Pressure Induced Structural Collapse of the Hydroquinone – Formic Acid Clathrate; a Pressure Medium Dependent Nonlinear Optical Phase Transition

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As of the beginning of the 21st century supramolecular chemistry and crystal engineering have become central areas for the development of organic materials, with applications as diverse as targeted drug delivery, chemical separation, sensors and catalysis. Yet, it is striking that the fundamental chemistry governing even simple self-assembly processes are not well understood.[1] The challenge of studying molecular aggregates are their inherent complexity, with even the simplest molecular crystal having numerous superimposed intermolecular interactions, all of which contribute to the cohesive energy of the solid. To better understand self-assembly processes, one needs to quantitatively determine the different intermolecular interactions energies. Spackman and co-workers have developed a computational approach to calculate accurate intermolecular interactions energies called energy frameworks. In this study energy frameworks are used to look at changes in host-guest interaction energies for the hydroquinone-formic acid clathrate system (HQ-HCOOH) when subjected to external pressure. Single crystal high-pressure crystallography is the perfect experimental method for probing intermolecular interactions by forcing the host and guest molecules together. Furthermore a new phase transition is found in which the host structure collapses and the guest molecules migrate out of the cavities. The high-pressure phase is a nonlinear optical material, interesting in its own right for developing photonic and optoelectric devices. The energy frameworks can here be used to explain the phase transition and why it only takes place when using a hydrostatic pressure medium.

Altogether this work presents a method for gaining quantitative information about different intermolecular interaction energies as a function of pressure. This will enable us to better understand the formation of more complex supramolecular aggregates.

1. S.I. Stupp and L.C. Palmer. Supramolecular Chemistry and Self-Assembly in Organic Materials Design. *Chemistry of Materials*, **2014**. 26, 507-518.