

Structural and spectroscopic studies on solid-state emissive organic fluorophores

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Fluorophores that emit in an aggregated state are useful for many applications, including biosensors, chemosensors and in optoelectronic devices. The Ritchie group has previously established a new family of zwitterionic organic molecules that are highly fluorescent in solution and the solid-state [1]. Building on this work, the incorporation of diphenylaminopyridine-based (DPAP) moieties imbues these betaines with environmental sensitivity, showing high quantum yields in the solid-state, as well as reversible changes in emission spectra when subjected to external stimuli, such as anisotropic force (mechanochromism - MFC) or temperature (thermochromism) [2,3]. In particular, these molecules show reversible, bathochromic shifts in emission peak maxima when the crystalline material is mechanically ground in a mortar and pestle (Fig. 1). To understand how these stimuli-responsive compounds work mechanistically, their optical properties are explored spectroscopically and their structures via a combination of powder X-ray diffraction, ambient and high-pressure crystallography. Crystal packing and analysis of intermolecular interactions help to rationalise the photophysical properties seen, allowing a rationale for the emission sensitivity to be proposed that is supported by time-dependent density-functional theory calculations. Understanding such mechanisms is key to optimising the design of future analogues with tailored optical properties and crystallographic techniques provide valuable insight at the molecular level. Overall, these novel molecules are bright and highly sensitive to their environment, which are desirable properties for their use in applications.

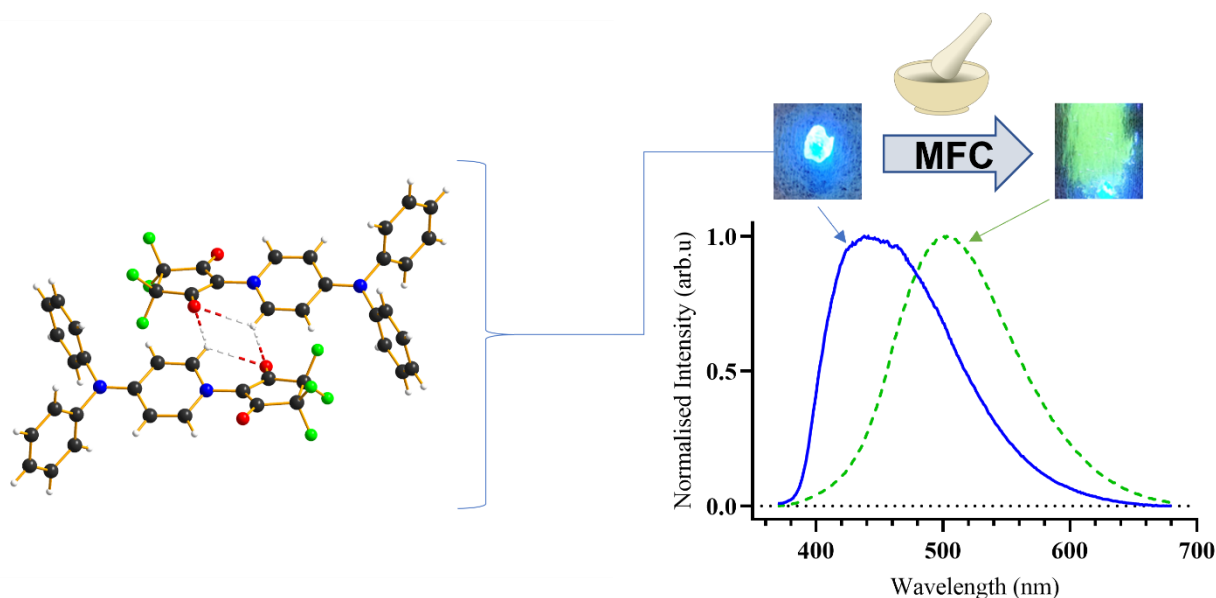


Figure 1. Crystal structure showing dimer-type interaction of a DPAP zwitterion and corresponding emission spectra of crystalline and mechanically ground physical forms (visual emission images inset).

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