View Article Online
DOI: 10.1039/C9TC06710H

ARTICLE

A Reversible Thermo-Responsive 2D Zn(II) coordination Polymer as a Potential Self-referenced Luminescent Thermometer

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A convenient, fast, and accurate temperature detection method is highly desirable in many biochemical processes and scientific research. Luminescence thermometry is one of the most currently studied approaches among the non-contact and non-invasive thermometry techniques. Here we present an intrinsic energy-based luminescent thermometer based on a stimuli-responsive coordination polymer, $[ZnL_2]_n \cdot nH_2O$ (H_2L=2,3-butanedionebisisonicotinylhydrazone). The temperature-dependent photophysical characteristic reveals that the thermochromic luminescence in the range 40-90 °C can be switched reversibly from yellow to red in an ambient atmosphere, thereby achieving the non-destructive sensing of temperature. Moreover, the material exhibits a linear relationship between wavelength/intensity and the absolute temperature in a wide range, thus presenting a rare solid-state luminescent thermometer based on both photoemission energy and intensity. The crystal structure reveals a 2D layer-structured framework, characterized by an unusual trigonal prismatic Zn center. The reversible thermochromic behavior is mainly attributed to the change of the coordination environment of Zn^{2+} ions during the dehydration/hydration process. The rapid response (less than 5 s), good reversibility and solvent-free procedure make the Zn(II) coordnation polymer an exceptional thermo-responsive material for use in temperature monitoring devices.

1. Introduction

As a new frontier for material research, the design and construction of the coordination polymers have attracted significant attention over the past few decades. They have demonstrated their huge potential as a functional material in miscellaneous fields such as sorption and storage, heterogeneous catalysis, drug delivery, luminescence, molecular recognition and chemical sensing.[1–4] The structural and functional tunability of these materials offer the potential to design a large variety of aesthetic structures and introduce desired functionalities that is not available with other conventional porous materials (zeolites, activated carbons).[5]

The strategy to construct coordination polymers involves self-assembly of metal ions and organic linkers of predefined stereochemistry and functionality. As it is known, there are several key elements that can influence the construction of coordination polymers, the linker design is a crucial factor. Highly symmetrical dicarboxylate or bipyridine functionalized polytopic ligands are often employed to produce extended frameworks. Conversely, our interest focuses on novel topological polymers with unorthodox polytopic ligands with high structural stability. On the basis of extensive studies, we have recently demonstrated the self-assembly of Cd^{2+} with a rigid compartmental polytopic ligand, 2,3-butanedionebisisonicotinylacidhydrazone (H_2L).[6] Besides, the role of linker in the formation if zeolitic structure and its thermo responsive and gelling behavior have been reported. Utilizing such observations, we planned to introduce Zn^{2+} to the compartmental ligand (H_2L), which could provide luminescent MOF with diversified structure and photophysical properties. Similar to cadmium, the pyridine groups and tetradentate compartment saturated the coordination sphere of the Zn^{2+}. Since the dimensionality and topology are highly dependent on linkers and metal nodes, the incorporation of Zn atom reduced the complexity of the porous structure (Fig. 1). Furthermore, the pores of the Zn(II) polymer were much smaller than those of the metal organic framework (MOF) obtained when employing Cd^{2+}.

Taking advantage of external stimuli like temperature, light, pressure, pH, and electric/magnetic field to switch the color of luminescent materials in a foreseeable way has been a hot topic worldwide for the development of smart photoactive materials for various technological applications. Among them, thermochromic materials have aroused a great deal of attention owing to their applications in areas such as fluorescent switches, data storage, sensors, and optical devices.[7–9] Dual responsive thermochromic materials, which exhibit reversible modification of emission wavelength in response to temperature change can contribute significant breakthroughs in the field of luminescent temperature sensors.[10–12] Since temperature is an extremely important physical parameter in almost all fields of science, its precise measurement is crucial in both scientific research and technological applications.[13] Many types of thermometers including liquid-filled glass thermometers, thermistors and thermocouples, which utilize various kinds of temperature dependent physical properties,

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Electronic Supplementary Information (ESI) available: CCDC:1968474 . For crystallographic data in CIF format see DOI: 10.1039/x0xx00000x