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Exploring the use of imine-functionalized silica nanoparticles as nanosensors for imidacloprid: A computational and experimental study

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Introduction: The Imidacloprid (IMD) Dilemma

Maintaining a balance between agricultural demands and environmental survival is critical. Neonicotinoid insecticides such as Imidacloprid, acetamiprid, thiamethoxam, clothianidin, amongst others, are highly effective at protecting various food crops¹⁻², making them essential for global food security, yet their overapplication threatens the very ecosystems we rely on. Imidacloprid application is like a double-edge sword, the same features (potency, efficacy, selectivity) that promotes its usage are the same features that do great harm if misused (Figure 1). Hence the need for rapid detection and monitoring systems to provide critical data such as the presence and levels of these toxic chemicals in various matrices at the right velocity, veracity and variety. Such systems foster quick and resolute data-driven decision-making and action at several levels – from the common man to policy makers – aiding the achievement of the sustainable development goals.

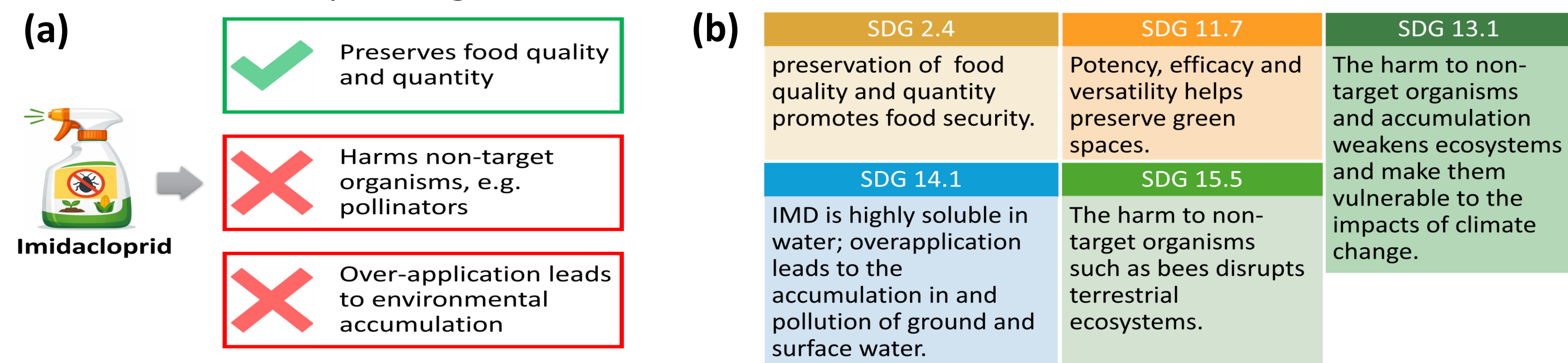


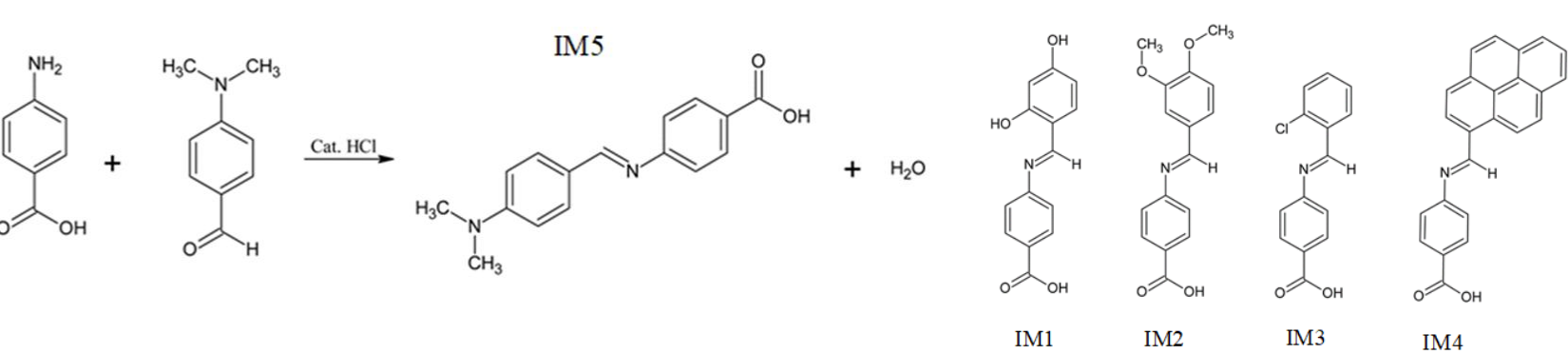
Figure 1 (a) The impact of Imidacloprid application and (b) their influence on certain SDGs.

Materials and Methods

Silica nanoparticle synthesis (sol-gel)

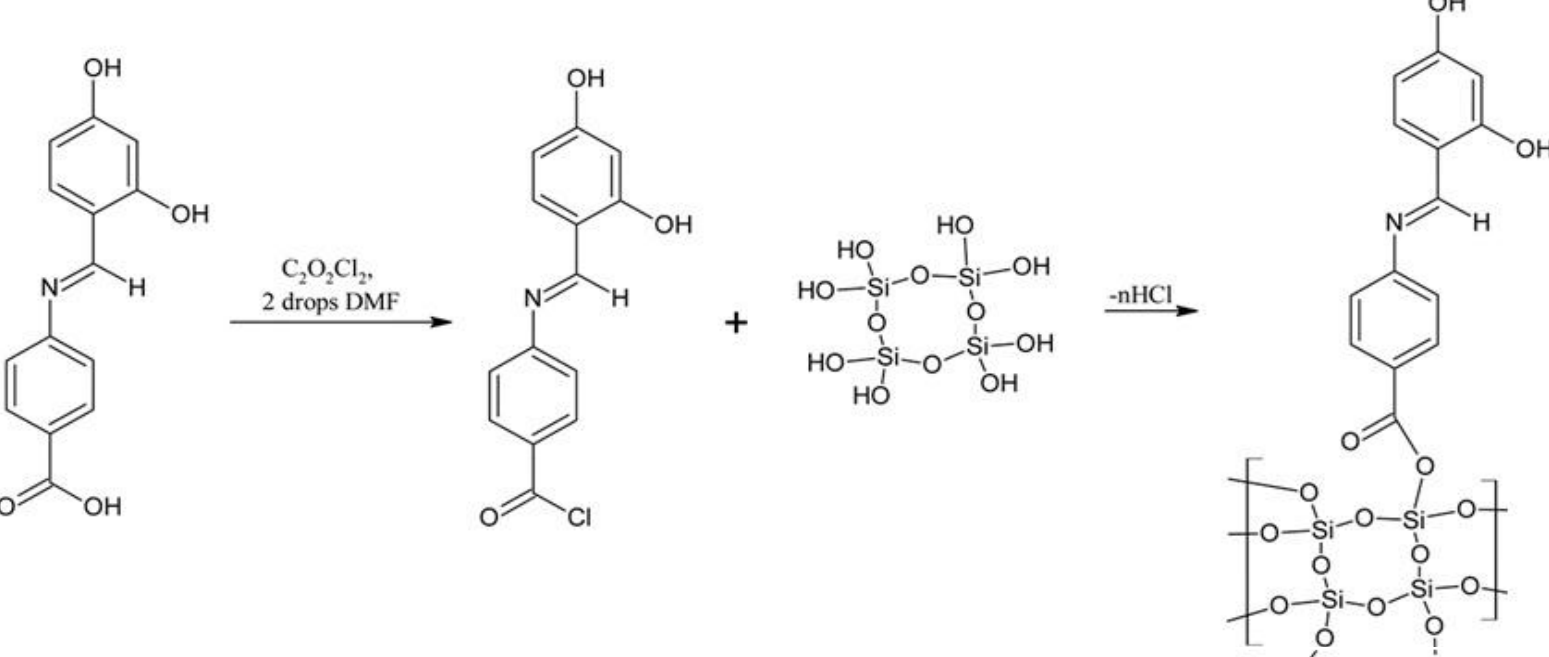


Imine Synthesis

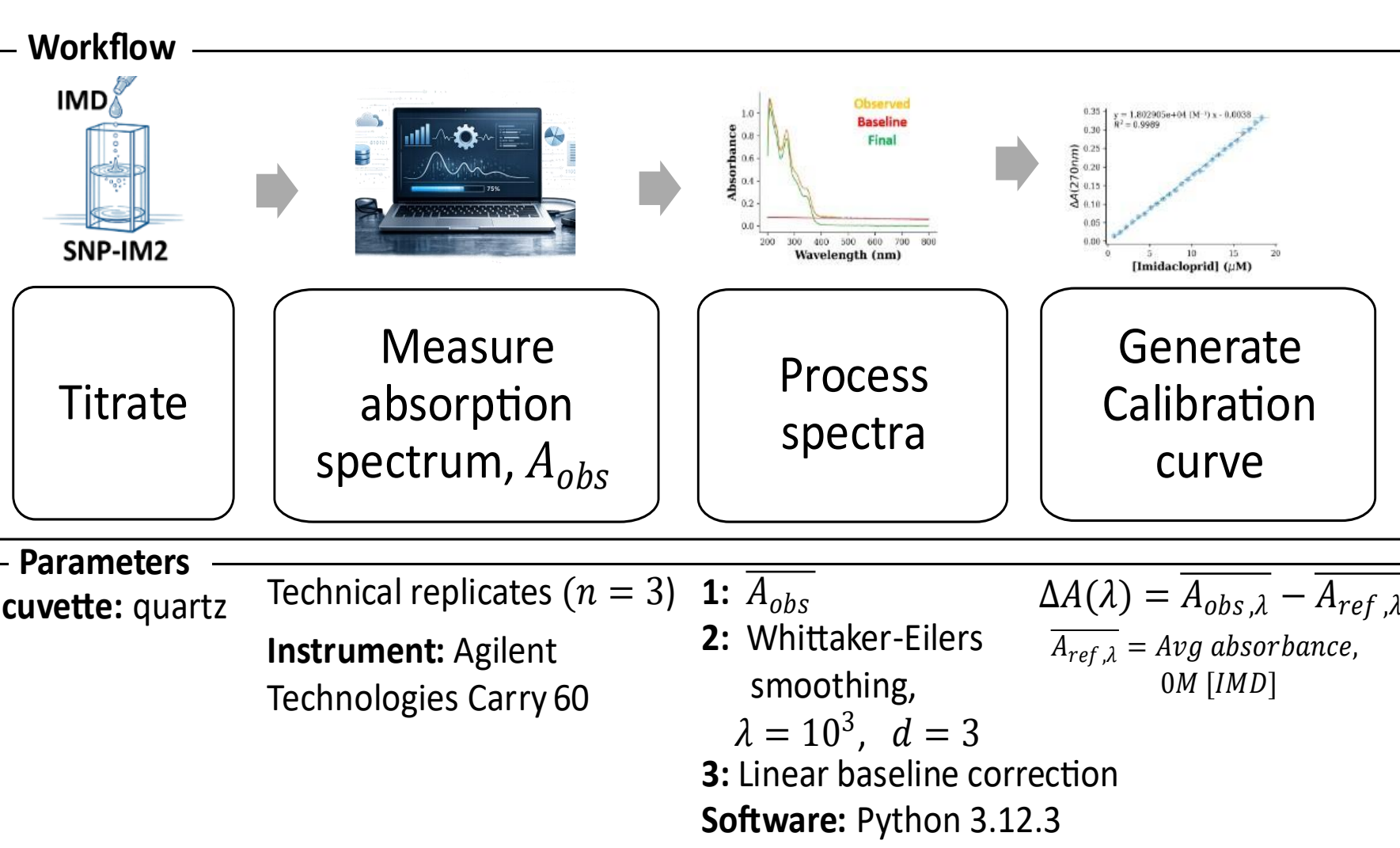


Imines

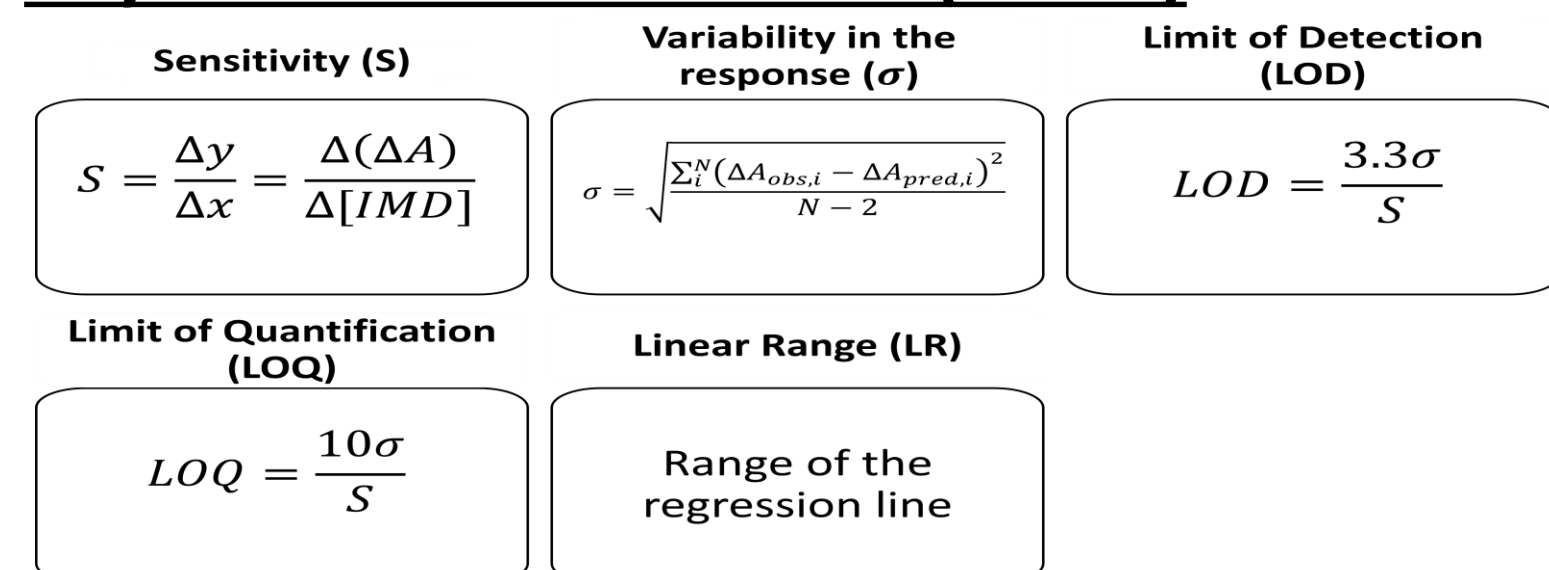
Functionalization



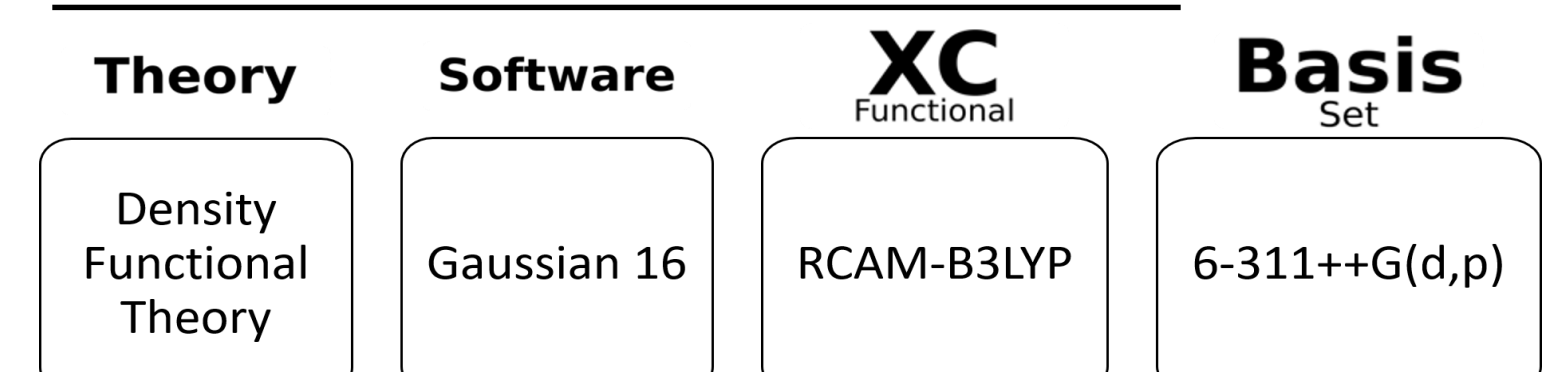
Sensor Calibration Framework



Key Performance Metrics (KPMs)



Electronic structure calculations



Results and Discussion

Morphology, composition, structure and optical properties of silica nanoparticles:

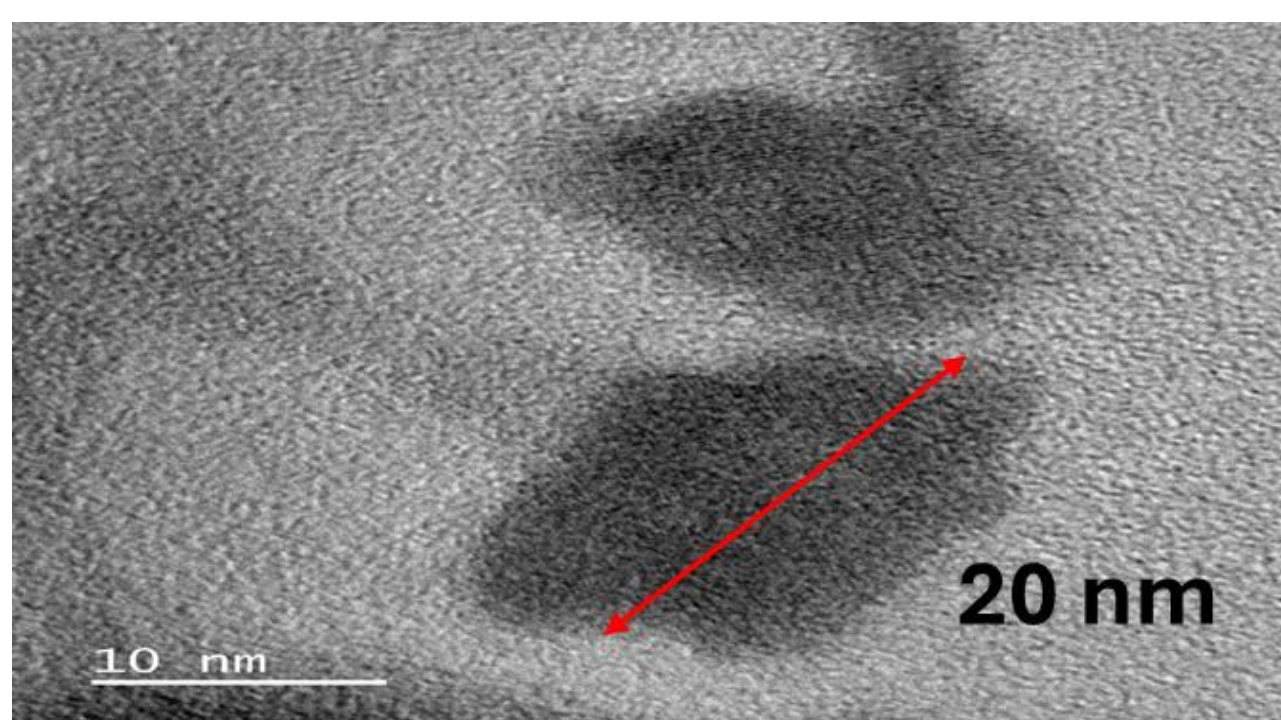


Figure 2 plate-like shape, 20 nm in diameter (HR-TEM).

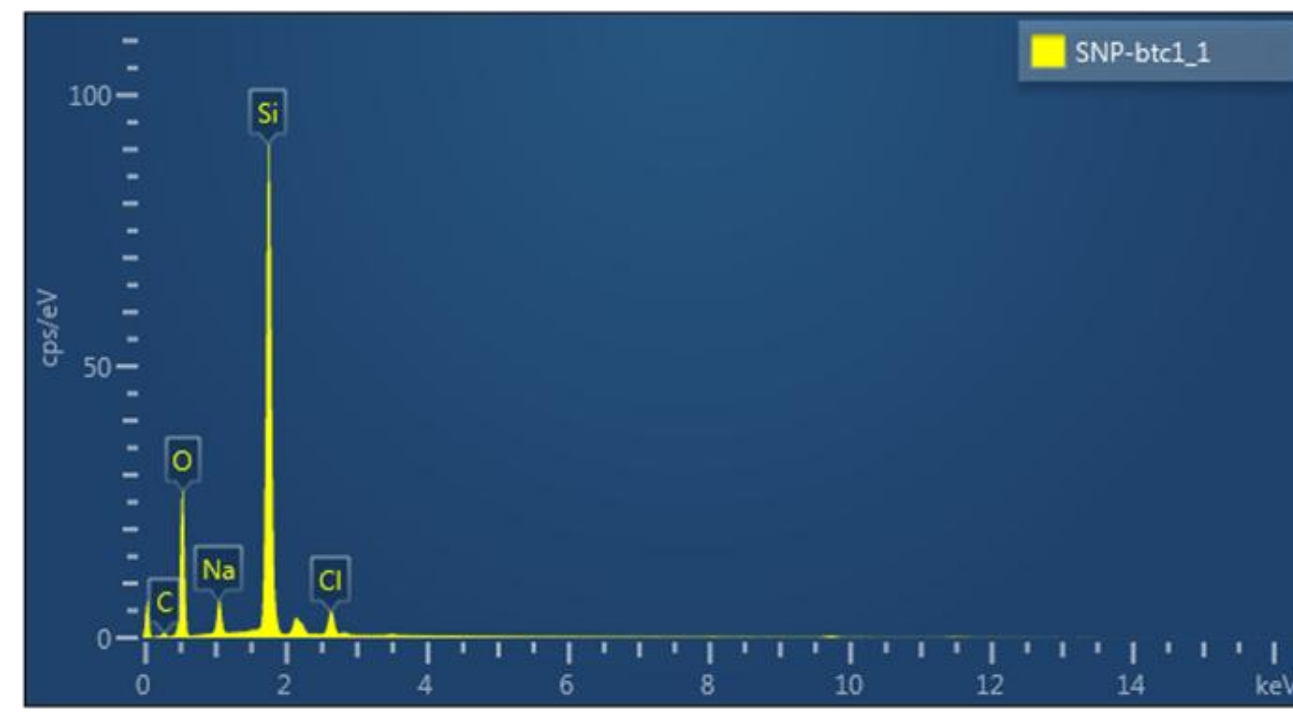


Figure 3 SNP primarily Silicon and Oxygen, minor trace of impurities from synthesis (EDX).

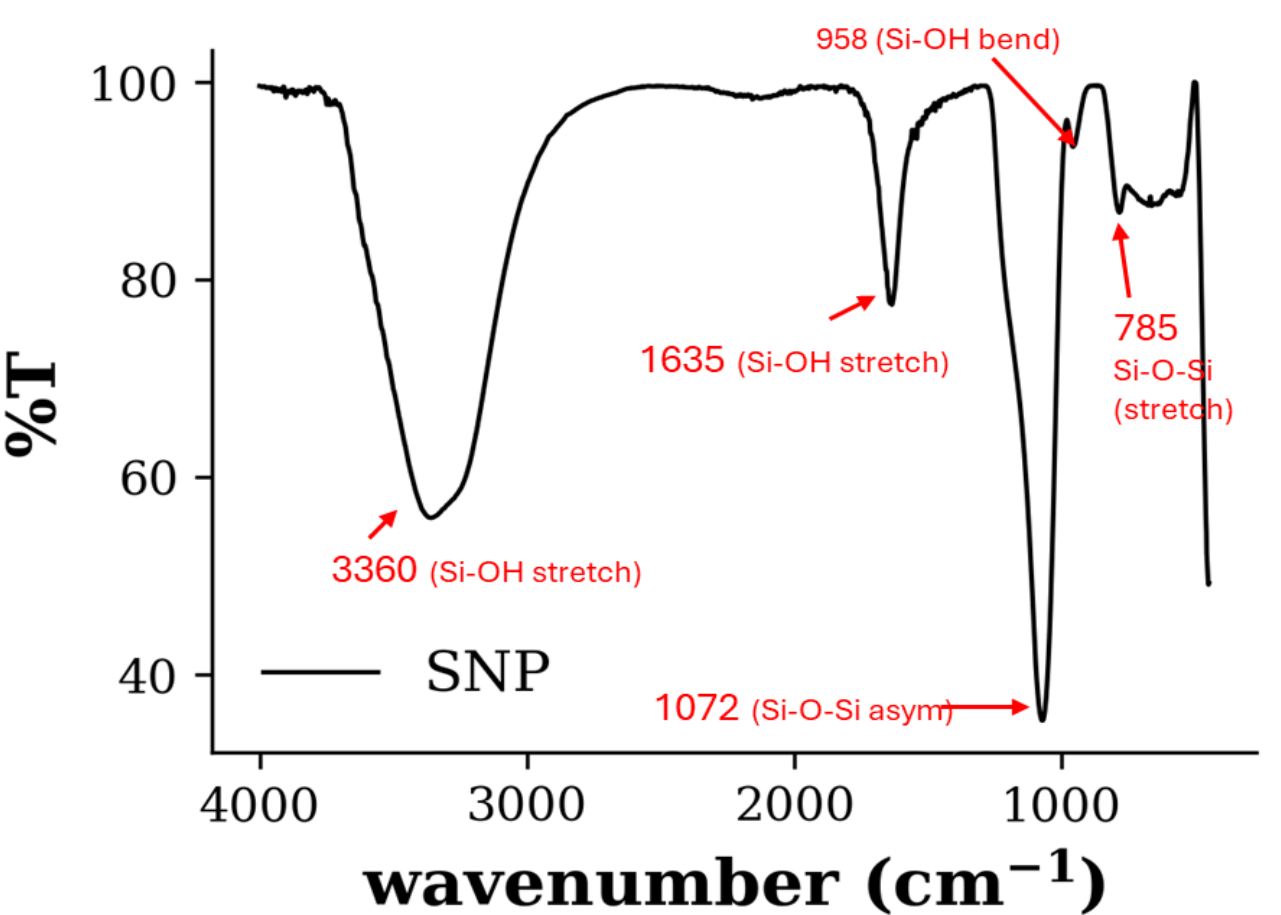


Figure 4 Vibrational bands (siloxane; silanol) consistent with literature reports of silica (FT-IR).

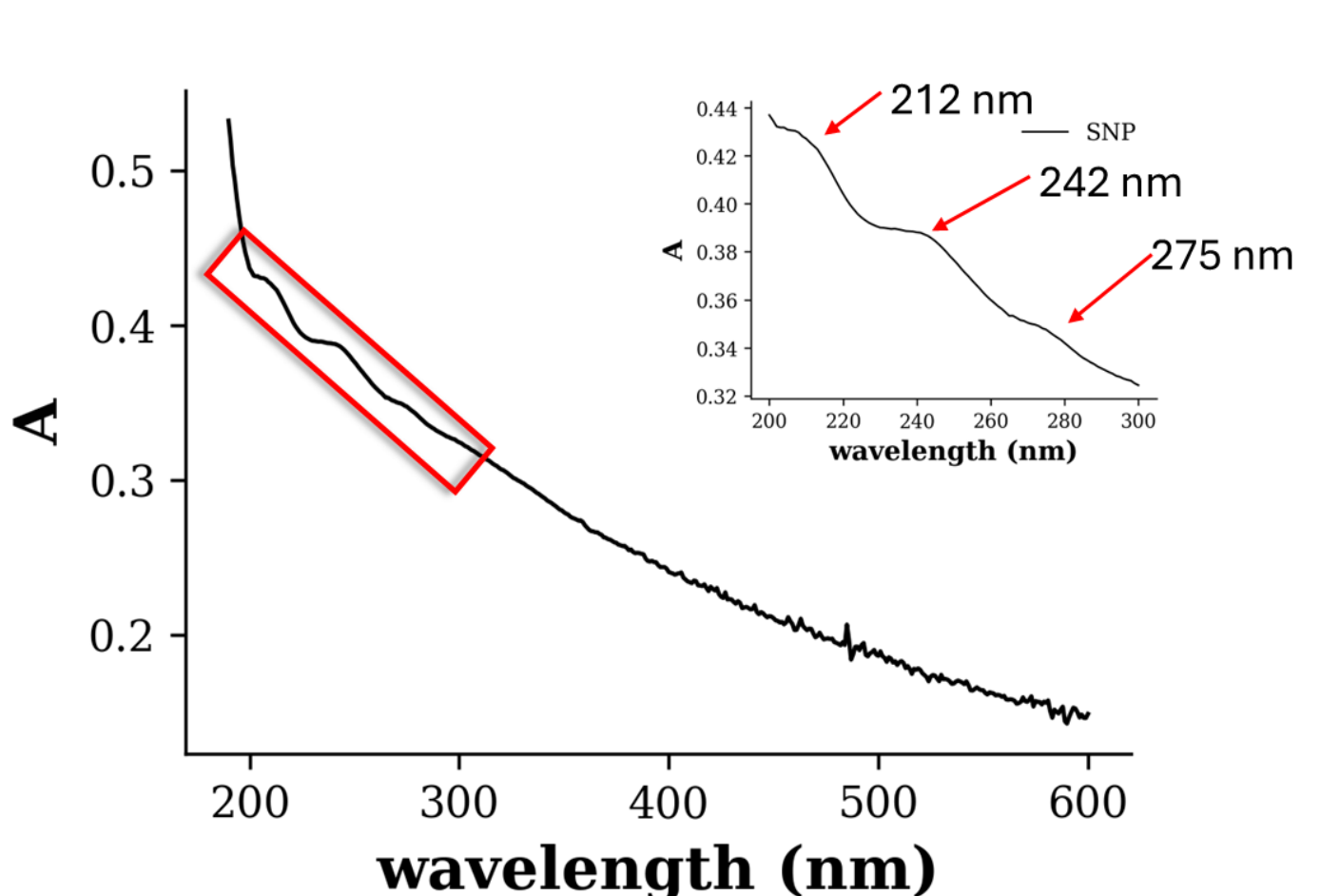


Figure 5 Three major absorption features consistent with the formation of defect states (UV-Vis).

Sample titration and calibration curve:

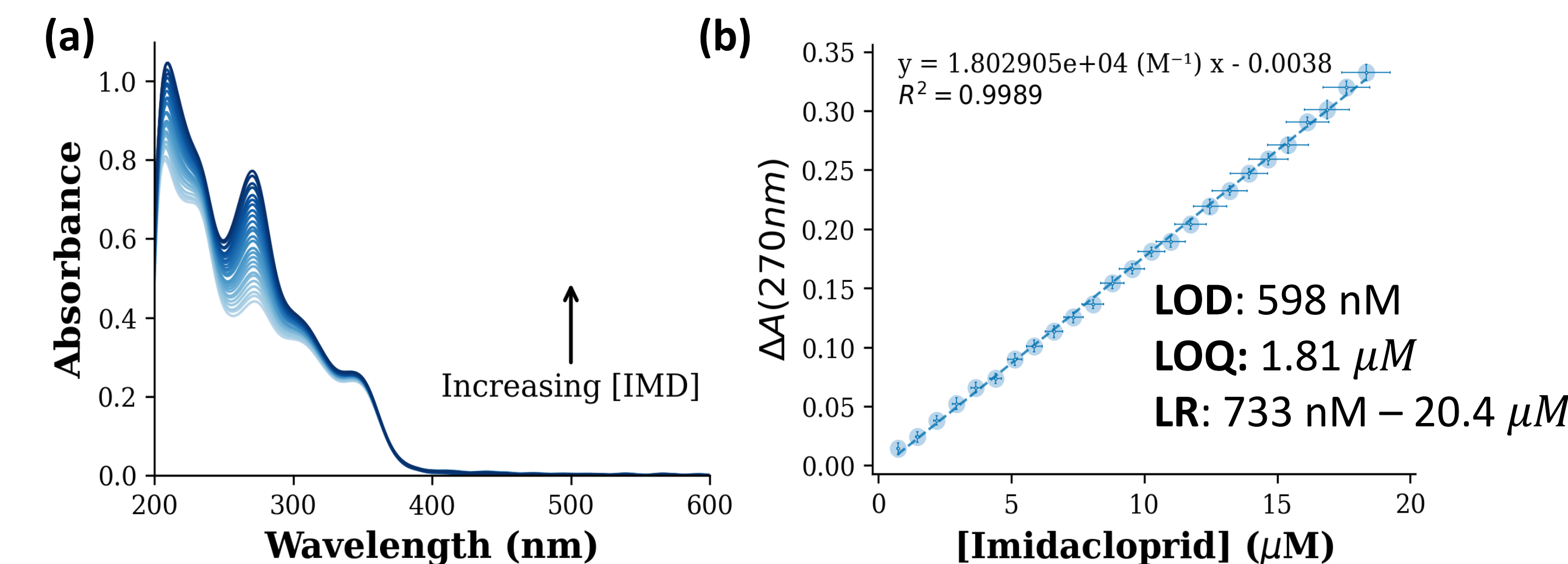


Figure 6 (a) Titration of Imine 2-functionalized silica nanoparticles (SNP-IM2) with IMD in methanol and (b) calibration curve (X-bars: $\pm 5\%$ of the analyte concentration; Y-bars: $\pm 1SD$, values calculated by the root sum of squares from $n = 3$ technical replicates).

Comparing KPMs across the undoped nanosensor series:

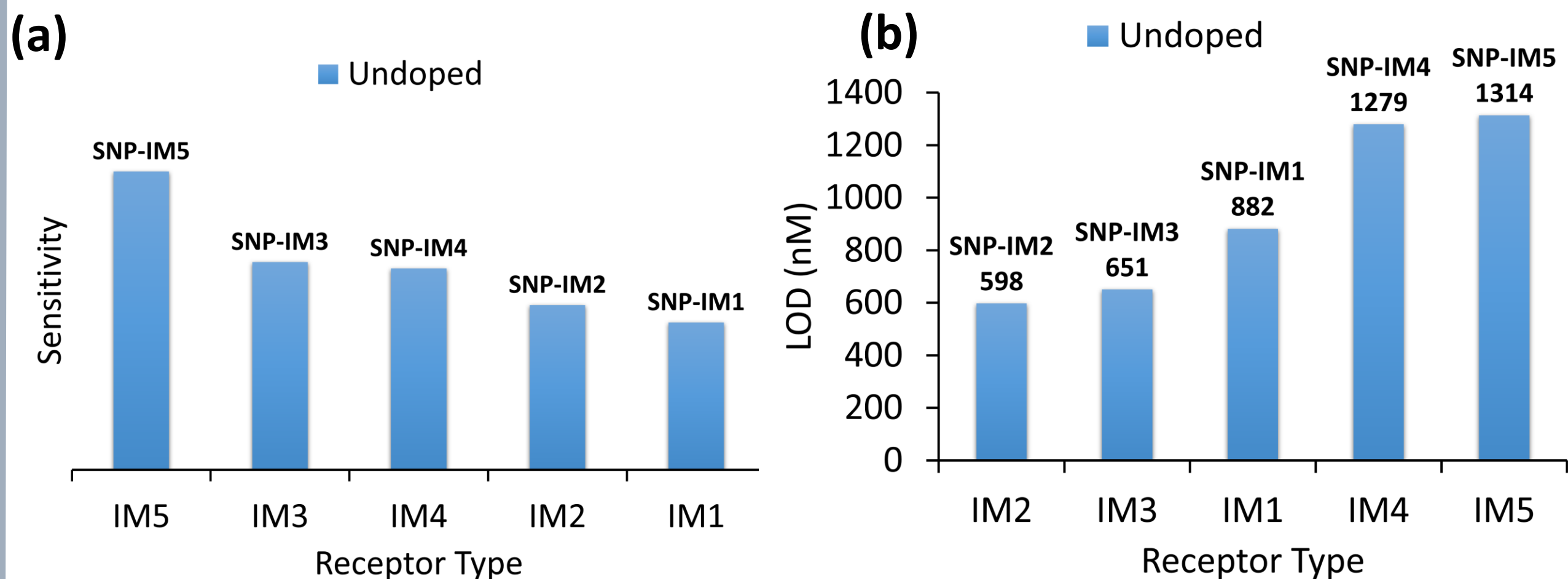


Figure 7 (a) Sensitivity and (b) Limit of Detection (LOD) across all nanosensors as a function of the type of receptor on that sensor.

Investigating the receptor-analyte interaction at a molecular level:

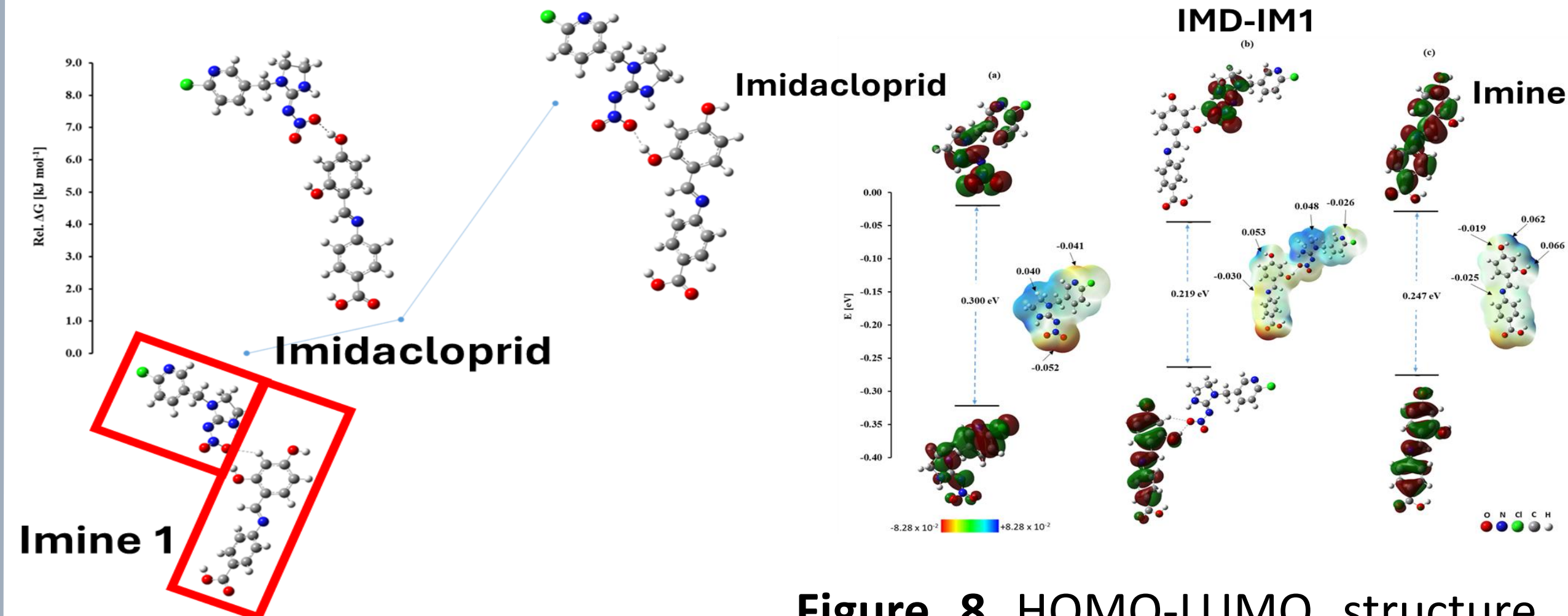


Figure 8 Free energy comparison across various configurations of the interaction between Imine 1 and Imidacloprid.

Figure 8 HOMO-LUMO structure and gap, and electrostatic potential map for (a) Imidacloprid, (b) lowest free energy configuration between Imidacloprid and Imine 1 and (c) Imine 1.

Conclusion and Future Work

- The silica nanoparticle-imine combinations are sensitive to Imidacloprid with linear ranges spanning the high nanomolar to micromolar range and limits of detection as low as 598 nM.
- The variability in the response signal is a key driver in the observed LODs across the nanosensor series.
- Next steps include:**
 - Assessing the selectivity of these nanosensors.
 - Assessing the influence of the silica surface on the electronic structure will be assessed.

Key Trends:

- The imine 5-functionalized silica nanoparticles (SNP-IM5) achieved the best Sensitivity but worst LOD.
 - SNP-IM2 displayed the second worst sensitivity but the best LOD.
 - The variability in the response (σ) is playing a key role in the observed LODs.
- Key Trends:**
- Of these three configurations, the most favourable interaction occurs when the nitro group of Imidacloprid forms two hydrogen bonds with the Imine.
 - HOMO-LUMO are situated on different fragments of the IMD-IM1 complex suggesting that electronic transition might possess significant charge transfer character.

References

- Morrison, B. A.; Xia, K.; Stewart, R. D. Evaluating Neonicotinoid Insecticide Uptake by Plants Used as Buffers and Cover Crops. *Chemosphere* **2023**, *322*, 138154. <https://doi.org/10.1016/j.chemosphere.2023.138154>.
- Buszewski, B.; Bukowska, M.; Ligor, M.; Staneczko-Baranowska, I. A Holistic Study of Neonicotinoids Neuroactive Insecticides—Properties, Applications, Occurrence, and Analysis. *Environ. Sci. Pollut. Res.* **2019**, *26* (34), 34723–34740. <https://doi.org/10.1007/s11356-019-06114-w>.