

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Trace Water Mediated Growth of Oriented Single-Crystalline

Mesoporous Metal–Organic Frameworks on Gold Nanorods

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Experimental Section

Chemicals: A Hexadecyltrimethylammonium bromide (CTAB, $\geq 99\%$) was bought from Acros. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99%) was bought from Macklin. N,N-dimethylformamide (DMF) was bought from J&K. 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin ($\text{H}_2\text{T CPP}$) was bought from TCI. Benzoic acid (BA, 99.5%), silver nitrate (AgNO_3 , 99.8%), and sodium borohydride (NaBH_4 , 98%) were purchased from Aladdin. Polyvinylpyrrolidone (PVP, M.W.=40000), L-ascorbic acid (AA, $\geq 99\%$), and zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%) were purchased from Sigma-Aldrich. Deionized water (Millipore Milli-Q grade) with resistivity of 18.2 M Ω was used. All chemicals were used as received without further purification.

Synthesis of PVP-modified AuNRs: The gold nanorods were prepared via the well-established seed-mediated growth method with some minor modifications.^{1,2} In a typical process, the seed solution was first prepared. HAuCl_4 solution (0.125 mL, 10 mM) was mixed with CTAB solution (5 mL, 0.1 M) under stirring. Then fresh prepared NaBH_4 solution (0.3 mL, 0.01 M) was added. The solution was kept stirring for another 2 min, and aged at room temperature at least 1 hour before further use. For the growth solution, AgNO_3 solution (0.27 mL, 0.06 mM) was mixed with CTAB solution (40 mL, 0.1M) at room temperature, followed by the addition of HAuCl_4 solution (2 mL, 10 mM) and fresh prepared ascorbic acid solution (0.45 mL, 0.064 M) into the mixture. The seed solution (0.45 mL) was then added into the growth solution. The reaction was left undisturbed for 12 h. The AuNRs were collected by centrifugation, washed with deionized water three times and re-dispersed in deionized water for further use. AuNRs were then coated with PVP according to the previously reported methods with minor modifications.³ As-prepared AuNRs (2 mL, 9.0 nM) were mixed with an aqueous solution of PVP (M.W.=40000, 2 mL, 1 wt%) and shaken overnight at room temperature. The PVP-AuNRs were washed by centrifugation.

Synthesis of AuNR@MOFs: Typically, a 20 μL volume of a concentrated aqueous solution of PVP-AuNRs (0.45 μM) was added to 2 mL of a DMF solution containing $\text{H}_2\text{T CPP}$ (2.0 mg, 2.5 μmol), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (6.0 mg, 18.6 μmol) and benzoic acid (56 mg, 0.46 mmol) in the 5-mL round-bottom flask (with final 1% v/v amounts of water). After brief sonication, the mixture

was heated at 90 °C for 5 h. Finally, the products were collected by centrifugation, washed with DMF three times and re-dispersed in 1 mL DMF for further use. Pure MOF NPs were synthesized under the same reaction condition but without adding of PVP-AuNRs.

Cell culture and bioimaging: Murine 4T1 breast cancer cells were seeded in chamber slides at a density of 4×10^5 cells/well in RPMI 1640 supplemented with 10% FBS and 1% penicillin-streptomycin at 37 °C in CO₂ incubator, and grown overnight to allow for cell adherence. The medium was replaced with fresh Opti-MEM containing AuNR@MOFs (10 µg mL⁻¹). After 2 h incubation in the dark, cells were washed to remove excess materials for imaging with confocal microscope.

Instrumentation: Transmission electron microscopy (TEM) images were taken on the HT7700 transmission electron microscope (Hitachi Co. Ltd., Japan) with an accelerating voltage of 120 kV. Scanning electron microscopy (SEM) images were taken on the SU8220 scan electron microscope (Hitachi Co. Ltd., Japan) with an accelerating voltage of 1kV. UV/Vis spectra were recorded on the Hitachi 5300 spectrophotometer (Hitachi Co. Ltd., Japan). Fluorescent spectra were recorded on the Hitachi F-4600 spectrometer (Hitachi Co. Ltd., Japan). Powder X-ray diffraction patterns were measured on the D/MAX-TTRIII(CBO) X-ray diffractometer (Rigaku Co. Ltd., Japan) at 40 kV and 200 mA. Small angle X-ray diffraction patterns were tested on Xeuss SAXS/WAXS system (XENOCS Co. Ltd., France). Infrared-radiation (IR) thermal images were monitored through the E40 infrared-radiation thermal camera (FILR Systems, Inc. America). N₂ adsorption-desorption isotherms at 77K were measured using a Micromeritics ASAP 2020 system (Micromeritics Instrument Corp., America). The confocal laser scanning microscopy (CLSM) images were obtained using an Olympus FV1000 (Olympus Co. Ltd., Japan) equipped with a two-photon laser (Spectra-Physics MaiTai Deepsee, (Newport Co. Ltd., America)).

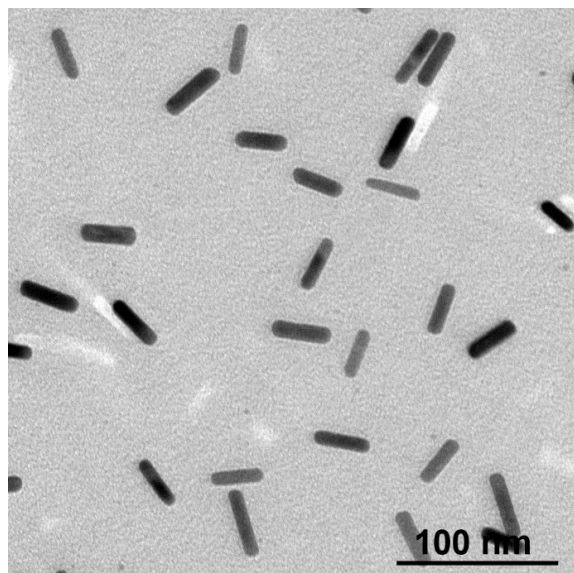


Fig. S1 TEM images of the as-synthesized AuNRs.

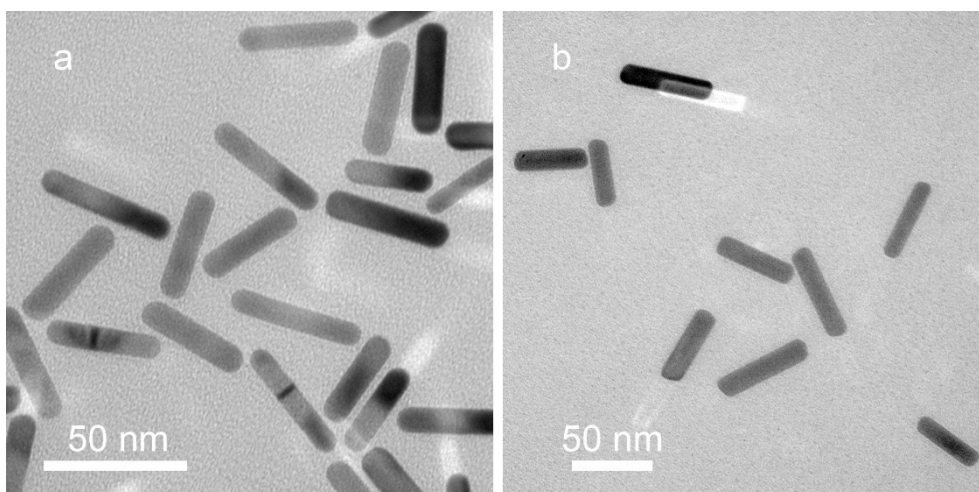


Fig. S2 TEM images of the PVP-AuNRs dispersed in (a) water and (b) DMF.

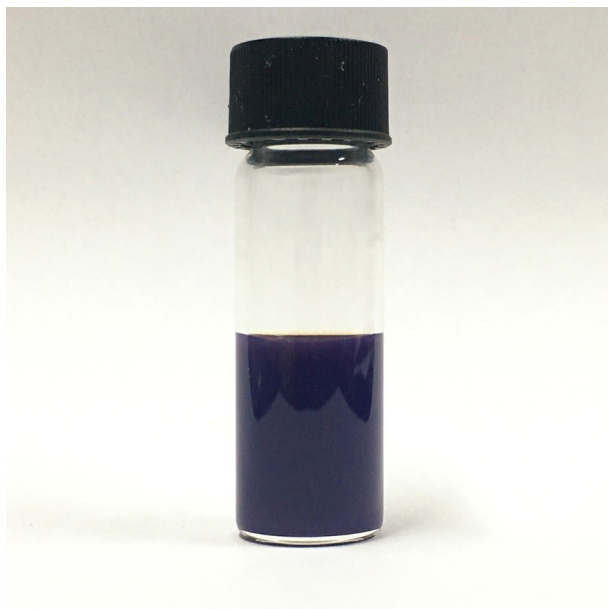


Fig. S3 Photograph of AuNR@MOFs nanoparticles dispersed in DMF solution.

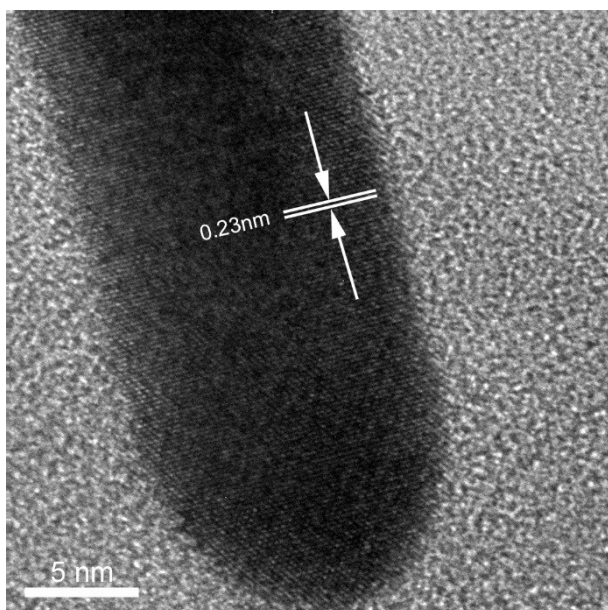


Fig. S4 HRTEM image of AuNR@MOFs. The interplanar spacing of 0.23 nm in the HRTEM image was corresponding to the typical (002) plane of the cubic Au.

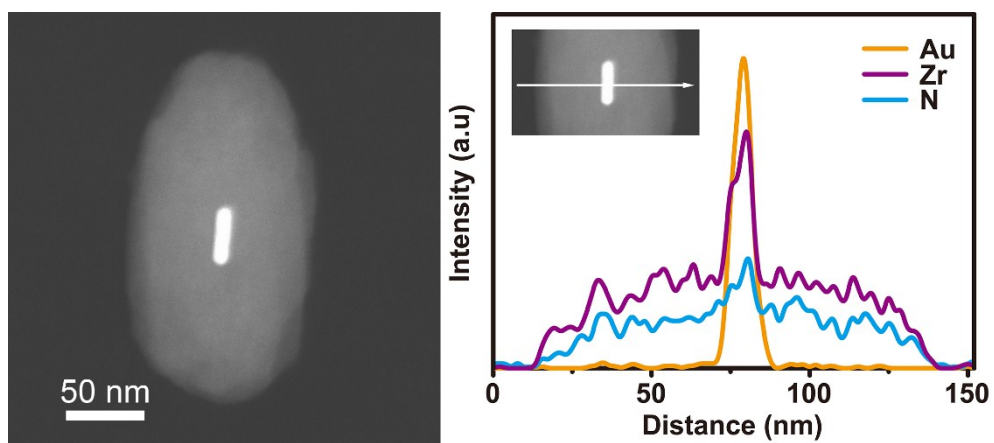


Fig. S5 (left) HAADF-STEM image and (right) EDS line scan profile of a single AuNR@MOF NP along the arrowed line shown in HAADF-STEM image (inset).

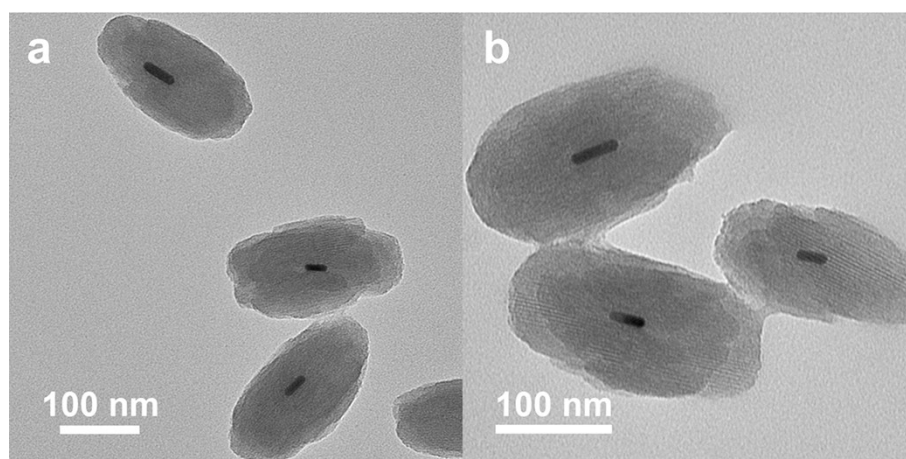


Fig. S6 TEM images of AuNR@MOFs incubated in water (pH=7.4) for (a) 0h and (b) 24h, respectively.

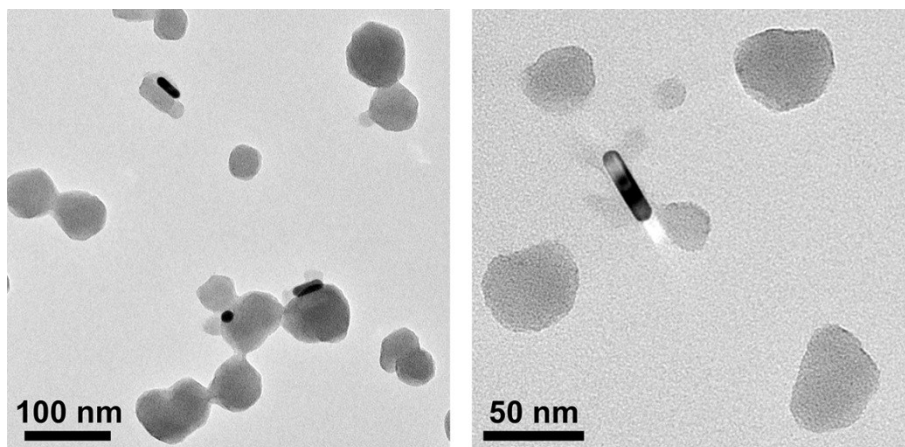


Fig. S7 TEM images of products synthesized under the same reaction conditions but without introducing any water.

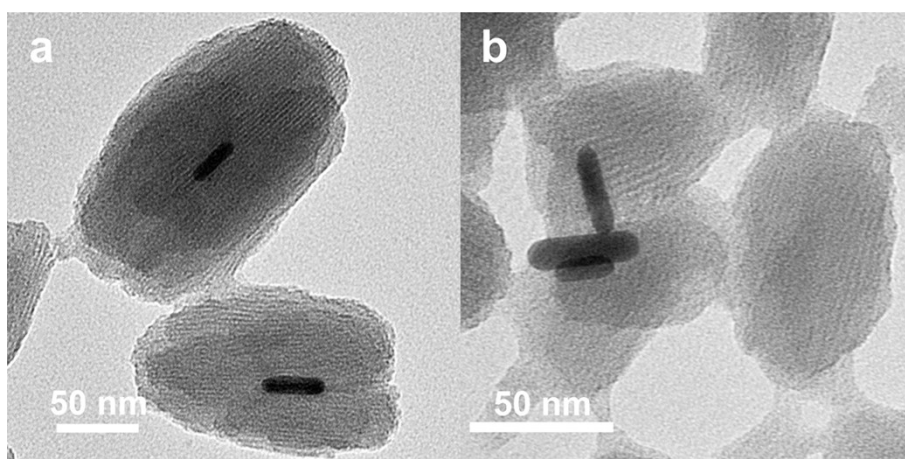


Fig. S8 TEM images of AuNR@MOFs synthesized with introducing (a) 1.5% and (b) 2% v/v water.

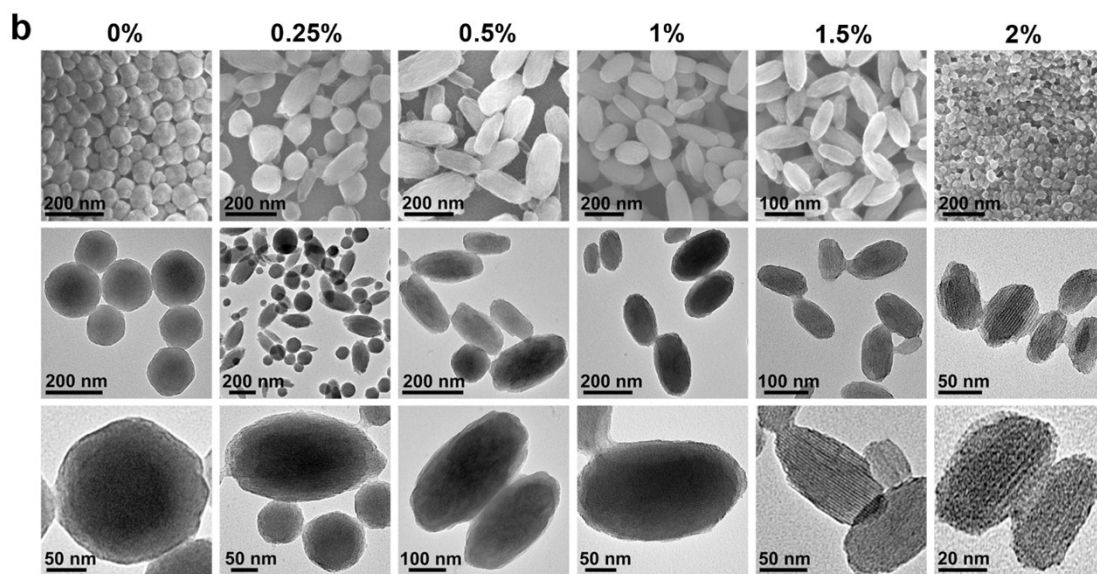
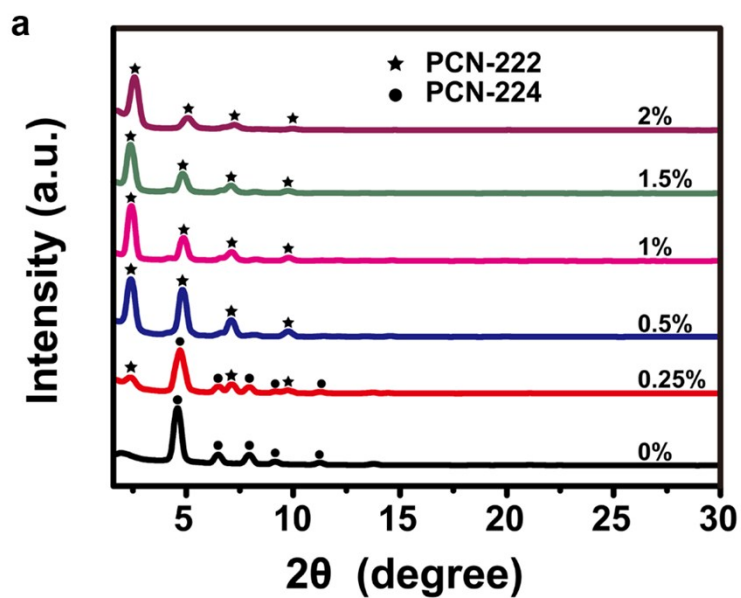


Fig. S9 a) Powder XRD patterns MOFs synthesized in DMF with different amounts of water additive. b) SEM and TEM images of pure MOFs synthesized in DMF with different amounts of water additive.

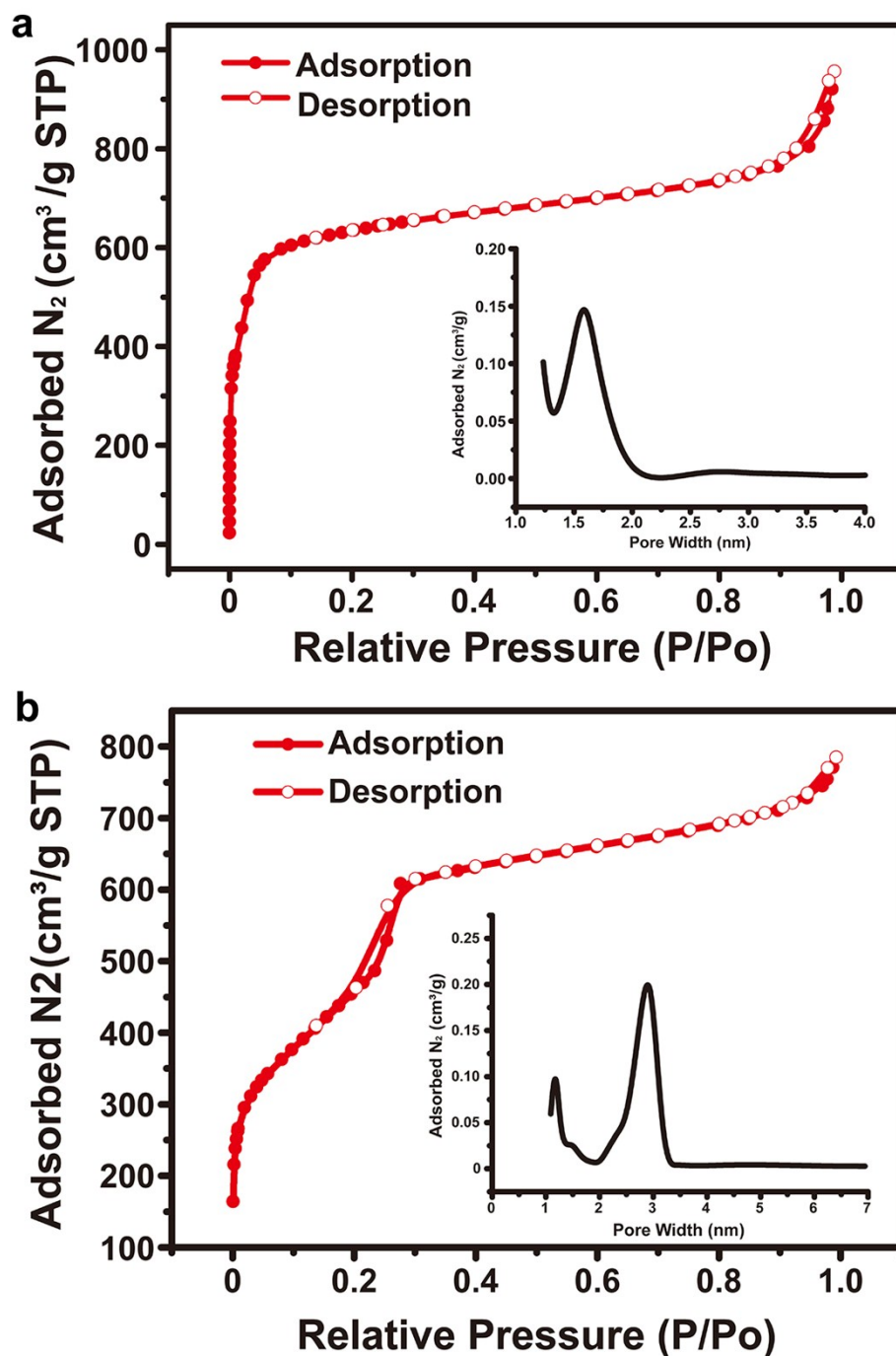


Fig. S10 N_2 adsorption isotherms for the MOF PCN-224 nanoparticles (a) and MOF PCN-222 nanorods synthesized with 1% v/v water (b). Inset shows their DFT pore size distribution.

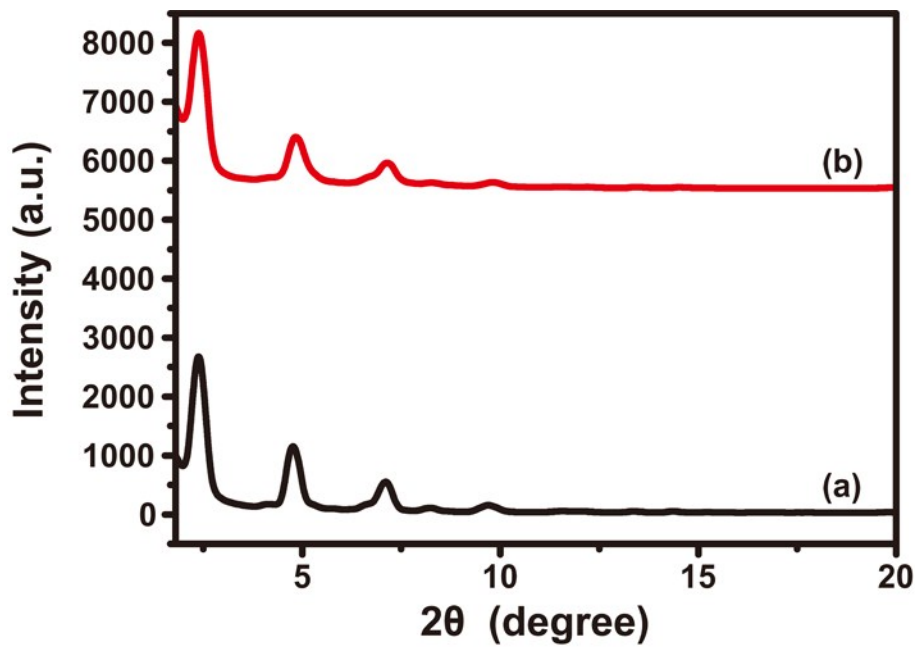


Fig. S11 Powder XRD patterns of AuNR@MOFs synthesized at (a) 12 min and (b) 3h.

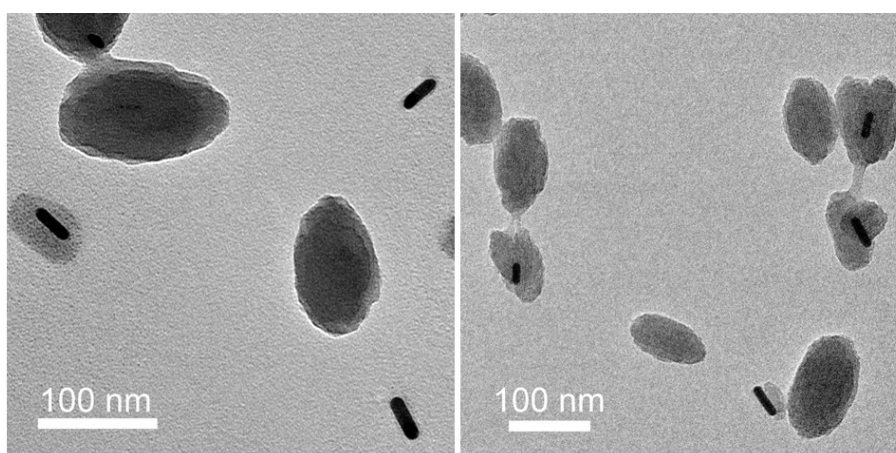


Fig. S12 TEM images of products when free PVP were added into the reaction solution in a control experiment.

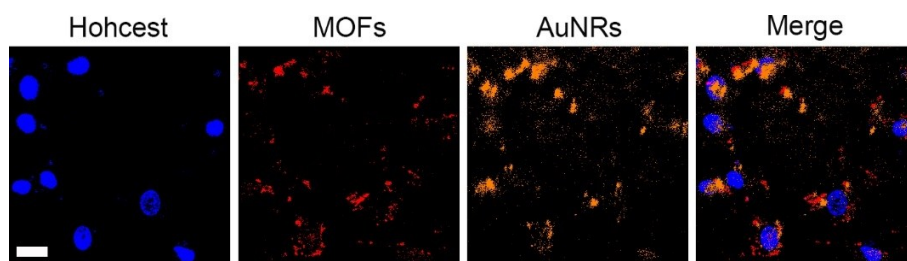


Fig. S13 Dual-modality imaging of 4T1 cells treated with AuNR@MOFs. For MOFs imaging channel, $\lambda_{\text{ex}} = 405 \text{ nm}$, and $\lambda_{\text{em}} = 600 - 700 \text{ nm}$. Scale bars = $50 \mu\text{M}$. As shown in Fig. S13, the cells treated with the AuNR@MOFs showed both strong fluorescence and light scattering signals. The well overlap of the two imaging signals confirms the cellular uptake of the heterostructures.

Notes and References

- 1 K. Lu, C. He and W. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 16712-16715.
- 2 D. K. Roper, W. Ahn and M. Hoepfner, *J. Phys. Chem. C.*, 2007, **111**, 3636-3641.
- 3 E. Carbó-Argibay, B. Rodríguez-González, J. Pacifico, I. Pastoriza-Santos, J. Pérez-Juste and L. M. Liz-Marzán, *Angew. Chem. Int. Ed.*, 2007, **46**, 8983-8987.