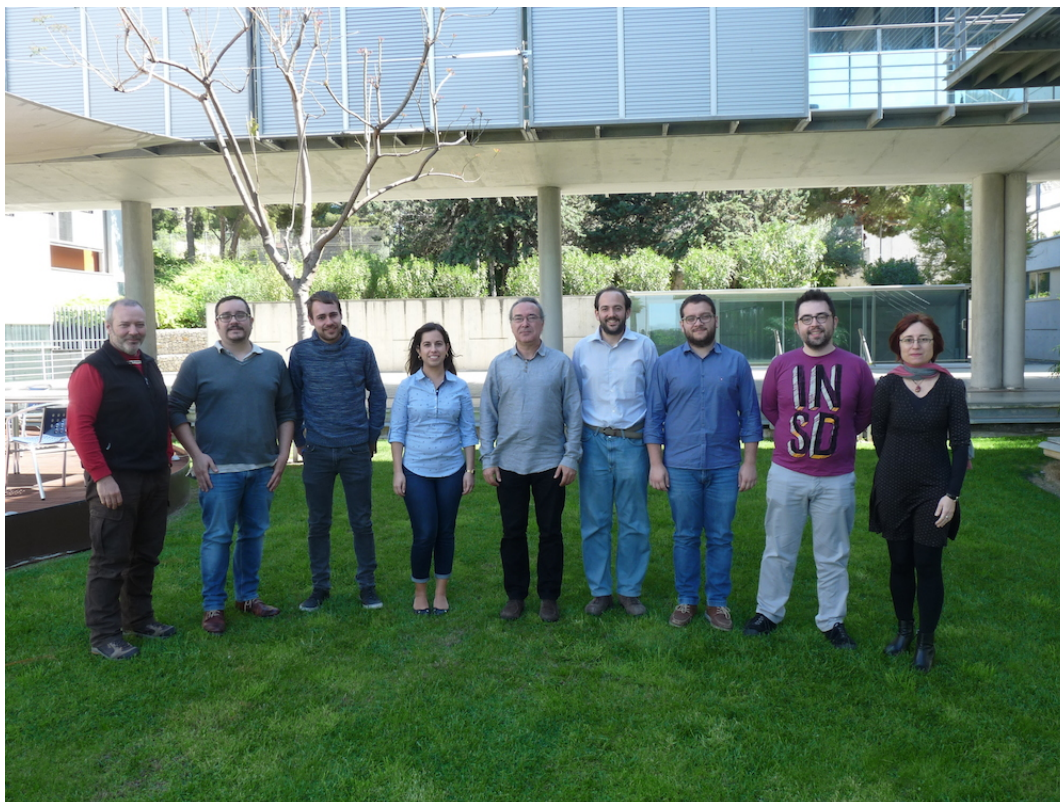


Prof. Carles Bo's Group



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Abstract

Our research deals with the application of computational chemistry methods to a variety of subjects. In most cases, we work in close collaboration with experimental groups both at ICIQ and at other institutions. We also develop computational tools to assist our research needs.

Research topics usually fall into three main categories:

- Polyoxometalates (POMs): electronic structure, mechanisms of catalytic oxidation reactions,

dynamic structure of cations and solvent water molecules around and inside POMs.

- Supramolecular Chemistry: structure of host-guest systems, assessment of non-bonding interactions and supra-molecular catalysis.

- Homogeneous catalysis, both metal-catalysed and organocatalysed transformations, such as characterisation in-silico of reactive intermediates, elucidation of reaction mechanisms, origin of the chemo-, regio- and enantioselectivity, ligand effects, ligand design and structure-selectivity relationships.

Polyoxometalates

During the last decade, polyoxometalates (POMs) chemistry enabled growing impressive new giant molecular metal oxide nanostructures. In some cases, the shape of the POM framework is such that it forms inner cavities, which are usually filled with other molecular species. These two characteristics are found in the family of Keplerales, spherical capsules that can assemble up to 132 metal atoms as shown in Figure 1. The most relevant member of this family is Mo_{132} , with general formula $[(\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_6)_{12}(\text{Mo}_2(\mu\text{-O})_2\text{O}_2(\text{L}^{n-}))_{30}]^{(12+n)-}$. This object contains twelve pentagonal Mo_6 units placed at the vertices of an icosahedron and linked by thirty binuclear Mo_2 units. This structure leads to capsules with twenty pores and a cavity where a large quantity of water molecules, cations or other species can be confined and even react within. In the recent years, our group is pioneering the theoretical treatment of these giant molecular capsules.

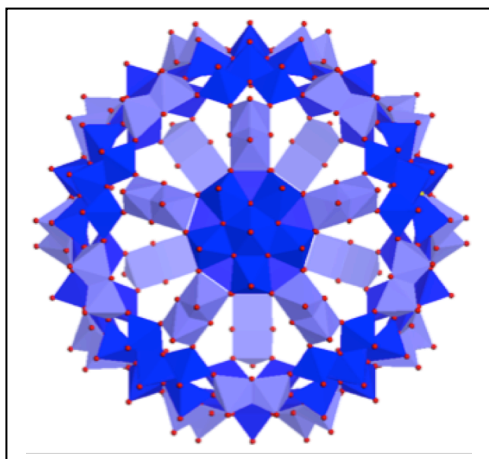


Fig. 1 – Polyhedral representation of Mo_{132}

In collaboration with Cadot's group (Université de Versailles Saint-Quentin, France) we showed [1] that lipophilic cations associate specifically with the $\{\text{Mo}_9\text{O}_9\}$ pores of the Keplerales-type ion, which behaves like 20 independent effective receptors in aqueous solution.

By using molecular dynamics simulations, computed self-diffusion coefficients revealed that the major factor dictating selectivity in trapping is the so-called "hydrophobic effect". This suggests that a fine control of the exchange mechanism at the $\{\text{Mo}_9\text{O}_9\}$ pores is achievable, which will have broad implications in supramolecular chemistry for (i) a regulated access to the large inner cavity, (ii) the functionalization of the surface of the capsule, and (iii) the development

of immobilization strategies of Keplerales-type ions on surfaces or within specific matrices.

Müller and coworkers reported recently a novel way for sequestering and transforming CO_2 into carbonate (or bicarbonate) by encapsulation within this unique molybdenum oxide nanocapsules. The novelty hinges on the fact that the approach uses only aqueous, room temperature and open-air chemistry. By considering a model system, we evaluated different reactive sites, different pH conditions, and compared the activation energies with those of the reaction outside the capsule. Our DFT studies demonstrated that the in situ bicarbonate formation, promoted by the Mo^{V} centres, inside the capsule is kinetically more favourable than direct carbonate uptake from aqueous solution.[2]

Supramolecular Chemistry

Prof. Ballester at ICIQ synthesized a new calix[4]arene host equipped with two bis-[Zn(salphen)] complexes, which self-assembles into a capsular complex in the presence of a chiral diamine guest with an unexpected 2:1 ratio between the host and the guest. Effective chirality transfer from the diamine to the calix-salen hybrid host was observed by circular dichroism (CD) spectroscopy. We carried out density functional calculations to investigate the origin of the stability of the host-guest system and the experimental CD spectrum compared with those calculated for both possible diastereoisomers showing that the M,M isomer (Figure 2) is the one that is preferentially formed, in full agreement with experiment.[3]

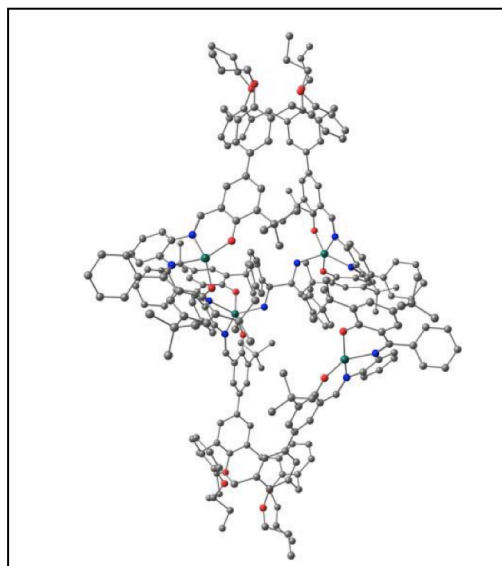


Fig. 2 - ONIOM structure for the supramolecular complex. The most stable *M,M* diastereoisomer (2:1) is shown. H atoms omitted.

Catalysis and Reactivity

The collaboration with Prof. Fernández (URV) on the metal-free activation of boranes, which started years ago, has continued. By following the same concept that we developed for activating diboranes without metals and make diboranes react with α,β -unsaturated carbonyl substrates, we showed that β -unsaturated imines, formed in situ, can be borated in effective and even stereoselective way. [4]

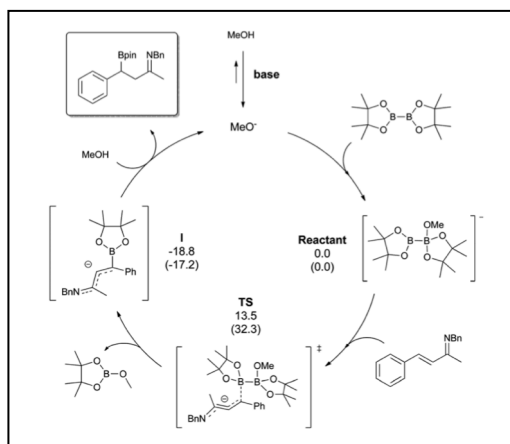


Fig. 3 - Mechanistic proposal for the organocatalytic β -boration of imines.

We predicted computationally that sulphur-boranes could be directly activated by α,β -unsaturated carbonyl substrates (Figure 4), without the need to use any base or any metal catalyst. Indeed, this was the case and this process could be applied to a broad range of carbonyl and aldehyde substrates. [5]

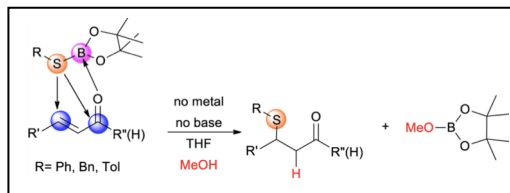


Fig. 4 - Direct addition of sulphur-boranes to α,β -unsaturated carbonyl substrates.

Moreover, the same concept was extended to ynone substrates for both sulphur- and selenium-boranes (Figure 5). [6]

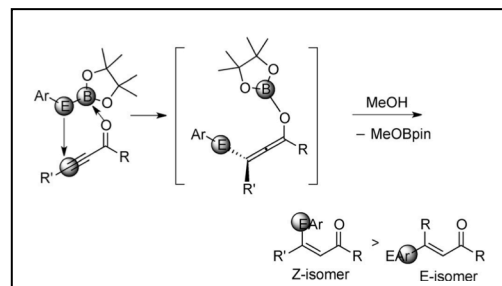


Fig. 5 - New synthesis of vinyl sulphides and selenides through chalcogenoborates.

Encouraged by the discovery of nucleophilic catalysis of diboryl additions, we carried out a broad analysis of uncatalysed additions of B_2X_4 to alkenes. This included the relative reactivity of several B-B reagents with ethene, and that of B_2Cl_4 vs. B_2F_4 additions, including benzene, naphthalene and C_{60} as reactants. This allowed the analysis of relative reactivity vis-à-vis substitution on boron, and also direct comparison with hydroboration by $HBCl_2$. [7]

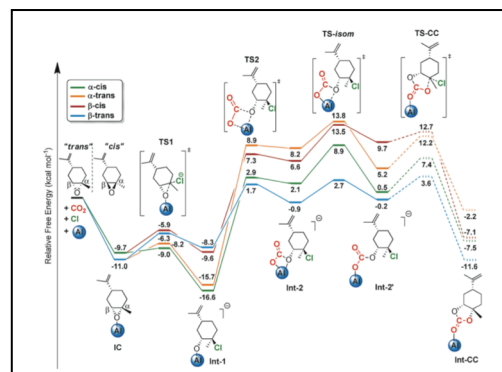


Fig. 6 - Gibbs free-energy profiles for the initiation reaction of copolymerisation between *cis/trans*-(*R*)-limonene oxide and CO_2 catalysed by the Al-complex 2/chloride binary system

The collaboration with Prof. Kleij (ICIQ) on the reaction of CO_2 with epoxides catalysed by amino-triphenolate Al(III) complexes pointed us to study the coupling of limonene oxide and carbon dioxide to obtain alternating polycarbonates. (Figure 6) These catalysts produced stereoregular, perfectly alternating trans-polymers from *cis*-limonene oxide, whereas the pure *trans* isomer and *cis/trans* mixture gave rise to lower degrees of stereoregularity. Our computational studies revealed unique features of the binary catalyst system, among which is the preferred nucleophilic attack on the quaternary carbon center in the limonene oxide substrate. [8]

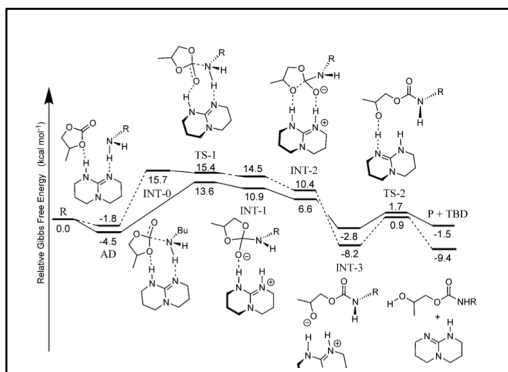


Fig. 7 - Gibbs free energy profile for the TBD-catalyzed reaction mechanism of PC with aniline (solid line) and butylamine (dashed line).

Kleij's group also found that cyclic carbonates, which were obtained by coupling CO₂ and epoxides with suitable catalysts, could be directly transformed into N-aryl carbamates through a metal-free unprecedented reaction catalyzed by TBD (triazabicyclodecene). The mechanism of this new transformation was unraveled computationally (Figure 7), revealing an interesting proton-relay mechanism. Both TBD acid/base properties and its geometrical characteristics are perfectly suited to operate as

a base first and as an acid later to catalyze this reaction. [9]

Last but not least, we presented the ioChem-BD platform (www.iochem-bd.org). This is a tool aimed to manage large volumes of quantum chemistry results (Figure 8).

This Web platform has an extensible structure and a user-friendly interface designed to keep safe output files from computational chemistry packages, to extract meaningful data from the raw results, and to publish the results from our studies in an open-access way. [11]



Fig. 8 – The ioChem-BD platform.

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2- "The mechanism of CO₂ hydration: A porous metal oxide nanocapsule catalyst can mimic the biological carbonic anhydrase role"

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3- "Highly Efficient Chirality Transfer from Diamines Encapsulated within a Self-Assembled Calixarene–Salen Host"

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4- "Asymmetric metal free β -boration of α,β -unsaturated imines assisted by (S)-MeBoPhoz"

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5- "Thioboration of α,β -Unsaturated Ketones and Aldehydes toward the Synthesis of β -Sulfido Carbonyl Compounds"

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9- "A Metal-Free Synthesis of N-Aryl Carbamates under Ambient Conditions"
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11- "Managing the Computational Chemistry Big Data problem: the ioChem-BD platform"
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