Microporous and Mesoporous Materials 268 (2018) 202–206

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Dye confined in metal-organic framework for two-photon fluorescent temperature sensing

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ARTICLE INFO

Keywords:
Size confinement
Electrostatic interaction
Two-photon luminescent
Metal-organic framework
Temperature sensing

ABSTRACT

In order to expand the application range of luminescent dye, metal-organic framework (MOF) is applied as a carrier to solve the problem such as low luminescent efficiency and poor stability. Here a two-photon luminescent dye-confined ionic metal-organic framework (iMOF) **ZJU-68⊃DMASM** was prepared through size confinement and electrostatic interaction. The dye loading content was investigated to obtain maximum luminescent efficiency and it was found that the change of two-photon emission intensity was consistent with that of quantum efficiency. In addition, the composite showed excellent physiological temperature sensing performance from 20 °C to 60 °C with a high relative sensitivity, good water stability and good biocompatibility, possessing great potential to be applied in biological field.

1. Introduction

Due to wide spectral range and good optical stability, luminescent dyes have wide application prospects in luminescent sensing [1,2]. Compared with single-photon luminescent dyes, two-photon luminescent dyes have many unique advantages [3]. First of all, water and haemoglobin in biological tissue will absorb photons, but with increasing of wavelength, the absorption is decreasing [4]. Therefore, the selection of near-infrared light as the excitation light source has better penetration ability instead of ultraviolet light or visible light, which can be used in deep region as detector [5]. Secondly, excited by near-infrared light can effectively reduce the interference of auto-fluorescence of biological materials, effectively improving the SNR (signal to noise ratio). In addition, two-photon luminescence can reduce the damage to biological tissues due to the low excitation energy and high spatial selectivity [6]. However, the luminescence quenching caused by aggregation of dye molecules has been a difficult problem all the time and poor stability as well as the toxicity to organisms limits its application as physiological sensing material as well [7,8].

Metal-organic framework (MOF) as a novel hybrid material composed of organic ligand and metal atom through coordination bond, possesses a plenty of advantages such as multi luminescent centres, adjustable pore structure, good biocompatibility and a variety of post modification methods [9–18]. Based on the above reasons, luminescent dyes can be loaded into pores of MOF in virtue of porous properties of MOF, which could also improve biocompatibility and the stability of dyes greatly. In addition, the chromospheres are uniformly dispersed in the pores of framework, which can effectively inhibit the interaction between dye molecules. It further weakens the luminescence quenching and improves the quantum efficiency of luminescent materials [19–21]. However, it's not enough to stabilize dye molecules just by size confinement and "dye leakage" becomes an annoying process [22–24]. The ionic MOF provides us with a good solution that restricting charged dyes through appropriate pore size and assisting with electrostatic interaction for closer combination are possible. Ionic metal-organic frameworks (iMOFs) have many advantages combining the ionic features and inherent characteristics of MOF [25]. As ionic framework, several oppositely charged guest objects can be loaded into pores of the framework by electrostatic interaction, which may ensure guest ordered-orientation in the pores with good stability and special optical properties [19].

Temperature is one of the most important parameters in our daily life and industry [26,27]. Here we synthesized a two-photon luminescent dye-loaded MOF **ZJU-68⊃DMASM** (ZJU-68 = $H_2[Zn_3O(C_{17}H_9NO_4)_3]{\cdot}2.5H_2O{\cdot}0.5DMF{\cdot}MeCN$, DMASM = 4-[p-(dimethylamino)styryl]-1-methylpyridinium) where size confinement and electrostatic interaction work together. The stability of the dye in the framework of MOF was characterized and dye loading content at maximum luminescent efficiency was studied. Temperature sensing properties of the composite were discussed in a range of 20–60 °C and

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https://doi.org/10.1016/j.micromeso.2018.04.032
Received 11 March 2018; Received in revised form 9 April 2018; Accepted 21 April 2018

thermal stability as well as the biocompatibility were also tested. Additionally, the composite shows great stability in water and good biocompatibility to cells compared to the pure dye, which indicates it has potential application in physiological temperature sensing filed.

2. Experimental section

2.1. Materials and synthesis

The ligand was synthesized according to the literature and MTT cell detection kit was purchased from Nanjing KaiJi biotech companies [19]. Other reagents or solvents used were commercially available unless otherwise specified. The synthesis of **ZJU-68⊃DMASM** is thus presented here in detail: Based on literature, $Zn(NO_3)_2{\cdot}6H_2O$ (100 mg, 0.34 mmol) and ligand (7-(4-carboxyphenyl)quinoline-3-carboxylate) (50 mg, 0.17 mmol) were mixed and dissolved in mixed solution of 10 mL DMF, 2 mL acetonitrile, 0.05 mL H_2O and 0.05 mL hydrofluoric acid. Different amount of DMASM (0.46 mg (0.1 mmol L^{-1}), 1.38 mg (0.3 mmol L^{-1}), 2.30 mg (0.5 mmol L^{-1}), 4.60 mg (1.0 mmol L^{-1}), 6.90 mg (1.5 mmol L^{-1}), 9.20 mg (2.0 mmol L^{-1}), 11.5 mg (2.5 mmol L^{-1}), 13.8 mg (3.0 mmol L^{-1}), 23.0 mg (5.0 mmol L^{-1})) were added in respectively before stirring evenly. The mixed solution was then loaded into a 20 mL sealed Teflon autoclave and kept at 100 °C for 24 h. Cooling slowly to room temperature and washing by DMF for 3 times before drying at 60 °C, we got red **ZJU-68⊃DMASM** crystal powder [19].

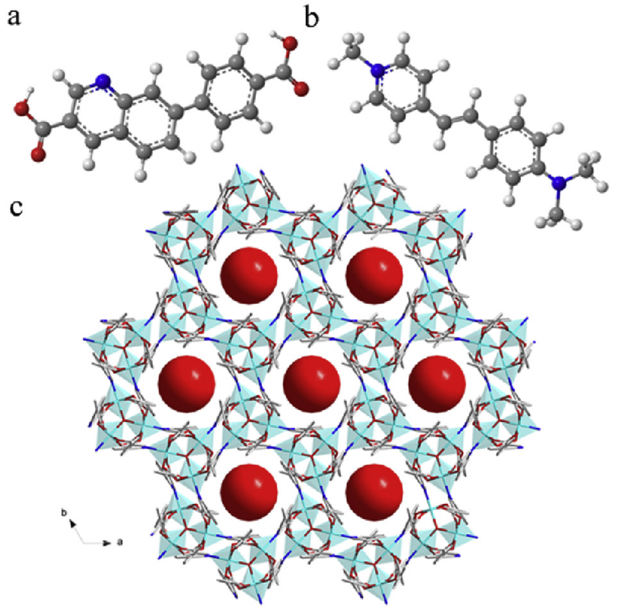
2.2. Characterization

Powder X-ray diffraction (PXRD) data were collected by X'Pert PRO diffraction machine, scanning range of 4–50° with Cu-K_α (λ = 1.542 Å) radiation. Thermo Fisher Nicolet iS10 spectrophotometer was used to test the infrared absorption spectrum and sample was tableted with KBr in ratio of 1:20. FTIR is mainly used for the detection of organic functional groups. Thermogravimetric analysis (TGA) was carried out on a Netzsch TG209F3 instrument at a heating rate of 5 °C·min^{-1} under N_2 atmosphere.

Using Edinburgh FLF920 multi-function fluorescence spectrometer, we got quantum efficiency of the sample in an absolute method with xenon lamp as the excitation light source and red PMT as detector. Excitation and emission slit size were 5 nm and 0.3 nm, respectively. Photoluminescence spectroscopy (PL) including excitation and emission spectra were obtained by Hitachi F4600 steady-state fluorescence spectrometer. Excitation light source was xenon lamp with excitation and emission slit size of 2.5 nm, 2.5 nm. PMT detector's voltage was 750 V and the scanning speed was 240 nm min^{-1}. Two-photon emission spectra were obtained by Nd:YAG laser at excitation wavelength of 1064 nm with frequency of 10 Hz and pulse energy of 3–4 mJ. The emission signals were collected by a fiber spectrometer and a PolyScience Temperature Control Solution PD07R-20 should be equipped if it is necessary. The fluorescent photograph were taken on an Olympus IX71 inverted fluorescence microscope excited by mercury lamp. The picture of two-photon luminescence of **ZJU-68⊃DMASM** was photographed were taken on Olympus IX71 inverted fluorescence microscope excited by a SpOne-8 laser equipped with Spirit-OPA PO15F4L.

We determined the concentrations of DMASM in ZJU-68 by UV–Vis absorption method. Weigh a certain amount of samples (about 5 mg) of **ZJU-68⊃DMASM**, then destroy the framework by adding HCl solution (about 0.01 mL) in order to release DMASM ions. After dissolving in DMF solution (about 20 mL), the concentration of dye in ZJU-68 was determined by UV–Vis spectroscopy.

MK3 type enzyme-linked immunosorbent assay from the United States Thermo company was utilized for MTT colorimetric test [28]. Taking the mouse adrenal nerve tumor cells (PC12 cells) as research object, firstly, we added **ZJU-68⊃DMASM** or DMASM with different amount in a 96-well plate (200 μL). After culturing for 24 h, MTT (50 μL) was added with 4 h of incubation and then we sucked the supernatant. DMASO (150 μL) was added to dissolve produced formazan by living cells. At last, light absorption value at 490 nm wavelength could be determined by Microplate Reader. In that way we determined the survival rate of cells with different conditions of treatments [29].



Scheme 1. (a) The structure of ligand; (b) The structure of dye (DMASM); (c) Crystal structure of ZJU-68, viewing from the *c* axis. The red balls represent DMASM.

For imaging experiments, 20 μg mL^{-1} **ZJU-68⊃DMASM** probes were added to the wells and incubated with the PC12 cells for 24 h in the incubator. DAPI was utilized for dyeing nucleus. Imaging of cells was conducted using a confocal laser scanning microscopes with a 60 × objective at room temperature with laser excitation wavelengths of 405 nm for DAPI.

The composite was incubated with PC12 cells for 4 h at 37 °C before washing by PBS for two times. The PC12 cells was then observed at 1040 nm on a photoelectricity deep imaging microscope FV MPE-RS.

3. Results and discussion

ZJU-68 is an anionic MOF whose ligand is 7-(4-carboxyphenyl) quinoline-3-carboxylate (Scheme 1a) and DMASM is a cationic two-photon luminescent dye (Scheme 1b). DMASM, metal nitrates and the ligand were mixed and reacted in-situ to obtain **ZJU-68⊃DMASM** crystal. According to reports, ZJU-68 crystal belongs to the space group of $P\bar{3}$. Secondary building unit (SBU) $[Zn_3O]^{4+}$ connect with each other by the ligand, producing an anionic framework [19]. There are one-dimensional hexagonal pores with pore size of 0.6 nm along the c axis (Scheme 1c). The cationic dye DMASM cannot pass through the window of the ZJU-68 pores through ion-exchange way due to a larger size of 0.35 × 0.63 × 1.43 nm^3 but only encapsulated in in-situ method, which provides two patterns of combination mode and is more reliable. The stability of the dye in the framework of MOF has been characterized by fluorescence spectroscopy and then photographed (Fig. 1). After immersing in DMF for one week, the luminescent intensity of the supernatant is much weaker than 10^{-6} M DMF solution of dye and is more close to that of pure DMF. It can also be seen from the photos that the supernatant is basically colourless and almost identical to the colour of DMF.

It is shown that the PXRD patterns of synthesized ZJU-68 crystals are consistent with that reported in literature, indicating that the pure