic versus hydrophilic, light emissive versus non-emissive, depending on the degree of aggregation, and temperature-dependent dielectric permittivity. The calculated values in some cases [48] of the hydrophilic-hydrophobic balance based on the well-determined structures of these compounds indicate a more or less amphiphilic character, at the boundary between watering and spreading agents and oil/water emulsifiers. This gives them surface activity and self-assembly capacity, as evidenced by spectral analysis (UV-Vis and fluorescence), tensiometry, nanoparticle tracking (NTA), dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) analyses [48–51], and which is the basis of specific morphological, thermal, optical and electrical characteristics. The attachment of a silane fragment, most often di- or triorganosilane, as a spacer or tail, to a coordination structure, due to the peculiarities of the Si-C bond mentioned above, also allows for greater conformational flexibility, and implicitly changes in behavior and properties. A representative example is the trimethylsilyl tail, which, through hydrophobicity, bulk, flexibility and electronic structure, increases hydrolytic stability and lipophilicity and influences the geometry, reactivity and electronic properties of the metal complexes. The introduction of the σSi-Si bond into π-conjugated compounds extends the conjugated system through the σ-π interaction [52].

Recent advances in the synthesis and functionalization of organosilicon scaffolds, through the formation of silicon-carbon, silicon-oxygen, or silicon-nitrogen bonds and the modification of their organic groups, considerably expand the range of applications, including in the coordination of metals in multifunctional architectures. Classical reactions from silicon chemistry, such as silylation and hydrosilylation, along with reactions known from organic chemistry, e.g., addition, substitution or elimination reactions, have been adapted and optimized for the development of new organosilicons. Among these, the following recent approaches can be mentioned: the use of copper catalysts in the synthesis of organosilicon compounds by substitution and addition reactions to imines, aldehydes, or C = C double bonds [53]; direct difunctionalization of unsaturated hydrocarbons with organosilicon reagents, for the formation of carbon-silicon/carbon-carbon or carbon-silicon/carbon-heteroatom bonds in a single step [54]; selective functionalization of the C–H bond in the beta position to silicon, by aminoalkylation, alkylation and arylation of simple silanes [55]; radical silylation of alkenes and alkynes, cheap and readily available, with the participation of silyl radicals, providing a powerful tool for the direct construction of organosilicon compounds [56]; dehydrogenative silylation of ubiquitous inactive C–H bonds catalyzed by Ni(0) dispersed in CeO_2 - an eco-friendly synthetic protocol for useful organosilicon compounds [57]; regio- and enantioselective Heck-type silylation of alkenes not activated with hydrosilanes, catalyzed by cobalt [58]; multicomponent cross-coupling of alkenes with silicon reagents to produce complex silicon-containing compounds from highly accessible chemicals [59]; nickel-catalyzed radical cross-coupling of vinylsiloxanes with pyridinium salts (a version of Hiyama coupling), which provides efficient access to (E), (Z), and (1,1')-alkenes with selectivity control, under mild conditions [60]; mild catalytic protocol for the preparation of stereogenic organosilanes by enantioselective intramolecular hydrosilylation catalyzed by Rh complex [61]; intramolecular hydrosilylation of alkenes or alkynes for their functionalization and easy access to silylated heterocycles [62]; metal-free, light-driven hydrosilylation reaction catalyzed by the synergistic effect of the organic photooxidation catalyst 2,4,6-tris(diphenylamino)−5-fluoroisophthalonitrile and the base N, N'-diisopropylethylamine [63]; asymmetric catalytic hydrosilylation of prochiral dihydrosilanes with internal diarylalkynes to obtain stereogenic hydrosilanes [64]; hydrosilylation catalyzed by transition metals instead of precious metal complexes, for the production of organosilanes, which have an essential role in organic chemistry and materials science [65]; thermal and photochemical reactions of organosilicon compounds approached through theoretical and experimental studies [66]; amine-catalyzed thiol-isocyanate click reaction allowing the obtaining of silanes with different functional groups [67]. In this context, some recent own results obtained in the direction of organosilicon derivatization, mainly at the organic groups, and in highlighting the potential that this structural motif has for inducing new, useful properties are presented below.

2.1 Organosilicon - Heterocycle Coupling Derivatives

Chemical coupling of flexible and hydrophobic silicon-based motifs with heterocycles such as triazoles or thiadiazoles, thioalkylation being a facile method for this, leads to structures with interesting properties. Combining 1,2,4-triazoles with a silicon derivative in the same molecule (Fig. 3a) appears to be a promising strategy for significantly improving their already well-known biological activity, especially in relation to the polarity of the environment (Fig. 3b). This also confers a certain degree of selectivity for metal ions, suggesting their potential as chemosensors for metal detection. The calculated binding energies for the metal M (Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}) coordinated through unsubstituted ligand molecules spaced by dimethylsilane, with binding energies values shown in Fig. 3c, indicate that Cu(II) chelation is the most favorable, consistent with the

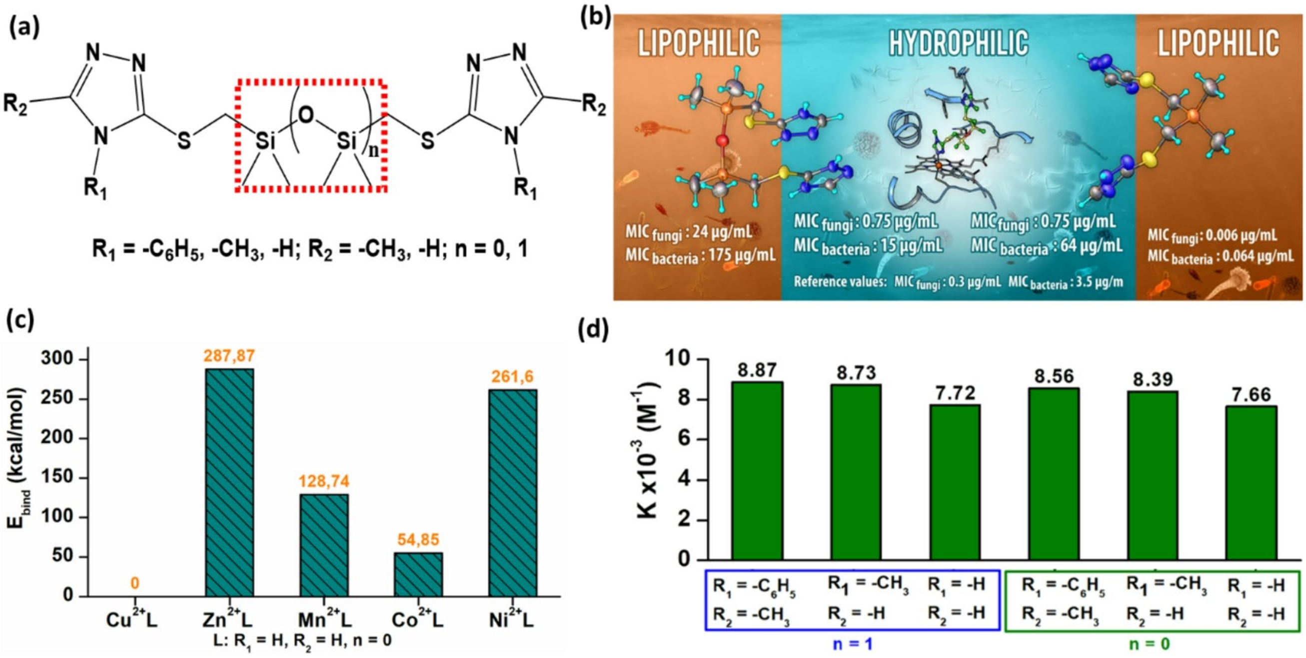

Fig. 3 Structures of silicon-triazole derivatives (**a**); antimicrobial activity values in media with different polarities (**b**); binding energies of M-L complexes (L-structure in Figure a with $R_1 = R_2 =$ H, $n = 0$, M = Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}) (**c**); binding constant values, K, for 1:1 complex formation of the triazole derivatives with Cu^{2+} in methanol solution at 25 ºC (**d**) [49]. Adapted from ref [49]., with permission from Elsevier, © 2019.

experimental results. Studies have shown that the synthesized bis-triazoles exhibit Cu^{2+} binding constants ranging from 7.66 $\times 10^3$ M^{-1} to 8.87 $\times 10^3$ M^{-1}, depending on the nature of the substituents on the triazole ring (Fig. 3d).

Compounds containing electron-donating groups, such as phenyl and methyl, enhance the complexing properties of the ligands, and siloxane derivatives consistently exhibit slightly higher binding constants than their silane counterparts, likely due to their greater conformational flexibility. Theoretical calculations results support the experimental results regarding metal binding capacity and biological activity, especially in the coordination of the ferric heme ion, as demonstrated in the case of 14α-Demethylase, chosen as a therapeutic target [49].

Another heterocycle, 1,3,4-thiadiazole, due to its electron-deficient nature and good electron-accepting capacity, exhibits notable optical, electronic, and chemical properties. Some of these intrinsic properties, determined by the electronic structure, are enhanced by its chemical association with silicon-based moieties. Attachment of 5-amino-2-mercapto-1,3,4-thiadiazole, for example, to a silicon derivative via S-alkylation, led to the formation of new amines that exhibit surface activity, self-assembly in solution, and aggregation-induced emission (AIE) phenomena, the latter - an optical phenomenon, in which certain molecules are weakly fluorescent (or completely non-fluorescent) in dilute solution, but become highly fluorescent when aggregated (Fig. 4). When these molecules are dispersed in dilute solution, their emission potentials are cancelled by internal motions (rotations, vibrations, etc.), which consume the energy absorbed through non-radiative pathways. When they aggregate, these motions are restricted, and the energy is released in the form of fluorescent light [68, 69].

The new resulted amines exhibit luminescence only when aggregated in solution or in the solid state, as their rigidity increases. Strong N−H•••N hydrogen bonds facilitate excited-state intramolecular proton transfer (pseudo-ESIPT), resulting in blue and green fluorescence, as well as near-infrared phosphorescence at room temperature. These compounds, which emit from higher-energy excited states, demonstrate light-harvesting capabilities within the UV−Vis−NIR spectrum. The large Stokes shift in this spectral range further enhances their potential for energy transfer of interest in photoactuators, for example. Flexible siloxane/silane spacers, which can adopt a highly twisted conformation, improve fluorescence efficiency compared to planar hydrocarbon spacers. By combining critical micelle concentration with fluorescence, photochemical processes can be effectively controlled at low levels of aggregation [70]. N and S heteroatoms with lone pairs of electrons provide active coordination sites for metal ions and hydrogen bond acceptors, forming extended supramolecular structures. Attachment of amino, mercapto, hydroxyl, phenyl, pyridyl or thiophene substituents can extend the use of thiadiazole in metal coordination chemistry. π-Conjugates systems and electron transfer between heteroatoms (N, S) and metals,

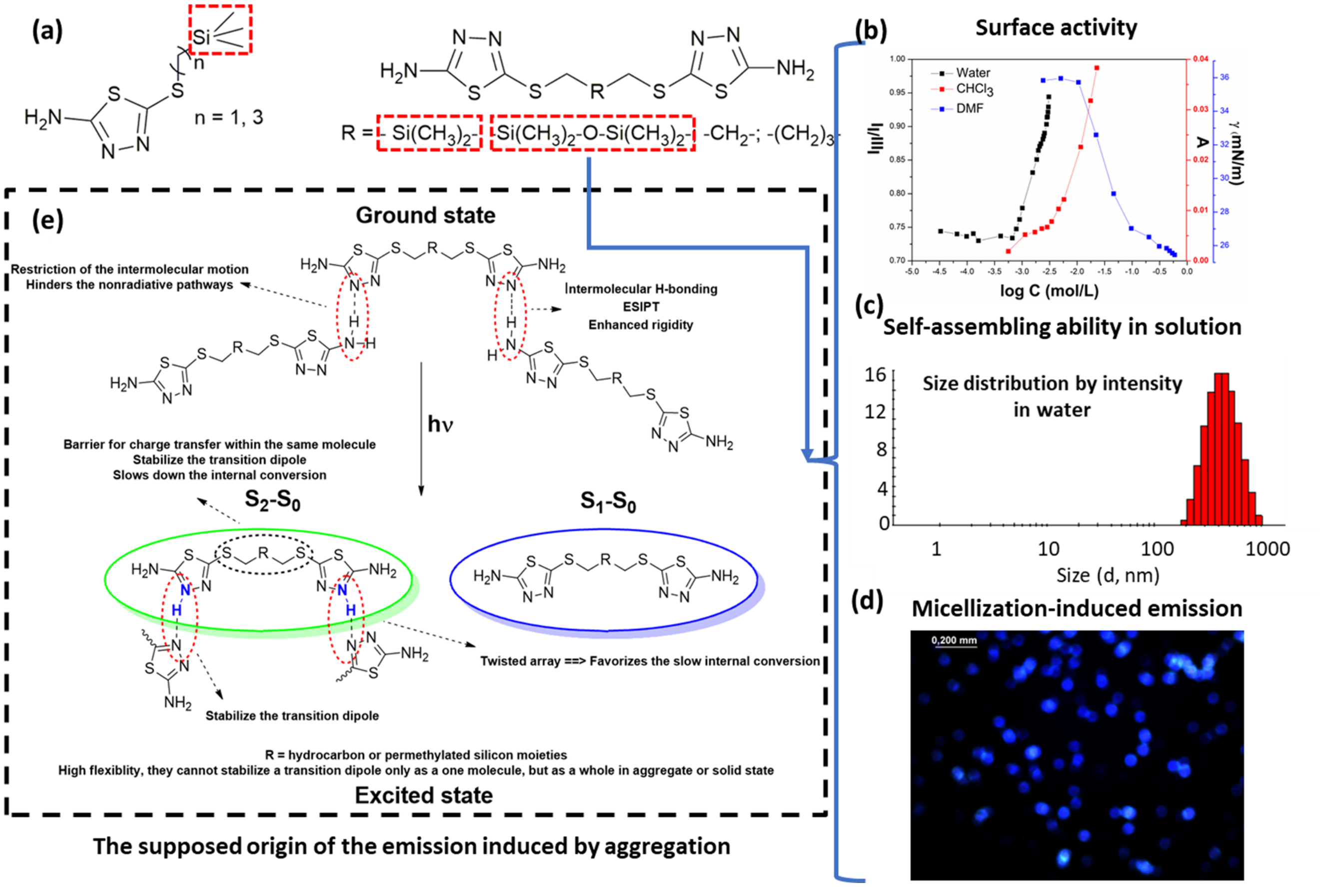

Fig. 4 Examples of 1,3,4-thiadiazole-containing organosilicon derivatives obtained (**a**); proofs of their behavior in solution: surface activity and aggregation (**b**, **c**), POM image with fluorescent micelles of the compound with R=$-Si(CH_3)_2-O-Si(CH_3)_2-$ in water (**d**), and the electronic processes supposed to be the basis of aggregated induced emission (**e**) [70]. Reprinted/adapted with permission from ref [70]. Copyright © 2023 American Chemical Society.

along with thermal stability, provide metal-organic frameworks containing thiadiazole motifs with potential applications in catalysis, luminescence, magnetism, nonlinear optics and electrical conductivity, sorption, ion exchange, etc [71]. In addition, the thiadiazole ring is a valuable pharmacophore, and its coupling with a lipophilic silicon moiety confers new properties.

2.2 Organosilicon – Substituted Aromatic Rings Coupling Derivatives

Further reaction of the above amines with 3,5-dibromosalicylaldehyde (Fig. 4a) leads to imines (Fig. 5a) exhibiting complex liquid crystal (LC) behavior, ranging from cholesteric, twisted, smectic boundaries to blue LC phases. Laterally located silane mobility units have been found to induce a greater decrease in phase transition temperatures than the siloxane spacer due to the geometric twist that produces more empty space. They exhibit characteristics such as supramolecular chirality, a concept in supramolecular chemistry that refers to the asymmetrical (chiral) organization of assemblies of molecules, even if the individual components are not necessarily chiral [72, 73]. In our case, the molecules do not contain a C or Si stereocenter, but they show chirality by breaking supramolecular symmetry. Supramolecular chirality occurs in the crystalline state, when the propyltrimethylsilyl tail is used, or in the LC state, regardless of the siloxane/silane moieties, as twisted, cholesteric, and blue boundary phases (Fig. 5b). Other features are the reentrant transitions, in which these molecules become more ordered upon thermal treatment and less ordered upon cooling (Fig. 5c, d). This is due to the strong dipolar heads (bromine) that favor electrostatic repulsions and strong nonpolar flexible moieties that promote attraction. Due to the weak intermolecular interactions of the latter, the most favorable phases at room temperature are the amorphous or LC states. Benefiting from their polar supramolecular structure, these molecules exhibit ferroelectricity of up to 2500 nC/cm^2 (Fig. 5e). Giant ferroelectricity arises from the same reason, as in the case of ferromagnetic ordering described previously [74].

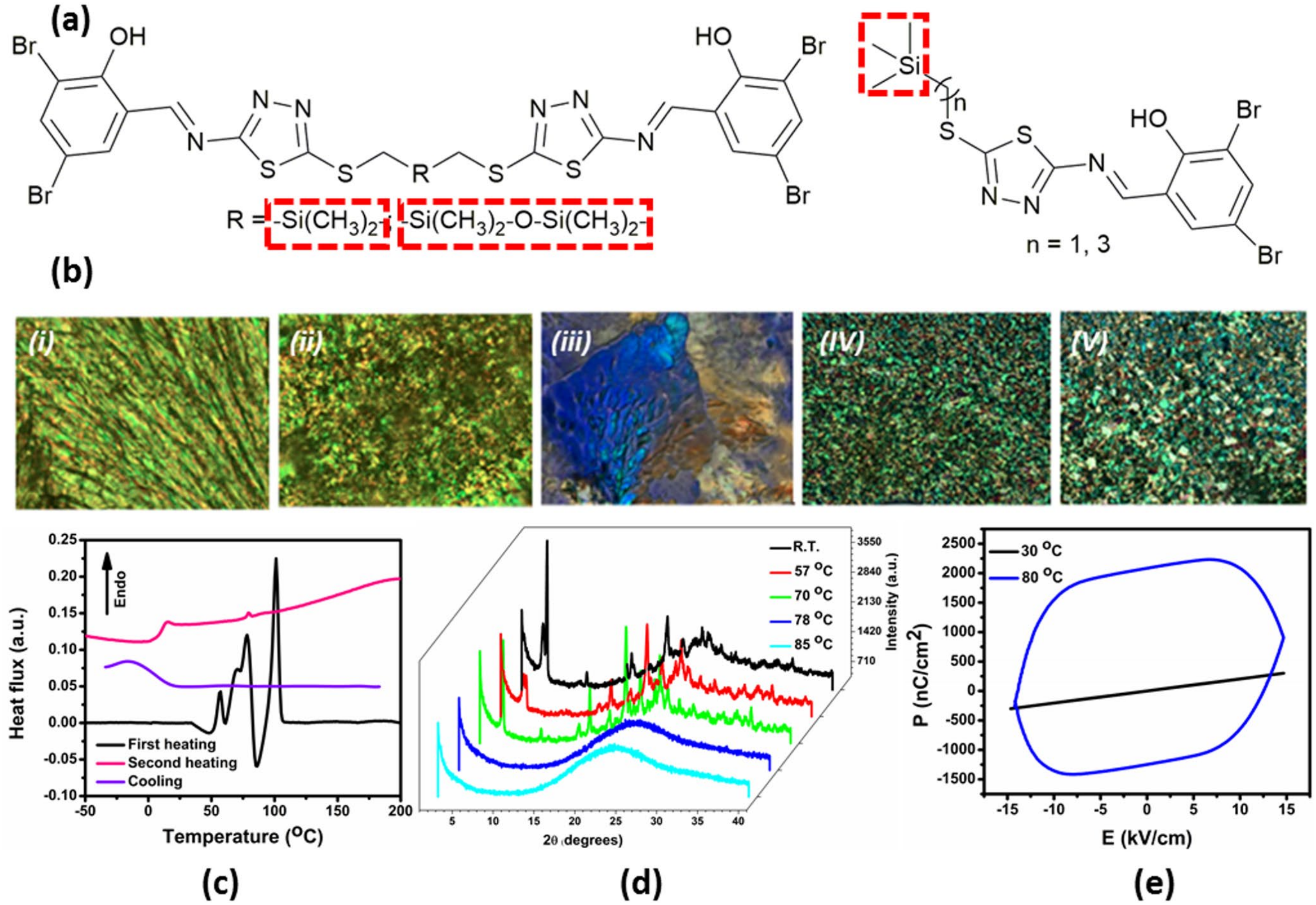

Fig. 5 Imines containing siloxane/silane fragments (**a**); Exemplified LCs mesophases for imine from Figure a with R =–Si(CH$_3$)$_2$: twist grain boundaries A (i) and C (ii), amorphous blue phase III (iii), cholesteric LCs (iv), and amorphous blue phase I (v) (**b**). Reentrant transitions highlighted through DSC and PXRD analyses (**c** and **d**). Ferroelectric LCs (**e**) highlighted through polarization-voltage loops [74]. Reprinted with permission from ref [74]. Copyright © 2023 American Chemical Society.

Salen-type Schiff bases, derived from highly flexible 1,3-bis(3-aminopropyl)tetramethyldisiloxane and salicylaldehyde derivatives (Fig. 6a), have been shown to exhibit surface activity and aggregation capacity in solution over critical micelle concentration (CMC) (Fig. 6b, c), attributed to the polarity difference between the organosilicon core and the azomethine arms. Critical micelle concentration values, ranging from 0.75 mol/L to 0.04 mol/L in DMF, were found for 3,5-dichloro and 3-hydroxy substituted derivatives of bis(salicylidene)aldimine, respectively [51]. These characteristics influence the kinetics and equilibrium of their synthesis reaction, resulting in slower processes (attributed to micellization of the organosilicon reagent), but higher yields (due to the isolation of imines in micelles as they form, which prevents the reversibility of the reaction), compared to those of forming fully organic counterparts. The metal binding capacity of these compounds is also higher compared to that of organic counterparts (i.e., those with C$_6$ or C$_{12}$ polymethylene spacers) [51] due to their flexibility and the possibility to surround the metal ion in an optimal geometry [75, 76].

Condensation with other carbonyl compounds, such as o-vanillin [77], pyrrole-2-carboxaldehyde [78], 3-formylsalicylic acid [79] or 2,6-diformyl-4-methylphenol [80], of 1,3-bis (3-aminopropyl)tetramethyldisiloxan [77–79] or trimethylsilyl *p*-aminobenzoate [81], has also been shown to be feasible, leading to interesting structures.

3 Coordination Compounds with Ligands Containing Passive Siloxane/Silane Fragments

3.1 Zero-Dimensional Coordination Compounds, 0D CCs

The metal (e.g., Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) complexes formed with the previous salen-type Schiff bases (Fig. 6a) are generally mononuclear, three-ring chelate type, one with 12

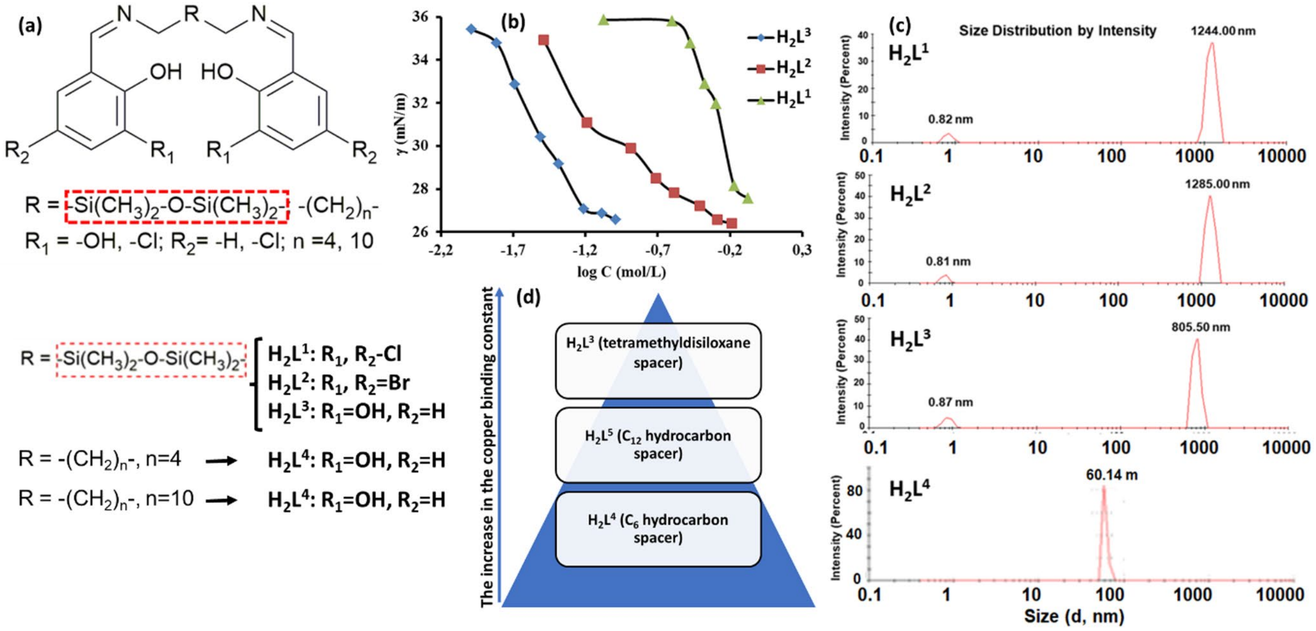

Fig. 6 Examples of salen-type Schiff bases obtained (**a**) and their micellization profile: surface tension-concentration dependence (**b**), and the dimensional distribution of the aggregates (**c**); variation of the copper binding constant in dependence on the nature and length of the salen spacer (**d**) [51]. Reprinted/adapted with permission from ref [51]., with permission from Elsevier, © 2020.

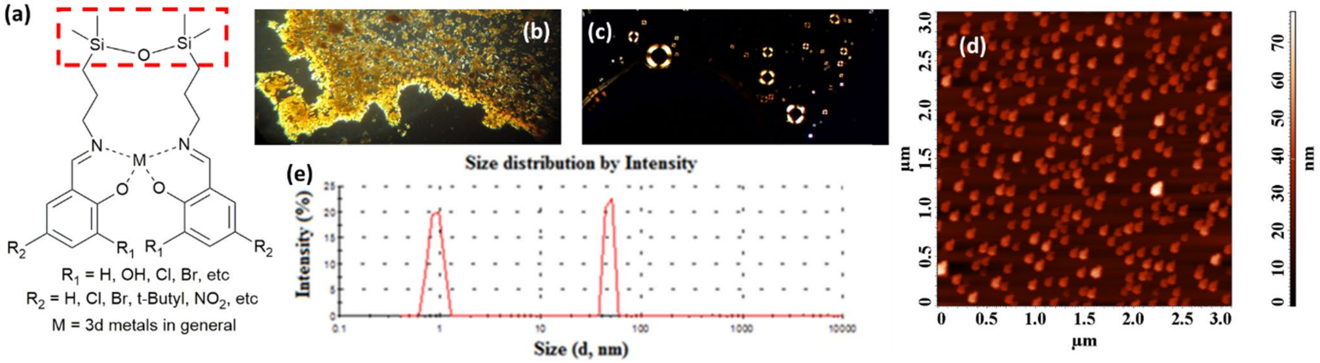

Fig. 7 General structure of coordination compounds with tetramethyldisiloxane-spaced salen-type Schiff bases (**a**); exemplification of the multiple phase states for the Cu complex with the Shiff base substituted with nitro groups, $C_{40}H_{66}CuN_2O_3Si_2$: crystalline (**b**) and nematic LC (**c**) shown by optical microscopy, self-assembly in DMF shown by DLS (**d**), preservation of aggregates by rapid evaporation of the solvent highlighted by AFM (**e**) [75, 76]. Reprinted/adapted with permission from Ref [76]., © 2021 Royal Society of Chemistry.

atoms and two with six atoms, the architecture dictated by length and flexibility of the spacer (Fig. 7a). The metal center is in a *trans*-N_2O_2 tetrahedral environment, with varying degrees of distortion, from slight to moderate. The values of the distortion parameter τ4 found for them vary between 0.14 and 0.84, while the value of the Si–O–Si angle is between 159–169°, depending on the metal ion and the substituents on the aromatic nucleus [82, 83]. But, as some research has already highlighted, there are wide possibilities for diversification by modifying the length and composition of the spacer, by controlling the reaction conditions, as well as by the nature of the carbonyl precursor, etc., which allow for obtaining more complex architecture. Thus, with derivatives of 2,6-diformyl-4-methylphenol, di- [80] or tetranuclear complexes [81] were obtained, while in the case of the 3-formylsalicylic acid derivative a hexanuclear complex was formed [79].

Like the siloxane-spaced ligands, the derived metal complexes have an amphiphilic character and can reduce the surface tension of a solvent, self-assembling in solution depending on the solvent polarity and concentration. For example, the copper complex of the derivative of 1,3-bis(3-aminopropyl)tetramethyldisiloxane with 3,5-di-tert-butyl-2-hydroxybenzaldehyde, $C_{48}H_{68}Cu_2N_4O_{10}Si_4$, is able to reduce the surface tension of DMF, from 37.1 to 26.4 mN/m at 1.5 g/dL) and forms aggregates above the critical micellar concentration [75]. This induces or enhances certain properties of metal complexes, well described in ref [82]. Micellization can be an effective method to increase the solubility and solution stability of coordination compounds.

These complexes can occur in an amorphous or crystalline state, or can exhibit LC behavior, depending on the isolation method and the treatment applied, their properties varying accordingly. Studies have shown that the dielectric permittivity and conductivity are higher in the amorphous state, while DSC measurements indicated a higher latent heat for the crystalline powder and the absence of isotropization in the amorphous state. Steady-state fluorescence revealed the AIE phenomenon, based on the thermotropic and lyotropic behavior of LCs. Fluorescence anisotropy measurements indicated a high degree of orientational order, with changes observed upon heating. These rare metallomesogens, which exist in both crystalline and amorphous states with intermediate LC behavior, have potential applications in energy, displays, photonics, and actuators [76].

Copper(II)–salen-type Schiff base complexes with a disiloxane moiety, particularly those with electron-withdrawing substituents (such as chloro, bromo, and nitro) on the aromatic ring, exhibit high catalytic activity and selectivity proven in the TEMPO radical-mediated aerobic oxidation of benzyl alcohol to benzaldehyde under mild conditions (aqueous acetonitrile at 50 °C) [83]. The amphiphilic nature of the tetramethyldisiloxane-spaced complexes can enhance the molecular interactions that favor the catalytic reaction [83, 84]. Studies have highlighted the antibacterial and antifungal activities of copper complexes with bis-azomethine ligands, attributing their efficacy to the increased lipophilicity, which facilitates the transport through lipid membranes of pathogenic microorganisms [77]. These complexes have also been shown to enhance the antioxidant activity of the extract of spirulina, suggesting potential applications in biotechnology. In addition, they exhibit electroactivity, undergoing both quasi-reversible and irreversible electron transfer processes involving the central Cu atom and the ligand. Substituents on the aromatic rings influence the values of the potential redox peak [85]. Depending on its nature, the metal ion can also induce specific properties, such as magnetic behavior [77].

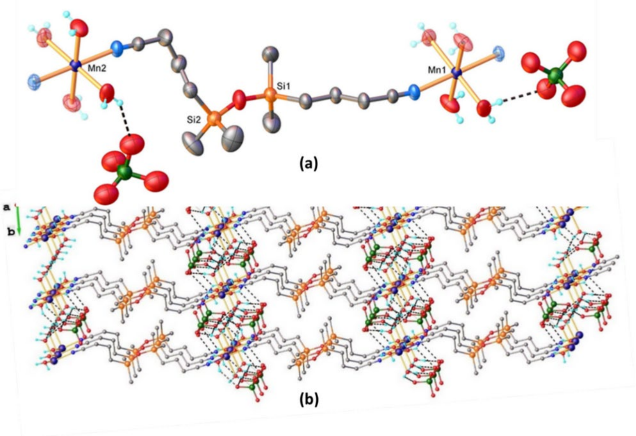

Fig. 8 Asymmetric unit and supramolecular structure of isostructural 1D CPs $\{[MCy(H_2O)_4](ClO_4)_2\}_n$ M: Mn^{2+}, Zn^{2+} and Cd^{2+}; Cy–1,3-bis(cyanpropyl)tetramethyldisiloxane) [74]

3.2 One-Dimensional Coordination Polymers, 1D CPs

One-dimensional coordination polymers (1D CP), formed by the unidirectional extension of coordination structures, are a class of compounds that, although not receiving the same attention as 3D MOFs (3D PCs), are useful as dynamic sorbents and for the separation of molecules larger than common gaseous species (N_2, CO_2, etc.), such as dyes or ions in aqueous solutions, due to their intrinsic flexibility and specific adsorption. Linear chains can assemble 3D through weak supramolecular interactions that allow easy access and orientation of guest molecules [86]. The use of siloxane-spaced ligands would provide more flexibility and adaptability, of interest for such a use of 1D PC. Such coordination polymers have been obtained using 1,3-bis(cyanopropyl)tetramethyldisiloxane (Cy) as a ligand for 3d metals [87, 88]. Their isolation in solid crystalline form, an otherwise difficult task in this case, can be achieved by using appropriate counterions, such as be perchlorate or iodide (Fig. 8).

Despite the hydrophobic nature of the spacer, the presence of these counterions gives the polymers a high water absorption capacity (about 75 wt%), of interest for certain applications [87]. Variations in the structure of the siloxane ligand and metal nature can allow the adjustment of some properties, according to the requirements.

3.3 Two-Dimensional Coordination Polymers, 2D CPs

Due to the surface activity of certain ligands with siloxane spacers, such as 1,3-bis(carboxypropyl)tetramethyldisiloxane (Cx) [89], promote the formation of 2D coordination polymers. These 2D materials are attractive due to their unique physical properties related to surface/interfaces and edge effects, inherent to the 2D structure. The infinitesimal thickness of 2D layers in two-dimensional coordination polymers (2D CPs) allows for significantly greater surface exposure, including metal centers, leading to higher permeability and improved electronic conductivity. This offers an advantage over bulky three-dimensional structures, where diffusion and access to active sites in the metal-organic framework (MOF) are often restricted. Such limitations can lead to lower internal surface area utilization and reduced efficiency of metal centers, ultimately leading to diminished performance in certain applications. To exhibit the specific characteristics of 2D materials, they should be isolated as single layers or a few layers with the lowest possible thickness-to-area ratio, the concept of 2D materials also encompassing this latter scenario.

2D coordination structures are also often obtained/separated as bulk crystals rather desired for their purity and for structural analysis. During crystallization, 2D PC nanosheets tend to stack vertically more than other 2D materials, generally due to their interpenetration or various types of interactions. This creates greater difficulties in exfoliation using methods similar to those used for conventional 2D materials. Consequently, the large-scale production of high-quality and stable 2D PCs of atomic or molecular-thick individual nanosheets remains a challenge. Incorporating methylsilicon segments into the structure of the complexes may be a solution to this [89].

In all 2D polymers obtained so far with such ligands, it has been found that the methyl groups are invariably oriented on one side and the other of the plane of the 2D structure, weakening the supramolecular interactions between the layers and increasing the distance between them, which facilitates their delamination. In 2D structures, obtained using 1,3-bis(carboxypropyl)tetramethyldisiloxane (Cx) with pyridyl derivatives (e.g., with 4,4`-azopyridine, AzoPy) as coligands and various 3d metal ions, interlayer distances of 2,3–3.0 Å were found [53]. Larger distances, around 14 Å, were observed when free Cx molecules were intercalated between the 2D layers via hydrogen bonds (Fig. 9).

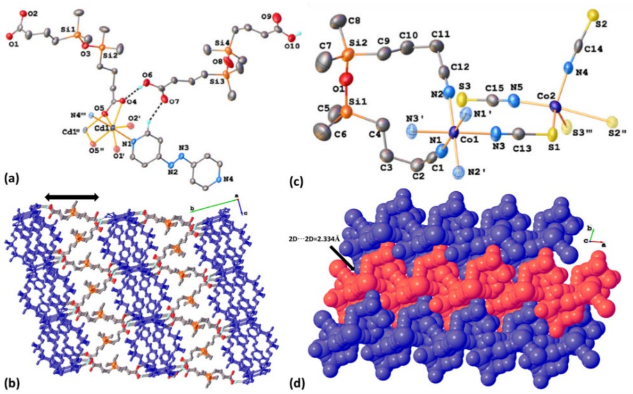

Fig. 9 The asymmetric unit and supramolecular interactions of the 2D coordination polymers with mixed ligands, one of them containing siloxane spacer: (**a**, **b**) - $[(CdCxAzoPy)\cdot H_2Cx]_n$; (**c**, **d**) - $\{CoCy_2[Co(SCN)_4]_2\}_n$; (Cx-1,3-bis(propyl)tetramethyldisiloxane; AzPy −4,4′-azopyridine, Cy −1,3-bis(cyanpropyl)tetramethyldisiloxane) [89]

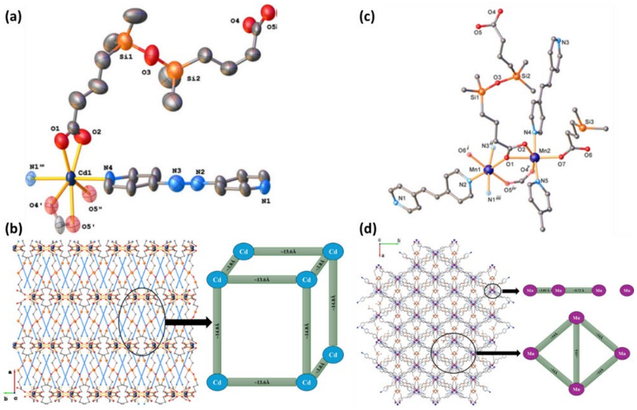

Fig. 10 The asymmetric unit and dimensional characteristics of two 3D coordination polymers (3D CPs) based on mixed ligands, one of them, 1,3-bis(carboxypropyl)tetramethyldisiloxane, containing siloxane spacer: (**a**, **b**) - $[Cd(Cx)(AzPy)\cdot 1.85H_2O]_n$ [92]; (**c**, **d**) - $\{[Mn_4(Cx)_3(etdipy)_5]\cdot 2\ ClO_4\}_n$ [95]

3.4 Three-Dimensional Coordination Polymers, 3D CPs

Although porosity is the most important characteristic that has established MOFs (consisting in principle of 3D coordination structures) since their discovery and promotion in the late 1990 s [90], it can sometimes dilute some sought-after properties, induced by the presence of the metal ion, such as magnetic [91] or thermal [92, 93]. For example, to be efficient in adiabatic refrigeration by magnetocaloric effect, magnetic density must be maximized by optimizing the packing pattern and minimizing the presence of non-magnetic elements that do not contribute to the physical processes [91]. In gas storage applications, where their ability to rapidly dissipate the heat generated during the exothermic adsorption process is sought, this is favored by high densities (> 1.0 g cm^{-3}), small pores (< 10 Å), and four-connected metal nodes [92] or by building doubly interpenetrated MOFs [93]. The use of highly flexible spacer siloxane ligands in the synthesis of 3D coordination polymers facilitates close packing, as demonstrated in MOFs based on 1,3-bis(propyl) tetramethyldisiloxane (Cx) with 4,4'-azopyridine (AzoPy) and Cd [94], or with 1,2-di(4-pyridyl)ethylene (etdipy) and Mn [95] (Fig. 10).

Both structures, $[Cd(CxAzoPy)\cdot 1.85\ H_2O]_n$ and $[Mn_4(Cx)_3(etdipy)_5]\cdot 2\ ClO_4\}$, were found to have low free volume values (13.0% and 2.3%, respectively) and to be highly hydrophobic, with water vapor sorption capacities of 2.7 wt% and 1.3 wt%, respectively, under equilibrium conditions at 90% RH.

4 Challenges and Perspectives

Although organosilicon compounds constitute an extremely versatile platform for structural diversification and obtaining valuable functional properties, their synthesis, characterization, and use frequently involve challenges, sometimes difficult to overcome.

Thus, despite the benefits of silicon-containing moieties – such as hydrophobicity, high steric bulk and conformational flexibility– their integration into organic systems often faces some synthetic and functional obstacles. The high reactivity of some silicon-based compounds or intermediates (e.g. halo-, alkoxy- or hydrosilane derivatives) requires the use of stringent reaction conditions to avoid unwanted reactions. Alternatives could be the use of temporary protecting groups, "one-pot" strategies or the development of more stable reagents. The sensitivity to hydrolysis or oxidation of Si–C and Si–O–Si bonds in strongly acidic or basic environments limits both the range of possible reactions and the applications under harsher conditions. Carrying out the reactions in a heterogeneous environment (emulsion), where appropriate, could be a solution.

High flexibility of the fragment allows structural adaptability, but complicates the prediction of molecular architecture (e.g., formation of cyclic vs. linear structures) and coordination geometry in the case of metal compounds. The use of rigid coligands could direct self-assembly into the desired shape. The presence of flexible and amorphous silicon fragments frequently hinders crystallization, making characterization by X-ray diffraction, crucial mainly for determining structures with metals, difficult. Co-crystallization with appropriate molecules would force ordering. But other methods available for structural analysis can be used: 2D NMR, MS, etc.).

Silicon-based fragments can negatively influence the compatibility with organic partners or the solubility of the products, thus affecting the yield, purification process and applicability of the compounds. To mitigate these effects, appropriate silicon-derivative precursors, generally bearing more polar substituents, could be used. Although organosilicon compounds, especially those containing permethylated silicon, are expected to have diverse applications and are considered relatively safe, there are concerns about ecotoxicological impacts, such as low biodegradability, possible bioaccumulation, or interference with biological processes. Also, for many new molecules, clear toxicological data are lacking, thus requiring systematic toxicity studies, evaluation of behavior in biological environments, and the development of "green" organosilicon compounds with controlled degradability.

Despite these challenges, there are promising prospects for the development of organosilicon compounds, such as: controlled functionalization of organosilicon compounds by introducing reactive groups that would expand the scope of applicability of these compounds, especially in modular synthesis and materials chemistry; modification of substituents on silicon and integration into advanced hybrid structures for fine-tuning of electronic, catalytic, optical, etc. properties; exploitation of the organosilicon fragment in supramolecular chemistry to promote self-assembly and generate useful structures in the design of nanostructured systems; use in bio-inspired applications, especially in drug delivery or controlled biomolecular interactions, due to the hydrophobic and bulky character of the organosilicon motif; more intensive approach to computational chemistry for the design of organosilicon compounds and prediction of their chemical behavior in complex systems. These perspectives highlight once again the fact that the silicon structural fragment has a potential that is still insufficiently explored.

5 Conclusions

Hybrid, organosilicon compounds, obtained by classical reactions between the functional groups of organic and silicon-derivative precursors, exhibit new or improved properties attributed to the silicon-containing moiety. Hybrid proligands with triazole units show an increased capacity for complexing metal ions. Organosilicons with aminothiadiazole units exhibit remarkable optical behaviors, such as aggregation-induced emission (AIE), efficient absorption in the UV-Vis-NIR, fluorescence and phosphorescence by intramolecular proton transfer, facilitated by hydrogen bonds, and increased quantum yields due to distorted conformations supported by silicon-based spacers. Additional functionalization with 3,5-dibromosalicylaldehyde generates bisimines with complex liquid-crystalline behavior, supramolecular chirality without stereogenic centers, reentrant transitions and ferroelectricity, due to the interaction between mobile siloxane side moieties, dipolar interactions and asymmetric supramolecular organization. Salen-type Schiff bases, based on 1,3-bis(3-aminopropyl)tetramethyldisiloxane and salicylic aldehyde derivatives, exhibit increased complexation capacity, favored by the flexibility of the siloxane spacer, surface activity, aggregation above the critical micellar concentration, with favorable effects, including on the yield of the reaction to obtain them (through self-isolation in micelles). The complexation of metals with these compounds, depending on their nature and reaction conditions, leads to various forms: small-molecular complexes (0D), one-dimensional (1D) chains, two-dimensional (2D) or three-dimensional (3D) networks. Schiff bases preferentially form mononuclear 0D complexes, with self-assembly potential and liquid-crystalline behavior, relevant in catalysis, electrochemistry and antimicrobial applications. 1D coordination polymers exhibit flexibility and self-organization, useful in the separation and adsorption of large molecules, and the presence of suitable counterions gives them water absorption capacity. 2D structures benefit from the spatial orientation of flexible and permethylated siloxane moieties, which reduce interlayer interactions and favor delamination, improving permeability and conductivity. 3D structures, made with ligands spaced by flexible siloxanes, allow dense packing, forming hydrophobic materials with small free volumes and high density of active centers, which increases their performance in some specific applications.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing Interests The authors declare no competing interests.

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