Abstract

This thesis investigates crystal engineering strategies for designing advanced functional materials based on hydrogen bonding and metal-ligand coordination, with an emphasis on their structural characteristics and emerging applications across diverse areas of chemistry. Four classes of organic ligands with distinct functionalities were systematically designed for this purpose: two carboxylic acid-based ligands and two pyridine-based ligands. A flexible tetracarboxylic acid ligand, H_4PAI, containing two olefinic double bonds, was explored for solid-state [2+2] photoreactions. The photoinduced single-crystal-to-single-crystal (SCSC) transformation converts the crystal into a softer polymeric phase. Notably, the molecular-level reorganization is translated to the macroscopic scale, resulting in pronounced photomechanical actuation. The work further focuses on the rational synthesis of coordination polymers (CPs), metal-organic frameworks (MOFs), and metal-organic gels (MOGs) incorporating metals from the s-, d-, and f-blocks, enabling systematic exploration of their structural diversity and functional properties. To bridge fundamental studies with the practical applications, mixed-matrix membranes (MMMs) were developed by integrating organic and inorganic components. A composite membrane-based piezoelectric nanogenerator was fabricated by embedding a photoreactive Sr-PAI MOF into a PVDF matrix, where the MOF acts as a nucleating agent to induce and stabilize the electroactive β-phase of PVDF. In addition, the first nickel-based MOG exhibiting an insulator-to-semiconductor transition via a [2+2] photoreaction, coupled with Li^+ doping through a gel-to-gel transformation, was demonstrated, achieving record-high Li^+-ion conductivity in the MMMs. Furthermore, imidazole- and sulfonate-containing proton-conducting CPs synthesized via a gel-to-crystal-to-crystal approach yielded low-cost, high-performance proton exchange membranes. On the other hand, essential metal-based MOF containing MMMs enabled turn-on fluorescent sensing of H_2S. Bromo- and free carboxylate-functionalized Ni-HBTM MOF-graphene hybrid nanosheets were developed for energy storage applications. Post-synthetic transmetallation with rare-earth metals enabled the conversion of Ni-HBTM into Ln-BTM MOFs with tunable magnetic and photoluminescent properties. LED light illumination underscores the commercial potential of the developed device.

Keywords: Photo-polymerization, [2+2] reactions, metal-organic frameworks, coordination polymers, metal-organic gels, piezoelectricity, semiconductivity, proton conductivity, H_2S sensing, supercapacitor, and magnetism.