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Iridium-Complex-Modified Upconversion Nanophosphors for Effective LRET Detection of Cyanide Anions in Pure Water

Liming Yao, Jing Zhou, Jinliang Liu, Wei Feng, and Fuyou Li**

Because of the extreme toxicity of cyanide anions, a great deal of effort has been invested in developing probes that use colorimetric and fluorometric methods to detect them. To date, most of the current optical probes require the use of organic solvents or a mixture of organic solvents and water. Upconversion nanophosphors (UCNPs) can serve as excellent emitters as a result of their sharp emission peaks and simple control of the emission wavelength. Here, the fabrication of hybrid material composed of iridium complex and UCNPs to detect cyanide anions selectively in pure water is described. In addition to the colorimetric detection, the upconversion luminescence emission can serve as a detection signal based on an effective luminescent resonance energy transfer (LRET) process within the hybrid nanoparticles.

1. Introduction

The cyanide anion (CN^-) is one of the most toxic anions because it can strongly interact with the active site of cytochrome a_3 and, thus, inhibit cellular respiration in mammalian cells.[1] On the other hand, large quantities of cyanide anions are widely used in industry, such as for the synthesis of nitriles, nylon, and acrylic plastics, fertilizers, and for precious metal mining and metal plating. As a result, finding methods to detect cyanide at the environmental level has attracted much attention. Recently, some methods have been developed, such as titrimetric, voltametric, potentiometric, and electrochemical methods. Unlike these methods, the optical method detects cyanide anions through a change in color and/or fluorescence intensity.[2–4] Such colorimetric and fluorometric changes are easily observed, even using the naked eye.[5–17]

A great deal of effort has been invested in developing easy-to-use colorimetric and fluorometric probes.[18,19] To achieve high selectivity, fluorescent chemodosimeters based on specific chemical reactions have been developed in organic solvents.[20–22] However, most cyanide-selective probes are insoluble in water because of their organic nature. As a result, most of the current optical methods need to be carried out in organic solvents or at least in a mixture of organic solvents and water. Such semi-aqueous detection methods are not very practical. To date, few methods have been reported for the fluorescent detection of the cyanide anion in water.[23–27] Martínez-Máñez and co-workers made a probe that could detect cyanide in water using a surfactant assisted method, in which the sensing molecules entered surfactant-formed micellar containers.[28] Moreover, most luminescent probes for CN^- are focused on conventional fluorescent dyes.

Compared with the conventional fluorescence method, upconversion luminescence (UCL) detection based on lanthanide-doped upconversion nanophosphors (UCNPs)[29–46] as probes has been shown to exhibit no autofluorescence (noise) from biosamples and greater penetration depth.[47–50] Therefore, UCNPs are good candidates for sensing and bioimaging. For example, Wolfbeis's group, Yan's group, Li's group, and our group have developed UCL-based sensors or probes to selectively respond to O_2,[51] NH_4,[52] DNA,[53] and Hg^{2+},[54] respectively.

Recently, we have developed an interface reaction strategy to provide highly sensitive detection of CN^- in a semi-aqueous system (dimethylformamide (DMF)/H_2O = 9:1, v/v) through modifying a CN^--responsive chromophoric complex on the surface of $NaYF_4$ with 20% Yb, 1.6% Er, 0.4% Tm upconversion nanoparticles using the upconversion luminescence emission as the output signal.[55] Unfortunately, this probe still does not work in pure water.

In light of the fact that the hydrophobic environment promotes the nucleophilic addition reaction of CN^-, we introduce a general method to fabricate hydrophilic hybrid nanoparticles with CN^--sensitive chemodosimeters in the hydrophobic layers. We coat amphiphilic block-polymer poly(maleic anhydride-alt-1-octadecene)-polyethylene glycol (C_{18}PMH-PEG) onto the surface of hydrophobic oleic acid (OA)-coated $NaYF_4$: 20%Yb, 2%Ho upconversion nanophosphors (UCNPs) to fabricate a hydrophilic nanostructure (denoted as PEG-UCNPs). In PEG-UCNPs, a hydrophobic layer composed of the long carbon chains from OA molecules and C_{18}PMH-PEG is formed. Then, the CN^--reactive iridium(III) complex ([$(ppy)_2Ir(dmpp)$]PF_6, **Ir1**), which was reported by Bian et al. to show high selectivity and sensitivity for CN^- in acetonitrile with significant color change from pink to colorless,[5] is loaded onto the hydrophobic layer to form the hybrid upconversion material (denoted as **Ir1**-UCNPs). This hybrid upconversion material can serve as

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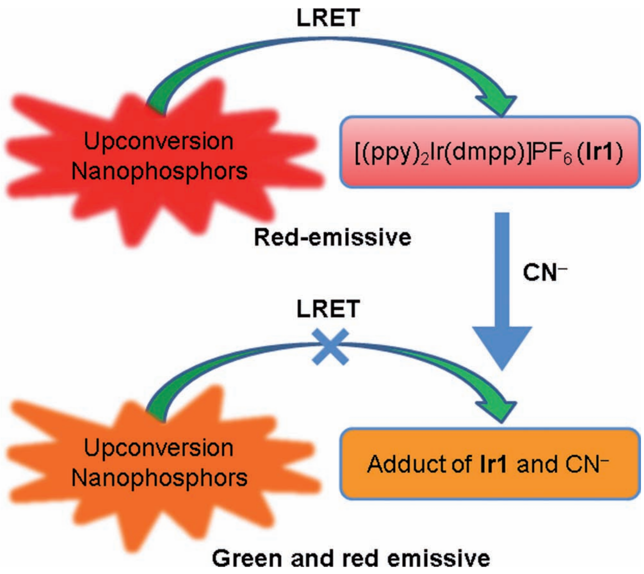


Scheme 1. Schematic illustration of the LRET process between UCNPs and **Ir1**.

an optical probe in pure water to detect CN$^-$ based on a luminescent resonance energy transfer (LRET) process with UCNPs and **Ir1** as energy donor and energy accepter, respectively.

2. Results and Discussion

The design of this work is based on the LRET process between UCNPs and **Ir1** (**Scheme 1**). LRET efficiency is determined by the distance between donor and accepter and the spectra overlap between the emission of energy donor and the absorption of energy accepter.[53,56–61] **Figure 1** shows the upconversion emission spectrum of UCNPs together with the absorption spectra of **Ir1** in the absence or presence of CN$^-$. The upconversion emission bands of UCNPs at 530–560 nm and 630–670 nm under 980 nm excitation can be attributed to the $^5F_5 \rightarrow {}^5I_8$ and ($^5S_2$, $^5F_4$) $\rightarrow {}^5I_8$ transitions of Ho^{3+}, respectively. **Ir1** has a significant absorbance with a maximum at 530 nm. This absorbance ideally overlaps the emission band of UCNPs at around 540 nm, which suggests that there will be a LRET process between them to quench the green emission of UCNPs. After addition of CN$^-$, the absorbance intensity bleaches dramatically after reaction with CN$^-$ (**Ir1**+CN$^-$), which will cause the LRET to be less effective and recover the green emission. Meanwhile, the red emission of UCNPs, which is not influenced by **Ir1**, can be taken as a reference to the green emission to allow ratiometric detection.

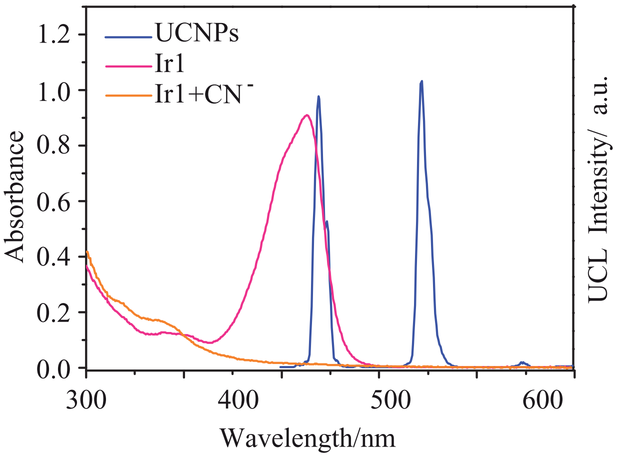
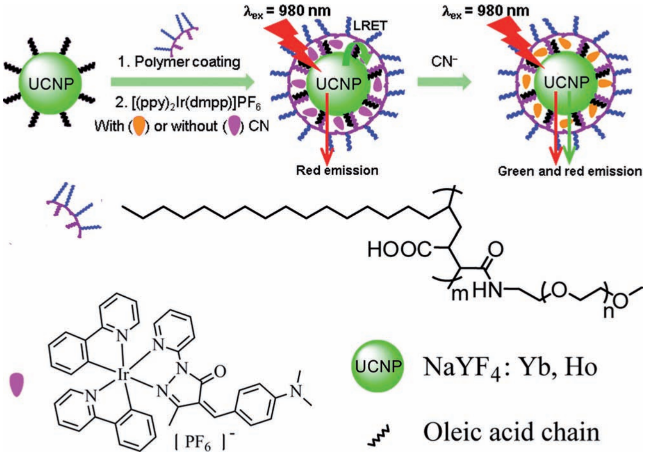


Figure 1. UV-vis absorption spectra of **Ir1** and **Ir1** upon addition of CN$^-$ and photoluminescence spectrum of UCNPs.



Scheme 2. Schematic illustration of the UCNPs-based color trigger system.

In order to fabricate a hybrid material composed of UCNPs and **Ir1**, we utilized a polymer-assisted self-assembly method.[62] The protocol is shown in **Scheme 2**. The as-prepared UCNPs have OA ligand on the surface. The carbon chains of the amphiphilic polymer have hydrophobic interactions with OA, therefore the polymer can be coated easily on the nanoparticles. After the coating process, a hydrophobic layer was formed between the UCNP surfaces and the hydrophilic layer of PEG moieties, so **Ir1** can get inside the hydrophobic layer in the second step through a basic mixing process.

Figure 2 shows transmission electron microscopy (TEM) image of the synthesized UCNPs and hybrid nanoparticles. The synthesized spherical UCNPs dispersed well in cyclohexane and had a diameter of about 20–40 nm. When coated with polymer and loaded with **Ir1**, the shape and size of the UCNPs did not change much and the hybrid materials could easily be dispersed by water. The composition and crystallinity of the UCNPs were investigated by X-ray diffraction. All diffraction peaks can be indexed to the hexagonal phase of NaYF$_4$ (JCPDS No.16-0334) (Figure 2g). Fourier transform infrared (FTIR) spectra were used to identify the specific groups in the polymer. In the FTIR spectra of PEG-UCNPs and **Ir1**-UCNPs (Figure S2, Supporting Information), the appearance of new peaks, located at 1262, 1024, and 802 cm^{-1} in the PEG-UCNPs and various additional peaks from 1686 to 556 cm^{-1} indicated the successful coating of C$_{18}$PMH-PEG and the modified **Ir1** on to the surface of the UCNPs. X-ray photoelectron spectroscopy (XPS) also suggested

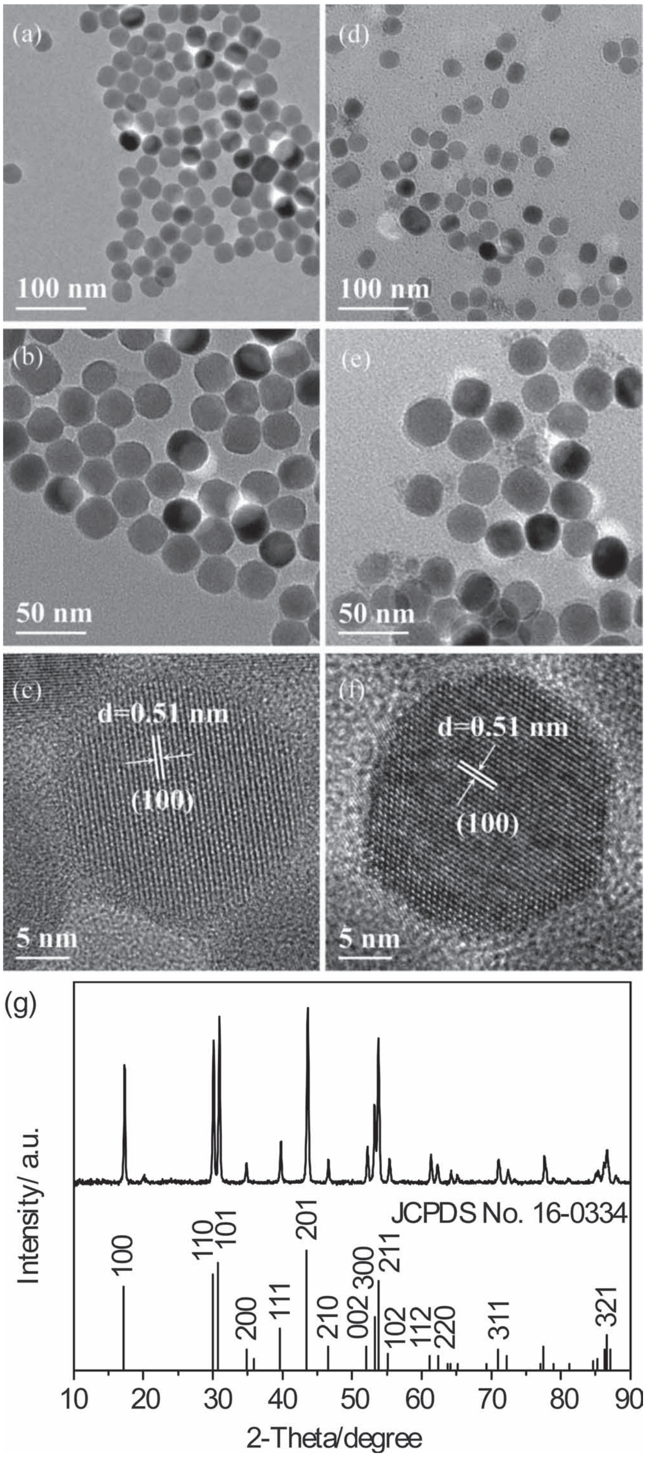


Figure 2. TEM images of UCNPs dispersed in cyclohexane (a–c), PEG-UCNPs dispersed in water (d–f), and XRD patterns of the synthesized UCNPs, the standard pattern of pure hexagonal $NaYF_4$ (JCPDS card No. 16-0334) (g).

that **Ir1** and UCNPs had been combined together in the final products (Figure S3, Supporting Information), by virtue of simultaneous observation of the elements Ir, Y, Yb, and F.

The amount of loaded **Ir1** in the hybrid material was determined by a UV-vis absorption technique. Because the hybrid materials were prepared by a self-assembly method based on the hydrophobic interaction, the polymer could easily break away from the UCNPs in an organic solvent such as chloroform or dichloromethane by ultrasonication if the loaded **Ir1** was dissolved in the solvent. By comparing the absorption intensity of the extraction solution with pure **Ir1** solutions with given different concentrations, the amount of **Ir1** in the extraction solution, that is, loaded-**Ir1** in the hydrophobic layer of the hybrid materials, was measured to be about 11.6 wt% (Figure S4, Supporting Information).

The colorimetric and luminescent responses of the nanosystem **Ir1**-UCNPs to cyanide ions are shown in **Figure 3**. The PEG-UCNPs dispersed well in water and formed a colorless solution. When **Ir1** was loaded, the aqueous solution of hybrid material changed to a dark red. The absorption peak located at 531 nm can quench the green upconversion emission of $NaYF_4$:Yb, Ho UCNPs in the hybrid materials, as shown clearly in the emission spectrum in Figure 3.

Moreover, the upconversion emission intensities were calculated to confirm the mechanism of energy transfer between UCNPs and **Ir1**. From emission spectra, the green UCL intensity decreased by a factor 84 in **Ir1**-UCNPs, compared to the

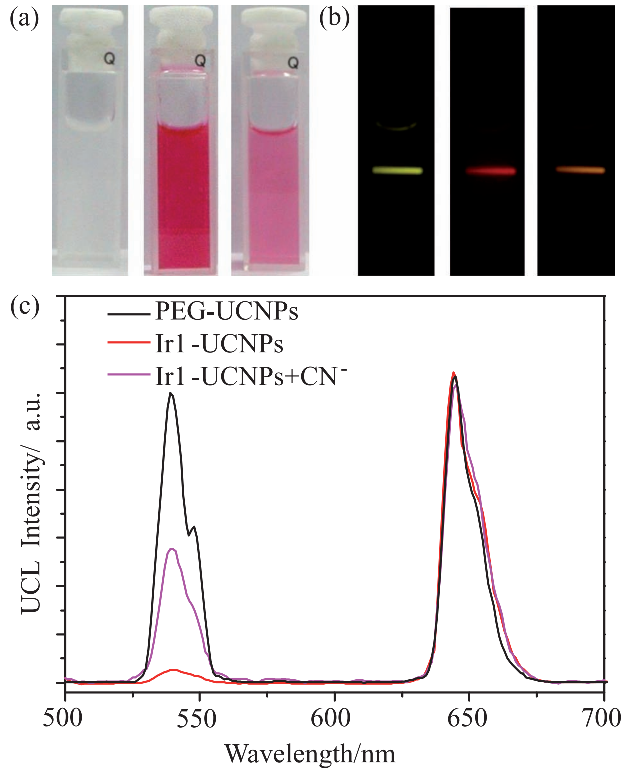


Figure 3. Photographs of water solutions (20 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer) of PEG-UCNPs, **Ir1**-UCNPs and after doped in 500 equiv. of CN^- (a). Corresponding photographs of emission (b) and photoluminescence spectra (c) of the materials with an excitation wavelength $\lambda = 980$ nm.

original UCNPs, while the absorption effect would only cause a 0.54-fold decrease of the green emission at 545 nm (calculated from A (absorbance) = 0.265, and the optical path of 0.5 cm). This result showed that the quenching effect in **Ir1**-UCNPs can be mainly attributed to the LRET process over a simply absorbed light process by **Ir1**. The LRET efficiency is approximately 98.7%, as deduced from the upconversion emission spectra of **Ir1**-UCNPs by the following equation:

$$E = 1 - \mathrm{UCL}_{\mathrm{Ir1-UCNPs}}/\mathrm{UCL}_{\mathrm{UCNPs}}$$

where E denotes the efficiency of quenching and $\mathrm{UCL}_{\mathrm{Ir1\text{-}UCNPs}}$ and $\mathrm{UCL}_{\mathrm{UCNPs}}$ are the integrated emission intensities from 520 to 560 nm of **Ir1**-UCNPs and UCNPs, respectively.

After addition of 500 equiv. of CN^-, the color of the **Ir1**-UCNPs solution weakened (Figure 3), which is in accordance with the dramatic decrease of the absorption peak at 531 nm shown in Figure 1. According to previous reports,[5,13] the color bleaching is assigned to chemical addition of CN^- to the α,β-unsaturated carbonyl site, corresponding to the disappearance of π-conjugation degree of the ligand for the iridium complex **Ir1**. Because the LRET efficiency is affected by the spectra overlap between the emission of energy donor and the absorption of energy accepter, the LRET effect was suppressed for **Ir1**-UCNPs upon addition of CN^-, resulting in the recovery of the green emission of the UCNPs (Figure 3).

These observations are clearly different from the complete recovery of luminescence observed in acetonitrile solution or other organic solutions. It can be understood as follows. The semipermeable and transparent nature of the matrix allows the cyanide to interact with **Ir1** through chemical addition of the cyanide anions to the α,β-unsaturated carbonyl site,[5,13] so the color intensity was reduced when the CN^- was added (as with the emission). However, **Ir1** in the hybrid material did not react completely, even when excess CN^- was present or when given a long time to react. These facts indicated that it is necessary for CN^- to permeate through the hydrophilic and hydrophobic layers of the coated polymer to react with **Ir1**, and CN^- do not permeate well through the hydrophobic layer. Therefore, the reaction mainly occurs in the outer part of the hydrophobic layer, but not completely.

For this reason, we studied the kinetic behavior of the reaction between **Ir1**-UCNPs and CN^- at different concentrations. The solution of **Ir1**-UCNPs (with concentration of **Ir1** at 10 μM, calculated as above) was adjusted to pH 7.0 in 20 mM HEPES buffer solution, with the addition of 10 equiv., 100 equiv., or 1000 equiv. of cyanide anions. As can be seen in **Figure 4**, the absorption intensity at 553 nm after 180 min was reduced to 85%, 64%, and 36%, respectively, compared to the initial intensity. From the kinetic behavior, we can clearly estimate the quantity of CN^- for titration to be several hundreds of equiv. and the time for reaction is rather longer than 180 min.

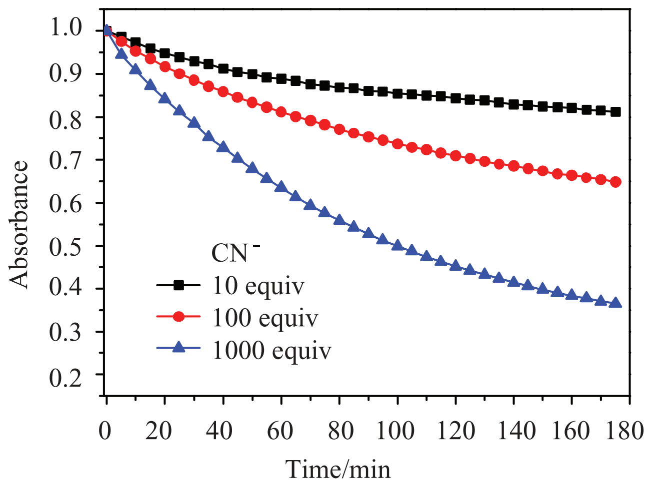


Figure 4. Absorption difference at λ_{max} versus the time at 25 °C.

By adding CN^- to a colored solution of hybrid materials (the calculated concentration of **Ir1** was 10 μM), the absorption at the wavelength λ_{abs} = 553 nm vanished gradually (**Figure 5**), which proposed the semiquantitative detection of CN^-. The absorbance bleached linearly with the CN^- concentration in the range 0 to 60 equiv., and the absorption change became slow after 100 equiv. cyanide anions were added. The detection limit was calculated to be 62.6 μM.

On the other hand, taking the green emission of the hybrid materials as the signal, there was a corresponding rise of the intensity at λ_{UCL} = 545 nm (**Figure 6**). The intensity increased linearly with the CN^- concentration in the range 0 to 60 equiv., in accordance with the result obtained in the absorbance measurement. Because the absorption of **Ir1** at 650 nm showed no obvious change during the addition of CN^-, the UCL emission band at 650 nm can be used as an internal standard to avoid the influence of changing concentration or other factors in the test process. The detection limit of the **Ir1**-UCNPs was estimated to be 37.6 μM using the green UCL emissions as detection signal (Figure S5, Supporting Information).

In addition to the sensitivity test, the selectivity of the anion sensing properties of the hybrid materials **Ir1**-UCNPs was also studied in solution by using water as solvent (HEPES,

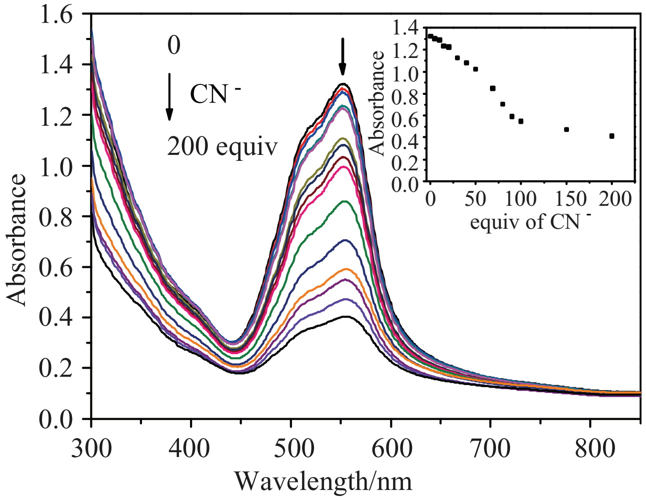


Figure 5. Absorption changes of **Ir1**-UCNPs with increasing amounts of cyanide in water. Inset: the absorbance at 553 nm.

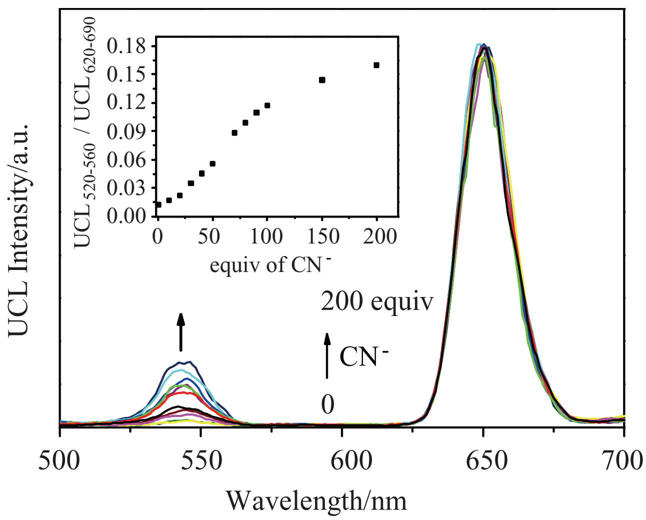


Figure 6. Emission intensity changes of **Ir1**-UCNPs with increasing amounts of cyanide in water. Inset: the ratio $\text{UCL}_{520}/\text{UCL}_{620}$ of the UCL emission bands.

20 mM). The anions selected for this study were NO_3^-, ClO_4^-, F^-, Cl^-, Br^-, NO_2^-, I^-, CH_3COO^-, SO_4^{2-}, and CN^-. A solution of the hybrid materials in water (10 μM) was treated with a fixed amount of different anions (300 equiv., aqueous form). Only the addition of CN^- caused an obvious change in the UV-vis absorption, with obvious bleaching of the red color (**Figure 7**), indicating that **Ir1**-UCNPs can selectively detect CN^- over other anions in pure aqueous surrounding.

3. Conclusion

In summary, we have demonstrated the fabrication of a cyanide-anions-responsive chromophoric iridium(III) complex modified $NaYF_4$: 20% Yb, 2% Ho upconversion nanophosphors and presented their utility as a colorimetric and upconversion luminescence ratiometric probe for cyanide detection. Using a self-assembly method based on hydrophobic–hydrophobic interaction, we have combined UCNPs, an amphiphilic polymer, and a CN-responsive Ir(III) complex in one nanosized hybrid structure to detect cyanide in pure water with high selectivity, based on a highly efficient LRET process. Although the proposed probe may not provide better sensitivity and detection limit than others reported in real use, the method is general and can be applied to similar chemodosimeters for the preparation of other probes that can be used in pure water.

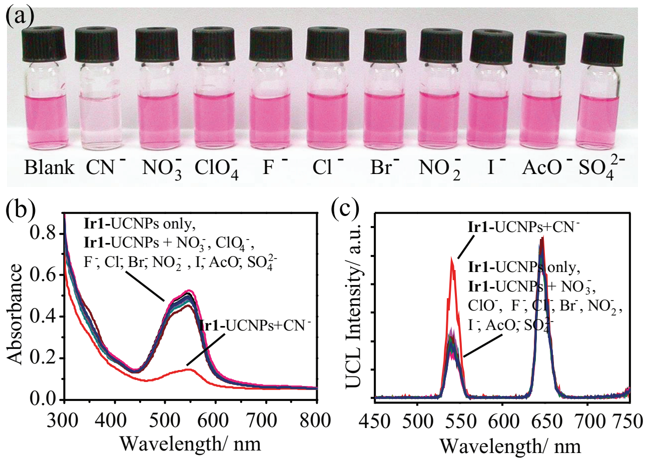


Figure 7. The photographs of color changes (a), absorption spectra (b), and UCL spectra (c) of **Ir1**-UCNPs in water upon addition 300 equiv. of various anions.

4. Experimental Section

Chemicals: Deionized water was used throughout. Rare earth oxides Y_2O_3 (99.999%), Yb_2O_3 (99.999%), Ho_2O_3 (99.999%), and Tm_2O_3 (99.999%) were purchased from Shanghai Yuelong New Materials Co. Ltd. OA and 1-octadecane (ODE 90%) were purchased from Alfa Aesar Ltd. Trifluoroacetic acid (99%), absolute ethanol, cyclohexane, chloroform, and dimethyl sulfoxide were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. All the materials were used without further treatment. $RE(CF_3COO)_3$,[63] $NaYF_4$:Yb, Ho UCNPs,[64] C_{18}PMH-PEG,[65] and ***Ir1***[5] were prepared according to the literature. The actual PEGylation ratio on the C_{18}PMH polymer was measured using NMR spectroscopy to be 86% (Figure S1, Supporting Information).

Synthesis of PEG-Functionalized UCNPs (PEG-UCNPs): In a typical procedure, C_{18}PMH-PEG (15 mg) and UCNPs (15 mg) were dispersed separately in chloroform (8 mL) and then mixed together and stirred for 2 h. After chloroform evaporated, the rest material dispersed easily in water. Large aggregates were removed by using a 0.22 mm syringe filters.[62]

Loading **Ir1** *in PEG-UCNPs*: **Ir1** (5 mg) dissolved in DMSO (50 μL) was added dropwise into of HEPES solution (2 mL, 20 mmol L^{-1}, pH 7.0) containing PEG functionalized UCNPs (20 mg). The solution was then stirred overnight. Free **Ir1** was removed by centrifugation at 14 000 rpm for 10 min. The precipitate was washed three times with HEPES by centrifugation. The as-obtained hybrid materials (**Ir1**-UCNPs) were re-suspended by a brief sonication to form a homogeneous clear solution and stored at 4 °C.

Instrumentation: Powder X-ray diffraction measurements were performed on a Bruker D4 diffractometer at a scanning rate of 1° min^{-1} with the 2θ from 10° to 80° (Cu Kα radiation, $\lambda = 1.54056$ Å). UCNPs were dispersed in cyclohexane or water and then dropped on the surface of a copper grid for TEM characterization, which was performed on a JEOL JEM-2010 low- to high-resolution TEM (HR-TEM) instrument operated at 200 kV. FTIR spectra were obtained using an IRPRESTIGE-21 spectroscope (Shimadzu) with KBr pellets. XPS experiments were carried out on a Perkin Elmer PHI-5000C ESCA system with Mg Kα radiation ($h\nu$ = 1253.6 eV) at a base pressure of 10^{-9} Torr. Upconversion luminescence spectra were recorded on an Edinburgh LFS-920 fluorescence spectrometer using an external 0–2 W adjustable continuous wave laser (980 nm, Connect Fiber Optics, China) as the excitation source, instead of the xenon source in the spectrophotometer. The images were obtained digitally on a Nikon multiple charge-coupled device (CCD) camera. UV-vis absorption spectra were measured using a Shimadzu UV-2550 ultraviolet-visible-near infrared spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer. Proton chemical shifts were reported in ppm downfield from tetramethylsilane (TMS).

Supporting Information

Supporting Information is available from the Wiley Online Library or fromt he author.

Acknowledgements

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