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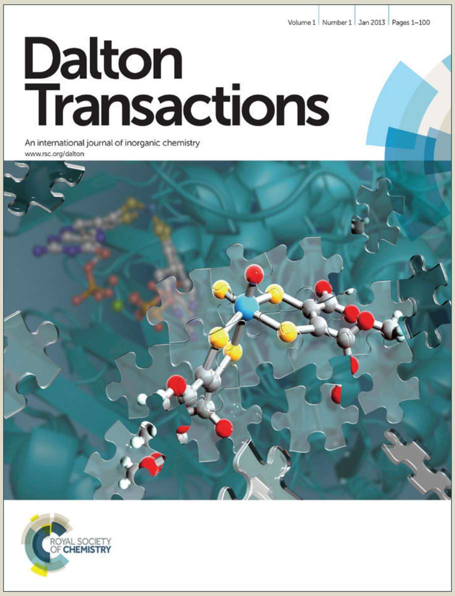

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Towards full-color-tunable emission of two component Eu(III)-doped Gd(III) coordination frameworks by variation of excitation light

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Abstract: A series of pyrazine-2,3,5,6-tetracarboxylate alkali-lanthanide coordination frameworks, namely, $[NaLn(pztc)(H_2O)_3]\cdot H_2O$ [Ln = Ce (**1**), Sm (**2**), Eu (**3**), Gd (**4**) and Tb (**5**); H_4pztc = pyrazine-2,3,5,6-tetracarboxylic acid] have been synthesized by reacting $Ln(NO_3)_3\cdot 6H_2O$ with H_4pztc in the presence of NaOH under room temperature. X-ray crystallographic analysis reveals that complexes **1**–**5** are isostructural featuring three-dimensional (3D) networks with a unique $(4^{11}\cdot 6^8\cdot 8^2)(4^3\cdot 6^2\cdot 8)(4^3)$ topology in which the ligand displays a novel μ_7-coordination mode. The photoluminescence (PL) spectra in the solid state reveal that complexes **2**, **3** and **5** exhibit the characteristic luminescence of Sm(III), Eu(III) and Tb(III) ions, respectively, while complex **4** displays a broad band in the range of 400–650 nm (λ_{max} = 505 nm) which exhibits about 103 nm red-shift and enhancement compared to the band of the free ligand. Further, the isostructural two component Eu(III)-doped Gd(III) complexes realize color-tunable luminescence from red to yellow, white, green and blue by variation of excitation wavelengths. It presents the first example towards full-color-tunable emission in lanthanide coordination frameworks by variation of excitation light.

Introduction

Full-color luminescent materials, especially those with white-light emission have recently merited considerable attention because of their potential applications in various important devices such as color-tunable phosphors,[1] white-light emitting devices,[2] and multicolor-light emitting diodes (LEDs).[3] Generally, white-light emitting materials can be produced through monochromatic,[4] dichromatic,[5] trichromatic[6] and tetrachromatic[7] approaches. The typical one is the trichromatic approach in which red, green and blue (RGB) light emitting components are incorporated into one complex, resulting in white-light emission.[8]

Lanthanide-based materials, owing to their high photoluminescence efficiency, unique sharp-emission bands, substantial Stokes shifts, and long luminescence lifetimes originated from the 4f electronic shells, have been extensively applied in optical, biomedical and magnetic devices.[9] Lanthanide coordination frameworks exhibiting numerous advantages, in particular, have attracted considerable interest and been effectively used in designing multi-color and white-light emitting materials.[10] For example, it has been shown recently that multi-color and white-light emission can be achieved by co-doping Eu(III) and/or Tb(III) ions into the corresponding isostructural frameworks through changing the composition of the lanthanide ions.[11] Rao *et al*. have reported isostructural Tb(III)- and Eu(III)-codoped La(III) coordination frameworks, whose colors can be easily tuned by different combinations of the doped Tb(III) and Eu(III) concentrations, generating white-light emitting materials.[12] Liu *et al*. constructed a series of Eu(III)-doped Tb(III) coordination frameworks emitting tunable three primary colors towards white-light emission by changing the doped ratio of Eu(III) ions.[13] However, it still remains a great challenge to synthesize white-light luminescent materials because different light emitters should compensate exactly by changing the composition of Ln(III) ions through the approach.[14]

Another alternative approach for designing color-tunable and white-light luminescence materials is based on varying excitation wavelengths[15] for either single-component materials[16] or doped lanthanide coordination frameworks,[17] which makes the fabrication of tunable luminescence much facile. For example, Li *et al*. have obtained tunable luminescence from yellow to white by varying excitation wavelengths through the doping of Eu(III) and Tb(III) ions into the La−Zn framework.[17a] Liu *et al*. have also realized tunable luminescence from yellow to white by a shift of the excitation wavelengths through the doping of Eu(III) and Tb(III) ions into the La(III) framework.[17b] Although these two lanthanide coordination frameworks have achieved color-tunable emitting by varying excitation wavelengths, the colors only can be tuned from yellow to white but not full-color region. Until now, there have no lanthanide coordination frameworks display full-color-tunable luminescence including three primary colors and white-light emission by variation of excitation light.

We are interested in the synthesis of new luminescent and color-tunable emitting lanthanide coordination frameworks.[18] Therefore, a rigid pyrazine-2,3,5,6-tetracarboxylic acid was chosen as the organic building blocks, not only for its versatile coordination directions in space making the design and prediction of the 3D networks possible, but also for the sensitization to the emission of lanthanide ions.[19] As a result, a family of new lanthanide coordination frameworks of $[NaLn(pztc)(H_2O)_3]\cdot H_2O$ [Ln = Ce (**1**), Sm (**2**), Eu (**3**), Gd (**4**) and Tb (**5**)] have been isolated and their luminescence have been studied. Notably, upon doping the Eu(III) ions into the isostructural Gd(III) complex, it realizes color-tunable emission from red to yellow, white, green and blue under variation of excitation wavelengths.

Experimental section

Materials and instrumentation. H_4pztc ligand was synthesized according to the literature.[20] $Ln(NO_3)_3{\cdot}6H_2O$ were prepared by reactions of lanthanide oxide and nitric acid. All the other reagents were of analytical grade and used without further purification. Elemental analysis for C, H and N was performed on a PerkinElmer 2400 analyzer. FT-IR data were collected on a PerkinElmer 100 spectrophotometer by using KBr pellets in the range of 4000−400 cm^{-1}. UV-vis spectra (in aqueous solutions) were recorded on a PerkinElmer Lambda 35 spectrometer. Thermal analysis was conducted on a PerkinElmer STA 6000 with a heating rate of 10 $^{\circ}C{\cdot}min^{-1}$ in a temperature range from 30 ºC to 800 ºC under atmosphere. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/Max-3B X-ray diffractometer with CuKα as the radiation source (λ = 0.15406 nm) in the angular range θ = 5−50º at room temperature. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) were performed on a HK-2000 spectrometer. Excitation and emission spectra were measured with an Edinburgh FLS 920 fluorescence spectrophotometer. Luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh Instrument (FLS 920) with microsecond pulse lamp as the excitation. The overall luminescent quantum yields of the solid-state samples were determined in powder forms by an absolute method developed by Molle and co-works,[21] using an integrating sphere (150 mm diameter, $BaSO_4$ coating) on Edinburgh Instrument FLS920. The basic principle of this method can be expressed by a simple formula equation:

$$\Phi_{overall} = \frac{A_H}{R_{ST} - R_H} \qquad (1)$$

where A_H is the area under emission spectrum of the sample and R_{ST} and R_H are diffuse reflectance of the reflecting standard and the sample, respectively. The Commission International de I'Eclairage (CIE) color coordinates were calulated on the basis of the international CIE standards.[21]

Synthesis of complexes 1−5. Complexes **1**−**5** were prepared in a similar manner. In a typical synthesis of **1**, a methanol solution (10 mL) of $Ce(NO_3)_3{\cdot}6H_2O$ (13.0 mg, 0.03 mmol) was layered on an aqueous solution (10 mL) of H_4pztc (7.7 mg, 0.03 mmol) and NaOH (4.8 mg, 0.12 mmol) in a long test tube. The tube was sealed and allowed to stand at room temperature. Colorless crystals of **1** suitable for X-ray analysis were obtained in about one month.

$[NaCe(C_8N_2O_8)(H_2O)_3]{\cdot}H_2O$ (1). Yield: 10.2 mg, 70%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaCe$ (487.27): C, 19.72; H, 1.65; N, 5.75%. Found: C, 19.75; H, 1.64; N, 6.36%. IR (KBr, cm^{-1}): 3421 (s), 1615 (s), 1455 (w), 1415 (w), 1308 (m), 1162 (m), 882 (w), 845 (w), 635 (w). UV-vis [H_2O, λ]: 239, 296 nm.

$[NaSm(C_8N_2O_8)(H_2O)_3]\cdot H_2O$ (2). Yield: 10.5 mg, 70%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaSm$ (497.51): C, 19.31; H, 1.62; N, 5.63%. Found: C, 19.30; H, 1.62; N, 6.15%. IR (KBr, cm^{-1}): 3412 (s), 1611 (s), 1461 (w), 1416 (w), 1309 (m), 1164 (m), 886 (w), 843 (w), 637 (w). UV-vis [H_2O, λ]: 239, 296 nm.

$[NaEu(C_8N_2O_8)(H_2O)_3]\cdot H_2O$ (3). Yield: 10.3 mg, 69%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaEu$ (499.11): C, 19.25; H, 1.62; N, 5,61%. Found: C, 19.26; H, 1.62; N, 6.10%. IR (KBr, cm^{-1}): 3411 (s), 1615 (s), 1462 (w), 1411 (w), 1309 (m), 1164 (m), 886 (w), 841 (w), 638 (w). UV-vis [H_2O, λ]: 239, 296 nm.

$[NaGd(C_8N_2O_8)(H_2O)_3]\cdot H_2O$ (4). Yield: 9.2 mg, 61%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaGd$ (504.40): C, 19.05; H, 1.60; N, 5.55%. Found: C, 19.04; H, 1.61; N, 6.08%. IR (KBr, cm^{-1}): 3399 (m), 1615 (s), 1463 (w), 1413 (w), 1310 (m), 1165 (m), 887 (w), 841 (w), 638 (w). UV-vis [H_2O, λ]: 239, 296 nm.

$[NaTb(C_8N_2O_8)(H_2O)_3]\cdot H_2O$ (5). Yield: 9.0 mg, 59%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaTb$ (506.08): C, 18.99; H, 1.59; N, 5.54%. Found: C, 19.01; H, 1.60; N, 6.09%. IR (KBr, cm^{-1}): 3439 (s), 1621 (s), 1462 (w), 1409 (w), 1314 (m), 1164 (m), 887 (w), 849 (w), 638 (w). UV-vis [H_2O, λ]: 296 nm.

For the isostructural Eu(III)-doped Gd(III) complexes, the synthetic methods are the same as mentioned above just by using $Eu(NO_3)_3\cdot 6H_2O$ and $Gd(NO_3)_3\cdot 6H_2O$ as the starting materials in stoichiometric ratios.

$[NaGd_{0\cdot90}Eu_{0\cdot10}(C_8N_2O_8)(H_2O)_3]\cdot H_2O$. Yield: 9.7 mg, 64%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaGd_{0\cdot90}Eu_{0\cdot10}$ (503.87): C, 19.07; H, 1.60; N, 5,56%. Found: C, 19.09; H, 1.61; N, 6.05%. IR (KBr, cm^{-1}): 3410 (s), 1616 (s), 1463 (w), 1410 (w), 1311 (m), 1165 (m), 887 (w), 840 (w), 639 (w). UV-vis [H_2O, λ]: 239, 296 nm.

$[NaGd_{0\cdot85}Eu_{0\cdot15}(C_8N_2O_8)(H_2O)_3]\cdot H_2O$. Yield: 9.8 mg, 65%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaGd_{0\cdot85}Eu_{0\cdot15}$ (503.6): C, 19.08; H, 1.60; N, 5.56%. Found: C, 19.10; H, 1.61; N, 6.08%. IR (KBr, cm^{-1}): 3406 (s), 1615 (s), 1462 (w), 1411 (w), 1310 (m), 1165 (m), 886 (w), 840 (w), 638 (w). UV-vis [H_2O, λ]: 239, 296 nm.

$[NaGd_{0\cdot95}Eu_{0\cdot05}(C_8N_2O_8)(H_2O)_3]\cdot H_2O$. Yield: 9.4 mg, 62%; *Anal.* Calcd for $C_8N_2H_8O_{12}NaGd_{0\cdot95}Eu_{0\cdot05}$ (504.13): C, 19.06; H, 1.60; N, 5,56%. Found: C, 19.09; H, 1.62; N, 6.09%. IR (KBr, cm^{-1}): 3408 (s), 1615 (s), 1463 (w), 1410 (w), 1311 (m), 1165 (m), 887 (w), 841 (w), 638 (w). UV-vis [H_2O, λ]: 239, 296 nm.

X−ray crystallography. Suitable single crystals of complexes **1−5** were selected for X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the SAINT processing program.[22] All data were collected at a temperature of 20 ± 2 ºC. The structures were solved by direct methods and all non-hydrogen atoms are anisotropically refined by full matrix least-squares on F^2 using the SHELXTL-97 program.[23] The topological analysis was performed with TOPOS.[24] The crystallographic data as well as the selected bond lengths and bond angles for complexes **1−5** are summarized in Table S1 and Tables S2−6. CCDC reference numbers 873443−873447 for complexes **1−5**, respectively.

Results and discussion

Characterization. FT-IR spectra for **1−5** and Eu(III)-doped Gd(III) complexes are similar (Fig. S1). In a typical spectrum of **1**, a broad strong band at 3427 cm^{-1} is assigned as the characteristic peak of O−H vibration from the water molecules. The asymmetric and symmetric stretching vibrations of the carboxylate groups are observed at 1615, 1455, and 1415 cm^{-1}. The absence of the characteristic band around 1726 cm^{-1} indicates a complete deprotonation of carboxylate groups and coordination to the metal ions.[25] UV-vis absorption spectra of all complexes and H_4pztc in aqueous solutions at room temperature were recorded and shown in Fig. S2. In the absorption spectrum of H_4pztc, there are two characteristic absorption peaks (239 and 294 nm), due to the K-band and B-band appearing separately, both corresponding to the π−π* transitions.[25] The absorption bands for all complexes are similar although the B-band (296 nm) red-shifted about 2 nm as compared to that (294 nm) of the free ligand. TG-DSC curves of complexes **1−5** are similar (Figs. S3−S7). In a typical curve of **1**, it exhibits a gradual weight loss of 16.7% in the range of 25−195 ºC, which corresponds to the loss of the lattice and coordinated H_2O molecules (calcd 14.7%). The powder X-ray diffraction patterns of complexes **1−5** and Eu(III)-doped Gd(III) complexes all match those simulated from single-crystal X-ray data, clearly indicating that the pure phases were obtained (Fig. S8).

Crystal structures. X-ray crystallographic analysis reveals that complexes **1−5** are isostructural featuring 3D open frameworks, crystallizing in orthorhombic system. In a typical structure of complex **1**, each Ce(III) ion is 9-coordinated in the coordination geometry of a mono-capped square antiprism (Fig. 1a) by eight oxygen atoms and one nitrogen atom from four pztc^{4-} ligands and two H_2O molecules. The Ce−O bond distances range from 2.414(9) to 2.572(9) Å and the Ce−N bond distance is 2.549(11) Å, which are comparable to those of the reported $\{[Ce(Hpdtc)(H_2O)_3]\cdot H_2O\}_n$ (H_4pdtc = pyridine-2,3,5,6-tetracarboxylate) complex.[26] The Na(I) ion is 5-coordinated in the coordination geometry of a square-pyramid by five oxygen atoms from three different pztc^{4-} ligands and two H_2O molecules, with an average

Na−O bond length of 2.582 Å. It is noteworthy that the fully deprotonated pztc^{4-} ligand adopts a novel μ_7-coordination mode connecting four Ce(III) ions and three Na(I) ions using its one monodentate N atom and four carboxylate groups with monodentate, μ_2-η^2:η^0-bidentate, μ_2-η^1:η^1-bidentate and μ_3-η^2:η^2-tridentate modes (Fig. 1b). It is different from that in the reported analog of [EuK(pztc)(H_2O)$_4$] complex in which the pztc^{4-} ligand acts as a μ_8-coordination mode.[27]

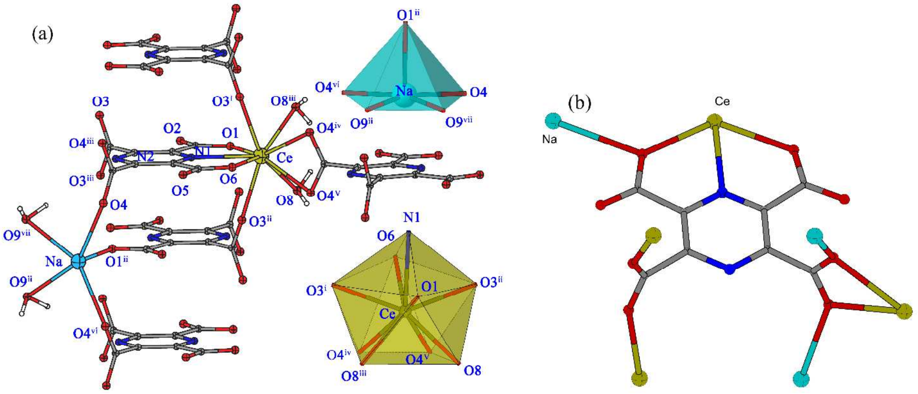

Fig. 1 (a) Coordination environments and the coordination geometries of Na(I) and Ce(III) ions in complex **1**. (b) Coordination mode of pztc^{4-} ligand in complex **1**. Symmetry codes: ^{i} = − x, − 1 − y, 1 − z; ^{ii} = − x, 0.5 + y, 1 − z; ^{iii} = x, − 0.5 − y, z; ^{iv} = − 0.5 + x, − 0.5 − y, 1.5 − z. ^{v} = − 0.5 + x, y, 1.5 − z; ^{vi} = x, 0.5 − y, z; ^{vii} = − x, − y, 1 − z.

The neighboring Ce(III) and Na(I) ions are bridged (up and down) by two carboxylate groups perpendicular to the pyrazine plane, respectively, forming a 1D square column along the *b* direction (Fig. 2a). Where the pztc^{4-} ligands are arranged alternately in a···b···a···b converting modes and both the Ce···Ce and Na···Na distances are 6.7180(13) Å. Then, the adjacent 1D square columns are connected by O4 atoms from μ_3-η^2:η^2-tridentate carboxylate groups into a 2D layer (Fig. 2b). As shown in Fig. 2c, there are still O4 atoms on the two sides of the layer, which further link the Ce(III) ions from the neighboring layers to generate a 3D framework (Fig. 3a). The 3D framework exhibits 1D channel along the *b* axis with dimensions of ~ 4.8 × 9.3 Å^2. A better insight into the nature of this intricate framework can be achieved by a topological approach. As depicted above, each Ce(III) ion can be regarded as being a 4-connected node and Na(I) ion can be regarded as a 3-connected node. Every pztc^{4-} ligand links four Ce(III) ions and three Na(I) ions to act as a 7-connected node. According to the simplification principle, the resulting structure of complex **1** is trinodal (3,4,7)-connected net with a $(4^{11}\cdot6^8\cdot8^2)(4^3\cdot6^2\cdot8)(4^3)$ topology (Fig. 3b) which is firstly reported.

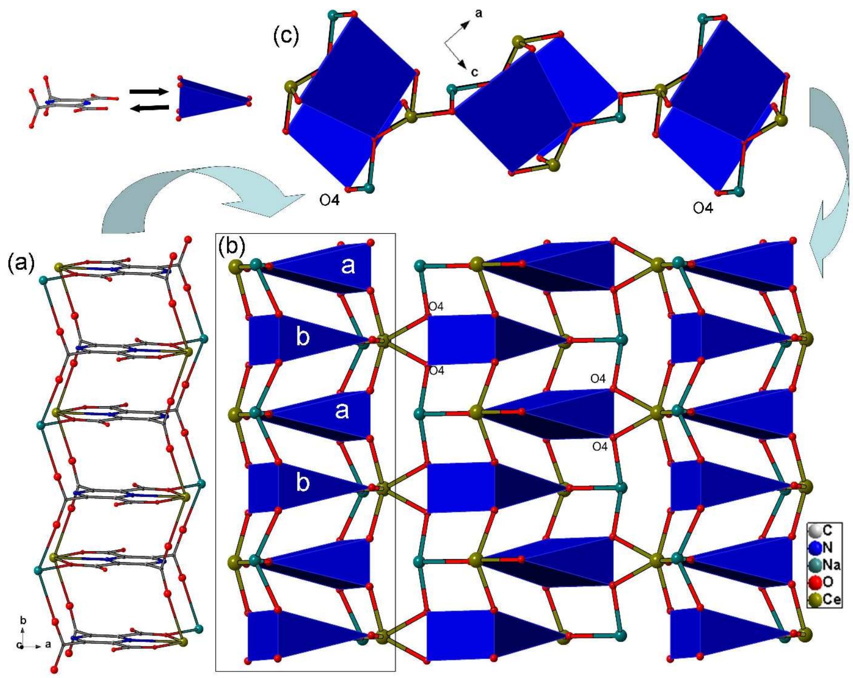

Fig. 2 (a) Infinite 1D square column in **1**. (b) View of the 2D layer structure along the *c* axis. (c) View of the 2D layer structure in **1** along the *b* axis. The pztc^{4-} ligand is represented as polyhedron. Coordinated and lattice H_2O molecules are omitted for clarity.

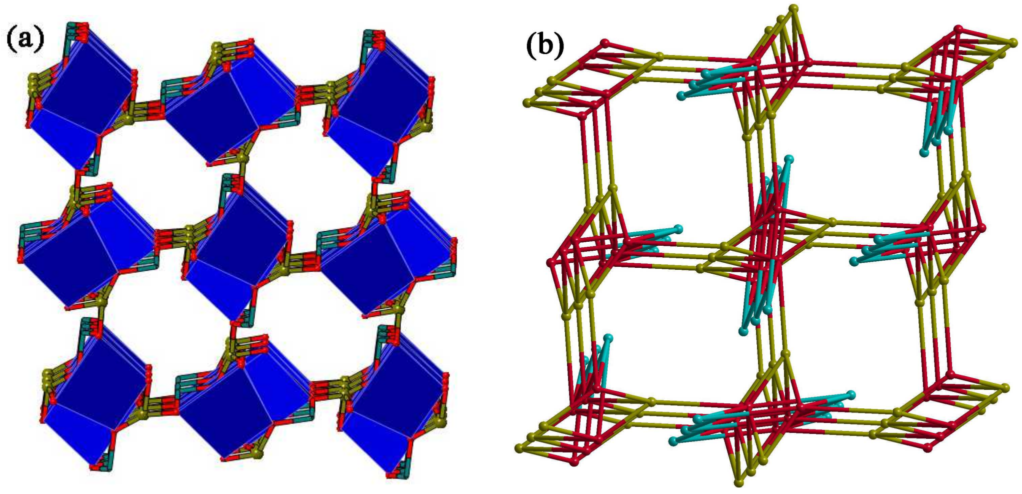

Fig. 3 (a) The 3D framework with 1D channels of **1** viewed along the *b* axis after removing the coordinated and lattice H_2O molecules. The pztc^{4-} ligand is represented as polyhedron. (b) Topological view of the 3D structure of **1**. Cerium atoms are shown in deep yellow, sodium atoms in teal and the ligand centroids in purple.

Photoluminescence properties. The solid state luminescence spectra of H_4pztc ligand and complexes **2–5** were recorded at room temperature as shown in Fig. 4. Upon excitation at 385 nm, free H_4pzdc ligand exhibits a blue light emission at 402 nm due to $\pi\rightarrow\pi^*$ transitions of the ligand (Fig. 4a).. However, complex **4** exhibits much enhanced blue-green emission and considerably shifts to 505 nm with the excitation at 356 nm in comparison to the band of the free ligand   It is known that the energies of the excited levels of Gd(III) ion are much higher than that for the typical energy of the ligand triplet states, inhibiting any ligand-to-metal energy transfer process.[28] The enhancement and about 103 nm red-shift of the emission band in complex **4** are attributed to the coordination of pztc^{4-} ligands to metal ions which has enabled the rigidity of the aromatic backbones and thus reduces the loss of energy by radiationless decay of the intraligand emission excited state.[15a, 29]

When excited at 330 nm, complex **2** exhibits four emission bands at 562, 595, 642 and 707 nm, which are attributed to $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$, $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ transitions of the Sm(III) ion, respectively (Fig. 4b). The luminescence lifetime τ value is 9.83 μs (Fig. S9) and the quantum yield Φ is 6.4%. Upon excitation at 334 nm, complex **3** displays intense red luminescence with five bands occurring at 580, 592, 614, 665, and 695 nm that can be assigned to $^5D_0\rightarrow{}^7F_J$ (J = 0−4) transitions, respectively (Fig. 4c). The lifetime and quantum yield are τ = 395.24 μs and Φ = 17.2%. Under excitation at 340 nm, complex **5** emits green luminescence with peaks located at 489, 544, 582 and 621 nm (Fig. 4d), coincident with the $^5D_4\rightarrow{}^7F_J$ (J = 6−3) transitions, respectively. The most intense emission at 544 nm is attributed to the $^5D_4\rightarrow{}^7F_5$ transition of the Tb(III) ion with the lifetime τ and quantum yield Φ values of 870.04 μs and 21.6%. Notably, obtained values of quantum yields and lifetimes of complexes **2**, **3** and **5** are higher than those of corresponding $\{[Ln_2(pmdc)_3(H_2O)_2]\cdot H_2O\}_n$ (H_2pmdc = Pyrimidine-4,6-dicarboxylate) and $[Ln_2(2,3\text{-}pzdc)_2(ox)(H_2O)_2]_n$ (2,3-H_2pzdc = 2,3-pyrazinedicarboxylate, H_2ox = oxalic acid) lanthanide analogue.[30] The absence of the ligand-based emission in the luminescence spectra of complexes **2**, **3** and **5** suggests that the energy transfer from the ligands to the lanthanide centers is very effective.[12]

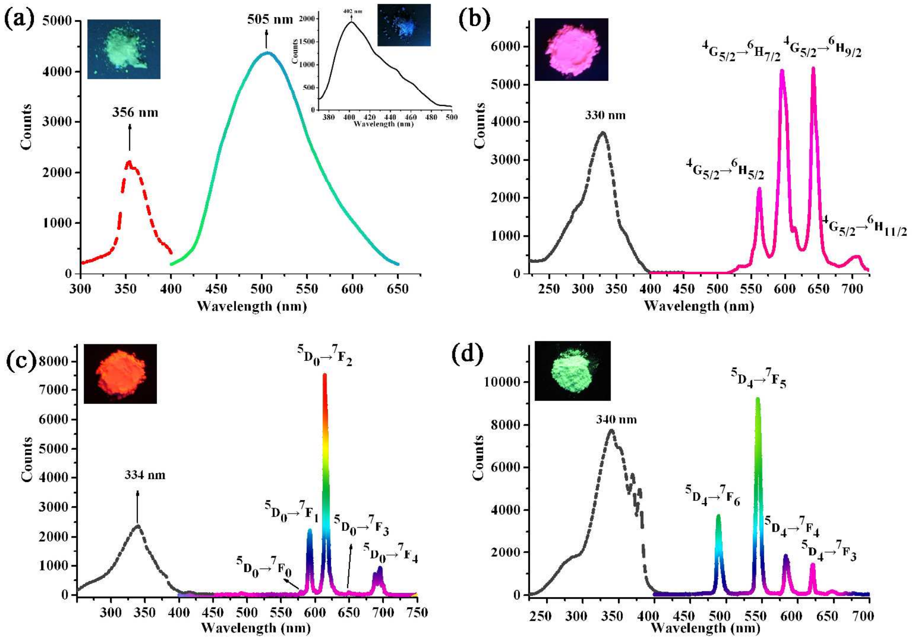

Fig. 4 Excitation and emission spectra of the complex **4** (a) and H_4pztc ligand [(a) insert] at 298K. Excitation and emission spectra of complexes **2** (b), **3** (c) and **5** (d) at 298K, respectively. Insert: The luminescence photograph of solid state complexes for **4** (a), **2** (b), **3** (c) and **5** (d) excited under UV lamp at 365 nm.

Triplet state of the ligand and energy transfer. According to the intramolecular energy transfer mechanism, the luminescence property of lanthanide complexes mainly depends on the energy match between the triplet state energy of ligands and the resonance emission energy level of lanthanide ions.[31] Herein, the low temperature phosphorescence of complex **4** at 77 K was measured to investigate the energy difference. It can be seen that the first phosphorescence band is around 434 nm and the triplet state energy of H_4pztc can be estimated to be 23 041 cm^{-1} (Fig. S10). The single state energy ($^1\pi\pi^*$) level of H_4pztc is estimated by referencing its absorbance edge, which is 29 412 cm^{-1} (340 nm). According to Reinhoudt's empirical rule,[15a] the intersystem crossing (ISC) process becomes effective when ΔE is at least 5000 cm^{-1}. The energy gap ΔE (S_1−T_1) for the ligand is 6371 cm^{-1}. Thus, the ISC is effective in this ligand. The energy differences between the triplet state of H_4pztc and the resonance energy level of Sm(III) ($^4G_{5/2}$, 17900 cm^{-1}), Eu(III) ($^5D_0$, 17300 cm^{-1}) and Tb(III) ($^5D_4$, 20500 cm^{-1}) can be calculated to be 5141, 5741 and 2541 cm^{-1}, respectively. Latva's empirical rule[32] states that an optimal ligand-to-metal energy transfer process for Ln(III) ions needs [$\Delta E = E(T_1) - E(^5D_J)$] 2500−4000 cm^{-1} for Eu(III) and 2500−4500 cm^{-1} for Tb(III). Hence, it can be predicted that H_4pztc ligand is more suitable for the sensitization for Tb(III) ion's luminescence than other Ln(III).

Color-tunable luminescence. Considering that both complexes **3** and **4** are isostructural and emit red and blue-green light, respectively, it will therefore be possible to construct the white-light or color-tunable emitting materials by means of doping Eu(III) ions into the Gd(III) frameworks. Thus, the Eu(III)-doped Gd(III) complex $Gd_{0.90}Eu_{0.10}$ has been synthesized and its phase purity was verified by PXRD analysis (Fig. S8). The content of Eu(III) and Gd(III) ions was confirmed by inductively coupled plasma (ICP) spectroscopy. The emission spectra of the complex $Gd_{0.90}Eu_{0.10}$ was recorded under varying UV light excitation from 330 to 390 nm (Fig. 5). Strikingly, tunable colors and white light have been observed along with the varying excitation wavelengths. When excited at 330 nm, the complex $Gd_{0.90}Eu_{0.10}$ mainly emits intense red luminescence from Eu(III) ions and very weak luminescence from the ligands. Obviously, the emission intensity from Eu(III) ions shows significant decrease with the excitation wavelengths varying from 330 to 390 nm, whereas, the emission intensity of the ligands enhances first and reaches its maximum at the excitation of 360 nm, then weakens with the increase of the wavelength. Upon varying the excitation light to 350 nm, the emission intensities from the ligands and Eu(III) ions are comparable resulting in white light to the naked eye. The calculated chromaticity coordinate (0.386, 0.378) fall within the white-light region of the 1931 CIE chromaticity diagram (for pure white x = 0.33, y =0.33) and the correlated color temperatures (CCT) is 3872 K. When adjusting the excitation light to 360−370 nm, the characteristic emission peaks from Eu(III) ions are very weak, and mainly exhibits green light emission from ligands. The wavelength of excitation light increase to 380−390 nm, it mainly displays blue light around 465 nm luminescence from the self-emission of the ligand.[15a] Therefore, the tunable colors from red to yellow, white light, green and blue are thus achieved by variation of excitation light, as evidenced by the photographs of the sample at different excitation wavelengths (Fig. 5a−g). The emission colors at different excitation wavelengths are illustrated in the CIE chromaticity diagram (Fig. 6), while the corresponding CIE color coordinates are listed in Table 1. For different doping concentrations of the Eu(III)-doped Gd(III) complexes ($Gd_{0.85}Eu_{0.15}$ and $Gd_{0.95}Eu_{0.05}$), they also achieved tunable colors from red to green and blue by variation of excitation light (Figs. S11 and S12). The luminescence lifetimes for complex $Gd_{0.90}Eu_{0.10}$ detected at $^5D_0\rightarrow{}^7F_2$ transition are in the range of 401−433 μs, while the corresponding quantum yields range from 15.5 to 0.5% when varying excitation light from 330 to 390 nm (Fig. S13 and Table 1). The quantum yield of white light emission (7.6%) for complex $Gd_{0.90}Eu_{0.10}$ is higher than those reported previously for white light emission of two-component lanthanide coordination frameworks.[5a, 33]

Notably, previously reported color-tunable emission of lanthanide coordination frameworks by variation of excitation light are all three-component lanthanide complexes and only reached tunable colors from yellow to white.[17] However, the two-component approach was rare for white-light emission and no reports about color-tunable emission by variation of excitation light on the basis of lanthanide coordination frameworks.[5a, 13, 33] To the best of our knowledge, the complex $Gd_{0.90}Eu_{0.10}$ in our work represents the first example towards full-color-tunable emission in lanthanide coordination frameworks by variation of excitation light.

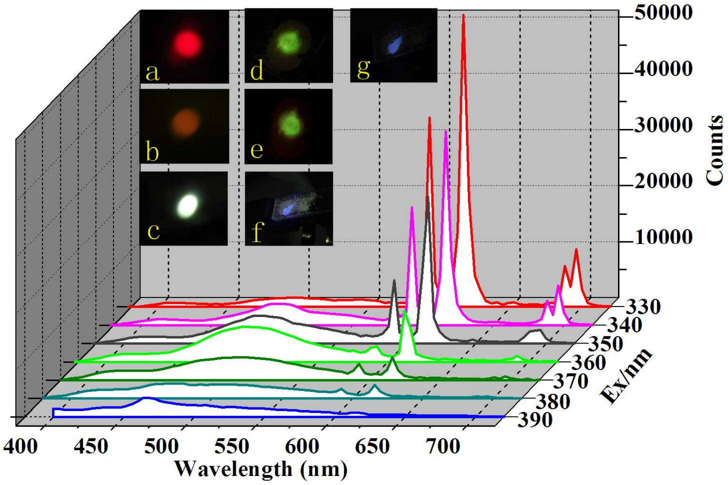

Fig. 5 Solid-state emission spectra of the complex $Gd_{0.90}Eu_{0.10}$ with excitation wavelengths varying from 330 to 390 nm. [Insert: The corresponding luminescence photograph under excitation wavelengths from 330 to 390 nm using fluorescence spectrophotometer (a–g, step size 10 nm)].

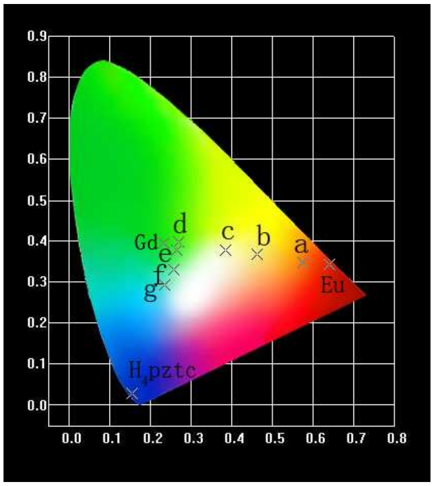

Fig. 6 The CIE chromaticity diagram for the complex $Gd_{0.90}Eu_{0.10}$ with excitation wavelengths varying from 330 to 390 nm (a–g, step size 10 nm) showing the location of the color-tunable chromaticity of visual emission image.

Table 1 Color coordinates according to CIE 1931, luminescence lifetimes and quantum yields of the complex $Gd_{0.90}Eu_{0.10}$ under different excitation wavelengths.

Ex/nm	CIE (x, y)	Approximate color regions	lifetimes/μs	Quantum yields Φ
330	a(0.575, 0.348)	Red	401.23	15.5%
340	b(0.462, 0.367)	Yellow	404.80	11.7%
350	c(0.386, 0.378)	White	407.44	7.6%
360	d(0.270, 0.398)	Green	411.65	3.8%
370	e(0.264, 0.378)	Green	415.43	1.9%
380	f(0.257, 0.330)	Blue	421.41	0.7%
390	g(0.235, 0.292)	Blue	433.26	0.5%

Conclusions

A series of pyrazine-2,3,5,6-tetracarboxylate alkai-lanthanide complexes with 3D open framework have been facilely synthesized. Structural analysis verifies that this series of complexes feature a unique $(4^{11}\cdot6^{8}\cdot8^{2})(4^{3}\cdot6^{2}\cdot8)(4^{3})$ topology structure by way of $pztc^{4-}$ ligands coordinating to lanthanide ions in a novel μ_7-coordination mode. The PL spectra in solid state reveal that the ligand of pyrazine-2,3,5,6-tetracarboxylate is able to sensitize the characteristic luminescence of Sm(III), Eu(III) and Tb(III) ions, respectively. As well, the Gd(III) complex displays strong blue-green emission with a broad band in the range 400−650 nm attributed to the rigidity of the 3D framework. Strikingly, the Eu(III)-doped Gd(III) complex exhibits towards full-color-tunable and white-light emission by variation of excitation light with considerable long lifetimes of 401 to 433 μs and the maximum quantum yield of 15.5%. This approach may provide a new route for design of lanthanide coordination frameworks with full-color-tunable materials by variation of excitation light. Future work will focus on the rational control of tunable colors with high quantum yield and ultimately the fabrication of emitting devices.

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Supplementary material

FT-IR spectra, UV spectra, TG-DTA curves, PXTD patterns, decay curves, CIE chromaticity coordinates diagram for complexes $Gd_{0.85}Eu_{0.15}$ and $Gd_{0.95}Eu_{0.05}$, crystal data and structure refinement, selected bond lengths and X-ray crystallographic files (CIF) for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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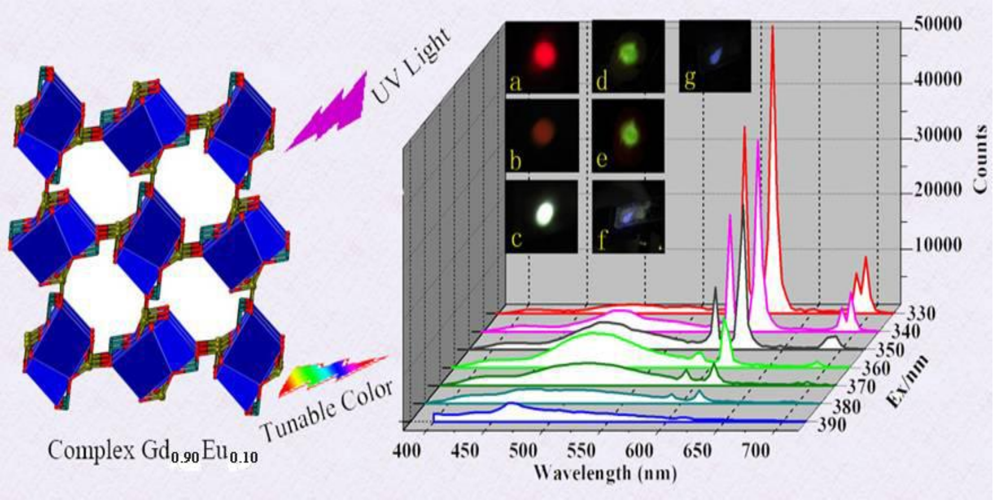
Graphic Abstract



Eu(III)-doped Gd(III) pyrazine-2,3,5,6-tetracarboxylate alkali-lanthanide metal-organic frameworks (LnMOF) with a unique $(4^{11}\cdot6^{8}\cdot8^{2})(4^{3}\cdot6^{2}\cdot8)(4^{3})$ topology present full color-tunable luminescence and white light by variation of excitation wavelengths.