2-5-14. Vapochromic Materials

Overview

Vapochromism refers to the phenomenon in which materials change color in response to vapors such as water and organic solvents. Although the phenomenon has been known for a long time, in recent years, luminescent metal complexes and organic crystals have been developed as sensor materials for detecting harmful substances in the environment. Meanwhile, as a visible phenomenon of the interaction between gas and solid, detailed studies on optical properties and structure have been conducted from the perspectives of intermolecular interactions, coordination structure changes, stereochemical changes, and crystalline phase transitions.

Figure 1. Vapochromism

Current Status and Frontiers

The phenomenon of color change in response to stimuli is known as chromism. For example, photochromism and thermochromism have been studied for a long time, but vaporochromism is relatively new and has gained attention since the end of the 20th century due to environmental issues.

Blue silica gel, which can detect the effectiveness of desiccants through color changes, is a vaporchromic material that utilizes the coordination of water molecules to cobalt ions. Additionally, vapochromic materials capable of detecting volatile organic compounds (VOCs) such as alcohols and toluene through color changes are commercially available as VOC sensors using porphyrins. For more sensitive and selective vapochromic materials, luminescent vapochromic materials have garnered attention. Based on the mechanism of color change, vaporochromic compounds are categorized into three types: 1) systems where vapor molecules induce changes in molecular arrangement, altering intermolecular interactions; 2) systems where vapor molecules directly coordinate with metal centers, changing the coordination structure; and 3) systems where various effects of vapor molecules cause changes in molecular stereochemistry. The types of vaporochromic materials utilizing these principles are diverse, including metal complexes, inorganic-organic composites, organometallic compounds, organic crystals, supramolecules, coordination polymers, and metal-organic frameworks (MOFs).

As a representative example of the first type of system, the term, vapochromism, was first used to describe the phenomenon found for stacked Pt(II) complexes. Square-planar platinum(II) complexes exhibit characteristic luminescence due to electronic interactions between platinum ions when the complex units are stacked in close metal-metal contact. Complexes containing π-conjugated ligands emit strong luminescence from the metal-metal-ligand charge transfer (^{3}MMLCT) state. When an external stimulus such as vapor is applied, a subtle change in the stacking structure causes a distinct change in luminescence color, i.e., vaporochromic luminescence. Not limited to intermetallic interactions, examples of vaporochromism have recently been reported in organic crystals where intermolecular interactions such as hydrogen bonding and π-π interactions effectively function. In systems where vapor molecules directly coordinate to metal complexes 2), vaporochromic luminescence has been observed in coordinatively unsaturated Pt(II), Au(I), and Cu(I) complexes. Additionally, there are interesting examples where the spin state of Ni(II) complexes is switched by the adsorption and desorption of vapor molecules, causing a color change, although they do not exhibit luminescence. In such cases, systems where color changes are accompanied by other physical property changes, such as magnetic or conductive properties, have been identified, and their application as high-performance materials is anticipated. The examples mentioned in 3) are common in organic crystals. For example, in molecules capable of flexible and diverse stereochemical configurations, structural changes induced by the inclusion of vapor molecules cause color changes. In molecular crystals with donor/acceptor sites that exhibit intramolecular charge transfer, vapor stimulation can induce changes in stereochemical configuration or charge transfer properties, leading to color changes. Furthermore, examples where luminescent molecules are embedded in MOFs to control vapor-chromic responses are also attracting attention.

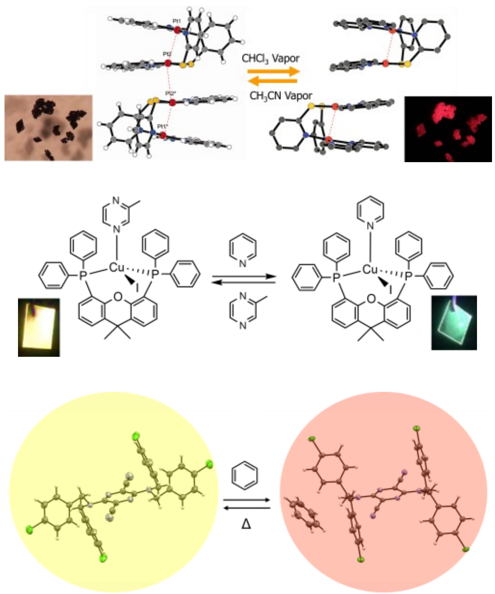

Figure 2. Examples of vapochromic luminescence.

References

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Future Perspectives and Directions

Issues to be resolved and realized within the next 10 years: Elucidation of the dynamics of vapor-induced phase transition phenomena, development of high-performance materials that combine luminescence with other physical properties, and other scientific advances and developments. Application of high-performance chromic materials and highly selective molecular sensors.

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