

Supplementary Information

Ligand-exchanged Metal Organic Frameworks Lenses for Super-Resolution Imaging

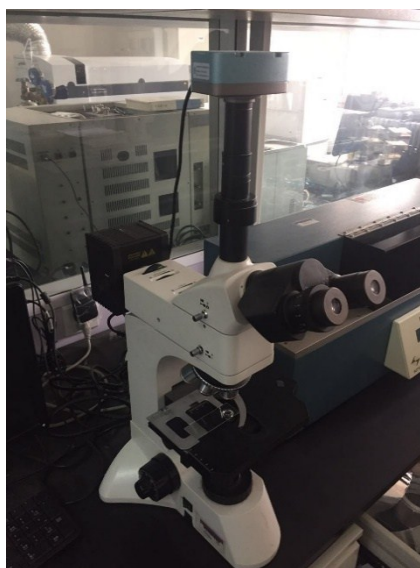
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1. Reagents and Chemicals

Bix was purchased from TCI (Tokyo, Japan), and all other reagents were purchased from Aladdin Chemicals (Shanghai, China). All water used in this work was 18 M Ω -cm deionized water (DIW) produced with a water purification Milli-Q system. All solutions were stored at 4 °C in the dark until use.

2. Instrumentation

The optical micrographs in Figure 1a, 2, S1, S5, S6 and videos was taken by using a laboratory optical microscope equipped with a 0.5X CCD camera. The optical micrograph in Figure 4, 5, S4, S8 was taken by using a Nikon Eclipse Ti-U equipped with a 2.11-megapixel CCD camera and an TU Plan Fluor EPI 50X/0.8 objective lens. The SEM images were obtained from a Hitachi SU-8010 scanning electron microscope (Tokyo, Japan). The mass spectrometry data were collected from a Thermo LTQ ion trap mass spectrometer (Thermo Scientific, San Jose, CA, USA), operated in the full mass mode.



Laboratory optical microscope and Nikon Eclipse Ti-U microscope

3. Synthesis experiment

Co(bpee)Mal: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.145 g) was dissolved in 4 mL of DMF in a 20 mL glass vial; to this, an aqueous solution (2 mL) of l/d-malic acid (0.5 mmol, 0.067 g) was added with stirring. Then ethanolic solution (2 mL) of bpee (0.25 mmol, 0.041 g) was added, and the mixture was stirred for 30 min to mix well. Then the vial was sealed and heated to 120 °C for 12 h. After being cooled to room temperature, red-colored crystals were isolated, washed with DMF, and dried in air.

Zn-Bix: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (150 mg, 0.5 mmol) in water (5 mL) to a solution of bix (121 mg, 0.5 mmol) in ethanol (25 mL), with sonication or vigorous stirring at room temperature. For a short time stirring, the MOFs were purified by centrifugation and washed three times with ethanol.

4. Illumination angle optimize

In the experiment, we also observed that the appropriate adjustment of the illumination angle could improve the imaging resolution, especially when the illumination angle between 20 and 40°, with the illumination direction perpendicular to the blu-ray disc track direction. The best resolution of imaging and highest magnification was shown in Fig S8. This result could be explained by the *Mie* scattering equation, and was consistent with the previously reported. The resolution of the super-resolution imaging was affected by the near-surface and near-field interaction of the microspheres, which transformed the high-space frequency evanescent waves of the bounded surface into propagating waves. This conversion process was highly sensitive to the distance between the microspheres and the surface of the target. The relevant theoretical and simulated calculations were reported previously by Wang' group^[1-3].

5. Figures and captions

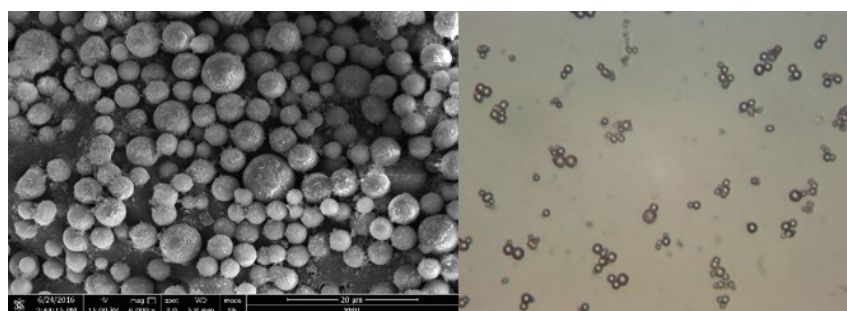


Figure S1. Co(bpee)Mal microsphere: left, SEM image; right, microscope image

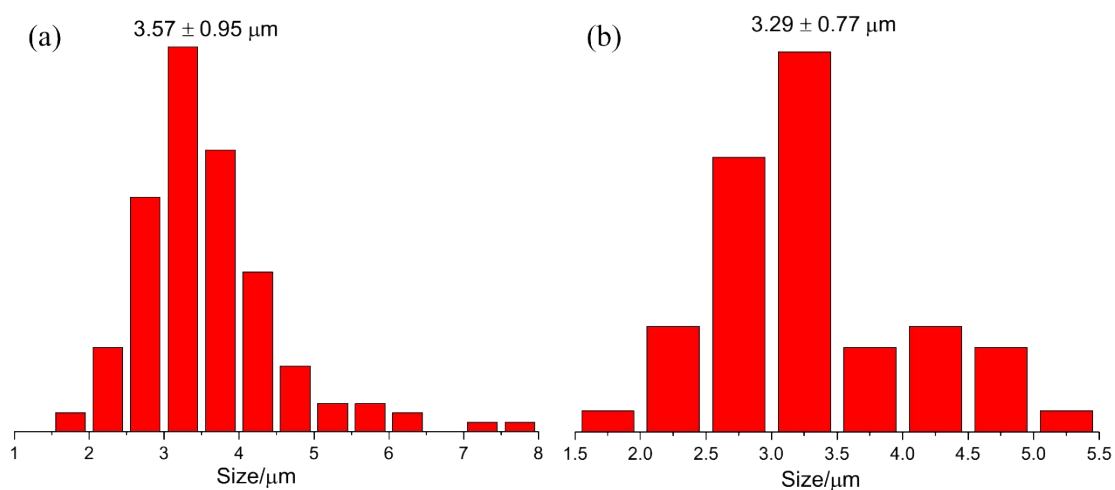


Figure S2. The size distribution of MOF spheres: a) **Co(bpee)Mal** and b) **Zn-Bix**

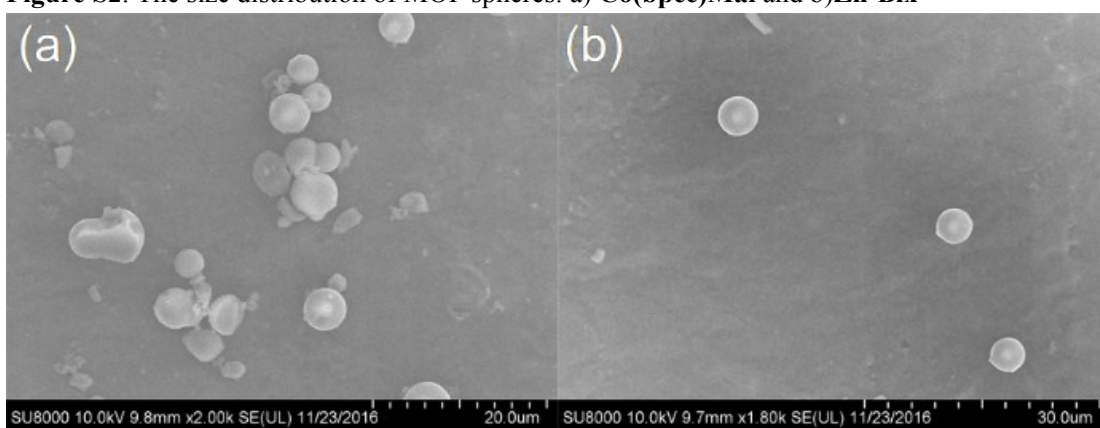


Figure S3. SEM images of a) **Co(bpee-HIM)Mal** and b) **Co(bpee-Bix)Mal**

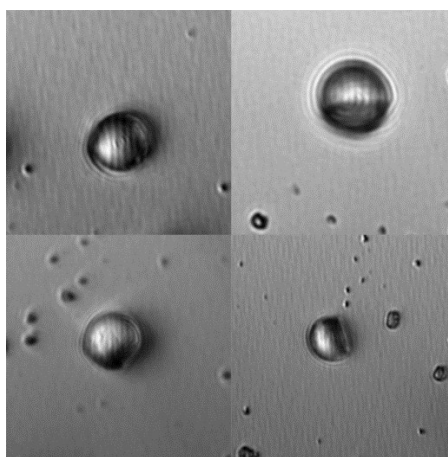


Figure S4. The super-resolution imaging of blu-ray disc with microsphere and ball crown **Co(bpee-HIM)Mal** crystal

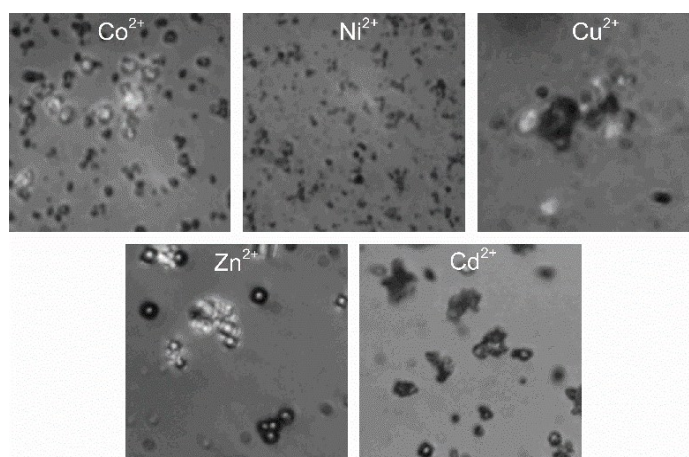


Figure S5. Microscopy images of five metal ions coordinated with Bix to form MOFs

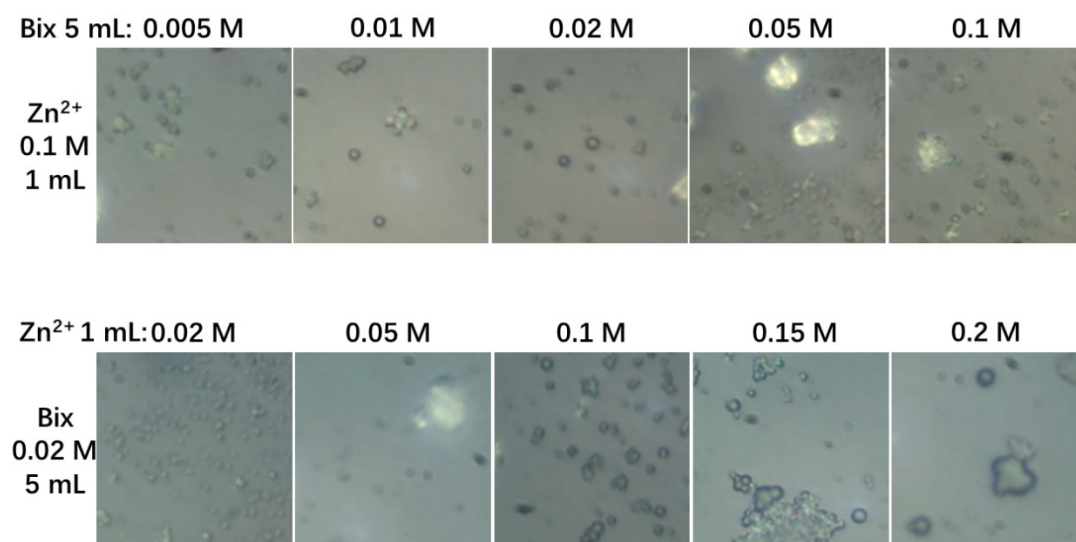


Figure S6. The optimized concentration of Zn^{2+} ions and Bix

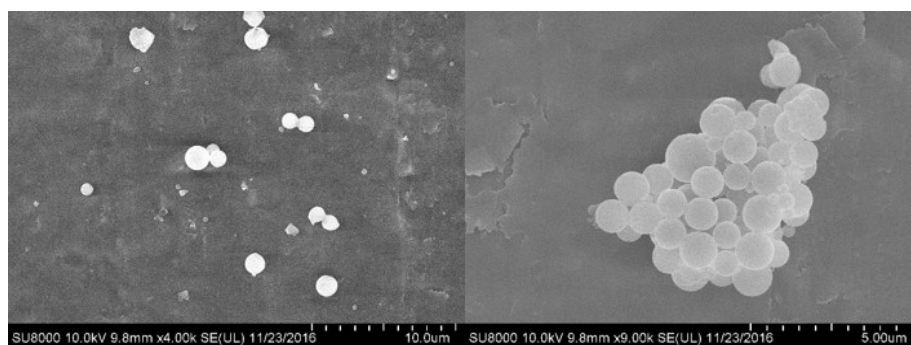


Figure S7. SEM images of **Zn-Bix** microspheres

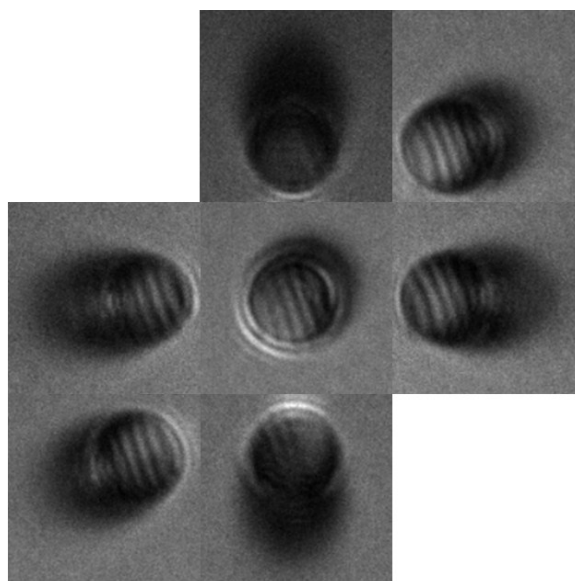


Figure S8. The effect of the illumination angle on the imaging contrast

1. H. Zhu, B. Yan, S. Zhou, Z. Wang and L. Wu, *J. Mater. Chem. C.*, 2015, **3**, 10907-10915.
2. Z. Wang, W. Guo, L. Li, B. Luk'yanchuk, A. Khan, Z. Liu, Z. Chen and M. Hong, *Nat. Commun.*, 2011, **2**, 218.
3. W. Fan, B. Yan, Z. Wang and L. Wu, *Sci. Adv.*, 2016, **2**, e1600901.