Computational study of the pressure-sensitive mechanoluminescent response in polymorphs of an anthracene derivative

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Smart technological systems are nowadays omnipresent in our everyday lives. By responding to various external stimuli they contribute to more sustainability, energy efficiency and comfort. They range from smart windows that can switch between transparent and dark states triggered by heat or light,[1] piezoelectric floors where the pressure of a human's footstep or vehicle's movement is turned into electrical energy[2] to responsive prostethic skin that detects pressure, temperature and touch giving a more natural sense to the patient.[3] To add an additional layer of functionality and visual confirmation to smart technologies, mechanoluminescent (ML) materials that emit light in response to a mechanical constraint are of unique interest. In these systems, the application of pressure triggers a change in the supramolecular arrangement and may alter the structure of the molecular units which consequently impacts the emission wavelength and intensity.

In this work, we report a computational study of the ML properties of recently synthesized 9,10-bis((E)-2-(pyrid-2-yl)vinyl)anthracene (BP2VA) crystal polymorphs, which evidence drastic changes in their photoluminescence color upon exertion of external pressure.[4]

The crystal structure of the BP2VA molecule at zero and applied pressure, including cell parameters and molecular arrangement, is calculated using periodic density functional theory (DFT). The choice of computational method is validated beforehand by comparing with experimental results.[4] In a next step, the optical properties of dimers extracted from the optimized crystals are calculated using a hybrid QM/MM scheme, where the central dimer is treated at the time-dependent DFT level of theory.

The results, which compare well to experimental data, demonstrate that intermolecular exciton couplings play a leading role in the photophysical properties of these materials. Decomposition of the optically active excited states on a diabatic basis further allows to characterize the electronic transitions according to their local and charge transfer nature.

Keywords: Mechanoluminescence, Density Functional Theory, QM/MM Hybrid Schemes, Excited States.

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