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Host-Guest Binding Hierarchy within Redox- and Luminescence Responsive Supramolecular Self-Assembly Based on Chalcogenide Clusters and \( \gamma \)-Cyclodextrin

Anton A. Ivanov, Clément Falaise, Pavel A. Abramov, Michael A. Shestopalov, Kaplan Kirakci, Kamil Lang, Mhamad A. Moussawi, Maxim N. Sokolov, Nikolay G. Naumov, Sébastien Floquet, David Landy, Mohamed Haouas, Konstantin A. Brylev, Yuri V. Mironov, Yann Molard, Stéphane Cordier and Emmanuel Cado
t*.

Abstract: Water-soluble salts of anionic \([\text{Re}_6\text{Q}(\text{CN})_6]^\text{5+}(\text{Q} = \text{S, Se, Te})\) chalcogenide octahedral rhenium clusters react with \( \gamma \)-cyclodextrin (\( \gamma \)-CD) producing a new type of inclusion compounds. Crystal structures determined through single-crystal X-ray diffraction analysis revealed supramolecular host-guest assemblies resulting from close encapsulations of the octahedral cluster within two \( \gamma \)-CDs. Interestingly, nature of the inner \( \text{Q} \) ligands influences strongly the host-guest conformation. The cluster \([\text{Re}_6\text{S}_4(\text{CN})_6]^\text{5+}\) interacts preferentially with the primary faces of the \( \gamma \)-CD while the bulkier clusters \([\text{Re}_6\text{Se}_4(\text{CN})_6]^\text{5+}\) and \([\text{Re}_6\text{Te}_4(\text{CN})_6]^\text{5+}\) exhibit specific interactions with the secondary faces of the cysyc host. Furthermore, analysis of the crystal packing reveals additional supramolecular interactions that lead to 2D infinite arrangements with \([\text{Re}_6\text{S}_4(\text{CN})_6]^\text{5+}\) or to 1D “bamboo-like” columns with \([\text{Re}_6\text{Se}_4(\text{CN})_6]^\text{5+}\) and \([\text{Re}_6\text{Te}_4(\text{CN})_6]^\text{5+}\) species. Solution studies, using multinuclear NMR methods, ESI-MS and isothermal titration calorimetry (ITC) corroborate nicely the solid state investigations showing that supramolecular pre-organization is retained in aqueous solution even in diluted conditions. Furthermore, ITC analysis showed that host-guest stability increases significantly ongoing from \( \text{S} \) to \( \text{Te} \). At last, we report herein that deep inclusion alters significantly the intrinsic physical-chemical properties of the octahedral clusters, allowing redox tuning and near IR luminescence enhancement.

Introduction

Self-assembly processes and structures driven by weak non-covalent interactions give rise to innumerable chemical events in living organisms.\(^{[1]}\) Resulting supramolecular organizations are of prime importance in functioning compartmentalized systems such as enzymes which conjugate sophisticated structures with highly specific molecular recognition involving cascade catalytic mechanisms.\(^{[2]}\) Thereby, self-assembly in biological systems have been often used as guiding models for designing “bio-inspired” sophisticated supramolecular complexes. Such a biomimicking approach has led to many efficient innovative systems in the field of artificial photosynthesis,\(^{[3]}\) catalysis\(^{[4]}\) or drug delivery.\(^{[5]}\)

Actually, development of new composite materials by controlling nature, specificity and strength of intermolecular interactions corresponds to an efficient strategy for the design of hierarchical hybrid assemblies with novel structures and emergent properties.\(^{[6]}\) In this context, host-guest type supramolecular arrangements are of particular interest, especially those that use cyclodextrins (CDs) as functional cavidades. Cyclodextrins are symmetrical macrocyclic cavatands consisting of six, seven, or eight glucopyranoside units named \( \alpha \)-, \( \beta \)-, or \( \gamma \)-CD, respectively.\(^{[7]}\) Due to their crown-like hydrophilic portals and hydrophobic inner cavity, CDs have received much interest as host receptors in encapsulations processes and hybrid assemblies.\(^{[8-10]}\) Their remarkable structural features have led to wide applications in separation, analysis, selective catalysis, materials and life sciences.\(^{[11]}\) Moreover, impressive inclusion capabilities and resulting synthetic host-guest systems create favorable conditions for substrate activation in the hydrophobic cavities of CDs via non-covalent interactions, thus mimicking enzymatic chemical reactions.\(^{[12]}\) Usually such biospired systems involve coordination\(^{[13]}\) or organometallic\(^{[14]}\) complexes closely embedded within the hydrophobic pocket of CDs. Nevertheless, little is known about supramolecular interactions of CDs with polynuclear species, such as metal clusters. Recently inclusion complexes with polyoxometalates\(^{[15]}\) and octahedral clusters\(^{[16,13]}\) were reported. Their structural investigations clearly demonstrate that stoichiometry,
conformation and spatial arrangement of the resulting host-guest adducts are highly sensitive to the nature of the guest, leading to highly contrasted behavior in solution, ranging from extremely labile assembly with \[\text{Re}^{\text{III}}\] to extremely highly sensitive to the nature of the guest, leading to adducts are highly sensitive to the nature of the guest, leading to highly contrasted behavior in solution, ranging from extremely labile assembly with \[\text{Re}^{\text{III}}\] to extremely high quantum yield, making this building blocks: a) Figure 1. Structural representation of the molecular components used as Figure 1. Structural representation of the molecular components used as secondary face (lined by the eight methanolic groups) and by the opposite primary face (lined by the eight methanolic groups) and by the opposite secondary face (lined by sixteen hydroxyl groups). b) octahedral cluster \[\text{Re}_6\text{Q}^{\text{III}}\] built from six rhenium \[\text{Re}^{\text{III}}\] ions located at the octahedron corners and mutually linked through metal-metal bonds (Re-Re = 2.64-2.69 Å). The resulting \[\text{Re}_6\text{Q}^{\text{III}}\] core is face capped by eight \[\mu_2\text{-Q}\] ligands (with \(Q = S, Se, or Te\)) and the coordination sphere of the six Re centers is completed by a cyano ligand in apical position. Color code: orange = rhenium, violet = \(Q\) (S, Se or Te), grey = carbon, blue = nitrogen, red = oxygen, white = hydrogen. In this paper we report on the formation of host-guest supramolecular complexes in aqueous solution involving \(\gamma\)-CD as host and anionic \[\text{Re}_6\text{Q}_2(\text{CN})_6^{2-}\] (\(Q = S, Se, or Te\)) clusters as guests (Figure 1). Structural models of supramolecular adducts have been obtained through single-crystal X-ray diffraction analysis, revealing the deep inclusion of the \[\text{Re}_6\text{Q}_2(\text{CN})_6^{2-}\] clusters within two \(\gamma\)-CD capsules. Furthermore, solution studies, using ESI-MS and multinuclear NMR techniques confirmed that supramolecular interactions are maintained in aqueous solution. Nevertheless, isothermal titration calorimetry experiments (ITC) revealed that efficiency of the supramolecular recognition process is strongly dependent upon the nature of the \(\mu_2\) chalcogenide ion (\(Q = S, Se, or Te\)) in the \[\text{Re}_6\text{Q}_2^{2-}\] cluster core. Such a contrasting behavior is also nicely supported by NMR conclusions that balance from highly labile associations with \(Q = S, Se, or Te\) to robust frozen arrangements with \(Q = Te\). Besides, we report herein that supramolecular \(\gamma\)-CD shells have noteworthy influences upon the electrochemical and luminescence properties of the embedded clusters, thus providing new arguments and opportunities for their deliberate integration within functioning systems useful in the area of biotechnological applications.

Results and Discussion

Formation of the \(\gamma\)-CD based adducts

Isolation of the supramolecular adducts has been carried out through systematic studies using different ratios of alkali salts of octahedral clusters \([\text{M}_6\text{Q}_6(\text{CN})_6\text{H}_2\text{O}] (\text{with } M = \text{Na or K and } Q = S, Se or Te) and varying procedures of crystallization such as slow evaporation of aqueous solution or vapor diffusion method. In short, this study showed that Se- and Te-containing clusters exhibit high propensity to form the 1:2 supramolecular adduct \([\text{Re}_6\text{Q}_2\text{CD}]_2\), consistent with X-Ray diffraction analysis or NMR solution studies. Compounds 1 and 2, corresponding to \(\text{Na}_1[\text{Re}_6\text{Te}_6(\text{CN})_6\text{CD}][\gamma\text{-CD}]_2\) (\(\gamma\)-CD)/3\(\text{H}_2\text{O}) and \(K_1[\text{Re}_6\text{Se}_6(\text{CN})_6\text{CD}][\gamma\text{-CD}]_2\) (\(\gamma\)-CD)/4\(\text{H}_2\text{O}) respectively, were obtained as single-crystals through slow evaporation of aqueous solutions. Conversely, applying similar procedures to the sulfur-containing cluster unit led systematically to formation of colorless cluster-free crystals corresponding to \(\gamma\)-CD, meaning that supramolecular interactions should give labile and highly soluble adducts reluctant to crystallize. Nevertheless, changing the crystallization conditions for slow ethanol vapor diffusion into aqueous solution containing cesium chloride produced single-crystals suitable for XRD. Structural analysis of compound \(\text{Cs}_5\text{K}_1[\text{Re}_6\text{S}_6(\text{CN})_6\text{CD}][\gamma\text{-CD}]_2\) 2[\(\text{Re}_6\text{S}_6(\text{CN})_6\text{CD}][\gamma\text{-CD}]_2\) 4\(\text{H}_2\text{O}) (3) revealed unexpected host-guest interactions as discussed below.

Single-crystal X-ray analysis

Main crystallographic parameters for structures of compounds 1, 2 and 3 which involves \(\gamma\)-cycloextrin and \([\text{Re}_6\text{Q}_2(\text{CN})_6]^{2-}\) with \(Q = Te, Se, or S\), respectively, are given in supporting information (SI §2.1, Table S1). X-ray diffraction study revealed three host-guest supramolecular adducts involving \(\gamma\)-CD and octahedral clusters \([\text{Re}_6\text{Q}_2(\text{CN})_6]^{2-}\) with \(Q = Te, Se, or S\). Nevertheless, depending upon conditions of crystallization and the nature of the octahedral-type cluster, CD:cluster stoichiometry and supramolecular interactions observed in the crystal structures differ strikingly.
Structural analysis of NaX[(Re8Se8(CN)8)(γ-CD)2]·(γ-CD)·30H2O and KX[(Re8Se8(CN)8)(γ-CD)2](γ-CD)·40H2O (noted 1 and 2, respectively) revealed two isostructural compounds which contain the octahedral cluster \([\text{Re}_8\text{Se}_8(\text{CN})_8]^2-\) closely embedded into two \(\gamma\)-CDs facing their wider rim (secondary face) and \([\text{Re}_8\text{Q}_8]^2+\) clusters range within those usually observed (see SI §2.2, Table S2). In addition, some weak intermolecular interacting mutually through hydrogen bonds (O⋯O ~ 2.8-3.1 Å) (see Figure 2a). Geometrical parameters of the encapsulated \([\text{Re}_8\text{Q}_8]^2+\) clusters range within those usually observed (see SI §2.2, Table S2). In addition, some weak intermolecular interactions can be identified within the solid state structures contributing to the stability of the supramolecular host-guest arrangements. Each equatorial cyano group interacts through hydrogen bonds with the three closest hydroxmo groups of the wider rim of \(\gamma\)-CD giving N⋯O distances in the 2.8-3.0 Å range while Q inner ligands (Q = Se or Te) participate also to the supramolecular cohesion (see Figures 2a-b), giving close contacts with inward-directed hydrogen H-3 labelled in the \(\gamma\)-CD (H⋯Se = 3.2-3.5 Å and H⋯Te = 3.1-3.4 Å). Furthermore, in the crystal packing, two supramolecular adducts \(\{\text{Re}_8\text{Q}_8(\text{CN})_8\}2\gamma\text{-CD})2+\) stack together through their primary faces along the [001] direction to give the typical tubular arrangement. At last, both sides are symmetrically closed by two additional free \(\gamma\)-CDs (see Figure 2c). The cohesion within such large enchainment is mainly ensured by a network of direct hydrogen bonding that interconnects alternately secondary rims and primary rims (O⋯O = 2.7-3.0 Å). This arrangement appears very similar to that reported previously by Nau et al. on inclusion complexes involving \(\gamma\)-CD and \([\text{Br}_3\text{Br}_2\text{I}_2]^2-\) dodecaborate cluster. Such similarities mean that in this case, crystal packing is mainly imposed by structural properties of the bulky \(\gamma\)-CD, while water molecules and disordered counter-cations (Na+ or K+ for Q = Se or Te, respectively) should be probably distributed within large voids between the tubular assemblies.

X-ray diffraction structural analysis of compound 3 containing the \([\text{Re}_8\text{Se}_8(\text{CN})_8]^2+\) octahedral type-cluster and \(\gamma\)-CD is graphically shown in Figure 3. Crystal structure of 3 reveals also host-guest arrangements built on the cluster unit bicapped by two \(\gamma\)-CD molecules, but here, both \(\gamma\)-CD face their two primary faces (see Figure 3a), instead of the secondary faces as observed in structure 1 and 2. It should be worth remarking that such host-guest disposition was already reported in systems involving bulky guests such as Keggin [PMo12O40]3- or Dawson [P2W18O62]6- anions. Furthermore, the relative disposition of the cluster within the two opposite CDs depicted in 3 differs from that observed in 1 or 2. The equatorial plane of the \([\text{Re}_8\text{Q}_8(\text{CN})_8]^2+\) -CD is perpendicular with respect to the faces of the \(\gamma\)-CDs while the two remaining opposite axial cyano ligands point between the two primary rings of the \(\gamma\)-CDs. Nonetheless, complete structural description of crystal 3 should mention an additional type of interactions wherein the cluster unit and \(\gamma\)-CD stack together to form regular planes (see Figure 3b). In such arrangement the cavity of \(\gamma\)-CD remains free while the clusters interact with the outer part of \(\gamma\)-CD torus (see Figure 3b). In summary, compound 3 exhibits an overall stoichiometry \(\text{cluster:}\gamma\text{-CD} = 3:4\) and contains two types of supramolecular interactions, leading to a quite typical 1:2 discrete host-guest arrangement involving the primary faces of the \(\gamma\)-CD tori. The second type of interaction appears less specific and allows the formation of regular plane paved from the strictly alternation of \([\text{Re}_8\text{Se}_8(\text{CN})_8]^2+\) anion and \(\gamma\)-CD tori. At last, the counter cations, K+ and Cs+, have been found and appear mainly located in the vicinity of the hydroxyl groups of the \(\gamma\)-CD and, thereby, quite far from the anionic clusters (not shown).
**FULL PAPER**

**NMR study**

Multinuclear NMR provides complementary informative analytical tools able to track supramolecular effects using available NMR probes either from the host (1H or 13C) or from the guests with 77Se and 125Te.[21] 1H NMR titrations were conducted for all clusters Q = S, Se or Te allowing to determine averaged cluster:CD stoichiometry in solution (Job plot analysis) and in some extend to give some insights about structures of supramolecular aggregates formed in aqueous solutions. 1H NMR titrations are shown in Figures 4a-c, and experimental details given in supporting information section. In the case of Te-containing cluster (Figure 4a), appearance of several new signals feature complex formation in a nearly frozen situation on the NMR time scale. For instance, H1 and H5 resonances clearly reflect the formation of the 1:2 host-guest arrangement in aqueous solution (see Figure 4a). Nevertheless, combination of slow exchange dynamics and restricted molecular movement due to aggregation cause significant line broadening (see, SI §3.1, Figure S2). In case of S or Se clusters, 1H NMR patterns behave differently, without excessive line broadening upon introducing up to 12 cluster equivalents (see Figures 4b and 4c), concomitant with the gradual variations of the 1H NMR resonances. These results are consistent with highly labile associations (extreme narrowing situation on the NMR time scale). These observations confirm quite strong interaction of the three clusters (Q = Te, Se or S) with the γ-CD torus which should correspond to inclusion complexes.

For Te- and Se-containing clusters, most important shifts for the inner H3 protons supported by NMR titration and Job plot analysis appear fairly consistent with the solid state structure 3 showing the ([Re6Q8(CN)34]·(γ-CD)2)4+ arrangement (see Figure 2a). In addition, the existence of the 1:2 supramolecular arrangements in diluted solutions has been confirmed by ITC experiments. For the S-containing cluster, NMR analysis shows clearly that in addition to H3 chemical shift variations, H5 inner proton appears also mostly affected by the inclusion process. Besides, NMR analysis is also consistent with 1:1 average stoichiometry nicely confirmed by ITC (see SI §3.2, Figures S3 and S4a). As these results differ from those obtained from X-ray diffraction analysis (see Figure 3), they could arise from weak selectivity of the supramolecular recognition process due to the smaller sized sulfur-containing cluster. Size volume calculation within the [Re6Q8(CN)34]-series gives 387, 419 and 473 Å3 for Q = S, Se and Te, respectively. Weak selectivity and affinity (see ITC results below) lead to predominant 1:1 associations in solution that could occur either from the secondary face (affecting the H3 inner proton) or from the primary face of the torus (leading to the H5 shift resonance).

Evidence for the inclusion complex formation is also provided by 1H DOSY NMR. The self-diffusion coefficient D of γ-CD drops from ca. 250 μm2/s for the free γ-CD[21]1 to ca. 220, 210, and 190 μm2/s for CD-[Re6Q8(CN)34]-solutions for Q = S, Se, and Te respectively, upon increasing the cluster to CD ratio (for further details, see SI, §3.3, Figure S5). However D changes are moderate because the hydrodynamic radii of supramolecular adducts are dominated mainly by the CD host, but significant decreases of self-diffusion coefficients indicate formation of labile host-guest aggregates.

77Se and 125Te NMR studies of solutions containing [Re6Q8(CN)34]- (Q = Se, Te) and γ-CD have been conducted at fixed cluster concentration (shown in Figure 5). In the case of Se cluster, a single signal is observed shifting progressively from δ = -389 ppm to the limiting value at -392.6 ppm (see Figure 5b). This indicates a fast exchange regime between the different cluster species, i.e. solvated or embedded within γ-CD. Besides, Job plot using the 77Se NMR data (see SI, §3.2, Figure S3) confirms the formation of the predominant 1:2 type complex in aqueous solution, still consistent with the solid state structure and 1H NMR analysis. Conversely, complexation of the [Re6Te3(CN)34]-cluster leads to two 125Te NMR resonances at δ = -1127 ppm and δ = -1165 ppm according to the slow chemical exchange regime observed by 1H NMR. While 125Te NMR titration gives also direct evidence for the 1:2 stoichiometry of the frozen CD-cluster conformation (see SI, §3.1 and 3.2, Figure S4b), such an experiment allows evidencing the formation of the highly labile 1:1 complex which causes the significant broadening of the δ = -1127 ppm 125Te resonances observed for CD/cluster ratio in the 0-1 range (see Figure 5a).
At last, $^{13}$C NMR spectra were also recorded to monitor the inclusion complex formation (see SI, §3.4, Figure S6) through the conformational changes of the $\gamma$-CD macrocycle. The spectra of Te cluster system showed broad signals due to slow exchange regime that makes the measurement and interpretation of the spectra difficult. However, narrow signals are obtained for S and Se cluster systems and their measurements are much easier. Actually, variations of $^{13}$C NMR chemical shifts reflect mainly the macrocycle distortions when accommodating the guest rather than the through-space host-guest contacts, as observed with $^{13}$C NMR: $^{13}$C atoms behave as hinge within the CD backbone, allowing in some extent expansion / contraction of the opposite rims. According to the solid state structure, host-guest interactions should provoke expansion of the secondary rim and the concomitant contraction of the primary one when $Q = Se$ while opposite trend holds for $Q = S$. It should be worth remarking that chemical shifts of the remaining C2, C3, C5 and C6 carbon atoms exhibits similar macrocycle distortions whatever the nature of the chalcogenide inner ligands ($Q = S$ or Se). Furthermore, the $^{13}$C NMR chemical shift of the outer cyano ligands appears quite unaffected for the sulfur-containing cluster while it undergoes significant deshielding when $Q = Se$. Such a difference arises probably from the hydrogen bonding network similar to that detected in the solid state which involves the equatorial cyano groups and the sixteen hydroxyl groups from the secondary rim (see Figure 2a). Such types of supramolecular interaction are prominent with the [Re$_8$Se$_6$(CN)$_3$]$_{2+}$ and fully cancelled in the host-guest conformations involving the S-containing cluster [Re$_8$Se$_3$(CN)$_3$]$_{2+}$ and the primary faces of the CDs (see Figure 3a).

**ESI-MS studies**

Solutions containing cluster and $\gamma$-CD have been investigated using ESI-MS. The results corroborate entirely the hypotheses and interpretations formulated from solid state analysis and multinuclear NMR investigations. In each case, the ESI-MS spectrum contains the 1:1 and 1:2 supramolecular complexes (see SI, §4, Figure S7 for further details). For $Q = S$ or Se, the 1:1 and 1:2 adducts are associated to two Na$^+$ cations to give [Na$_2$[Re$_8$Q$_6$(CN)$_3$]$_{3-}$(H$\gamma$-CD)$_3$]$_{2-}$ species with $x = 1$ or 2 while for $Q = Se$ the 1:1 and 1:2 adducts are associated to one proton in [H[Re$_8$Te$_6$(CN)$_3$]$(\gamma$-CD)$_3$]$_{2-}$ with $x = 1, 2$.

**Isothermal calorimetric titration**

ITC experiments were carried out to give thermodynamic insights about interactions between the $\gamma$-CD and the [Re$_8$Q$_6$(CN)$_3$]$_{2+}$ clusters as function of the nature of the chalcogenide inner ligand S, Se or Te. Selected ITC thermograms and isotherms obtained at 283 K are shown Figure 6 while full detailed data and related analytical treatments are given in Supporting information (SI, §5). ITC results including binding constants, enthalpy $\Delta H^\circ$ and entropy $\Delta S^\circ$ are given at 298 K in Table 1. They were analyzed using a two-site binding model involved within a sequential process, except for S-containing cluster for which the second 1:2 step is found negligible. For all the complexes, supramolecular binding is invariably an enthalpically driven process but as the size of the Q ligand increases from S to Te, the enthalpy of the complexion tends to decrease gradually. Such a tendency is exactly opposite to that observed by Nau et al. with dodecarbostil [Bi$_2$(S$_3$)$_6$]$_{2-}$ cluster (X = Cl, Br or I), who reasoned, logically, that such a behavior is in line with increasing donation between the cyano outer ligands and the [Re$_8$Q$_6$]$_{2+}$ core, while corresponding M-L bonding energy increases gradually from $Q = S$ to $Te$. [22] Such an apparent discrepancy means that solvation of the rhenium octahedral clusters is mainly governed by the six exposed cyano groups rather that the eight inner Q ligands. In short, increasing the $\sigma$ donor capability of the Q ligands toward the Re centers ongoing from S to Te weakens the Re-C $\sigma$ overlap which induces the increase of the (C=N) bond polarization and then the subsequent strengthening of the electrostatic interaction with water molecules of the solvation shell. Such a qualitative explanation was nicely supported by DFT calculations which clearly showed that bonding stabilization comes mainly from $\sigma$ donation between the cyano outer ligands and the [Re$_8$Q$_6$]$_{2+}$ core, while corresponding M-L bonding energy increases gradually from $Q = S$ to $Te$. [22] The enthalpic gain appears correlated to entropic penalty according to enthalpy-entropy compensation ($R^2 = 0.96$) that usually hold with CDs-based encapsulation process. [23] Actually, thermodynamic profile of the rhenium clusters series resembles that of the perhalogenated...
Figure 7. Enthalpy–entropy compensation plot for 1:1 γ-CD complexes with \([\text{Re}_6\text{Q}_8(\text{CN})_4]^{2+}\) (red circles) compared with those found for \([\text{B}_{12}\text{X}_2]^2-\) dodecaborates series and suggests that these ions behave as chaotropic species (water structure breakers). However, as shown in Figure 7, magnitude of the chaotropic character within the \([\text{Re}_6\text{Q}_8(\text{CN})_4]^{2+}\) series does not increase with the polarizability of the Q ligand, probably due to antagonist influence of the six outer cyano ligands which cancels partially dispersion forces involved within solvation process of the cluster. Nevertheless, the highest affinity was observed with the most bulky anion \([\text{Re}_6\text{S}_8(\text{CN})_4]^{2+}\), which optimizes the host-guest dispersion interactions compared to the S- or Se-containing cluster units.

### Table 1. Binding constants \(K\) involving rhenium octahedral cluster with γ-CD and associated thermodynamic parameters (in kJ mol\(^{-1}\)) at \(T = 298 K\)

<table>
<thead>
<tr>
<th>([\text{Re}_6\text{Q}_8(\text{CN})_4]^{2+})</th>
<th>Step</th>
<th>(K (\text{M}^{-1}))</th>
<th>(\Delta H^\circ)</th>
<th>(T \cdot \Delta S^\circ)</th>
<th>(\Delta G^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q = \text{S})</td>
<td>1:1</td>
<td>900</td>
<td>-63.2</td>
<td>-46.4</td>
<td>-16.8</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Q = \text{Se})</td>
<td>1:1</td>
<td>1500</td>
<td>-30.4</td>
<td>-12.3</td>
<td>-18.1</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>300</td>
<td>-56.5</td>
<td>-42.7</td>
<td>-13.8</td>
</tr>
<tr>
<td>(Q = \text{Te})</td>
<td>1:1</td>
<td>37700</td>
<td>-25.3</td>
<td>+0.8</td>
<td>-26.1</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>12700</td>
<td>-51.0</td>
<td>-27.7</td>
<td>-23.4</td>
</tr>
</tbody>
</table>

**Physical-chemical properties of the host-guest arrangements**

**Electrochemistry**

As \([\text{Re}_6\text{Q}_8]^3\) cores are redox active species, influence of γ-CD upon the electrochemical properties could be examined for the three compounds (\(Q = \text{S, Se or Te}\)). Previous studies reported electrochemical properties of the \([\text{Re}_6\text{Q}_8(\text{CN})_4]^{2+}\) anions in non-aqueous medium, such as acetonitrile or dichloromethane solvent showing that the 24-electron \([\text{Re}_6\text{Q}_8]^3\) cores undergo a quasi-reversible one-electron transfer leading to the 23-electron oxidized species.\(^{24}\) Besides, the oxidizing ability of the \([\text{Re}_6\text{Q}_8]^3\) core was revealed to be dependent on the α donating character of the Q inner ligands that increases ongoing from S to Te atom.\(^{25}\) Surprisingly, electrochemical properties of the \([\text{Re}_6\text{Q}_8(\text{CN})_4]^{2+}\) series in aqueous solution have never been reported while many supramolecular processes arise from the remarkable properties of water solvation. Herein, we report for the first time on the electrochemical properties of the \([\text{Re}_6\text{Q}_8(\text{CN})_4]^{2+}\) anions in aqueous solution and on their deep alteration in the presence of the γ-CD. Electrochemical study of the native \([\text{Re}_6\text{Q}_8(\text{CN})_4]^3\)\(\cdot\)n\(\text{H}_2\text{O}\) compounds has been carried out in 25 mmol L\(^{-1}\) \(\text{HClO}_4\) aqueous solution using various amounts of γ-CD. The corresponding cyclic voltammograms (CVs) are shown in Figures 8a-c and the related data given in Table 2. Each cluster undergoes a monoelectronic wave observed at \(E_{1/2} = 0.820, 0.580\) and 0.290 V v.s. SCE for \(Q = \text{S, Se and Te}\), respectively. Such a trend appears fully consistent with previous results obtained in CH3CN but a ~ 0.2 V systematic shift toward positive potential was observed in aqueous medium (see Table 2). Furthermore, variation of the anodic (\(E_a\)) and cathodic (\(E_c\)) peak currents exhibits a fair linear dependence upon square root of the potential scan rate \(\sqrt{v}\), consistent with a diffusion-controlled electron-transfer kinetic (see SI §6.1, Figure S11). Influence of γ-CD on the electrochemical properties was then investigated showing important changes related to the host-guest structures and solution behavior (see above). Upon gradual addition of γ-CD, the CVs of the sulfur-containing cluster \([\text{Re}_6\text{S}_8(\text{CN})_4]^{2+}\) retain its reversible shape but undergo a continuous decreasing of its half-wave potential \(E_{1/2}\) (see Figure 8a) associated to a substantial reduction of the peak currents. Such observations are consistent with i) fast formation / dissociation of the inclusion complexes that maintains equilibrium conditions over the time scale of the experiment and ii) a more slowly diffusing γ-CD-cluster based species. Furthermore, linear dependence of the anodic and cathodic peak currents upon square root of the potential scan rate \(\sqrt{v}\) is always maintained indicating that γ-CD complexion does not alter the fast kinetic of the electron transfers (see SI §6.1, Figure S12). Surprisingly, no attenuation of these variations was observed up to addition of 50 equivalents of γ-CD indicating that γ-CD is always involved within the redox reactions according to equation 1 and 2 (see SI §6.2, Figure S13). Actually, for large excess of γ-CD up to 10 equivalents, the speciation diagram established from the stability constant \(K_{5,1} = 900 \text{ M}^{-1}\) (see Table 1 and SI §6.3, Figure S14) shows that 1:1 host-guest species is prevalent, thus indicating that equation 2 should govern preferentially the redox process.

\[
[\text{Re}_6\text{S}_8\text{CD}]^{3+} + \text{CD} = ([\text{Re}_6\text{S}_8\text{CD}]^{2+} + 1\text{e}^-) + \text{CD}
\]

\[
([\text{Re}_6\text{S}_8\text{CD}]^{2+} + \text{CD} = ([\text{Re}_6\text{S}_8\text{CD}]^{+} + 1\text{e}^-)
\]

Table 2. Main electrochemical potentials (Volt vs. SCE) for chalcogenide clusters 1-3 and their related inclusion compounds in 25 mmol L\(^{-1}\) \(\text{HClO}_4\) aqueous solution at \(T = 298 K\).

<table>
<thead>
<tr>
<th>([\text{Re}_6\text{Q}_8(\text{CN})_4]^{2+})</th>
<th>(E_a)</th>
<th>(E_c)</th>
<th>(E_{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q = \text{S}) Free</td>
<td>0.850</td>
<td>0.785</td>
<td>0.820</td>
</tr>
<tr>
<td>([\text{Re}_6\text{S}_8\text{CD}]^{3+})</td>
<td>-</td>
<td>-</td>
<td>0.560</td>
</tr>
<tr>
<td>(Q = \text{Se}) Free</td>
<td>0.615</td>
<td>0.545</td>
<td>0.580</td>
</tr>
<tr>
<td>([\text{Re}_6\text{Se}_8\text{CD}]^{3+})</td>
<td>-</td>
<td>-</td>
<td>0.480</td>
</tr>
<tr>
<td>(Q = \text{Te}) Free</td>
<td>0.325</td>
<td>0.255</td>
<td>0.290</td>
</tr>
<tr>
<td>([\text{Re}_6\text{Te}_8\text{CD}]^{3+})</td>
<td>-</td>
<td>-</td>
<td>0.175</td>
</tr>
</tbody>
</table>
function (\(R\)) reduced species (see Table 1), then derived easily from the prevalent redox process (2) where \(E_{1/2}\) associated to equation (2).

In such a range of composition, a simple relationship between apparent half-wave potential \(E_{1/2}^{app}\) and \(p\)CD hold as expressed by equation 3 where \(p\)CD = -log[CD] and \(E_{1/2}^{CD}\) is the half-wave potential of the redox couple \([\text{Re}6\text{ox}\cdot2\text{CD}]^{\gamma}\) / \([\text{Re}6\text{red}\cdot\text{CD}]^{\gamma}\) associated to equation (2).

\[
E_{1/2}^{app} = E_{1/2}^{CD} + 0.059 p\text{CD}
\]

Actually, equation 3 is experimentally justified by a fair linear function (\(R^2=0.996\)) giving a slope of 0.0585V per pH value and \(E_{1/2}^{CD} = 0.560\) V (see SI §6.2, Figure S13). At last, equation 4 is then derived easily from the prevalent redox process (2) where \(K_{11}\) corresponds to the stability constant of the 1:1 host-guest reduced species (see Table 1), \(E_{1/2}^{CD}\) is the global formation constant related to equation 5 and \(E_{1/2}^{CD}\) is the half-wave potential of compound 3 in the absence of \(\gamma\)-CD.

\[
E_{1/2}^{CD} = E_{1/2}^{CD} + 0.059 \log \frac{p\text{CD}}{K_{11}}
\]

\([\text{Re}6\text{ox}]^{3+} + 2 \text{CD} = [\text{Re}6\text{ox}\cdot2\text{CD}]^{\gamma}\)

Using experimental values given in Table 1 and 2, \(K_{11}\) values have been determined from equation 7, giving \(K_{11} = 2.4 \times 10^5 \text{ M}^{-1}\) and \(K_{11}' = 1.0 \times 10^2 \text{ M}^{-1}\) for oxidized 1:1 inclusion complexes based on \([\text{Re}6\text{ox}\cdot\text{CN}]^{\gamma}\) and \([\text{Re}6\text{ox}\cdot\text{CN}]^{\gamma}\) clusters, respectively. Then at larger values of \(\gamma\)-CD equivalent number, the anodic peak potential shifts slowly toward positive values to reach limiting values. In this range of composition, speciation curves established from ITC experiments indicate gradual changes of the host-guest composition from 1:1 to 1:2 stoichiometry, thus in such conditions, this limiting anodic peak potential should be close to that of the 1:2 redox couple \([\text{Re}6\text{ox}\cdot2\text{CD}]^{\gamma}\) / \([\text{Re}6\text{ox}\cdot2\text{CD}]^{\gamma}\). Nevertheless, due to the irreversible character of the redox processes supported by the flattening of the anodic peaks observed for large \(\gamma\)-CD equivalents, any straight quantitative analysis remains quite difficult and requires further computational efforts.
investigations with regard to the oxidized forms behavior in the presence of the cyclodextrins. However, these preliminary results highlight important electrochemical features that are strongly related to the nature of the inner \( Q \) ligands in octahedral cyanido \( \text{[Re}_6\text{Q}_6(\text{CN})_8]^\pm \). Importantly, this study reveals that the sulfur-containing cluster leading to the less stable host-guest arrangement behaves as highly dynamic redox host-guest system while features of the other two clusters that exhibit higher host-guest stability are consistent with a frozen redox behavior. Besides, it should be worth mentioning that such a frozen behavior has been previously evidenced by \(^1\)H and \(^{135}\)Te NMR for the reduced host-guest complex based on the \( Q \)-containing cluster (see Figure 5a). Furthermore, for the three cluster units (\( Q = S, \text{Se} \) and \( \text{Te} \)), complexation by \( \gamma \)-CD leads in all cases to the decrease of the half-wave potential, meaning clearly that host-guest affinity of the oxidized species \( \text{[Re}_6\text{Q}_6(\text{CN})_8]^\pm \) is significantly greater than that of the reduced one \( \text{[Re}_6\text{O}_6(\text{CN})_8]^\pm \). Such a trend is nicely supported by quantitative analysis of the electrochemical data summarized in Table 2. Although the full understanding of this observation should require further investigations, especially about the thermodynamic contributors of the solvated oxidized derivatives, reducing of the ionic charge from 4- to 3- should have as main consequence the destabilization of the solvation shell by decreasing ion-dipole interactions. Similar observations were made previously with the ferrocene/ferrocenium as redox active guest interacting with \( \beta \)-CD as host.\(^{126}\) Lowering the ionic charge of the guest would make easier the cluster transfer from a solvated to an embedded situation. In other word, the driving force of the encapsulation process should be mainly governed by effective water structure recovery, a process highly orchestrated by the chaotropic nature of the octahedral clusters.

**Luminescence properties**

The UV-vis spectra of aqueous solutions of \( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \) and \( \text{[Re}_6\text{Se}_6(\text{CN})_8]^\pm \) are nearly unchanged in the presence of \( \gamma \)-CD. The supramolecular interaction between \( \text{[Re}_6\text{Te}_6(\text{CN})_8]^\pm \) ion and \( \gamma \)-CD is manifested by only a small red shift of the \( \text{[Re}_6\text{Te}_6(\text{CN})_8]^\pm \) absorption band from 416 nm to 420 nm (see §8.1, Figure 15). \( \text{[Re}_6\text{O}_6(\text{CN})_8]^\pm \) clusters and their inclusion complexes with \( \gamma \)-CD exhibit luminescence emission spectra in the red/NIR region with almost the same maxima, indicating that the nature of the cluster triplet states is not affected by interaction with \( \gamma \)-CD (see SI §7.2, Figure S15). In all cases, luminescence quantum yields and corresponding lifetimes (i.e., triplet state lifetimes) of inclusion complexes increase when compared with free (unbound) clusters in aqueous solutions. The changes are minor for \( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \), reflecting the weak effects of \( \gamma \)-CD on the cluster as described above (see SI §7.2, Figure S17). In contrast, the formation of inclusion complexes with \( \text{[Re}_6\text{Se}_6(\text{CN})_8]^\pm \) and \( \text{[Re}_6\text{Te}_6(\text{CN})_8]^\pm \) clusters enhances luminescence intensities as characterized by increasing luminescence quantum yields and extension of lifetimes (Table 3, see SI §7.2, Figures S16, S17). In the presence of \( \gamma \)-CD, the luminescence decay profile of \( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \) becomes biphasic with the increasing contribution of a long-lived component at higher \( \gamma \)-CD/\( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \) molar ratios (Figure 9B). This behavior may be interpreted by the contribution of at least two species with different luminescence lifetimes in the equilibrium, i.e., solvated \( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \) and corresponding inclusion complexes with \( \gamma \)-CD. Evidently, the 1:1 and 1:2 complexes are not spectroscopically distinguishable and have the same or very similar luminescence parameters. Nevertheless, introducing a large excess of \( \gamma \)-CD in the cluster solution leads to the recovery of the mono exponential behavior of the emission decay profile, consistent with predominant formation of the 1:2 complex.

The increase of luminescence parameters upon inclusion of the clusters to \( \gamma \)-CD can be attributed to the combination of two factors: exclusion of water molecules from the solvation shell of cluster molecules in the cyclodextrin cavity and reduction of collisional quenching by water molecules from the bulk.\(^{27}\) As shown recently by analyzing the magnitude of \( D \) or \( \Delta G \) isotopic effects on the triplet state behavior of these clusters,\(^{28}\) energy transfer from their excited states to \( \text{H}_2\text{O} \) vibrational modes leads to extensive non-radiative deactivation. Indeed, due to hydrophobic character inside the cyclodextrin cavity and the fact that water molecules are expelled from the interior and substituted with the cluster body, contacts of excited cluster molecules with water molecules are reduced.

![Figure 9](image-url)

**Figure 9.** Luminescence properties of \( 8 \times 10^{-5} \text{ mol L}^{-1} \) \( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \) aqueous solutions in the presence of \( \gamma \)-CD in water. A) Luminescence emission spectra in a) air-saturated water, b) oxygen-free water in the absence and in the presence of c) 2.8 or d) 5.4 mM \( \gamma \)-CD. B) Luminescence decay curves a) in oxygen-free water and in the presence of b) 1.0 or c) 5.4 mM \( \gamma \)-CD.

<table>
<thead>
<tr>
<th>( Q )</th>
<th>( \Phi_i[^{[a]} )</th>
<th>( \Phi_i(\text{CD})[^{[b]} )</th>
<th>( \tau_i(\mu\text{s})[^{[c]} )</th>
<th>( \tau_i(\mu\text{s})(\text{CD})[^{[d]} )</th>
<th>( \tau_{i0}(\mu\text{s})[^{[e]} )</th>
<th>( \tau_{i0}(\mu\text{s})(\text{CD})[^{[f]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.09[^{[a]}</td>
<td>&lt; 0.01</td>
<td>1.17[^{[b]}</td>
<td>1.06[^{[b]}</td>
<td>1.27[^{[e]}</td>
<td>1.15[^{[e]}</td>
</tr>
<tr>
<td>Se</td>
<td>0.015[^{[a]}</td>
<td>0.03</td>
<td>2.12[^{[b]}</td>
<td>1.50[^{[b]}</td>
<td>4.29[^{[e]}</td>
<td>2.53[^{[e]}</td>
</tr>
<tr>
<td>Te</td>
<td>0.004[^{[a]}</td>
<td>0.01</td>
<td>0.43[^{[b]}</td>
<td>0.34[^{[b]}</td>
<td>0.75[^{[e]}</td>
<td>0.69[^{[e]}</td>
</tr>
</tbody>
</table>

[^{[a]} data from ref. \[^{[26]} \).[^{[b]} Recorded at 720 nm. \[^{[c]} Recorded at 740 nm. \[^{[d]} \text{in oxygen-free water.} \[^{[e]} \text{in air-saturated water.}

In order to represent accurately how the inclusion of the clusters into the \( \gamma \)-CD cavity affects the efficiency of oxygen quenching of the triplet states, we used the relationship \( 1 - (\tau_i/\tau_{i0}) \) to yield the fraction of the triplet states quenched by oxygen under air-saturated conditions (see Table 3). In agreement with negligible effects of \( \gamma \)-CD on the properties of \( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \), the cluster triplet states of inclusion complex are minimally affected by oxygen with a low fraction of \( 9\% \), which is the same as for free

---

**Table 3.** Luminescence properties of \( \text{[Re}_6\text{Q}_6(\text{CN})_8]^\pm \) clusters in water at room temperature. \( \Phi_i \) is the luminescence quantum yield, \( \Phi_i(\text{CD}) \) is the luminescence quantum yield in the presence of \( \gamma \)-CD (> 5 mM, measured for excitation wavelengths varying from 340 to 420 nm), \( \tau_i \) and \( \tau_{i0} \) are the lifetimes of the triplet states, \( \tau_{i(\text{CD})} \) and \( \tau_{i0(\text{CD})} \) are the lifetimes of the triplet states of bound clusters with \( \gamma \)-CD (> 20 mM).

---

\( ^{[a]} \) data from ref. \[^{[26]} \).[^{[b]} Recorded at 720 nm. \[^{[c]} Recorded at 740 nm. \[^{[d]} \text{in oxygen-free water.} \[^{[e]} \text{in air-saturated water.}

In order to represent accurately how the inclusion of the clusters into the \( \gamma \)-CD cavity affects the efficiency of oxygen quenching of the triplet states, we used the relationship \( 1 - (\tau_i/\tau_{i0}) \) to yield the fraction of the triplet states quenched by oxygen under air-saturated conditions (see Table 3). In agreement with negligible effects of \( \gamma \)-CD on the properties of \( \text{[Re}_6\text{S}_6(\text{CN})_8]^\pm \), the cluster triplet states of inclusion complex are minimally affected by oxygen with a low fraction of \( 9\% \), which is the same as for free
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[Re$_2$Se$_6$(CN)$_{12}$]$^{6-}$. On the other side, the fraction increases from 29 to 40 % in the case of [Re$_2$Se$_6$(CN)$_{12}$]$^{6-}$ inclusion complexes, whereas it decreases from 21 to only 8 % for [Re$_2$Te$_6$(CN)$_{12}$]$^{6-}$ complexes with γ-CD. These effects reflect nicely the fact that while the formation of inclusion complexes increases the lifetimes of the triplet states, thus promoting higher fractions of their quenching by oxygen, it is also accompanied with the drop of diffusion coefficients (see previous paragraph), leading to less effective collisional quenching of the triplet states with oxygen. In the case of [Re$_2$Se$_6$(CN)$_{12}$]$^{6-}$, the increase of the lifetime overcomes the effect of slower diffusion of the inclusion complex. For [Re$_2$Te$_6$(CN)$_{12}$]$^{6-}$ complexes with γ-CD, the increase of the lifetime is limited due to deactivation of the excited states through internal conversion and cannot compensate for slower diffusion, resulting in a small fraction of the triplet states quenched by oxygen.

Conclusions

The self-assembly between native γ-CD and octahedral [Re$_2$Q$_6$(CN)$_{12}$]$^{6-}$ clusters (with Q = S, Se and Te) has been observed and studied both in solid state and in aqueous solution. Varying systematically the inner face-capping chalcogenide ligands of these clusters allowed evidencing key parameters required for the molecular recognition efficiency. In addition to size-fitness, preorganization or attractive host-guest interactions, the chaotropic nature of these clusters should probably have a decisive contribution to the supramolecular association involving water-soluble host and guest species. For instance, the smallest cluster which contains sulfur as inner ligand interacts preferentially with the primary faces of the γ-CD to give a 1:2 supramolecular assembly while the bulkier [Re$_2$Se$_6$(CN)$_{12}$]$^{6-}$ and [Re$_2$Te$_6$(CN)$_{12}$]$^{6-}$ ions appear closely embedded through the secondary faces of the host. Such structural features observed in the solid state from X-ray diffraction analysis are nicely correlated to solution studies which reveals the host-guest stability increases significantly in the following order S < Se < Te.

Experimental Section

Materials and Methods. All reagents were purchased from commercial sources and used without further purification. A$_2$[ReX$_6$(CN)$_{12}$] (A = K, Na; X = S, Se, Te) were synthesized as described in literature.[17b, 29]

Fourier Transformed Infrared (FT-IR) spectra were recorded on a Vertex 80 spectrometer. Elemental analyses (C, H, N, S) were carried on an Euro EA 3000 instrument. Energy-dispersive X-ray spectroscopy (EDX) measurements were performed using a SEM-FEG (Scanning Electron Microscope) equipped with a Field Emission Gun (JSM 7001-F, Jeol). The measures were acquired with a SDD XMax 50 mm$^2$ detector and the Aztec (Oxford) system working at 15 kV and 10 mm working distance. The quantification is realized with the standard library provided by the constructor using Lo lines. Water and cyclodextrin contents were determined by thermal gravimetric (TGA) analysis with a Mettler Toledo TGA/DSC 1, STAR$^{\circ}$ System apparatus or with a NETZSCH TG 209 F1 device under oxygen flow (50 mL min$^{-1}$) at a heating rate of 5°C min$^{-1}$ up to 700°C. NMR studies: All NMR spectra were measured on a Bruker Avance 400 spectrometer in D$_2$O at 300 K. $^1$H and $^{13}$C NMR spectra were recorded at 400.1 and 100.6 MHz respectively, referenced to the TMS signal. $^{75}$Se and $^{125}$Te NMR spectra were measured at Larmor frequencies of 76.3 and 126.3 MHz, using H$_2$SeO$_4$ in alkaline solution (1272.6 ppm) and aqueous H$_2$TeO$_4$ (713 ppm) as external secondary references, respectively. Translational diffusion measurements were performed using Bruker’s “ledbpgs2s” stimulated echo DOSY pulse sequence including bipolar and spoil gradients. Apparent diffusion coefficients were obtained using an adapted algorithm based on the inverse Laplace transform stabilized by maximum entropy.[58] ElectrospRAY Ionization Mass Spectrometry: ElectrospRAY ionization (ESI) mass spectra were collected using a Q-TOF instrument supplied by WATERS. Samples were solubilized in water at a concentration of 10$^{-3}$ M and were introduced into the MS via an ACQUITY UPLC WATERS system whilst a Leucine Enkephalin solution was co-injected via a micro pump as internal standard. Isothermal Titration Calorimetry (ITC): Formation constants and inclusion enthalpies were simultaneously determined for each γ-CD[Re$_2$Q$_6$(CN)$_{12}$]$^{6-}$ systems by the use of an isothermal calorimeter (ITC200, MicroCal Inc., USA). See supplementary information for further details.

Electrochemistry. Purified water was used throughout. It was obtained by passing water through a ROs 8 unit followed by a Millipore-Q Academic purification set. All reagents were of high-purity grade and were used as purchased without further purification. Cyclic voltammetric (CV) experiments were carried out with an Autolab Autolab PGSTAT12 potentialstat/galvanostat associated with a GPES electrochemical analysis system (EcoChemie). Measurements were performed at room temperature in a conventional single compartment cell. A glassy carbon (GC) electrode with a diameter of 3 mm was used as the working electrode. The auxiliary electrode was a Pt plate placed within a fritted-glass isolation chamber and potentials are quoted against a saturated calomel electrode (SCE). The solutions were deaerated thoroughly for at least 30 minutes with pure argon and kept under a positive pressure of this gas during the experiments.

Single-crystal X-ray diffraction analysis. The crystal structures of compound 1 and 2 were determined by X-ray analysis on an Xcalibur (Agilent Technologies) and Oxford Diffraction Xcalibur II graphite-monochromated Mo (λ = 0.71073 Å) radiation. The reflections intensities were measured ϕ-scanning of narrow (0.5°) frames. Intensity data collection of compound 3 was carried out at T = 200(2) K with a Bruker D8 VENTURE diffractometer equipped with a PHOTON 100 CMOS bidimensional detector using a high brilliance iMRS microfocus X-ray Mo Kα monochromated radiation (λ = 0.71073 Å). Empirical absorption correction was applied with SCALES3 ABSPACK program[31] or using the SADABS program.[32] The structure was solved by direct method and refined with full-matrix least-squares treatment, anisotropically for non-hydrogen atoms in SHELXL[33] using OLEX2.[34] Crystals were glued in paratone to prevent any loss of crystallization water. The remaining non-hydrogen atoms were located from Fourier differences and were refined with anisotropic thermal parameters. Positions of the hydrogen atoms belonging to the γ cyclodextrins were calculated and refined isotropically using the gliding mode. Crystallographic data for 1: Tetragonal, a = b = 23.8046(2), c = 57.1588(7) Å, V = 32389.5(7) Å$^3$, R$_1$ = 0.0479, wR$_2$ = 0.1460, GOF = 1.100 for 15244 independent reflections with I > 2I$(hkl)$. Crystallographic data for 2: Tetragonal, a = b = 23.8608(2), c = 57.4481(9) Å, V = 32707.4(8) Å$^3$, R$_1$ = 0.0534, wR$_2$ = 0.1622, GOF = 1.146 for 14796 independent reflections with I > 2I$(hkl)$. Crystallographic data for 3: Monoclinic, C2, a = 63.823(4), b = 17.8218(11), c = 17.7578(11) Å, V = 104.248(2) cm$^3$, I = 19577(2) Å$^3$, R$_1$ = 0.0545, wR$_2$ = 0.1267, GOF = 1.034 for 47105 independent reflections.
with h·2s(l). For the compounds 1 and 3, disorder is observed on the encapsulated clusters. In the compound 1, two positions are observed for \([\text{Re}_8\text{Te}_6\text{CN}_4\text{S}_2]^{6-}\) (occupancy of site 1 = 94% and occupancy of site 2 = 6%). In case it was not possible to locate the cyano group of the cluster with occupancy of 6%. In the compound 3, the encapsulated cluster \([\text{Re}_8\text{Si}_8\text{CN}_4\text{S}_2]^{6-}\) is three fold disordered on three positions (occupancy of site 1 = 90%, occupancy of site 2 = 5%, occupancy of site 3 = 5%). In this, the \([\text{Re}_8\text{Si}_8\text{CN}_4\text{S}_2]^{6-}\) site is well defined. For the sites 2 and 3, only the \([\text{Re}_8\text{S}]^0\) cores have been located. Selected Crystallographic data for single-crystal X-ray diffraction studies are summarized in Table S1. CCDC-1813565, CCDC-1813564 and CCDC-1813563 for compounds 1, 2 and 3, respectively, also contain the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

**Optical measurements.** UV-vis absorption spectra of solutions were recorded on a Perkin Elmer Lambda 35 spectrometer. Luminescence properties of the compounds were monitored on a Fluorolog 3 spectrometer equipped with a cooled TBX-05-C photon detection module (Horiba Jobin Yvon). The same instrument was used for luminescence lifetime experiments using an excitation at 390 nm (SpectrasLED-390, Horiba Scientific). Decay curves were fitted to exponential functions by the iterative reconvolution procedure of the DAS6 software (v. 6.8, Horiba Jobin Yvon). Absolute photoluminescence quantum yields were measured using a Quantaurus QY C11347-1 spectrometer (Hamamatsu). 8·10⁻¹⁵ mol·L⁻¹ Cluster aqueous solutions were investigated using excitation wavelength between 340 and 420 nm. For all measurements, oxygen was removed by saturating the solutions with a continuous flow of argon.

**Synthesis of Na[Re₁₂Te₁₁CN₁₄(C)-Cd(C)-3O·(CD)-OH]** (1). 0.1 g (0.04 mmol) of Na[Re₆Te₅CN₄] was dissolved in 10 mL of distilled water, after that 0.163 g (0.126 mmol) of γ-CD was added under stirring and gentle heating at 50 °C. Final solution was allowed to slowly evaporate which gave orange cubic crystals of Na[Re₁₂Te₁₁CN₁₄(C)-Cd(C)-3O·(CD)-OH]. Yield: 0.25 g (86%) of pure crystalline product. Anal. Calcd for Na[Re₆Te₅CN₄]: Cs = 11.81%, Te = 15.95%, O = 11.81%. Found: Cs = 11.57%, Te = 15.05%, O = 11.57%. IR (KBr, cm⁻¹): ν = 3406 (s), 2927 (m), 1636 (w), 1244 (w), 1159 (m), 1028 (s), 941 (w), 856 (w), 760 (w), 708 (w), 1413 (w), 1369 (w), 1340 (w), 1305 (w), 1244 (w), 1201 (w), 1159 (m), 1078 (w), 999 (w), 941 (w), 850 (w), 760 (w), 708 (w), 528 (w), 405 (w). EDS shows: R : S : K : Cs ratio = 18 : 23.8 : 7.9 : 3.8. Thermogravimetric analysis revealed a weight loss of about 7.7% from 50 to 200 °C (the theoretical weight loss of 49 H₂O is 7.67%).

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**Keywords:** metal cluster complex • cycloextrin • supramolecular self-assembly • luminescence • electrochemistry

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Supramolecular recognition dictated by chaotropic effect. Water-soluble [Re₆Q₈(CN)₆]⁴⁻ (Q = S, Se, Te) octahedral clusters react with γ-cyclodextrin producing supramolecular inclusion systems. The nature of the inner Q ligands influences strongly the water structure-breaking character of the clusters, resulting in different host-guest stability. The encapsulation modifies significantly the intrinsic physical-chemical properties of the inorganic guest (redox & luminescence).