Viologen Guest-Mediated Luminescence Emission Tuning and Photochromic Behavior by a Series of Viologen@Zn-MOF Materials

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ABSTRACT: The encapsulation of various guest molecules into the pores of metal-organic frameworks (MOFs) to form hybrid materials has attracted significant attention due to their unique spatial distribution and certain preferential geometry of the guests inside the MOFs. This arrangement often results in the guests exhibiting unique physical and chemical properties due to their intramolecular interactions with the host. In this article, five viologen derivatives were introduced as guests in a Zn-MOF with different benzene ring lengths, resulting in the formation of host-guest three-dimensional (3D) MOFs. The five compounds exhibited guest-dependent emission wavelength, color, and excellent photochromic behavior upon ultraviolet (UV) light radiation due to the distinct electronic transfer and $\pi \cdots \pi$ stacking interactions between the viologen guests and the host framework. This study provides a host-guest strategy for designing color-tunable luminescent and highly sensitive photochromic materials.



KEYWORDS: host–guest, viologen-based MOFs, $\pi \cdots \pi$ stacking interactions, modulating emission, photochromic behavior

1. INTRODUCTION

Electron transfer (ET) smart materials, such as tunable luminescent and photochromic materials based on a host– guest platform, have attracted significant attention due to their potential applications in light sensing, detectors, information storage, anticounterfeiting, and others.^{1–3} Various host–guest platforms have been documented through well-developed design and synthesis technology.^{4–6} The luminescent and photochromic properties of the materials depend on their components and the interactions between hosts and guests. Consequently, researchers can exercise significant control over these and other chemical and physical properties. Therefore, selecting hosts and guests and designing an ideal host–guest platform are key to controlling the physical and chemical properties of the materials.

Metal–organic frameworks (MOFs) are well-developed crystalline porous materials self-assembled from inorganic nodes and organic ligands. They have been extensively used in catalysis, chemical sensing, biomedicine, and other fields owing to their significant chemical stability and high surface areas.^{7–9} Moreover, the crystalline structures, pore sizes, and functionality of MOFs can be modulated at the molecular level by choosing the appropriate organic components, making them promising candidates as donors. Further, viologen derivatives, as cationic electron-deficient organic ligands, can react sensitively and rapidly to various external stimuli accompanied by a wealth of coloration phenomena. Previously, different smart materials have been constructed using viologen

derivatives.^{10–12} Hence, it is a logical choice to construct ET smart materials with MOFs as hosts and viologen ligands as guests.^{13–16}

Previous studies have demonstrated that loading different functional guest molecules into MOFs results in tunable emission colors via intermolecular interactions between the guest molecules and the MOF skeleton. This tunable color property has been used in sensing and luminophore applications.^{17–19} For example, Bu et al. loaded a series of electron-rich aromatic guests into an electron-deficient MOF, realizing charge-transfer-based emission color changes.²⁰ Li et al. presented a new strategy to encapsulate multiple dyes into nanocrystalline ZIF-8 pores. Using this strategy, they achieved a finely tuned white emission color by varying the components and concentrations of encapsulated dyes.²¹

These reports demonstrate that viologens present in the pores of MOFs can significantly impact emissions from electronic interactions between viologens and the framework. However, reports of viologen guest molecules modulating the emission color are rare. Furthermore, the photoluminescence (PL) modulations of some ET smart materials are limited to

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Figure 1. (a) Preparation of Zn-MOF-0. The coordinate DMA molecules are omitted for clarity. (b) Five viologen molecules used in this study (arranged by length). (c) Encapsulation of guest molecules forming host-guest materials.

simple on/off switching with coloring/bleaching behaviors, with no change in the emitted colors.^{22–24} Most viologenbased MOFs are reported to be sensitive to ultraviolet (UV) light. They can detect sunlight with a minimum detection intensity of 1 μ W/cm⁻² (Table S1).^{25,26} Natural and room light detection by the viologen-based MOFs are rarely reported due to the high detection limit toward UV light. In addition, the reported sensors for UV light decolor to the original color expending several tens of hours or even several days, restricting their convenience and portability in daily life (Table S2).^{22–26}

Herein, a three-dimensional (3D) Zn-MOF containing well–defined two-dimensional (2D) channels was utilized as a host framework. Five viologen molecular derivatives served as guest molecules, forming host–guest materials. Consequently, these five host–guest materials, named Zn-MOFs-1–5 based on viologen molecules, revealed highly tunable guest-dependent emissions from green to yellow and excellent photo-chromic properties. Further, Zn-MOF-3 detected natural and room light with a minimum detection intensity of 0.1 μ W/ cm⁻², successfully developed in photosensitive reagents' warning labels. Zn-MOF-1 showed fast recovery from the color saturation state to the initial color state toward UV light and could be used as a portable UV-sensitive card for UV light detection.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Zn-MOFs-0–5. 2.1.1. $[Zn_4(pdda)_2(H-DMA)-(H_2O)_2(OH)]\cdot[DMA]_5$ (Zn-MOF-0). Colorless single crystal blocks of Zn-MOF-0 were obtained by the solvothermal reaction of the mixture of ZnCl₂·6H₂O (0.05 g, 0.1 mmol), 5,5'-(pyridine-3,5-diyl)-diisophthalic acid (0.025 g, 0.06 mmol, H₄pdda), N,N-dimethylace-tamide (DMA) (2.0 mL), and water (3.0 mL) in a 15 mL Teflon-

lined autoclave which was heated to 130 °C for 3 days. Subsequently, the autoclave was slowly cooled to 20 °C at 4 °C·h⁻¹. The crystals were collected by filtration. Yield: 36% based on H₄pdda. Elemental analysis: calcd (%) for $[Zn_4O_{25}N_8C_{66}H_{79}]$ (including disordered solvent molecules): C 48.19, H 4.74, and N 6.81; found: C 49.26, H 4.25, and N 6.53. FT-IR (cm⁻¹) (Figure S1): 3388(w), 1618(s), 1572(s), 1432(m), 1403(m), 1355(s), 1317(w), 1274(s), 1182(w), 1112(w), 1079(w), 1091(w), 928(m), 806(m), 776(s), 728(s), 657(s), and 632(w).

2.1.2. $[Zn_8(pdda)_4(DMA)(H_2O)_7(OH)_2]^{2-} \cdot [DdMA]_{10}$ (*Zn*-*MOF-1*). Light yellow single crystal blocks of Zn-MOF-1 were obtained by the solvothermal reaction of the mixture of ZnCl₂·6H₂O (0.05 g, 0.1 mmol), H₄pdda (0.025 g, 0.06 mmol), 1,1'-diethyl-[4,4'-bipyridine]-1,1'-diium.dibromide (debpy·Br₂, 0.02 g, 0.05 mmol), *N*,*N*-dimethylacetamide (DMA) (2.0 mL), and water (3.0 mL) in a 15 mL Teflon-lined autoclave which was heated to 110 °C for 1 day. Subsequently, the autoclave was slowly cooled to 20 °C at 4 °C·h⁻¹. The crystals were isolated by filtration, which were washed with DMA and then dried in air. Yield: 19% based on debpy·Br₂. Elemental analysis: calcd (%) for $[Zn_8O_{51}N_{17}C_{142}H_{169}]$ (including disordered solvent molecules): C 49.39, H 4.90, and N 6.90; found: C 49.85, H 4.25, and N 6.62. FT-IR (cm⁻¹) (Figure S2): 3371(w), 1615(s), 1571(s), 1396(s), 1353(s), 1271(s), 1181(m), 1080(m), 1012(m), 924(m), 820(m), 772(s), 725(s), 651(s), and 564(m).

2.1.3. **Zn-MOF-2**. Yellow single crystal strips of Zn-MOF-2 were obtained by the solvothermal reaction of the mixture of ZnCl₂·6H₂O (0.05 g, 0.1 mmol), H₄pdda (0.025 g, 0.06 mmol), 150 μ L of a H₂O solution of 4,4'-(1,4-phenylene)bis(1-ethylpyridin-1-ium)·dibromide (0.1 g/mL, pbepy·Br₂), *N*,*N*-dimethylacetamide (DMA) (2.0 mL), and water (3.0 mL) in a 15 mL Teflon-lined autoclave which was heated to 110 °C for 1 day. Subsequently, the autoclave was slowly cooled to 20 °C at 4 °C·h⁻¹. The crystals were isolated by filtration, which were washed with DMA and then dried in air. Yield: 16% based on pbepy·Br₂. FT-IR (cm⁻¹) (Figure S3): 3381(w), 3219(w), 1615(s), 1571(s), 1430(m), 1403(m), 1356(s), 1275(s), 1184(m),

 $1110(m),\ 1019(m),\ 924(m),\ 803(s),\ 776(s),\ 725(s),\ 655(s),\ and 567(m).$

2.1.4. $[Zn_5Cl_2(pdda)_2(OH)_2]^{2-} \cdot [Dbk]^{2^+} \cdot [DMA]_5$ (*Zn-MOF-3*). Yellow single crystal blocks of Zn-MOF-3 were obtained under the same reaction conditions as those for Zn-MOF-1, except for replacing debpy·Br₂ with 1,1'-dibenzyl-[4,4'-bipyridine]-1,1'-diium·dichloride (dbbpy·Cl₂) (0.01 g, 0.02 mmol). The crystals were isolated by filtration, which were washed with DMA and then dried in air. Yield: ca. 23% based on dbbpy·Cl₂. Elemental analysis: calcd (%) for Zn₅Cl₂O₂₃N₉C₈₆H₈₅ (including disordered solvent molecules): C 51.39, H 4.23, and N 6.27; found: C 51.64, H 4.04, and N 6.37. FT-IR (cm⁻¹) (Figure S4): 3523(w), 3293(m), 3055(m), 1618(s), 1568(s), 1430(m), 1406(m), 1362(s), 1353(s), 1275(m), 1072(m), 921(m), 823(m), 820(m), 776(s), 739(s), 655(s), and 564(m).

2.1.5. $[Zn_8(pdda)_4(H_2O)_8[OH]_2]^{2-} \cdot [pbbpy]^{2+} \cdot [DMA]_6$ (Zn-MOF-4). Flat-shaped yellow single crystals of Zn-MOF-4 were obtained under the same reaction conditions as Zn-MOF-0, except for adding 1,1"-(1,4-phenylenebis(methylene))bis(([4,4'-bipyridin]-1-ium))·dichloride (pbbpy·Cl₂) (0.01 g, 0.02 mmol). The crystals were isolated by filtration, which were washed with DMA and then dried in air. Yield: ca. 14% based on pbbpy·Cl₂. Elemental analysis: calcd (%) for [Zn₈O₄₈N₁₂C₁₃₆H₁₂₈] (including disordered solvent molecules): C 50.72, H 3.97, and N 5.22; found: C 50.09, H 3.85, and N 5.16. FT-IR (cm⁻¹) (Figure S5): 3208(w), 3058(m), 1615(s), 1571(s), 1430(m), 1400(m), 1359(s), 1353(s), 1268(m), 1072(m), 924(m), 776(s), 725(s), 655(s), and 567(m).

2.1.6. Zn-MOF-5. Flat-shaped yellow single crystals of Zn-MOF-5 were obtained under the same reaction conditions as Zn-MOF-0 except for adding 1,1''-([1,1'-biphenyl]-4,4'-diylbis(methylene))bis-(([4,4'-bipyridin]-1-ium))·dichloride (bdbpy·Cl₂) (0.01 g, 0.02 mmol). The crystals were collected by filtration. Yield: 13% based on bbpyCl₂. FT-IR (cm⁻¹) (Figure S6): 3267(w), 3055(w), 1622(s), 1568(s), 1575(w), 1430(m), 1392(m), 1353(m), 1271(m), 1171(w), 1103(m), 1005(m), 921(m), 719(s), 651(s), 625(m), and 560(m).

2.2. UV Doses Detection Procedures. For the UV-dependent coloration measurements, a 15 W light lamp (365 nm UV type, PhilipsHolland) was used as the irradiation source. The UV light intensity was measured by a UV-A photometer (Beijing Shida Optoelectronics Technology Co., Ltd.) and controlled with the distance between the lamp and crystals sample. In order to simulate sunlight, the irradiation sources were used by UVA and UVB lamps (UVA20WT12–600320–400 nm and UVB20WT12–600 280–320 nm LONGPRO China) measured by a 340A UV light meter (Lutron, America).

2.3. H₂O₂ **Decomposition Rate Measurement Procedures under Different Times.** In order to measure unknown H₂O₂ concentrations under different times, we used UV-visible (UV–vis) absorption spectra of the TMB-derived oxidation product in the presence of the ZnMnFe₂O₄ nanomaterial as a catalyst under 30, 20, and 15% wt of H₂O₂ at room temperature.²⁷ Afterward, standard curves are plotted based on the relationship between maximum values of the TMB-derived oxidation product absorbance and concentrations of H₂O₂. In the end, the unknown H₂O₂ concentrations are determined at different times based on standard curves.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Molecular Structures. $ZnCl_2 \cdot 6H_2O$ and H_4pdda were reacted in a mixture of dimethylacetamide (DMA) and water (H_2O) under solvothermal conditions that provided flat-shaped colorless crystals of Zn-MOF-0 (Figure 1a). Zn-MOF-0 consists of a 2D square channel with an approximate diameter of 1.3 nm × 1.0 nm, which is suitable for encapsulating viologen molecular derivatives with proper dimensions. As a result, five hybrid materials Zn-MOFs-1-5 were successfully obtained by introducing five viologen molecules of varying lengths between 10.4 and 20.4 Å into the reaction system through a self-assembly mode (Figure 1b,1c). The successful fabrication of five crystalline materials

demonstrates that the inclusion of guest molecules does not interfere with the relatively stable coordination-directed assembly inherent in Zn-MOF-0. In addition, we also attempted a postsynthesis method to prepare viologen-based host-guest compounds, but we could not obtain them due to DMA solvent molecules occupying the pores of Zn-MOF-0, which prevents the entry of viologen derivatives. Single-crystal diffraction experiments revealed that compound Zn-MOF-0 crystallizes in the triclinic space group with the space group P-1. As shown in Figure S7, the asymmetric unit is constituted by four crystallographically independent Zn²⁺ ions and two pdda⁴⁻ ligands. The Zn1 site shows tetrahedral geometry with one OH⁻ and three O atoms from three different pdda⁴⁻ ligands. Zn2 and Zn3 are both five-coordinated, but their coordination environments are different: Zn2 is coordinated by one OH⁻, one H₂O molecule, and three O atoms from three different pdda⁴⁻ ligands; Zn3 is coordinated by one OH⁻ and three O atoms from three different pdda⁴⁻ ligands. Zn4 is fourcoordinated by one H₂O molecule, one O atom from a coordinated DMA molecule, and two O atoms from two different pdda⁴⁻ ligands. The carboxyl O atoms from the pdda⁴⁻ ligands have monodentate and bidentate coordination modes and each Zn^{2+} ion connects two pdda⁴⁻ ligands to form a 3D framework (Figure S8). Zn-MOF-1 crystallizes in the triclinic space group P-1. Zn-MOF-1 contains square channels with a pore size of 1.2 nm \times 1.1 nm with the debpy²⁺ guest immobilized in the channels and produces a nonporous hostguest architecture (Figure S9a). As shown in Figure S9b, the asymmetric unit of Zn-MOF-1 possesses one debpy²⁺ guest molecule, eight crystallographic Zn2+ ions, and four pdda4ligands. Zn1 is five-coordinated by one OH-, one H2O molecule, and three O atoms from three different pdda4ligands. Zn2 is also five-coordinated by one OH⁻, two H₂O molecules, and two O atoms from two different pdda⁴⁻ ligands. Zn3 is four-coordinated by one OH⁻, one H₂O molecule, and two O atoms from two different pdda⁴⁻ ligands. Zn4 is sixcoordinated by one OH⁻, two H₂O molecules, and three O atoms from three different pdda4- ligands. Zn5 is fivecoordinated by one OH- and four O atoms from three different pdda⁴⁻ ligands. Zn6 is four-coordinated by one OH⁻ and three O atoms from three different pdda⁴⁻ ligands. Zn7 is six-coordinated by three H₂O molecules and three O atoms from two different pdda⁴⁻ ligands. Zn8 is five-coordinated by one H₂O molecule, one O atom from the coordinated DMA molecule, and three O atoms from two pdda⁴⁻ ligands. The carboxyl O atoms from four pdda⁴⁻ ligands have two different coordination modes. The first is the coordination mode in case, that is, both carboxylic acid oxygen atoms from pdda⁴⁻ are involved in coordination and are coordinated to two different Zn^{2+} ions. Another mode is only where one O atom from $pdda^{4-}$ is coordinated by one Zn^{2+} ion (Figure S10). Neighboring pdda⁴⁻ ligands link Zn²⁺ ions to form a 3D supramolecular framework. Zn-MOF-3 crystallizes in the monoclinic system with the space group C2/c. Zn-MOF-3 has one-dimensional (1D) channels and guest molecules accommodated in channels which possess rhomboid pores of 0.8 nm \times 0.7 nm (Figure S11a). In an asymmetrical unit, there are three crystallographic Zn^{2+} ions, one pdda⁴⁻ ligand, and half of the dbbpy²⁺ cation (Figure S11b). Zn1 is six-coordinated through two OH⁻ and four O atoms from two different pdda⁴⁻ ligands, displaying a distorted octahedral geometry. Zn2 is four-coordinated by one OH⁻ and three O atoms from three pdda⁴⁻ ligands. Zn3 exhibits tetrahedral



Figure 2. Top: the channel of Zn-MOFs occupied by guests and the $\pi \cdots \pi$ stacking interactions between guests and the host structure in Zn-MOFs. d_1 : 3.58 Å and d_2 : 3.65 Å. Bottom: the dihedral angles between the H₄pdda ligand and ligand planes in Zn-MOFs.

geometry with one Cl-, one OH-, and two atoms from two different pdda⁴⁻ ligands. The carboxyl O atoms from pdpa⁴⁻ ligands also have two coordinate modes and each pdda4ligand connects with seven Zn²⁺ ions, forming a nonporous 3D host-guest complex. Zn-MOF-4 has an identical space group with P-1, as shown in Figure S13a. The distorted guests pbbpy²⁺ occupy one-dimensional channels with the diameters being 1.2 nm \times 1.0 nm. As shown in Figure S13b, the asymmetric unit is constituted by eight crystallographically independent Zn²⁺ ions, four pdda⁴⁻ ligands, and one pbbpy² guest. Zn1 and Zn2 are four-coordinated by one OH- and three O atoms from pdda⁴⁻ ligands. Zn3 is five-coordinated by one OH⁻, one H₂O molecule, and three O atoms from pdda⁴⁻ ligands. Zn4 is five-coordinated by one OH⁻, three H₂O molecules, and one O atom from one pdda⁴⁻ ligand. Zn5 is five-coordinated by one OH⁻, two H₂O molecules, and two O atoms from two pdda⁴⁻ ligands. Zn6 is also five-coordinated by one OH⁻ and four O atoms from three pdda⁴⁻ ligands. Zn7 and Zn8 are six-coordinated by three H₂O molecules and three O atoms from two pdda⁴⁻ ligands. The carboxyl O atoms from pdda⁴⁻ ligands adopt three coordinate modes with Zn²⁺ ions, forming a nonporous three-dimensional host-guest complex (Figure S14). Furthermore, through careful observation of the structures of Zn-MOFs-1, 3, and 4, we discovered that the arrangement of the guest molecules in the MOFs was variable. In Zn-MOFs-1 and 4, the guest molecules filled the pores uniformly (Figure 2), although their arrangement within the pores of Zn-MOFs-1 and 4 was slightly different. In Zn-MOF-1, there was a distinct angle formed between the guest molecules and the host structure. Conversely, in Zn-MOF-4, the guest molecules situated themselves parallel to the channels, occupying rectangular cavities within the 3D framework (Figure 2). Notably, in Zn-MOF-3, the guest molecules partially filled the one-dimensional channels in a direction perpendicular to the channels and were parallel to each other. In addition, the X-ray diffraction data also suggested that intermolecular forces existed between the guest molecules and the host structures in Zn-MOFs-1, 3,

and 4. The $\pi \cdots \pi$ interactions between the guests and H₄pdda ligands were 3.81 Å in Zn-MOF-1, 3.58 and 3.65 Å in Zn-MOF-3, and 3.67 Å in Zn-MOF-4 (Figure 2). The close stacking of viologens and H4pdda ligands indicates relatively strong interactions between them, which could facilitate donor-acceptor interactions. Besides, compared with the structures of Zn-MOFs-0, 1, and 4, the structure of Zn-MOF-3 has changed slightly. Therefore, we explored the degree of distortion of the H₄pdda ligands in these compounds. The degree of distortion of the benzene ring of H₄pdda ligands in Zn-MOFs-1 and 4 is slight and the dihedral angle between the H₄pdda ligand and ligand planes is similar to that of Zn-MOF-0, yet the dihedral angle of Zn-MOF-3 between the H₄pdda ligand and ligand planes through the benzene ring is 59.5°, which results in slightly different structures compared to Zn-MOF-0. These results also indicate that strong $\pi \cdots \pi$ stacking interactions (3.58 and 3.65 Å) between the viologen guest and H4pdda ligand play an important role in forming molecular crystals of Zn-MOF-3. However, the single-crystal X-ray diffraction structures of Zn-MOFs-2 and 5 could not be obtained, may be due to the guests' irregular arrangement within the crystal lattices and low occupancy, resulting in a low scattering intensity of X-rays by the guest molecules. Therefore, their structures were confirmed by powder X-ray diffraction, appearance color, fluorescence, and thermogravimetric analysis (TGA). The phase purity of bulk samples of Zn-MOFs-0-5 was confirmed by powder Xray diffraction (PXRD) (Figures S15-S20). TG analysis reveals that all compounds have similar TG behaviors (Figure S21); that is, five compounds showed a slow weight loss with the release of the lattice solvent molecules until 360 °C and then a steep weight loss due to the decomposition of the compound. The similar TG behaviors would be due to their similar structures, expect of the guest molecules. Additionally, Zn-MOFs-1-5 showed a slower weight loss than that of Zn-MOF-0 due to the inclusion of viologen molecules in Zn-MOFs-1-5.



Figure 3. Guest-dependent optical (top) and luminescent (middle) images of crystals and the CIE color coordinates of the Zn-MOFs (bottom).



Figure 4. (a) Solid-state photoluminescence (PL) spectra of Zn-MOFs-0–5 (λ_{ex} = 365 nm for Zn-MOFs-1–5 and λ_{ex} = 364 nm for Zn-MOF-0). (b–f): PL spectral changes after irradiation with 365 nm UV light (0.5 mw/cm² for Zn-MOFs-1, 3, 4, and 5 and 2.5 mw/cm² for Zn-MOF-2) at different times.

3.2. Fluorescent Properties. Viologen-based compounds have been reported to exhibit special luminescence emissions originating from the charge transfer between the framework

and viologen molecules.^{28–30} Thus, their luminescent properties were first investigated. Notably, Zn-MOFs-1–5 showed guest-dependent luminescence compared with Zn-MOF-0

(Figure 3). The corresponding CIE coordinates of their emissions were calculated; the values spanned a wide range from green to yellow (Figure 3). As shown in Figure 4a, Zn-MOF-0 emitted at 454 nm when excited with a 364 nm laser. The emissions of Zn-MOFs-1-5 (496-565 nm) were redshifted compared with Zn-MOF-0, and the extent of the red shift depended on the encapsulated guests, which may be ascribed to the charge transfer between guest viologen molecules and the host framework. The average lifetime (τ_{av}) of Zn-MOF-0 was 4.75 ns, and the average lifetimes of Zn-MOFs-1-5 were in the range of 1.4-37.69 ns (Figure S22; Table S4, Supporting Information). The photoluminescence quantum yield (PLQY) (%) of Zn-MOF-0 was 12.9%, while that of the other MOFs was 2.2-22.7%. These results indicate that a typical charge-transfer interaction occurs between viologen guests and the host framework. Moreover, the broad emission range of the five hybrid materials suggests that fluorescence emission modulation can be achieved by using the MOF as a host and different viologen molecules as guests. Additionally, Zn-MOFs-1-5 simultaneously exhibited luminescence quenching phenomenon and photochromic transition with PL color evolution upon continuous 365 nm UV irradiation (Figure 4b-4f). Under continuous 365 nm UV irradiation, the emission intensities of the Zn-MOFs-1, 3, 4, and 5 drastically decreased to 73.0, 86.8, 57.6, and 36.8% of the original intensity, respectively, upon 900 mJ/cm² irradiation (0.5 mw/cm², 30 min). Meanwhile, Zn-MOF-2 is less sensitive toward UV light than the other Zn-MOFs. The emission intensity of Zn-MOF-2 decreased to 85.2% of the original intensity upon 4.5 J/cm² irradiation (2.5 mw/cm², 30 min). Therefore, among the five hybrid materials, Zn-MOF-3 has the highest quenching efficiency, which is attributed to the rapid charge-transfer ability between the MOF host and the viologen guest. Besides, compared with Zn-MOF-0, Zn-MOFs-1, 3, 4, and 5 were blue-shifted by 24, 14, 38, and 6 nm, respectively; Zn-MOF-2 was red-shifted by 3 nm (See Figure S23; Table S5, Supporting Information). The changes mentioned above can also be visualized by the gradual transition of the emission color from pinkish green to pine forest green for Zn-MOF-2, patina to light green-gray for Zn-MOF-4, and stone green to blue for Zn-MOF-5, resulting in photomodulated luminescence (Figure 5a). Wavelength shifts of 38 nm for Zn-MOF-4 upon exposure to external stimuli are rarely reported for viologen-based MOFs. Consequently, these materials could be potentially applied in photomodulated color switching by an easy UV light irradiation mode.

3.3. Photochromism. The photochromism of Zn-MOFs-1-5 was examined in air at room temperature since viologenbased compounds possess excellent photochromic properties. Under continuous UV light exposure, Zn-MOFs-1-5 showed evident color changes (Figure 5b). After 60 min of UV irradiation, the color of Zn-MOFs-1-5 reached saturation and then turned gray, brown, dark green, dark blue, and light blue, respectively. The five MOFs showed different photochromic abilities. Among all of the MOFs, Zn-MOF-3 produced the best photochromic abilities. After 10 s of UV irradiation at a low intensity of 0.5 mw/cm², a clear color change from yellow to cyan blue was observed. A response was observed with a UV irradiance intensity as low as 0.1 μ W/cm² (Figure S24), which is comparable to commercialized UV light radiation devices, lower than that reported for ultraviolet light detection materials.^{25,26,31-34} The color-saturated samples of Zn-MOFs-1-5 were completely decolored after being kept in



Figure 5. (a) Photomodulated luminescence over time under 365 nm light exposure. Zn-MOFs-1–5 were loaded on a quartz slide with a dimension of $1.5 \times 1.5 \text{ cm}^2$. (b) Photochromism of Zn-MOFs-1–5 upon 365 nm UV irradiation over different times.

the dark for 9, 28, 41, 25, and 47 h at room temperature, respectively (Figure S25). This reversible color conversion could be repeated three times without a significant color loss.

3.4. Application in Direct Readout UV Colorimetric Dosimeters. Photosensitive reagents are photolyzed under natural or sunlight irradiation. However, protective photosensitive colorimetric dosimeters toward these reagents are rarely documented due to the requirement of low light detection limits. Zn-MOF-3 displays fast and sensitive responses toward low doses of natural and room light (Figures S26-S27). This property is suitable for applications as a photosensitive colorimetric dosimeter for photosensitive reagents. To explore the practical applications of Zn-MOF-3, a color matching chart was prepared with 30 mg of Zn-MOF-3 on a silicone board $(2 \times 2 \text{ cm}^2)$. A color matching chart was prepared by exposing samples to natural light at different times and used as a reference for an unknown concentration of H_2O_2 (Figures S28–S31). Then, the matching chart was attached to the top of a H₂O₂ reagent bottle and exposed to natural light for varying time periods. As shown in Figure 6a, when a H_2O_2 reagent bottle is exposed to natural light for 0.5, 4, and 9 h, respectively, the concentration of H₂O₂ decreases from 30 wt % to 29.7, 26.6, and 19.1%, accompanied by a color change from yellow to light green, green, and dark green in the matching chart. The low limit of the H₂O₂ decomposition rate was 0.3%. Meanwhile, the changed color of the matching chart remained unchanged for at least 24 h when kept in the dark. These results indicated that Zn-MOF-3 could be utilized as a warning label for the decomposition rate of H₂O₂ in natural light. Due to the fast recovery from the color saturation state to the initial color state toward UV light for Zn-MOF-1, we developed a portable UV colorimetric dosimeter. As is well known, ultraviolet (UV) rays in the sunlight are primarily responsible for skin damage and are categorized into UVA (400-320 nm), UVB (315-280 nm), and UVC (290-100



Figure 6. (a) Zn-MOF-3 as a photosensitive colorimetric dosimeter for the H_2O_2 decomposition rate under natural light (Feb 25, 2023, in Jining, China). (b) Zn-MOF-1 made as a UV-sensitive card by MED (Feb 24, 2023, in Jining, China).

nm) rays; the ozone layer completely filters UVC. A UV colorimetric dosimeter alerts users against excessive solar UVA-UVB exposure and can operate in the range of the minimal erythemal dose (MED). MED is the minimum amount of UVR likely to cause erythema for most Asians, i.e., with skin type V (600 J/m^2).^{35,36} Based on this, a sunlight colorimetric dosimeter was developed to determine personal UVA and UVB radiation doses in real time (Figure 6b). As shown in Figure 6b, 20 mg of samples were loaded in a thin film as a colorimetric dosimeter, and the film was attached on the surface of the user's clothing. Similarly, a color matching chart was also prepared by exposing samples to UVA and UVB at different MEDs and used as a reference for an unknown MED (Figure S32). From the color changes of the colorimetric dosimeter on the user's clothing, the user can obtain information about sunlight radiation doses. Further, the dosimeter can decolor to the original color when kept in the dark for 5 h or heated at 50 °C for 30 min, making it suitable for practical applications.

3.5. Mechanism of Photochromism and Photoluminescence Modulation. The powder X-ray diffraction (PXRD) patterns observed in both the preirradiation and postirradiation samples closely matched those of the originally synthesized sample (Figures S33-S37). Similarly, the IR spectra of complexes Zn-MOFs-1-5 before and after exposure to UV-vis light showed a high degree of overlap (Figures S38-S42). These results suggest that the observed photochromism was not a result of structural alterations or photolysis. The UV-vis diffuse reflectance and electron spin resonance (ESR) spectra of the Zn-MOFs were recorded before and after UV light treatment to explore the mechanism of their photochromic behaviors. Upon UV light irradiation, the UV-vis spectra showed new strong bands centered at 627-751 nm (Figures S43-S47), while the ESR spectra showed stronger and symmetric single-peak radical signals, confirming the existence of photogenerated radicals (Figures S48-S52).^{31-34,37,38} For Zn-MOFs-1, 3, and 4, the shortest

distances between the O of carboxylate groups and the N of the pyridinium unit were 3.48, 3.83, and 3.56 Å, respectively, satisfying the photoinduced electron paths. The shorter distances are more favorable for electron transfer. Additionally, as previously reported, the small dihedral angles between the two pyridinium rings were more conducive to the photoinduced reduction of viologens and the stability of free radicals.^{39,40} Zn-MOF-3 showed the smallest dihedral angle (the dihedral angles between the two pyridinium rings for Zn-MOFs-1, 2, and 3 are 29.4, 0, and 11.95°, respectively) and showed the strongest $\pi \cdots \pi$ stacking interactions. The small dihedral angle and strong $\pi \cdots \pi$ stacking interactions between the bipyridinium ring and H4pdda ligand lead to fast photochromism of Zn-MOF-3 in the presence of UV light. X-ray photoelectron spectroscopy (XPS) spectra were collected to further explore the photochromic mechanism. As shown in Figures S53–S57, the core-level spectra of both C 1s and Zn 2p of Zn-MOFs-1-5 are almost the same before and after UV light irradiation. However, the variation in those of the oxidants of O 1s and N 1s is discernible. The O 1s binding energy signal of Zn-MOFs-1-5 increases after UV irradiation compared to its pre-UV irradiation state. This elevation results from the dissociation of electrons from the ions on the O atoms. Conversely, Zn-MOFs-1-5 experience a noticeable shift toward a lower N 1s binding energy position after UV irradiation, as it receives electrons in this process. This further confirms that the electron transfer occurs between the O of carboxylate groups and the N of the pyridinium unit in Zn-MOFs-1-5. It is worth noting that Cl⁻ also acts as an electron donor and participates in the electron transfer process in Zn-MOF-3. Despite the long distance of 4.61 Å from Cl⁻ to N of the pyridinium unit exceeding the maximum electron transfer distance of 4 Å, some reported viologen-based complexes longer than that distance can facilitate electron transfer.⁴¹⁻⁴³ Moreover, the photoluminescence of the H₄pdda ligand and viologen guests was investigated to understand the fluorescence emission mechanism of Zn-MOFs. The free H₄pdda

ligand showed weak photoluminescence emission at 394 nm, indicating that the fluorescence of Zn-MOF-0 could be attributed to the ligand-to-metal charge transition (LMCT) (Figures S57-S58). Additionally, the five viologen guests displayed photoluminescence emission bands at 486, 484, 517, 522, and 489 nm (Figures S57-S58). The luminescence emission of the compounds Zn-MOFs-1-5 can be attributed to the ligand-to-ligand charge transition (LLCT) and the presence of $\pi \cdots \pi$ stacking interactions between viologen guests and the host framework.^{44–49} Moreover, the principles of controlled modulation of fluorescent properties in this system were further investigated by determining the relationship between the emission of Zn-MOFs and the electron affinity (E_a) of the guest molecules (Table S6). As we all know, in the luminescent MOF-based charge-transfer system, luminescence emission is determined by the charge-transfer nature.^{30,-52} Therefore, the wavelength signifies the energy gap between the exciplex's excited state and the ground state, primarily defined by the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. As the E_a of the guest corresponds to its LUMO energy level and the HOMO of H₄pdda remains similar in five hybrid compounds, a guest having a higher E_a value may generate an emission featuring a higher wavelength. For instance, the E_a values of $[dbbpy]^{2+}$ and $[debpy]^{2+}$ molecules are 8.5 and 8.8 eV, respectively, which are higher than the E_a values of other viologen guest molecules. Hence, Zn-MOF-4 and Zn-MOF-2 show higher emission wavelength (centered at 565.3 and 549.6 nm). Conversely, the [bdbpy]²⁺ molecules possess minimum E_a values, and the compound Zn-MOF-5 has the lowest emission wavelength (centered at 491.9 nm). However, linear correlations could not be obtained between the emission maximums of the Zn-MOFs and the E_{a} values of the corresponding guests (Figure 7a). This is probably credited to the varying $\pi \cdots \pi$ interaction levels between the viologen guests and H4pdda ligands (Figure 7b). In the previously reported luminescent MOFs or multicomponent crystal systems, the $\pi \cdots \pi$ interactions between the host and guest can affect the charge-transfer process, thereby impacting the luminescent properties of these compounds.^{53–56} In Zn-MOFs-2, 3, and $\overline{4}$, the varying degrees of $\pi \cdots \pi$ interactions between viologen molecules and H₄pdda ligands affect the respective Zn-MOFs emissions. Therefore, in these viologen-based host-guest compounds, both the E_a values of the viologen guests and the $\pi \cdots \pi$ interactions between the viologen guests and H4pdda ligands determine fluorescence emissions. Besides, luminescence quenching could be attributed to the partial overlap between the emission bands of the initial sample and the absorption bands of the colored sample.

4. CONCLUSIONS

In summary, the five viologen-based host–guest materials were constructed with viologen as guests and 3D Zn-MOF as a host. These composite materials showed guest-dependent color-tunable emissions and photomodulated luminescence upon UV light radiation. Specifically, Zn-MOF-3 displayed excellent photochromism at intensities as low as 0.1 μ w/cm². This property was successfully applied in a readout UV colorimetric dosimeter. Zn-MOF-1 was used as a real-time sunlight sensor for personal UVA and UVB radiation doses. These MOFs showed fast recovery when kept in the dark for 5 h or heated at 50 °C for 30 min, which is suitable for practical applications.



Figure 7. (a) Correlation between the emission maxima of Zn-MOFs-1–5 and E_a of guests. (b) $\pi \cdots \pi$ interactions between the guests and H₄pdda ligands.

The mechanisms of photochromism and photoluminescence modulation are also discussed. Successful syntheses of these host-guest compounds based on viologen are expected to encourage the discovery of other molecules for constructing host-guest composite materials for applications in photomodulated color switching and UV sensing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.3c12012.

Materials synthesis and characterization; FT-IR spectra; TGA analyses; experimental section; single-crystal X-ray diffraction; structural figures; XRD analyses; luminescence lifetimes and photoluminescence quantum yield analyses; photoluminescence and photochromism; ESR spectra; UV–vis spectra; XPS spectra analyses; DFT computation (PDF)

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Notes

The authors declare no competing financial interest.

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Orthogonal Trichromatic Upconversion with High Color Purity in Core-Shell Nanoparticles for a Full-Color Display

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Abstract: Materials with tunable emission colors has attracted increasing interest in both fundamental research and applications. As a key member of lightemitting materials family, lanthanide doped upconversion nanoparticles (UCNPs) have been intensively demonstrated to emit light in any color upon nearinfrared excitation. However, realizing the trichromatic emission in UCNPs with a fixed composition remains a great challenge. Here, without excitation pulsed modulation and three different near-infrared pumping, we report an experimental design to fine-control emission in the full color gamut from core-shell-structured UCNPs by manipulating the energy migration through dual-channel pump scheme. We also demonstrate their potential application in full-color display. These findings may benefit the future development of convenient and versatile optical methos for multicolor tuning and open up the possibility of constructing full-color volumetric display systems with high spatiotemporal resolution.

Introduction

In recent years considerable attention has been given to multicolor-emitting materials due to their applications in the fields of graphics imaging, biological sensing, optical memory, as well as anticounterfeiting and display.^[1-5] On the basis of the potential to present more information at a time than monochrome display, full-color display has experienced rapid development and enormous progress over the past

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Angew. Chem. Int. Ed. 2023, 62, e202218491 (1 of 7)

decades.^[6-10] Conventional color display technology, including 2D pixilated red-green-blue (RGB) and volumetric 3D full-color display, always rely on blending pixels of RGB three primary colors as one color pixel, which suffer from some limitations such as low resolution and specific pixel arrangement.^[11–13]

As representative of multicolor emissive and responsive materials, organic dyes, carbon dots, and semiconducting quantum dots are highly attractive on account of their unique properties such as high photoluminescence quantum yield, color tunable, high color purity, and solution processability.^[14-16] However, current multicolor-emitting system generally require the physical blending of individual monochromatic luminescent units, which may be constrained by rigorous composition optimization and complex color modulation.^[17-19] In particular, controlling light emission over a wide color range in a single material still remains a great challenge.

Upconversion nanoparticles (UCNPs) doped with lanthanide ions that feature ladder-like energy levels can produce multiple emissions span from ultraviolet to nearinfrared, making them ideal candidates for full-color tuing.^[20-25] Intriguingly, the significant development of coreshell structural design over the past few years provides an effective platform for color modulation in a single upconversion nanoparticle by tailoring the emission profiles of different lanthanide centers.^[26–33] Despite the enticing prospect, the current development of full-color upconversion nanoparticles is hindered by the harsh need of excitation setup, such as complex three-channel photo upconversion and complicated pulse width modulation.[34-37] Here, we demonstrate a dual-channel orthogonal upconversion system pumping at 808 nm and 980 nm, in which the specific emissions of different lanthanide dopants can be selectively and exquisitely produced on a single upconversion nanoparticle. In contrast to previously reported RGB upconversion systems in which three different lanthanide luminescent centers are needed,^[35-37] our design provides a precise control over the emission color by tuning the power density of the excitation, avoiding the deleterious interaction between multiple luminescence centers, thereby offering the possibility to improve spectral purity of RGB emission without the excitation pulse modulation.

In our proposal, a specially designed multilayer coreshell structured NaYF₄:Yb/Tm (20/0.2 mol%)@NaYF₄:Yb/ Nd (20/20 mol%)@NaYF₄@NaYbF₄:Ho (1 mol%)@NaYF₄ were proposed for dual-channel pumping (Figure 1a). Each layer has its own role and they work together to generate

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Figure 1. a) Schematic illustration of the core-shell nanoparticle for orthogonal RGB luminescence under 808 and 980 nm excitation. b) Transmission electron microscope (TEM) images of NaYF₄:Yb/Tm, NaYF₄:Yb/Tm@NaYF₄:Yb/Nd, NaYF₄:Yb/Tm@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Po/Nd@NaYF₄:Yb/Nd@NaYF₄:NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:NaYF₄:Yb/Nd@NaYF₄:Yb/Nd@NaYF₄:NaYF₄:Yb/Nd@NaYF

orthogonal upconversion. The inner Nd³⁺ and outer Yb³⁺ ions were used as sensitizes for harvesting the excitation at 808 and 980 nm, respectively. Tm³⁺ was confined in the core to make blue emission possible under 808 nm excitation, while Yb3+ and Ho3+ were codoped into shell layer to generate the power-dependent red or green emission under 980 nm excitation.^[38] An inert interlayer of NaYF₄ between Yb/Nd and Yb/Ho codoped shell layer was applied to block the energy transfer pathways of $Nd^{3+} \rightarrow Yb^{3+} \rightarrow Ho^{3+}$ and prevent the cross-relaxation process between Tm³⁺ and Ho³⁺. To eliminate the surface-related energy loss, we introduce the NaYF₄ coating at the outermost layer of the nanoparticles. By tuning the shell thickness of NaYbF4:Ho layer and the power density of 980 nm laser, we obtain orthogonal RGB luminescence with a high spectral purity, which was further used for full-color display.

Results and Discussion

In a typical experiment, a layer-by-layer epitaxial growth procedure was adopted to synthesize the core-shell nanoparticles. X-ray powder diffraction (XRD) study of the assynthesized samples at each step confirms the hexagonal phase (Figure S1). Transmission electron microscopy (TEM) micrographs show spherical shape of the nanoparticles after each growth step with the average diameter increasing from 21.2 nm of core to 71.5 nm of the final multilayer nanoparticles (Figure 1b and Figure S2). The high-resolution TEM image of the as-synthesized NaYF₄:Yb/Tm@NaYF₄: Yb/Nd@NaYF₄@NaYbF₄:Ho@NaYF₄ sample exhibits lattice fringes of the (100) planes of hexagonal-phase NaYF₄ and NaYbF₄ with *d*-spacing of ~0.5 nm. The corresponding Fourier transform pattern with sharp diffraction spots further confirms that the nanoparticles are highly crystalline (Figure 1c).

We then investigated the luminescence properties of the multilayer nanoparticles under ambient conditions. Under 808 nm laser excitation, the as-prepared nanoparticles exhibit two strong blue band emissions, which can be attributed to the ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$ and ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ transitions of Tm³⁺. However, strikingly, upon switching the excitation wavelength to 980 nm, the blue emissions of these nanoparticles are almost fully suppressed, only Ho3+ emission bands came from the green ${}^{5}F_{4}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ and red ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ transitions were observed. Remarkably, the emission profiles of these colloidal nanoparticles, especially the red/green (R/G) emission intensity ratio was greatly influence by 980 nm excitation power. For instance, a relatively low power (1 W cm^{-2}) gave rise to a green emission with R/G ratio less than 1. In stark contrast, on lifting the excitation power density to 200 W cm⁻², the as-synthesized nanoparticles present an intense red emission, which can be ascribed to a markedly enhanced red/green ratio (~8) (Figure 1d and Figure S3).

 Yb^{3+} ion has an inherent absorption band around 980 nm. To achieve the aforementioned orthogonal upconversion, the pathway of 980 nm photons to the Yb^{3+} ions

doped in the particle's core and Yb/Nd codoped inner shell layer need to be blocked. The shell-mediated excitation exhaustion has been proven efficient to cut off the absorption of input pump photons in inner shell layer.^[39-41] To validate this effect in our multilayer systems, four batches of core-shell nanoparticles with different thicknesses of NaYbF₄:Ho shell layer were prepared in our experiments (Figure 2a, b). Photoluminescence study revealed that the emission intensities of Tm³⁺ decrease with increasing shell thickness of NaYbF₄:Ho layer upon 980 nm excitation. Most notably, after coating NaYF₄:Yb/ Tm@NaYF₄:Yb/Nd@NaYF₄ nanoparticles with 8.8 nm layer of NaYbF₄:Ho, the emission of Tm³⁺ doped in the core is completely eliminated and the as-prepared sample merely showed the characteristic emission bands of Ho³⁺ (Figure 2c). We proposed that most of 980 nm photons were exhausted by the absorption of Yb^{3+} in outer shell and thus was insufficient to upconvert Yb^{3+}/Tm^{3+} pairs in the core. Therefore, only Ho³⁺ emission was detected under 980 nm excitation.

The luminescence properties of the multilayer nanoparticles upon near-infrared excitation with different power were then investigated. By tuning the pumping power of 980 nm laser from 1 to 200 W cm⁻², the as-prepared nanoparticles with 8.8 nm thick layer of NaYbF₄:Ho revealed power-dependent upconversion luminescence with the corresponding emission color changes from green to red (Figure 2d and Figure S3). The curves of red and green emission intensities as a function of excitation power were further plotted (Figure 2e). We found that the slope for red



Figure 2. a) Scheme showing the dual-channel orthogonal upconversion through shell thickness tuning. Five-tier from left to right refers to NaYF₄: Yb/Tm, NaYF₄:Yb/Nd, NaYF₄, NaYbF₄:Ho, and NaYF₄ layer, respectively. b) Representative TEM images of the as-synthesized nanoparticles with different thickness of NaYbF₄:Ho shell layer. scale bar, 100 nm. c) Upconversion emission spectra of NaYF₄:Yb/Tm@NaYF₄:Yb/ Nd@NaYF₄@NaYbF₄:Ho@NaYF₄ nanoparticles as a function of NaYbF₄:Ho shell thickness under 980 nm excitation. d) Power-dependent emission spectra of the as-synthesized nanoparticles by 980 nm excitation. Note that the emission spectra in (d) are normalized to Ho³⁺ 646 nm emission. e) The dependence of photoluminescence intensity on laser excitation power at emission wavelengths of 540 nm and 646 nm, performed for the as-prepared nanoparticles. f) Numerical simulation results of red and green emission intensity ratio (R/G ratio) versus excitation power density and Yb³⁺ concentration based on a simplified energy transfer model involving Yb³⁺ and Ho³⁺ ions. g) Power-dependent emission. Luminescence photographs (h) and the corresponding CIE chromaticity diagram (i) showing multicolor tuning (1-11) of the sample under combined irradiation at wavelengths of 980 and 808 nm. Note that the outer and inner triangle shown in (i) represents the color spaces from the as-synthesized sample and from the conventional sRGB projectors, respectively.

Angew. Chem. Int. Ed. 2023, 62, e202218491 (3 of 7)

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emission is much higher relative to that for green, which could explain the dominant red emission of the as-synthesized nanoparticles upon excitation at high power. To investigate the pump power sensitivity of the red/green ratio in Yb³⁺/Ho³⁺ codoped systems, a population kinetic model involving the energy level of ${}^{5}F_{4}$, ${}^{5}S_{2}$ and ${}^{5}F_{5}$ was numerically constructed (Figure S4 and Table S1, see Supporting Information for more details). Simulation results show that red/ green ratio exhibit high excitation power sensitivity, confirming that the enhanced red/green ratio likely occurs in heavily Yb doped systems with higher-power 980 nm laser pumping (Figure 2f). By contrast, upon turning the excitation light to 808 nm, the as-synthesized nanoparticles present power-independent blue luminescence, which was purely ascribed to the electronic transitions of Tm³⁺ (Figure 2g). Taken together, in contrast to other othogonal upconversion systems, our design provides a convenient way to allow orthogonal RGB emission with high spectral purity by tuning the excitation power through two-channel pump scheme (Table S2). More interestingly, when combining the 980 nm laser excitation with that of 808 nm, the dual-channel optical pumping enabled us to achieve multicolor luminescence with tunable emission and wide color gamut (Figure 2h and Figure S5). Highly saturated RGB colors are available in our multilayer nanoparticles due to the narrow emission bandwidths of lanthanide emitters, leading to a realization of wider color space than accessible by conventional sRGB projectors (Figure 2i and Table S3).^[42]

It is worth noting that the multilayer design is essential for attaining orthogonal RGB emission with high spectral purity. Two control experiments on codoped nanoparticles (NaYF₄:Yb/Nd/Tm/Ho@NaYF₄) and nanoparticles without isolating layer (NaYF4:Yb/Tm@NaYF4:Yb/ inert Nd@NaYbF4:Ho@NaYF4) revealed the intermixing upconversion emissions of Tm and Ho, indicating that the multilayer structure is effective to minimize the cross relaxation and regulate the energy migration pathways between different lanthanides (Figure 3a and Figure S6). In addition, the orthogonal RGB emission is unavailable based on the homogeneous mixture of NaYF₄:Yb/Tm@NaYF₄:Yb/ Nd@NaYF4 and NaYF4@NaYbF4:Ho@NaYF4 nanoparticles as well (Figure S7).

We next proposed a plausible upconversion mechanism of the orthogonal RGB emission from the as-synthesized nanoparticles (Figure 3a and Figure S8). Under 808 nm laser excitation, the blue emission from Tm^{3+} in the core can be generated through the successive energy transfer process of $Nd^{3+} \rightarrow Yb^{3+} \rightarrow Tm^{3+}$. Specifically, Nd^{3+} ions absorb the 808 nm photons first to populate the ${}^{4}F_{5/2}$ state and then relax rapidly to their ${}^4\!F_{3/2}$ state, from which the energy transfer to Yb^{3+} ions occur via a process of ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ (Nd³⁺): ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ (Yb³⁺). Subsequently, Yb³⁺ ions return to the ground state and transfer energy successively to Tm³⁺ to populate their ${}^{3}H_{5}$, ${}^{3}F_{2, 3}$, and ${}^{1}G_{4}$ levels in turn to produce blue emission.^[43,44] In addition, by introducing inert isolating layer between NaYF4:Yb/Nd and NaYbF4:Ho shell layer, the energy trasfer pathways from excited Nd³⁺ to outer Yb³⁺/Ho³⁺ pairs are blocked due to the large interionic distance, which is critical to the implementation of orthogonal upconversion.

Upon changing the excitation wavelength to 980 nm, Yb^{3+} in the NaYbF₄:Ho shell layer captured excitation energy and then transferred to neighboring Ho³⁺ ions via Yb^{3+} -sensitized upconversion process to populate the excited states of Ho³⁺ for producing color-tunable emission. Although Yb³⁺ ions in the core and NaYF₄:Yb/Nd shell layer are effective to absorbe 980 nm photons for Tm³⁺ upconversion in principle (Figure 2c), however, with increasing shell thickness of NaYbF₄:Ho, most of the 980 nm excitation photons are consumed by Yb³⁺ absorption in the NaYbF₄:Ho shell, leading to inadequate excitation of Yb³⁺ ions in the core and inner shell. Therefore, only Ho³⁺ emission was observed upon 980 nm laser pumping.

In general, the population of the excited states of lanthanides is executed sequentially from low- to high-lying energy levels in the upconversion process. In the case of 980 nm excitation with low-power, the weak pump only allows the two-photon upconversion of Ho³⁺ to be achieved, thus enabled green emission from the ⁵F₄, ⁵S₂ states through direct two-step energy transfer from Yb³⁺ (Figure 3b). It should be noted that an extra step of nonradiative relaxation of ${}^{5}I_{6} \rightarrow {}^{5}I_{7}$ is required to populate the intermediate ${}^{5}I_{7}$ state of Ho^{3+} , from which the ${}^{5}F_{5}$ state can be further filled for red emission. Additionally, the energy transfer from the ${}^{5}I_{6}$ to ${}^{5}I_{7}$ state is a slow process because of the large energy gap $(\sim 3400 \text{ cm}^{-1})$, it may take more time for populating the ${}^{5}\text{F}_{5}$ state to reach its steady state than that of ${}^{5}F_{4}$, ${}^{5}S_{2}$ states. Therefore, a weak red emission was generated in the assynthesized nanoparticles under low power excitation. By comparison, when elevating the excitation power to a high level, the higher-lying ${}^{5}G_{3}$ and ${}^{5}F_{1}$, ${}^{5}G_{6}$ states of Ho³⁺ can be pumped through three-step energy transfer from Yb³⁺ ions (Figure S9). More importantly, considering the larger slope of the red emission in the double-logarithmic plot of pump power and emission intensity (Figure 2e), we believe that a subsequent back energy transfer from Ho³⁺ (${}^{5}F_{1}$, ${}^{5}G_{6} \rightarrow {}^{5}F_{5}$) to Yb^{3+} (${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$) is efficient in the highly doped system to populate the ⁵F₅ state for enhanced red emission (Figure 3b). This result is also confirmed by our numerical simulations (see Supporting Information for more details).

Regarding the high-purity orthogonal RGB emission at the single particle level, we then applied the as-synthesized NaYF₄:Yb/Tm (20/0.2 mol %)@NaYF₄:Yb/Nd (20/ $20 \mod \%)$ @NaYF₄@NaYbF₄:Ho (1 mol %)@NaYF₄ nanoparticles with 8.8 nm thick layer of NaYbF4:Ho to full-color display. As a proof of concept, we prepared a transparent polydimethylsiloxane (PDMS) matrix of upconversion nanoparticles as the display unit, which showed the same luminescence profiles as the pristine multilayer nanoparticles (Figure S10). As expected, under near-infrared irradiation, images with various shapes can be generated by laser beam scan within the nanoparticles/PDMS composite monolith (Figure 4a and Figure S11). The application of this principle of laser scanning also enabled full-color display by combining the 808 nm laser with a 980 nm one. Using this approach, we obtained multicolor images of pet paws, "SCNU" text, and Olympic rings with high spatial resolution



Figure 3. a) Upconversion luminescence profiles of NaYF₄:Yb/Nd/Ho/Tm@NaYF₄ and NaYF₄:Yb/Tm@NaYF₄:Yb/Nd@NaYbF₄:Ho@NaYF₄ nanoparticles upon excitation at 808 nm and 980 nm, respectively. Schematic designs of the nanostructures and the corresponding luminescence photographs of the nanoparticles are displayed in the insets. b) Proposed energy transfer pathways for producing blue emission of Tm³⁺ under 808 nm laser excitation and green/red emissions of Ho³⁺ under 980 nm laser excitation.

(Figure 4b). Unlike the existing solid-state volumetric color display techniques, which usually require complicated stacked layers or complex optical holography,^[45-48] our design provides a convenient way for multicolor tuning and imaging, making them ideal for full-color volumetric display.

Conclusion

In conclusion, we have demonstrated a multilayer core–shell design principle of upconversion nanoparticles to achieve orthogonal RGB emission with high color purity. The NaYF₄ nanoparticles codoped with Tm^{3+} and Ho^{3+} at different layers are capable of dual-channel orthogonal luminescence through Nd³⁺- and Yb³⁺-sensitized upconver-

sion process upon excitation at 808 and 980 nm. Mechanistic studies suggest that the shell thickness and pump power tuning can be harnessed to regulate the energy migration and adjust the emission color on a single-particle level. The ability of our multilayer nanoparticles to emit RGB luminescence on demand in response to near infrared excitation enables us to realize full-color volumetric display. Importantly, our findings not only provide new insights into the precise control of emission color upon multi-channel pumping, but also will broaden the utility of upconversion nanoparticles for advanced anticounterfeiting, multiplexed biological sensing, and color display applications.

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Figure 4. a) Schematic of the synchronous galvanometric scanning system equipped with two laser beams for full-color display. Note that the multilayer nanoparticles are incorporated into a polydimethylsiloxane (PDMS) monolith to construct a transparent display matrix for drawing images. b) The photograph of a PDMS monolith composed of 0.2 wt% NaYF₄:Yb/Tm@NaYF₄:Yb/Nd@NaYF₄@NaYbF₄:Ho@NaYF₄ nanoparticles, showing a disc shape with diameter of 8.5 cm and luminesce color images of pet paws, "SCNU" text, and Olympic rings generated in the nanoparticles/PDMS composite monolith.

Experimental Section

The experimental details are provided in the Supporting Information.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Color Purity · Core–Shell Nanoparticles · Crystal Engineering · Full-Color Displays · Orthogonal Upconversion

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