

## Kleij Research Group



**Group Leader:** Arjan Kleij

**Postdoctoral Researchers:** Carmen Martín / Christopher Whiteoak (until Dec.) / Nicola Kielland (until April) / Antonello Decortes (until March) / Robert haak (until July) / Martha Escárcega (until Sep.)

**PhD Students:** Jeroen Rintjem / Leticia Peña / Luís martínez / Víctor Laserna / Giovanni Salassa (until May) / Daniele Anselmo (until Feb.)

**Visiting Students:** Margerita Dimitrova (Msc Student from URV) / Jonathan Rojas (Msc Student from URV) / Blerina Gjoka (University of Parma, Italy)

**Summer Fellows:** Leire de Juan Fernández

**Administrative Support:** Ingrid Mateu

### Abstract

Our current research activities are split into two main directions: (1) the use of carbon dioxide as a  $C_1$  building block in organic synthesis using new and improved catalytic strategies, and (2) the application of appropriate building blocks for the development of smart materials. In the first area, we have been active in the preparation of organic carbonates for a number of years, focusing on sustainable solutions and improving activity and stereo-selectivity profiles. We are currently expanding our activities to other

classes of compounds such as oxazolidinones,  $CO_2$ -based (bio)polymers and more complex organic matter derived in tandem approaches. In the second area, we have developed systems that have allowed us to study chirality transfer effects and the development of new electronic materials. Connected to this latter activity, we wish to design systems that are able to control the nanoscopic features of self-assembled molecules either in the solution phase or on surfaces (single-molecule studies), with an aim to develop materials with interesting functions and/or catalytic properties.

### Carbon dioxide chemistry

Our current activities in the area of CO<sub>2</sub> conversion focuses on the development of powerful, selective and attractive methodology for the synthesis of organic compound with added value. In this regard, specific attention is given to the preparation of organic carbonates (either “monomeric” cyclic carbonates or polycarbonates). Also, we wish to develop new catalytic processes that can address the overall sustainability of the process, taking into account the atom-efficiency, reaction conditions (solvent, reagent, temperature, pressure) and toxicity of the involved reaction partners. With this in mind we have now developed a series of new catalysts that are based on a next generation of seemingly privileged ligand scaffolds known as amino-triphenolates (Figure 1).

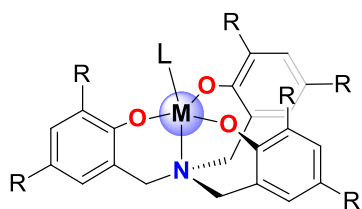
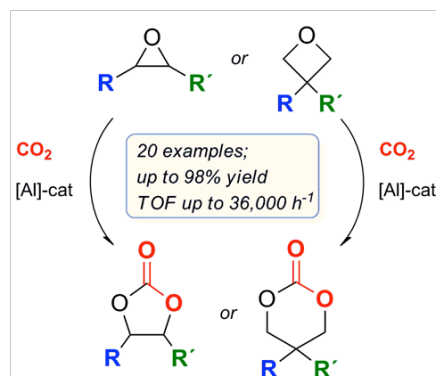
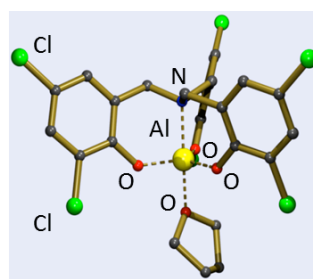


Fig. 1 – General structure of an amino-triphenolate complex used in our work.

With the aim to create powerful, highly active catalysts, we have designed an Al(III) based aminotrisphenolate complex that shows exceptional reactivity in the formation of functional organic carbonates (Figure 2). The highest initial turnover frequencies (TOFs) and total turnover numbers (TONs) to date were reported upon using this Lewis acidic complex in combination with a suitable nucleophile. The scope of the reaction was studied in great detail and showed that oxiranes with a range of functional groups that could potentially compete for coordination to the metal center were conveniently converted. The steric impediment around the oxirane ring was also varied to a large extent and the Al(III) complex also exhibited good activity for the formation of the corresponding cyclic organic carbonates.

In a separate study, Fe(III) aminotrisphenolate complexes have been employed in an effort to convert internal epoxides stereo-selectively. In this regard, first *cis* and *trans* 2,3-epoxybutane were considered as substrates and their conversion was studied using a single Fe(III) complex/TBAB (TBAB = tetrabutylammonium bromide) binary catalyst systems. Systematic

variation of the catalyst/nucleophile ratio showed that both substrates could be either converted into their *cis* or *trans* carbonate product with high diastereo-selectivity (Figure 3). The mechanistic rationale behind this observation is the possible occurrence of two distinct ring-closing steps (cf., the selectivity-determining step) leading to (1) an expected double inversion pathway when the TBAB concentration is relatively high, and (2) a *pseudo*-S<sub>N</sub>1 pathway when the TBAB concentration is relatively low. The latter is likely to be mediated by the Fe(III) complex and more specifically the ability of the metal to switch between penta- and hexa-coordinated coordination geometries during the catalysis event.



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Fig. 2 – A powerful Al(III) complex for the synthesis of highly functional organic carbonates.

A small set of *trans* internal epoxides were then converted in high yield using this Fe(III) based catalyst system in high selectivity. A future outlook in this area is the conversion of enantiomerically pure oxiranes into two both organic carbonate enantiomers using a single catalyst with stereo-divergent potential.

Despite the fact that organocatalysts have intrinsically less activation potential when compared to metal-based systems, we have also been involved in the use and development of efficient organic mediators for organic carbonate formation combining both good activities (i.e., high turnovers at relatively low temperature and pressure) with attractive recycling features. As such we have previously reported that (commercially available and cheap) pyrogallol (1,2,3-trishydroxybenzene) is an excellent organocatalyst for the hydrogen-bond activation of epoxides; more recently, we have designed a polystyrene-supported bifunctional organocatalyst based on pyrogallol that incorporates also a reactive nucleophilic site (Figure 4). This catalyst was probed for its substrate scope, recyclability and successfully used in a multi-substrate conversion campaign.

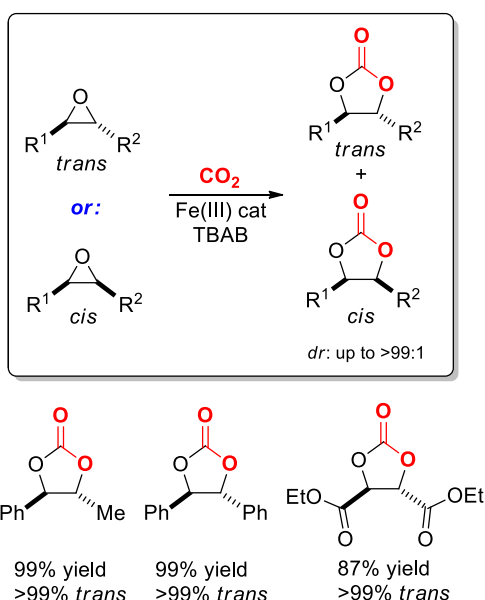


Fig. 3 – Stereo-divergent behavior using  $Fe(III)$  catalysis using epoxides and  $CO_2$ .

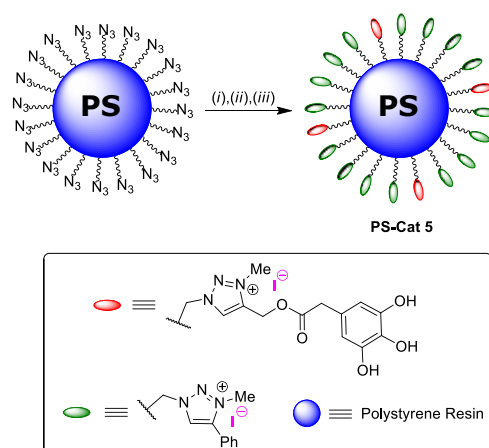


Fig. 4 – Supported bifunctional organocatalyst for organic carbonate formation.

Our first efforts in polycarbonate formation using  $Fe(III)$  catalysts have revealed that high chemo-selectivity can be attained for the polymer (cf., cyclic carbonate formation) under supercritical  $CO_2$  conditions. Observed TOFs (around  $200\ h^{-1}$ ) are rather competitive compared with the state of the art, but moreover, further studies suggest that the selectivity for the polycarbonate is retained at much lower reaction temperatures/pressures. The highest  $M_n$  obtained so far is an appreciable 18 KDa with a polydispersity index  $M_w/M_n$  of 1.1-1.3. Currently, we are focusing on bio-based polymers that can incorporate  $CO_2$  making these polymer targets fully fully renewable.

### New materials

In order to address and develop recyclable catalysts for  $CO_2$  conversion we have designed a supramolecular system (Figure 5) that comprises three Lewis acidic metal centers and two nucleophilic halides that are associated to the Lewis acids via reversible coordinative interactions. This trimetallic system was then probed as a catalyst for cyclic carbonate formation with the aim to recycle the bifunctional catalyst. The product of the reaction could be easily extracted after the reaction and after some optimization the best catalyst system could be reused 5 times without significant drop in activity. Therefore, the design of non-covalent catalysts that incorporate both Lewis acidic functions as well as nucleophilic sites shows promise in this area, taking into account the modularity of the metal ions and nucleophiles that can be chosen *a priori*. It should also be possible to amplify the catalyst potential considering other types of Lewis acid mediated transformations (e.g. polyester formation).

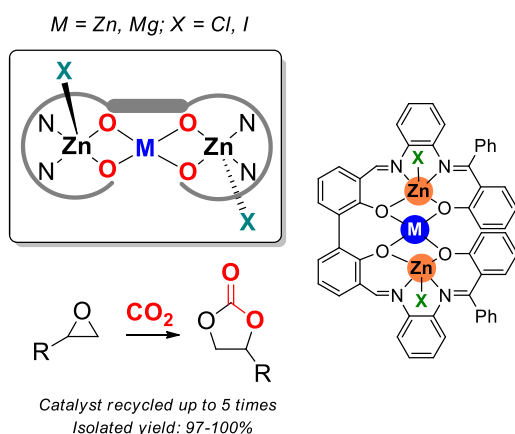


Fig. 5 – A supramolecular bifunctional catalyst for organic carbonate formation.

The overall ligand structure depicted in Figure 5 (right-hand side) proved to be a versatile framework for its use as a molecular building block in the self-assembly of unusual, large structures that resemble a neural network (Figure 6). The self-assembly of these networks apparently does not depend on the type of metal used nor does it seem that this is warranted for network formation. The formation of these networks has been investigated by a large number of spectroscopic and microscopic techniques including AFM, TEM, ESEM, SERS, FTIR-RAMAN, UV-Vis, DLS, and XRD among others (for some examples see Figure 6).

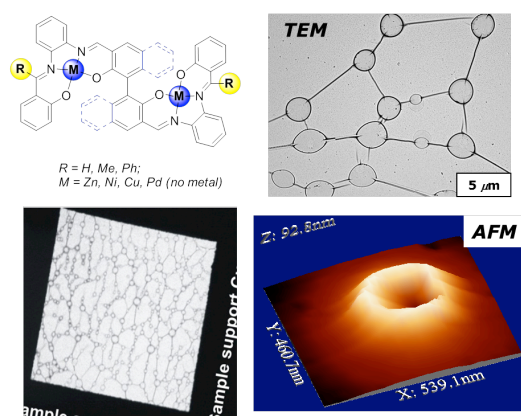


Fig. 6 – Self-assembled neural-like networks using molecular building blocks.

These combined studies (together with extensive computational analyses) have resulted in a mechanistic proposal showing how these networks may form. Interestingly, the use of these networks has resulted in a much better dispersion of carbon nanotubes (CNTs), also in polymeric matrices.

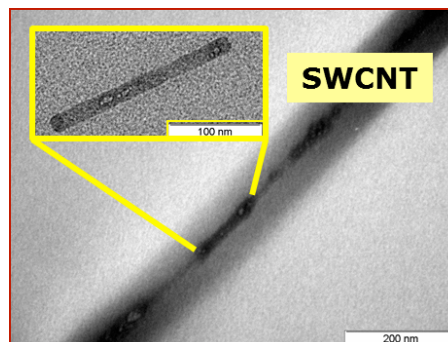


Fig. 7 – Directional assembly of CNTs through interaction with the self-assembled network. SWCNT stands for single-walled CNT.

The importance of this finding is reflected by an increase in the electrical conductivity behavior (2 orders of magnitude) of the CNTs once co-assembled onto the network structure (Figure 7). Therefore, these new self-assembled networks hold great promise for the development of conducting materials and applications related to that. Currently this proprietary technology is expanded to a larger series of building blocks and its commercial value evaluated through a collaboration with an industrial partner.

## Articles

“Metal Mediated Coupling of Carbon Dioxide and Aryl/Vinyl Chlorides under Ambient Conditions”

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*Dalton Trans.* (2013) 42, 1427-1436

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“A Trinuclear Bifunctional Catalyst Derived from a Tetraoxo Bis-Zn(salphen) Metalloligand”

*Chem. Eur. J.* (2013) 19, 2641-2648

Martha V. Escárcega-Bobadilla, Marta Martínez Belmonte, Eddy Martin, Eduardo C. Escudero-Adán, Arjan W. Kleij

“Conformational Studies of Template-Assisted Self-Assembled Molecular Capsules and the Use of their Rhodium Complexes in Hydroformylation reactions”

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“A Powerful Aluminium Catalyst for the Synthesis of Highly Functional Organic Carbonates”

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Christopher J. Whiteoak, Nicola Kielland, Victor Laserna, Eduardo C. Escudero-Adán, Eddy Martin, Arjan W. Kleij

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*Dalton Trans.* (2013) 42, 7595-7603

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