

## Video Article

# A Facile Synthesis of Upconversion Metal-Organic Framework Heterodimers

Bei Liu<sup>1</sup>, Yifan Li<sup>1</sup>, Yulei Shao<sup>1</sup>, Lele Li<sup>1</sup>

<sup>1</sup>CAS Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety and CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology (NCNST)

Correspondence to: Lele Li at [lilele@nanocr.cn](mailto:lilele@nanocr.cn)

URL: <https://www.jove.com/video/57571>

DOI: [doi:10.3791/57571](https://doi.org/10.3791/57571)

Keywords: Nanostructures, heterodimers, synthesis, metal-organic frameworks, upconversion nanoparticles, anisotropic growth

Date Published: 10/26/2018

Citation: Liu, B., Li, Y., Shao, Y., Li, L. A Facile Synthesis of Upconversion Metal-Organic Framework Heterodimers. *J. Vis. Exp.* (), e57571, doi:10.3791/57571 (2018).

## Abstract

The synthesis of nanostructures with asymmetric configurations in terms of both geometries and compositions has attracted extensive interest in recent years. In this work, we describe a protocol for the synthesis of high quality heterodimers made of upconversion nanoparticles (UCNPs) and porphyrinic nanoscale metal-organic frameworks (nMOF). Tuning the surface chemistry of UCNPs plays a key role for the formation of heterodimers in a controllable fashion. The hydrophobic UCNPs are firstly coated with polyvinylpyrrolidone to convert them into hydrophilic ones and to facilitate subsequent nucleation and growth of nMOFs on their surface. Then, UCNP-MOF heterodimers (UCMOFs) are synthesized through the anisotropic growth of nMOFs on UCNPs in the presence of optimal precursors in dimethyl formamide solution. To demonstrate the versatility of the approach, core-multishell structured UCNPs are also prepared to serve as seeds for the growth of UCNP-MOF heterodimers. Such UCNP-MOF heterodimers hold a great promise for various applications, such as NIR-induced photodynamic therapy, drug delivery, photocatalysis, and solar cell.

## Video Link

The video component of this article can be found at <https://www.jove.com/video/57571/>

## Introduction

Constructing multicomponent hybrid nanoparticles (NPs) has attracted extensive interest due to their architecturally defined collective properties<sup>1,2,3</sup>. NP dimers are emerging as an important family of hybrid nanostructures due to their cooperative properties that cannot be observed either for single component or their physical mixtures<sup>4,5</sup>. Surface-directed nucleation is a powerful approach in the preparation of such heterostructures, and the as-obtained NP dimers can exhibit unexpected optic, electronic and magnetic communication between adjacent components. In particular, heterodimers, in which two NPs of distinct nature are connected through a junction area, have facilitated a variety of applications such as solar energy conversion, catalysis, cancer diagnosis and therapy<sup>6,7</sup>. However, as most heterostructures are limited to pure inorganic components, the fabrication of organic-inorganic NP dimers with controlled structures still remains a great challenge.

Among the various types of building blocks, lanthanide-doped upconversion nanoparticles (UCNPs) are becoming an exciting candidate due to their unique properties, such as upconversion luminescence (converting NIR light into tunable shorter-wavelength emissions), multicolored emissions, and high photostability<sup>8,9,10,11,12,13,14,15</sup>. In the past few years, synthetic approaches for the preparation of UCNP-based nanocomposite materials have attracted significant research interest in this field, as evidenced from the rapid upsurge of reports on UCNP-based nanohybrids. For example, mesoporous silica, zinc oxide and titanium dioxide have been successfully integrated into UCNPs to form discrete core-shell nanocomposites<sup>16,17,18</sup>, which could act as multifunctional "theranostic" platforms for biological labeling, disease diagnosis and therapy. However, the synthesis of asymmetric UCNP-based heterostructures with synergistically enhanced properties has not been achieved.

Metal-organic frameworks (MOFs), a class of crystalline solid materials possessing uniform and tunable pore structures, are attracting great attention due to their intriguing features, including chemical and structural versatility, porous structure, high surface area, and multiple coordination sites<sup>19,20,21</sup>. Owing to these excellent structure and properties, MOFs show promise for a variety of applications, including gas storage, chemical separation, catalysis, and drug delivery<sup>21,22,23,24</sup>. Most recently, researchers have made remarkable achievements in growing MOFs on various kinds of NPs, such as gold NPs, quantum dots, and UCNPs, for the construction of multifunctional NPs<sup>21,25,26,27</sup>. However, in these reports, nanoparticles were often encapsulated in the pores of MOFs or coated by MOFs to form isotropic heterostructures (e.g., core@shell geometry). We recently reported an asymmetric heterodimer made of UCNPs and porphyrinic nanoscale MOFs (nMOFs). The UCMOFs-mediated combination of photodynamic therapy and chemotherapy has been demonstrated for synergetic treatment of tumors<sup>28</sup>. To the best of our knowledge, this is the first example of UCNP- or MOF-based heterodimers. Herein, we provide a detailed protocol for the synthesis of UCMOF heterodimers to avoid common pitfalls associated with the synthesis.

In a typical synthesis of UCMOFs (**Figure 1**), oleic acid (OA)-capped UCNPs are firstly coated with polyvinylpyrrolidone (PVP) to convert them into hydrophilic ones. UCMOFs are synthesized by adding an optimal amount of PVP-coated UCNPs into a dimethyl formamide (DMF) solution of 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , and benzoic acid. Then, the reaction mixture is stirred at 90 °C for 5 h.

Morphology characterization of UCMOFs is carried out via transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM).

## Protocol

**CAUTION:** Please consult all relevant material safety data sheets (MSDS) before use. Several of the chemicals used in these syntheses can cause skin irritation or serious eye irritation. Nanomaterials may have additional hazards compared to their bulk counterparts. Please use all appropriate safety practices when performing a nanocrystal synthesis at high temperature, including the use of engineering controls (fume hood, glovebox) and personal protective equipment (safety glasses, gloves, lab coat, full length pants, closed-toe shoes).

## 1. Preparation of Rare-earth Trifluoroacetates<sup>29</sup>

### 1. Preparation of the yttrium trifluoroacetates ( $\text{Y}(\text{CF}_3\text{COO})_3$ )

1. Add 10 mmol of the rare earth oxide  $\text{Y}_2\text{O}_3$  (3.94 g) to 50 mL deionized water into a 100 mL round bottom flask equipped with a stir bar and a reflux condenser.
2. Cautiously add, dropwise, 80 mmol (6.2 mL) of trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ) into the reaction system while stirring.
3. If needed, scale up reactants (including rare earth oxide, deionized water and trifluoroacetic acid) between 1 and 10 times. For example, for 20 mmol of the rare earth oxide  $\text{Y}_2\text{O}_3$  (7.88 g), add to 100 mL of deionized water in a 250 mL round bottom flask equipped with a stir bar and a reflux condenser. Then cautiously add, dropwise, 160 mmol (12.4 mL) of trifluoroacetic acid into the reaction system while stirring.
4. Heat the solution to 110 °C in an oil bath until the rare earth oxide powder is dissolved completely.
5. Transfer the as-obtained transparent solution into a 100 mL breaker. Then, put the breaker into a drying oven (or heated in an oil bath) at 80 °C for 10 h in order to evaporate the solvent absolutely.
6. Collect the white powder into a bottle or centrifuge tube and store at room temperature for further use.

### 2. Preparation of the gadolinium trifluoroacetates ( $\text{Gd}(\text{CF}_3\text{COO})_3$ )

1. Add 10 mmol of the rare earth oxide  $\text{Gd}_2\text{O}_3$  (3.62 g) to 50 mL deionized water in a 100 mL round bottom flask equipped with a stir bar and a reflux condenser.
2. Repeat steps 1.1.2-1.1.6.

### 3. Preparation of the erbium trifluoroacetates ( $\text{Er}(\text{CF}_3\text{COO})_3$ )

1. Add 10 mmol of the rare earth oxide  $\text{Er}_2\text{O}_3$  (3.82 g) to 50 mL deionized water in a 100 mL round bottom flask equipped with a stir bar and a reflux condenser.
2. Repeat steps 1.1.2-1.1.6.

### 4. Preparation of the thulium trifluoroacetates ( $\text{Tm}(\text{CF}_3\text{COO})_3$ )

1. Add 10 mmol of the rare earth oxide  $\text{Tm}_2\text{O}_3$  (3.86 g) to 50 mL deionized water in a 100 mL round bottom flask equipped with a stir bar and a reflux condenser.
2. Repeat steps 1.1.2-1.1.6.

### 5. Preparation of the ytterbium trifluoroacetates ( $\text{Yb}(\text{CF}_3\text{COO})_3$ )

1. Add 10 mmol of the rare earth oxide  $\text{Yb}_2\text{O}_3$  (3.94 g) to 50 mL deionized water in a 100 mL round bottom flask equipped with a stir bar and a reflux condenser.
2. Repeat steps 1.1.2-1.1.6.

### 6. Preparation of the neodymium trifluoroacetates ( $\text{Nd}(\text{CF}_3\text{COO})_3$ )

1. Add 10 mmol of the rare earth oxide  $\text{Nd}_2\text{O}_3$  (3.36 g) to 50 mL deionized water in a 100 mL round bottom flask equipped with a stir bar and a reflux condenser.
2. Repeat steps 1.1.2-1.1.6.

## 2. Synthesis of $\text{NaGdF}_4\text{:Yb,Er}$

### 1. Synthesis of $\alpha$ -phase $\text{NaGdF}_4\text{:Yb,Er}$

1. Inspect all the glassware carefully to ensure there is no damage and cracking before the high temperature experiments.
2. Combine  $\text{CF}_3\text{COONa}$  (1 mmol, 0.136 g),  $\text{Gd}(\text{CF}_3\text{COO})_3$  (0.78 mmol, 0.387 g),  $\text{Yb}(\text{CF}_3\text{COO})_3$  (0.2 mmol, 0.1024 g) and  $\text{Er}(\text{CF}_3\text{COO})_3$  (0.02 mmol, 0.0105 g) with a mixed solution of OA (10 mmol, 2.82 g), oleylamine (OM, 10 mmol, 2.67 g) and octadecylene (ODE, 20 mmol, 5.04 g) in a three-neck round bottom flask equipped with a stir bar, a thermocouple, a reflux condenser, and a rubber septum. NOTE: Fit the thermocouple to the three-neck round bottom flask by puncturing a rubber septum and let its tip touch the solution.
3. Degas the mixed solution at 30 °C under vacuum while stirring. When the bubbles have almost disappeared after 10 min, raise the temperature to 110 °C. Keep stirring at 110 °C under vacuum for 15 min or longer.
4. Fill the flask with nitrogen. Increase the temperature to 310 °C and keep the temperature at 310 °C for 50 min. Then stop the hot plate and remove the flask to allow the reaction mixture to cool down slowly in room temperature while stirring. Be careful of the high-temperature hot plate to avoid severe burns upon skin contact.
5. Transfer the mixture in the flask to two 50 mL centrifuge tubes. Rinse the flask with 60 mL of ethanol and divide the solution equally into each centrifuge tube. Centrifuge the product at  $5000 \times g$  for 5 min at room temperature and discard the supernatant.
6. Add 10 mL of cyclohexane to each centrifuge tube and re-disperse the product with sonication for 5 min. Add 30 mL ethanol into each tube. Centrifuge the product at  $5000 \times g$  for 5 min at room temperature and discard the supernatant.
7. Re-disperse the white precipitate in 5 mL of cyclohexane.

8. Stock the transparent cyclohexane solution in a 20 mL sealed glass bottle for future use.  
NOTE: The cyclohexane solution of UCNP can be stocked for several months.
9. Collect transmission electron microscopy (TEM) images to characterize the  $\alpha$ -phase  $\text{NaGdF}_4\text{:Yb,Er}$ .

## 2. Synthesis of $\beta$ -phase $\text{NaGdF}_4\text{:Yb,Er}$

1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.
2. Carefully combine  $\text{CF}_3\text{COONa}$  (0.5 mmol, 0.068 g),  $\text{Gd}(\text{CF}_3\text{COO})_3$  (0.39 mmol, 0.194 g),  $\text{Yb}(\text{CF}_3\text{COO})_3$  (0.1 mmol, 0.051 g) and  $\text{Er}(\text{CF}_3\text{COO})_3$  (0.01 mmol, 0.005 g) with a mixed solution of OA (20 mmol, 5.64 g) and octadecylene (ODE, 20 mmol, 5.04 g) into the 3-neck round bottom flask.
3. Add 5 mL of the as-prepared  $\alpha$ -phase  $\text{NaGdF}_4\text{:Yb,Er}$  colloidal solution into the mixture.
4. Equip the 3-neck round bottom flask with a thermocouple, a reflux condenser and a rubber septum.
5. Repeat steps 2.1.3-2.1.8.
6. Collect TEM images to characterize the  $\beta$ -phase  $\text{NaGdF}_4\text{:Yb,Er}$ .

## 3. Synthesis of $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$

1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.
2. Carefully combine  $\text{CF}_3\text{COONa}$  (1 mmol, 0.136 g) and  $\text{Y}(\text{CF}_3\text{COO})_3$  (1 mmol, 0.428 g) with a mixed solution of OA (20 mmol, 5.64 g) and ODE (20 mmol, 5.04 g) into the 3-neck round bottom flask.
3. Add 5 mL of the as-prepared  $\beta$ -phase  $\text{NaGdF}_4\text{:Yb,Er}$  colloidal solution into the mixture.
4. Equip the 3-neck round bottom flask with a thermocouple, a reflux condenser and a rubber septum.
5. Repeat steps 2.1.3-2.1.8.
6. Collect TEM and HAADF-STEM images<sup>28</sup> to determine the core-shell structure of the  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$ .

## 4. Synthesis of $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{@NaYF}_4\text{:Yb,Tm}$

1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.
2. Carefully combine  $\text{CF}_3\text{COONa}$  (1 mmol, 0.136 g),  $\text{Y}(\text{CF}_3\text{COO})_3$  (0.08 mmol, 0.034 g),  $\text{Yb}(\text{CF}_3\text{COO})_3$  (0.9 mmol, 0.461 g) and  $\text{Tm}(\text{CF}_3\text{COO})_3$  (0.02 mmol, 0.01 g) with a mixed solution of OA (20 mmol, 5.64 g) and ODE (20 mmol, 5.04 g) in the 3-neck round bottom flask.
3. Add 5 mL of the as-prepared  $\text{NaGdF}_4\text{:Yb,Er@NaGdF}_4$  colloidal solution to the mixture.
4. Equip the 3-neck round bottom flask with a thermocouple, a reflux condenser and a rubber septum.
5. Repeat steps 2.1.3-2.1.8.
6. Collect TEM and HAADF-STEM images to determine the core-shell structure of the  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{@NaYF}_4\text{:Yb,Tm}$ .

## 5. Synthesis of UCMOFs

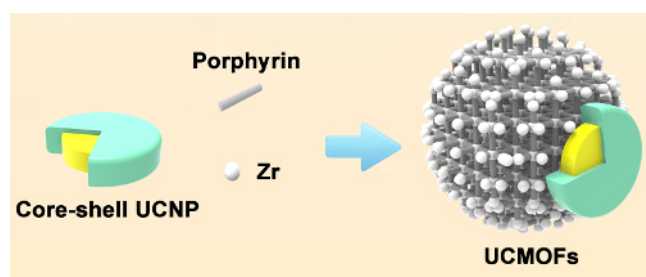
1. **Synthesis of nitrosonium tetrafluoroborate ( $\text{NOBF}_4$ ) modified UCNP<sup>30</sup>**
  1. Store the  $\text{NOBF}_4$  at 4 °C. In order to increase the weighing accuracy, take the  $\text{NOBF}_4$  out from freezer at least 10 min before weighing.
  2. Dissolve 20-30 mg of  $\text{NOBF}_4$  into 1 mL of DMF.
  3. Add 1 mL cyclohexane solution of UCNP to the stirring DMF solution of  $\text{NOBF}_4$ .
  4. Stir the resulting mixture until UCNP are transferred from the upper hexane layer to the bottom acetonitrile layer, typically within 5 hours. Use a 980 nm laser to characterize the successful phase transfer of UCNP from cyclohexane to DMF. Ideally, upon 980 nm irradiation, the cyclohexane phase has no light, while DMF phase has a bright green luminescence.
  5. Isolate the  $\text{NOBF}_4$  modified UCNP by centrifugation at  $15,800 \times g$  for 10 min. After removing the supernatant carefully, re-disperse the precipitates in 1 mL of DMF.
2. **Synthesis of PVP-coated UCNP**
  1. Dissolve 40 mg of PVP ( $M_w = 8,000$ ) into 1 mL DMF.
  2. Add 1 mL DMF solution of the  $\text{NOBF}_4$  modified UCNP to the PVP solution dropwise.
  3. Keep stirring overnight.
  4. Add 2 mL of acetone to flocculate the UCNP's dispersion.
  5. Transfer the mixture solution to centrifuge tubes and centrifuge at  $15800 \times g$  for 10 min.
  6. Remove the supernatant carefully, and re-disperse the precipitates in 2 mL of DMF/acetone mixture solution (1:1 by volume).
  7. Centrifuge at  $15,800 \times g$  for 10 min for washing.
  8. Re-disperse the precipitate in 2 mL of DMF.
3. **Synthesis of UCMOFs**
  1. Prepare a 90 °C oil bath in advance.
  2. Prepare a clean 5 mL round bottom flask with a stir bar.
  3. Carefully combine 2 mg TCPP (0.0260 mmol), 6 mg  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (0.186 mmol) and 56 mg benzoic acid (0.460 mmol) with 1 mL DMF solvents into the 5 mL round bottom flask.
  4. Add 1 mL DMF solution of PVP modified UCNP into the flask.
  5. Stir the reaction mixture at 90 °C for 5 h. During the stirring process, the color of the solution will change from red to dark purple.
  6. Transfer the mixture solution to centrifuge tubes and centrifuge at  $13,500 \times g$  for 30 min immediately.
  7. Remove the supernatant and re-disperse the precipitates in 1.5 mL of DMF solution.
  8. Centrifuge at  $13,500 \times g$  for 30 min for washing.
  9. Repeat the washing process 2 - 3 times.

10. Re-disperse the final precipitates in 2 mL of DMF.
11. Collect TEM images for characterization of UCMOFs.

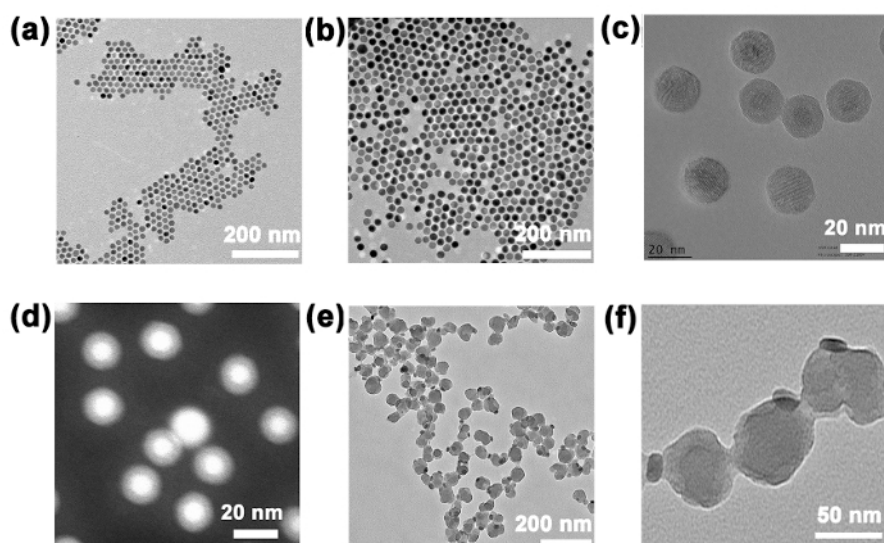
## Representative Results

Transmission electron microscopy (TEM) images of monodispersed oleate-capped  $\text{NaGdF}_4\text{:Yb,Er}$  UCNPs (**Figure 1a**) and core-shell structured  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$  UCNPs (**Figure 1b,c**) were collected, which revealed that the as-prepared UCNPs were monodisperse nanoplates with an average particle size of #12 nm for  $\text{NaGdF}_4\text{:Yb,Er}$  core and #19 nm for  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$  core-shell UCNPs. The core-shell structure was further confirmed by HAADF-STEM (**Figure 1d**). **Figure 1e,f** clearly demonstrates the asymmetric structure of the UCMOFs with MOF domains of lower contrast on UCNPs.

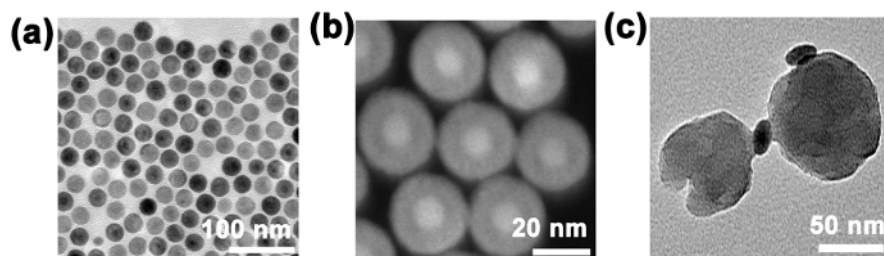
$\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{:Yb,Tm}$  core-multishell structured UCNPs (#27 nm) were synthesized for the growth of UCMOFs (**Figure 3a**). Two-shelled structure of such UCNPs can be clearly observed in their HAADF-STEM image (**Figure 3b**). The TEM image in **Figure 3c** shows that the growth of nMOFs on this two-shelled UCNP was successfully achieved.



**Figure 1:** Schematic illustration of the synthesis of UCMOFs. [Please click here to view a larger version of this figure.](#)



**Figure 2: Synthesis of UCMOFs based on  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$  UCNPs as seeds.** TEM images of (a)  $\text{NaGdF}_4\text{:Yb,Er}$  and (b,c)  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$  UCNPs. (d) HAADF-STEM image of  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$  UCNPs. (e,f) TEM images of the UCMOFs synthesized from  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$ . [Please click here to view a larger version of this figure.](#)



**Figure 3: Synthesis of UCMOFs based on  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{:Yb,Tm}$  UCNPs as seeds.** (a) TEM image and (b) HAADF-STEM image of  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{:Yb,Tm}$  UCNPs. (c) TEM image of the UCMOFs synthesized from  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{:Yb,Tm}$ . [Please click here to view a larger version of this figure.](#)

## Discussion

In this protocol, oleate-capped core-shell structured  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4$  UCNP s were prepared using a high temperature pyrolysis method<sup>31</sup>. The core-shell structure design of UCNP s can avoid environmental quenching effects, thus guaranteeing a high upconversion luminescence (UCL) efficiency of UCNP s<sup>32</sup>. The hydrophobic UCNP s were transferred into DMF phase through replacing OA molecules on the surface of UCNP s with  $\text{NOBF}_4$ . The resulted OA-free UCNP s were then modified with polyvinylpyrrolidone (PVP), which acts as directing agent to promote the growth of nMOFs on the surface of UCNP s. Interestingly, a majority of the resulted heterodimers exhibit selective growth of nMOFs on the top faces of the UCNP s (**Figure 1e,f**). In order to investigate the versatility of the approach,  $\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{:Yb,Tm}$  core-multishell structured UCNP s with larger size were synthesized for the growth of UCMOFs (**Figure 3a,b**). The results showed that UCMOFs were successfully synthesized (**Figure 3c**).

There are several critical steps in the synthesis of UCMOFs. First, when preparing the rare-earth trifluoroacetates, the temperature should be kept at 110 °C in an oil bath until the rare earth oxide power is dissolved completely (step 1.1.3). This process may take several hours. If no transparent solution is obtained after a long time stirring (>10 h), more trifluoroacetic acid (1-2 mL) can be dropped into the reaction system while stirring. Second, the precise control of both the temperature and the heating time (step 2.1.4) guarantees the high-yield preparation of anisotropically shaped UCNP s. Third, for the PVP-modification of UCNP s, 2 mL of acetone should be added after the overnight stirring (step 5.2.4) to flocculate the UCNP s dispersion.<sup>30</sup> The direct centrifugation after the stirring can cause heavy loss of UCNP s. Fourth, a high yield can be achieved by adjusting the amount of UCNP seeds used for the growth of UCMOFs (step 5.3.4).

Recently, several types of heterodimers have been reported, and most of them are limited to pure inorganic components, such as metal-metal, metal-semiconductor, and metal-metal oxide combinations<sup>4,5,6,7,33</sup>. The synthesis procedures involved are generally based on seeded growth techniques, which are conducted at two steps, namely the preparation of the starting NP seeds, and the subsequent growth of foreign materials onto their surface. To the best of our knowledge, this is the first example of a MOF- or UCNP-based heterodimer. Our method described allows for anisotropic growth of nMOFs on the surface of upconversion nanoplates which can be tuned in size based on a sequential epitaxial shell growth strategy. The successful construction of such heterodimers is because of two reasons: (i) PVP on the surfaces of UCNP s not only stabilizes the NPs in the reaction solution, but also induces the binding of Zr ions to the UCNP surface for subsequent nMOF growth; and (ii) the anisotropic structure of UCNP s and facet-selected absorption of PVP play key roles for the preferential nucleation and growth of nMOFs on the top (001) facets of UCNP s<sup>28</sup>. This work highlights the importance of surface chemistry for the synthesis of MOF-based asymmetric nanostructures. Since the MOFs grew onto the facet of UCNP s that can selectively bind with PVP, we anticipate that the approach could be applied to growth of MOFs on other anisotropically shaped NPs.

## Disclosures

We have nothing to disclose.

## Acknowledgements

This work was financially supported by the NSFC (No. 21771044), the Young Thousand Talented Program and the start-up supports from CAS.

## References

- Nie, Z., Petukhova, A., Kumacheva, E. Properties and Emerging Applications of Self-Assembled Structures Made from Inorganic Nanoparticles. *Nat. Nanotechnol.* **5**, 15-25 (2010).
- Costi, R., Saunders, A. E., Banin, U. Colloidal Hybrid Nanostructures: A New Type of Functional Materials. *Angew. Chem., Int. Ed.* **49** (29), 4878-4897 (2010).
- Wang, C., Xu, C., Zeng, H., Sun, S. Recent Progress in Syntheses and Applications of Dumbbell-like Nanoparticles. *Adv. Mater.* **21** (20), 3045-3052 (2009).
- Sun, Y., Foley, J. J., Peng, S., Li, Z., Gray, S. K. Interfaced Metal Heterodimers in the Quantum Size Regime. *Nano Lett.* **13** (8), 3958-3964 (2013).
- Hu, Y., Sun, Y. A Generic Approach for the Synthesis of Dimer Nanoclusters and Asymmetric Nanoassemblies. *J. Am. Chem. Soc.* **135** (6), 2213-2221 (2013).
- Amirav, L., Oba, F., Aloni, S., Alivisatos, A. P. Modular Synthesis of a Dual Metal-Dual Semiconductor Nano-Heterostructure. *Angew. Chem., Int. Ed.* **54** (24), 7007-7011 (2015).
- Zhu, H., *et al.* Pressure-Enabled Synthesis of Hetero-Dimers and Hetero-Rods through Intraparticle Coalescence and Interparticle Fusion of Quantum-Dot-Au Satellite Nanocrystals. *J. Am. Chem. Soc.* **139** (25), 8408-8411 (2017).
- Liu, Y., Tu, D., Zhu, H., Chen, X. Lanthanide-doped luminescent nanoprobe: controlled synthesis, optical spectroscopy, and bioapplications. *Chem. Soc. Rev.* **42**, 6924-6958 (2013).
- Liu, Y. *et al.* Hypoxia Induced by Upconversion-Based Photodynamic Therapy: Towards Highly Effective Synergistic Bioreductive Therapy in Tumors. *Angew. Chem. Int. Ed.* **54** (28), 8105-8109 (2015).
- Dong, H., Sun, L., Feng, W., Gu, Y., Li, F., Yan, C. Versatile Spectral and Lifetime Multiplexing Nanoplatfrom with Excitation Orthogonalized Upconversion Luminescence. *ACS Nano.* **11** (3), 3289-3297 (2017).
- Li, Z., Zhang, Y. Monodisperse Silica-Coated Polyvinylpyrrolidone/ $\text{NaYF}_4$  Nanocrystals with Multicolor Upconversion Fluorescence Emission. *Angew. Chem. Int. Ed.* **45**, 7732-7735 (2006).
- Ai, X. *et al.* In Vivo. Covalent Cross-Linking of Photon-Converted Rare-Earth Nanostructures for Tumour Localization and Theranostics. *Nat. Commun.* **7**, 10432-10441 (2016).

13. Xiang, J. *et al.* Antigen-Loaded Upconversion Nanoparticles for Dendritic Cell Stimulation, Tracking, and Vaccination in Dendritic Cell-Based Immunotherapy. *ACS Nano.* **9** (6), 6401-6411 (2015).
14. Li, L., Lu, Y. Regiospecific Hetero-assembly of DNA-Functionalized Plasmonic Upconversion Superstructures. *J. Am. Chem. Soc.* **137** (16), 5272-5275 (2015).
15. Li, C. X. *et al.* Multifunctional Upconversion Mesoporous Silica Nanostructures for Dual Modal Imaging and *In vivo*. Drug Delivery. *Small.* **9** (24), 4150-4159 (2013).
16. Zhou, J., Liu, Q., Feng, W., Sun, Y., Li, F. Upconversion Luminescent Materials: Advances and Applications. *Chem. Rev.* **115** (1), 395-465 (2015).
17. Gu, Z., Yan, L., Tian, G., Li, S., Chai, Z., Zhao, Y. Recent Advances in Design and Fabrication of Upconversion Nanoparticles and Their Safe Theranostic Applications. *Adv. Mater.* **25**, 3758-3779 (2013).
18. Zhou, B., Shi, B., Jin, D., Liu, X. Controlling Upconversion Nanocrystals for Emerging Applications. *Nature Nanotech.* **10**, 924-936 (2015).
19. Furukawa, H., Cordova, K. E., O'Keeffe, M., Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science.* **341**, 1230444-1230456 (2013).
20. Zhou, H. C., Long, J. R., Yaghi, O. M. Introduction to Metal-Organic Frameworks. *Chem. Rev.* **112**, 673-674 (2012).
21. Lu, G., *et al.* Imparting Functionality to a Metal-Organic Framework Material by Controlled Nanoparticle Encapsulation. *Nature Chem.* **4** (4), 310-316 (2012).
22. Son, H. *et al.* Light-Harvesting and Ultrafast Energy Migration in Porphyrin-Based Metal-Organic Frameworks. *J. Am. Chem. Soc.* **135** (2), 862-869 (2013).
23. Jin, S., Son, H. J., Farha, O. K., Wiederrecht, G. P., Hupp, J. T. Energy Transfer from Quantum Dots to Metal-Organic Frameworks for Enhanced Light Harvesting. *J. Am. Chem. Soc.* **135** (3), 955-958 (2013).
24. Maza, W. A., Padilla, R., Morris, A. J. Concentration Dependent Dimensionality of Resonance Energy Transfer in a Postsynthetically Doped Morphologically Homologous Analogue of UiO-67 MOF with a Ruthenium(II) Polypyridyl Complex. *J. Am. Chem. Soc.* 2015, **137** (25), 8161-8168 (2015).
25. Sindoro, M., Granick, S. Voids and Yolk-Shells from Crystals That Coat Particles. *J. Am. Chem. Soc.* **136** (39), 13471-13473 (2014).
26. He, L. *et al.* DNA-Assembled Core-Satellite Upconverting-Metal-Organic Framework Nanoparticle Superstructures for Efficient Photodynamic Therapy. *Small.* **13**, 1700504-1700511 (2017).
27. Khaletskaia, K. *et al.* Integration of Porous Coordination Polymers and Gold Nanorods into Core-Shell Mesoscopic Composites toward Light-Induced Molecular Release. *J. Am. Chem. Soc.* **135**, 10998-11005 (2013).
28. Li, Y. *et al.* Heterodimers Made of Upconversion Nanoparticles and Metal-Organic Frameworks. *J. Am. Chem. Soc.* **139** (39), 13804-13810 (2017).
29. Liu, B. *et al.* Poly(Acrylic Acid) Modification of Nd<sup>3+</sup>-Sensitized Upconversion Nanophosphors for Highly Efficient UCL Imaging and pH-Responsive Drug Delivery. *Adv. Funct. Mater.* **25**, 4717-4729 (2015).
30. Dong, A. *et al.* A Generalized Ligand-Exchange Strategy Enabling Sequential Surface Functionalization of Colloidal Nanocrystals *J. Am. Chem. Soc.* **133**, 998-1006 (2011).
31. Mai, H. *et al.* High-Quality Sodium Rare-Earth Fluoride Nanocrystals: Controlled Synthesis and Optical Properties. *J. Am. Chem. Soc.* **128** (19), 6426-6436 (2006).
32. Dong, H. *et al.* Lanthanide Nanoparticles: From Design toward Bioimaging and Therapy. *Chem. Rev.* **115** (19), 10725-10815 (2015).
33. Wu, H. *et al.* Formation of Heterodimer Nanocrystals: UO<sub>2</sub>/In<sub>2</sub>O<sub>3</sub> and FePt/In<sub>2</sub>O<sub>3</sub>. *J. Am. Chem. Soc.* **133**, 14327-14337 (2011).