Polyoxometalate–cyclodextrin assembly

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Cyclodextrin-Induced Auto-Healing of Hybrid Polyoxometalates

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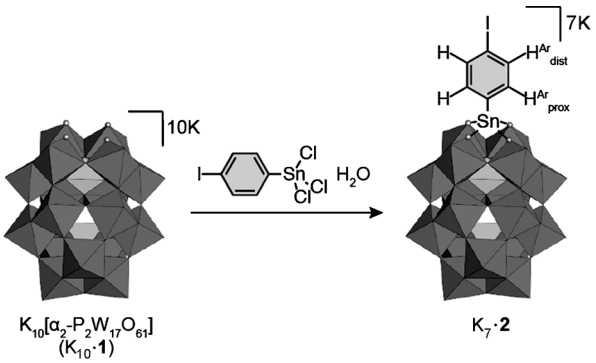
Polyoxometalates (POMs) form a remarkable class of well-defined nanoscale molecular oxides with a great diversity of molecular structures and properties.[1] They currently receive considerable attention as their field of applications ranges from biology to molecular spintronics, with remarkable breakthroughs in water oxidation catalysis[2] and in the design of POM-based single-molecule magnets.[3] However, to further employ their chemical and physical properties, POMs will have to be processed and integrated into functional devices or materials.[4] This issue has so far been mainly addressed by replacing POM counterions by cationic polyelectrolytes or surfactants,[5] but the use of covalently functionalized POMs with elaborate remote functions is now emerging as a powerful alternative.[6] An important class of such hybrids is obtained by anchoring an organic function on a lacunary POM through organic derivatives of group 14 elements (e.g., Si, Ge, Sn).[6a,7] However, the inherent base sensitivity of these assemblies, affording metal hydroxide derivatives, which lead to insoluble polynuclear species,[8] narrows the scope of their post-functionalization and operating purposes. To overcome this drawback, we decided not to look for a putatively more solid anchorage, but—inspired by the auto-healing ability found in biological or artificial systems[9]—we envisaged to find conditions under which a POM–organotin hybrid could re-form on its own after a basic degradation. To ensure the reversible disanchoring/anchoring of the organotin function of the POM hybrid, the operating conditions had to involve a solubilizing/protecting agent able to stabilize and prevent the oligomerization of adventitiously released organotin fragments. We logically turned our attention to cyclodextrins (CDs), concave molecules, known to form water-soluble inclusion complexes with simple organic functions, stable to both acidic and basic conditions.

To the best of our knowledge, no host–guest complex involving a POM hybrid has been described. Therefore we embarked upon the study of the interaction of α-CD and β-CD with a Dawson-type POM hybrid displaying an aromatic moiety, $K_7[\alpha_2\text{-}P_2W_{17}O_{61}\{Sn(C_6H_4I)\}]$ (K_7·**2**), as the potential guest for the CD cavity. We present the structures and the thermodynamic values of the POM/CD adducts and describe how damage caused by a basic stress on the functionalized POM could be fully repaired upon neutralization in the presence of the CD.

The POM hybrid K_7·**2** was synthesized by adapting a general procedure[10] through reaction of monovacant $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ (K_{10}·**1**) with 1-iodo-4-(trichlorotin)benzene in a slight excess (1.5 equiv) in water (Scheme 1). Association between CDs and K_7·**2** was then investigated in D_2O using ^{1}H NMR spectroscopy. For both α- and β-CD, only one set of signals was observed during titration, indicating a host–guest exchange that is fast on the NMR timescale. Successive additions of the POM hybrid to the CD solution led to specific complexation-induced shifts (Figure 1) that afforded the corresponding isothermal binding constants $K_{\alpha\text{-}CD\supset 2} = (780 \pm$



Scheme 1. Synthetic route to the POM hybrid K_7·**2**.

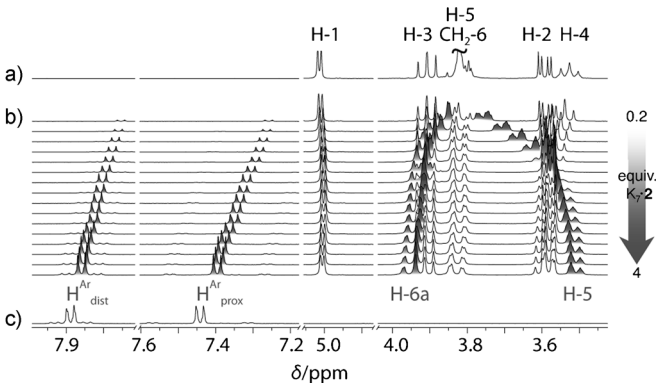


Figure 1. ^{1}H NMR spectra (400 MHz, D_2O) of β-CD (5 mM) a) before, b) after successive additions of K_7·**2** (from 0.2 to 4 equiv) and c) of K_7·**2** (5 mM).

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50) M^{-1} and $K_{\beta\text{-CD}\supset\mathbf{2}} = (1020 \pm 50)\,M^{-1}$ with a 1:1 binding profile.[11]

A careful analysis of the chemical shifts gave more information about the position of the aromatic unit inside the cavity. Indeed, upon complexation with α-CD, the distal aromatic protons (H^{Ar}_{dist}, see Scheme 1) of the POM derivative underwent a deshielding ($\Delta\delta[H^{Ar}_{dist}] = +0.21$ ppm, for a 6:1 ratio of α-CD/K_7·**2** in a 5 mM D_2O solution of K_7·**2**) due to the proximity with the secondary hydroxy groups, while the proximal ones (H^{Ar}_{prox}, see Scheme 1), being farther from the secondary rim and located outside the cavity, were less affected ($\Delta\delta[H^{Ar}_{prox}] = +0.09$ ppm). Concomitantly, the CD inner protons experienced inverse effects since the signals of the H-3 protons directed toward the aromatic moiety shifted upfield ($\Delta\delta$[H-3] = −0.12 ppm), while the H-5 protons shifted downfield ($\Delta\delta$[H-5] = +0.16 ppm), owing to their vicinity with the iodine atom. These observations are consistent with a partial inclusion of the POM aromatic part through the secondary face of the α-CD.

In the case of β-CD, a totally different ^{1}H NMR behavior was observed for both the POM derivative and the β-CD (Figure 1). Upon complexation, the aromatic protons underwent a shielding ($\Delta\delta[H^{Ar}_{dist}] = -0.11$ ppm and $\Delta\delta[H^{Ar}_{prox}] = -0.14$ ppm, for a 5:1 ratio of β-CD/K_7·**2** in a 5 mM D_2O solution of β-CD), indicative of a deep inclusion of the aromatic substituent in the CD. Moreover, the strong shielding of the inner H-5 protons ($\Delta\delta$[H-5] = −0.29 ppm), together with the weak effect on the H-3 signals ($\Delta\delta$[H-3] < + 0.01 ppm), suggested that the aromatic unit was close to the primary rim. Further 2D-ROESY and -NOESY experiments clearly evidenced the orientation of the inclusion complex showing a set of correlations between H-5 protons and both H^{Ar}_{prox} and H^{Ar}_{dist} protons, while H-3 protons correlated only with the H^{Ar}_{dist} protons. Finally, the H-6 protons underwent a slight deshielding ($\Delta\delta$[H-6] = +0.11 ppm) and experienced weak NOE correlations with H^{Ar}_{prox} confirming the deep inclusion of the POM aromatic part through the primary face of the β-CD. Incidentally, this constitutes a rare case of face selection in CD complexation[12] (Figure 2).

The geometries of both α-CD⊃**2** and β-CD⊃**2** adducts were fully confirmed by X-ray diffraction analysis. Slow diffusion of an aqueous solution of dimethylammonium (DMA) chloride into a solution containing K_7·**2** (5 mM) and α-CD (20 mM) afforded single crystals of $K_{1.5}DMA_{5.5}$·α-CD⊃**2.** Similarly, single crystals of $K_{2.5}Rb_{4.5}$·β-CD⊃**2** were grown by diffusion of a solution of rubidium chloride into a solution of K_7·**2** (5 mM) and β-CD (20 mM). The α-CD adduct structure was properly solved (Figure 3), while the structure resolution of the β-CD adduct revealed some disorder in the cyclodextrin preventing the analysis from being completed, but still confirmed the orientation of the inclusion complex.[11] In the case of α-CD⊃**2**, the structure shows the aryl moiety of the polyanion **2** half included in the center of the CD torus. The structure of **2** is similar to the already reported structure of $[\alpha_2\text{-}P_2W_{17}O_{61}\{SnC_6H_5\}]^{7-}$,[13] the Sn^{IV} atom of the polyanion residing in a distorted C_{4v} local environment. All glucose units are in $^4C_1$ conformation and the geometry of the complex is in full agreement with the chemical shifts observed by ^{1}H NMR spectroscopy (Figure 3).

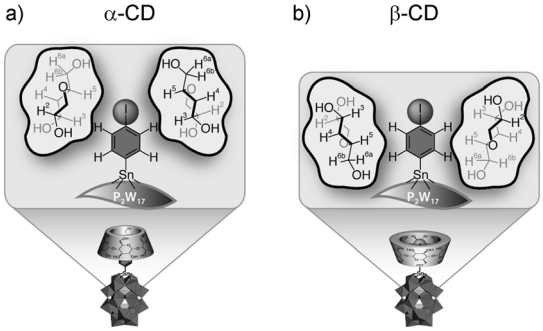

Figure 2. Representation of a) α-CD⊃**2** and b) β-CD⊃**2** adducts.

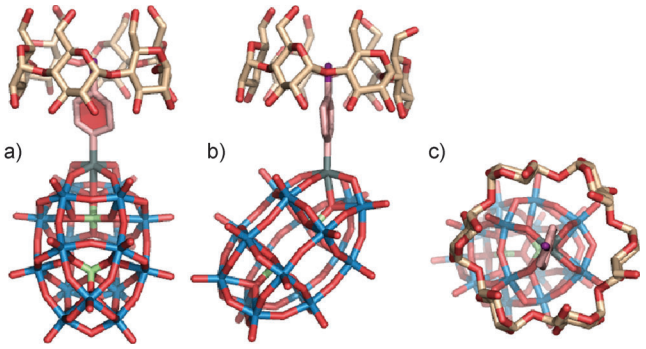

Figure 3. a) Front, b) side, and c) top views of the crystal structure (sticks representation) of the α-CD⊃**2** adduct. Solvent molecules and counterions have been omitted for clarity. The W, P, Sn, C, and I atoms are shown in blue, green, grey, yellow/pink, and purple, respectively.

After the POM–CD complexes were characterized and evidenced, we next investigated the effect of CD complexation on the solubilization and the protection of the organostannyl moiety under a basic degrading stress. As expected, in the absence of β-CD and upon action of LiOH (4 equiv), hybrid **2** was instantly and quantitatively converted into its monolacunary precursor **1**, while a concomitant precipitation of organotin species appeared. Upon neutralization through addition of trichloroacetic acid (TCA, 4 equiv), only partial re-formation of hybrid **2** (ca. 65%) was observed, **1** being also partly converted into the complete POM species $[P_2W_{18}O_{62}]^{6-}$ (**3**) by reaction with the acid, while some organotin derivatives remained as a precipitate. After four cycles of basic degradation followed by neutralization, about 20% of the starting POM was present in solution (A in Figure 4). In striking contrast, when the hydrolysis of **2** was performed in the presence of β-CD (5 equiv), no precipitation was observed after addition of LiOH, while the POM was again fully converted into **1**. However, after neutralization with TCA, **2** was fully recovered, with no trace of **1** or **3**. After four consecutive cycles of basic degradation followed by neutralization, the hybrid was fully present in solution (B in Figure 4), the amount of the complete species **3** being estimated to be less than 1%. When the same experiment was carried out with α-CD, a slight formation of **3** (ca. 5%)

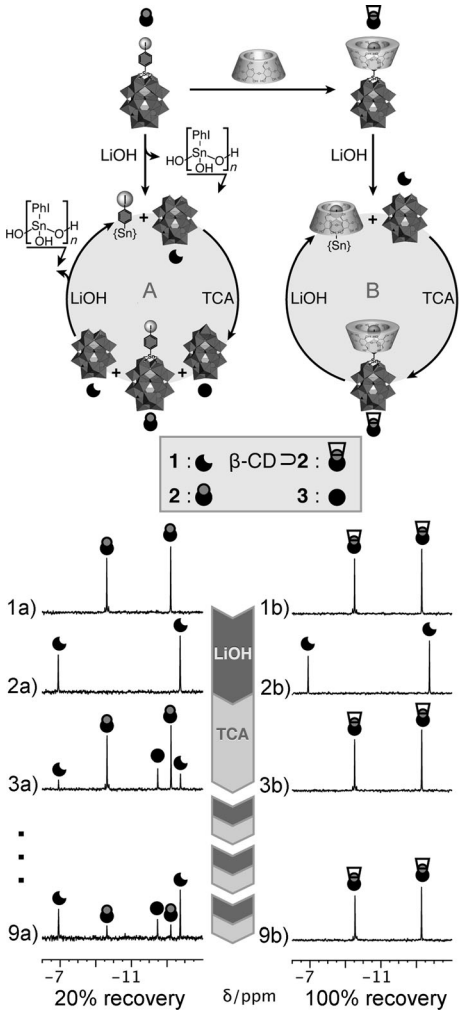

Figure 4. Action of LiOH and TCA neutralization on **2** (A) and on β-CD⊃**2** (B). 1)–9) ^{31}P NMR spectra (121.5 MHz, D_2O) of a solution of **2** (5 mM, a) or of β-CD⊃**2** (5 mM of **2** with 5 equiv of **β**-CD, b), 1) before, 2) after addition of LiOH (4 equiv), 3) after neutralization with TCA (4 equiv), showing coexistence of **1**, **2**, and **3** (a) or only β-CD⊃**2** (b). After four consecutive LiOH degradations and neutralizations only 20% of **2** is recovered (9a) and 100% of β-CD⊃**2** (9b).

was detected after four consecutive basic degradations followed by neutralization. Hence the disanchoring of the organostannyl moiety triggered by a basic stress can be harmless in the presence of β-CD, which encapsulates the organotin derivative and prevents it from oligomerization or disproportionation.[14]

We have thus uncovered the first supramolecular inclusion complex between a POM hybrid and a concave macrocycle. Associations between the POM-based hybrid K_7·**2** and α- and β-CD have been characterized, and their intimate molecular structures have been inferred both from solution and solid-state studies. These inclusion complexes allow the restoration of the anchored organic moiety after a basic stress, a process otherwise not fully reversible. The full recovery of the original material after four successive basic degradations qualifies this process as auto-healing.

This observation broadens the scope of post-functionalization of POM-based hybrids, which was up to now limited to non-basic conditions. This work also paves the way for self-assembled constructions driven by host–guest interactions between CD organic linkers and POM hybrids.

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[11] See the Supporting Information.

[12] For face selection through methylation, see for example: K. Harata, K. Uekama, M. Otagiri, F. Hirayama, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3904 – 3910; S. Immel, F. W. Lichtenthaler, *Starch/Staerke* **1996**, *48*, 225 – 232; T. H. Fenger, M. Bols, *Chem. Commun.* **2010**, *46*, 7769 – 7771.

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