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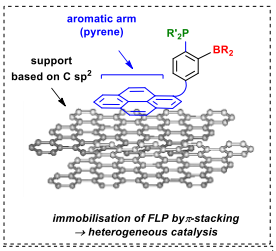
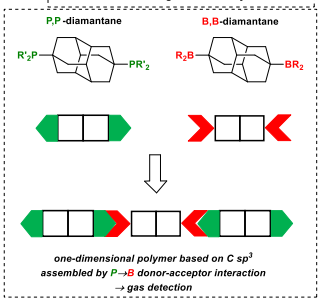
Phosphine-boranes and carbon materials

Keywords: catalysis, P→B interactions, FLP, π-stacking, molecular assembling

Context: This project is at the interface of two growing research fields, Lewis pairs and carbon materials. The frustrated association of Lewis bases and acids (FLP), typically phosphines and boranes, has opened new opportunities in catalysis for the metal-free activation of small molecules.[1] Furthermore, the formation of Donor-Acceptor adducts allows the self-assembly of materials, as recently demonstrated for self-repairing gels.[2] Carbon materials have very peculiar properties and are used in many fields. In particular, the materials based on sp^2 carbon (such as graphenes), are widely used as supports for heterogeneous catalysis. Furthermore, diamondoids, sp^3 carbon-based materials derived from diamantane, are also the subject of many studies, in particular for the development of devices allowing the detection of toxic gases such as NO_2 or NH_3.[3]





In collaboration with Prof. J.-C. Hierso in Dijon, we have initiated a project aiming to combine phosphine-boranes and carbon materials. The first topic consists in the use sp^2 carbon-based materials as supports to immobilize phosphine-boranes by π-stacking. Here, the goal is to heterogenise organic FLP-type catalysts in order to ease their separation and recycling. The second objective deals with the preparation of nanostructured materials by self-assembly of elementary bricks, diamantanes functionalized by phosphines and boranes, for applications as sensors.

Research program: The project will address these 2 research axes. It will consist in preparing carbon compounds functionalized with phosphines and / or boranes. The derivatives based on C sp^2 will be grafted by π-stacking on graphite-type supports, and applied in heterogeneous catalysis. In particular, we seek to synthetize recyclable versions of the FLP type catalysts that we have developed in homogeneous version for the reduction of CO_2 and the dehydrogenation of amine-boranes.[4] On the other hand, the molecular bricks based on C sp^3 will be used to achieve one-dimensional polymers by P→B donor-acceptor interactions. The self-assembly conditions and the structure of the obtained materials will be studied in detail.

This project combines synthesis, heterogenization and assembly of Lewis pairs, their characterization and application in catalysis. The successful applicant will have a strong background in molecular chemistry. A previous experience in main group chemistry and/or catalysis will be a plus. Dedication for research, curiosity and ability to engage into a cooperative project will be appreciated. Applicants are asked to send a detailed CV with at least one reference and a cover letter indicating their abilities and motivation.

NB: The project is funded by ANR. the PhD is expected to start in September-October 2021.

1. For a general review on FLP, see: Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2015**, *54*, 6400.
2. For self-assembly and self-repairing polymer thanks to P→B interaction, see: Wang, M.; Nudelma, F.; Matthes, R. R.; Shaver, M. P. *J. Am. Chem. Soc.* **2017**, *139*, 14232.
3. For gas sensing by diamontane based materials, see: Moncea, O.; Casanova-Chafer, J.; Poinsot, D.; Ochmann, L.; Mboyi, C. D.; Nasrallah, H. O.; Llobet, E.; Makni, I.; El Atrous, M.; Brandès, S.; Rousselin, Y.; Domenichini, D.; Nuns, N.; Fokin, A. A.; Schreiner, P. R.; Hierso, J.-C. *Angew. Chem. Int. Ed.* **2019**, *58*, 9933.
4. For catalysis mediated by FLP, see: a) Boudjelel, M.; Sosa Carrizo, E. D.; Mallet-Ladeira, S.; Massou, S.; Miqueu, K.; Bouhadir, G.; Bourissou, D. *ACS Catal.* **2018**, *8*, 4459. b) Declercq, R.; Bouhadir, G.; Bourissou, D.; Légaré, M. A.; Courtemanche, M. A.; Nahi, K. S.; Bouchard, N.; Fontaine, F. G.; Maron, L. *ACS Catal.* **2015**, *5*, 2513.