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1 **NMR Spectroscopy to Study Cyclodextrin-Based Host-Guest Assemblies**
2 **with Polynuclear Clusters**

3

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10 **ABSTRACT.** Natural cyclodextrin (CD) macrocycles are known to form diverse inclusion
11 complexes with a wide variety of organic molecules, but recent work has revealed that inorganic
12 clusters also form multicomponent supramolecular complexes and edifices. Such molecular
13 assemblies exhibit a high degree of organization in solution governed by various chemical
14 processes including molecular recognition, host-guest attraction, hydrophobic repulsion, or
15 chaotropic effect. Nuclear magnetic resonance (NMR) spectroscopy is one of the most efficient
16 and practical analytical technique to characterize the nature, the strength and the mechanism of
17 these interactions in solution. This review provides a brief overview on recent examples of the
18 contribution of NMR to the characterization of hybrid systems in solution based on CD with
19 polynuclear clusters, including polyoxometalates (POMs), metallic clusters and hydroborate
20 clusters. The focus will be first on using ^1H (and ^{13}C) NMR of the host, *i.e.*, CD, to identify the
21 nature of the interactions and measure their strength. Then, 2D NMR methods will be illustrated
22 by DOSY as a means of highlighting the clustering phenomena, and by NOESY/ROESY to
23 evidence the spatial proximity and contact within the supramolecular assemblies. Finally, other
24 NMR nuclei will be selected to probe the inorganic part as a guest molecule. Attention will be paid
25 to classical host-guest complexes Cluster@CD, but also to hierarchical multi-scale, multi-
26 component assemblies such as Cluster@CD@Cluster.

27

28 **1. Introduction**

29 Molecular recognition in biology, which exploits the high affinity of bindings/interactions between
30 specific pairs of host and guest molecules, is an infinite source of inspiration for innovation in
31 materials science.^{1,2} Molecular signal detection is probably one of the most important bioinspired
32 functions, which may be of interest in various fields such as medical engineering, therapeutic

33 treatment, and sensing.³⁻⁵ The processes involved are mainly based on supramolecular chemistry,
34 where self-assembly through weak chemical bonds, *i.e.*, hydrophobic, electrostatic, and ionic-
35 dipole interactions, is the driving force behind stable systems.⁶⁻⁹ The spontaneous association of
36 two or more components in solution to produce hybrid systems by coordination or supramolecular
37 chemistry requires favorable physicochemical phenomena with minimal energy cost.^{10,11} The
38 construction of multifunctional assemblies based on supramolecular complexes usually involves
39 the use of macrocyclic molecules to host various guest species.^{5,12,13}

40 Cyclodextrins (CDs) represent a group of macrocyclic oligosaccharides mainly constituted of 6,
41 7, or 8 D-glucopyranoside units.¹⁴ Thus, the three renowned corresponding forms, *i.e.*, α -, β -, and
42 γ -CD, present a hydrophobic cavity of different diameter sizes depending on the number of the
43 repeating glucopyranose group. While CDs are known for a long time to interact with various
44 hydrophobic substances, it is now admitted that CDs are also capable of forming host-guest
45 adducts with a wide variety of hydrophilic polynuclear metallic clusters.¹⁵ Such self-assembly
46 properties of CDs have proven useful for the development of smart materials based on
47 supramolecular hybrid systems.^{16,17} Hybrid associations between CDs and inorganic species can
48 be divided into two categories. The first results from the strong affinity of the CD with a
49 hydrophobic group grafted to the inorganic moieties. Such a mode of interaction fits into the well-
50 established classical hydrophobic effect.¹⁸⁻²¹ The second type involves native inorganic species
51 such as polyoxometalates (POMs) or ionic cluster compounds which were found to form unusually
52 stable host-guest adducts with CDs. In 2015, both Nau's and Stoddart's groups reported that γ - or
53 β -CD interacts strongly with hydrophilic ions such as $[B_{12}X_{12}]^{2-}$ clusters (with X = H, F, Cl, Br or
54 I) and $[PMo_{12}O_{40}]^{3-}$ anions, as revealed by single-crystal X-ray diffraction (XRD).^{22,23} These solid-
55 state arrangements showed a 2:1 sandwich-type complex where the inorganic ionic species, *i.e.*,

56 either the dodecaborate anions or the POM, appears surrounded by two CDs. It is interesting to
57 note that depending on the anionic guest, the interaction of the CD involves its secondary face in
58 the case of the cluster or its primary face in the case of POM. This molecular recognition behavior
59 thus appears as a distinctive feature of CD in the inclusion phenomenon with inorganic clusters.
60 The inclusion phenomenon involving hydrophilic ionic species has been recently well documented
61 and explained as a solvent effect that arises from the chaotropic nature of the ionic guest.^{24,25} Such
62 a chaotropic effect occurring in aqueous solution gives a characteristic thermochemical fingerprint.
63 Low charge density species locally cause the breakdown of the water structure, characterized by a
64 high-enthalpy and a high-entropy solvation shell. Throughout the aggregation process leading to
65 guest encapsulation, the release of water from the hydration shell to the bulk is associated with
66 strong decreases in enthalpy and entropy, *i.e.*, $\Delta_r H < 0$ and $\Delta_r S < 0$. Despite the entropy penalty,
67 the aggregation process remains highly favorable and enthalpically driven ($T\Delta_r S > \Delta_r H$ and $\Delta_r G <$
68 0). Thus, several POM-based chemical systems with low charge density, including the Lindqvist
69 ions $[M_6O_{19}]^{2-}$,²⁶ the Preyssler-type anion $[P_5W_{30}O_{110}]^{15-}$,²⁷ the Dawson-type anion $[P_2W_{18}O_{62}]^{6-}$,²⁸
70 and even, the giant Mo blue wheel $[Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$, abbreviated $\{Mo_{154}\}$,^{29,30} have verified
71 such affinity. The phenomenon can then be generalized regardless of the structure, composition,
72 size and shape of the POM.^{24,25} Although the chaotropic effect was identified by Hofmeister in
73 1888 for small ions, this property has been clearly associated with cluster anions only very recently
74 and opens a new avenue for the design of CD-based smart supramolecular materials.^{7,31-36}
75 The characterization of CD complexation by polynuclear clusters is of paramount importance to
76 understand the driving forces of the phenomena involved in solutions such as self-assembly, host-
77 guest inclusion, and aggregation process. Various analytical techniques such as calorimetric
78 titration,³⁷ ESI-mass spectrometry,^{38,39} X-ray scattering and diffraction,^{1,40} circular

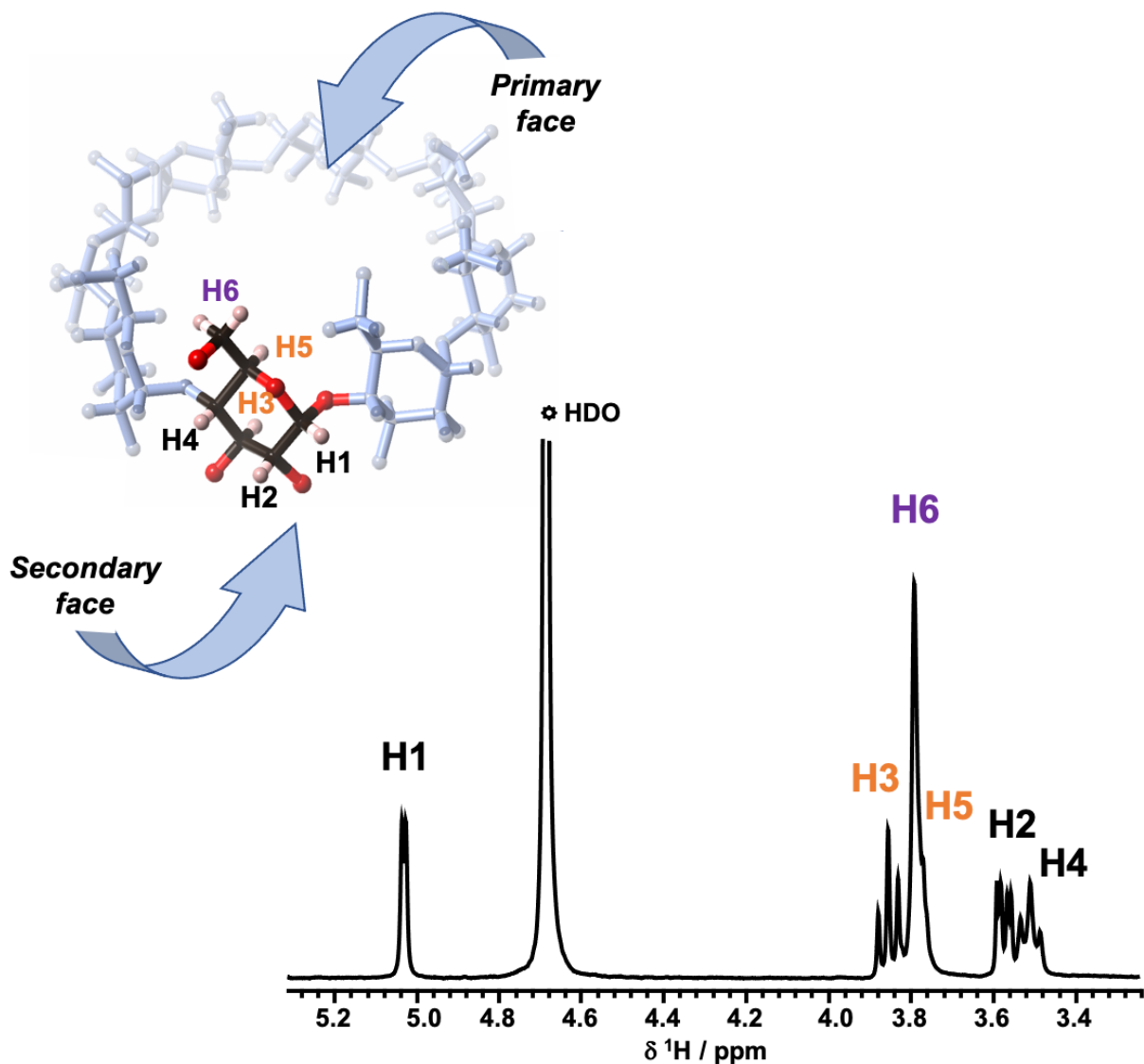
79 dichroism,^{21,36,41} voltammetry⁴¹ and fluorescence spectroscopy⁴² were applied to study the
80 reactivity of CDs with different guest molecules. Furthermore, NMR spectroscopy is one of the
81 most frequently used methods for studying self-assembly processes with CDs,⁴³⁻⁴⁶ allowing to
82 determine not only quantitative information, e.g., the stoichiometry of adducts and their binding
83 constants but also structural and dynamic data of the complex and its constituent parts, e.g., the
84 regioselectivity of the binding sites and their equilibria and exchanges. This mini-review focuses
85 on the recent use of NMR methodology to study complexation of CD with inorganic polynuclear
86 species.

87
88

89 **2. Probing host-guest interaction by ¹H and ¹³C NMR of cyclodextrin**

90 Cyclodextrins are highly symmetrical molecules consisting of identical D-glucopyranoside
91 motifs. The ¹H NMR in aqueous solution thus shows the signature of this glucopyranoside unit
92 which has six distinctive proton sites, labeled H1 (anomeric position), H2, H3, H4, H5 and H6
93 (See Fig. 1).⁴⁶ The three hydroxyl groups are not distinguishable and merge with the water signal
94 due to their chemical exchange. Because the molecules are cyclic H2 and H4 are exposed to the
95 outside, while H3 and H5 are located inside the central cavity of the tori. The H6 protons
96 correspond to the methanolic arms at the top of the primary face of the macrocycles. Fig. 1 is a
97 representative ¹H NMR spectrum in D₂O of 3 mM solution of γ -CD. The anomeric proton H1
98 appears strongly deshielded at ca. 5 ppm, while the other protons are only partially resolved and
99 divided into two groups, at 3.4-3.6 ppm (outward protons H2 and H4) and 3.7-3.9 ppm (inward
100 protons H3, H5, and H6). The latter are obviously the most sensitive to interaction with guest
101 molecules and are often used as probes for host-guest complexation.

102



103

104 Fig. 1. ^1H NMR spectrum of 3 mM γ -CD in D_2O showing the six signals of the macrocycle: the
 105 anomeric proton H1, the outward protons H2 and H4, the inward protons H3 and H5, and the
 106 methanolic H6 protons on the primary face.

107

108 One of the simplest experiments to identify the host-guest interaction in solution between CD and

109 inorganic species is the ^1H NMR titration of the host molecule by the guest species to observe the

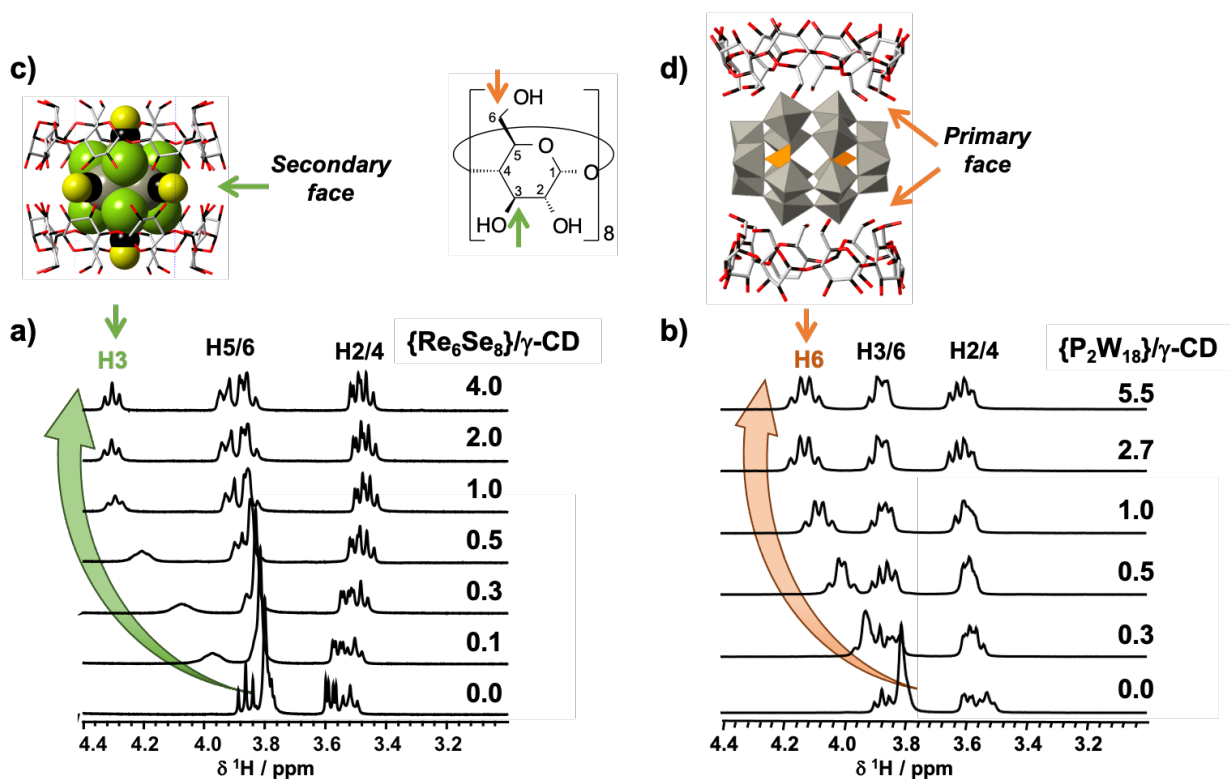
110 effects on the resonances of the most exposed protons, those present on the inner surface of the

111 cavity. Fig. 2 shows an example of titration of 3 mM D_2O solution of γ -CD by two anionic clusters:

112 the selenide octahedral rhenium cluster $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ and the Dawson-type POM $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$

113 ^{6,28} Two antagonist behaviors are observed. With the rhenium cluster complex, the most affected

114 resonance upon addition of 4 eq. corresponds to the H3, down-field shifting from ca. 3.9 to 4.3
 115 ppm, whereas in case of the POM, this resonance did not move so much, and instead, H6
 116 underwent up to 0.3 ppm downfield shift. This illustrates the difference in supramolecular
 117 recognition process in solution. CD reacts with the rhenium cluster to form inclusion complex
 118 involving their secondary face, which differs from the sandwich adduct through its primary rim
 119 obtained with the Dawson-type POM (see Fig. 2). These observations in aqueous solution are
 120 consistent with the molecular organization in the solid-state, but has to consider the dynamics
 121 aspect of the host-guest association equilibria. As evidence of molecular recognition, competition
 122 occurs in the simultaneous presence of two guests, Dawson-type POM and octahedral rhenium
 123 cluster.⁴⁷
 124

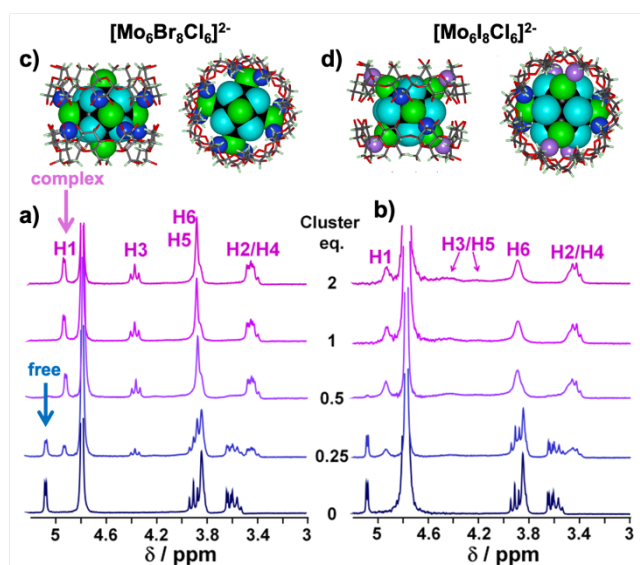


125

126 Fig. 2. ^1H NMR titration of 3 mM γ -CD in D_2O by (a) $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4+}$ and (b) $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ in the
127 range 3.0-4.4 ppm. (c) and (d) the crystallographic structures of the adducts obtained in each
128 system. Adapted from references.^{6,28}

129
130 The dynamic aspect of the host-guest association could also inform the strength of the interaction
131 between the two components. Generally speaking, a slow dissociative process usually indicates
132 a strong complexation. This can be easily observed in the NMR titration experiment. When the
133 equilibria are fast relative to the NMR time scale, the CD signals appear as a weighted average
134 situation between free and bound species. This is manifested by a continuous shift of some
135 specific resonances, as observed in the cases of $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4+}$ and $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ with γ -CD in
136 Fig. 2. The scenario is different with molybdenum clusters $[\text{Mo}_6\text{X}_8\text{Cl}_6]^{2-}$ ($\text{X} = \text{Br}$ or I) when the
137 NMR signatures of γ -CD exhibit slow exchange regime,⁴⁸ as shown in Fig. 3. Here, the signals
138 of free and complexed CD are observed together, allowing even the stoichiometry of the final
139 adduct to be easily determined. Indeed, consumption of free CD occurs at 0.5 eq. of cluster
140 confirming a 2:1 sandwich complex in agreement with the XRD structures (Fig. 3).

141



142

143 Fig. 3. ¹H NMR titration of 2 mM γ -CD in D₂O by (a) [Mo₆Br₈Cl₆]²⁻ and (b) [Mo₆I₈Cl₆]²⁻. (c) and
144 (d) the crystallographic structures (top and side views) of the adducts obtained in each system.
145 Color code: black = Mo, light blue = X (Br or I), green = Cl. H3 and H5 involved in close host-
146 guest interactions are in dark blue and pink, respectively. Adapted from reference.⁴⁸

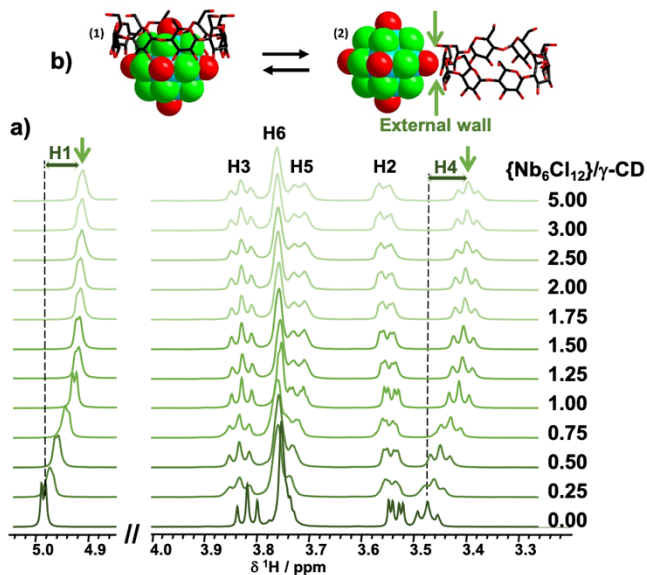
147
148 The interaction of octahedral metal clusters with γ -CD often leads to sandwich-like host-guest
149 complexes, as revealed by XRD analysis. However, the behavior in solution may differ
150 dramatically from one cluster to another. Some clusters like [Re₆X₈(CN)₆]⁴⁺ (X = S or Se) showed
151 labile complexes indicating moderate association affinity ($K_{1:1} < 2000 \text{ M}^{-1}$), while others like
152 [Mo₆X₈Cl₆]²⁻ (X = Br or I) are characterized by frozen complexation in solution due to strong
153 attraction between the two components. Such behavior comes from a chaotropic effect induced
154 complexation where the guest dehydration and its association with neutral surfaces such as
155 hydrophobic CD cavities are very favorable processes.^{24,25,49} Here, the overall charge of the
156 polyanion plays a crucial role, and the general trend shows that the lower the charge density, the
157 stronger the host-guest association. In comparison, POMs can have a very strong chaotropic
158 character, but they lead almost exclusively to dynamically labile systems. It seems therefore
159 difficult to reconcile the thermodynamic stability of these supramolecular associations and their
160 dynamics in solution, even if the general tendency shows that frozen complex reflects a strong
161 association.

162 Internal dynamics can also be detected in a frozen system, as in the case of molybdenum chloride
163 clusters with γ -CD shown in Fig. 3.⁴⁸ The NMR spectra of the iodine derivative are broader than
164 those obtained with Br-based clusters. This would indicate a different rotational dynamic within
165 the host-guest assembly, induced by a reorientation of the cluster in the CD cavities after a 45°
166 tilt from the central axis of the CD (Fig. 3). With iodide compound, all the six apical chlorine
167 ligands are located inside the cavities of the capping CDs, maximizing the weak attractive forces

168 with the host and thus restricting internal molecular movement within the supramolecular
169 framework. Host size may also play a key role in these associations and their dynamics since the
170 volume of cluster $[\text{Mo}_6\text{X}_8\text{Cl}_6]^{2-}$ increases from 395 to 447 \AA^3 by substituting X with Br and I,
171 respectively.

172 Interaction of cyclodextrins with cationic transition metal octahedral clusters has also been
173 studied, and their behavior in solution has been found mostly to depend on the nature of their
174 inner ligands like with anionic clusters. For instance, very different results were obtained with
175 $[\text{Nb}_6\text{Cl}_{12}(\text{H}_2\text{O})_6]^{2+}$ when compared to $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$ although both had led to isostructural
176 sandwiched inclusion 2:1 complexes with γ -CD in the solid-state.^{1,28} While titration experiment
177 with $[\text{Ta}_6\text{Br}_{12}(\text{H}_2\text{O})_6]^{2+}$ showed frozen complexation in solution, the ^1H NMR spectra in the case
178 of $[\text{Nb}_6\text{Cl}_{12}(\text{H}_2\text{O})_6]^{2+}$, shown in Fig. 4, clearly indicate no host-guest inclusion happened and only
179 weak contacts took place at the external peripheral wall of the CD. Indeed, the signals of H3 and
180 H6 protons at the two different rims did not undergo any significant alteration, while resonances
181 of H1 and H4 protons pointing outward the cavity shifted significantly in the presence of the
182 cluster. In a similar way, no interaction has been recorded with the chloride derivative of
183 $[\text{Mo}_6\text{Cl}_8\text{Cl}_6]^{2-}$,⁵⁰ while the bromide and iodide cluster complexes $[\text{Mo}_6\text{X}_8\text{Cl}_6]^{2-}$ (X = Br or I)
184 interact strongly with γ -CD.⁴⁸

185



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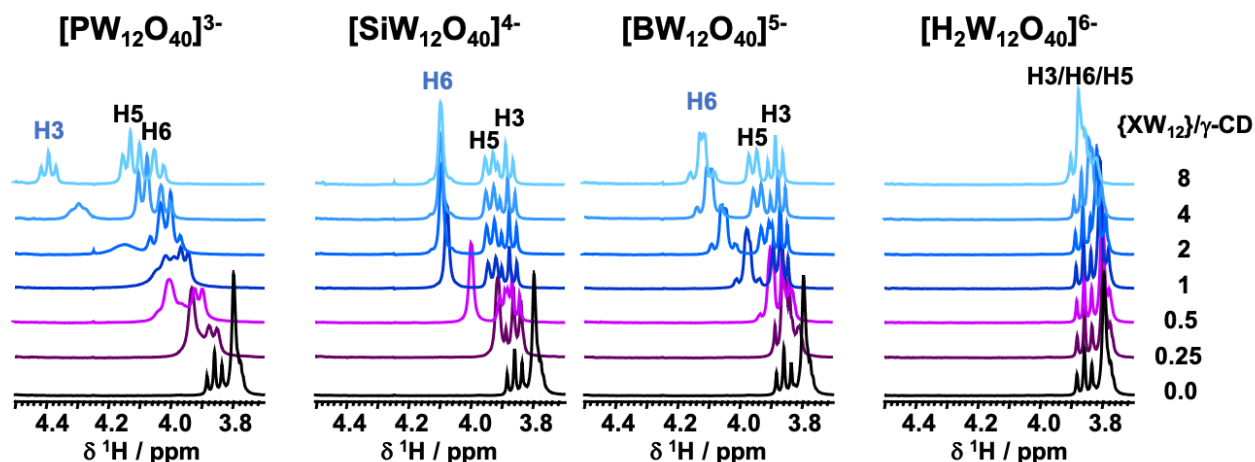
187 Fig. 4. (a) ¹H NMR titration of 1 mM γ-CD in D₂O by [Nb₆Br₁₂(H₂O)₆]²⁺. (b) A schematic
 188 illustration of the dynamic dissociation of the host-guest complex observed in the solid state (1)
 189 occurring in solution (2). Adapted from reference.¹

190

191 Given their spherical shape and nanoscale size, Keggin-type POMs are expected to react with
 192 CDs to readily form host-guest inclusion complexes in a similar way to octahedral metal-atom
 193 clusters. Nonetheless, the isolation of well-defined supramolecular assemblies is rather rare with
 194 POMs. The interaction in solution was found to be strongly dependent on the charge of the POM
 195 as shown in Fig. 5,²⁵ depicting the ¹H NMR titration of 2 mM γ-CD with four different Keggin-
 196 type POMs [XW₁₂O₄₀]ⁿ⁻, X = P, Si, B, and H₂, whose overall charge *n* varied from 3- to 6-.
 197 Almost no effect can be detected with the most charged POM [H₂W₁₂O₄₀]⁶⁻, indicating very weak
 198 interaction between the POM and organic macrocycle. With the boron and silicon derivatives
 199 moderate effects on H6 signal can be seen, comparable to that observed with the Dawson-type
 200 POM (Fig. 2), indicative of supramolecular contact of the POM with the primary face of the CD.
 201 The situation is even more different with the Keggin-type dodecatungstophosphate [PW₁₂O₄₀]³⁻
 202 where H3 exhibited the strongest effect as clear evidence of embedment of the POM within the

203 central cavity of the CD. Indeed, among the four Keggin-type POMs studied, only $[\text{PW}_{12}\text{O}_{40}]^{3-}$
 204 had conducted to crystal structure of host-guest adduct where the POM is deeply embedded
 205 within the central cavity through the secondary face of the γ -CD. The X-ray structure with the
 206 boron derivative showed co-crystallization of the POM and the CD side-by-side without
 207 inclusion complexation. Again, these results are explained by the chaotropic nature of the
 208 polyanions. When the hydration network is loosely defined and weakly organized, desolvation
 209 can occur easier. Obviously, the charge density of the POM affects the solvation properties and
 210 the higher the charge density, the lower the desolvation ability (or the chaotropic power).

211

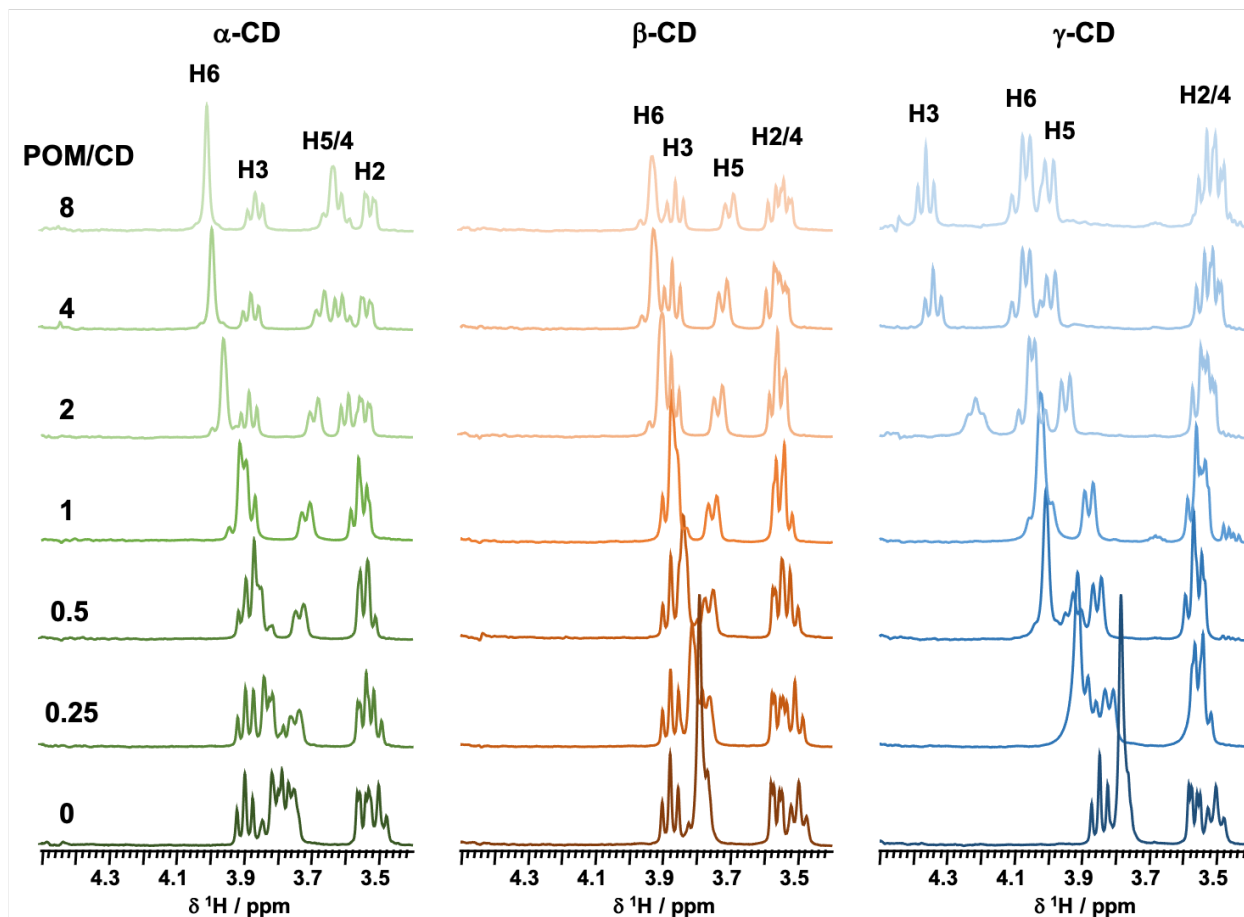


212
 213 Fig. 5. ^1H NMR titration of 2 mM γ -CD in D_2O by Keggin POMs $[\text{XW}_{12}\text{O}_{40}]^n$: X = P, Si, B, H_2 ,
 214 and n = 3, 4, 5, 6. Adapted from reference.²⁵

215
 216

217 Similar results were obtained with the molybdenum Keggin POMs, confirming that the nature
 218 of the metal center, *i.e.*, Mo^{6+} or W^{6+} , does not affect much the interaction with the CD. However,
 219 the effects of POM on the ^1H NMR response are different depending on the size of the CD
 220 highlighting the importance of the host-guest size matching in the encapsulation process. Fig. 6
 221 displays the obtained ^1H NMR titration of three different solutions of α -, β -, and γ -CD by

222 [PMo₁₂O₄₀]³⁻ (4 mM in D₂O).⁵¹ The evolution of the spectra of γ -CD is very similar to that
223 observed with [PW₁₂O₄₀]³⁻ (see Fig. 5), where H2 and H4 show only a negligible effect by
224 comparison to H3, and to a lesser extent to H5 and H6, experiencing all strong deshielding
225 effects. On the other hand, no significant effect can be seen on H3 resonance in α - and β -CD
226 solutions, and only moderate shifts are detected for H6 and H5 signals. These results indicate
227 that interactions occur mainly with the primary face of the CD without deep inclusion within the
228 organic macrocycle since the chemical shift of the internal H3 proton remains unaffected. It
229 appears therefore clear that the α - and β -CD interact mostly with the POM through their outer
230 surface, while γ -CD leads to the usual host–guest inclusion, involving its internal cavity. The α -
231 and β -CD are too small to entirely accommodate Keggin-type POM in their central cavity.
232



233
 234 Fig. 6. ^1H NMR titration of 4 mM α -, β -, and γ -CD in D_2O by Keggin-type POM $[\text{PMo}_{12}\text{O}_{40}]^{3-}$.
 235 Reproduced from reference.⁵¹

236

237 The use of ^{13}C NMR in titration is rather rare due to the very poor sensitivity compared to ^1H

238 NMR despite the considerable gain in resolution. As an example of such experiments, Fig. 7

239 shows the obtained $^{13}\text{C}\{^1\text{H}\}$ NMR of 3 mM γ -CD titrated by the rhenium clusters $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$

240 and $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ up to 8 equivalents.⁶ The behavior of the CD in the presence of the two

241 clusters is different. First, C1 and C4 signals undergo deshielding with the selenide cluster, while

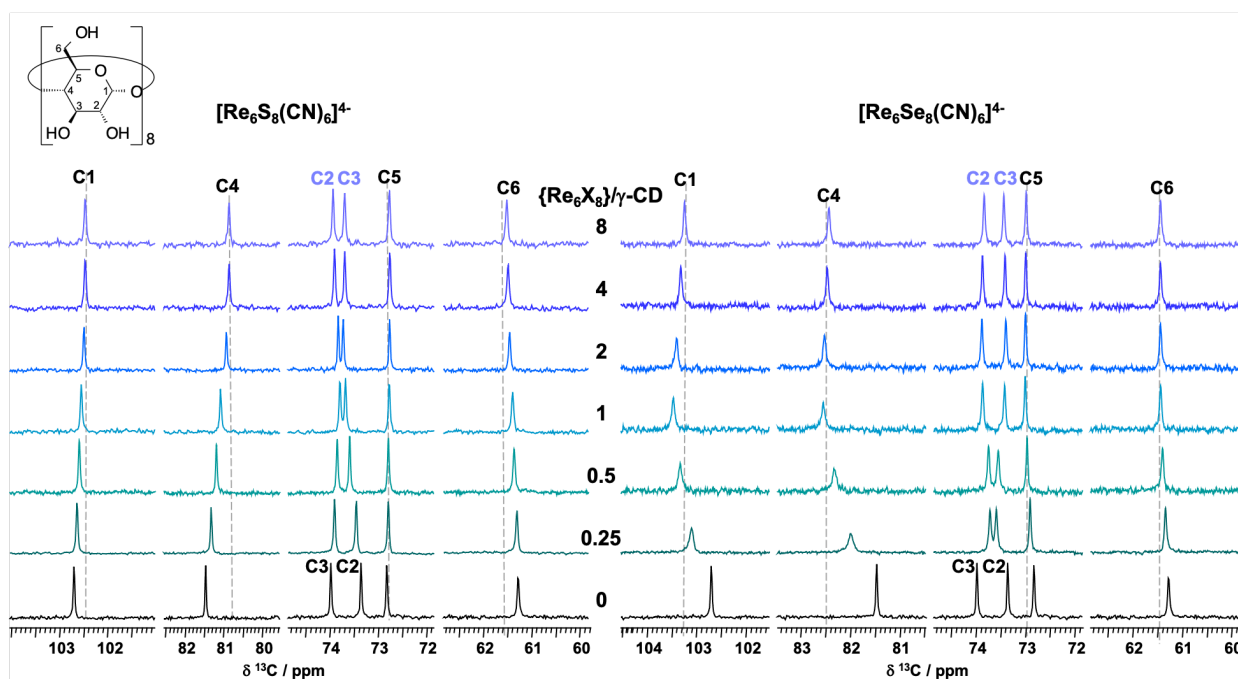
242 these signals evolve toward the reverse shielding direction with the sulfide cluster. Secondly,

243 the variations of signal position are faster (lower cluster equivalents) with the Se-based cluster

244 than the S-based cluster. For instance, the crossing of the C2 and C3 signals happens at ca. 0.25

245 equivalent of $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$, while it occurs at ca. 2 equivalents of $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$. This result

246 indicates stronger affinity between the CD and $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ than $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ in agreement
 247 with the difference in association constants measured for these clusters, $K_{1:1} = 1500$ vs 900 M^{-1} ,
 248 respectively (see Table 2).
 249



250
 251 Fig. 7. $^{13}\text{C}\{^1\text{H}\}$ NMR titration of 3 mM γ -CD in D_2O by (left) $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ and (right)
 252 $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$.

253
 254
 255

3. Quantitative analysis: Determination of binding constants

256 NMR is a quantitative analytical tool for studying chemical equilibria and dynamic phenomena.⁵²
 257 The association constants between the polynuclear cluster and the host CD can be determined from
 258 NMR titration by applying mathematical approach.^{53,54} In the case of a fast chemical exchange
 259 regime relative to the NMR time scale, when a single NMR signal representative of all the different
 260 binding states is observed, the variation in the apparent chemical shift (δ_{obs}) of the CD resonances
 261 should correspond to a linear combination of the individual chemical shifts of the CD in its

262 different states, *i.e.*, the free CD and the 1:1, 1:2, ... etc. adducts, noted respectively δ_0 , $\delta_{1:1}$, $\delta_{1:2}$
 263 , ... etc. This relationship illustrated by equation (1) implies mole fractions x_0 , $x_{1:1}$, $x_{1:2}$, ... etc. of
 264 each CD species in free and adduct forms of 1:1, 1:2, ... etc.

$$265 \quad \delta_{obs} = x_0\delta_0 + x_{1:1}\delta_{1:1} + x_{1:2}\delta_{1:2} + \dots etc. \quad (1)$$

266 In the simplest case of a 1:1 adduct, the association constant K is given by equation (2), using the
 267 CD molar fractions x_0 and $x_{1:1}$ and expressed as a function of the initial CD concentration C^0 and
 268 the molar ratio $R = [\text{Cluster}]/[\text{CD}]$.

$$269 \quad K = \frac{x_{1:1}}{x_0 \left(R - \left(\frac{1 - x_0 + x_{1:1}}{2} \right) \right) C^0} \quad (2)$$

270 By combining equations (1) and (2), and assuming that $x_0 + x_{1:1} = 1$, we can deduce the expression
 271 of the observed chemical shift as a function of binding constant K (eqn (3)).

$$272 \quad \delta_{obs} = \delta_0 \left[\frac{KC^0 - KC^0R - 1 + \sqrt{(KC^0R - KC^0 + 1)^2 + 4KC^0}}{2KC^0} \right] + \delta_{1:1} \left[\frac{KC^0 + KC^0R + 1 - \sqrt{(KC^0R - KC^0 + 1)^2 + 4KC^0}}{2KC^0} \right] \quad (3)$$

273 Modeling the experimental data ($\delta_{obs} = f(R)$) with equation (3) enables us to estimate the binding
 274 constant K for the 1:1 complexation model. The individual chemical shifts (δ_0 and $\delta_{1:1}$) can be
 275 measured from independent experiments of a free CD solution and a solution with a large excess
 276 of Cluster over CD, respectively. For a more complex model, such as a 1:2 adduct, it becomes
 277 difficult to use this NMR approach to resolve the binding constants $K_{1:1}$ and $K_{1:2}$ due to the
 278 overparameterization. Indeed, prior knowledge of the individual chemical shifts $\delta_{1:1}$ and $\delta_{1:2}$, is
 279 required, that are difficult to determine in fast exchange spectra. In this case, other experimental
 280 techniques such as ITC would be more appropriate.

281 Thus, ¹H NMR is a useful internal probe to identify the nature and the strength of the
 282 supramolecular interaction between CD and inorganic clusters. In particular, the binding sites
 283 (e.g., secondary *versus* primary face), the location of the interaction (e.g., the interacting proton),
 284 and the association constants are the most valuable information determined. As a result, several
 285 types of CD-cluster hybrids are obtained from weak surface contact adducts to deeply
 286 encapsulated host-guest complexes.^{30,41,55} Tables 1-3 summarize the main CD-based hybrid
 287 adducts and complexes observed with POM, boron, and octahedral metal-atom clusters studied
 288 in solution by NMR.

289

290 Table 1. Summary of reported CD-POM adducts studied in solution by NMR.

CD	POM	CD•POM adduct ^a	binding site ^b	Most affected H	Δδ (ppm) ^c	Binding constant $K_{1:1}$ (10^3 M ⁻¹) ^d	Ref.
α-CD	[PW ₁₂ O ₄₀] ³⁻	CD•POM	P. F.	H6	+0.20	0.98	51,56
	[P ₂ W ₁₇ O ₆₁ {Sn(C ₆ H ₄ I)}] ⁷⁻	POM@CD	S. F.	H5	+0.16	0.78	19
	[P ₂ Mo ₅ O ₂₃] ⁶⁻	CD•POM	E. W.	-	0	-	57
	[AlMo ₆ (OH) ₆ O ₁₈] ³⁻	3CD•4POM	E. W.	H2	+0.06	-	58
	[PMo ₁₂ O ₄₀] ³⁻	-	P. F.	H6	+0.20	0.26	51
	[V ₆ O ₁₃ ((OCH ₂) ₃ C-CH ₂ CH ₃) ₂] ²⁻	-	S. F.	H5	-0.04	0.23	59
	[V ₆ O ₁₃ ((OCH ₂) ₃ C-NO ₂) ₂] ²⁻	POM@CD	P. F.	H3	-0.01	0.30	59
	[V ₆ O ₁₃ ((OCH ₂) ₃ C-CH ₂ OH) ₂] ²⁻	-	-	-	0	-	59
	[V ₆ O ₁₃ ((OCH ₂) ₃ C-NH(BOC)) ₂] ^{2-e}	-	P. F.	H5	+0.12	0.36	59
[MPd ₁₂ O ₈ (PhAsO ₃) ₈] ^{2-f}	POM@2CD	S. F.	H3	-0.03	-	35	
β-CD	[PW ₁₂ O ₄₀] ³⁻	-	P. F.	H6	+0.15	0.43	51
	[P ₂ W ₁₇ O ₆₁ {Sn(C ₆ H ₄ I)}] ⁷⁻	POM@CD	P. F.	H5	-0.29	1.0	19
	[P ₂ Mo ₅ O ₂₃] ⁶⁻	CD•POM	E. W.	-	0	-	57
	[MnMo ₉ O ₃₂] ⁶⁻	POM@CD	E. W.	H1/H2	-0.07	-	60
	[PMo ₁₂ O ₄₀] ³⁻	POM@2CD	P. F.	H6	+0.15	0.39	23,51
	[V ₆ O ₁₃ ((OCH ₂) ₃ C-CH ₂ CH ₃) ₂] ²⁻	-	S. F.	H5	-0.17	0.70	59
	[V ₆ O ₁₃ ((OCH ₂) ₃ C-NO ₂) ₂] ²⁻	POM@CD	S. F.	H5	-0.15	0.47	59

	$[\text{V}_6\text{O}_{13}((\text{OCH}_2)_3\text{C}-\text{CH}_2\text{OH})_2]^{2-}$	POM@2CD	S. F.	H5	-0.10	0.29	59
	$[\text{V}_6\text{O}_{13}((\text{OCH}_2)_3\text{C}-\text{NH}(\text{BOC}))_2]^{2-e}$	POM@2CD	S. F.	H5	-0.10	1.2	59
γ -CD	$[\text{W}_6\text{O}_{19}]^{2-}$	POM@CD	I. C.	H5	+0.50	-	26
	$[\text{PW}_{12}\text{O}_{40}]^{3-}$	POM@CD	S. F.	H3	+0.53	140	25,51,54,61
	$[\text{SiW}_{12}\text{O}_{40}]^{4-}$	-	P. F.	H6	+0.30	17	25,38
	$[\text{BW}_{12}\text{O}_{40}]^{5-}$	CD•POM	P. F.	H6	+0.33	1.1	25
	$[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$	-	P. F.	H6	+0.07	0.023	25
	$[\text{SiW}_{11}\text{MoO}_{40}]^{4-}$	-	P. F.	H6	+0.29	11	54
	$[\text{SiW}_{11}\text{MoO}_{40}]^{5-}$	-	P. F.	H6	+0.10	0.73	54
	$[\text{PW}_{11}\text{VO}_{40}]^{4-}$	-	P. F.	H6	+0.31	7.8	54
	$[\text{PW}_{11}\text{VO}_{40}]^{5-}$	-	P. F.	H6	+0.10	0.86	54
	$[\text{SiW}_{11}\text{VO}_{40}]^{5-}$	-	P. F.	H6	+0.28	0.39	54
	$[\text{SiW}_{11}\text{VO}_{40}]^{6-}$	-	-	-	0	0.13	54
	$[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$	POM@2CD	P. F.	H6	+0.30	3.2	28
	$[\text{P}_3\text{W}_{30}\text{O}_{110}]^{15-}$	CD•POM	S. F.	H6	+0.05	0.43	27
	$[\text{P}_2\text{Mo}_5\text{O}_{23}]^{6-}$	CD•POM	E. W.	-	0	-	57
	$[\text{Mo}_6\text{O}_{19}]^{2-}$	POM@CD	I. C.	H5	+0.65	-	26
	$[\text{AlMo}_6(\text{OH})_6\text{O}_{18}]^{3-}$	CD•POM	E. W.	H2	+0.02	-	58
	$[\text{An}-\text{AlMo}_6(\text{OH})_3\text{O}_{18}]^{3-g}$	-	I. C.	H5	-0.40	-	18
	$[\text{An}_2-\text{MnMo}_6\text{O}_{18}]^{3-g}$	-	I. C.	H5	-0.40	-	18
	$[\text{MnMo}_9\text{O}_{32}]^{6-}$	POM@2CD	E. W.	H2	-0.11	-	60
	$[\text{PMo}_{12}\text{O}_{40}]^{3-}$	POM@2CD	S. F.	H3	+0.70	56	23,51
	$[\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$	CD@POM	E. W.	H2	+0.50	-	30
	$[\text{V}_6\text{O}_{13}((\text{OCH}_2)_3\text{C}-\text{CH}_2\text{CH}_3)_2]^{2-}$	-	P. F.	H6	+0.11	0.32	59
	$[\text{V}_6\text{O}_{13}((\text{OCH}_2)_3\text{C}-\text{NO}_2)_2]^{2-}$	POM@2CD	P. F.	H5	+0.24	1.4	59
	$[\text{V}_6\text{O}_{13}((\text{OCH}_2)_3\text{C}-\text{CH}_2\text{OH})_2]^{2-}$	POM@2CD	P. F.	H6	+0.12	0.090	59
	$[\text{V}_6\text{O}_{13}((\text{OCH}_2)_3\text{C}-\text{NH}(\text{BOC}))_2]^{2-e}$	-	P. F.	H6	+0.22	1.0	59

291 a) From crystal structure when available. b) P. F. = primary face, S. F. = secondary face, E. W.
292 = external wall, I. C. = internal cavity. c) difference in NMR chemical shift of most affected
293 CD proton between its free and bound states, $\Delta\delta = \delta_{\text{bound}} - \delta_{\text{free}}$. d) calculated by NMR or
294 ITC. e) BOC = N-tert-butoxycarbonyl. f) M = Co, Ni, Zn. g) An = anthracene group.

296

297 Table 2. Summary of reported CD-octahedral metal cluster adducts studied in solution by NMR.

CD	{M ₆ } cluster	CD-Cluster adduct ^a	binding site ^b	Most affected H	Δδ (ppm) ^c	Binding constant K _{1:1} (10 ³ M ⁻¹) ^d	Ref.
α-CD	[Re ₆ S ₈ (CN) ₆] ⁴⁺	Cluster@2CD	S. F.	H3	+0.15	0.27	41
	[Re ₆ Se ₈ (CN) ₆] ⁴⁺	CD•POM	S. F.	H3	+0.15	0.030	41
	[Re ₆ Te ₈ (CN) ₆] ⁴⁺	2CD•POM	E. W.	-	0	0	41
β-CD	[Re ₆ S ₈ (CN) ₆] ⁴⁺	Cluster@2CD	S. F.	H3	+0.30	0.64	41
	[Re ₆ Se ₈ (CN) ₆] ⁴⁺	Cluster@2CD	S. F.	H3	+0.45	0.78	41
	[Re ₆ Te ₈ (CN) ₆] ⁴⁺	Cluster@2CD	S. F.	H3	+0.15	0.084	41
γ-CD	[Re ₆ S ₈ (CN) ₆] ⁴⁺	Cluster@2CD	S. F.	H3	+0.40	0.90	6
	[Re ₆ Se ₈ (CN) ₆] ³⁻	Cluster@2CD	S. F.	H3	+0.2	225	49
	[Re ₆ Se ₈ (CN) ₆] ⁴⁺	Cluster@2CD	S. F.	H3	+0.45	1.5	6
	[Re ₆ Te ₈ (CN) ₆] ⁴⁺	Cluster@2CD	S. F.	H5	+0.35	38	6
	[Re ₆ S ₈ (H ₂ O) ₆] ²⁺	Cluster@2CD	S. F.	-	0	-	62
	[Nb ₆ Cl ₁₂ (H ₂ O) ₆] ²⁺	Cluster@2CD	E. W.	H1/H4	-0.08	2.2	1
	[W ₆ Br ₈ Cl ₆] ²⁻	Cluster@2CD	S. F.	H3	+0.46	-	48
	[W ₆ I ₈ Cl ₆] ²⁻	Cluster@2CD	S. F.	H3	+0.60	-	48
	[Mo ₆ Br ₈ Cl ₆] ²⁻	Cluster@2CD	S. F.	H5	+0.40	-	63
	[Mo ₆ I ₈ Cl ₆] ²⁻	Cluster@2CD	S. F.	H5	+0.60	-	63
	[Mo ₆ Cl ₁₄] ²⁻	Cluster@2CD	S. F.	H3/H5	+0.04	-	50
	[Ta ₆ Br ₁₂ (H ₂ O) ₆] ²⁺	Cluster@2CD	S. F.	H3	+0.60	150	28

298 a) From crystal structure. b) S. F. = secondary face, E. W. = external wall. c) difference in NMR
 299 chemical shift of most affected CD proton between its free and bound states, Δδ = δ_{bound} –
 300 δ_{free}. d) calculated by NMR or ITC.

301

302 Table 3. Summary of reported CD-boron cluster adducts studied in solution by NMR.

CD	Boron cluster	CD-Cluster adduct ^a	binding site ^b	Most affected H	Δδ (ppm) ^c	Binding constant K _{1:1} (10 ³ M ⁻¹) ^d	Ref.
α-CD	[B ₁₀ H ₁₀] ²⁻	Cluster@CD	S. F.	H3	+0.05	0.035	55
	[B ₁₀ H ₉ NCCH ₃] ⁻	-	S. F.	H3	+0.06	0.034	53
	[B ₁₂ H ₁₂] ²⁻	-	-	-	0	-	22
	[B ₁₂ H ₁₁ SH] ²⁻	-	-	-	0	-	22
	[(1,2-C ₂ B ₉ H ₁₁) ₂ -3,3'-Co] ⁻	-	S. F.	H3	+0.25	-	42

	[(1,2-Me ₂ -1,2-C ₂ B ₉ H ₉) ₂ -3,3'-Co]	-	S. F.	H3	+0.10	-	42
	[(8,8'-Cl ₂ -(1,2-C ₂ B ₉ H ₁₀) ₂ -3,3'-Co]	-	S. F.	H3	+0.10	-	42
	[(8-I-1,2-C ₂ B ₉ H ₁₀)(1',2'-C ₂ B ₉ H ₁₁)-3,3'-Co]	-	S. F.	H3	+0.15	-	42
β-CD	[B ₁₀ H ₁₀] ²⁻	Cluster@CD ^e	I. C.	H5	+0.19	0.11	55
	[B ₁₀ H ₉ NCCH ₃]	-	P. F.	H5	+0.15	0.30	53
	[B ₁₂ H ₁₂] ²⁻	-	-	-	0	-	22
	[B ₁₂ H ₁₁ SH] ²⁻	-	S. F.	H5	+0.32	-	22
	[B ₁₂ I ₁₂] ²⁻	-	P. F.	H6	+0.15	-	22
	[B ₁₂ I ₁₁ -NH ₂ C ₆ H ₄ -m-NO ₂] ¹⁻	-	-	H3	+0.10	18	64
	[B ₁₂ I ₁₁ -NH ₂ C ₆ H ₄ -p-NO ₂] ¹⁻	Cluster@CD ^e	S. F./I. C.	H3	-0.15	19	64
	[B ₁₂ I ₁₁ -S ₂ C ₆ H ₂ -N ₂ O-p-NO ₂] ¹⁻	Cluster@CD ^e	S. F.	H1/H2	-0.10	270	65
	[B ₁₂ I ₁₁ -S ₂ C ₄ H ₈ N-C ₆ H ₂ -N ₂ O-p-NO ₂] ¹⁻	-	-	H6	-0.15	260	65
	[B ₁₂ Br ₁₂] ²⁻	-	S. F.	H3	+0.08	-	22
	[(1,2-C ₂ B ₉ H ₁₁) ₂ -3,3'-Co]	-	S. F.	H3	+0.20	26	42
	[(1,2-Me ₂ -1,2-C ₂ B ₉ H ₉) ₂ -3,3'-Co]	-	S. F.	H3	+0.30	21	42
	[(8,8'-Cl ₂ -(1,2-C ₂ B ₉ H ₁₀) ₂ -3,3'-Co]	-	S. F.	H3	+0.27	19	42
	[(8-I-1,2-C ₂ B ₉ H ₁₀)(1',2'-C ₂ B ₉ H ₁₁)-3,3'-Co]	-	S. F.	H3	+0.25	24	42
γ-CD	[B ₁₀ H ₁₀] ²⁻	Cluster@CD ^e	I. C.	H5	+0.19	0.060	55
	[B ₁₀ H ₉ NCCH ₃]	-	P. F.	H5	+0.18	0.72	53
	[B ₁₂ H ₁₂] ²⁻	Cluster@CD ^e	S. F.	H5	+0.15	2.0	22
	[B ₁₂ H ₁₁ SH] ²⁻	Cluster@CD ^e	S. F.	H5	+0.32	7.8	22
	[B ₁₂ Cl ₁₂] ²⁻	Cluster@CD ^e	S. F.	H3	+0.35	17	22
	[B ₁₂ Br ₁₂] ²⁻	Cluster@2CD	S. F.	H5	+0.70	960	22
	[B ₁₂ I ₁₂] ²⁻	Cluster@CD ^e	S. F.	H1	+0.10	67	22
	[B ₁₂ H ₁₁ OH] ²⁻	-	S. F.	H5	+0.10	0.62	22
	[B ₁₂ H ₁₁ NH ₃] ²⁻	-	S. F.	H3	+0.05	1.7	22
	[B ₁₂ H ₁₁ N(CH ₂ CH ₂ CH ₃) ₃] ²⁻	-	P. F.	H6	+0.05	1.1	22
	[B ₁₂ H ₁₁ O(CH ₂) ₄ C(NH ₂)CO ₂ H] ²⁻	-	S. F.	H5	+0.20	-	22
	[B ₁₂ I ₁₁ -NH ₂ C ₆ H ₄ -m-NO ₂] ¹⁻	-	-	H5	+0.20	9.6	64
	[B ₁₂ I ₁₁ -NH ₂ C ₆ H ₄ -p-NO ₂] ¹⁻	-	-	H5	+0.15	7.6	64
	[B ₁₂ I ₁₁ -NH ₂ C ₆ H ₄ -m-NO ₂] ¹⁻	-	-	H6	+0.20	150	65
	[B ₁₂ I ₁₁ -NH ₂ C ₆ H ₄ -p-NO ₂] ¹⁻	-	-	H6	+0.15	590	65
	[(1,2-C ₂ B ₉ H ₁₁) ₂ -3,3'-Co]	-	P. F.	H6	+0.10	191	42

[(1,2-Me ₂ -1,2-C ₂ B ₉ H ₉) ₂ -3,3'-Co]	-	S. F.	H3	+0.10	300	42
[(8,8'-Cl ₂ -(1,2-C ₂ B ₉ H ₁₀) ₂ -3,3'-Co]	-	S. F.	H3	+0.15	3600	42
[(8-I-1,2-C ₂ B ₉ H ₁₀)(1',2'-C ₂ B ₉ H ₁₁)-3,3'-Co]	-	S. F.	H3	+0.15	1300	42

303 a) From crystal structure when available. ^{b)} P. F. = primary face, S. F. = secondary face, I. C.
304 = internal cavity. ^{c)} difference in NMR chemical shift of most affected CD proton between
305 its free and bound states, $\Delta\delta = \delta_{\text{bound}} - \delta_{\text{free}}$. ^{d)} calculated by NMR or ITC. ^{e)} From DFT
306 calculation.

307

308

309 4. Relaxation and line broadening

310 Supramolecular contact may induce line broadening due to dipolar coupling between neighboring
311 nuclear spins, and linewidths could be used as a probe to assess the strength of these interactions
312 and the interatomic distances. In presence of paramagnetic atoms, the effect should even be
313 amplified since the dominant NMR relaxation mechanisms are connected to the coupling of the
314 strong magnetic moment of the unpaired electron with the adjacent nuclear magnetic moment.
315 Examples of NMR studies involving paramagnetic species include reduced POMs and oxidized
316 octahedral clusters.^{49,54} Dramatic line broadening of NMR signals of the CD has been observed
317 upon host-guest complexation, particularly those present in the inner sites (H3 and H5).
318 Furthermore, relaxation studies showed significant decreases of relaxation rates T_1 and T_2 for these
319 specific protons up to two-order of magnitude.⁴⁹ Interestingly, longitudinal relaxation T_1 was found
320 to discriminate interacting protons better than the transverse relaxation T_2 .

321

322

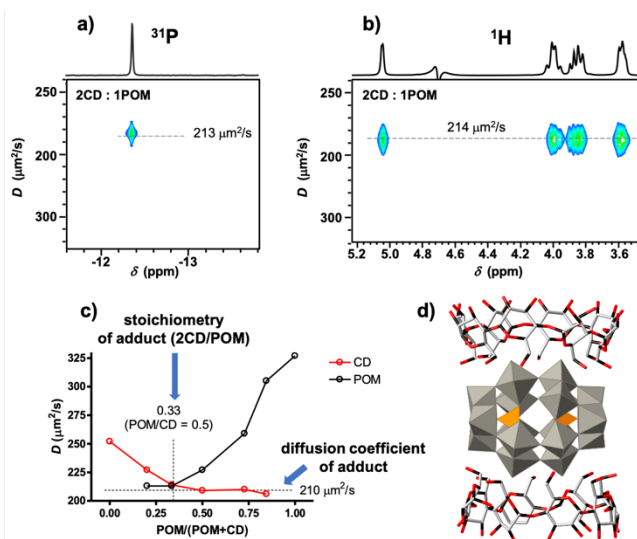
323 5. DOSY and 2D NMR tools to track aggregation and self-assembly

324 Diffusion Ordered Spectroscopy (DOSY) and Nuclear Overhauser Effect Spectroscopy
325 (NOESY) or Rotating frame Overhauser Effect Spectroscopy (ROESY) are the most used 2D

326 NMR techniques to study the interaction of CD with organic, inorganic and hybrid guests. DOSY
327 is the 2D version of pulsed field gradient (PFG) NMR measurement, used to determine the self-
328 diffusivity of dissolved species. Thus, DOSY experiment correlates the chemical shift with the
329 diffusion coefficient in the second dimension. This technique can allow differentiation between
330 free and aggregated CD to other species or between them, and thus provide information about
331 binding and exchange in CD-based supramolecular systems. As an example, the ¹H DOSY
332 experiment revealed the host-guest complex formation between the Lindqvist-type functionalized
333 hexavanadate [V₆O₁₃((OCH₂)₃C-NO₂)₂]²⁻ and γ -CD.⁵⁹ The diffusion coefficient of the free hybrid
334 POM in 2 mM D₂O drops from around 450 to 300 $\mu\text{m}^2/\text{s}$ when complexed with γ -CD, as a clear
335 indication of the POM encapsulation process within the macrocycle. The diffusion coefficient of
336 the free CD also decreased in the presence of POM, but only slightly, as the volume/size of the
337 complex is dominated by that of CD. Nonetheless, the diffusion coefficient of hybrid POM is not
338 perfectly aligned with that of the host molecule, indicating dynamic dissociation in solution.
339 DOSY has thus proved an efficient technique for quantitatively studying chemical equilibria and
340 exchange processes in CD-based hybrids with inorganic nanoclusters.^{25,28}

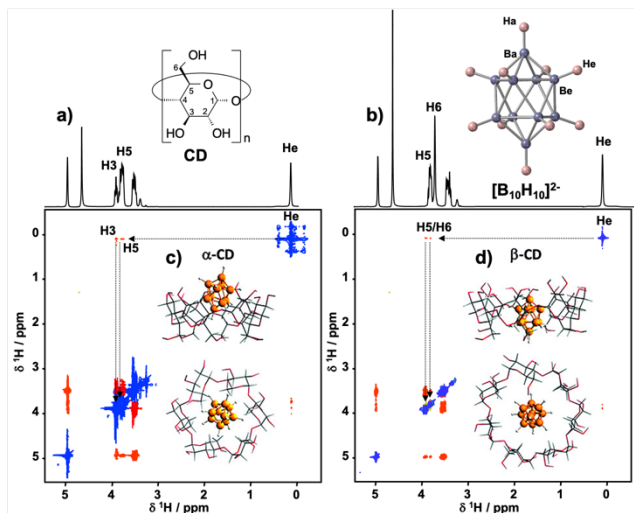
341 For example, the formation of aggregates between γ -CD and Dawson-type POM [P₂W₁₈O₆₂]⁶⁻
342 has been well demonstrated by ¹H and ³¹P DOSY NMR, providing simultaneous access to the self-
343 diffusion coefficient of γ -CD and that of the POM species, respectively.¹⁵ The DOSY
344 investigation, graphically shown in Fig. 8 reveals that the self-diffusion coefficients of the
345 interacting substrates decrease significantly in the POM/ γ -CD mixture that underline the formation
346 of stable aggregates in solution. Interestingly, the *D* value of both interacting components reaches
347 together the same minimum value at *D* = 210 $\mu\text{m}^2/\text{s}$ observed for the composition range close to
348 the 1:2 ratio ($\frac{POM}{POM+CD} = 0.33$). This result highlights that stable aggregates are formed provoking

349 large changes of self-diffusion coefficients of each component in the presence of large excess of
 350 the corresponding partner (see Fig. 8c). These DOSY NMR data corroborate nicely the analysis
 351 given by Stoddart et al. from SAXS/WAXS measurements carried out on aqueous solution
 352 containing the Keggin-type anion and γ -CD.¹⁰ However, it is interesting to note that structural
 353 analysis by XRD (Fig. 8d) reveals that POM and CDs assemble through weak interactions
 354 highlighted by minimal variations in NMR chemical shifts (^1H , ^{183}W , and ^{31}P), while DOSY or
 355 SAXS/WAXS studies demonstrate that these hydrophilic species form stable aggregates in
 356 aqueous solution. This demonstrates the high sensitivity of the DOSY technique to supramolecular
 357 interaction.
 358



359
 360 Fig. 8. 2D DOSY (a) ^{31}P and (b) ^1H spectra of a mixture of 2:1 γ -CD (3 mM): Dawson POM
 361 $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ (1.5 mM) revealing common diffusion coefficient at ca. $214 \mu\text{m}^2/\text{s}$. (c) Diffusion
 362 coefficients of the host (CD) and the guest (POM) measured by ^1H and ^{31}P DOSY as a function of
 363 POM fraction in POM-CD system. The two curves cross at POM/CD ratio of 0.5 corresponding
 364 to the stoichiometry of (d) the sandwich adduct evidenced by single crystal XRD. Adapted from
 365 reference.¹⁵
 366

367 NOE-based experiments such as NOESY and ROESY are techniques of choice for studying
368 non-covalent interactions in supramolecular systems involving cavitand molecules such as CDs.
369 Such NMR methodologies based on “through space” interactions (or dipolar coupling) allow
370 insight into which parts of a guest molecule are in spatial proximity to the hosting unit. ROESY
371 is generally preferred to NOESY for the study of nanoscopic assemblies built with CD, as it
372 enables to probe longer distances up to 5 Å and provides positive ROE signal for
373 macromolecules and large chemical complexes. The sign of the NOE/ROE signals is an
374 important parameter for differentiating other dynamic phenomena such as spin diffusion and
375 exchange process, which lead to negative cross-peaks like the diagonal signals. Fig. 9 shows an
376 example of application of ROESY experiment to the CD/[B₁₀H₁₀]²⁻ systems.⁵⁵ For a 1:1 mixture
377 of α-CD/[B₁₀H₁₀]²⁻, the interactions between equatorial protons of the boron cluster He, with H3
378 and H5 internal protons of the α-CD are revealed through the occurrence of cross NOE peaks.
379 For β-CD, the cross ROE peaks between the unresolved resonances of H5/H6 of the CD and
380 both Ha and He of [B₁₀H₁₀]²⁻ indicate interactions between hydrogen atoms of the boron cluster
381 and the CD. These results are fully consistent with the DFT-optimized structures of the adducts
382 showing partially embedded cluster through the secondary face of α-CD and fully encapsulated
383 cluster within the β-CD cavity. ROESY NMR technique has been employed successfully to
384 probe the host-guest contacts through space occurring in solution between β-CD and Lindqvist-
385 type hybrid hexavanadates.⁵⁹ Strong correlations were generally observed between the organic
386 part of [V₆O₁₃((OCH₂)₃C-R)₂]²⁻ derivatives, R = CH₂OH, CH₂CH₃, NO₂, and internal protons of
387 the CD (mostly H3 and H5) fairly consistent with the host-guest structures observed in the solid-
388 state. Recent examples of zirconium oxoclusters have also been reported.⁶⁶
389



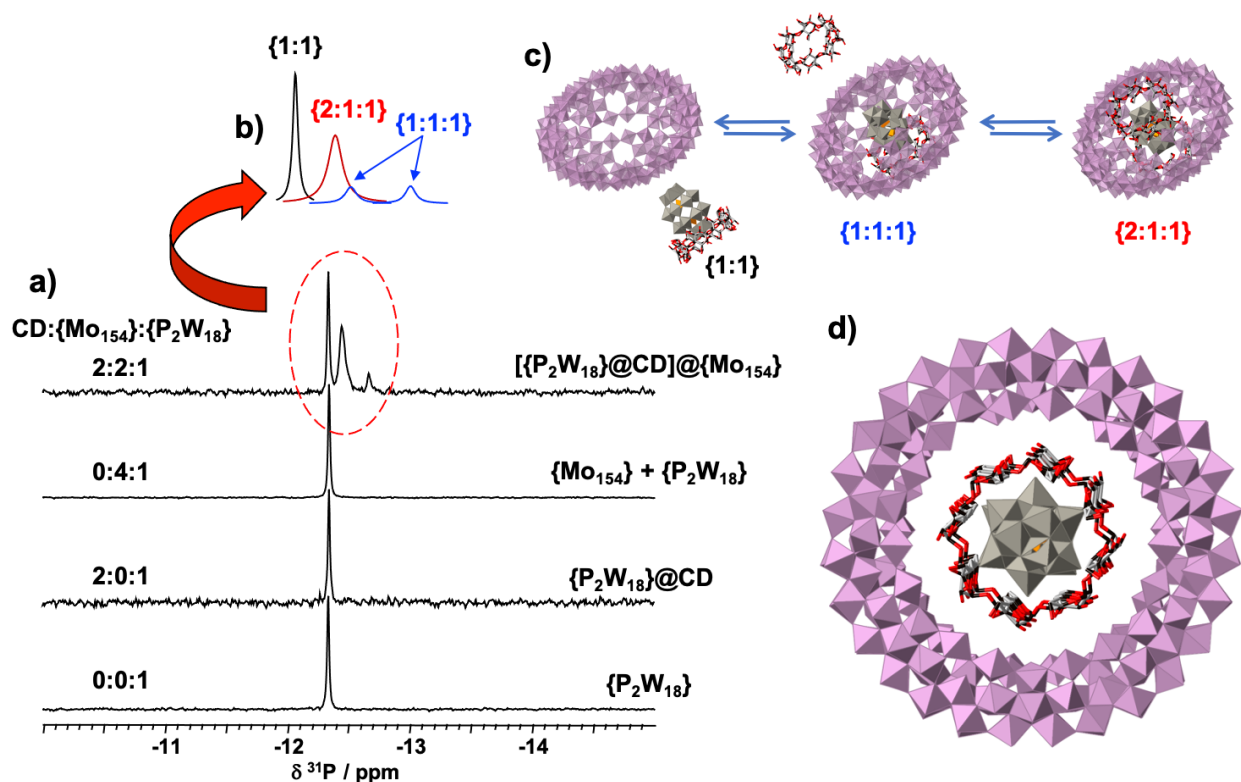
390
 391 Fig. 9. 1D and 2D ^1H - $^1\text{H}\{^{11}\text{B}\}$ ROESY NMR spectra in D_2O of a 1:1 mixture of (a) $\alpha\text{-CD}/[\text{B}_{10}\text{H}_{10}]^{2-}$
 392 and (b) $\beta\text{-CD}/[\text{B}_{10}\text{H}_{10}]^{2-}$. (c) and (d) the corresponding optimized DFT structures of the CD-cluster
 393 adducts. Adapted from reference.⁵⁵

394

395

396 6. Use of guest NMR probes

397 When available other NMR nuclei than ^1H and ^{13}C of the host can be used to probe the
 398 supramolecular interaction between the CD and the inorganic guest. These NMR nuclei should
 399 then be present in the cluster part of the hybrid assembly, providing additional characterization
 400 from the guest's point of view. For example, ^{31}P NMR is used to follow the Dawson-type POM in
 401 the ternary system $\gamma\text{-CD}:[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}:[\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$.³⁰ In the binary system $\gamma\text{-CD}:$
 402 $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, the characteristic signal of the POM appeared similar to that of the free species at -
 403 12.3 ppm as an indication of labile dynamic $\{1:1\}$ complex (Fig. 10). Introducing the giant blue
 404 wheel $\{\text{Mo}_{154}\}$ had led to resolved three additional signals assigned to POM@POM assembly with
 405 one and two capping CDs, $\{1:1:1\}$ and $\{2:1:1\}$, respectively (Fig. 10). Such a frozen three-
 406 component assembly is made possible by the CD binding ability, which enables to bring two
 407 anionic species closer together. Indeed, no interaction could be observed in the absence of CD.



409

410 Fig. 10. (a) ^{31}P NMR spectrum in D_2O of Dawson POM $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ in the presence of γ -CD and
 411 the molybdenum blue wheel $[\text{Mo}_{154}\text{O}_{462}\text{H}_{14}(\text{H}_2\text{O})_{70}]^{14-}$ compared to the spectra in the absence of
 412 one of them or both of them. The spectrum in the ternary system can be decomposed into (b) three
 413 components corresponding to the labile $\{1:1\}$ CD: $\{\text{P}_2\text{W}_{18}\}$, and the ternary complexes $\{1:1:1\}$ and
 414 $\{2:1:1\}$ in the CD: $\{\text{P}_2\text{W}_{18}\}$: $\{\text{Mo}_{154}\}$ system in (c) equilibrium in solution. The crystallographic
 415 structure of the $\{2:1:1\}$ adduct (d) is consistent with a “host in host” hierarchical
 416 POM@CD@POM structure. Adapted from reference.³⁰

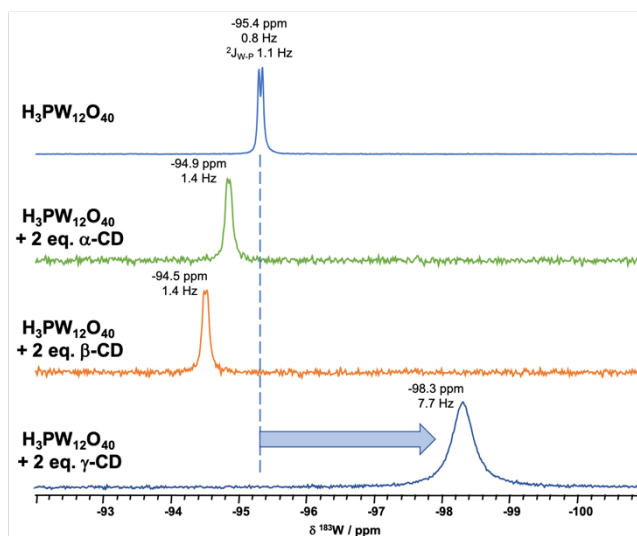
417

418 In labile dynamically systems, ^{31}P NMR could not sense efficiently the host-guest interaction
 419 between the POM and the CD when the phosphorus is located in the internal pocket of the POM.

420 The nucleus is in somehow shielded by the surrounding metal atoms, which protect the heteroatom
 421 from interaction with the surrounding environment. This is the case of the Dawson-type POM
 422 shown in Fig. 10 when exposed to CDs. However, external nuclei at the surface of the POM, such
 423 as ^{183}W NMR, should exhibit higher sensitivity towards supramolecular interaction at their surface.

424 Fig. 11 shows the effect of presence of α -, β -, and γ -CD on the ^{183}W NMR of $[\text{PW}_{12}\text{O}_{40}]^{3-}$.⁵¹

425



426

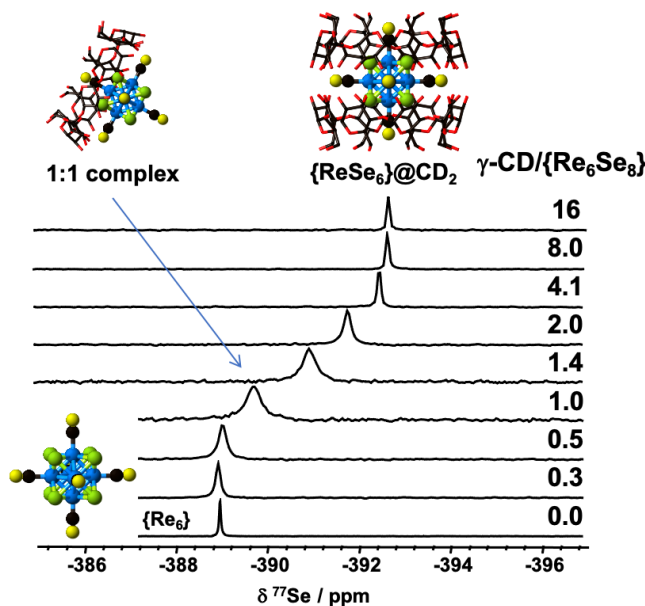
427 Fig. 11. ^{183}W NMR spectra in D_2O of 7.5 mM Keggin-type POM $[\text{PW}_{12}\text{O}_{40}]^{3-}$ in the absence and
 428 presence of 2 equivalents of α -, β -, and γ -CD. Adapted from reference.⁵¹

429

430 The Keggin POM $[\text{PW}_{12}\text{O}_{40}]^{3-}$ is characterized by a single sharp ^{183}W signal at -95.4 ppm
 431 corresponding to the 12 W equivalent nuclei of the POM structure (Fig. 11). This signal is actually
 432 a doublet due to the scalar coupling with the neighboring P heteroatom ($^2J_{\text{W-P}} = 1.1$ Hz). With the
 433 addition of two equivalents γ -CD, this signal broadens and shifts toward high fields of about 3
 434 ppm. These effects clearly indicate the formation of the inclusion complex with a very strong
 435 association, which provides a significant shielding on the W nuclei. The line broadening of the
 436 ^{183}W signal recalls that of the H3 proton of the CD (see Fig. 5) resulting from a strong host–guest
 437 contact. This interaction can therefore be tracked from the host side by ^1H NMR or the guest side
 438 by ^{183}W NMR. Furthermore, these effects are not observed with the other smaller CDs (Fig. 11),
 439 confirming the unique behavior of γ -CD highlighted by the formation of the inclusion complex.
 440 These effects are only moderately perceived by ^{31}P NMR, with a maximum variation of 0.4 ppm
 441 (from -14.3 to -14.7 ppm),⁵¹ while ^{183}W NMR recorded a difference of ca. 3 ppm, as the outer metal
 442 centers are more exposed to interaction with CD than the inner heteroatom.

443
 444 The metal transition octahedral clusters can also contain interesting active NMR nuclei. For
 445 instance, the $\frac{1}{2}$ -I nucleus ^{77}Se (7.63% natural abundance) has been used to study the interaction of
 446 the selenide rhenium cluster $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ with γ -CD.⁶ Fig. 12 shows the NMR titration of 24
 447 mM solution by increasing the amount of the CD progressively up to 16 equivalents. A single
 448 signal is observed shifting progressively from $\delta = -389$ ppm to the limiting value of -392.6 ppm.
 449 This indicates a fast exchange regime between the different cluster-based species, that is, solvated
 450 or embedded within γ -CD. The line broadening observed at intermediate CD equivalents (ca. 0.5
 451 to 2) is indicative of formation of 1:1 intermediate labile complex. Similar behavior is observed in
 452 ^1H NMR titration of the same system shown in Fig. 2a, where the most affected H3 resonance
 453 experienced major line broadening at intermediate cluster equivalents. Job plots shown in Fig. 13
 454 confirm the formation of the predominant 2:1 CD:Cluster type complex in aqueous solution as in
 455 the XRD structure.⁶

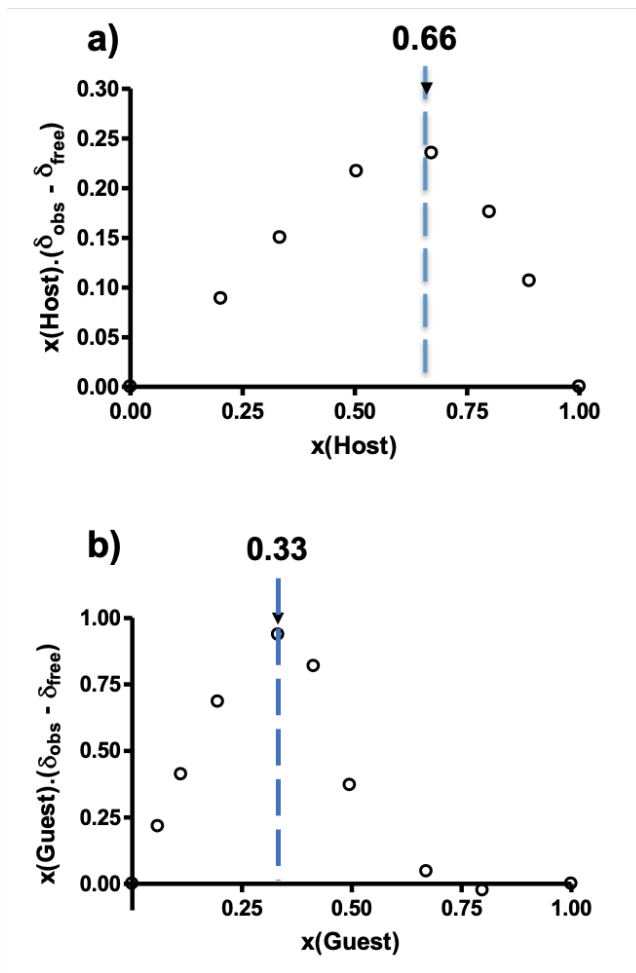
456



457
 458 Fig. 12. ^{77}Se NMR titration of 24 mM $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ in D_2O by γ -CD. Adapted from references.³⁶

459
460 Job plot allows determining the stoichiometry of the adducts in solution, and can be applied either
461 on the host or the guest. By plotting the product of the molar fraction of the host (CD) or the guest
462 (cluster) in the mixture by the difference between observed chemical shift of the host (H3) or the
463 guest (^{77}Se) in presence and absence of the cluster or the CD as a function of the molar fraction in
464 the host or the guest, respectively, maxima indicate the stoichiometry. Job's plots drawn in Fig. 13
465 both give consistent results with the formation of 2:1 adduct.

466



467
468 Fig. 13. Job plots obtained from NMR titration of (a) the host by the guest, or (b) the guest by the
469 host in the host-guest system $\gamma\text{-CD}:[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4+}$, by using ^1H NMR signal H3 of $\gamma\text{-CD}$ in (a)
470 (spectra shown in Fig. 2a), or ^{77}Se NMR signal of the cluster in (b) (spectra shown in Fig. 12).

471 **7. Concluding remarks and outlook**

472 Over the past decade, significant progress has been made in the development of host-guest
473 assemblies based on CDs and inorganic molecules, and this area of research continues to attract
474 growing interest. Understanding the phenomena at play in solution in these systems, and
475 characterizing them in their original environment, is essential for the search of new, more elaborate
476 and complex supramolecular functional materials. NMR has proven to be a versatile, flexible and
477 easy-to-implement technique for probing the weak interactions between these macrocycles and
478 inorganic cluster molecules such as POMs, octahedral metal-atom clusters or boron clusters.
479 Qualitative and quantitative information can be extracted by measuring the strength of mutual
480 interaction, identifying binding sites, and studying chemical equilibria and molecular exchange.

481 Future research should focus on a better understanding of the role of water in host-guest
482 complexation driven by solvent effect. NMR nuclei such as ^1H , ^2H , and ^{17}O would be excellent
483 probes for identifying local interaction sites and monitoring dynamic behavior. Of particular
484 interest, relaxation (T_2 and linewidth) and diffusion (DOSY) experiments could provide valuable
485 information. Variable-temperature NMR experiments can also shed light on molecular motions.
486 Finally, the gradual change in the nature of the medium from water to organic solvents (*e.g.*,
487 DMSO) may also bring insight on the proton exchange process involving the hydroxyl groups in
488 CD.

489 Nevertheless, with the ever-increasing complexity of these systems, the limits of the
490 technique could be rapidly reached as of the size of the aggregates increases and the viscosity of
491 the native medium decreases, as in hydrogels and supramolecular polymers. The restriction of
492 molecular motion is the main drawback of high-resolution NMR spectroscopy. In this case, other

493 techniques more suited to semi-fluids and soft matter systems, such as cryo-TEM, DLS, SAXS,
494 SANS, and solid-state NMR, can take over.

495 **Conflicts of interest**

496 The authors declare no competing financial interest.

497

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505

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