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Probing dynamic library of metal-oxo building blocks with γ -cyclodextrin

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Supporting Information Placeholder

ABSTRACT: Formation of one of the most representative polyoxometalate (POM) archetypes, namely the Lindqvist anion $M_6O_{19}^{2-}$ with $M = Mo^{VI}$ or W^{VI} , was considered as elusive in aqueous solution. Herein, we report on the supramolecular host-guest stabilization of the $M_6O_{19}^{2-}$ species with $M = Mo$ or W from aqueous solution. The adduct $\{M_6O_{19}@ \gamma\text{-CD}\}^{2-}$ reveals remarkable stability over a wide pH range ($0 < \text{pH} < 7$) that offers new opportunities for exploring potentialities of molybdates or tungstates in the field of biology and medicine, since CDs are known as efficient drug carrier/delivery agents.

The early transition metals of groups V and VI in their highest oxidation state behave singularly, forming large and discrete anionic polynuclear metal-oxygen anions with terminal oxo groups.^{1,2} Formation of these molecular entities, named polyoxometalates (POMs) proceeds generally in aqueous solution through acidic condensation of tetraoxometalates MO_4^{2-} ($M = Mo$ or W) driven mainly by pH, concentration as well as the ionic strength.³ Polyoxometalates represent a unique class of all-inorganic metal-oxygen species which exhibit extremely high structural diversity in relationship with cumulative potentialities useful for a wide variety of applications in catalysis,⁴ medicine^{5,6} or energy storage.^{7,8}

Mo^{VI} or W^{VI} polynuclear oxo-clusters can be found in molybdenum storage proteins (MoSto).^{9,10} X-ray diffraction analysis of metal-loaded proteins revealed various discrete polynuclear species embedded into protein pockets acting as supramolecular hosts.^{10,11} Analogous to POMs, these polynuclear species (e.g. Mo_{5-7} or W_6) could exhibit unusual arrangements never isolated synthetically from aqueous solution. It means that these biological pockets engineer naturally directed self-condensation processes or protect against hydrolytic attack. Such a scenario offers a promising synthetic approach to trap novel species from the dynamic virtual library of constitutive metal-oxo building blocks. In this context, we re-investigated speciation of molybdates and tungstates in aqueous solution in the presence of γ -cyclodextrin (γ -CD), composed of eight glucopyranoside units, forming a doughnut-shaped molecules of about 9 Å in diameter. Recently our group and others showed the strong ability of γ -CD to interact with POMs in aqueous solution.¹²⁻¹⁵ Herein we present that presence of γ -CD interferes within the well-established interconversion condensation diagram of tungstates or molybdates, generating straightforwardly the Mo and W based $M_6O_{19}^{2-}$ Lindqvist ion.

The latter is known to be highly unstable in water³ and formed exclusively in solvents with lower dielectric constants.^{16,17}

Acidification of sodium molybdate solution containing γ -CD with aqueous HCl solution involves color change (colorless to pale yellow) for $H_3O^+ : Mo$ ratio higher than 1.5 featuring the formation of the $Mo_6O_{19}^{2-}$ ion. Interestingly, similar experiments, carried out in absence of γ -CD or in the presence of smaller cyclodextrins (α and β -CD) does not provoke any color change. This indicates clearly the specific role of γ -CD unit in the formation of the $Mo_6O_{19}^{2-}$ Lindqvist ion. These observations can be extended to the condensation of tungstates and confirmed by X-ray structure analysis and solution characterizations (see below for details). Large crystals of $Na_2\{M_6O_{19}@ \gamma\text{-CD}\} \cdot 18H_2O$ (noted **1** for $M = W$ and **2** for $M = Mo$) suitable for X-ray diffraction analysis appear after slow evaporation of acidic solution ($\text{pH} = 2$) containing metalate ions and γ -CD in 6:1 stoichiometric ratio.

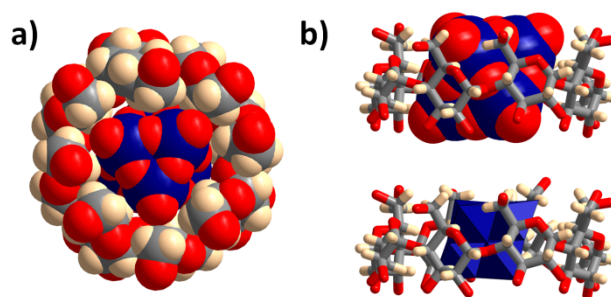


Figure 1. Structural representation of the 1:1 inclusion complex $M_6@ \gamma\text{-CD}$ built from one Lindqvist anion $M_6O_{19}^{2-}$ with $M = Mo^{VI}$ or W^{VI} closely embedded into one γ -CD torus. a) Top view of $M_6@ \gamma\text{-CD}$ highlighting the perfect size matching between the inorganic guest and the tori host; b) Side view: showing the deep inclusion of the Lindqvist anion fully hidden into the γ -CD.

Structural analysis reveals two isostructural 1:1 supramolecular host-guest complexes, abbreviated $Mo_6@ \gamma\text{-CD}$ and $W_6@ \gamma\text{-CD}$. The supramolecular arrangement exhibits a Lindqvist anion deeply embedded into the γ -CD torus. As depicted in Figure 1, the $M_6O_{19}^{2-}$ guest species appears tightly trapped within the γ -CD host, strongly anchored through a convergent 24 $O \cdots H$ hydrogen bonding network. The numerous weak hydrogen bonding interactions involve hydrogen atoms (H3, H5 and H6) from the γ -CD and oxygen atoms (terminal and bridging oxo groups) from the POM unit. Although the host-guest assembly exhibits a quite perfect

matching, it should be worth remarking that the 24 H•••O contacts exhibit average distances in the range 2.7-2.9 Å, consistent with rather weak hydrogen bonds (supporting information §2.2).

The ^1H NMR spectra of $\text{Mo}_6@ \gamma\text{-CD}$ and $\text{W}_6@ \gamma\text{-CD}$ in D_2O are shown in Figure 2 and compared to the ^1H NMR spectrum of the native $\gamma\text{-CD}$. Both spectra exhibit similar NMR fingerprints featuring the close host-guest encapsulation. Important down-field shifts appear for the H3 and H5 inner protons. Strikingly, the initial singlet of H6 protons splits into two doublets, meaning that the free rotation of the H6 protons from the methylenic group is frozen. These overall observations confirm the deep inclusion of the guest. As previously depicted by the structure analysis, the internal protons H5, H3 and H6 correspond to those that involved in hydrogen bonding contact with the oxo groups of the Lindqvist unit.

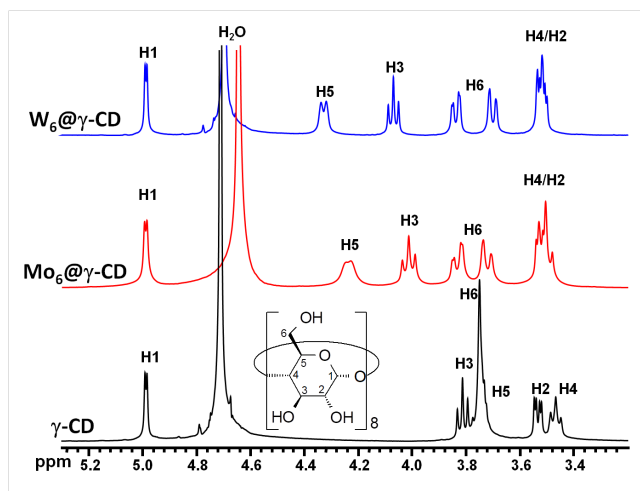


Figure 2: ^1H NMR spectra of $\gamma\text{-CD}$ solution (16 mM in D_2O) and dissolved crystals of **1** ($\text{W}_6@ \gamma\text{-CD}$) and **2** ($\text{Mo}_6@ \gamma\text{-CD}$) in D_2O (16 mM), showing clearly the shifts of signals associated to the interior protons (H3 and H5) of the host.

Careful examination reveals sharper ^1H NMR linewidths for $\text{W}_6@ \gamma\text{-CD}$ resonances than those observed for $\text{Mo}_6@ \gamma\text{-CD}$ assembly. Such observation suggests higher lability for the Mo-containing host-guest assembly compared to $\text{W}_6@ \gamma\text{-CD}$ arrangement. This was further investigated by ^{183}W and ^{95}Mo NMR, UV-visible spectroscopy, and ESI-MS.

^{183}W NMR of $\text{W}_6@ \gamma\text{-CD}$ (16 mM in D_2O) exhibits a single signal at 45.1 ppm (Figure S3), characteristic of Lindqvist anion while almost other archetypical polyoxotungstates give rise negative chemical shifts.¹⁸⁻²⁰ The spectrum does not change over a wide range of pH from 0.5 to 6 revealing a remarkable stability of the $\gamma\text{-CD}$ protected $\text{W}_6\text{O}_{19}^{2-}$ anion (Figure S14). ESI-MS method reveals the supramolecular adduct $\text{W}_6@ \gamma\text{-CD}$ is stable in diluted conditions (Figure S17-S18), indicating the feasibility to investigate its electrochemical behavior. In aqueous solution (sulfate buffer, pH = 2), the $\text{W}_6@ \gamma\text{-CD}$ assembly undergoes a quasi-reversible monoelectronic wave at $E_{1/2} = -0.65$ V vs SCE (Figure S24).

Solution behavior of $\text{Mo}_6@ \gamma\text{-CD}$ compound exhibits a quite different scenario (Figure S15). At its native pH (2.3), the ^{95}Mo NMR spectrum reveals three signals, corresponding to a mixture of $\text{Mo}_6\text{O}_{19}^{2-}$,^{21,22} and $\beta\text{-Mo}_8\text{O}_{26}^{6-}$.²³ After decreasing the pH down to 0.6, the Lindqvist signature is accompanied by signals of other species ($\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}^{8-}$ at pH 1.3 and MoO_2^{2+} at pH 0.6). Formation of the polyoxomolybdate ions as side-products indicates that the host-guest dissociation process involves consecutive hydrolysis of the Lindqvist anion according to the pH-dependant molybdate speciation. As expected, the dissociation of host-guest

entities is more pronounced and faster at lower concentrations as confirmed by ESI-MS (Figure S19) and UV-visible (Figure S23). Nevertheless, the dissociation-decomposition process appears fully suppressed by excess of $\gamma\text{-CD}$. As shown in Figure S4, the ^{95}Mo NMR spectrum of 16 mM solution of $\text{Mo}_6@ \gamma\text{-CD}$ containing five equivalents of $\gamma\text{-CD}$ shows a single signal characteristic of $\text{Mo}_6\text{O}_{19}^{2-}$ (120 ppm).

To understand the formation process of the encapsulated Lindqvist anions, we reinvestigate speciation of tungstates and molybdates using ^{183}W or ^{95}Mo NMR, respectively (supporting information §3.3-§3.8). Interconversion scheme of metalate species in the presence or in absence of $\gamma\text{-CD}$ is given in Figure 3. In short, acidification of sodium orthotungstate aqueous solutions in the absence of $\gamma\text{-CD}$ gives WO_4^{2-} (pH > 7), $\text{W}_7\text{O}_{24}^{6-}$ ($5 < \text{pH} < 7$), isomers α - and β - $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ ($2 < \text{pH} < 6$) and $\text{W}_{10}\text{O}_{32}^{4-}$ (pH < 1), in accordance with the literature.^{24,25} In the presence of $\gamma\text{-CD}$ ($\text{W}/\gamma\text{-CD} = 6/1$), the ^{183}W NMR fingerprint of the encapsulated Lindqvist $\text{W}_6\text{O}_{19}^{2-}$ appears within a quite wide pH range ($1 < \text{pH} < 6$). Interestingly, the formation of the host-guest adduct is always accompanied by the presence of $\text{W}_{10}\text{O}_{32}^{4-}$ anion. Furthermore, kinetic study reveals slow equilibration rate that leads invariably to the complete conversion of $\text{W}_{10}\text{O}_{32}^{4-}$ anion into the encapsulated $\text{W}_6\text{O}_{19}^{2-}$ species (Figure S9). This suggests that the $\text{W}_{10}\text{O}_{32}^{4-}$ anion would be the main species directly involved within the host-guest supramolecular process. Contrary to polyoxotungstates, self-condensation of molybdates proceeds with fast equilibration rates²⁶ and involves five main species identified as MoO_4^{2-} (pH > 6), $\text{Mo}_7\text{O}_{24}^{6-}$ ($4 < \text{pH} < 6$), $\beta\text{-Mo}_8\text{O}_{26}^{6-}$ ($2 < \text{pH} < 4$), $\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}^{8-}$ ($1 < \text{pH} < 2$), and MoO_2^{2+} (pH < 1). In presence of $\gamma\text{-CD}$, encapsulated $\text{Mo}_6\text{O}_{19}^{2-}$ complex is observed as a new species arising in a reduced 2.5 - 1 pH range.

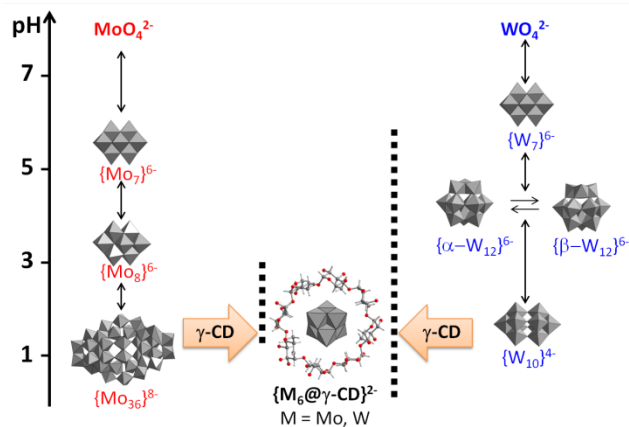


Figure 3: Illustration of the W^{VI} and Mo^{VI} speciation in absence and in presence of $\gamma\text{-CD}$ ($[\text{M}^{6+}] = 0.1\text{M}$). The dashed line indicates the pH domain where the Lindqvist anion is observed in presence $\gamma\text{-CD}$.

The formation of $\text{W}_6@ \gamma\text{-CD}$ adduct occurs over a wide pH range, while the stability scale of the Mo analog appears significantly shrunk. Such an observation is supported by a previous reports, showing experimentally and theoretically higher stability for the W-containing Lindqvist anion.^{27,28} The formation/degradation scheme of the encapsulated Lindqvist anion can be described reasonably as two main consecutive steps, one corresponding to the conversion of the predominant building units into intermediate species, able to be encapsulated within the $\gamma\text{-CD}$ in a second step to give the resulting stable $\text{M}_6@ \gamma\text{-CD}$ supramolecular complex. Analysis of the tungstate speciation diagrams suggests that the decatungstate $\text{W}_{10}\text{O}_{32}^{4-}$ ion should correspond to the identified unit able to generate $\text{W}_6@ \gamma\text{-CD}$. Similar analysis of molybdate speciation diagrams leads up to identify $\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}^{8-}$ anion as the precursor of pre-encapsulated

species. Even if there is quite perfect size-matching between $M_6O_{19}^{2-}$ and γ -CD, the supramolecular cohesion forces remain weak and cannot be the main contributor that explains the extremely high stability of the $M_6@ \gamma$ -CD assembly in aqueous solution. Solvation / desolvation processes occurring along the host-guest inclusion must be therefore taken into account as the main contributor to the supramolecular association. Such a scenario was nicely discussed by Nau et al. who considered halogeno dodecaborate clusters $B_{12}X_{12}^{2-}$ ($X = Cl, Br, I$) as superchaotropic entities to explain their extremely high affinity for the γ -CD pocket.²⁹ Chaotropic character of polynuclear ions disturbs the water structure in their hydration shell, featured by a loss of hydrogen bonds and concomitant positive entropy change. Such an effect becomes stronger in POMs when charge density (charge/size) decreases.^{30,31} Interestingly, the highly negatively charged $Nb_6O_{19}^{8-}$ Lindqvist ion almost does not interact with γ -CD as supported by 1H NMR titrations (Figure S16), while changing water for DMF as solvent precludes any formation of supramolecular adduct between the preformed weakly negatively charged Lindqvist $Mo_6O_{19}^{2-}$ as tetrabutylammonium salt and γ -CD. These two observations shed light on the solvent / ion complementary prerequisites to give rise to any significant chaotropic behavior at the origin of remarkable and counter intuitive aggregation phenomena in water.¹⁴ Herein, the encapsulation is directly coupled to metalate ions polycondensation and occurs within pH window that favors formation of low charge density / chaotropic species i.e pre-encapsulated units able to give $M_6@ \gamma$ -CD. Furthermore, Mo and W based Lindqvist anions exhibit contrasted stabilities while direct comparison of the structural features of $Na_2[M_6O_{19}@ \gamma$ -CD]•18H₂O does not show any difference in the host-guest binding modes. Therefore, the origin of such difference must be still found considering solution behavior of solvated pre-encapsulated species. Kinetic stability gain can be expected with regard to the low equilibration rates generally observed for condensation of tungstates compared to the Mo analog system.³ In addition, tungstates differ from molybdates in their M-O bonds properties, being less polar for $M = W$ with consequence to lower further the charge density at the surface of the polyoxotungstate ion. For instance, this induces high Brønsted acidity for $H_3PW_{12}O_{40}$, considered among the strongest acid catalysts.³² Therefore, polyoxotungstate ions are expected to exhibit pronounced chaotropic character, giving rise to significant thermodynamic stability gain for W-containing inclusion complexes in contrast to the Mo analogues.

In summary, we demonstrated for the first time that Mo and W Lindqvist anions can exist in aqueous solution as supramolecular inclusion complexes with γ -CD. Importantly, this report highlights that the biocompatible cyclodextrins can be used as efficient drug carrier/delivery agents to promote the biological activity of metalates, known to present antitumoral and antiretroviral properties.^{5,6} Such host-guest systems should give new opportunities for exploring potentialities of metalates in medicine. Beside, stabilization of polynuclear cores through host-guest trapping can be extended to other relevant elusive synthetic targets such as the Posner's cluster^{33,34} (size 8-10 Å), considered as prenucleation cluster in the bioapatites growth process.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Materials and methods.

Crystallographic data for **1** (CIF)

Crystallographic data for **2** (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Long, D.-L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105.
- (2) Pope, M.; Müller, A. *Angew. Chem.-Int. Edit.* **1991**, *30*, 34.
- (3) Pope, M. *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, Heidelberg, 1983.
- (4) Wang, S.-S.; Yang, G.-Y. *Chem. Rev.* **2015**, *115*, 4893.
- (5) Rhule, J. T.; Hill, C. L.; Judd, D. A.; Schinazi, R. F. *Chem. Rev.* **1998**, *98*, 327.
- (6) Yamase, T. *J. Mater. Chem.* **2005**, *15*, 4773.
- (7) Chen, J. J.; Symes, M. D.; Fan, S. C.; Zheng, M. S.; Miras, H. N.; Dong, Q. F.; Cronin, L. *Adv. Mater.* **2015**, *27*, 4649.
- (8) Nishimoto, Y.; Yokogawa, D.; Yoshikawa, H.; Awaga, K.; Irlle, S. *J. Am. Chem. Soc.* **2014**, *136*, 9042.
- (9) Fenske, D.; Gnida, M.; Schneider, K.; Meyer-Klaucke, W.; Schemberg, J.; Henschel, V.; Meyer, A. K.; Knochel, A.; Müller, A. *ChemBiochem* **2005**, *6*, 405.
- (10) Kowalewski, B.; Poppe, J.; Demmer, U.; Warkentin, E.; Dierks, T.; Ermler, U.; Schneider, K. *J. Am. Chem. Soc.* **2012**, *134*, 9768.
- (11) Schemberg, J.; Schneider, K.; Demmer, U.; Warkentin, E.; Müller, A.; Ermler, U. *Angew. Chem.-Int. Edit.* **2007**, *46*, 2408.
- (12) Wu, Y.; Shi, R.; Wu, Y.-L.; Holcroft, J. M.; Liu, Z.; Frascioni, M.; Wasielewski, M. R.; Li, H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 4111.
- (13) Zhang, B.; Guan, W. M.; Yin, F. F.; Wang, J. X.; Li, B.; Wu, L. X. *Dalton Trans.* **2018**, *47*, 1388.
- (14) Moussawi, M. A.; Haouas, M.; Floquet, S.; Shepard, W. E.; Abramov, P. A.; Sokolov, M. N.; Fedin, V. P.; Cordier, S.; Ponchel, A.; Monflier, E.; Marrot, J.; Cadot, E. *J. Am. Chem. Soc.* **2017**, *139*, 14376.
- (15) Moussawi, M. A.; Leclerc-Laronze, N.; Floquet, S.; Abramov, P. A.; Sokolov, M. N.; Cordier, S.; Ponchel, A.; Monflier, E.; Bricout, H.; Landy, D.; Haouas, M.; Marrot, J.; Cadot, E. *J. Am. Chem. Soc.* **2017**, *139*, 12793.
- (16) Fournier, M. *Inorganic Syntheses*; John Wiley and Sons: Hoboken, NJ, ed., 1990; Vol. 27, 80.
- (17) Hur, N. H.; Klemperer, W. G.; Wang, R.-C. *Inorganic Syntheses*; John Wiley and Sons: Hoboken, NJ, ed., 1990; Vol. 27, 77.
- (18) Chen, Y. G.; Gong, J.; Qu, L. Y. *Coord. Chem. Rev.* **2004**, *248*, 245.
- (19) Proust, A.; Thouvenot, R.; Roh, S.-G.; Yoo, J.-K.; Gouzerh, P. *Inorg. Chem.* **1995**, *34*, 4106.
- (20) Balamurugan, K.; Corinne, W.; William, M.; William, C.; W., H. R.; Antonio, R.-F.; M., P. J.; G., B. P.; John, E. R. *Chem. Eur. J.* **2012**, *18*, 59.
- (21) Haouas, M.; Trebosc, J.; Roch-Marchal, C.; Cadot, E.; Taulelle, F.; Martineau-Corcós, C. *Magn. Reson. Chem.* **2017**, *55*, 902.

- (22) Strong, J. B.; Yap, G. P. A.; Ostrander, R.; Liable-Sands, L. M.; Rheingold, A. L.; Thouvenot, R.; Gouzerh, P.; Maatta, E. A. *J. Am. Chem. Soc.* **2000**, *122*, 639.
- (23) Maksimovskaya, R. I.; Maksimov, G. M. *Inorg. Chem.* **2007**, *46*, 3688.
- (24) Himeno, S.; Nakajima, K.; Eda, K. *Polyhedron* **2010**, *29*, 2595.
- (25) Smith, B. J.; Patrick, V. A. *Aust. J. Chem.* **2000**, *53*, 965.
- (26) Schaffer, C.; Todea, A. M.; Gouzerh, P.; Müller, A. *Chem. Commun.* **2012**, *48*, 350.
- (27) Vila-Nadal, L.; Wilson, E. F.; Miras, H. N.; Rodriguez-Fortea, A.; Cronin, L.; Poblet, J. M. *Inorg. Chem.* **2011**, *50*, 7811.
- (28) Vila-Nadal, L.; Rodriguez-Fortea, A.; Yan, L. K.; Wilson, E. F.; Cronin, L.; Poblet, J. M. *Angew. Chem.-Int. Edit.* **2009**, *48*, 5452.
- (29) Assaf, K. I.; Ural, M. S.; Pan, F.; Georgiev, T.; Simova, S.; Rissanen, K.; Gabel, D.; Nau, W. M. *Angew. Chem.-Int. Edit.* **2015**, *54*, 6852.
- (30) Buchecker, T.; Schmid, P.; Renaudineau, S.; Diat, O.; Proust, A.; Pfitzner, A.; Bauduin, P. *Chem. Commun.* **2018**, *54*, 1833.
- (31) Naskar, B.; Diat, O.; Nardello-Rataj, V.; Bauduin, P. *J. Phys. Chem. C* **2015**, *119*, 20985.
- (32) Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171.
- (33) Posner, A. S.; Betts, F. *Acc. Chem. Res.* **1975**, *8*, 273.
- (34) Dey, A.; Bomans, P. H. H.; Müller, F. A.; Will, J.; Frederik, P. M.; de With, G.; Sommerdijk, N. A. J. M. *Nature Mater.* **2010**, *9*, 1010.

Table of Contents (TOC)

