

Towards CO₂-fueled Molecular Machines

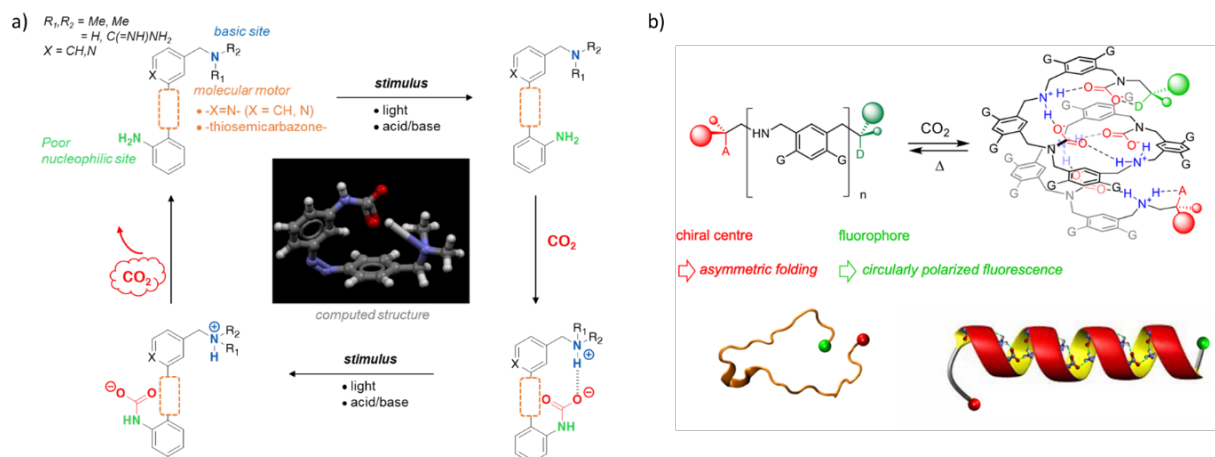
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This new research project focuses on the preparation and study of a new family of Synthetic Organic compounds displaying controlled molecular motion upon CO₂ capture/release



Research topic: The general objective of the PhD is to design and study molecular systems absorbing CO₂ by unconventional pathways, which are directed by intramolecular non-covalent interactions. These synthetic and soluble absorbents will be of two types: either multivalent and intrinsically cooperative or activated by an external physical (light) or chemical (effector) stimulus. In both cases, CO₂ fixation will be accompanied by self-organization of matter, which constitutes a valorisation of the captured CO₂.

In this first part of the project, a dyad resulting from the coupling of non-nucleophilic Brønsted base (tertiary benzylic amine or guanidine) and a modest non-basic nucleophilic end group (aniline) through a photoisomerizable central linkage (diazo or imino) will be synthesized and studied for the photo-induced capture and release of CO₂ coupled to molecular motion (figure a). The principle of the design resides in the fact the aniline-bound carbamate is insufficiently stable to capture CO₂ when the backbone adopts the *E* configuration but may be stabilized through single- or multiple H-bond salt bridge in the *Z* configuration. Therefore, irradiation at an absorption wavelength which is selective of the *Z* (resp. *E*) stereoisomer form should trigger the isomerization into the *E* configuration (resp. the *Z*) i.e. the release into CO₂-poor (resp. the capture from CO₂ rich) media.

The second part of the PhD project consists in the solution-phase synthesis of monomers and their solid-phase oligomerization into linear polyamine strands of controlled sizes bearing a chiral initiator such as an amino acid (figure b). Design and synthesis of the monomeric units is based on the work of A. Hamilton (*Org. Lett.*, 2019, 21, 7763) and have both been validated in the framework of two undergraduate projects. G groups can be chosen to be hydro-phobic/philic or even to bear chirogenic elements, enabling to tune the solubility or helicity of the architecture. The principle, of what should be the first cooperative absorbent for CO₂ in water, is that the strand lacks strong intramolecular structuring interaction in the absence of CO₂ and that these interactions arise upon conversion of neutral amines to ammonium carbamates, thereby inducing helical folding. In agreement with modelling data, an enantiopure monomer bearing a strong H-bond acceptor (A) or donor (D) at the end of the strand should initiate the sequence of CO₂/H⁺ fixation and the sense of the helicity. With this scenario, not only does CO₂ capture triggers matter structuration. In addition, CO₂ capture should be cooperative, i.e. its uptake and release should be facilitated as the extent of the reaction progresses.

Candidate profile: As the proposed topic is in the field of supramolecular chemistry, the recruited candidate will have a research master's degree or equivalent in organic chemistry and a solid knowledge of organic physical-chemistry.

Keywords: Organic synthesis, Supramolecular chemistry, CO₂ Capture, Molecular machines

Our recent publications in the field: (1) *Chem. Sci.* **2016**, 7, 4379-4390, (2) *Green Chem.* **2016**, 18, 6436 – 6444, (3) *Acc. Chem. Res.* **2017**, 50, 1692-1701, (4) *Green Chem.* **2018**, 22, 5058-5508, (5) *Curr. Opin. Green Sustain. Chem.* **2019**, 16, 71-76, (6) *Nature Chem.* **2020**, 12, 202-212, (7) *Chem. Eur. J.* **2021**, 28, e202104377 (8) Fr. Patent **2016**, FR16 53968, (9) Fr. Patent **2017**, FR1758538, (10) WO patent **2017**, PCT EP 2017060166, (11) WO patent **2018**, PCT EP 2018 074789.