Colour properties of fluorescein: an interplay of tautomerism and crystal packing

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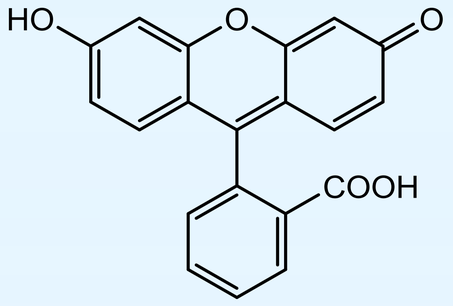
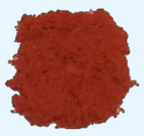
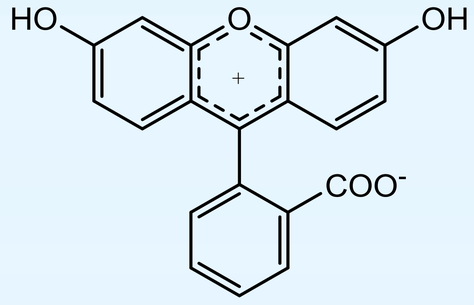
Introduction

In the solid state fluorescein exists in three tautomeric forms, quinoid (flsQ), zwitterionic (flsZ) and lactoid (flsL) all showing different colours.[1] By analogy to the lactoid form of a closely related compound diacetylfluorescein, the lactoid form of fluorescein is expected to be colourless although it has never been crystallised in pure form. The known cocrystals and solvates of flsL, on the other hand, display a variety of colours ranging from orange to green. Two potential explanations could be used to rationalise the observation: the colour may be caused by either the electronic interactions between the fluorescein and guest molecules or by the presence of zwitterionic impurities at the crystal surface. The present study shows how a combination of experimental and computational methods can be used to rationalise the colour properties of this organic pigment system, and in particular the possible role of the zwitterionic impurity influenceing the colour properties of the observed crystal forms of flsL.

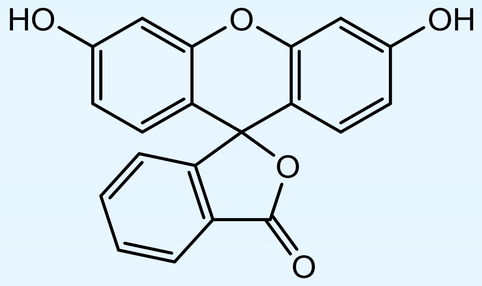




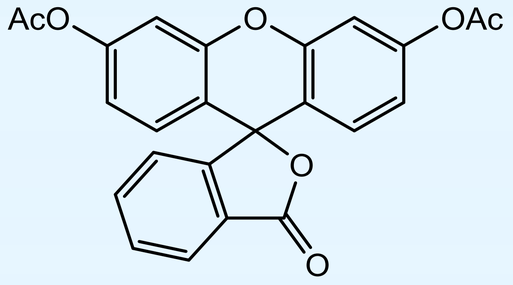
Quinoid form, flsQ



Zwitterionic form, flsZ



Lactoid form, flsL, from left to right, in:
acridine cocrystal, dioxane solvate, pyrazine cocrystal



Pure diacetylfluorescein,
lactoid form

Measurement of the band gaps

The colour of a material is strongly dependent on the value of band gap: photons with energy lower then the band gap will be reflected, while photons with higher energy will be absorbed.
The values of band gaps of all the available solid forms of fluorescein were measured using solid state UV/Vis spectroscopy. The measured band gap of the zwitterionic form was 2.30 eV, with the band gaps of all lactoid the samples being at the range of 2.7-4.0 eV.

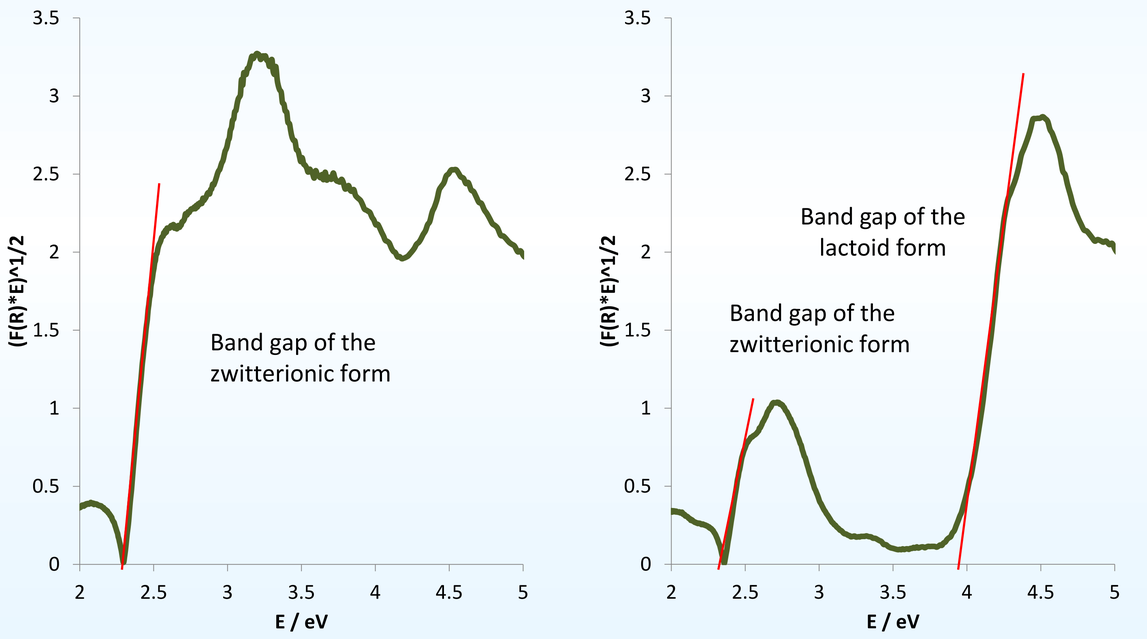


Figure 1. The Tauc plots[2] constructed from the UV/Vis spectrum of flsZ (left) and flsL dioxane solvate (right) were used to measure the band gaps . Spectra of all lactoid forms contain a small feature at 2.3 eV, which indicates the presence of flsZ impurity. This impurity is responsible for the yellow colour of the materials.

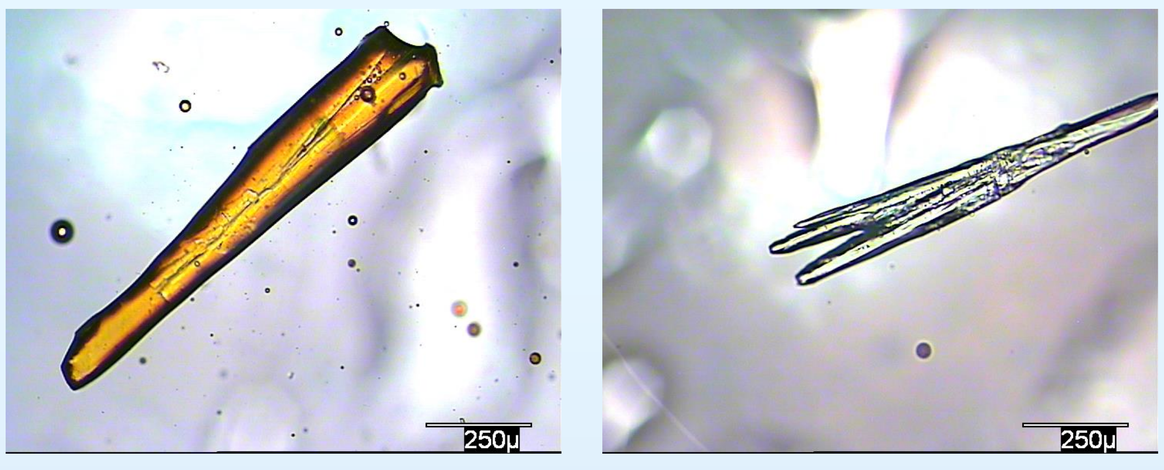


Figure 2. Crystal of the fluorescein dioxane solvate before (left) and after (right) washing in silicon oil. The oil removes the surface layer, making the crystal colourless. The experiment proves that the zwitterion impurity is concentrated at the surface of the crystals.

Conclusions

- With the help of solid state UV/Vis measurements it was found that crystals of lactoid fluorescein are coated with the layer of zwitterionic molecules. This layer is responsible for the yellow colour of the materials.
- Although the existence of the zwitterionic layer has been proven, the mechanism of its formation remains unclear.
- Presence of coformers with extended pi-systems leads to a lowering of the band gap, often bringing it into visible light region. The effect is especially pronounced for the pyrazine cocrystal.
- The influence of coformer molecules in controlling the value of the band gap can be established with the aid of band structure calculations.

Band structure calculations

Band structure calculations were performed using a plane-wave DFT code CASTEP 7.[3] The theoretical band gaps were estimated from the calculated density of states (DOS). The calculation was performed using a semi local PBE functional[4] which is known to underestimate the band gap due to the self-interaction error. Nonetheless it has been shown that the calculated band gaps correlate well with the experimental values. Once the difference between the calculated and measured band gap is known, it is possible to correct the calculated DOS by shifting the energies of the unoccupied bands. This modified DOS should provides a basis for the calculation of optical properties such as reflectance spectra.

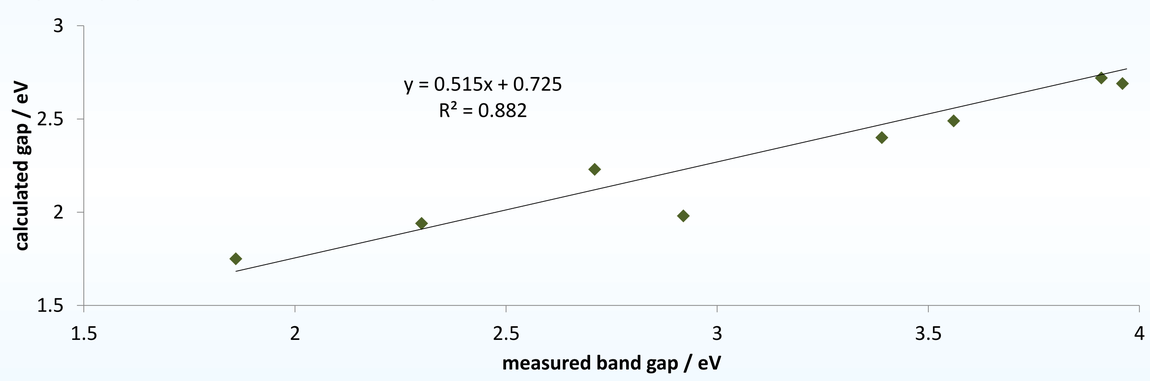


Figure 3. Comparison between the calculated and measured band gaps of the solid forms of fluorescein.

Specific effect of the coformer on the optical properties of cocrystals

The yellow colour of cocrystals and solvates of fluorescein arises from the zwitterion layer coating the surface of the crystals. The green colour of the pyrazine cocrystal, however, cannot be explained that way. It was noted that the band gap for this cocrystal is the lowest among all crystal forms of lactoid fluorescein (2.7 eV).
In order to establish the role of the pyrazine molecule in the optical properties of the cocrystal, the DOS was analysed in more detail. It was shown that the lowest energy unoccupied bond is formed exclusively from the orbitals of pyrazine, meaning that the unusually low band gap of the cocrystal can be attributed to the action of the coformer.
The calculated reflectance spectrum has shown a maximum at 460 nm, suggesting a blue colour for the bulk phase of the cocrystal. Mixing of the colour of the bulk phase with the yellow colour of the flsZ surface layer results in the observed green colour.

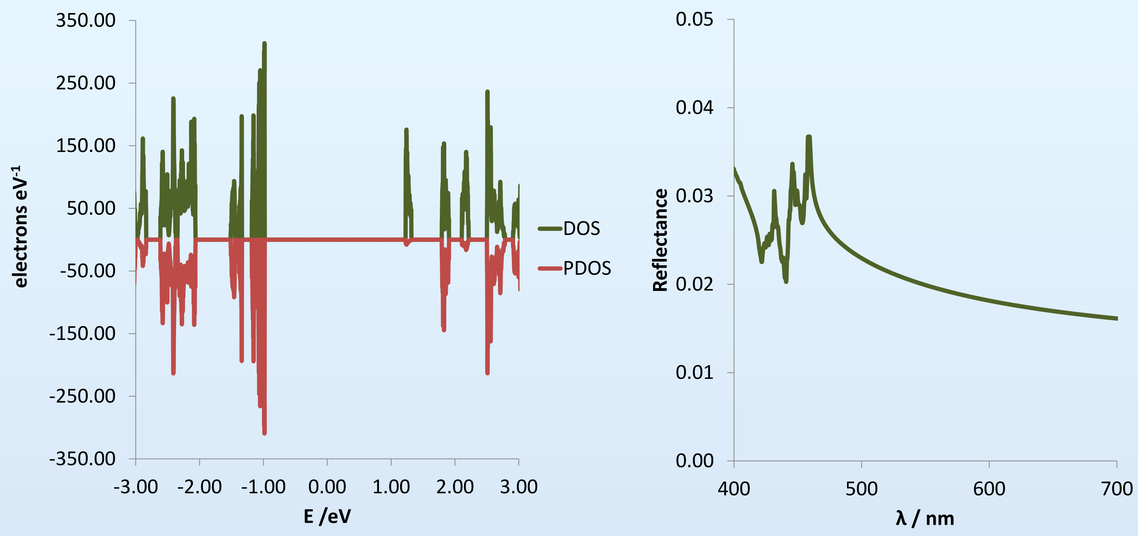


Figure 4. Comparison of the full and partial DOS (right) shows that the lowest unoccupied band is formed of pyrazine orbitals. The calculated reflectance spectrum (left) shows a maximum at 460 nm (blue light region).

References and acknowledgements

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