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Facile synthesis of silver alkynide cluster and coordination polymers using picolinic acid as a co-ligand

Studying the reactions of picolinic acid, silver salts and various acetylenes reveals the rich chemistry of these multi-dentate and bridging ligands. The silver fountain delivered crystals of coordination polymers and discrete clusters; the latter tridecanuclear Ag-species are also persistent in solution.

As featured in:

See Arvind Kumar Gupta and Andreas Orthaber, Dalton Trans., 2019, 48, 16518.
Facile synthesis of silver alkynide cluster and coordination polymers using picolinic acid as a co-ligand†

Arvind Kumar Gupta‡ and Andreas Orthaber‡

We describe five 1D-coordination polymers and two discrete silver clusters consisting of alkynides and picolinic carboxylates as co-ligands. In some cases, DMSO or EtOH further solvated the structural motifs. Utilising the sterically demanding tri-isopropylsilyle acetylene afforded a tridecanuclear cluster that possessed an unprecedented core with a silver center surrounded by six octahedrally arranged silver atoms. Can also have a great impact on which structures are formed, in particular when coordinating counterions, e.g. oxo-anions are used. Their ability to act as (bridging) ligands or being encapsulated in the direct coordination sphere of clusters and coordination polymers has led to interesting structural motifs and host–guest cage compounds.9–11 Phosphane-based co-ligands are often used to steer the formation of larger cluster motifs,12 while the use of harder donor co-ligands such as N- or O-based Lewis bases is significantly less explored.13 Only very few silver coordination compounds using picolinic acid (and related pyridine carboxylic acid derivatives) have been reported to date, however recent examples clearly illustrate the possibilities offered by this co-ligand class. Various groups have reported the coordination of two ortho-pyridine carboxylates as the O,N-bidentate ligand towards one silver centre in the form of homoleptic coordination compounds14−17 or as a heteroleptic motif with one pyridine carboxylate and two monodentate ligands, e.g. PPh3.18 On the other hand, pyridine dicarboxylates have led to an assembly of the homoleptic structural motif into 2D-layered structures via additional hydrogen bonding (2),19 while in other cases carboxylate oxygen atoms also engage in bridging coordination modes yielding interesting Ag2O2-cyclic motifs (3).20,21 To the best of our knowledge, there is only one example in which alkynide coordination is combined with a pyridine carboxylate motif. Zhang and co-workers reported the reaction of 5-ethyl nicotinic acid and 5-ethyl-picolinic acid with silver salts. The combination of the pyridine carboxylate and the various alkynide coordination modes led to fascinating high nucularity coordination compounds displaying argentophilic interactions. What is noteworthy is that in these clusters there is the tridentate (N,O,O′) binding of the pyridine carboxylates (picolinic and nicotinic acids), which is assisted by various alkynide coordination modes.22

Introduction

Alkynides are very versatile ligands giving multinuclear coinage metal coordination compounds.1 In particular for silver, alkynides can ligate one or more silver centres in various combinations of end-on (η1) or side-on (η2) fashion. Alkynides bridging up to four and in extremely rare cases even five silver centres have been previously reported, with μ3-η1η11 and μ3-η2η11 being the most prominent coordination modes.2 Although slightly weaker than those of gold clusters, metallocophilic interactions in silver assemblies, i.e. argentophilic interactions,3 are a fundamental force for crystal engineering.4 In analogy to aurophilic interactions, a typical criterion used in the current literature for argentophilic interactions is a sub-Ångström, Uppsala distances of 3.0 Å.5 Importantly, in most cases, no higher numbers of partners can be achieved, also due to the omnidirectionality of these interactions.

Bridging mono- and multidentate ligands play an important role in forming these assemblies. For example, the μ3-η1η11 and μ3-η2η11 trinuclear structural motifs are found in highly symmetric alkynide-only larger clusters,6 but also in co-ligand stabilized smaller clusters. For example, bidentate phosphane ligands stabilize the cationic [Ag2(CCR)2L3]3− motif having one (for R = (CMe2OH), n = 1, L = dppm, bis(diphenylphosphino)methane)7 or two (for R = Ph, n = 2, L = dppm, 1)8 alkynide ligands. Variation of silver salts in the cluster synthesis

†Electronic supplementary information (ESI) available: Additional experimental data and synthetic procedures. CCDC 1902309–1902312 and 1953779–1953781. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C9DT03697K.
In this report, we elaborate on how the interplay of picolinic acid as an N,O,O'-tridentate ligand and various alkyne ligands leads to the formation of different coordination polymers and discrete tridecanuclear clusters. Different metal salts and synthesis conditions lead to commonly observed silver motifs, which arrange into a variety of structural motifs. The multifacility of picolinic acid, various bridging alkyne coordination modes and argentophilic interactions give rise to a complex coordination chemistry with prominent coordination motifs found in both 1D-polymeric and discrete systems.

**Results and discussion**

This study reveals the formation of five different coordination compounds obtained by using different acetylene ligands (-CC-R, where R = Si(i-Pr3) subsequently abbreviated as TIPS, t-Bu, i-Pr, Ph) in the presence of silver salts (AgClO4 or AgTfO), picolinic acid and triethylamine. Variation of the steric demand as well as the cations impacts how the silver centres assemble and which coordination compounds are formed upon crystallisation (Scheme 1).

In order to solubilize the reactants and intermediates during the product formation, a binary (or ternary) solvent mixture is used consisting of dichloromethane (DCM) and ethanol (EtOH). As discussed later, for compound 3, dimethylsulfoxide (DMSO) was added to facilitate the solubilisation of intermediates during the cluster formation (Fig. 1).

Firstly, we performed the reaction using t-Bu acetylene, picolinic acid, and silver triflate, with triethylamine acting as a base in a DCM/EtOH solvent mixture. Initially we isolated the single crystal of a coordination polymer (1a, [Ag-C≡C(t-Bu),]-pic[EtOH])(CF3SO3), Fig. 2). The reaction mixture was filtered and evaporation of the solvents gave small colorless blocks suitable for SC-XRD.† The unit cell contains seven silver atoms, coordinated by one ethanol, four t-BuCC₂, and two picolinic carboxylate ligands in the asymmetric unit (Fd3d, no. 43, Z = 16). The metal core of 1a displays the unusual µ₁⁻η₁⁻η₁ coordination mode of acetylide ligands (Fig. 2c). The

† 1a (CCDC 1902312): C26H26AgN3O5[S2Ag2 (M = 1518.96 g mol⁻¹): orthorhombic, space group Fd3d (no. 43), a = 38.82(4) Å, b = 53.26(4) Å, c = 9.606(15) Å, V = 20.64(5) Å³, Z = 16, T = 150.15 K, µ(MoKα) = 2.697 mm⁻¹, Dcalc = 1.956 g cm⁻³, 41 117 reflections measured (3.058° ≤ 2θ ≤ 50.492°), 8717 unique (Rint = 0.0880, Rsigma = 0.0217) which were used in all calculations. The final Rf was 0.0645 (I > 2σ(I)) and wRf = 0.1321 (all data).

1b (CCDC 1953779): C26H34Ag2N3O7S2Ag2 (M = 1919.64 g mol⁻¹): monoclinic, space group C2/c (no. 15), a = 27.92(3) Å, b = 19.999(9) Å, c = 15.639(5) Å, β = 73.10(10)°, V = 5502(4) Å³, Z = 4, T = 150.15 K, µ(MoKα) = 3.286 mm⁻¹, Dcalc = 2.317 g cm⁻³, 41 200 reflections measured (2.98° ≤ 2θ ≤ 50.00°), 4858 unique (Rint = 0.0959, Rsigma = 0.0649) which were used in all calculations. The final Rf was 0.0492 (I > 2σ(I)) and wRf was 0.0902 (all data).

2a: (CCDC 1902311): C26H34Ag2N3O7S2Ag2 (M = 2876.96 g mol⁻¹): triclinic, space group P1 (no. 2), a = 13.969(3) Å, b = 15.629(3) Å, c = 20.922(4) Å, α = 74.668(2)°, β = 77.661(2)°, γ = 84.863(2)°, V = 4300.9(15) Å³, Z = 2, T = 150.15 K, µ(MoKα) = 3.416 mm⁻¹, Dcalc = 2.222 g cm⁻³, 48 854 reflections measured (2.00° ≤ 2θ ≤ 50.00°), 15 153 unique (Rint = 0.0535, Rsigma = 0.0623) which were used in all calculations. The final Rf was 0.0794 (I > 2σ(I)) and wRf was 0.0380 (all data).

2b: (CCDC 1953780): C26H34Ag2N3O7S2Ag2 (M = 2876.96 g mol⁻¹): monoclinic, space group C2/c (no. 15), a = 13.412(5) Å, b = 24.726(9) Å, c = 126.986(6)°, V = 4289(3) Å³, Z = 2, T = 150.15 K, µ(MoKα) = 3.755 mm⁻¹, Dcalc = 2.438 g cm⁻³, 47 797 reflections measured (3.35° ≤ 2θ ≤ 50.00°), 3773 unique (Rint = 0.1244, Rsigma = 0.0818) which were used in all calculations. The final Rf was 0.0603 (I > 2σ(I)) and wRf was 0.1711 (all data).

3: (CCDC 1902310): C30H38Ag2Cl2N2O2S2Ag2 (M = 2616.60 g mol⁻¹): orthorhombic, space group P2₁2₁2₁ (no. 19), a = 18.77(2) Å, b = 18.77(2) Å, c = 25.470(5) Å, V = 7882(3) Å³, Z = 4, T = 123.15 K, µ(MoKα) = 2.762 mm⁻¹, Dcalc = 2.205 g cm⁻³, 96 189 reflections measured (2.696° ≤ 2θ ≤ 50.00°), 13 905 unique (Rint = 0.0243, Rsigma = 0.0927) which were used in all calculations. The final Rf was 0.0703 (I > 2σ(I)) and wRf was 0.1893 (all data).

4a (CCDC 1902309): C31H44N2O2Si4N4AgCl2Ag (M = 3441.10 g mol⁻¹): monoclinic, space group C2/c (no. 15), a = 29.148(6) Å, b = 16.308(4) Å, c = 28.317(6) Å, β = 91.7990(10)°, V = 13550.3(5) Å³, Z = 4, T = 150.15 K, µ(MoKα) = 1.975 mm⁻¹, Dcalc = 1.687 g cm⁻³, 56 034 reflections measured (4.014° ≤ 2θ ≤ 49.996°), 11 916 unique (Rint = 0.0354, Rsigma = 0.0929) which were used in all calculations. The final Rf = 0.0335 (I > 2σ(I)) and wRf = 0.0859 (all data).

4b (CCDC 1953781): C31H44Ag2Cl2N2O2Si4N4Ag (M = 3497.29 g mol⁻¹): triclinic, space group P1 (no. 2), a = 16.217(4) Å, b = 16.611(4) Å, c = 29.328(6) Å, α = 91.319(7)°, β = 94.827(7)°, γ = 117.772(7)°, V = 6948(3) Å³, Z = 2, T = 150.15 K, µ(MoKα) = 1.927 mm⁻¹, Dcalc = 1.673 g cm⁻³, 285 113 reflections measured (1.39° ≤ 2θ ≤ 50.00°), 24 428 unique (Rint = 0.0691, Rsigma = 0.0337) which were used in all calculations. The final Rf = 0.0864 (I > 2σ(I)) and wRf = 0.2530 (all data).

**Scheme 1** Synthesis of coordination polymers 1–3 and discrete cluster 4. Experimental details are summarized in the ESI.†

**Fig. 1** Typical µ₁⁻η₁⁻η₁ coordination motif of supported alkyne clusters (I). Different pyridine carboxylic acid Ag(II) coordination compounds (II–III). Combination of both coordination motifs into 5-ethynyl picolinic acid (IV). This work: picolinic acid combined with sterically different acetylene ligands.

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μ of five silver atoms arranged in a distorted pyramid. Two sides that the major product of this reaction di-coordination polymer stretching along the crystallographic 1D-polymer. These three ligand environments form a rather complex 1D-cc coordination polymer with a coordinated ethanol at the apex and an almost linear CC–Ag–CC fragment.

Ag–carbon distance in the almost linear arrangement is the shortest (2.153(17) Å) of the three η¹-coordinations (2.286(19) and 2.37(2) Å), while the η² coordination mode is rather long (2.33(2) and 2.63(2) Å). Besides this unusual coordination, the very common “pyramidal” arrangement of silver atoms with two acetylides coordinating in μ₁η¹η¹ is realized. Interestingly, the apical silver atom is further coordinated by an ethanol (EtOH) solvent molecule (Fig. 2d). Lastly, the picolinic acid bridges four silver centres acting as a tridentate ligand in the μ₁η¹η¹N,1-2-3κ²O,4κ²O’ coordination mode (Fig. 2b). These three ligand environments form a rather complex 1D-coordination polymer stretching along the crystallographic [001]-direction.

Powder XRD (PXRD) of the bulk material however suggested that the major product of this reaction differs from the isolated single crystals (see ESI Fig. S87). Indeed for more than one week after initial crystallisation, differently shaped crystals of another coordination polymer 1b were obtained (Fig. 3). The unit cell contains nine silver centers, two coordinating triflate counter ions, two t-butyl acetylides and four picolinate ligands (C2/c, no. 15, Z = 4). The core of this structure consists of five silver atoms arranged in a distorted pyramid. Two sides of the pyramid are capped by a silver dimer unit via a μ₃-η¹η¹η² acetylide coordination forming the nonanuclear building block of this coordination polymer. The other two sides of the pyramid are coordinated by two picolinic acids in a complex μ₃-1κ¹N,1-2-3κ²O,4-5κ²O’ fashion. The basal plane of the central pyramid is coordinated by the carboxylates of the remaining two picolinic ligands, and the nitrogen atom and one oxygen atom link to a neighbouring unit (μ₃-1κ¹O,2-3κ²O’,3κ²N). Furthermore, one triflate acts as a bridging ligand between the nonanuclear silver units, which are not connected via short Ag–Ag distances. The 1D polymer stretches along the crystallographic c-axis (see ESI Fig. S13 and S14).

Changing to silver perchlorate and subtle variation of the steric demand of the acetylidy ligand, i.e. changing to an i-propyl acetylene, gives a completely different reactivity. We were able to identify a set of 1D-coordination polymers (2a, Fig. 4a and 2b Fig. 5) amongst other unidentified products during the reaction of AgClO₄, i-PrCC-H, NEt₃, in DMC/EtOH. Crystals suitable for SC-XRD for both species are obtained by slow evaporation from DCM/EtOH. The 15 silver atoms in the asymmetric unit of 2a are coordinated by four picolinic acids and ten acetylidy ligands. While two of the picolinic acids are in a μ₃-1κ¹N,1-2-3κ²O,3κ²O’ mode (Fig. 4b), the other two bridge four silver centres in the μ₄-1κ¹N,1-2-3κ²O,4κ²O’ coordination mode (Fig. 4c). The acetylidy ligands mainly have a three-centre bridging environment (Fig. 4d and e), while some exhibit a four-centre coordination mode (Fig. 4f). In the latter, three silver atoms and the acetylene (C6=C7) form an almost co-planar arrowhead with Ag1 as the tip, while the fourth silver atom (Ag2) locates above, forming an almost per-
The observed arrangement of the six nearest silver atoms around Ag2 is highly distorted due to the asymmetric unit contains ten silver atoms, three picolinic carboxylates, four phenyl acetylides, and three non-coordinating perchlorates. The ligand shell of the coordination polymer forms regimes of higher polarity \( i.e. \) where the DMSO ligands and perchlorates are grouped and areas dominated by π-interactions between the pyridyl fragments (containing N1, N2 and N3) (Fig. 6a). The centroid and shift distances between the rings are 3.592, 3.565 Å and 1.109, 1.356 Å, respectively. The picolinic carboxylates act as tridentate ligands aligning eight silver centres, in which the two outermost show the \( \mu \eta^1 \kappa^1 \eta^1 \xi^1 \) coordination of \( \mu \eta^1 \kappa^1 \eta^1 \xi^1 \) around Ag2 and Ag4 (Fig. 4g), albeit incorporated into two different silver environments. While for \( \text{2b} \) the silver atom Ag2 is quite regularly surrounded by six silver atoms, the six closest silver atoms around Ag4 are highly distorted due to the additional bridging coordination mode of the three perchlorate ions (Fig. 5a). The observed arrangement of the six nearest silver atoms around Ag2 is quite remarkable (Fig. 5b). These are octahedrally arranged around a silver center. This motif is stabilized by a \( \mu_3^\kappa_1 \eta^1 \xi^1 \) bridging picolinate coordination mode and the \( \eta^1 \kappa^1 \xi^1 \) bridging acetylide ligands (\textit{vide infra} coordination of 4). This silver packing motif alternates with the irregular environment around Ag4 in the 1D polymer along the crystallographic [101] direction (see Fig. S15 in the ESI).
central silver atom (Ag5), which is surrounded by six silver atoms forming an octahedral arrangement around Ag5. Furthermore, two acetylide ligands are coordinated to Ag5 in a μ3 bridging mode (Fig. 7b). This structural motif is remarkably similar to the Ag2 environment in cluster 2b, however the smaller i-Pr acetylene ligands allows the formation of a coordination polymer, while the increased steric demand of the TIPS acetylene ligands leads to the formation of discrete clusters.

The first layer of six silver atoms forms an almost octahedral environment with Ag5–Ag distances of 2.8980(4), 2.9297(4), 3.147(5) Å, and Ag–Ag5–Ag angles close to right angles: 85.69(1), 93.13(1), and 92.25(1)°. The inner acetylide ligands exhibit the rarer μ3-η2-η1-η1 coordination mode with a short Ag5–C distance (2.112(4) Å) and slightly longer distances to the first layer of silver atoms (2.28687(5) & 2.44570(4) Å for the η2- and 2.37383(4) & 2.51499(4) Å, for the η1 coordination modes, Fig. 7d). This is similar to the previously observed μ3-coordination modes. The silver cluster is expanded by two Ag3 units located in two opposite octants. The Ag3 units are linked to the central octahedral motif with three acetylide ligands coordinating trigonal faces (two in μ3-η2-η1-η1 and one in a μ3-η1-η1-η1) as well as four picolinic acids acting as the μ3-1-x1′N,1-2-x2′O,3-x′O′ tridentate bridging ligand (Fig. 7c). Related, octahedral motifs without a central silver atom are commonly found in silver clusters (e.g. in [Ag₆(CCR)₄L₂])₆ and in expanded motifs as the outer shell of a cubane core (see for example the [XC₈Ag₁₄(C≡C₉Bu)₁₂]⁺ series, where X = Cl, Br, I).23,24 However such an octahedral cluster with a central silver atom is to the best of our knowledge the first Ag(I) cluster that features such a structural motif. Surprised by these findings we wanted to investigate if minor changes in the picolinate ligand would alter its coordination behaviour. We identified from the solid-state X-ray analysis that substitution at the 4-position of picolinic acid, i.e. 4-methylpyridine-2-carboxylic acid, should have no impact on the coordination and packing of the discrete cluster. Indeed, this ligand affords an almost identical motif 4b, which crystallizes as colourless blocks in the monoclinic space group P1 (no. 2, Z = 2) as two halves of the tridecanuclear cluster in the asymmetric unit. One of the discrete clusters shows a slight disorder around the central silver atom, which is modelled as a position disorder with 1/2 occupancy. In the non-disordered moiety, we see silver distances of 2.910(1), 3.028(1) and 3.050(1) Å from the central to
the first shell of six silver atoms, and angles in the range of 88.43(3)° to 91.76(3)° closely matching the metric parameters observed in cluster 4a. As expected, the methyl groups do not disturb the coordination of the picolinate moieties during the formation of the tridecanuclear assembly (Fig. 7e).

Due to the discrete nature of these clusters, we performed solution studies using NMR spectroscopy (see also Fig. S1–S6 in the ESI†). Surprisingly, the clusters are sensitive towards chloroform solutions. Solution studies of 4a were performed in DCM-d2, while 4b could only be studied in a 1:1 mixture of DCM-d2 and C6D6. For both compounds 4a and 4b, a broadening in the proton NMR of the signals for the picolinic carboxylate (8.41, 8.15, 7.80, and 7.43 ppm for 4a and 8.08, 7.83, 6.84, and 1.98 ppm for 4b) and multiple signals for the TIPS (1.19, 0.97, 0.83 ppm for 4a and multiple signals around 0.91 ppm for 4b) environments are observed. This is also seen in 13C-NMR spectra, where two (4a) sets of signals for the i-Pr-group are observed; the quaternary acetylide signals are however not detected, presumably due to Ag–C couplings. The observed broadening either indicates a dynamic behaviour in solution, represents the different environments seen in the solid-state structure or originates from the large size of the cluster. In order to probe the persistence of the cluster in solution, we performed further 1H-NMR DOSY and 1D-NOE measurements. Selective irradiation of the 2-H (8.18 ppm) and 4-H (8.48 ppm) of the picolinic acid in cluster 4a indicates close proximity to the i-Pr groups with a chemical shift of 0.97 ppm, while both protons 3-H and 4-H show no NOE correlation. These findings are in agreement with the spatial arrangement of the i-Pr groups with respect to the picolinic fragment in the solid-state structure (see also Fig. S7 in the ESI†). DOSY measurements have previously been used to confirm stability as well as the dissociation behaviour of various silver coordination compounds in solution.25–27 Measurements of 4a using mesitylene as an internal reference give similar diffusion rates for the picolinate and the acetylide ligands (D = 12.12 × 10−9 m2 s−1), suggesting that both ligands are part of the same entity (Fig. 8).§ The calculated hydrodynamic radius (ρh) of 12.1 Å is slightly larger than expected from the solid-state structure, in which the longest axis in the approximately prolate spheroid structure of 4a is approx. 19.5 Å and the shorter axis falls between 15–17 Å. Re-crystallization from the NMR solutions again affords single crystals of 4a, supporting its solution stability. Similarly, 1H-DOSY measurements of 4b using the residual solvent peaks as internal standards give a diffusion coefficient of D = 12.13 × 10−9 m2 s−1 (ρh = 12.6 Å), which is, as expected, slightly larger than that for 4a, but is within the error of the measurements. Comparing these values with the dimensions of the cluster also indicates significant interaction of the solvent molecules with the cluster, leading effectively to a larger hydrodynamic radius. It must be stated that these findings do not completely rule out a dynamic situation in solution, but can only confirm that the entity observed in solution is of similar size compared to the original clusters 4a and 4b, and complete fragmentation and aggregation (dimers or oligomers) can be excluded. Although not directly comparable, the ESI-MS analysis shows significant fragments that involve the loss of acetylide ligands, and/or the addition of chloride (from the solvent) and/or silver ions.¶

Conclusions

In this manuscript we describe the synthesis and solid state structures of silver(i) coordination compounds stabilized by picolinic carboxylates and acetylide ligands. We illustrate how subtle variations of the silver salt and the steric demand of the acetylene ligand lead to the formation of complex 1D-coordination polymers or afford discrete cluster, when a sterically demanding TIPS acetylene is used. The obtained clusters show a very regular octahedral core of six silver atoms grouped around a silver centre, which is further expanded by two Ag3 units. The integrity of the discrete cluster in solution has been corroborated by solution NMR studies (1D proton and carbon as well as 2D-DOSY). The different ligand binding modes reoccur in this series of coordination compounds illustrating how subtle ligand, metal salt, and solvent variations can lead to a variety of silver coordination compounds. Notably, the combination of the cluster-directing acetylide ligands and the

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§ The DOSY analysis points towards similar diffusion of both the acetylide and picolinate ligands, indicating their presence in one discrete entity in solution on an NMR time scale. Based on the calculated size (ρh) we can exclude small components and larger assemblies, however an equilibrium of multiple interchanging species cannot be ruled out completely.

¶ General procedure for the synthesis of compound 4b. A solution of (iPr)3SiC≡CH (50 mg, 0.27 mmol) in CH3CN/EtOH was treated with AgClO4 (92 mg, 0.44 mmol) and a few drops of triethylamine (Et3N) were added. To the resulting solution, 4-methylpyridine-2-carboxylic acid (19 mg, 0.14 mmol) was added and stirred for 2 h. The reaction mixture was filtered through Celite pad and the solution was kept for crystallization. Colourless crystals were obtained after one week by slow evaporation. Yield 80% (96 mg).
multidenticity of picolinic acid, together with the notably short Ag–Ag distances indicative of argentophilic interactions, gives rise to the diverse coordination chemistry reported herein.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
The authors would like to thank the EU-COST action on Smart Inorganic Polymers (CM1302, SIPs), the Swedish Research Council (Vetenskapsrådet), Byggmästare-Olle-Engkvist Foundation.

Notes and references