Towards the prediction of novel biogenic crystals and co-crystals with target properties

Parfaite SENOU, Carlo ADAMO and Frédéric LABAT

Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences, Chemical Theory and Modelling Group, F-75005 Paris, France
parfaite.senou@chimieparistech.psl.eu

ABSTRACT

Biogenic crystals are used by animals for a variety of purposes, including the production of structural colors for camouflage or display, as mirror components in visual systems, or as thermoregulators for protection against extreme heat[1, 2, 3]. Among the few biogenic organic crystals known so far, guanine crystals are the most widespread in animals due to their unusually high refractive indices along certain crystallographic directions, but other crystals such as xanthine, xanthopterin or uric acid for instance, which all crystallize into highly birefringent crystals [4], are also thought to be used by animals to manipulate light. Although significant efforts to characterize and elucidate the optical function of biogenic crystals in living organisms have been made in recent years, many aspects remain however largely unknown, such as how organisms can generate and modulate specific optical effects.

In this context, we first studied the three already-known polymorphs of anhydrous guanine (AG), namely α, β and γ, and identified a fourth stable and close in energy one (γ')[5], which could potentially contribute to AG polymorphism. Their structural, electronic, vibrational and optical properties were systematically investigated with different DFT models under periodic boundary conditions and their absorption spectra were studied with TD-DFT combined with electrostatic embedding techniques. Although important structural differences could be evidenced between these four AG forms, their refractive indices (RIs) as well as their UV-Vis spectra did not reveal significant differences. In a second step therefore, we considered a broader polymorphism of such crystals as well as the possibility to form co-crystals based on AG and xanthine using an approach based on an evolutionary algorithm. However, the optical properties of the newly generated crystals and co-crystals were found very similar to the pure AG polymorphs ones. Work is in progress to consider other combinations of purine bases in order to better rationalize the structure/property relationship of such crystals and co-crystals.

References

[1] A. Levy-Lior, E. Shimoni, O. Schwartz, E. Gavish-Regev, D. Oron, G. Oxford, S. Weiner, and L. Addadi, "Guanine-based biogenic photonic-crystal arrays in fish and spiders," *Advanced Functional Materials*, vol. 20, no. 2, pp. 320–329, 2010.

[2] J. Teyssier, S. V. Saenko, D. Van Der Marel, and M. C. Milinkovitch, "Photonic crystals cause active colour change in chameleons," *Nature communications*, vol. 6, no. 1, p. 6368, 2015.

[3] B. A. Palmer, D. Gur, S. Weiner, L. Addadi, and D. Oron, "The organic crystalline materials of vision: structure–function considerations from the nanometer to the millimeter scale," *Advanced Materials*, vol. 30, no. 41, p. 1800006, 2018.

[4] R. De, T. Tao, W. Tang, and J. Gong, "Emerging biomineralization of organic photonic crystalline materials: Ultrastructure, formation mechanism, and optical function," *Chemistry of Materials*, vol. 36, no. 13, pp. 6321–6346, 2024.

[5] P. Senou, C. Adamo, and F. Labat, "First-principles modeling of the electronic and optical properties of biogenic crystals: The case of anhydrous guanine," *The Journal of Physical Chemistry C*, vol. 129, no. 17, pp. 8404–8416, 2025.