Enabling country food monitoring through a fluorescent Hg(II)-responsive sensor

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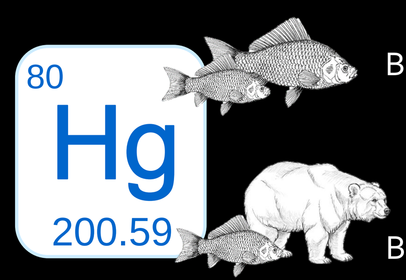
Research context [1]

Mercury pollution in water sources and its bioaccumulation in marine species is a worldwide issue. Since exposure leads to negative health effects, probing this contaminant is essential. Although North Americans are generally not at risk from poisoning, diets rich in fish and marine mammal can lead to an increased hazard.



- Significant presence in the food chain
- High toxicity
- Crossing of biological barriers

Health Canada dietary recommendations[2]

Drinking water	Fish sold at retail
1 ng/mL	0.5 – 1.0 mg/kg

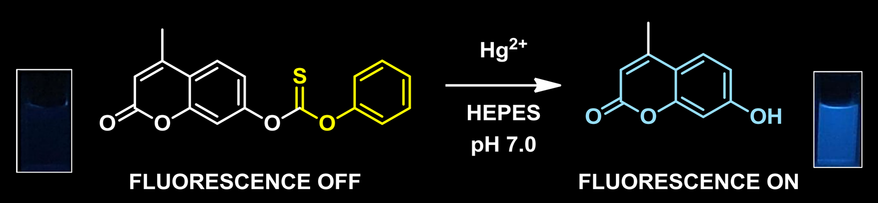
Atmospheric circulation carries Hg species to polar regions, where monitoring is more laborious.

The current approaches to quantify mercury are efficient, but are costly and require bulky instrumentation. Hence, many research advances rely on fluorimetry as a more portable alternative for rapid and selective in-the-field sensing.

Fluorophores

Thanks to interesting photophysical properties, many fluorophores have been chemically modified to be Hg(II)-responsive. In fact, fluorescence can be induced or prevented by exploiting the affinity of Hg towards sulfur atoms.

Example for Hg-assisted hydrolysis of a coumarin compound[3]



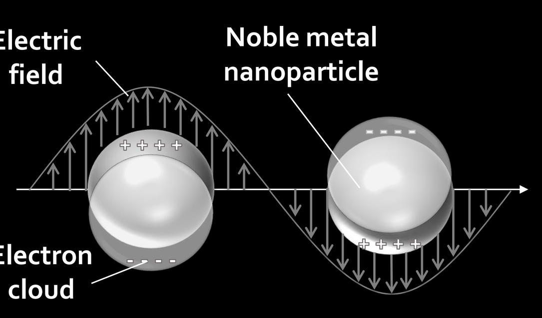
Detection limit 146 ng/mL

- Functional in water
- Selective towards Hg(II)
- Tunable λ_{ex} and λ_{em} through fluorophore selection

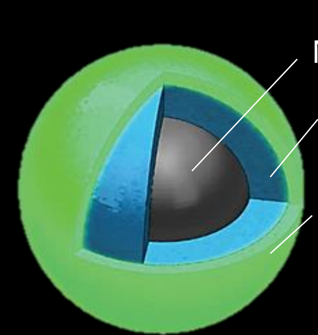
- Irreversible mechanism
- Response time ≥ 10 min
- Lack of sensitivity (high detection limit)

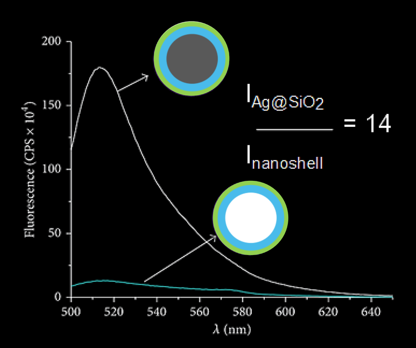
Plasmonic nanoparticles

Noble metal nanoparticles can show a collective oscillation of its conduction electrons when under an incident light. This phenomenon is called **localized surface plasmon resonance (LSPR)** and leads to an amplification of the electric field at the particle's suface.



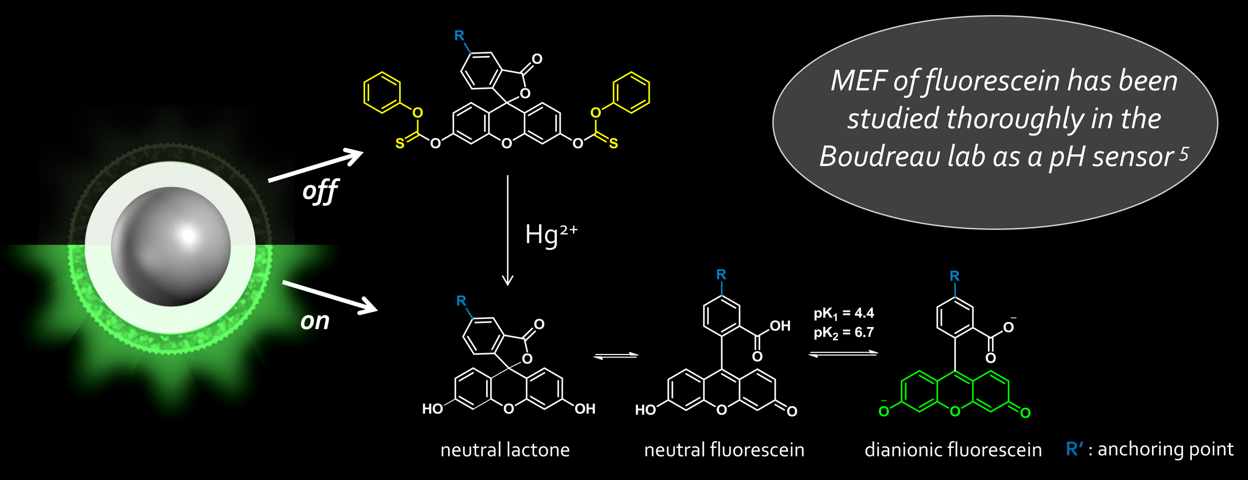
Combining fluorophores into a concentric nano-architecture can lead to **metal-enhanced fluorescence (MEF)**, allowing a better sensitivity for detection.[4]





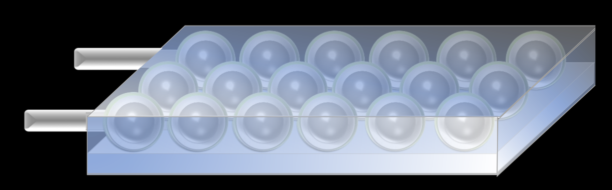
Objective and Strategy

The project targets the development of a Hg(II)-responsive fluorescent probe providing an enhanced performance in terms of sensitivity and reusability to replace the bulky lab-based instruments for in-field applications.



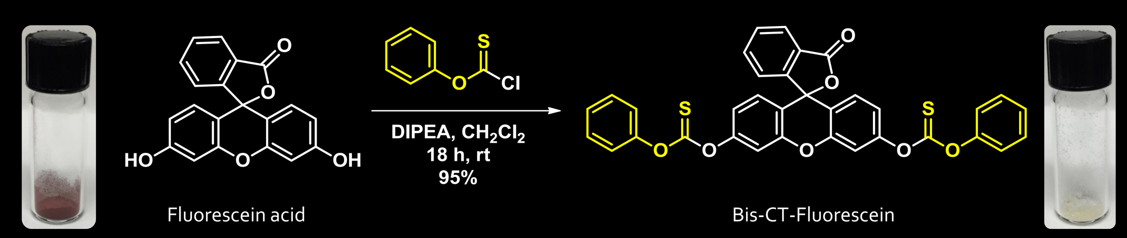
Tasks

- Synthesis of the Hg-responsive probe
- Evaluation of its analytical performance
- Implementation onto substrates for MEF
- Regeneration of the Hg-sensitive surface
- Implementation into a μfluidic chamber

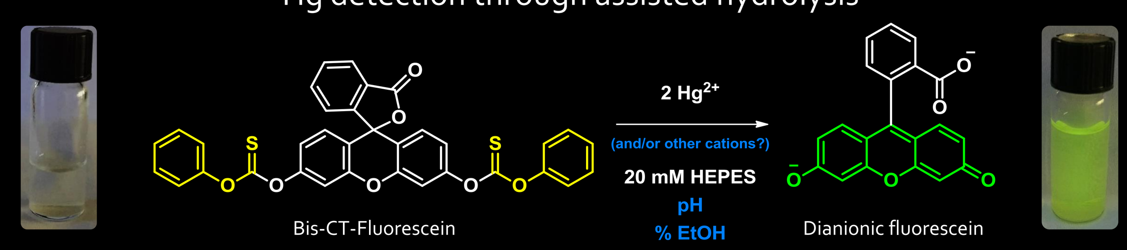


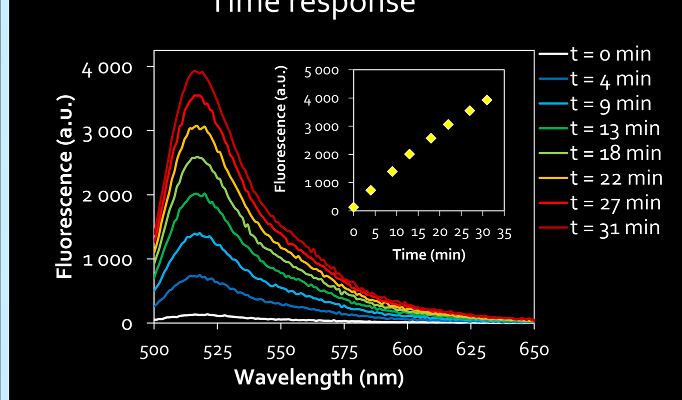
Molecular probe and its Hg-sensing properties

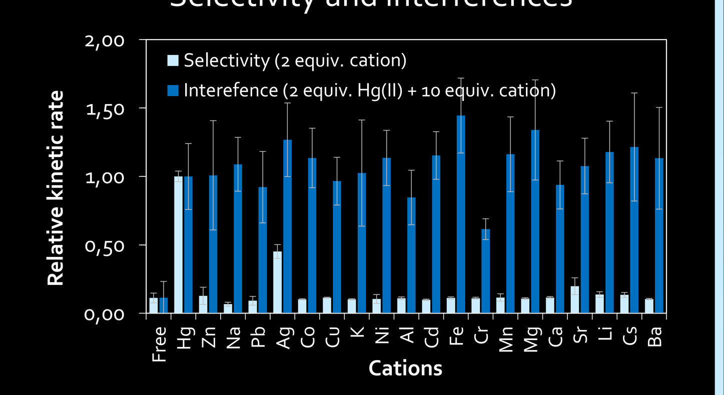
Probe synthesis through a one-step, high yield procedure[3]

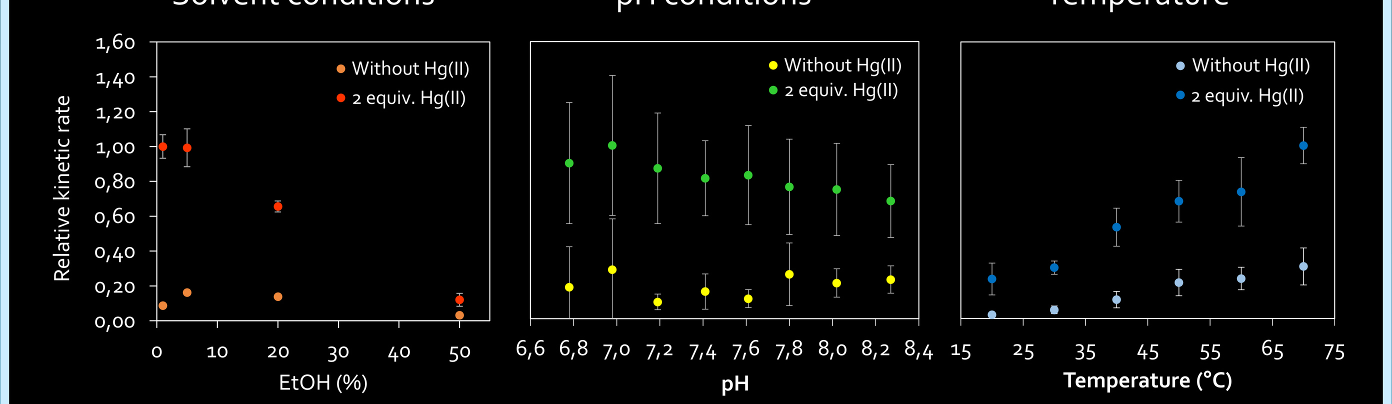


Hg detection through assisted hydrolysis









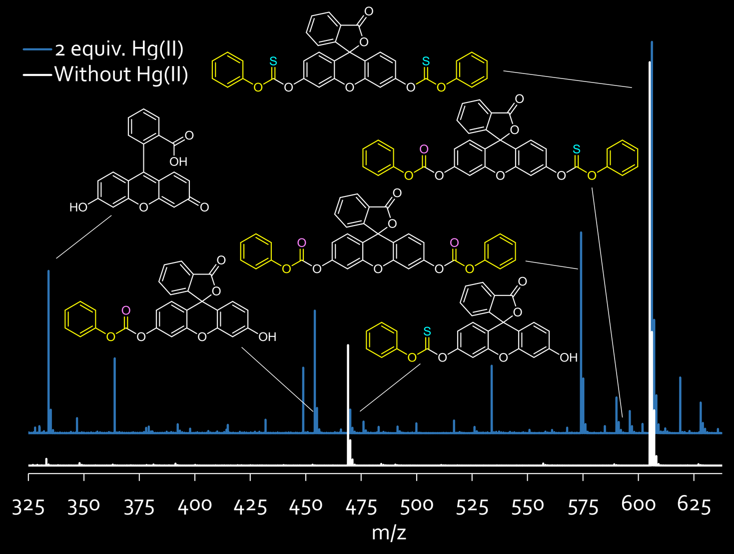
Optimized conditions :

- 1 μM Bis-CT-Fluorescein
- $\lambda_{ex,\ max}$ = 490 nm
- $\lambda_{em,\ max}$ = 516 nm
- 1% EtOH in water
- pH 7.4
- 25°C

Hg-sensing mechanism

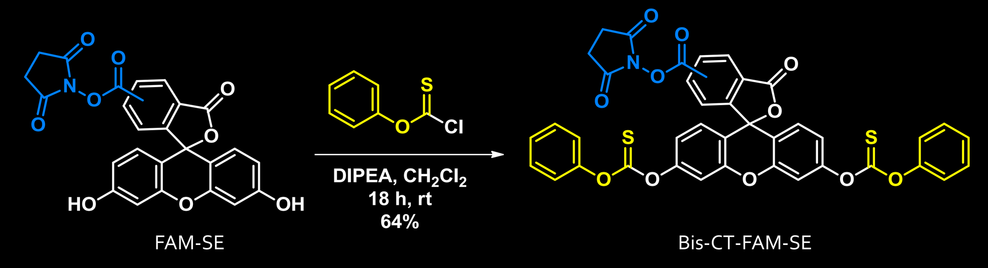
Mass spectrometry (MS) allows ionization of chemical species in order to identify them as a mass to charge (m/z) ratio.

After analyzing Bis-CT-fluorescein by MS, the results suggest its slow but spontaneous hydrolysis in pure water. However, addition of Hg(II) leads to desulfurized intermediates which accelerate the hydrolysis and allows detection of fluorescein rapidly.

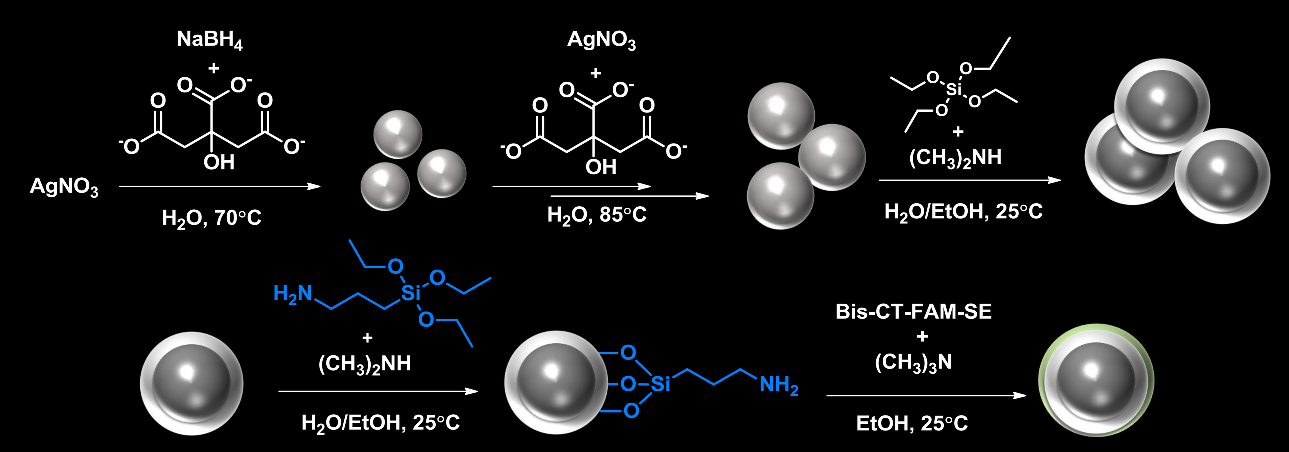


Implementation to substrates

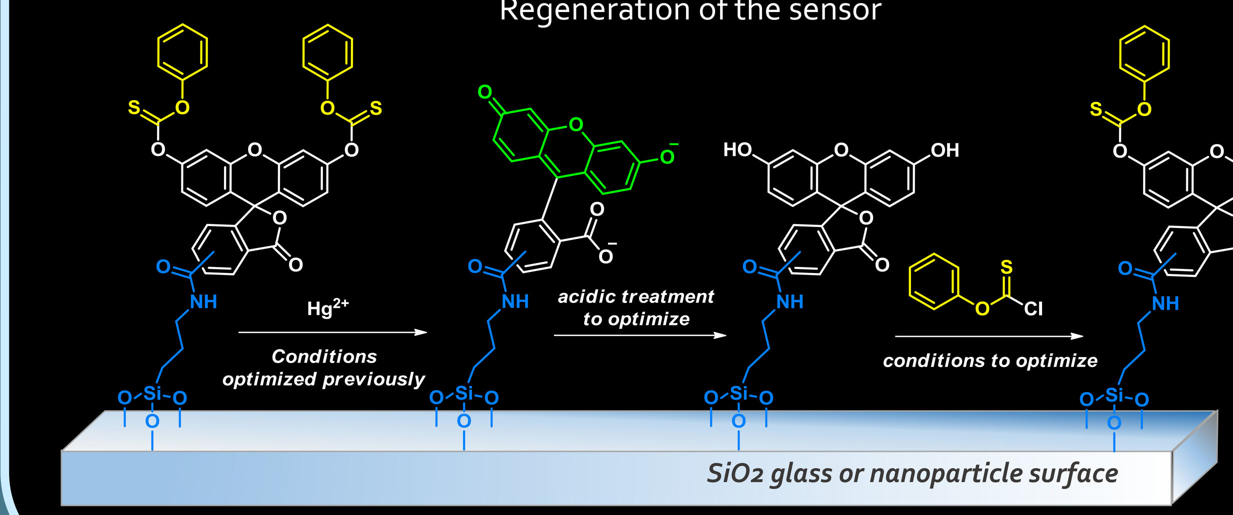
Synthesis of a functionalized molecular probe to allow grafting onto surfaces



Implementation onto nanoparticles for MEF detection[6]



Regeneration of the sensor



Conclusions

A new Hg-sensitive molecule based on fluorescein has been synthesized and proved quite selective towards Hg(II) across a series of competitive cations. The strategy can be applied to a functionalized fluorescein derivative, allowing immobilisation on silica.

Current work includes quantification of Hg(II) using the molecular probe and its grafting on AgNPs to study MEF. By combining these results with further reversibility studies, a fluidic detection chamber will be built as a preliminary reusable and sensitive platform.

References

1. This thesis is part of the thematic project 3.4 of Sentinel North, aiming to enable the monitoring of food quality in the Northern environment. *Sentinellenord.ulaval.ca/en/research/enabling-tools-monitoring-food-quality-northern-environment*
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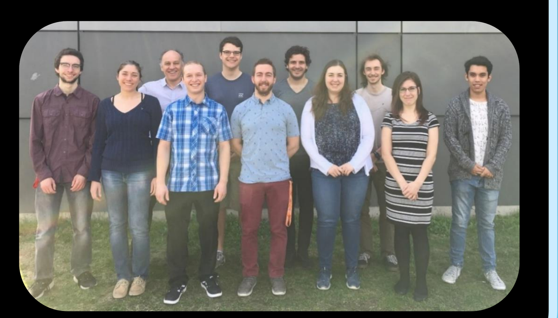

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