

# Layer-by-Layer Grafting Dye on Chiral MOF Thin Films for Circularly Polarized Luminescence

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**ABSTRACT** Metal-organic frameworks with chiral feature (chirMOFs) are attracting great attention on circularly polarized luminescence (CPL). However, developing new efficient strategy to achieve or improve CPL properties is an urgent task. Herein, new chiral MOF thin films prepared by liquid-phase epitaxial layer by layer (lbl) growth method (SURchirMOF) are composed of D- or L-camphorate (D/Lcam) and aminopyrazine (Pr-NH<sub>2</sub>) by using liquid phase epitaxial layer by layer (lbl) method. The resulted Zn<sub>2</sub>(D/Lcam)<sub>2</sub>Pr-NH<sub>2</sub> SURchirMOF shows strong chirality and luminescence but weak CPL emission at 390 nm. After lbl modifying a dye molecule FluoresceinIsothiocyante (FITC), the chiroptical Zn<sub>2</sub>(D/Lcam)<sub>2</sub>Pr-NH-FITC SURchirMOFs with ~7 times CPL signal improvement and ~3 times *g*<sub>lum</sub> value amplification are obtained. This work provides a new strategy to develop chiral MOF thin films for CPL improvement using lbl grafting approach.

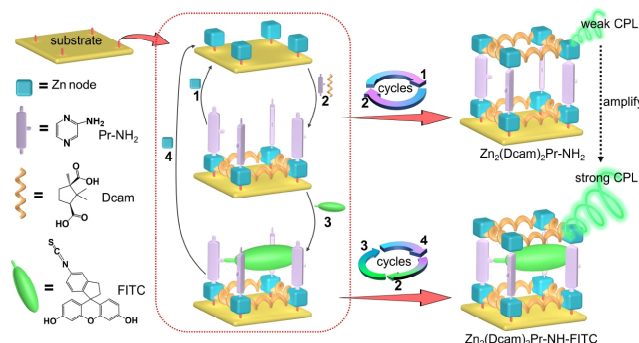
**Keywords:** metal-organic frameworks, liquid-phase epitaxy, thin film, circularly polarized luminescence

## INTRODUCTION

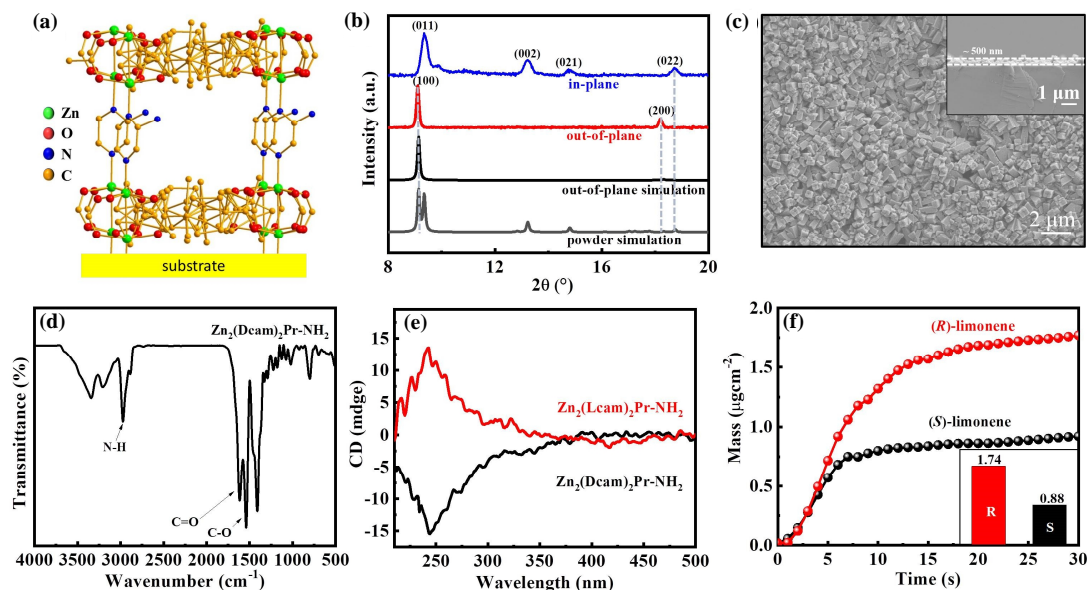
Metal-organic frameworks (MOFs) materials<sup>[1-4]</sup> constructed from metal ions (clusters) and organic ligands have been widely concerned, because of their diverse structures and fascinating potential of applications in broad fields of catalysis,<sup>[5,6]</sup> adsorption/separation,<sup>[7-9]</sup> optical,<sup>[10,11]</sup> energy storage<sup>[12,13]</sup> and so on. As a subclass of MOFs materials, chiral MOFs (chirMOFs)<sup>[14,15]</sup> have attracted great attention on the potential applications in asymmetric catalysis,<sup>[16,17]</sup> enantioselective adsorption/separation<sup>[18]</sup>, nonlinear optics,<sup>[19,20]</sup> and drug delivery<sup>[21]</sup>. In order to meet the requirement of practical applications in many fields, recently chiral MOFs with the form of thin films or membranes have been realized to be advanced candidates for chiral recognition,<sup>[22,23]</sup> enantiomers separation,<sup>[24]</sup> and photoelectronic applications.<sup>[25,26]</sup> Particularly liquid-phase epitaxial (LPE) layer-by-layer (lbl) growth approach<sup>[27,28]</sup> affords an advanced approach to grow high-quality MOF thin films on the substrate surfaces (also known as surface-coordinated MOFs, SURMOFs) which promote the resulting MOF thin films to have the advantages of controllable growth orientation, tunable thickness and highly-homogeneous surface, providing a promising thin film material for the study in fundamental research and the application on sensors and devices applications. Especially, the development of SURMOFs with chiral function (called chiral SURMOF, SURchirMOFs) is very important for chiral related applications but their preparation was rarely reported. The previous work showed that the pillar-layered homochiral MOFs M<sub>2</sub>(D/Lcam)<sub>2</sub>L (M = Zn or Cu; D/Lcam = camphoric acid; L = pillared ligands) could easily grow chiral SURMOFs using LPE lbl methods.<sup>[29,30]</sup>

As the emerging chiroptical applications, circularly polarized

luminescence (CPL)<sup>[31-34]</sup> of chiral thin films has aroused great interest.<sup>[35,36]</sup> Supramolecular self-assembly, upconversion materials and liquid crystals have been reported to achieve CPL amplification of 1~2 orders of magnitude.<sup>[37-39]</sup> However, the use of MOF thin films to study CPL amplification has not been reported yet. In addition, MOFs with chiral feature have diverse structures, ordered nanopores and tunable functionalities, providing excellent candidates for developing CPL materials by selecting both inorganic and organic components. Particularly, SURchirMOFs have homogeneous films and can have large surface, resulting in good candidates for CPL applications. So far, organic molecules/supramolecular<sup>[40-42]</sup> and the related chiral thin films have been widely studied for CPL. Recently, developing the chiral SURMOF for promising chiroptical devices and sensors applications has attracted great interest in CPL study. For example, the first chiral



**Scheme 1.** The assembly process of Zn<sub>2</sub>(Dcam)<sub>2</sub>Pr-NH<sub>2</sub> and Zn<sub>2</sub>(Dcam)<sub>2</sub>Pr-NH-FITC prepared by lbl grafting method.



**Figure 1.** (a) The structural model of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ ; (b) Out-of-plane and in-plane XRD patterns of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ ; (c) Surface and cross-sectional SEM images of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ ; (d) IR spectra of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ ; (e) CD spectra of  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$ ; (f) Comparison of (R)- or (S)-limonene adsorption uptakes for  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  measured by QCM technique with the histogram of ee%.

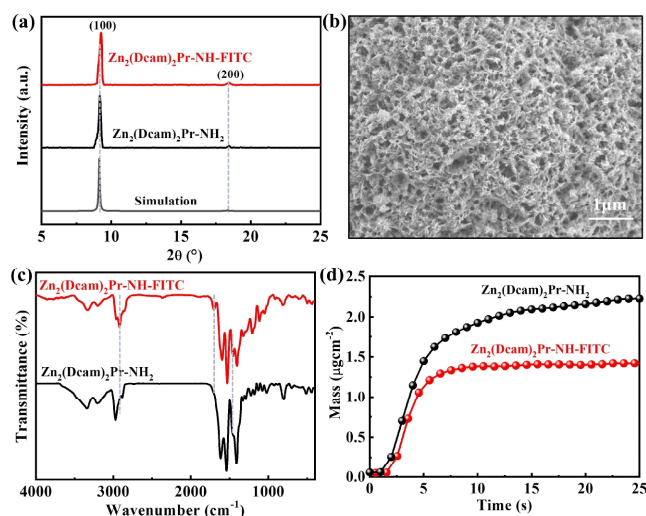
SURMOFs,  $\text{Zn}_2(\text{D/Lcam})_2\text{DAP}^{[43]}$  constructed with chiral ligand and luminescent ligand zapyrene-based was prepared on quartz substrates for CPL. However, the assembly of chiral SURMOFs consisting of chiral and luminescent ligands directly is difficult and the prediction of CPL properties is also challenging. Therefore, developing an efficient method to achieve or improve CPL of chiral SURMOFs is significant to expand CPL applications.

Based on above considerations, in this work a new pillar-layered homochiral SURMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  grown successfully on the substrate surfaces is composed of chiral ligand D- or L-camphoric acid (D/Lcam) and pillared ligand aminopyrazine (Pr-NH<sub>2</sub>) using LPE lbl dipping method. More importantly, the chiral SURMOFs with amino group can be post-modified with thiocyanate containing fluorescent dye molecule to enhance CPL. The prepared SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  with high orientation and homogeneous surface exhibits good enantioselective adsorption toward limonene enantiomers and strong chirality but weak CPL emission at 390 nm. By using lbl-modifying approach, the FITC with green emission can be grafted on SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  skeleton by the lbl polyurethane reaction, which fails to use direct post-modification method. The modified SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  keeps the chirality and shows CPL emission at about 540 nm. The present work provides a facile strategy to develop the chiral MOF thin films for CPL improvement by using lbl grafting fluorescent molecules.

## n RESULTS AND DISCUSSION

**SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ .** The hydroxyl functionalized substrates (quartz substrates and Au wafer) are chosen as the SURMOFs growth in this work. A new SURchirMOF assembled by aminopyrazine and Dcam = (1R,3S)-(+)-camphorate or Lcam = (1S,3R)-(-)-camphorate, is prepared on the substrates using a

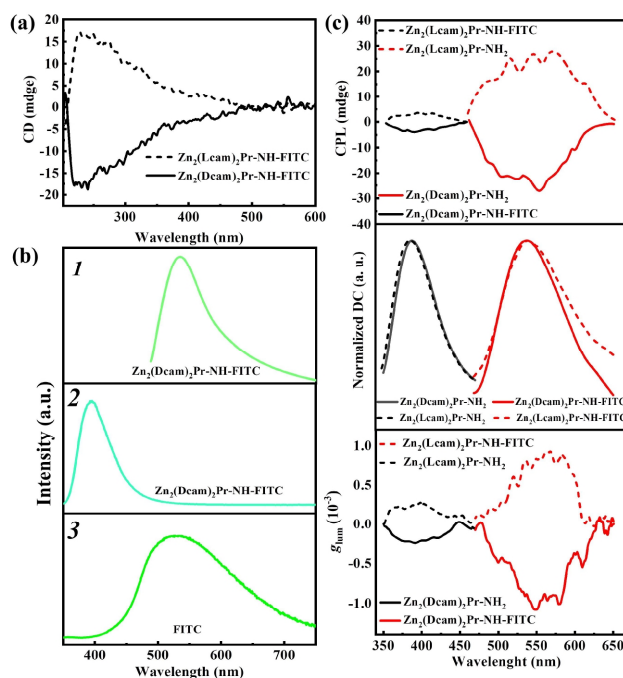
LPE lbl approach, named  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$ . As the homochiral MOF with pillar-layered structure,  $\text{Zn}_2(\text{D/Lcam})_2$  acts as the 2D layer, while the Pr-NH<sub>2</sub> serves as the bridging pillar.<sup>[44]</sup> X-ray diffraction (XRD) patterns for the SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  in an out-of-plane mode (Figure 1(b)) show diffraction peaks at 9.2 and 18.4°, corresponding to the (100) and (200) peaks of simulated MOF. The in-plane XRD patterns of the samples at 9.3, 13.2, 14.8, and 18.8° are in accord with the simulated XRD peaks at (011), (002), (021), and (022). The XRD patterns clearly demonstrate a preferentially oriented growth of SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  along the [100] orientation, revealing a good agreement with the simulated XRD pattern calculated from the structures of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  (Figure 1(a)). The scanning electron microscopy (SEM) images (Figure 1(c)) of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  show a highly homogeneous crystalline film of the obtained SURchirMOF and the cross-sectional SEM image displays the thickness to be ~500 nm when the LPE lbl dipping cycles are 30. The infrared (IR) spectra (Figure 1(d)) for  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  show that the appearance of the band at 1538  $\text{cm}^{-1}$  corresponds to C-O stretching vibration, and those at 1613 and 2976  $\text{cm}^{-1}$  belong to the C=O and N-H groups, respectively. The chiral characteristic of the SURMOFs is characterized by circular dichroism (CD) (Figure 1(e)) spectrometer. The CD spectra show that  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  has a strong and opposite CD signal at ~230 nm in  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{Lcam})_2\text{Pr-NH}_2$ , indicating the chiral MOF thin films with enantiomers. In order to study the SURchirMOFs on enantioselectivity of enantiomers, a gas phase quartz crystal microbalance (QCM) technique is used to monitor mass changes with pure argon by detecting the change of resonance frequency, which has been developed for investigating the enantioselectivity of homochiral MOF thin films.<sup>[45-47]</sup> The Au coated QCM electrode is used as the growth substrate. By using



**Figure 2.** (a) XRD pattern of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$ ; (b) Surface SEM images of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$ ; (c) The IR spectra of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$ ; (d) Ethanol adsorption uptake for  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$  measured by QCM technology.

the lbl dipping method, the SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  is prepared for further experiment. The QCM adsorption results (Figure 1(f)) show that the adsorption amount of (*R*)- or (*S*)-limonene for  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  is 1.74 and 0.88  $\mu\text{g cm}^{-2}$ , which exhibit an ee value<sup>[48,49]</sup> (32.8%). The  $\text{Zn}_2(\text{Lcam})_2\text{Pr-NH}_2$  adsorption results exhibit enantioselective adsorption for (*S*)-limonene over (*R*)-limonene (ee = 42.4%) with 2.25 and 0.91  $\mu\text{g cm}^{-2}$  (Figure S1,2), respectively. In addition, the photoluminescent spectra show the SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  has photoluminescent emission (Figure 3(b(2))) at 390 nm, which is different from the ligand  $\text{Pr-NH}_2$  (Figure S3) (370 nm).

**SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$ .** In order to improve the CPL property of SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$ , here we further introduce the amino containing fluorescent dye molecules FITC by liquid-phase epitaxial lbl modification method, which is named  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$ . The lbl-modified chiral thin film was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), IR spectra and UV-vis spectra. From the XRD patterns (Figure 2(a) and S4), we can find that the chiral thin film still has the preferential growth orientation after the lbl modification of dye molecule. Compared with the as-prepared SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ , the SEM images (Figure 2(b)) of SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$  show the flat and uniform morphology with 30 LPE lbl dipping cycles, and the extra absorbance bands at 1456, 1702 and 2914  $\text{cm}^{-1}$  of IR spectra (Figure 2(c)), as well as the increased absorption intensity at ~500 nm in UV-vis spectra (Figure S5), which proves that SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$  is lbl-modified by FITC dye successfully. The QCM adsorption amount of ethanol with the lbl-modified chiral thin film is significantly reduced compared with the as-prepared SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  from 2.1 to 1.4  $\mu\text{g cm}^{-2}$  (Figure 2(d)). Similarly, the same QCM adsorption result of ethanol uptake is obtained when comparing with that of SURchirMOF  $\text{Zn}_2(\text{Lcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{Lcam})_2\text{Pr-NH-FITC}$  (Figure S6).



**Figure 3.** (a) The CD spectra of  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$ ; (b) The photoluminescent emission spectra of FITC (1),  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  (2) and  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$  (3); (c) The CPL spectra of  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  and CPL dissymmetric factor ( $g_{\text{lum}}$ ) of  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$ .

**Chiroptical Properties.** To investigate the chiroptical properties of lbl-modified SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$ , the CD absorption spectra of SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$  display one positive band at ~230 nm and  $\text{Zn}_2(\text{Lcam})_2\text{Pr-NH-FITC}$  thin film exhibits mirror images of CD signal (Figure 3(a)). In the test, to demonstrate that the CD and CPL signals are not influenced by linear dichroism and birefringence, we get average signal of front and back from one sample.<sup>[50]</sup> As a green fluorescent dye molecule, FITC has good fluorescence property (Figure 3(b(3)) and S7), which can promote the photoluminescent intensity of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  (Figure 3(b(2)) and S8, 9). As shown in Figure 3(b(1)) and S10, 11), the photoluminescent spectra of SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  exhibit an intense green emission with bands located at ~540 nm, with excitation at ~340 nm. In addition, the SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  has strong CD signal, which is similar to SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$ . This also reveals that the lbl-modification of the SURchirMOF does not affect the chiral signal.

The CPL spectra with almost mirror images for the enantiomers  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  are found that both of them have CPL signal. As shown in Figure 3(c),  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  exhibits negative CPL sign at 390 nm, while  $\text{Zn}_2(\text{Lcam})_2\text{Pr-NH}_2$  also shows positive CPL sign, with  $g_{\text{lum}}$  of about  $\pm 0.0003$ . Compared with as-prepared SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$ ,  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  has a stronger CPL signal at ~540 nm under excitation of ~340 nm, showing a mirror image of green emission with  $g_{\text{lum}}$  of about  $\pm 0.001$ . This preparation strategy can effectively achieve energy transfer be-



tween FITC and SURchirMOF, resulting in an amplification of CPL performance.<sup>[51,52]</sup>

In order to demonstrate the feasibility of this lbl grafting strategy, the as-prepared SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$  is immersed into FITC solution for post-modification of dye molecule FITC, which is named  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$ . Unfortunately, such post-modification strategy is not available in this SURchirMOF, which is demonstrated by the unchanged XRD, SEM, and IR as well as QCM adsorption of ethanol. The unchanged XRD patterns (Figure S12) show the crystallinity of MOF is maintained, which can also be seen in the SEM image (Figure S13). The IR spectra (Figure S14) of  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH-FITC}$  are similar to that of as-prepared SURchirMOF  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ , and the almost unchanged QCM adsorption of ethanol (Figure S15) demonstrates that the dye (FITC) does not enter into the cavity of SURchirMOF to modify the skeleton of  $\text{NH}_2$ -functionalized MOF. As a result, due to the small pore size of the chiral  $\text{Zn}_2(\text{Dcam})_2\text{Pr-NH}_2$ , such post-modification strategy is unsuccessful for CPL enhancement of the chiral thin film.

## CONCLUSION

In summary, the proof-of-concept chiral MOF thin films (SURchirMOFs) with CPL amplification have been successfully fabricated by lbl grafting luminescent dye molecules onto the skeleton of chirMOF thin films. By using LPE lbl dipping method, homochiral MOFs thin film containing free-coordinated amino group is successfully grown on the OH-functionalized substrates. The obtained  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  SURchirMOF shows weak CPL performance. By lbl modification growth approach with the carboxyl containing dye molecule, the lbl-modified SURchirMOFs  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  have strong chirality and intense luminescent emission. The CPL spectra show that  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  exhibits obvious improvement performance on CPL, which is ~7 times stronger CPL signal and more than ~3 times  $g_{\text{lum}}$  value than that of  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$ , comparable to the performance of the reported materials. The lbl-modified chiral SURMOFs provide an effective and facile strategy to achieve the CPL amplification on the MOF thin film materials.

## EXPERIMENTAL

**Materials and Methods.** All the chemical reagents employed in this work were commercially available. Zinc acetate dihydrate ( $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , Sinopharm Chemical), Dcam = (1*R*,3*S*)-(+)-camphorate, Lcam = (1*S*,3*R*)-(-)-camphorate ( $\text{C}_{10}\text{H}_{16}\text{O}_4$ , Sigma-Aldrich, 99%), Pr-NH<sub>2</sub> = aminopyrazine ( $\text{C}_4\text{H}_5\text{N}_3$ , Aladdin, 99%), (*R*)- or (*S*)-limonene (TCI, 98%) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , Sinopharm Chemical, 99.7%).

The samples grown on Au substrate were characterized with powder X-ray diffraction (PXRD) analysis performed on a Mini-Flex2 X-ray diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ). The samples grown on functionalized Au/SiO<sub>2</sub> wafer and quartz substrates were characterized by Fourier transformation infrared (FTIR) spectra and scanning electron microscope (SEM). Fluorescence photoluminescent spectra for the samples were performed on an Edinburgh Analytical instrument FLS920. The bare quartz substrate was used as the reference for CD, LD and CPL

measurements. Circularly polarized luminescence (CPL) spectra were obtained using JASCO CPL-300.

Mass uptake results of (*R*)- or (*S*)-limonene and ethanol for the samples grown on Au-coated QCM electrodes were obtained by BELQCM instrument.

**Substrate Pretreatment.** The quartz substrates were cleaned and treated with a mixture of sodium hydrate (1 mM) and hydrogen peroxide (30%) with a volume ratio 3:1 at 80 °C for 30 minutes, as well as the Au and Au-coated QCM electrodes were immersed into 11-mercapto-1-undecanol (MUD) ethanolic solution (20  $\mu\text{M}$ ) at room temperature for 2 days, then cleaned with deionized water or ethanol and dried under nitrogen flux to obtain OH-functionalized substrates for the next preparation.

**Synthesis of SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$ .** The SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  was grown by the layer-by-layer (lbl) automatic dipping method and fabricated with the following ethanolic solutions at 50 °C: 1.0 mM zinc acetate ( $\text{Zn}(\text{OAc})_2$ ), 0.4 mM H<sub>2</sub>Dcam/H<sub>2</sub>Lcam and 0.4 mM aminopyrazine (Pr-NH<sub>2</sub>) mixed solution. The amount of solution can be enough to cover the substrate. The detailed experimental steps: firstly, functionalized quartz substrate was immersed in a solution of  $\text{Zn}(\text{OAc})_2$  for 15 min, and then was immersed in a solution of equimolar H<sub>2</sub>Dcam/H<sub>2</sub>Lcam and a Pr-NH<sub>2</sub> mixed solution for 20 min. After each step, the sample was washed with pure ethanol for 2 min to remove residual reactants. The above details represent one growth cycle. The ChirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  thin films were obtained by 30 growth cycles.

**Synthesis of SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$ .** The SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  was synthesized by the layer-by-layer automatic dipping method at 50 °C. The functionalized quartz substrates were immersed in 1.0 mM  $\text{Zn}(\text{OAc})_2$ , 0.4 mM equimolar H<sub>2</sub>Dcam/H<sub>2</sub>Lcam, Pr-NH<sub>2</sub> and 0.1 mM fluorescein isothiocyanate with the immersion time to be 20, 30, and 10 min, respectively. A total of 30 growth cycles are used for the  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  thin films.

### Quartz Crystal Microbalance Adsorption of the Thin Films.

The quartz crystal microbalance (QCM) has been used to monitor the mass of probe species with good volatility in gas phase by monitoring the resonance frequency changes on the electrode thin film. The gold-coated QCM sensors used as substrates were functionalized by 11-mercapto-1-undecanol (MUD) SAMs. The 20 cycles SURchirMOF  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH}_2$  and  $\text{Zn}_2(\text{D/Lcam})_2\text{Pr-NH-FITC}$  were prepared on the substrates using the same condition and growth procedure mentioned above. In this work, the pure argon was used for the baseline, (*R*)- or (*S*)-limonene and ethanol were chosen as the loading analyte.

## ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (21872148), the Youth Innovation Promotion Association of the Chinese Academy of Sciences (2018339), and Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (2021ZR131).

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## n COMPETING INTERESTS

The authors declare no competing interests.

## n ADDITIONAL INFORMATION

Supplementary information is available for this paper at <http://manu30.magtech.com.cn/jghx/EN/10.14102/j.cnki.0254-5861.2022-0023>.

For submission: <https://www.editorialmanager.com/cjschem>

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Received: February 5, 2022

Accepted: April 4, 2022

Published online: April 15, 2022

Published: September 22, 2022