Photosalient Crystal Structures of Cinnamalites

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Introduction

The energy released from photosalient crystals could drive photo-actuators.^[1] The photodimerization of 4-Fluoro cinnamylidene malononitrile (4FCM), one of the strongest photosalient materials, can lift 200,000 times its own weight.^[2] Derivatives of cinnamylidene malononitrile (CM) are polymorphic with photo-active head-to-tail and non-reactive head-to-head configurations as shown in Figure 1.^[2]



Figure 1. The polymorphism and photoreactivity of 4FCM and CM.

However, only 4FCM is known to be polymorphic, while CM crystals have only been found to exist in the head-to-tail orientation. To understand the polymorphism and photoreactivity of CM and 4FCM, shown in figure 1, crystal structure prediction (CSP) has been performed. However, this data predicts low energy polymorphs not experimentally discovered. This could be due to the limitations inherent in plane-wave density functional theory, the model chemistry previously used.^[3]

Hypothesis

Applying spin-component-scaled and dispersion-corrected MP2 (SCS-MP2D) could improve lattice energy predictions, leading to a more accurate CSP landscape.

Methods

CSP is a process used to find polymorphs viable for synthesis.^[4] A Python script is used to produce hundreds of thousands of crystal structures using the General Atomic Force Field. The structures are then optimized by increasing levels of model chemistry to find the lowest energy structures.

Planewave density functional theory (pwDFT) satisfies the periodic boundary conditions, which simulates a crystal lattice. The B86bPBE-XDM model, a plane-wave density functional with the exchange-hole dipole moment dispersion model was utilized to obtain accurate geometries. However, delocalization errors known in DFT under-estimate π -stacking interactions and conjugation which negatively impacts the prediction of lattice energies of 4FCM and CM derivatives.

MP2 is a second order perturbation on Hartree-Fock (HF) and thus covers many of the weakpoints of HF. MP2 specifically does well with electron correlation without introducing delocalization error. SCS-MP2D, which has been shown to provide accurate lattice energies, is used.^[5] However, a drawback of MP2 is its high computational cost, as MP2 cannot be applied to a unit cell.^[3] Thus, it is not feasible for crystals. Instead, a SCS-MP2D monomer correction to the plane-wave DFT lattice energies will be applied via the following equation.^[5]

$$E_{\text{crystal}}^{\text{corrected}} = E_{\text{crystal}}^{\text{DFT}} + \sum_{i} \left(E_{\text{mon},i}^{\text{SCS-MP2D}} - E_{\text{mon},i}^{\text{DFT}} \right)$$

The energy of the unit cell is calculated with pwDFT. Monomers are then taken from the unit cell, and SCS-MP2D is used to calculate the monomers' energy in the gas phase. Thus we are given proper values for electron correlation and delocalization. Then the monomer energies are calculated with pwDFT. The resulting sum of energy is subtracted from the SCS-MP2D energy. The final corrected energies are plotted on a CSP landscape.

Results

A CSP landscape plots relative energy over density. Each point represents a polymorph created through CSP of CM or 4FCM, respectively. pwDFT provided a questionable CSP landscape, depicted by figure 2, as experimental structures were not shown to be the lowest energy polymorphs. Thus, there must be limitations inherent in the model chemistry, pwDFT, causing this discrepancy. So, a higher level of theory, SCS-MP2D, was applied.



The SCS-MP2D correction provides a more accurate landscape associated with CM and 4FCM derivatives, depicted by figure 3. As predicted, 4FCM experimental structures are shown as the lowest energy polymorphs. However, CM HT is not shown to be the lowest energy polymorph. Thus, CSP predicts that there exist undiscovered polymorphs of CM.

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Conclusion

The SCS-MP2D CSP landscape in figure 3 agrees with the hypothesis.

Experimental polymorphs of 4FCM corresponded to the lowest energy CSP structures, which suggests that all 4FCM polymorphs have been discovered. However, CSP predicted polymorphs of CM lower energy than experimental HT CM, which indicates there exist crystal structures not yet discovered. These undiscovered structures may hold photosalient effects that could be key in the creation of a photo-actuator. Further research would include attempting to crystalize CM in the lower energy configurations and testing their photo-reactivity.



Figure 4. The photodimerization of 4FCM in the HT orientation.^[2]

This research was conducted mostly on the reactants of the photodimerization, depicted in figure 4. To gain a more thorough understanding, similar tests could be done on the photodimers formed during the reaction.

Overall, this work used a method of calculating energies for crystals wherein pw-DFT and SCS-MP2 are used to capture the lattice structure and to model the monomers within the cinnamalmalononitrile crystals respectively. The improved energy calculation confirmed the experimental results by realistically predicting a non-photosalient form. So, these discoveries made a significant contribution to work published in an official physical chemistry journal, *Crystal Growth and Design*.^[6]

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