The photophysical properties of chromophores assembled into metal-organic framework thin-films

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DISSERTATION

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Metal-organic frameworks (MOFs) are hybrid porous materials consisting of a metal center connected with an organic linker via coordination bonds. Virtually infinite possibilities of metal-linker combination have resulted in a large number of MOF structures (>100,000) to date, with different structural topologies. The properties of MOFs can be tuned by the rational selection of the metal centers and organic linkers to design specific MOFs to be adequate to the in-demand applications. Regarding more advanced applications, the bulk MOFs synthesized via conventional solvothermal method are not always suitable. Heterogeneous morphology, weaker adhesion to substrate, and high defect densities present in the powder MOFs greatly influence the structure property correlation. One approach used to fabricate monolithic, crystalline, and well-controlled thickness is the layer-by-layer (LbL) method via the liquid phase epitaxy technique. So, in the present thesis, I used this technique to build a highly crystalline, monolithic, and orientated a surface-anchored metal-organic frameworks (SURMOFs) thin films. One type of organic linkers was used here is called a photoactive compound. The spatial arrangement of these photoactive molecules in the SURMOF leads to materials with distinguished photophysical properties. In the present work, I studied bianthryl chromophoric linker, equipped with metal-coordinating groups, to construct a photoluminescent Zn-bianthryl based surface-anchored MOF (SURMOF) thin film. The Znbianthryl SURMOF has a 2D-layer stacked structure and shows cyan luminescence upon excitation with ultraviolet (UV) light. In response to the prolonged UV irradiation under ambient conditions, the Zn-bianthryl based SURMOF exhibited a prominent change in the ground and excited-state optical properties, without losing its crystalline structure. A detailed spectroscopic study using UV-Vis, FTIR, Raman, EPR, and NEXAFS indicated the formation of stable oxidation products of bianthryl (endoperoxide bianthryl) in the SURMOF. The present study identifies the key factors of the bianthryl oxidation process which involve a self-sensitized photochemical pathway. Also, redox-active viologen-based metal-organic frameworks (MOFs) have received an increasing interest in recent years, from the perspective of smart optically active materials. In this respect, a dicarboxylate functionalized viologen, $1,1 \square$ -bis (4-(carboxylic acid) phenyl)-[4,4 \square -bipyridine]-1,1 \square -diium dichloride (Viologen) is used as a linker to construct a surface-anchored metal-organic framework (SURMOF) thin

film using a layer-by-layer liquid-phase epitaxy method. This technique produces a highly crystalline, oriented viologen-based SURMOF-2. The oriented, monolithic, crystalline SURMOF exhibits fast reversible photochromism, compared to the previously reported viologen-based powder MOFs. The photochromism in the SURMOF is investigated by the UV-Vis, EPR and XPS.