PhD offer

Sustainable and recyclable photoluminescent alkali lanthanide-free polyoxometalate salts for water detection

Keywords: Polyoxometalates, hydrates, photoluminescence, water sensing, recycling.

Context: The detection and quantification of water either as trace in liquids, or as relative humidity (RH) in air are highly critical for industrial process controls, solvent manufacture, food and drug storage, lithium-ion batteries life extension, and indoor air quality improvement.[1–5] In the last years, photoluminescent (PL) solid sensors, that can respond to the presence of water with a detectable change in their PL signal, have been considered as an attractive potential alternative to traditional analytical technics due to their faster response, higher sensitivity and ability of *in situ* and real-time detection.[6–9] However, many investigated materials still suffer from non-trivial synthesis approaches using toxic reagents or highly critical elements, limited stability over storage time, low selectivity or poor reusability. Moreover, their recycling has never been considered. **Therefore, new sustainable, reusable and recyclable PL water sensors are highly desirable, to be able to use them in real-world applications.**

Position: This PhD project aims at investigating the potentiality of new PL anhydrous alkali salts of the $[SbW_6O_{24}]^{7-}$ (**SbW_6**) lanthanide-free polyoxometalate (Fig. 1a) to sense RH in the air and trace amounts of water in organic solvents. These materials can be elaborated in water *via* low-energy and eco-friendly procedures.[10] Upon exposure to water molecules, they rehydrate quickly causing strong PL quenching effects (Figs. 1a-b). The variation of the light signal is correlated to the water content of the medium, which these phases detect with high sensitivity and selectivity. As a proof of concept, a recent study has highlighted that $Na_7[SbW_6O_{24}]$ quantitatively senses RH with a limit of detection (LOD) of 2.2% RH (Fig. 1c) which is among the best values of recent PL humidity sensors.[11] Moreover, the PL-active anhydrous phases are regenerable after use by soft thermal treatments (T ≤ 200 °C), and they can be easily recycled via a one-step procedure in water.

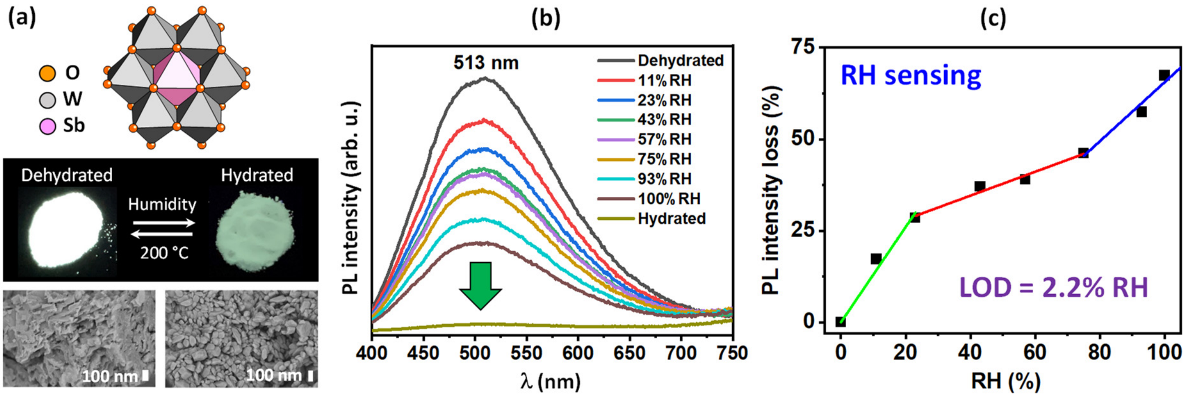

Fig. 1 (a) The $[SbW_6O_{24}]^{7-}$ unit, PL properties (λ_{ex} = 254 nm) and particle morphologies of $Na_7[SbW_6O_{24}]$ (dehydrated) and $Na_7[SbW_6O_{24}]\cdot16H_2O$ (hydrated). (b) PL intensity of $Na_7[SbW_6O_{24}]$ exposed for 1 h at different RH levels. (c) % PL intensity loss vs RH variation, and limit of detection (LOD) value of $Na_7[SbW_6O_{24}]$.

Further investigations are required to streamline the complex reactivity of these materials towards water, and to ultimately understand their detection mechanism. Indeed, the hydration/dehydration processes of the anhydrous phases involve the formation of intermediary hydrates. Their PL response varies with their degree of hydration, and their stability depends on the temperature and water content of the medium.

Project description: The first objective is to enrich this class of materials by performing a prospective research of new alkali **SbW_6** salts whose chemical composition will vary with the nature and the ratio of the alkali ions, and with their degree of hydration. New crystallization routes of intermediary hydrates will be developed thanks to experimental elaborations of binary and/or ternary phase diagrams between salts, water and/or anhydrous solvent. The crystal structures of the water-sensitive (an)hydrated/deuterated phases will be determined by performing advanced X-ray, neutron (for deuterated materials) and electron diffraction analyses. Advanced structural analyses methods such as the Maximum Entropy Method (MEM) based on single-crystal X-ray diffraction data will be managed to accurately characterize the H-bonding networks involving water molecules and the **SbW_6** surface, responsible of PL quenching effects. In addition, the recycling procedures of the sensors will be optimized.

The second objective consists in streamlining the hydration/dehydration processes of the alkali **SbW_6** salts. Thanks to experimental techniques dedicated to the study of thermodynamic solid/vapor equilibria, *i.e.* gravimetric vapor sorption (GVS) experiments, X-ray diffraction and microscopy under variable RH, the RH-dependent thermodynamic stability domains of each phase will be investigated. A kinetic study of the phase conversions during the hydration/dehydration processes will be also carried out to correlate the microstructure of solids with their hydration rates.

The third objective is the characterization of the water sensing performances of the anhydrous alkali **SbW_6** salts as such or incorporated into polymer matrices in order to elaborate new water sensing devices with improved applicability. This will be realized by studying the photophysical properties (absorption and emission) of the alkali **SbW_6** salts, and by compiling them with their chemical composition and their crystal structure to evidence pertinent relationships. The ability of the anhydrous phases to trace water will be then examined by performing *in situ* PL experiments under variable RH in the air or water content in a wide range of organic solvents. This would allow correlating composition, crystal structure, particle size and morphology of the salts with their sensing parameters (detection range, LOD, sensitivity, detection rate).

Environment: This PhD work is a part of the **ALPS-Water** project (ANR-24-CE08-4167) funded by the French National Research Agency. Its consortium gathers three academic partners with complementary cultures, skills and resources. The Institut des Matériaux de Nantes (IMN) Jean Rouxel (http://www.cnrs-imn.fr) has a recognized expertise in photoactive POM-based materials.[10–13] The Separative Sciences and Methods (SMS) Laboratory (https://labsms.univ-rouen.fr) is expert in phase diagrams elaboration and in the physico-chemistry of hydrates.[14–16] The Polymers, Biopolymers, Surfaces (PBS) Laboratory (https://www.pbs.cnrs.fr) brings its expertise in design and elaboration of polymer materials.[17,18] The PhD candidate will mainly conduct their research activities at IMN, in the Innovative Materials for Optics, Photovoltaics and Storage (MIOPS) team, and he will undertook several short stays at SMS. He will also perform at IMN PL characterization of alkali **SbW_6** salt/polymer composite sensors previously elaborated at PBS. This research project offers the candidate the opportunity to acquire knowledge and multidisciplinary know-how in inorganic chemistry for the preparation of the alkali **SbW_6** salts, in physico-chemistry of hydrates for the study of their reactivity towards water, as well as in photophysical characterizations to evaluate their sensing performances. In addition, the candidate will gain experience in a wide variety of characterization techniques: single-crystal and powder X-ray diffraction analyses, thermal and GVS analyses, vibrational (IR, Raman) and optical (UV-visible absorption, steady-state and time-resolved photoluminescence) spectroscopies, scanning electron microscopy (SEM) and transmission electron (TEM) microscopy. Furthermore, he will have the opportunity to present his results in national and international congresses.

Candidate profile and skills required: The profile sought is that of a young scientist holding or in the process of obtaining a Master's degree (or equivalent) focused on materials or/and solid-state chemistry, extremely motivated by exploratory synthesis, and possessing a strong interest in interdisciplinary subjects (inorganic chemistry, physico-chemistry of hydrates, photophysics, materials science). Expected and necessary skills include experience in inorganic synthesis (M1 and/or M2 internship), proficiency with common tools for characterizations of materials. Additional skills in photophysical characterizations (absorption, emission) will be appreciated but not essential.

Start of PhD: October 2025

The application package (Curriculum Vitae, transcripts of Master 1 and 2 degrees or equivalents, letter of motivation) should be sent to the three PhD supervisors.

PhD supervision:

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