**Title:**

**A Facile Synthesis of Upconversion** **Metal−Organic Framework Heterodimers**

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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 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 heterostuctures 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 NPs21,25-27. 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 synergetic 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, ZrOCl2•8H2O, 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**29
   1. **Preparation of the yttrium trifluoroacetates (Y(CF3COO)3)**
      1. Add 10 mmol of the rare earth oxide Y2O3 (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 (CF3COOH) 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 Y2O3 (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 (Gd(CF3COO)3)**
      1. Add 10 mmol of the rare earth oxide Gd2O3 (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 (Er(CF3COO)3)**
      1. Add 10 mmol of the rare earth oxide Er2O3 (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 (Tm(CF3COO)3)**
      1. Add 10 mmol of the rare earth oxide Tm2O3 (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 (Yb(CF3COO)3)**
      1. Add 10 mmol of the rare earth oxide Yb2O3 (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 (Nd(CF3COO)3)**
      1. Add 10 mmol of the rare earth oxide Nd2O3 (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 NaGdF4:Yb,Er**
   1. **Synthesis of** **α-phase NaGdF4:Yb,Er**
      1. Inspect all the glassware carefully to ensure there is no damage and cracking before the high temperature experiments.
      2. Combine CF3COONa (1 mmol, 0.136 g), Gd(CF3COO)3 (0.78 mmol, 0.387 g), Yb(CF3COO)3 (0.2 mmol, 0.1024 g) and Er(CF3COO)3 (0.02mmol, 0.0105 g) with a mixed solution of OA (10 mmol, 2.82 g), oleylamine (OM, 10 mmol, 2.67g) 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.

* + 1. 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. 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.
    3. 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 × g for 5 min at room temperature and discard the supernatant
    4. 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 × g for 5 min at room temperature and discard the supernatant.
    5. Re-disperse the white precipitate in 5 mL of cyclohexane.
    6. 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.

* + 1. Collect transmission electron microscopy (TEM) images to characterize the α-phase NaGdF4:Yb,Er.
  1. **Synthesis of β-phase NaGdF4:Yb,Er**
     1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.
     2. Carefully combine CF3COONa (0.5 mmol, 0.068 g), Gd(CF3COO)3 (0.39 mmol, 0.194 g), Yb(CF3COO)3 (0.1 mmol, 0.051 g) and Er(CF3COO)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 α-phase NaGdF4: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 β-phase NaGdF4:Yb,Er.

1. **Synthesis of NaGdF4:Yb,Er@NaYF4**
   1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.
   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. Add 5 mL of the as-prepared β-phase NaGdF4: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 images28 to determine the core-shell structure of the NaGdF4:Yb,Er@NaYF4.
2. **Synthesis of NaGdF4:Yb,Er@NaYF4@NaYF4:Yb,Tm**
   1. Prepare a clean 100 mL 3-neck round bottom flask with a high-temperature stir bar.
   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.
   3. Add 5 mL of the as-prepared NaGdF4:Yb,Er@NaGdF4 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 NaGdF4:Yb,Er@NaYF4@NaYF4:Yb,Tm.
3. **Synthesis of UCMOFs**
   1. **Synthesis of nitrosonium tetrafluoroborate (NOBF4) modified UCNPs**30
      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.
      2. Dissolve 20-30 mg of NOBF4 into 1 mL of DMF.
      3. Add 1 mL cyclohexane solution of UCNPs to the stirring DMF solution of NOBF4.
      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. 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.
   2. **Synthesis of PVP-coated UCNPs**
      1. Dissolve 40 mg of PVP (Mw = 8,000) into 1 mL DMF.

* + 1. Add 1 mL DMF solution of the NOBF4 modified UCNPs to the PVP solution dropwise.
    2. Keep stirring overnight.
    3. Add 2 mL of acetone to flocculate the UCNPs’ dispersion.
    4. Transfer the mixture solution to centrifuge tubes and centrifuge at 15800 × g for 10 min.
    5. Remove the supernatant carefully, and re-disperse the precipitates in 2 mL of DMF/acetone mixture solution (1:1 by volume)
    6. Centrifuge at 15,800 × g for 10 min for washing.
    7. Re-disperse the precipitate in 2 mL of DMF.
  1. **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 ZrOCl2•8H2O (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 UCNPs 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 × 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 × 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 NaGdF4:Yb,Er UCNPs (**Figure 1a**) and core-shell structured NaGdF4:Yb,Er@NaYF4 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 NaGdF4:Yb,Er core and ∼19 nm for NaGdF4:Yb,Er@NaYF4 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.

NaGdF4:Yb,Er@NaYF4@NaYF4: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 and Table Legends:**

**Figure 1:** Schematic illustration of the synthesis of UCMOFs.

**Figure 1: Synthesis of UCMOFs based on NaGdF4:Yb,Er@NaYF4 UCNPs as seeds.** TEM images of (a) NaGdF4:Yb,Er and (b,c) NaGdF4:Yb,Er@NaYF4 UCNPs. (d) HAADF-STEM image of NaGdF4:Yb,Er@NaYF4 UCNPs. (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 UCNPs as seeds.** (a) TEM image and (b) HAADF-STEM image of NaGdF4:Yb,Er@NaYF4@NaYF4:Yb,Tm UCNPs. (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 UCNPs were prepared using a high temperature pyrolysis method31. The core-shell structure design of UCNPs can avoid environmental quenching effects, thus guaranteeing a high upconversion luminescence (UCL) efficiency of UCNPs32. The hydrophobic UCNPs were transferred into DMF phase through replacing OA molecules on the surface of UCNPs with NOBF4. The resulted OA-free UCNPs were then modified with polyvinylpyrrolidone (PVP), which acts as directing agent to promote the growth of nMOFs on the surface of UCNPs. Interestingly, a majority of the resulted heterodimers exhibit selective growth of nMOFs on the top faces of the UCNPs (**Figure 1e,f**). In order to investigate the versatility of the approach, NaGdF4:Yb,Er@NaYF4@NaYF4:Yb,Tm core-multishell structured UCNPs 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 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 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 combinations4-7,33. 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 UCNPs 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 UCNPs and facet-selected absorption of PVP play key roles for the preferential nucleation and growth of nMOFs on the top (001) facets of UCNPs28. 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.

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**Disclosure:**

We have nothing to disclose.

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