DESIGN OF FIRST POM-BOX HYBRID MATERIALS WITH EFFICIENT SOLID-STATE HALOCHROMIC PROPERTIES

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The benzazolo-oxazolidine (BOX) derivatives represent an interesting family of multiswitchable molecules (Fig 1.a). Exhibiting a colourful open and closed a colorless closed form, they can respond in solution to different kinds of stimulations such as electrochemical potential, pH variation or light irradiation leading to a strong modulation of their optical characteristics [1]. In order to efficiently transpose their properties into the solid state, the coupling of BOXs with polyoxometalates (POMs), which are anionic metal-oxide clusters [2], into new hybrid organic-inorganic supramolecular switchable materials is a promising but still unexplored approach.

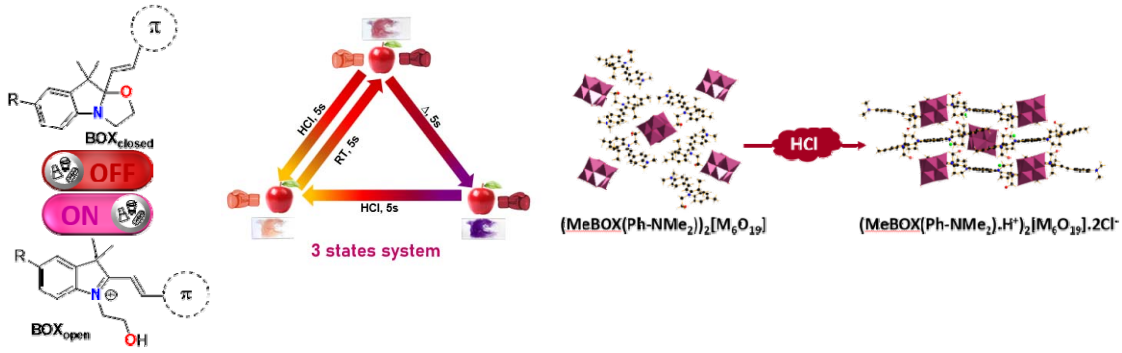

Fig 1: a) Multi-switchable properties of BOX derivatives, b) Halochromic behaviour of (MeBOX(Ph-NMe_2))$_2$[M_6O_{19}] (M= Mo, W), c) Crystal structure of (MeBOX(Ph-NMe_2))$_2$[M_6O_{19}] and (MeBOX(Ph-NMe_2).H^+)$_2$[M_6O_{19}].2Cl^-

In such context, we report here our success in designing the first hybrid supramolecular assemblies combining POM and BOX units. They exhibit a large versatility in their synthesis pathways, chemical compositions and crystal structures. Among them, (MeBOX(Ph-NMe_2))$_2$[M_6O_{19}] (M= Mo, W) materials exhibit efficient reversible halochromic properties upon acid vapours exposure at room temperature, leading to a three-states coloured system (Fig 1.b). The colour-change effect is due to the capture of HCl into the hybrid networks, which has been successfully characterised by single-crystals X-Ray diffraction analyses (Fig 1.c). Furthermore, assemblies containing $[W_6O_{19}]^{2-}$ unit, exhibit solid-state photoluminescence modulation upon acid exposure, in contrast with their isostructural molybdenum analogues. These behaviours make these hybrid materials highly relevant for the development of new optical sensors to detect acid gases and for optoelectronic applications [3].

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[1] Photon-Working Switches. Tokyo: *Springer Japan*; **2017**. p. 69-91

[2] *J. Mater. Chem. C* **2020**, 8, 637-649; *J. Mater. Chem. C*, **2022**, 10, 899-907.

[3] Article under preparation