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A Facile Synthesis of Upconversion Metal–Organic Framework Heterodimers

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Title:**A Facile Synthesis of Upconversion Metal–Organic Framework Heterodimers****Authors & Affiliations:**

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Summary:

A protocol for the synthesis of heterostructural nanoparticle dimers consisting of upconversion nanoparticles and porphyrinic nanoscale metal–organic frameworks is presented.

Long 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.

Introduction:

Constructing multicomponent hybrid nanoparticles (NPs) has attracted extensive interest due to

their architecturally defined collective properties¹⁻³. 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 mixtures⁴⁻⁵. 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 therapy⁶⁻⁷. 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 photostability⁸⁻¹⁵. In the past few years, synthetic approaches for the preparation of UCNPs-based nanocomposite materials have attracted significant research interest in this field, as evidenced from the rapid upsurge of reports on UCNPs-based nanohybrids. For example, mesoporous silica, zinc oxide and titanium dioxide have been successfully integrated into UCNPs to form discrete core-shell nanocomposites¹⁶⁻¹⁸, 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 sites¹⁹⁻²¹. Owing to these excellent structure and properties, MOFs show promise for a variety of applications, including gas storage, chemical separation, catalysis, and drug delivery²¹⁻²⁴. 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^{21,25-27}. 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 synergistic treatment of tumors²⁸. 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 Trifluoroacetates²⁹

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

1.1.1. Add 10 mmol of the rare earth oxide Y_2O_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.

1.1.2. Cautiously add, dropwise, 80 mmol (6.2 mL) of trifluoroacetic acid (CF_3COOH) into the reaction system while stirring.

1.1.3. 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 Y_2O_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.

1.1.4. Heat the solution to 110 °C in an oil bath until the rare earth oxide powder is dissolved completely.

1.1.5. 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.

1.1.6. Collect the white powder into a bottle or centrifuge tube and store at room temperature for further use.

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

1.2.1. Add 10 mmol of the rare earth oxide Gd_2O_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.

1.2.2. Repeat steps 1.1.2-1.1.6.

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

1.3.1. Add 10 mmol of the rare earth oxide Er_2O_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.

1.3.2. Repeat steps 1.1.2-1.1.6.

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

1.4.1. Add 10 mmol of the rare earth oxide Tm_2O_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.

1.4.2. Repeat steps 1.1.2-1.1.6.

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

1.5.1. Add 10 mmol of the rare earth oxide Yb_2O_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.

1.5.2. Repeat steps 1.1.2-1.1.6.

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

1.6.1. Add 10 mmol of the rare earth oxide Nd_2O_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.

1.6.2. Repeat steps 1.1.2-1.1.6.

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

2.1. Synthesis of α -phase $\text{NaGdF}_4\text{:Yb,Er}$

2.1.1. Inspect all the glassware carefully to ensure there is no damage and cracking before the high temperature experiments.

2.1.2. Combine CF_3COONa (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.

2.1.3. 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.

2.1.4. 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.

2.1.5. 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

2.1.6. 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.

2.1.7. Re-disperse the white precipitate in 5 mL of cyclohexane.

2.1.8. Stock the transparent cyclohexane solution in a 20 mL sealed glass bottle for future use.

Note: The cyclohexane solution of UCNPs can be stocked for several months.

2.1.9. Collect transmission electron microscopy (TEM) images to characterize the α -phase $\text{NaGdF}_4\text{:Yb,Er}$.

2.2. Synthesis of β -phase $\text{NaGdF}_4\text{:Yb,Er}$

2.2.1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.

2.2.2. Carefully combine CF_3COONa (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.

2.2.3. Add 5 mL of the as-prepared α -phase NaGdF₄:Yb,Er colloidal solution into the mixture.

2.2.4. Equip the 3-neck round bottom flask with a thermocouple, a reflux condenser and a rubber septum.

2.2.5. Repeat steps 2.1.3-2.1.8.

2.2.6. Collect TEM images to characterize the β -phase NaGdF₄:Yb,Er.

3. Synthesis of NaGdF₄:Yb,Er@NaYF₄

3.1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.

3.2. Carefully combine CF₃COONa (1 mmol, 0.136 g) and Y(CF₃COO)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.

3.3. Add 5 mL of the as-prepared β -phase NaGdF₄:Yb,Er colloidal solution into the mixture.

3.4. Equip the 3-neck round bottom flask with a thermocouple, a reflux condenser and a rubber septum.

3.5. Repeat steps 2.1.3-2.1.8.

3.6. Collect TEM and HAADF-STEM images²⁸ to determine the core-shell structure of the NaGdF₄:Yb,Er@NaYF₄.

4. Synthesis of NaGdF₄:Yb,Er@NaYF₄@NaYF₄:Yb,Tm

4.1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.

4.2. Carefully combine CF₃COONa (1 mmol, 0.136 g), Y(CF₃COO)₃ (0.08 mmol, 0.034 g), Yb(CF₃COO)₃ (0.9 mmol, 0.461 g) and Tm(CF₃COO)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.

4.3. Add 5 mL of the as-prepared NaGdF₄:Yb,Er@NaGdF₄ colloidal solution to the mixture.

4.4. Equip the 3-neck round bottom flask with a thermocouple, a reflux condenser and a rubber

septum.

4.5. Repeat steps 2.1.3-2.1.8.

4.6. Collect TEM and HAADF-STEM images to determine the core-shell structure of the NaGdF₄:Yb,Er@NaYF₄@NaYF₄:Yb,Tm.

5. Synthesis of UCMOFs

5.1. Synthesis of nitrosonium tetrafluoroborate (NOBF₄) modified UCNPs³⁰

5.1.1. Store the NOBF₄ at 4 °C. In order to increase the weighing accuracy, take the NOBF₄ out from freezer at least 10 min before weighing.

5.1.2. Dissolve 20-30 mg of NOBF₄ into 1 mL of DMF.

5.1.3. Add 1 mL cyclohexane solution of UCNPs to the stirring DMF solution of NOBF₄.

5.1.4. Stir the resulting mixture until UCNPs 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 UCNPs from cyclohexane to DMF. Ideally, upon 980 nm irradiation, the cyclohexane phase has no light, while DMF phase has a bright green luminescence.

5.1.5. Isolate the NOBF₄ modified UCNPs by centrifugation at 15,800 × g for 10 min. After removing the supernatant carefully, re-disperse the precipitates in 1 mL of DMF.

5.2. Synthesis of PVP-coated UCNPs

5.2.1. Dissolve 40 mg of PVP (Mw = 8,000) into 1 mL DMF.

5.2.2. Add 1 mL DMF solution of the NOBF₄ modified UCNPs to the PVP solution dropwise.

5.2.3. Keep stirring overnight.

5.2.4. Add 2 mL of acetone to flocculate the UCNPs' dispersion.

5.2.5. Transfer the mixture solution to centrifuge tubes and centrifuge at 15800 × g for 10 min.

5.2.6. Remove the supernatant carefully, and re-disperse the precipitates in 2 mL of DMF/acetone mixture solution (1:1 by volume)

5.2.7. Centrifuge at $15,800 \times g$ for 10 min for washing.

5.2.8. Re-disperse the precipitate in 2 mL of DMF.

5.3. Synthesis of UCMOFs

5.3.1. Prepare a 90 °C oil bath in advance.

5.3.2. Prepare a clean 5 mL round bottom flask with a stir bar.

5.3.3. 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.

5.3.4. Add 1 mL DMF solution of PVP modified UCNPs into the flask.

5.3.5. 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.

5.3.6. Transfer the mixture solution to centrifuge tubes and centrifuge at $13,500 \times g$ for 30 min immediately.

5.3.7. Remove the supernatant and re-disperse the precipitates in 1.5 mL of DMF solution.

5.3.8. Centrifuge at $13,500 \times g$ for 30 min for washing.

5.3.9. Repeat the washing process 2 - 3 times.

5.3.10. Re-disperse the final precipitates in 2 mL of DMF.

5.3.11. 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.

$\text{NaGdF}_4\text{:Yb,Er@NaYF}_4\text{@NaYF}_4\text{:Yb,Tm}$ core-multishell structured UCNPs (~ 27 nm) were

synthesized for the growth of UCMOFs (**Figure 3a**). Two-shelled structure of such UCNP 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 and Table Legends:

Figure 1: Schematic illustration of the synthesis of UCMOFs.

Figure 1: Synthesis of UCMOFs based on NaGdF₄:Yb,Er@NaYF₄ UCNP as seeds. TEM images of (a) NaGdF₄:Yb,Er and (b,c) NaGdF₄:Yb,Er@NaYF₄ UCNP. (d) HAADF-STEM image of NaGdF₄:Yb,Er@NaYF₄ UCNP. (e,f) TEM images of the UCMOFs synthesized from NaGdF₄:Yb,Er@NaYF₄.

Figure 3: Synthesis of UCMOFs based on NaGdF₄:Yb,Er@NaYF₄@NaYF₄:Yb,Tm UCNP as seeds. (a) TEM image and (b) HAADF-STEM image of NaGdF₄:Yb,Er@NaYF₄@NaYF₄:Yb,Tm UCNP. (c) TEM image of the UCMOFs synthesized from NaGdF₄:Yb,Er@NaYF₄@NaYF₄:Yb,Tm.

Discussion

In this protocol, oleate-capped core-shell structured NaGdF₄:Yb,Er@NaYF₄ UCNP were prepared using a high temperature pyrolysis method³¹. The core-shell structure design of UCNP can avoid environmental quenching effects, thus guaranteeing a high upconversion luminescence (UCL) efficiency of UCNP³². The hydrophobic UCNP were transferred into DMF phase through replacing OA molecules on the surface of UCNP with NOBF₄. The resulted OA-free UCNP were then modified with polyvinylpyrrolidone (PVP), which acts as directing agent to promote the growth of nMOFs on the surface of UCNP. Interestingly, a majority of the resulted heterodimers exhibit selective growth of nMOFs on the top faces of the UCNP (**Figure 1e,f**). In order to investigate the versatility of the approach, NaGdF₄:Yb,Er@NaYF₄@NaYF₄:Yb,Tm core-multishell structured UCNP 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. Third, for the PVP-modification of UCNP, 2 mL of acetone should be added after the overnight stirring (step 5.2.4) to flocculate the UCNP dispersion.³⁰ The direct centrifugation after the stirring can cause heavy loss of UCNP. Fourth, a high yield can be achieved by adjusting the amount of UCNP seeds used for the growth of UCMOFs (step 5.3.4).

370
371 Recently, several types of heterodimers have been reported, and most of them are limited to pure
372 inorganic components, such as metal–metal, metal–semiconductor, and metal–metal oxide
373 combinations^{4-7,33}. The synthesis procedures involved are generally based on seeded growth
374 techniques, which are conducted at two steps, namely the preparation of the starting NP seeds,
375 and the subsequent growth of foreign materials onto their surface. To the best of our knowledge,
376 this is the first example of a MOF- or UCNP-based heterodimer. Our method described allows for
377 anisotropic growth of nMOFs on the surface of upconversion nanoplates which can be tuned in
378 size based on a sequential epitaxial shell growth strategy. The successful construction of such
379 heterodimers is because of two reasons: (i) PVP on the surfaces of UCNPs not only stabilizes the
380 NPs in the reaction solution, but also induces the binding of Zr ions to the UCNP surface for
381 subsequent nMOF growth; and (ii) the anisotropic structure of UCNPs and facet-selected
382 absorption of PVP play key roles for the preferential nucleation and growth of nMOFs on the top
383 (001) facets of UCNPs²⁸. This work highlights the importance of surface chemistry for the
384 synthesis of MOF-based asymmetric nanostructures. Since the MOFs grew onto the facet of
385 UCNPs that can selectively bind with PVP, we anticipate that the approach could be applied to
386 growth of MOFs on other anisotropically shaped NPs.

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391 **Disclosure:**

392 We have nothing to disclose.

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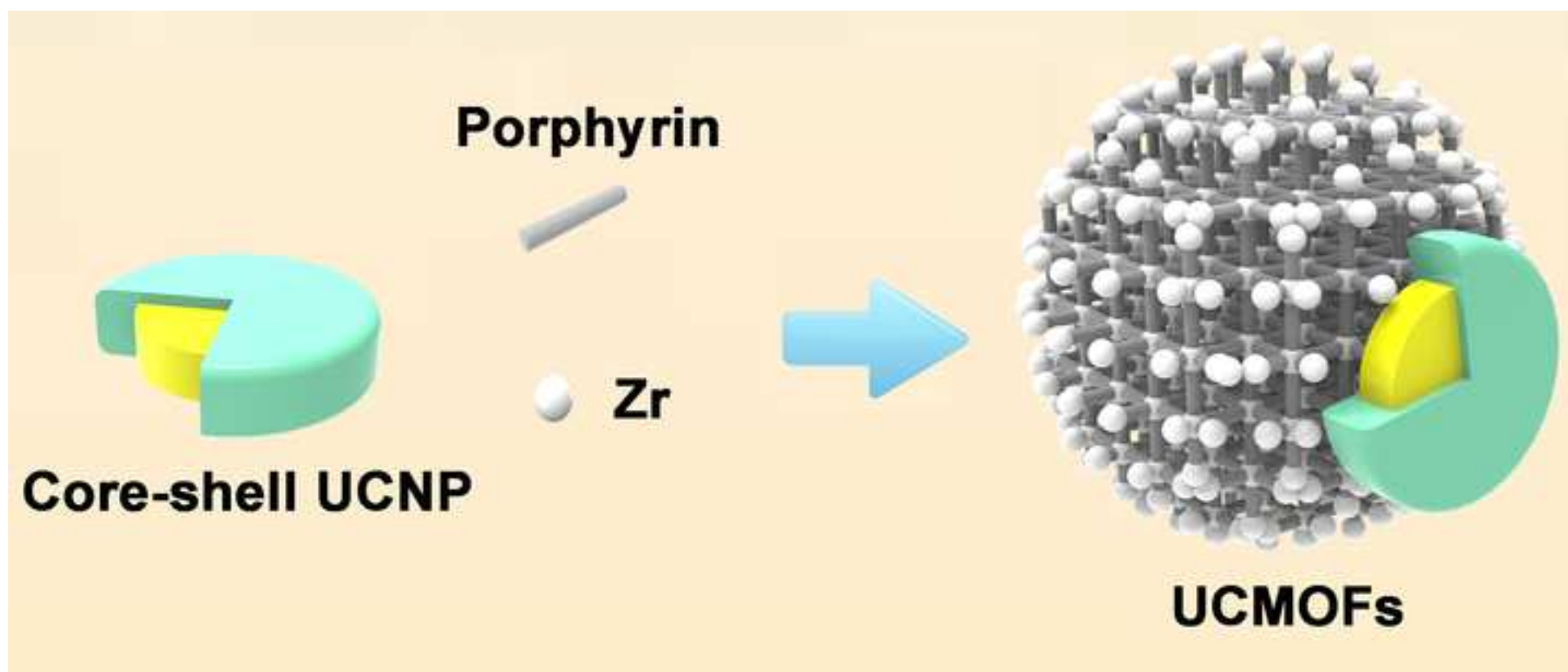
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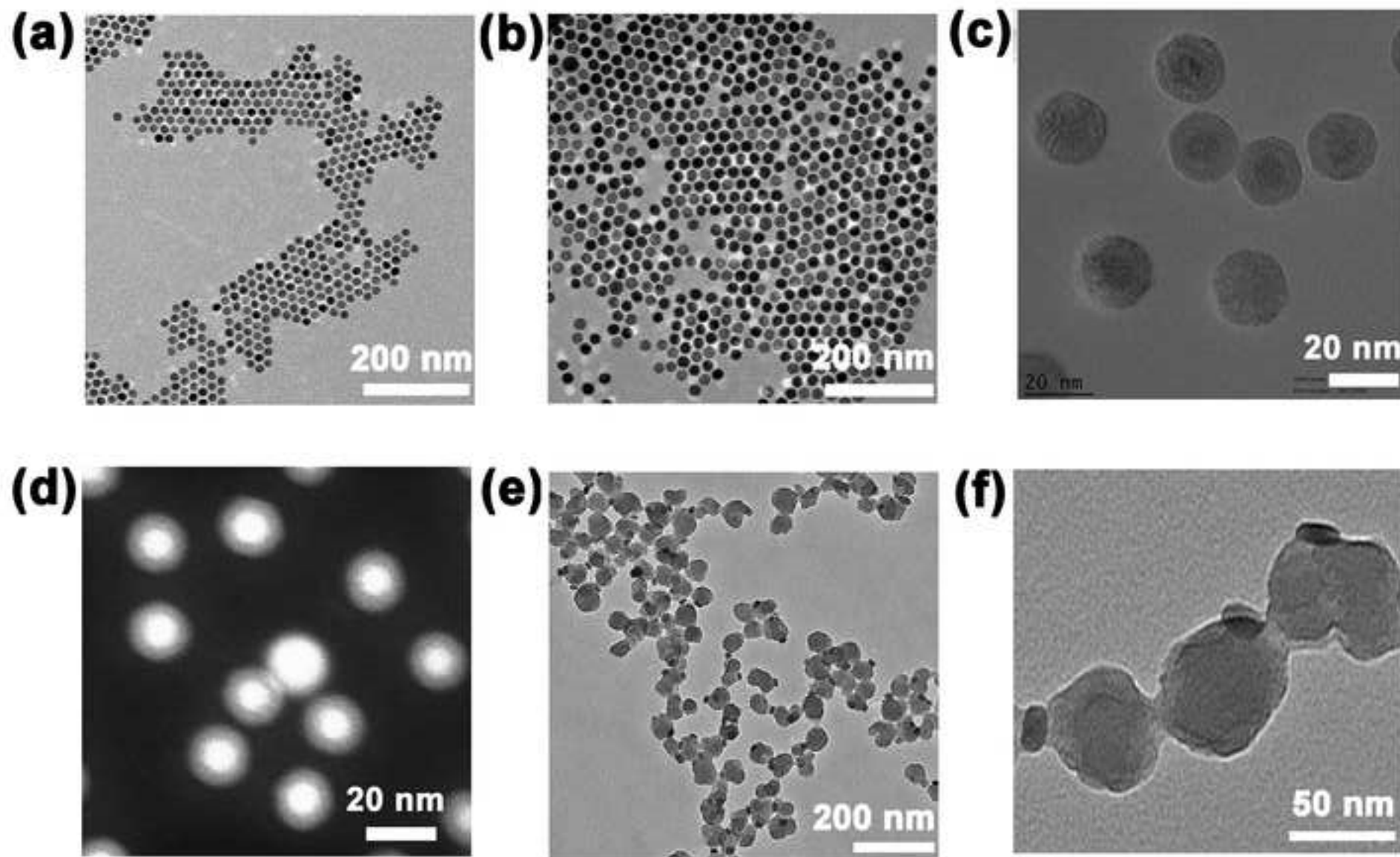
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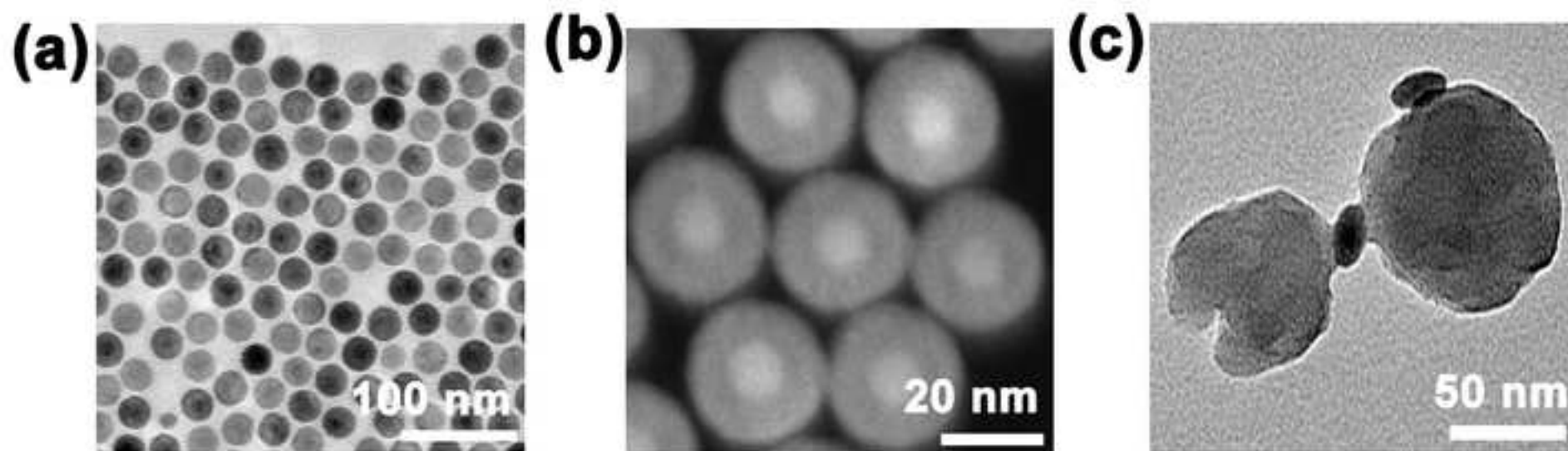
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Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Yttrium oxide (Y ₂ O ₃ , 99.99%)	Acros	194610500	
Gadolinium oxide (Gd ₂ O ₃ , 99.9%)	Acros	315510250	
Erbium oxide (Er ₂ O ₃ , ≥99.99%)	Aldrich	203238	
Thulium oxide (Tm ₂ O ₃ , 99.9%)	Aldrich	289167	
Ytterbium oxide (Yb ₂ O ₃ , 99.9%)	Macklin	Y820617	
Neodymium oxide (Nd ₂ O ₃ , 99.9%)	Acros	211580250	
Trifluoroacetic acid (99%)	Acros	139721000	
Sodium trifluoroacetate (CF ₃ COONa, >98%)	TCI	T1336	
Oleylamine (OM, 90%)	Acros	129540010	Causes skin irritation; Causes serious eye irritation.
1-octadecene (ODE, 90%)	Acros	129310010	
Oleic acid (OA, 90%)	Aldrich	364525	Causes skin irritation; Causes serious eye irritation.
	Beijing Chemical		
Anhydrous Ethanol (99.5%)	Works Beijing Chemical		
Cyclohexane (≥99.5%)	Works		
N,N-Dimethylformamide (DMF, 99.9%)	J&K Beijing Chemical	133682	
Acetone (99.9%)	Works Sigma-		
ZrOCl ₂ •8H ₂ O (98%)	Aldrich	224316	
Benzoic acid (99.5%)	Aladdin	B116255	

Nitrosyl tetrafluoroborate (NOBF ₄ , 95%)	Aldrich	175064	Stored in 4 °C; Atmosphere Sensitive;
Polyvinylpyrrolidon (PVP, 8000)	Alfa Aesar	41626	
Tetrakis (4-carboxyphenyl)porphyrin (H ₂ TCPP, >97%)	TCI	A5015	Stored in 4 °C; Atmosphere Sensitive;
H ₂ O (HPLC grade)			Distilled H ₂ O filtered by a Milli-Q purification system



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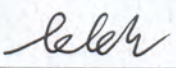
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February 28, 2018

Dear Dr. Phillip Steindel,

In response to your e-mail of February 8, 2018, I am sending you a revised manuscript (Ms No.: **JoVE57571R1**) entitled “A Facile Synthesis of Upconversion Metal–Organic Framework Heterodimers”.

We wish to thank you for the careful evaluation of the manuscript and the helpful comments. We have revised the manuscript according the comments. A detailed list of the editorial comments and our responses is shown starting on the next page. In addition, we have provided copies of the manuscript in which the changes are marked in red colored font.

We believe the revised manuscript has addressed the editorial comments and are suitable for publication in *JoVE*.

Thank you for your continued attention and we look forward to hearing from you.

Sincerely,

Le-Le Li

Professor of Chemistry
National Center for NanoScience and Technology, China

Responses to the Referees' Comments and the Corresponding Revisions

We appreciate the editor for the careful evaluation of the manuscript. A thorough and detailed reply to each point raised by the editor together with the changes made to the manuscript is listed below.

Response to Editorial comments:

Comment: Please proofread; there are still a few errors in grammar and usage, some of which have been noted.

Response: We thank the editor for the suggestions. Following the editorial suggestion, we proofread the manuscript thoroughly, and some grammar or usage issues have been corrected.

Comment: Please provide references for TEM and HAADF-STEM (the latter in particular).

Response: Following the editorial suggestion, we have provide Ref.28 for TEM and HAADF-STEM.

“3.6. Collect TEM and HAADF-STEM images²⁸ to determine the core-shell structure of the NaGdF₄:Yb,Er@NaYF₄.” (page 6)

Comment: 1.1.3: This is rather vague-how much should the dosage be increased or decreased, and which reactants might vary? What requirements might vary?

Response: Following the editorial suggestion, we corrected it (page 3):

“1.1.3 Scaled up of reactants (including rare earth oxides, deionized water and trifluoroacetic acid) on demand (1~10 times). For example, disperse 20 mmol of the rare earth oxides Y₂O₃ (7.88 g) in 100 mL deionized water in a 250 mL of 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.”

Comment: 1.2.2 (and others): Do you mean to say ‘Repeat steps 1.1.2-1.1.6’ (and other)? Please edit if so (and if the protocol varies, say how).

Response: Following the editorial suggestion, we have made it clear in the revised manuscript:

“1.2.2. Repeat steps 1.1.2-1.1.6.” (page 4)

“2.2.5. Repeat steps 2.1.3-2.1.8.” (page 6)

...

Comment: Most of the steps in the protocol should be in the imperative tense (e.g., 1.1.1 should be ‘Disperse 10 mmol of the rare earth oxide Y₂O₃ (3.94 g) in 10 mL...’).

Response: Following the editorial suggestion, we proofread the protocol thoroughly, and some steps have been revised in the imperative tense:

“1.1.1. Disperse 10 mmol of the rare earth oxides Y₂O₃ (3.94 g) in ...” (page 3)

“1.1.5. Transfer the as-obtained transparent solution into a...” (page 4)

“1.2.1. Disperse 10 mmol of the rare earth oxides Gd₂O₃ (3.62 g) in...” (page 4)

...

Comment: Discussion: This should be oriented towards a prospective experimenter who wants to repeat your work. Specifically, address the following:

a) Critical steps: Which steps should the experimenter pay close attention to and why?

- b) Troubleshooting: What are common mistakes in carrying out this protocol, and how can they be corrected or avoided?
- c) Modifications: How can this protocol be modified from what is presented (if applicable)?
- d) Limitations: What can't this protocol do that an experimenter may want to keep in mind?
- e) Significance/comparison with other methods: What other protocols might achieve similar results to this one, and how do they differ?

Response: Following the editorial suggestions, we revised Discussion part (page 9):

“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 powder was dissolved completely (step 1.1.3). This process may cost several hours. If no transparent solution 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 UCNPs. Third, for the PVP-modification of UCNPs, 2 mL of acetone should be added after the overnight stirring (step 5.2.4) to flocculate the UCNPs dispersion.³⁰ The direct centrifugation after the stirring can cause heavy loss of UCNPs. Fourth, a high yield could 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.^{4-7,33} The involved synthesis procedures 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 UCNPs not only stabilizes the NPs in the reaction solution, but also induce the binding of Zr ions to the UCNP surface for subsequent nMOF growth; and (ii) the anisotropic structure of UCNPs and facet-selected adsorption of PVP play key roles for the preferential nucleation and growth of nMOFs on the top (001) facets of UCNPs.²⁸ This work highlights the importance of surface chemistry for the synthesis of MOF-based asymmetric nanostructures. Since the MOFs grew onto the facet of UCNPs that can selectively bind with PVP, we anticipate that the approach could be applied to growth of MOFs on other anisotropically shaped NPs.”