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Heteroepitaxial Growth of Multiblock Ln-MOF Microrods for Photonic Barcodes

Yinan Yao⁺, Zhenhua Gao⁺, Yuanchao Lv, Xianqing Lin, Yingying Liu, Yuxiang Du, Fengqin Hu,* and Yong Sheng Zhao*

Abstract: Micro/nanoscale multicolor barcodes with unique identifiability and a small footprint play significant roles in applications such as multiplexed labeling and tracking systems. In this work, we report a strategy to design multicolor photonic barcodes based on 1D Ln-MOF multiblock heterostructures, where the domain-controlled emissive colors and different block lengths constitute the fingerprint of a corresponding heterostructure. The excellent heteroepitaxial growth characteristics of MOFs enable the effective modulation of the coding structures, thereby remarkably increasing the encoding capacity. The as-prepared multicolor barcodes enable an efficient authentication and exhibit great potential in fulfilling the functions of anti-counterfeiting, information security, and so on. The results will pave an avenue to novel hybrid MOFs for optical data recording and security labels.

Micro/nanoscale barcodes have attracted great attention due to their promising applications in multiplexed bioassays, materials tracking, and information security.^[1] The ever-increasing demand for high security level in anti-counterfeiting applications calls for micro/nanoscale multicolor barcodes with accurate recognition and high encoding capacity.^[2] One-dimensional (1D) segmented structures with domain-controlled colors, can be readily distinguished by the identifiable patterns, which have shown great potential for achieving multicolor barcodes.^[3] Recently, the 1D segmented structures have been demonstrated inorganic semiconductors through integrating emitting in components with distinct optical bandgaps.^[4] Unfortunately, these materials with strong covalent or ionic bonds always require fabrication conditions of (ultra-)high temperature and vacuum. Compared with their inorganic counterparts, organic materials, with excellent flexibility and processability, have also been utilized to construct numerous 1D segmented structures with various optoelectronic functionalities.^[5] However, the fabricated structures often suffer from low thermal instability due to the weak intermolecular interactions, which would hinder their practical applications.

Metal-organic frameworks (MOFs), a kind of crystalline

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[*] These authors contributed equally to this work. Supporting information for this article is given via a link at the end of the document. materials constructed from metal ions and organic linkers,^[6] not only possess the high stability of inorganic materials but also ensure the excellent processability of organic materials, representing an effective solution to the above problems. For example, the outstanding ability to flexibly self-assemble into various 1D micro/nanostructures,^[7] such as wires, tubes, and rod, makes MOFs a fundamental model for designing novel optical barcodes. The versatile spectra from luminescent MOFs, which origins from the organic ligand or metal ion, enable the generation of a large library of optical encoding.^[8] In addition, the excellent compatibility of MOFs allows for fabricating hybrid nanostructures, making it possible to integrate different identifiable patterns in a single nanostructure.^[9] Especially, incorporating diverse lanthanide (Ln) ions with a series of wellresolved emission peaks, would offer a good platform for digital encoding.^[10] Therefore, the 1D Ln-MOF heterostructures would provide an innovative encoding scheme for the development of multicolor barcodes with high coding capacity.

Herein, we propose a strategy to design microscale barcodes with high coding capacity based on the 1D Ln-MOF multiblock heterostructures, which were prepared through a stepwise epitaxial growth. The as-prepared Ln-MOF heterostructures exhibit the domain-controlled emissive colors and identifiable block lengths, which constitutes the intrinsic fingerprint of a heterostructure and allows for the definition of a practical barcode. Furthermore, the well controllable growth of Ln-MOFs enabled us to obtain distinct barcodes through tuning the block lengths and the number of blocks in the heterostructures, which remarkably enlarges the encoding capacity. The as-designed microscale barcodes facilitate an efficient authentication and exhibit great potential in fulfilling data recording and information tracking. These results offer a comprehensive understanding of the function-oriented construction of hybrid MOF materials and open up a new way to achieve miniaturized security labels.

The strategy for multicolor barcodes based on Ln-MOF heterostructures is schematically illustrated in Figure 1a. Under UV radiation, spatially separated colors are emitted along the 1D Ln-MOF heterostructures. When each segment of the heterostructure is excited locally with a focused laser beam, the photoluminescence (PL) spectra of each block exhibits the specific sharp peaks corresponding to characteristic emission bands of the Ln ion, which constitutes a fingerprint of the structure and might be utilized to create a multicolor barcode. Moreover, the doping flexibility during the growth of MOFs allows to modulate the geometry of the heterostructures by alternately introducing different Ln ions, which may endow the multicolor barcodes with high coding capacity. Therefore, controlled preparation of 1D Ln-MOF heterostructures with axially tunable composition is a necessary prerequisite for producing multicolor barcodes.

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Here, 1,3,5-benzenetricarboxylic acid (BTC) was selected as organic linker to construct 1D Ln-MOF heterostructures due to the following reasons: (1) the self-assembly of BTC and Ln ions would benefit the construction of 1D microrod owing to their 1D preferential packing interactions (Figure S1-2),^[7b] providing the fundamental building blocks for the fabrication of 1D Ln-MOF heterostructures; (2) the Ln-BTC MOFs exhibit characteristic lanthanide-centre luminescence due to the effective ligand-tometal energy transfer process (Figure S3); (3) different Ln-BTC MOFs with distinct emission characteristics show the isomorphous structures (Figure 1b, Table S1). making it possible to realize the 1D multicolor Ln-MOF heterostructures without lattice mismatch;[11] (4) The Ln-MOFs demonstrate excellent thermostability and high stibility under various environments, which enable their applications as security labels (Figure S4-6).



Figure 1. (a) Schematic illustration of a multicolor barcode based on a single Ln-MOF heterostructure. (b) X-ray powder diffraction (XRD) patterns of the simulated Tb-BTC, the Ln-BTC. The XRD patterns of Ln-BTC powder well match those of the simulated results from the single crystal diffraction of Tb-BTC, clearly indicating that pure Ln-BTC phase was obtained and the two kinds of MOFs have the isomorphous structures. (c) Schematic representation of the epitaxial growth process in a solvothermal reactor containing seeding crystals, BTC and different Ln ions. (d-f) PL images of the triblock heterostructures showing visually emissive colors. UV band (330-380 nm) of a mercury lamp was used to excite the samples. Scale bars are 10 µm.

The 1D multicolor Ln-MOF heterostructures were fabricated via a facile stepwise solvothermal synthesis (Figure 1c). In a typical preparation, Tb-MOFs with green emitting colors were initially synthesized, which can be used as seeds for the growth of the second MOF. Then the solution of Eu³⁺ ions was subsequently added into the as-prepared Tb-MOF microcrystals. The isostructural Ln-MOFs with high crystallinity can be beneficial for the epitaxial growth of the Eu-MOFs (Figure S7). After aging for 2 hours, the hybrid Ln-MOF microstructures were

finally obtained. As shown in Figure 1d, the as-assembled Ln-MOF microstructures exhibit red-green-red triblock heterostructures under UV radiation, which confirmed the successful epitaxial growth of the preformed MOFs. The scanning electron microscopy (SEM) image (Figure S8) reveals that the Ln-MOF heterostructures exhibit 1D microrod-like morphology with smooth and continuous surface, confirming the strong coordination interaction at interfaces without lattice mismatch.

According to the step-by-step assembly process, the emissive color of each segment strongly depends on the composition of the corresponding block. Therefore, by adjusting the emissive centers in each segment, we could modulate the diversity of the multicolor heterostructures. For instance, the green-red-green triblock heterostructures can be further acquired by changing the addition sequence of the Ln ions precursors into the reaction (Figure 1e). In addition, PL of the mixed Ln-MOFs has been proved to be tuned through controlling the proportional variation of Eu³⁺ and Tb³⁺ in the host frameworks.^[12] Here, the mixed Ln-MOFs with highly efficient orange luminescence were fabricated by co-doping Eu³⁺ ions into the Tb-BTC host microrods (Figure S9). The elemental mapping results indicate that the Eu distribution is nearly overlapped with Tb mapping, suggesting that Eu³⁺ ions are well dispersed within the Tb-BTC microrods (Figure S10). The obtained mixed Ln-MOFs can subsequently act as seeds for the epitaxial growth of the Eu-MOFs, resulting in the formation of the red-orange-red triblock heterostructures (Figure 1f). These as-prepared multicolor microstructures exhibit excellent emissive colors, which should be attributed to the efficient ligand-to-metal energy transfer in each segment.



Figure 2. (a) Jablonsky energy level diagram for schematic illustration of the ligand-to-metal energy transfer process. (b) Bright-field and PL images of a Ln-MOF heterostructure. Scale bar is 10 μ m. (c) Schematic illustration of a heterostructure excited with a focused laser beam. (d-f) The corresponding PL

spectra collected from three different areas (marked as 1, 2, 1' shown in Figure 2c).

Figure 2a depicted the energy transfer process between BTC and Ln ions according to their intrinsic energy levels. The organic ligand BTC with high molar absorption coefficient can efficiently absorb the energy of the excitation light, resulting in the transition to its singlet state (30488 cm⁻¹).^[7b] The gap (6098 cm⁻¹) between the singlet and triplet excited states (24390 cm⁻¹) of BTC is favorable for an efficient intersystem crossing process, according to Reinhoudt's empirical rules.^[13] Furthermore, the energy level of the triplet excited state matches well with the ⁵D₀ of Eu³⁺ and ⁵D₄ of Tb³⁺, which would facilitate energy transfer from BTC to these Ln ions, and thus lead to the strong luminescence with a high quantum yield (Figure S11).

The segregated Ln-MOF heterostructures with recognizable features provide an opportunity to encode each microstructure. Taking the Tb@Eu-MOF microcrystal as an example (Figure 2b), the PL of a single heterostructure at different micro-area was characterized with а home-built far-field microphotoluminescence system (Figure S12). Each part (marked as 1, 2, 1' in Figure 2c) of the heterostructure was selectively focused and excited with a continuous-wave (CW) laser beam (375 nm), and the corresponding PL spectra were exhibited in Figure 2d-f. The two red-emitting tips (1 and 1') show a series of sharp peaks located at about 590, 615, 652 and 700 nm, corresponding to the transitions from ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1, 2, 3 and 4, respectively) of Eu³⁺ centers. By contrast, the middle greenemitting block (marked as 2) exhibits four sharp peaks located at about 487, 543, 580 and 620 nm, which are ascribed to the transitions from ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 6, 5, 4 and 3, respectively) of the Tb³⁺ ions. These sharp peaks constitute the fingerprint of a specific microstructure; therefore, we can distinguish each microstructure based on their intrinsic PL spectrum, just like the recognition of the commodity by a specific barcode. A typical barcode contains a series of black bars with different widths representing consecutive digits. The obtained Ln-MOF heterostructures are ideally suited for spectroscopic encoding based on these well-resolved PL spectra. Here, the barcodes are defined as follows: each solid bar is located in the wavelength position, and the bar width is defined by the relative PL intensity of the same wavelength. Therefore, the PL spectrum from each segment can be expediently converted into a specific barcode, which would enable the digital identification of each segment in the heterostructure.

In addition to the spectroscopic encoding based on the recognizable PL spectra, each segment with different colorlength endows the heterostructure with length-encoded character, which provides a platform to develop graphical encoding. As shown in Figure 3a, according to different block lengths in the heterostructure, the as-designed barcodes were compressed with the corresponding length ratio, which can be defined as the sub-barcodes. The built-up barcode was subsequently generated by combining the three parts of the sub-barcode and the Ln-MOF heterostructure, thus we can deduce a specific barcode from a Ln-MOF heterostructure by integrating the spectroscopic and graphical encoding. The encoding information of a specific barcode strongly depends on both the PL spectra and block length of each segment. Therefore, effective modulation of the coding structures is essential to the generation of distinct barcodes.

According to the above-mentioned growth mechanism, the Ln-MOF heterostructures with specific block length is resulted from the flexible co-assembly process of the Ln ions and the organic ligand. The length of each segment is primarily associated with the concentration of the precursor solutions. It was found that the increase of the precursor concentration would induce the formation of longer 1D MOFs (Figure S13), making it possible to produce multiblock heterojunctions with tunable length of each block. In a typical synthesis, the seeds with approximately uniform length were first synthesized, and subsequently, by tuning the concentration of the epitaxy precursor solution (the epitaxy precursor-to-seed molar ratio: 0.3, 0.6, 1.0, respectively), the red-green-red triblock heterostructures with different block lengths were successfully obtained (Figure 3b-d). Therefore, the optimized assembly method provides opportunity for controllably fabricating diverse Ln-MOF heterostructures, which enables the production of countless unique and irreproducible barcodes (Figure 3e-g).



Figure 3. (a) Schematic illustration of the encoding strategy based on the Ln-MOF heterostructure. (b-d) PL images of segmented structure with varied block lengths. The block length can be precisely controlled by adjusting the epitaxy precursor-to-seed ratio in the reaction system. Scale bars are 10 μ m. (e-g) Different barcodes corresponding to the heterostructures in Figure b-d. (h) Schematic illustration for the epitaxial growth of the penta-block structures. (i) PL image of the 1D penta-block heterojunctions. Scale bar is 5 μ m. (j, k) The magnified PL image and corresponding barcode of the structure. Scale bar is 5 μ m.

Benefiting from the flexible stepwise co-assembly process, the heterojunctions with more blocks might be fabricated via a multi-step assembly process (Figure 3h), which would further

increase the coding capacity. For instance, by feeding the triblock Tb@Eu-MOFs heterostructures again with the precursor of Tb³⁺ ions in the reaction system, we were able to synthesize 1D penta-block heterostructures exhibiting alternate green/red emissions (Figure 3i, j). Based on the proposed coding rule, the barcode with more encoding information can be generated as shown in Figure 3k. Considering the diversity and flexibility of the multicolor-banded microstructures, these tiny barcodes are expected to be expediently identifiable and difficult to replicate, showing great potential to function as the "security tag" with practical anti-counterfeiting applications.^[14]

The application of as-prepared Ln-MOF heterostructures as barcodes in commodity circulation is demonstrated in Figure 4. As a proof-of-concept illustration, a Ln-MOF heterostructure was embedded into an artwork as the "security tag" by the manufacturer (Figure 4a). The corresponding PL spectrum and length information of each segment were recorded from the Ln-MOF heterostructure (Figure 4b). According to the coding rule, the Barcode-1 can be acquired. The Barcode-1 was further input into a cloud for future reference (Figure 4c), and then the artwork, together with the tag, went into circulation (green arrow). The Barcode-2 can be obtained by means of encoder from the heterostructure and input into the cloud for an online inquiry (Figure 4d-g). If Barcode-2 is consistent with the Barcode-1, the matching result is TRUE, confirming that the artwork is authentic; otherwise, the artwork is counterfeit. Furthermore, the multicolor Ln-MOF barcodes generated from the specific synthetic methods and encoding rules can enhance the security protection, which can further be extended to other secret media, such as identity documents and banknotes.



Figure 4. Proof-of-concept demonstration of a Ln-MOF heterostructure-based multicolor barcode for artwork anti-counterfeiting. (a–c) The acquisition procedure of Barcode-1 before circulation. (a) Digital photograph of an artwork

with a Ln-MOF heterostructure. (b) PL spectra of the heterostructure collected from different blocks. (c) Obtained Barcode-1 generated from the spectra shown in (b) according to the coding rule. An authenticated artwork can circulate in the supply chain (green arrow). The unknown artwork may be introduced directly to the purchaser (red arrow). (d) Digital photograph of an unknown artwork with a heterostructure. (e) PL spectra of the heterostructure from the unknown artwork. (f) The Barcode-2 generated from the spectra in (e). (g) The comparison between Barcode-1 and Barcode-2 for artwork authentication.

In summary, we have constructed a type of Ln-MOF for multicolor barcode. heterostructure The Ln-MOF heterostructures were controllably fabricated by using a stepwise heteroepitaxial growth. The as-prepared Ln-MOF demonstrated distinct multiblock emissive colors that constitute a unique signature of the heterostructure and allow for the definition of a barcode. Different barcodes were designed through modulating the types of the heterostructure, which can further increase the coding capacity. Moreover, the as-designed microscale barcodes can enhance the security as the labels and exhibit great potential in anti-counterfeiting applications. We hope these results would provide enlightenment for the rational design and controllable synthesis of hybrid MOFs with precise heterostructures for applications of data recording and information security.

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Keywords: heteroepitaxial growth • Ln-MOF • metal-organic framework • photonic barcodes • anti-counterfeiting

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