

Thesis Abstract

This thesis elucidates the central role of crystal engineering strategies specifically hydrogen bonding, halogen bonding, and coordination interactions in the rational design of supramolecular functional materials capable of undergoing controlled solid-state photochemical [2+2] di- and polymerization reactions. A series of Co(II)-based coordination polymers constructed from the rigid linear diene and various rigid and flexible dicarboxylate co-ligands exhibit distinct dimensionalities and network topologies. Upon UV irradiation, single-crystal photodimerization is observed; however, deviations from ideal geometrical parameters lead to unexpected reactivity, including dimerization instead of polymerization or complete photo-inactivity. Notably, one system undergoes a rare single-crystal-to-single-crystal transformation, yielding a three-dimensional coordination polymer upon photodimerization, accompanied by quenched photoluminescence and a blue-shifted emission profile. The thesis further demonstrates the functional relevance of photopolymerization through the fabrication of a transparent polymer thin film *via* single-crystal-to-single-crystal [2+2] photopolymerization of a flexible diene coordination polymer. The resulting film exhibits outstanding third-order nonlinear optical properties, including a high two-photon absorption coefficient and a low optical limiting threshold. Structure-property correlations in low-molecular-weight organogelators (LMOGs) derived from cinnamic acid salts reveal that gelation behaviour is governed by the nature and dimensionality of supramolecular hydrogen-bonded networks. Although primary ammonium cinnamate salts do not favour solid-state [2+2] reactions, systematic incorporation of competing hydroxyl groups enables the development of a new class of organogelators with tunable supramolecular architectures. Alkyl/aryl diammonium salts of dichlorocinnamates further display halogen-bond-assisted solid-state photodimerization, photomechanical responses, organogel formation, and iodine capture ability. Finally, the thesis reports, a rare gel-to-gel transformation driven by [2+2] photopolymerization in metal-organic gels composed of transition metal halides and rigid dienes. Contrary to conventional gel behaviour, photopolymerization enhances gel rigidity, opening new avenues for accessing mechanically robust metal-organic gels *via* post-synthetic photochemical modification.