Project 1: Artificial Photosynthesis: transformation of water and carbon dioxide into fuels

Group leaders: Marc Fontecave, Caroline Mellot-Draznieks

Permanent staff involved in the project:

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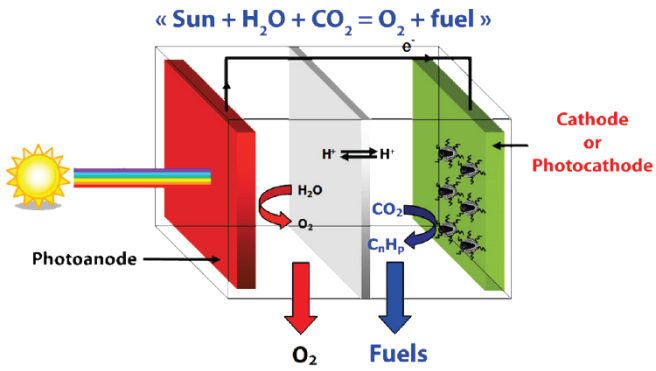
One of the challenges of the 21st century is energy. The limitation of fossil fuels (oil, gas and coal) and the need to limit emissions of CO_2, a greenhouse gas, require the development of technologies aimed at valorizing CO_2, in particular by converting it into energy-dense organic molecules such as hydrocarbons. One of the most fascinating strategies is that used by nature. The complex process of photosynthesis uses solar energy to realize a thermodynamically unfavorable reaction: the reduction of CO_2 by H_2O. Photosynthesis thus can store solar energy in the form of biomass with high energy content, and also in the form of hydrogen by water splitting. These reactions require photosensitizers for photon absorption and charge separation, as well as catalysts to accelerate multi-electronic processes required in water oxidation, CO_2 and H^+ reduction.

An artificial photosynthetic system must first include an efficient photon collector absorbing a broad spectrum of visible sunlight. These can be molecular photosensitizers or semiconductor materials. They allow charge conduction and separation, stabilization of excited states, and have to be interfaced with catalysts. The latter are the other important elements of the device. They use the holes for water oxidation and the excited electrons to bind and transform the CO_2 molecule or to reduce protons. One may use solid metal-based electrodes that provide both electron conducting and catalytic functions, or soluble molecular catalysts, which are then grafted on electrodes.

Towards Artificial Photosynthesis



The bio-inspired approach is not much implemented so far. This is the strategy followed in our laboratory to develop new solid and molecular metal catalysts preferably based on non-noble and abundant metals (Fe, Cu, Co, Ni) for (photo)electro-oxidation of water and -reduction of protons or CO_2. We also study hydrogenases, fascinating metalloenzymes, and artificial hydrogenases for the production of hydrogen. Various strategies for the heterogenization of the molecular and enzymatic catalysts are undertaken to build solid materials for electrodes and photo-electrodes.

This project is developed along several directions:

- **Synthesis and characterization of molecular complexes as catalysts for the reduction of CO_2 or water (homogeneous catalysis)**

- New molecular mononuclear catalysts based on Cobalt (Co), Nickel (Ni), Rhodium (Rh) and Rhenium (Re) **(Figure 1a-c**)
- Dithiolene complexes of Molybdenum (Mo) or Tungsten (W), which are inspired by the active sites of formate dehydrogenase (**Figure 1d**)
- Polynuclear complexes of Mo and Copper (Cu) inspired by active sites of class II of CO dehydrogenases

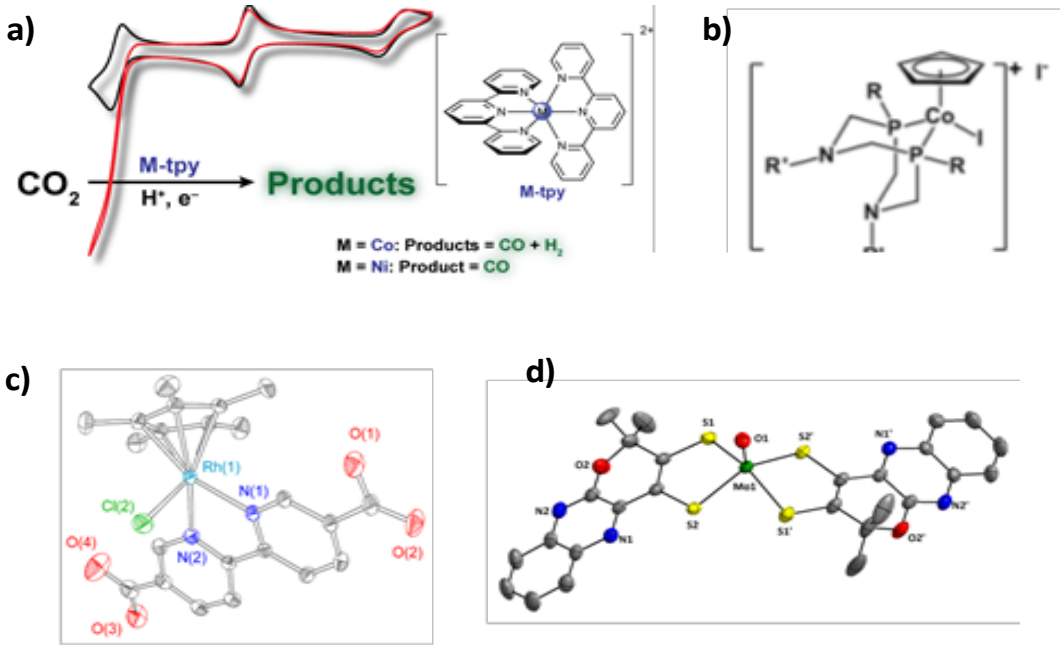


Figure 1: a) Terpyridine complexes of cobalt and nickel are electrocatalysts for the reduction of CO_2 to CO, as shown in the cyclic voltammogram in the presence of CO_2 (*Chem Soc. Rev.* **2017**, 46, 761-796); b) A cobalt complex catalyzing reduction of CO_2 to formic acid (*J. Am. Chem. Soc.* **2017**, 139, 3685-3696); c) A rhodium-based catalyst for reduction of CO_2 into formic acid (*Inorg. Chem.* **2019**, 58, 6893-6903); d) A Molybdenum-dithiolene complex that mimics the active site of formate dehydrogenase (*Angew. Chem. Int. Ed. Engl.* **2018**, 57, 17033-17037).

- **Towards heterogeneous catalysts for water oxidation, proton reduction and CO_2 reduction**

- By covalent grafting of molecular complexes on the electrode surfaces and by electrodeposition of metals from molecular or salt precursors
- By incorporating, covalently or not, catalytic or photosensitive complexes in coordination polymers or in MOFs (Metal Organic Frameworks) and shaping them into thin films. Examples are polyoxometallates encapsulated in MOFs (POM@MOFs) for the oxidation of water (**Figure 2**) or encapsulated photosystems into MIL-101 for the reduction of CO_2 (**Figure 3**)
- By electrodeposition of metals and metallic oxides (copper for example) from metallic salts, leading to dendritic porous catalysts (**Figure 4a**)
- By doping carbon graphite-like (nano)materials with nitrogen and metals (Fe, Cu) (**Figure 4b**).

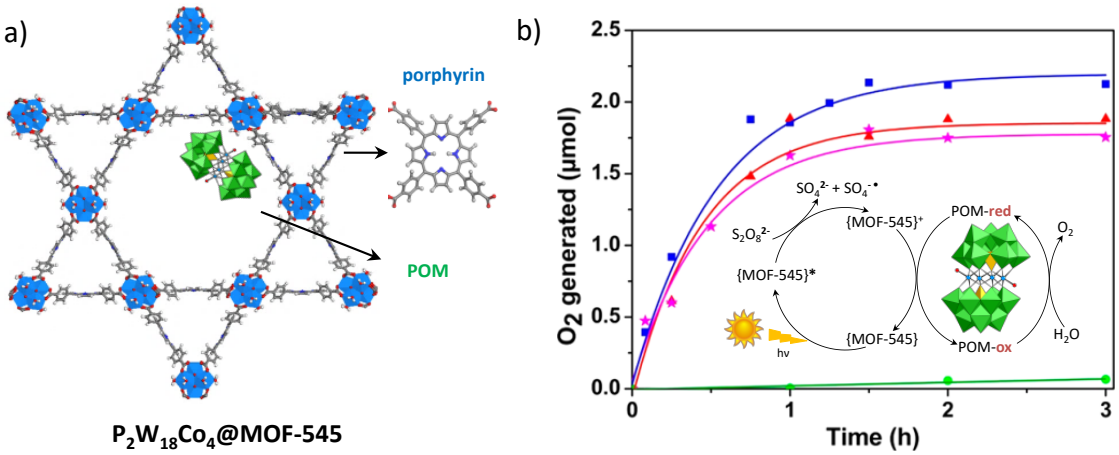


Figure 2: a) Components of $P_2W_{18}Co_4$@MOF-545. The position of the POM is obtained from computations (see Figure 6). Colour code: WO_6, green polyhedra; ZrO_8, blue polyhedral or spheres; Co, cyan spheres; O, red spheres; C, H, grey; N, dark blue. b) Kinetics of visible-light-driven O_2 production measured by GC analysis over 0.5 mg of $P_2W_{18}Co_4$@MOF-545 (blue square), $P_2W_{18}Co_4$@MOF-545 recycled once (red triangle), twice (pink stars), 131 µM TCPP-H_2 and 13 µM $P_2W_{18}Co_4$ in solution (green circle). Reaction conditions: 5 mM $Na_2S_2O_8$ in 2 mL of 80 mM borate buffer solution, pH 8, visible light (λ > 420 nm, 280 W). Inset: Schematic representation of the proposed mechanism for the light-driven OER by $P_2W_{18}Co_4$@MOF-545 (*J. Amer. Chem. Soc.* **2018**, 140, 10, 3613-3618).

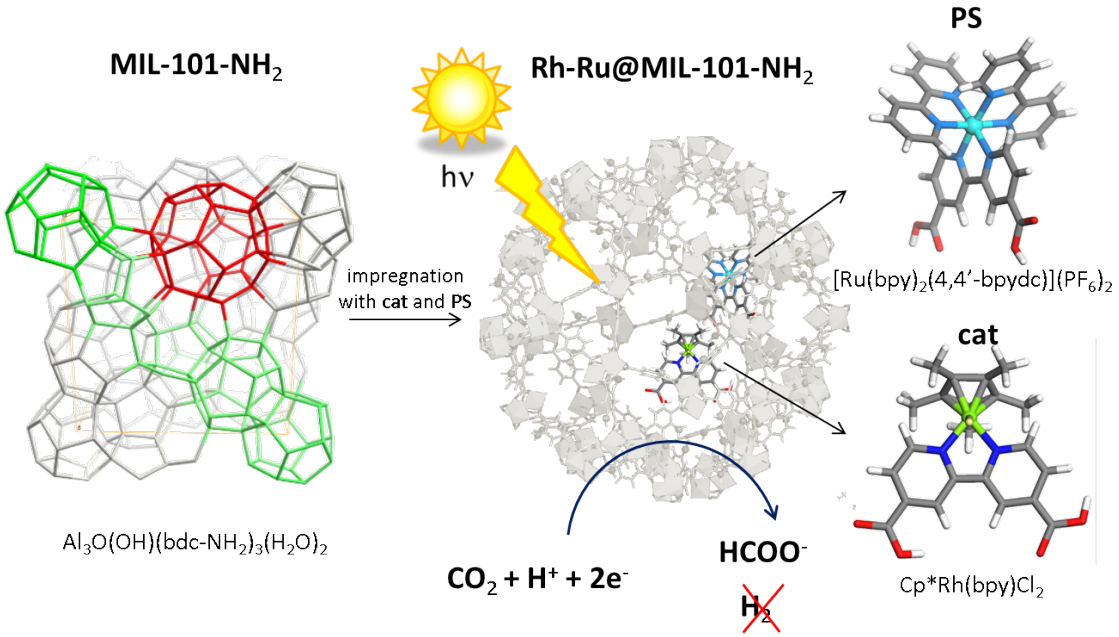


Figure 3: Schematic representation of co-immobilized photosystem in very large pore MIL-101-NH_2 showing the host topology with its small (green) and large (red) cages (left part) and enlarged large cage of Rh-Ru@MIL-101-NH_2 (middle part). The enlarged structures of photosensitizer (PS) $Ru(bpy)_2(4,4'\text{-bpydc})](PF_6)_2$, and catalyst (cat) $Cp^*Rh(4,4'\text{-bpydc})Cl_2$ (O: red, N: blue, Ru: cyan, Rh: green, C: grey, H: white) are shown on the left (*ChemSusChem.* **2018**, 11, 3315-3322).

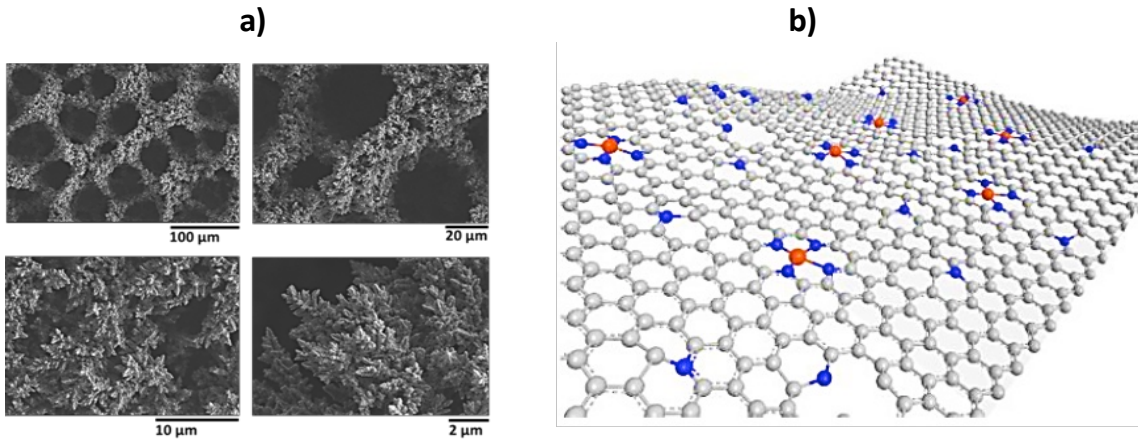


Figure 4 : a) Porous dendritic copper-based materials for the reduction of CO_2 into ethylene (*Proc. Natl. Acad. Sci.* **2019**, 116, 9735-9740; *Nature Materials* **2019**, 18, 1222-1227) and the oxidation of water (*Angew. Chem. Int. Ed.*, **2017**, 56, 4792–4796); b) N- and Cu-doped carbon materials, containing Cu single sites, as catalysts for CO_2 reduction to ethanol (*Angew. Chem.* **2019**, 58, 15098-15103).

The preparation and study of artificial hydrogenases

The combination of well-selected receptor proteins and catalysts can lead to new "enzymes" called “artificial enzymes”. They have the advantage of being optimized both by chemical modification of the catalyst and by protein engineering (site-directed mutagenesis). This original approach is used for the construction of artificial hydrogenases (**Figure 5**) but also CO_2 reductase which catalyze the reduction of CO_2 into CO.

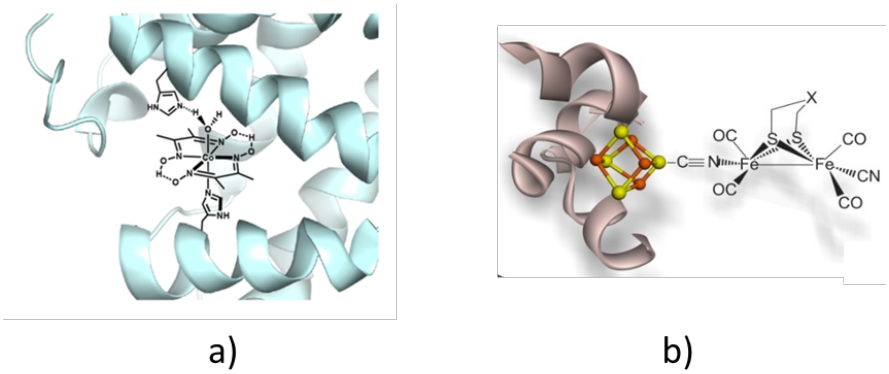


Figure 5. a) An artificial hydrogenase resulting from the combination of myoglobin in its *apo* form and a synthetic complex, cobaloxime (*Inorg. Chem*. **2014**, 53, 8071 ; *Curr. Op. Chem. Biol.* **2015**, 25, 36–47 ; *ChemPlusChem* **2016**, 81, 1083-1089). b) An artificial hydrogenase with an active site mimicking the active site (see figure 4b) of [FeFe]-hydrogenases (*ACS Catal.* **2019**, 9, 4495-4501).

The evaluation of these chemical or enzymatic systems

- For their electro-catalytic properties for the reduction of protons and carbon dioxide and for water oxidation (electrochemical analysis such as cyclic voltammetry and electrolysis)
- For their photochemical catalytic properties in combination with organic or inorganic photosensitizers, and a sacrificial electron donor/acceptor.
- For the structure determination of hybrid porous solids through diffraction techniques and PDF (Pair Distribution Function) techniques (**Figure 6**).
- For elucidating electronic properties and reaction pathways through Density Functional calculations (**Figure 7**).

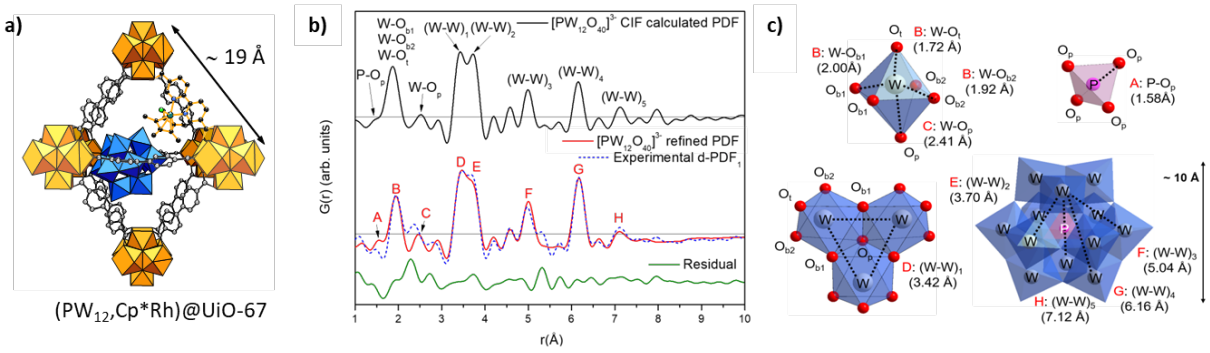


Figure 6. (a) Details of the structural model for (PW_{12},Cp*Rh)@UiO-67 as obtained from simulated annealing and DFT-D3 level geometry optimizations. (b) Comparison of the calculated PDF of an isolated PW_{12} (black) and the experimental d-PDF of PW_{12} in UiO-67 (blue dotted line), superimposed with the refined d-PDF (red) fitted using the $[PW_{12}O_{40}]^{3-}$ structural model from CIF file (JCPDS 00-050-0304) and residual profile (green). A-H labels of peaks correspond to the indicated refined distances in the POM components as illustrated in (c) for the PO_4 tetrahedron, the WO_6 octahedron, the trimer of WO_6 octahedra, and within the full PW_{12} polyoxometalate structure. WO_6, blue octahedra, PO_4, pink tetrahedron, O, red spheres, W, grey spheres, P pink sphere (Mellot-Draznieks et al. *J. Am. Chem. Soc.* **2020**, 142, 9428–9438).

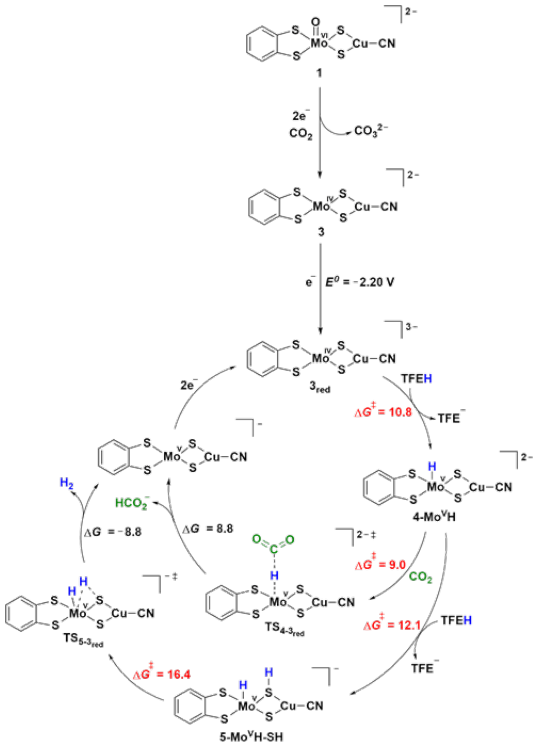


Figure 7: Mechanism proposed for the reduction of CO_2 into formic acide by a dinuclear Mo-Cu complex, mimicking the active site of the CO-dehydrogénase (*Chem. Sci*. **2020**, 11, 5503–5510).

The implementation of these systems within technological devices

The most efficient molecules (photosensitizers and catalysts) and materials (semiconductors and catalysts) are exploited to develop an electrochemical or a photoelectrochemical cell to couple water oxidation (anode) to the reduction of CO_2 or protons (cathode), the source of electrons being preferentially an external photovoltaic system (see *Proc. Natl. Acad. Sci.* **2019**, 116, 9735-9740). Different types of electrodes/electrolyzers (H cells, flow cells and gas diffusion electrodes) are developed (**Figure 8**).

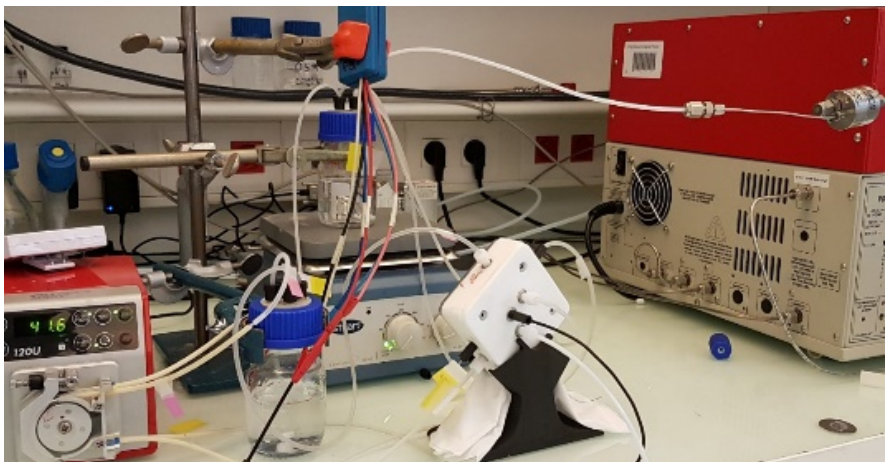


Figure 8: Electrochemical flow cell coupled with a chromatograph for the detection of reaction products (*Proc. Natl. Acad. Sci.* **2019**, 116, 9735-9740).

Methods and competences

- Organic and organometallic synthesis
- Materials synthesis and characterization
- Coordination chemistry
- Electrochemistry
- Photochemistry
- Hydrogenation reactors
- Analytical Platform (gas chromatography, ion exchange, HPLC ...)
- Platform for protein crystallography (glove box, robots ...)
- Optical Spectroscopy
- Computational chemistry (VASP, Gaussian ...)
- Protein cloning, expression and purification
- Molecular biology: directed mutagenesis...

Academic collaborations

- Vincent Artero, CEA Grenoble (électrodéposition de métaux, hydrogénases, complexes de cobalt)
- Carlos Sanchez-Sanchez, Sorbonne Université (électrochimie moléculaire)
- Mohamed Atta, CEA Grenoble (hydrogénases)
- Capucine Sassoye, UPMC (PDF des MOFs)
- Jérôme Canivet, IRCE Lyon (MOFs)
- Florian Wisser, Regensburg University , Allemagne (polymères poreux)
- Anna Proust, UPMC Paris (POMs)
- Anne Dolbecq, Pierre Mialane UVSQ, Versailles (POM@MOF)
- Céline Pagis, Audrey Bonduelle, IFPEN, Lyon (Photocatalyse des MOFs)
- Christophe Léger, CNRS Marseille (hydrogénases)
- Andrea Zitolo, Synchrotron Soleil (XAS spectroscopy)
- Dario Taverna, Sorbonne Université (microscopy)

Industrial partnership

A tight collaboration between the laboratory and the company TOTAL aims at developing catalysts for electrolysis of carbon dioxide into hydrocarbons (ethylene) and alcohols (ethanol).

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