Metal-organic frameworks as a platform for controlling triplet exciton dynamics

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論文内容の要旨

In Chapter 1, the background and motivation of this thesis are introduced. Of the 30,000 metal-organic framework (MOF)-related publications to date, one-tenth (almost 4,000) focuses on the luminescent properties of MOF. Among them, triplet excitons in purely aromatic molecules that are used as the organic linkers or that are trapped in a MOF as guest molecules have barely been investigated despite the unique environment that a MOF provides. The goal of this thesis is to develop new ways to control the harvesting of triplet excitons for luminescence including thermally activated delayed fluorescence (TADF) and phosphorescence by exploiting the rigid environments provided by MOFs.

In Chapter 2, triplet excitons were harvested as TADF originating from ligand-based emission. A Zr-based MOF (namely UiO-68-dpa) was firstly synthesized based on the newly designed organic linker with TADF properties (4,4”-Dicarboxyl-2’-diphenylamino-[1,1’:4’,1”]terphenyl: H_2tpdc-dpa). The linker consists of diphenylamine as an electron-donating moiety and carboxyl groups as both electron-accepting moieties and linkers that bond to the Zr clusters. From this new MOF, TADF characteristics were obtained at room temperature. The interactions among organic linkers, neighboring organic linkers, and metal clusters were discussed in terms of their effects on the emission spectrum, self-quenching, and photoluminescence quantum yield (Φ_{PL}).

In Chapter 3, long-lived room-temperature phosphorescence from MOFs having guest-related emission was obtained. Long-lived phosphorescence was demonstrated with an emission lifetime of 22.4 s at room temperature from coronene-d_{12} encapsulated in the zeolitic imidazolate framework ZIF-8 (coronene-d_{12}@ZIF-8). The guest emitter coronene-d_{12} was well isolated in the rigid framework of ZIF-8, enabling long-lived triplet excitons even at higher than 300 K. Thermally activated delayed fluorescence was also demonstrated at temperatures over 300 K.

In Chapter 4, a new strategy to control the dynamics of triplet excitons in organic emitters was demonstrated by encapsulating the emitters in a metal organic framework. Because MOFs intrinsically have pores that can accommodate gases and aromatic molecules, the heavy-atom gas xenon (Xe) can be introduced into coronene-d_{12}@ZIF-8 to influence the emission properties of coronene. Triplet excitons accumulated by photoexcitation of coronene-d_{12} under vacuum can be converted into emission immediately after introduction of Xe. It was easy to regulate the timing and speed of extraction of the accumulated triplet excitons as emission by introducing gas mixtures with various concentrations of Xe.

In Chapter 5, the thesis is summarized, and future prospects are discussed.