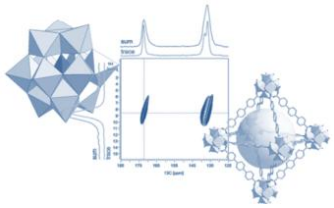
Visit of Prof. Guangjin Zhang and his team of research
August 27, 2025
Pavillon Panhard, UFR des Sciences, UVSQ



TimeTable
Scientific exchanges MIM-IPE, August, 27th 2025
Pavillon Panhard, UFR des Sciences, UVSQ

9:00-9:15	Presentation of the ILV and the MIM research team (E. Cadot)
9:15-9:30:	General presentation of the IPE (G. Zhang)
9.30-9:55	Pr. Guanjin Zhang : "Electrocatalytic Nitrogen Fixation: From Ammonia to Urea"
9:55-10:20	Gabrielle Mpacko Priso: "Deeply Reduced Polyoxometalates: Investigating the Attainability of Metalate Oxidation States"
10:20-10:50	Coffee Break
10:50-11:15	Navaneeth Gowda: "Design of Chiral Porous Bio-hybrid Materials as catalysts for CO_2 Conversion"
10:15-11:40	Zijian Gao: "Jahn-teller distortions induced by in situ Li migration in λ-MnO_2 for boosting electrocatalytic nitrogen fixation"
11:40-12:05	Sana Aniba: "Immobilization of Keggin anions in cyclodextrin-based polymers: a road to develop heterogeneous catalysts"
12:05-12:30	Yu Sun: "Revitalizing lithium-mediated ammonia electrosynthesis activity over heterogeneous lithiophobic-lithiophilic solid electrolyte interphase"
12:30-14:00	Lunch (Pavillon Panhard)
14:00-14:25	Jeremy Delafoulhouze: "CO_2 Reduction by a Conjugated Iron Porphyrin / Polyoxometalate Dyad "
14:25-14:50	Xuehua Zhang: "Efficient ammonia synthesis from electrocatalytic reduction of nitrate over conjugated nickel phthalocyanine under a wide potential"
14:50-15:15	Arnaud Tillet: "Supramolecular self-assembly of nanotubes based on inorganic nano-ions and organic macrocycles"
15:15-16:00	Round table and discussions about future collaboration between IPE and ILV institutions

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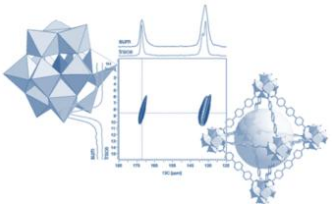


Participants:

Chinese delegation:

1. Guangjin Zhang
2. Zijian Gao
3. Yu Sun
4. Xuehua Zhang

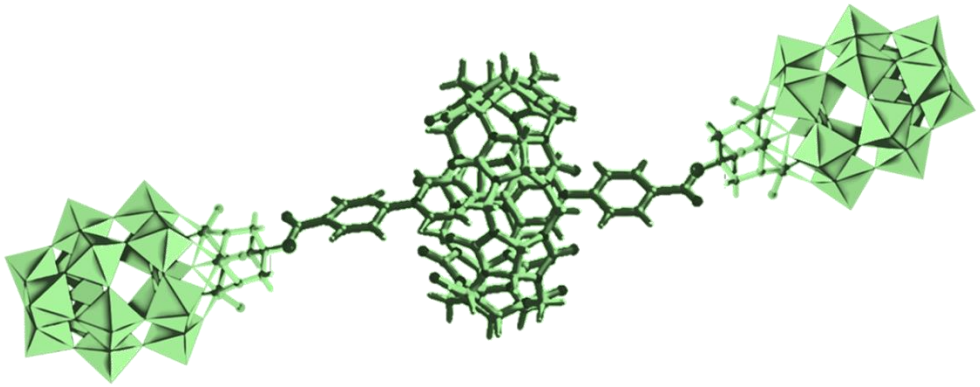
Permanents ILV

5. Anne Dolbecq (CNRS)
6. Clément falaise (CNRS)
7. Clémence Sicard (UVSQ)
8. Mohamed Haouas (CNRS)
9. Emmanuel Cadot (UVSQ)
10. Nathalie Guillou (CNRS)
11. Nathalie Steunou (UVSQ)
12. Maxime Laurans (UVSQ)

Non-Permanent ILV

13. Gabrielle Mpacko-Priso (PhD)
14. Maxime Lajoye (PhD)
15. Arnaud Tillet (PhD)
16. Navaneeth Gowda (PhD)
17. Abdur Rehman Sheikh (PhD)
18. Jérémie delafoulhouze(PhD)
19. Sana Aniba (PhD)
20. Khaled Dassouki (PhD)
21. Irène Mangialomini (PhD)

Abstracts of the presentations



1.

Electrocatalytic Nitrogen Fixation: From Ammonia to Urea

Guangjin Zhang

The electrochemical conversion of nitrogen (N_2) into value-added products like ammonia (NH_3) and urea offers a sustainable alternative to energy-intensive industrial processes such as the Haber-Bosch synthesis. This presentation explores recent advances in electrocatalytic nitrogen fixation, focusing on two key pathways: (1) direct N_2 reduction to NH_3 using transition metal catalysts (e.g., Ni, Fe) under ambient conditions, and (2) the electrosynthesis of urea from CO_2 and N_2-derived intermediates. Key challenges, including competing hydrogen evolution reactions (HER), low Faradaic efficiency, and catalyst stability, will be discussed alongside innovative strategies such as electrolyte engineering, atomic-site catalysts, and dual-sites catalysts designs. By bridging fundamental mechanistic insights with scalable reactor configurations, this talk highlights the potential of electrocatalysis to decarbonize nitrogen chemistry and enable distributed fertilizer production.

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2.

Deeply Reduced Polyoxometalates: Investigating the Attainability of Metalate Oxidation States

G. Mpacko Priso,[a] K. Kozma,[a] J. Puiggalí-Jou,[b] M. Haouas,[a] N. Leclerc,[a] E. Cadot,[a] J. J. Carbó,[b] V. Briois,[c] and C. Falaise[a]

[a] *Université Paris-Saclay, UVSQ, CNRS, UMR8180, Institut Lavoisier de Versailles, 78000, Versailles, France*
[b] *Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcellí Domingo 1, 43007 Tarragona, Spain*
[c] *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192, Gif-sur-Yvette, France*
gabrielle.mpacko-priso@universite-paris-saclay.fr

Keywords: Polyoxometalates, Electrochemistry, Spectroscopy

Polyoxometalates (POMs) represent one class of fascinating inorganic molecules built from transition metals in their highest oxidation states. One of the most striking properties of POMs is their ability to exchange massively electrons in aqueous solution. Understanding this storage capacity is a pivotal question that carries substantial implications for energy storage and conversion. Previous results shew Keggin-type[1] and pseudo Dawson-type[2] POMs were able to store 6 electrons on one metal triad, while Cronin's team demonstrated that the Wells-Dawson anion $[P_2W_{18}O_{62}]^{6-}$ can accept up to 18 electrons. [3][4] We unveiled thus the super-reduction process of Dawson-type POMs $[P_2W_{15}Mo_3O_{62}]^{6-}$, containing a trimolybdic unit $\{Mo_3O_{13}\}$ sustained by a polyoxotungstate core. Using the synergic combination of *in-situ* measurements (XANES/EXAFS) and *ex-situ* techniques (X-ray diffraction, UV-vis spectroscopy, voltammetry and multinuclear NMR), we reveal that: (i) the super-reduction of Dawson-type POMs can lead to the formation of metal-metal bonds between Mo centers, and out of the blue, (ii) the molybdic centers can be reduced to their trivalent state, having thus the possibility to reach a total of four oxidation states, which had never been demonstrated in the field of POMs.

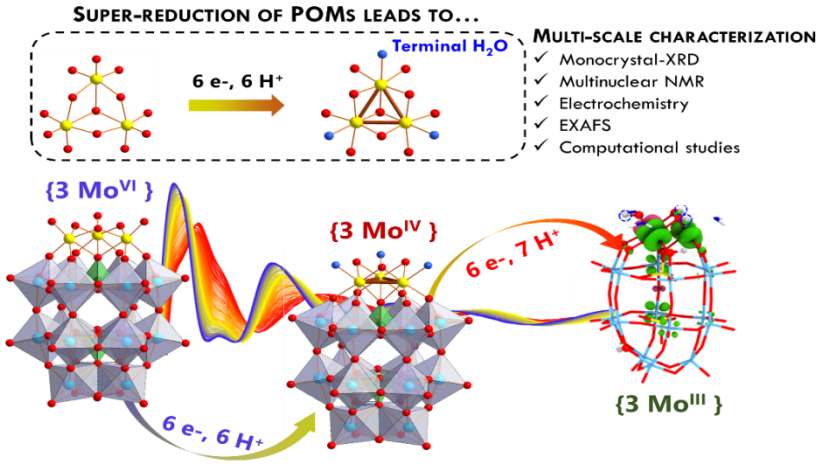
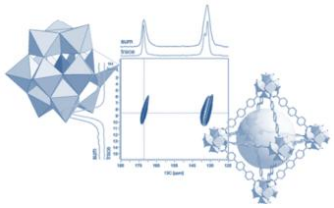


Figure - Schematic representation showing the 12-electrons-reduction of Dawson-POM

[1] C. Falaise and al. *Inorg. Chem.* 2023, *62*, 2494
[2] G. Mpacko Priso and al. *Angew. Chem. Int. Ed.* **2023**, e202312457
[3] L. Cronin, and al. *Nature Chem* **2018**, *10*, 1042
[4] L. Cronin, and al. *J. Am. Chem. Soc.* **2022**, *144*, 8951



3.

DESIGN OF CHIRAL POROUS BIO-HYBRID MATERIALS AS CATALYSTS FOR CO_2 CONVERSION

Navaneeth Gowda[1,2], Khaled Dassouki[1], Subharanjan Biswas[1,3], Rémy Ricoux[3], Nathalie Guillou[1], Juliette Blanchard[2], Nathalie Steunou[1]

[1]Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles St Quentin en Yvelines, Université Paris Saclay - Versailles (France)

[2]Laboratoire de Réactivité de Surface, LRS UMR 7197, Sorbonne Université - Paris (France)

[3]Institut de Chimie Moléculaire et des Matériaux d'Orsay, ICMMO UMR 8182, Université Paris Saclay,-Orsay (France)

Metal Organic Frameworks (MOFs) are used for various applications including gas storage/separation, catalysis, biomedicine etc… [1]. In recent years, significant attention has been focused on reducing their environmental impact by prioritizing using safer solvents or reaction media, sustainable and non-toxic metal ions, and biocompatible organic linkers derived from biomolecules or biomass. Biomolecules such as amino acids and peptides are attractive building blocks to design MOFs, commonly known as bioMOFs, which still represent only a marginal fraction of 3D MOFs discovered so far [2]. The cycloaddition of CO_2 to epoxides to form cyclic carbonates (CAs) is a promising approach for CO_2 conversion, offering efficient resource utilization and 100% atom economy, which finds applications in manufacturing various fine chemicals. Although a large variety of MOF catalysts have been proposed for the CO_2 cycloaddition to epoxides under ambient conditions, they generally operate with a high amount of homogeneous halide co-catalyst [3]. In this project, we have synthesized MOF-based nanocomposites and bioMOFs following different strategies in solution. Their chemical/thermal stability, homochirality, Lewis/ Brønsted acid-base properties, and CO_2 adsorption properties are currently characterized by coupling multiple advanced characterization techniques. The catalytic performance of these materials is also evaluated for the CO_2 cycloaddition to epoxides. Our objective is to develop a series of chemically stable MOF-based heterogeneous catalysts for CO_2 cycloaddition to epoxides that can operate under ambient and eco-compatible solvent-free conditions and with a minimal amount of co-catalyst. Moreover, this project also aims to evaluate the promises of these materials as asymmetric catalysts for synthesizing enantiomerically pure or enantio-enriched CAs.

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[2] José Navarro-Sánchez, Ana I. Argente-García, Yolanda Moliner-Martínez, Daniel Roca-Sanjuán, Dmytro Antypov, Pilar Campíns-Falcó, Matthew J. Rosseinsky, and Carlos Martí-Gastaldo J. Am. Chem. Soc.2017 139 (12), 4294-4297

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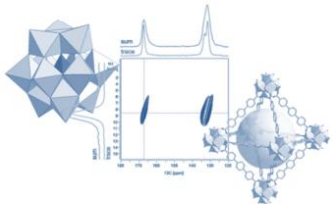


4.

Jahn-teller distortions induced by in situ Li migration in λ-MnO_2 for boosting electrocatalytic nitrogen fixation

Zijian Gao

Lithium-mediated electrochemical nitrogen reduction reaction (Li-NRR) completely eschews the competitive hydrogen evolution reaction (HER) occurred in aqueous system, whereas the continuous deposition of lithium readily blocks the active sites and further reduces the reaction kinetics. Herein, we propose an innovative in situ Li migration strategy to realize that Li substitutes Mn sites in λ-MnO_2 instead of evolving into the dead Li. Comprehensive characterizations corroborate that the intercalation of Li^+ at high voltage breaks the structural integrity of MnO_6 octahedron and further triggers unique Jahn-Teller distortions, which promotes the spin state regulation of Mn sites to generate the ameliorative eg orbital configuration and accelerates N≡N bond cleavage via e_g-σ and e_g-π* interaction. To this end, the resulted cationic disordered $LiMnO_4$ delivers the recorded highest NH_3 yield rate of 220 μg h^{-1} cm^{-2} and a Faradaic efficiency (FE) 83.80% in organic electrolyte.

5.

Immobilization of Keggin anions in cyclodextrin-based polymers: a road to develop heterogeneous catalysts

Sana Aniba,[a, b] Nathalie Leclerc,[b] Clément Falaise,[b] Samah Akriche,[a] Emmanuel Cadot,[b] and Mohamed Haouas[b]

[a] *Laboratory of Chemical Materials LR13ES08, Faculty of Sciences of Bizerte, Carthage University, 7021, Zarzouna, Tunisia*

[b] *Institut Lavoisier de Versailles, UMR 8180 CNRS, UVSQ, Université Paris-Saclay, Versailles, France*

E-mail: sana.aniba@uvsq.fr

Recent works have demonstrated that polyoxometalates (POMs) interact strongly with γ-cyclodextrin (γ-CD) to form stable supramolecular host-guest complexes in water.[1] Therefore, incorporating this macrocyclic organic host within materials paves the way toward the entrapment and immobilization of POMs through the molecular recognition process, offering POM-doped materials with potentialities in biology and catalysis.

In this communication, we will discuss our work aiming to prepare POM-CD composites as heterogeneous catalysts for the oxidative reaction of organic substrates. Insoluble γ-CD-based polymers crosslinked with epichlorohydrin (EPI) were synthesized and used as host matrices to immobilize Keggin-type POMs, including $[PW_{12}O_{40}]^{3-}$, $[PVW_{11}O_{40}]^{4-}$, $[PVW_{11}O_{40}]^{5-}$, and $[H_2W_{12}O_{40}]^{6-}$.[2] The resulting materials were characterized by infrared spectroscopy, solid-state NMR, and thermogravimetric analysis (TGA). The adsorption kinetics and equilibrium isotherms were assessed, revealing that the maximum adsorption capacity varied between 75 to 135 µmol.g^{-1}, depending on the charge of the POM. These adsorption performances are comparable to those observed with mesoporous materials such as MOFs. Then, the POM@CD-EPI composites were tested as heterogeneous catalysts for the oxidation of benzyl alcohol to benzoic acid under mild conditions (60°C, 24h) using tert-butyl hydroperoxide as the oxidizing agent. The results show complete conversion, maximum selectivity (100%), and excellent recyclability over five cycles.

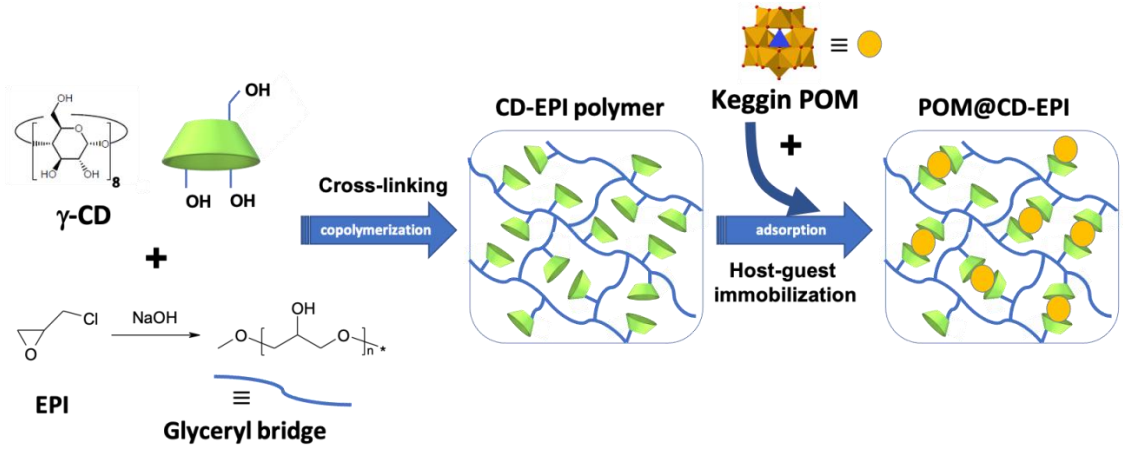
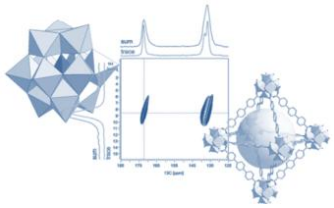


Figure . Schematic representation of immobilization of Keggin POM in organic network of γ-CD copolymerized with epichlorohydrin.

1. S. Yao, C. Falaise, A. A. Ivanov, N. Leclerc, M. Hohenschutz, M. Haouas, D. Landy, M. A. Shestopalov, P. Bauduin, E. Cadot *Inorganic Chemistry Frontier* **2021**, *8*, 12.
2. S. Khlifi, S. Yao C. Falaise, P. Bauduin, V. Guerineau, N. Leclerc, M. Haouas, H. Salmi-Mani, P. Roger, E. Cadot *Chemistry-European Journal* **2024**, *30*, e202303815.



6.

Revitalizing lithium-mediated ammonia electrosynthesis activity over heterogeneous lithiophobic-lithiophilic solid electrolyte interphase

Yu Sun

Compared to aqueous-phase electrocatalytic nitrogen reduction reaction (NRR), lithium-mediated NRR (Li-NRR) theoretically enhances the intrinsic activity of NH_3 production through spontaneous exothermic reactions between Li and N_2. However, the in-situ generated solid electrolyte interphase (SEI) during the reaction slows down the Li^+ transport and nucleation kinetics, which further hinders the subsequent activation and protonation processes. Herein, a sophisticated amorphous-crystalline heterostructured SEI of Zn-LiF is formed by additive engineering. The concerted electron interplay between amorphous and crystalline domains is prone to generate lithiophobic Zn and lithiophilic LiF sites, where lithiophobic Zn accel erates Li^+ diffusion within the SEI and avoids high concentration polarization, and lithiophilic LiF ensures homogeneous nucleation of diffused Li^+ and its participation in subsequent reactions. Therefore, compared to conventional SEI, a more than 8-fold performance improvement is achieved in the additive-engineered heterogeneous lithiophobic-lithiophilic SEI, which exhibits a high NH_3 yield rate of 11.58 nmol s^{-1} cm^{-2} and a Faradaic efficiency of 32.97%. Thus, exploiting the synergistic effects in heterogeneous lithiophobic-lithiophilic structures to achieve functional complementarity between different components opens a new avenue toward high-performance Li-NRR.

7.

CO_2 Reduction by a Conjugated Iron Porphyrin/Polyoxometalate Dyad

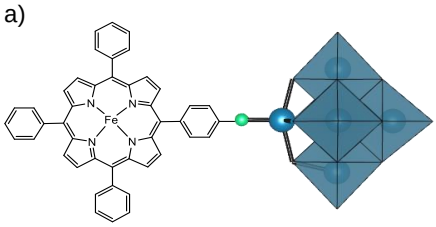
J. Delafoulhouze[1,2], M. Guergueb[1], F. Penas Hidalgo[2], A. Solé-Daura[3], A. Rehman Sheikh[1], A. Robinson[1,2], A. Damond[1], Z. Halime[4], C. Mellot-Draznieks[2], A. Dolbecq[1], W. Leibl[4], P. Gotico[4], O. Oms[1] and P. Mialane[1]

[1] *Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles Saint-Quentin en Yvelines, Université Paris-Saclay, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France ;*
[2] *Laboratoire de Chimie des Processus Biologiques, UMR CNRS 8229, Collège de France, Sorbonne Université, 11 place Marcelin Berthelot, 75231 Paris Cedex 05;*
[3]*Departament de Química Física iInorgànica, UniversitatRovira i Virgili, 43005 Tarragona,Spain*
[4]*Université Paris Saclay, CEA, CNRS, Institute for Integrative Biology of the Cell 91198 Gif Sur Yvette, France.*

Jeremy.delafoulhouze@uvsq.fr

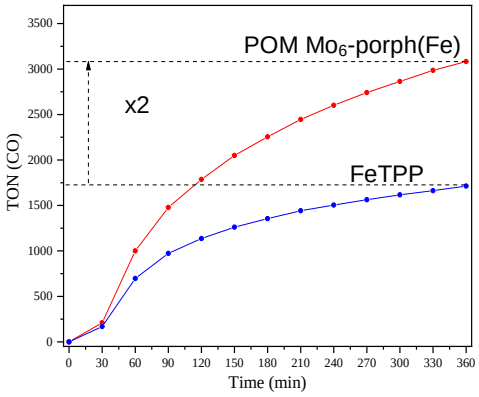
CO_2 can be seen as a costless C1-feedstock, which makes its conversion into high value-added synthetic fuels particularly attractive. In this way, various strategies have been developed for the CO_2 reduction reaction (CO_2RR), especially in the field of photocatalysis. A key challenge in this area remains the identification of efficient catalysts capable of selectively converting CO_2.
In this work, we explore the photocatalytic reduction of CO_2 to CO using a novel iron-based catalyst (**POM Mo_6-porph(Fe)**), which results from the covalent grafting of an iron tetraphenylporphyrin (FeTPP) derivative, a well-known photocatalyst for CO_2RR,[1] to the Lindqvist-type polyoxometalate (POM) $[Mo_6O_{19}]^{2-}$. This system leverages the electron-storage capacity of the Mo_6 POM to act as a multi-electron reservoir, facilitating efficient electron transfer under visible-light irradiation during the CO_2RR, a strategy that our groups have already exploited in MOF-based photocatalytic systems.[2] Our present approach highlights the synergistic interaction between the covalently bounded porphyrin core and the redox-active POM fragment, offering a new pathway toward the design of high-performance molecular photocatalysts for CO_2 valorization.

a)



a) Representation of the compounds **POM Mo_6-porph(Fe)**

b)



b) CO TONs for **POM Mo_6-porph(Fe)** (4 µM) and **FeTPP** (4 µM) in the presence of $[Ru(dmbpy)_3](PF_6)_2$ (500 µM) and BIH (48 mM) in DMF:TEOA (5:1) solutions obtained under irradiation with a blue LED (10 mW.cm²).

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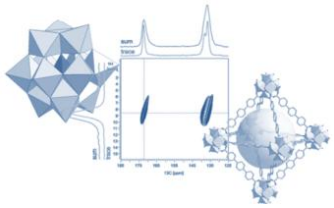


8.

Efficient ammonia synthesis from electrocatalytic reduction of nitrate over conjugated nickel phthalocyanine under a wide potential

Xuehua Zhang

Electrocatalytic reduction of nitrate to ammonia (NO_3^--RR to NH_3) can both provide a green ammonia production strategies and alleviate the ground water pollution. The development of highly efficient catalysts for NO_3^--RR to NH_3 under a wide potential is of great importance for utilizing intermittent renewable electricity. Herein, a conjugated nickel phthalocyanine polymer (NiPcP) was prepared by vacuum calcination, which showed highly efficient and selective NO_3^--RR to NH_3 under a wide operating potential window of -1.2 V to -0.6 V vs. RHE. The highest faradaic efficiency (FE) exceeding 95% and ammonia yield up to 9.2 g g_{cat}^{-1} h^{-1} were got based on NiPcP electrocatalyst at -0.7 V vs. RHE, obviously higher than that of NiPc monomer. The suitable electronic and hydrophobic conjugated structure of NiPcP can enhance the adsorption and activation of NO_3^-, and inhibit the competitive hydrogen evolution reaction, thereby improving the catalytic activity and selectivity for NO_3^--RR to NH_3 production.

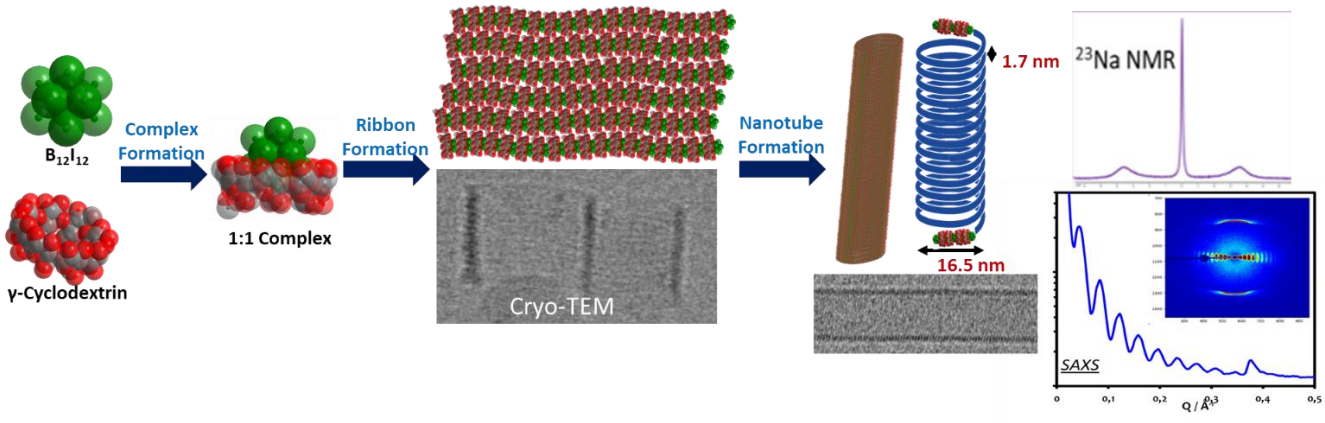
9.

Supramolecular self-assembly of nanotubes based on inorganic nano-ions and organic macrocycles

A. Tillet, C. Falaise, M. Haouas, N. Leclerc and E. Cadot

Institut Lavoisier de Versailles, UMR 8180 CNRS, UVSQ, Université Paris-Saclay, Versailles, France
arnaud.tillet@universite-paris-saclay.fr

Nano-ions represents a broad class of inorganic compounds that include polyoxometalates, metal-atom clusters, or closo-borates. A key feature of these nano-ions is their low volumetric charge density, which imparts remarkable supramolecular properties in aqueous solutions.[1] These arise from a powerful solvent effect, namely the chaotropic effect, which gives them ability to self-assemble with non-ionic organic substances like cyclodextrins or surfactants, leading to host-guest complexes or hybrid vesicles.[2] Recent publication showed formation of discrete supramolecular host-guest complex between γ-cyclodextrin and the dodecaborate anions $[B_{12}X_{12}]^{2-}$ with X = Cl, Br or I.[3] Our reinvestigation revealed that these systems can undergo supramolecular polymerization, producing in fine either crystalline materials built from 1D-bamboo chains or water-soluble hybrid nanotubes.
In this communication, we present multi-scale characterizations of these systems, discussing both their structures and formation pathways. Solution studies were conducted using multinuclear NMR (1H, 11B, and 23Na), dynamic light scattering, and small- and wide-angle X-ray and neutron scattering. Direct observation of the nanotubes was achieved using cryogenic electron microscopy, which revealed highly monodisperse self-assembled nanotubes. This data set shows that the local structure of the hybrid nanotubes closely is reminiscent to that of the 1D bamboo chains, as determined by single-crystal X-ray diffraction.



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