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# Polyoxometalate, Cationic Cluster, and $\gamma$ -Cyclodextrin: From Primary Interactions to Supramolecular Hybrid Materials

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Mhamad Aly Moussawi,<sup>†</sup> Nathalie Leclerc-Laronze,<sup>†</sup> Sébastien Floquet,<sup>†</sup> Pavel A. Abramov,<sup>⊥,#</sup> Maxim N. Sokolov,<sup>⊥,#</sup> Stéphane Cordier,<sup>§</sup> Anne Ponchel,<sup>‡</sup> Eric Monflier,<sup>‡</sup> Hervé Bricout,<sup>‡</sup> David Landy,<sup>∥</sup> Mohamed Haouas,<sup>\*,†</sup> Jérôme Marrot,<sup>†</sup> and Emmanuel Cadot<sup>\*,†</sup>

<sup>†</sup>Institut Lavoisier de Versailles, UMR 8180, UVSQ, Université Paris-Saclay, 78035 Versailles, France

<sup>§</sup>Institut des Sciences Chimiques de Rennes, UMR 6226, Université de Rennes 1, 35042 Rennes, France

<sup>‡</sup>Unité de Catalyse et Chimie du Solide, UMR 8181, Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille 1, 62300 Lens, France <sup>||</sup>Unité de Chimie Environnementale et Interactions sur le Vivant EA 4492, SFR Condorcet FR CNRS 3417, Université du Littoral Côte d'Opale, 59140 Dunkerque, France

<sup>1</sup>Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia <sup>#</sup>Novosibirsk State University, Novosibirsk 630090, Russia



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# **Different types of polyoxometalates**







## Applications





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# **Complexation of Polyoxometalates with Cyclodextrins**

Yilei Wu,<sup>†</sup> Rufei Shi,<sup>†,||</sup> Yi-Lin Wu,<sup>†</sup> James M. Holcroft,<sup>†</sup> Zhichang Liu,<sup>†</sup> Marco Frasconi,<sup>†</sup> Michael R. Wasielewski,<sup>†</sup> Hui Li,<sup>\*,†,‡</sup> and J. Fraser Stoddart<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, United States <sup>‡</sup>Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing Institute of Technology, Beijing 100081,

P. R. China

<sup>II</sup>Department of Chemistry, Loras College, 1450 Alta Vista Street, Dubuque, Iowa 52001, United States



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#### Host–Guest Complexes

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## Water Structure Recovery in Chaotropic Anion Recognition: High-Affinity Binding of Dodecaborate Clusters to γ-Cyclodextrin\*\*

Khaleel I. Assaf, Merve S. Ural, Fangfang Pan, Tony Georgiev, Svetlana Simova, Kari Rissanen,\* Detlef Gabel,\* and Werner M. Nau\*



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## In this paper

- They showed the existence of relevant supramolecular associations between γ-CD and POM and between γ-CD and {Ta<sub>6</sub>} separately in aqueous solutions as well as in the solid state.
- Most importantly, They demonstrated that such interactions could be combined in a rational way to give rise to ordered supramolecular hybrid organic-inorganic network based on [P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup>, {Ta<sub>6</sub>}<sup>2+</sup>, γ-CD as primary building units.



Structural representation of the molecular components used as building blocks: (a) Dawson anion  $[P_2W_{18}O_{62}]^{6-}$  (POM), (b)  $\gamma$ -cyclodextrin  $C_{48}H_{80}O_{40}$  ( $\gamma$ -CD), and (c) octahedral cluster  $[Ta_6Br_{12}(H_2O)_6]^{2+}$  ({Ta<sub>6</sub>}).



Structural representation of the supramolecular POM@nCD along their X-ray diffraction analysis showing (a) the 1:1, (b) 1:2, and (c) 1:3 arrangements.



Mixed representations of the solid-state structure of the supramolecular host–guest { $[Ta_6Br_{12}(H_2O)_6]@2\gamma-CD$ }<sup>2+</sup> complex: (a) side view and (b) top view highlighting close interactions between inner H-3 hydrogen (white sphere) and four bromide ligands (yellow sphere) with H···Br = 2.83 Å; (c) focus on the intermolecular hydrogen-bonding network involving the four in plane aquo ligands of the cluster and the hydroxo groups of  $\gamma$ -CD secondary faces (O···O = 3.0–3.1 Å).



ESI-MS spectra of the inclusion compounds in aqueous solution. (a) POM@3CD showing the 1:1 and the 1:2 adducts while the 1:3 complex is not observed. (b)  $\{Ta_6\}$ @2CD containing the m/z peak related to the 1:2 (red trace) and 1:1 (green trace) adducts. The side peaks separated from each other by m/z = 9 are unambiguously attributed to either hydrated or dehydrated complexes.



Microcalorimetric titration data obtained at 298 K from sequential injections of 3.33 mM  $\gamma$ -CD solution into a 0.33 mM [Ta<sub>6</sub>Br<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>]Br<sub>2</sub> solution showing ITC thermogram (left) and isotherm (right). Dots and full lines correspond to experimental and calculated heats obtained from thermodynamic parameters describing a two-step sequential binding process (bottom).



Cyclovoltammograms of  $[Ta_6Br_{12}(H_2O)_6]^{2+}$  (0.5 mM, 298 K, scan rate 10 mV s<sup>-1</sup>; 2.5 × 10<sup>-2</sup> mol L<sup>-1</sup> HClO<sub>4</sub> aqueous solution) in the presence of increasing amounts of  $\gamma$ -CD (from 0 to 5 equiv). Inset: plot of the first anodic peak potential versus equivalent number of  $\gamma$ -CD showing a break point for the stoichiometric conditions.

## NMR DATA





**Figure S19**. UV-vis spectra of  $[Ta_6Br_{12}(H_2O)_6]^{2+}$  aqueous solution in presence solution in presence 0, 2, 4 and 10  $\gamma$ -CD equivalents. For amount of  $\gamma$ -CD upper than 2 equivalents, the UV-vis features of the  $\{Ta_6\}^{2+}$  cluster remain almost unchanged.



Structural representations resulting from the single-crystal X-ray diffraction analysis of the three-component system  $\{Ta_6@2CD\cdotPOM\}$ : (a) tubular chain showing periodic alternation of the ditopic cation  $\{Ta_6@2CD\}^2 + \text{ and the } [P_2W_{18}O_{62}]^{6-}$  POM running along c axis with c = 89.17 Å; (b) highlight of the tubular chain packing in the ab plane; (c) POM moieties within the tubular chain are symmetrically related through 41 helicoidal axis generating successively four equivalent POM units colored in yellow, green, red, and blue, respectively; (d) highlight of two POM units sandwiching the  $\{Ta6\}^2$ + cluster through short hydrogen bonds such as O–O = 2.64 Å (the two  $\gamma$ -CDs have been omitted for clarity).



ITC thermograms (upper part) and isotherms (lower part) for the titration of a mixture of  $\gamma$ -CD (22.5  $\mu$ M) and  $[Ta_6Br_{12}(H_2O)_6]^{2+}$  (90  $\mu$ M) by a 200  $\mu$ M POM solution. Dots correspond to the experimental heats. Red line corresponds to the theoretical heats when considering the presence of {Ta<sub>6</sub>}@CD, {Ta<sub>6</sub>}@2CD, POM[{Ta<sub>6</sub>}@CD], POM[{Ta<sub>6</sub>}@CD]<sub>2</sub>, and POM[{Ta<sub>6</sub>}@CD]<sub>3</sub>.

## Conclusion

- > They have shown that recognition process of  $\gamma$ -cyclodextrin in host-guest binding can be used for building hierarchical noncovalent materials using POMs and octahedral clusters.
- > They have reported the discovery of a remarkable versatility featuring interactions between the Dawson anion  $[P_2W_{18}O_{62}]^{6-}$  and the primary portal of  $\gamma$ -CD, allowing the selective isolation of the 1:1, 1:2, or 1:3 adducts in the solid state.
- > They have studied on the first inclusion complex built from a cationic octahedral cluster  $[Ta_6Br_{12}(H_2O)_6]^{2+}$  and  $\gamma$ -CD wherein the structural model displays the conventional host-guest 1:2 assembly involving close intermolecular contacts.
- Finally, both building blocks, i.e., the ditopic supramolecular cation {[Ta<sub>6</sub>Br<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>]@2CD}<sup>2+</sup> and the Dawson-type anion, react together to give a three-component, well-ordered hybrid material derived either as a supramolecular single crystals.