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Near-Infrared Luminescent Lanthanide MOF Barcodes

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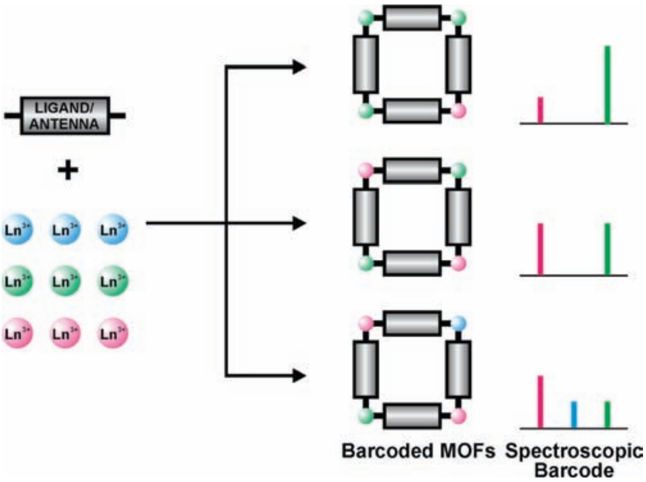
Barcoded materials are attractive as labels in multiplexed bioanalytical assays and as encryption tags.[1−9] Such systems provide an unambiguous way to recognize the identity of a biological entity or of an object. These materials can play an important role in applications related to national security purposes, such as tracking and identifying objects at airports, in transit, in storage, and on the battlefield. An ideal barcoded material should meet the following specifications: It should be robust and available in large scale, and its synthesis should be straightforward, highly reproducible, and configurable to provide numerous possible encoding combinations. In addition, its spectral signature should be easily and rapidly acquired and unambiguously interpreted with inexpensive and portable equipment.

In this communication, we report a new conceptual approach for creating luminescent barcoded systems based on the use of metal−organic frameworks (MOFs) that contain multiple near-IR (NIR)-emitting lanthanides and have well-controlled compositions and photophysical properties (Scheme 1).[10−18]

Luminescent lanthanide cations have unique advantages for the creation of barcoded luminescent materials. They exhibit sharp, nonoverlapping, and easily identifiable emission bands in both the visible[19] and NIR.[20] More specifically, they have much narrower bandwidths than organic fluorophores and semiconductor fluorescent nanocrystals (NCs) [Figure S6 in the Supporting Information (SI)]. In addition, the wavelengths of the emission bands of lanthanide cations are not affected by their environment,[21] unlike those of organic fluorophores and NCs, which may change emission wavelengths on the basis of conditions such as the nature of the solvent[22] or the pH. These advantages permit their use in various materials and solvents where their emission wavelength depends only on the nature of the lanthanide, not on its environment. Since free lanthanides have very low extinction coefficients, chromophoric molecules ("antennae") must be placed in close proximity to the lanthanides to allow for their sensitization so the compound can emit a sufficient number of photons for sensitive detection.[23] For practical applications, a common antenna for the sensitization of several different lanthanide cations would be advantageous in order to generate simultaneous emission of several wavelengths using one excitation wavelength. In addition, it would be beneficial if all of the lanthanide cations were embedded in a well-defined unit that could be well-characterized and would retain its properties over time. However, creating polymetallic lanthanide compounds with well-defined and easily reproducible structures is challenging.

Scheme 1. Controlled Preparation of Barcoded MOFs



The synthesis of barcoded polymetallic lanthanide complexes as MOFs addresses these challenges and is attractive for several reasons: (i) Unlike lanthanide-doped nanocrystals,[24−26] MOFs have easily characterizable crystalline structures, allowing for a high degree of spatial organization of multiple different cations[17,27] and organic sensitizers.[28] The crystalline nature of these materials allows for unambiguous determination of their structures in terms of the precise locations of the cations and sensitizers. This aspect permits reproducible formation of the material and rationalization of its luminescence properties on the basis of its structure.[18] (ii) MOFs have a high density of lanthanide cations and sensitizers and can therefore emit a large number of photons per unit volume.[18,29] Herein we report highly reproducible barcoded MOF materials with NIR emissions based on the controlled composition of MOFs incorporating several different lanthanide cations.

We recently reported two new Yb^{3+}-based MOFs (**Yb-PVDC-1** and **Yb-PVDC-2**) and demonstrated that we can (i) use the chromophoric group within these MOFs to sensitize Yb^{3+} and (ii) tune and optimize their luminescence properties by tailoring the MOF architecture.[18] We further showed that these materials have relatively long luminescence lifetimes and high quantum yields relative to other Yb^{3+}-based systems under solvent. Here we have adapted our synthesis of **Yb-PVDC-1** (Figure 1a) to yield barcoded frameworks containing both ytterbium and erbium. Yb^{3+} and Er^{3+} were chosen because they have very distinguishable emission profiles in the NIR. Specif-

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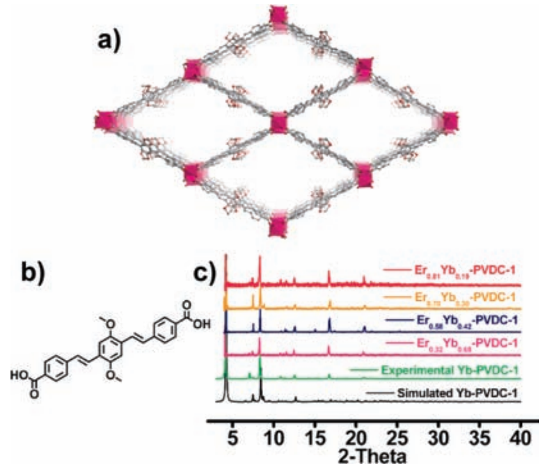

Figure 1. (a) Crystal structure of **Yb-PVDC-1** viewed along the crystallographic *c* axis. (b) **H_2-PVDC**. (c) PXRD patterns for **Yb-PVDC-1** and analogues **1**−**4**.

Table 1. Relative Ln^{3+} Content for the Er_xYb_{1-x}-PVDC-1 MOFs **1**−**4** during Synthesis (theor) and As Determined by EDS and ICP Analysis of the Final Product

	synthesis amount (mmol)		% Er^{3+}		
MOF	$Er(NO_3)_3$	$Yb(NO_3)_3$	theor	EDS[a]	ICP
1	0.00125	0.00250	33	32 (±2)	30
2	0.00375	0.00250	60	58 (±2)	63
3	0.00625	0.00250	71	70 (±2)	68
4	0.00625	0.00125	83	81 (±3)	78

[a] Errors are given in parentheses.

ically, we reacted 4,4′-[(2,5-dimethoxy-1,4-phenylene)-di-2,1-ethenediyl]bisbenzoic acid (**H_2-PVDC**) (Figure 1b), our chosen antenna, with $Er(NO_3)_3 \cdot 5H_2O$ and $Yb(NO_3)_3 \cdot 5H_2O$ to produce yellow needles of four luminescent frameworks with varying lanthanide ion stoichiometries: $Er_{0.32}Yb_{0.68}$-PVDC-1 (**1**); $Er_{0.58}Yb_{0.42}$-PVDC-1 (**2**); $Er_{0.70}Yb_{0.30}$-PVDC-1, (**3**); and $Er_{0.81}Yb_{0.19}$-PVDC-1, (**4**). Each framework is isostructural with **Yb-PVDC-1**, as revealed by comparison of their powder X-ray diffraction (PXRD) patterns (Figure 1c). The lanthanide compositions in the resulting products were determined by energy-dispersive X-ray spectroscopy (EDS), confirmed by inductively coupled plasma (ICP) analysis, and directly correlated to the amounts of each lanthanide salt used during the corresponding syntheses (Table 1). The EDS measurements were performed on a minimum of four independently synthesized samples for each MOF and showed highly reproducible results for each lanthanide composition. These results indicate that any desired lanthanide composition in the final product can be obtained in a predictable and reproducible fashion simply by controlling the stoichiometry of the reactants. Moreover, they suggest that the MOF structure does not preferentially include either lanthanide cation and thus that any Er/Yb ratio can be obtained. This predictable aspect of the synthesis is highly advantageous for a barcoded material, and in this case it allows for the preparation of multiple barcodes simply by varying the ratios of two emitters.

Photoluminescence studies were performed on each sample to determine whether the different lanthanide compositions would result in materials having unique and discernible barcoded signals. MOFs **1**−**4** were suspended in chloroform, and their respective excitation and emission spectra were recorded. The

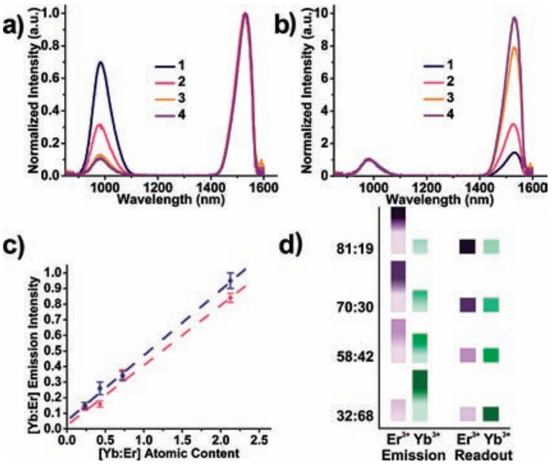

Figure 2. (a, b) Yb^{3+} (980 nm) and Er^{3+} (1530 nm) emission spectra recorded upon 490 nm excitation: (a) normalized to the Er^{3+} signal; (b) normalized to the Yb^{3+} signal. (c) Plot of the ratio of integrated emission intensities vs their atomic ratio as measured by EDS (blue, $\lambda_{ex} = 370$ nm; pink, $\lambda_{ex} = 490$ nm). (d) Color-coded schematic of the barcode readout.

MOFs displayed sharp signals from both erbium and ytterbium. The excitation spectrum of either the erbium or ytterbium emission band contains two similar bands with apparent maxima at 370 and 470 nm, as observed for **Yb-PVDC-1**. These results indicate that the chromophore embedded in the MOF is able to sensitize these two different cations. Excitation through either of these bands simultaneously produces the characteristic Yb^{3+} emission band centered at 980 nm and the Er^{3+} band centered at 1530 nm. As expected, with an increase in the amount of Er^{3+} and a decrease in the amount of Yb^{3+}, their respective emission intensities increase and decrease accordingly (Figure 2a,b). Thus, we have demonstrated that by controlling the lanthanide composition, we can quantitatively control the resulting luminescence intensities of the individual signals of the two NIR-emitting lanthanide cations.

A plot of the ratio of the integrated intensities of the emissions of the two different lanthanides with respect to the metal cation ratio reveals a linear relationship between 32:68 and 81:19 Er/Yb (Figure 2c). This trend is similar when either excitation band is used and reproducible across multiple samples. This feature provides the advantage of offering two excitation wavelengths for verifying the authenticity of an encryption tag. Importantly, PXRD showed that these materials maintained their crystallinity throughout the photoluminescence experiments (Figures S2−S4 in the SI), demonstrating the possibility for extended use, which is another important requirement for applications. To facilitate interpretation, we generated a color-coded barcode readout (Figure 2d), because the Er^{3+} and Yb^{3+} luminescence bands in the NIR range cannot be detected by the naked eye. Therefore, the signal can be monitored only spectroscopically, and the signal intensities must be artificially correlated with two different visible colors for facile human interpretation and quantification. Here, purple was used to represent the Er^{3+} signal and green the Yb^{3+} signal. Their relative intensities are reflected in the display, creating four distinct barcodes, one correlating to each MOF.

The number and diversity of barcodes can be increased by using a larger number of Ln/Ln ratios or by incorporating additional lanthanide cations into the material. As a first step in this direction, we demonstrated the latter concept by preparing

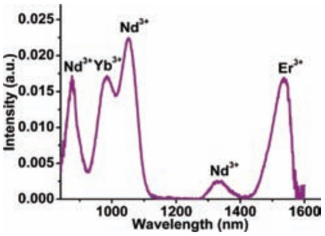

Figure 3. Yb^{3+}, Er^{3+}, and Nd^{3+} emission from **5** ($\lambda_{ex} = 490$ nm).

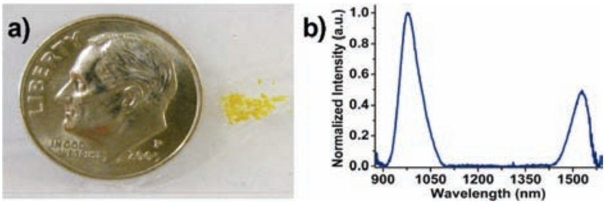

Figure 4. (a) Sample of **2** dried and glued to a microscope slide (the dime is included for size perspective). (b) Yb^{3+} (980 nm) and Er^{3+} (1530 nm) emission spectra for this sample ($\lambda_{ex} = 490$ nm).

$Nd_{0.09}Er_{0.55}Yb_{0.36}$-PVDC-1 (**5**). As expected, it displays a more sophisticated barcode signal consisting of NIR signals from its three component lanthanide cations (Figure 3). We are currently preparing additional barcoded MOFs incorporating Nd^{3+}. We note, however, that predicting the resulting Nd^{3+} content of these materials may be less straightforward than the Er^{3+}/Yb^{3+} materials because of possible size selectivity.

For practical applications, barcoded materials need to be incorporated into objects (e.g., money or clothing) in ways that do not detrimentally affect their signals. To evaluate this possibility, we coated **2** in Superglue (Figure 4a) and observed that upon excitation at 490 nm, the Yb^{3+}/Er^{3+} barcode was easily detected in the NIR range (Figure 4b).

In conclusion, we have created a new barcoded system based on polymetallic lanthanide MOFs that simultaneously emit several independent NIR signals arising from different lanthanide cations. We have demonstrated that by controlling reactant stoichiometry we can predict and tune the lanthanide composition of the MOF and therefore control the resulting individual emission intensities. Further, we have shown that excitation at a single wavelength produces concurrent ytterbium and erbium emission bands that are linearly correlated to the lanthanide ratio. Investigation of the possible ytterbium-to-erbium energy transfer for these systems is currently underway and will be presented at a later time. Er_xYb_{1-x}-PVDC-1 MOFs have the required properties to serve as barcoded luminescent materials, and we expect that these materials and others produced using the concepts presented herein will be useful for many practical applications.

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Supporting Information Available: Experimental procedures and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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