Research Article

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Nucleotide-based green synthesis of lanthanide coordination polymers for tunable white-light emission

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Abstract: White-light emitting lanthanide(III) metal-organic coordination polymers (LMOCPs) were prepared via a green synthesis method performed in pure aqueous solution at room temperature without using toxic solvent and reagents. This kind of LMOCP, denoted as adenosine monophosphate (AMP)/Ln-CIP, was composed of Ln^{3+} {Ln = Tb (1), Eu (2), and Gd (3)}, hydrosoluble biomolecule of AMP, and nonpoisonous antenna ligand of CIP (ciprofloxacin). The complex of Tb(1), Eu(2), and Gd(3) in AMP/Ln-CIP emits strong green, red, and blue light, respectively. With careful adjustment of the doping mole ratio of the three lanthanide ions {Ln = Tb:Eu:Gd = 0.1:0.9:99.0} in one framework, white light-emission can

indeed be achieved. AMP/Ln-CIP is network-structural and amorphous by transmission electron microscope and X-ray diffraction analysis. The fluorescence lifetime and quantum yield of AMP/Ln-CIP are 4.36 ms and 36.5%, respectively.

Keywords: white light, metal-organic coordination polymers, green synthesis

1 Introduction

White light-emitting materials have received tremendous attention because they can be applied in many practical domains, such as light-emitting diodes, electrochemical cells, and many other types of light-emitting devices [1–6]. The white-light-emitting materials reported to date were mainly concentrated on metal-organic hybrid materials [7–10], inorganic nanocrystals [11,12], quantum dots [13,14], and small organic molecules [15]. Generally, these white light materials were obtained through three strategies: (1) a single component emitting in the whole visible region from 400 to 700 nm, (2) a two-chromophore containing component emitting blue and yellow or orange, and (3) a three-chromophore containing emitting primary colors [6–8,16–18]. In comparison, the single-component white-light-emitting phosphors have many advantages such as high color rendering index, high luminescence efficiency, and low manufacturing cost [19,20]. However, the acquisition of single-component materials capable of white-light production is of great challenge. Lanthanide inorganic phosphors have been the domain of two-chromophore white emitting materials in the last decades due to the advantages of lanthanide ions, including large Stokes shift, sharp emission, long fluorescence lifetime, high photochemical stability, and low toxicity [1,21,22]. Currently, the white LED based on the emission of blue light InGaN chip and yellow light from lanthanide

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inorganic materials of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG:Ce) is most widely used and commercially available [23,24]. However, some defects still remain due to the lack of a red-emitting light component, which severely limits its versatile applications [25].

Recently, lanthanide-based metal-organic coordination polymers have attracted great interests for white light applications [7–9,26]. As an organic-inorganic hybrid material, lanthanide(III) metal-organic coordination polymer (LMOCP) is more compatible with organic matrices for organic light-emitting diode applications than inorganic metal oxide and nitride powders [7–9,26–29]. Compared with crystal metal-organic framework, amorphous LMOCP possesses higher tailorable properties, milder reaction conditions, and wider diversity of composition [30]. These facts would afford an infinite number of possible white light-emitting materials and improve the overall optical features. Europium and terbium compounds with specific red and green emission bands, respectively, are regarded as so excellent fluorescence materials and widely used in diverse optical fields [31]. Several white-light LMOCPs have been synthesized to take advantage of the unique optical features of terbium and europium ions; however, the organic ligand in these LMOCPs was toxic, and the synthesis was conducted at high temperature [32,33]. Challenges still remain in the development of white LED with good performance, especially with the green synthesis method and nontoxic reagents.

Nucleotides, as a kind of non-poisonous, rigid, water-soluble biomolecules, not only have been widely used as a building block for constructing metal-organic coordination polymer via nitrogen and oxygen atoms but also can enhance the fluorescence of lanthanide complexes on basis of the hydrophobic environment of the polymer interior [34–36]. In this work, by a green synthetic method, we prepared an amorphous LMOCP of AMP/Ln-CIP with tunable white light emission using adenosine monophosphate (AMP) as an organic ligand. In the solid framework of AMP/Ln-CIP, Ln = Tb(1), Eu(2), and Gd(3); CIP is able to coordinate to lanthanide ions through O atoms of the carbonyl group and/or carboxyl group for building lanthanide complexes and absorb energy in the UV range to sensitize the green emission of Tb^{3+} and the red emission of Eu^{3+} [37–39]. Especially, CIP ligand presents a blue emission under UV excitation [37]. With careful adjustment of the relative concentration of the lanthanide ions and excitation wavelength, the white light-emitting phosphor can be obtained via the red emission of Eu^{3+} and green emissions of Tb^{3+} combined with blue luminescence of CIP (Scheme 1).

2 Experimental

2.1 Materials and reagents

The following chemical reagents were purchased from J&K Scientific Co. Ltd (Beijing, China): $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), adenosine-5-monophosphate disodium salt (AMP, 98%), tyrosine, and ciprofloxacin. Ultrapure water (18 M Ω) was used for the preparation of all aqueous solutions. Unless otherwise stated, all chemicals used were of analytical reagent grade and were used as received without further purification.

2.2 Synthesis of AMP/ $\text{Tb}_{0.1}\text{Eu}_{0.9}\text{Gd}_{99.0}$ -CIP(4)

The aqueous solutions of 2 mL of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Tb}^{3+} = 0.01$ mM, $\text{Eu}^{2+} = 0.09$ mM, $\text{Gd}^{3+} = 9.9$ mM), 2 mL of AMP (10 mM), and 2 mL of CIP (2.5 mM) were mixed together and incubated for 20 min. The white precipitate was formed immediately. After stirring for 4 h at room temperature, the white precipitate was collected by centrifugation at 13,000 rpm for 5 min, and then washed with ultrapure water for several times to remove unreacted reactants. Finally, the obtained precipitate of AMP/ $\text{Tb}_{0.1}\text{Eu}_{0.9}\text{Gd}_{99.0}$ -CIP(4) was dried in an oven at 60°C. For comparison, the single Tb/AMP-CIP(1), Eu/AMP-CIP(2), and Gd/AMP-CIP(3) were also prepared by a similar procedure using $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mM), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mM), and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mM) as the precursors, respectively.

2.3 Apparatus and characterization

The morphology of LMOCP was examined by scanning electron microscope (SEM) (JSM-6490LV, Japan). The elemental analysis was performed on an energy-dispersive X-ray spectrometer (EDX, X-Max Oxford, UK) and inductively coupled plasma atomic emission spectrometer (ICP-AES, USA). A D8 advance diffractometer (Bruker, Germany) was used for the collection of diffraction data which were useful for phase determination. The fluorescence spectra were recorded on an Agilent CaryEclipse fluorescence spectrophotometer (USA) with a xenon lamp as an excitation source. The fluorescence lifetime was measured by F-7000 FL spectrophotometer. The detection solution was placed in a microscale quartz cuvette. UV-visible absorption spectra

Scheme 1: Schematic diagram of the synthesis process for white-light emissive AMP/Ln-CIP.

were recorded on an Agilent Cary 60 UV-visible spectrophotometer (USA). Nicolet FTIR IS 10 spectrometer (USA) was employed to record the Fourier transform infrared (FTIR) spectra. The Commission International de L'Eclairage (CIE) color coordinates were calculated based on the international CIE standards.

2.4 Quantum yield of AMP/ $\text{Tb}_{0.1}\text{Eu}_{0.9}\text{Gd}_{99.0}\text{-CIP}$

The relative quantum yields of AMP/ $\text{Tb}_{0.1}\text{Eu}_{0.9}\text{Gd}_{99.0}$ were determined using tyrosine as a standard. The values of quantum yield were calculated by the following equation:

$$\Phi_x = \Phi_s (F_x A_s n_x^2 / F_s A_x n_s^2), \quad (1)$$

where Φ is the quantum yield, F is the fluorescence integral intensity, A is the absorbance intensity, and n is the refractive index of the solvent. The subscripts s and x are the reference fluorophore of known quantum yield and the sample, respectively.

3 Results and discussion

3.1 Synthesis and characterization

AMP/ $\text{Tb}_{0.1}\text{Eu}_{0.9}\text{Gd}_{99.0}\text{-CIP}$ was prepared by the self-assembling of Ln^{3+} ions, AMP, and CIP in aqueous solution. SEM images

showed that AMP/ $\text{Tb}_{0.1}\text{Eu}_{0.9}\text{Gd}_{99.0}\text{-CIP}$ was the same network-exterior as the single AMP/Ln-CIP $\{\text{Ln} = \text{Tb}(1) \text{ or } \text{Eu}(2) \text{ or } \text{Gd}(3)\}$ (Figure 1). This result indicates that different kinds of lanthanides ions involved in the same framework have no influence on its appearance. No diffraction peak appeared in the images of X-ray diffraction (XRD) spectra (Figure 2), proving that these LMOCPs were all amorphous. The energy-dispersive X-ray (EDX) confirmed that Ln^{3+} , AMP, and CIP were all involved in the formation of LMOCP (Figure S1). With same lanthanide ratios in LMOCP, we also compared the fluorescence of the mixtures of LMOCP 1, 2, and 3 with that of LMOCP 4. The results indicated that the mixtures of LMOCP 1, 2, and 3 do not emit pure white light (Figure S2). Therefore, to obtain white-emitting material, current synthesis strategy is perfect. Furthermore, the metal compositions analyzed by ICP-AES (mole ratio, $\text{Tb}:\text{Eu}:\text{Gd} = 0.1:0.9:99.0$) are matched with the initial compositions of the Ln^{3+} ions. However, the element analysis of C, H, N, O, and P is not accordant with the initial appending amount of AMP and CIP because (1) during washing and centrifugation, excess AMP and/or CIP was eliminated, which is unproportional with the original ratio and (2) the sensitivity of different elemental analysis instrument to each element is not completely identical (Table S1). The UV-Vis absorption spectra of AMP and CIP and AMP/ $\text{Tb}_{0.1}\text{Eu}_{0.9}\text{Gd}_{99.0}\text{-CIP}$ are also shown in Figure S3; it is observed that AMP displays a characteristic absorption peak at 260 nm and free CIP exhibits two maximum absorption peaks at 270 and 323 nm, respectively. In the absorption peaks of LMOCP 4, these peaks shifted to 268

Figure 1: SEM images of (1) AMP/Tb-CIP, (2) AMP/Eu-CIP, (3) AMP/Gd-CIP, and (4) AMP/Tb_{0.1}Eu_{0.9}Gd_{99.0}-CIP.

Figure 2: XRD analysis of (1) AMP/Tb-CIP, (2) AMP/Eu-CIP, (3) AMP/Gd-CIP, and (4) AMP/Tb_{0.1}Eu_{0.9}Gd_{99.0}-CIP.

and 320 nm, respectively. These changes confirmed that both AMP and CIP had coordinated with Ln^{3+} . Furthermore, the peaks that correspond to the absorption spectrum of LMOCP 4 are stronger, indicating an efficient energy transfer and luminescence sensitization between CIP and Ln^{3+} .

To confirm the chemical coordination between ligands and Ln^{3+} , FTIR was conducted (Figure S4). The characteristic absorption peaks corresponding to C2–N1 stretching vibrations, NH_2 scissoring vibrations, and P–O

stretching of AMP were observed at 1,576, 1,654, and 978 cm^{-1} , respectively. These peaks shifted to 1,566, 1,643, and 996 cm^{-1} in the spectra of LMOCP 4, suggesting both nucleobase moieties and phosphate groups of AMP are involved in the coordination to Ln^{3+} [36]. Furthermore, when compared with pure CIP, the disappearing of the band at 1,708 cm^{-1} (ν_{COOH}) and the shifting of the peak from 1,627 cm^{-1} ($\nu_{\text{C=O}}$) to 1,579 cm^{-1} reflects the coordination between Ln^{3+} and CIP via carboxylate O and carbonyl groups [37–39].

3.2 Photoluminescence properties

The solutions and solid-state photoluminescent properties of LMOCP [1–4] were investigated (Figure 3). In the fluorescence spectrum of AMP/Tb-CIP(1), the peaks at 488, 545, 584, and 619 nm are the characteristic emissions of the Tb^{3+} ions from the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 3-6$) transitions, respectively. For AMP/Eu-CIP, typical peaks at 545, 589, 616, and 696 nm were also observed [40,41], which were associated with the 4f–4f transitions of $^5\text{D}_0$ excited state to the low lying $^7\text{F}_j$ ($j = 1-4$) of Eu^{3+} . LMOCP

Figure 3: Excitation and emission spectra of AMP/Tb-CIP(a), AMP/Eu-CIP (b), and AMP/Gd-CIP (c). Inset is the corresponding images of their solutions and solid powder under a common UV lamp.

1 and 2 display strong green and red emission at room temperature, respectively. Furthermore, the characteristic emission of CIP ligand at 412 nm disappeared in spectra of LMOCP 1 and 2, indicating the efficient energy transfer from CIP to Tb^{3+} and Eu^{3+} (Figure S5 and Figure 3a, b). However, AMP/Gd-CIP(3) does not display the typical emission of Gd^{3+} at 340 nm but a single broad blue emission peak at 412 nm originates from the $\pi-\pi^*$ transition of free CIP (Figure S4 and Figure 3c). We contribute this result to the energy mismatch between the absorption band of Gd^{3+} and the emission of CIP, leading the characteristic 4f–4f transition of Gd^{3+} at 340 nm is invisible.

To obtain a pure white light emission, the molar ratio of Tb^{3+} , Eu^{3+} , and Gd^{3+} ions doped into LMOCP 4

was optimized. According to three primary color theory, green, red, and blue light are all needed for obtaining white emission. However, in LMOCP of 1 and 2, the blue emission of CIP ligand is completely suppressed by the strong red and green luminescence of the Eu^{3+} and Tb^{3+} ions, an excess amount of nonluminescent Gd^{3+} ion is required to dilute these two Ln^{3+} ions in the solid state. With an increase in the concentration of Gd^{3+} , the emission intensities of blue light components gradually raised, when the mole ratio of $\text{Tb}:\text{Eu}:\text{Gd}$ was adjusted to 0.1:0.9:99.0 (Figure 4), a white emission with CIE chromaticity coordinates of (0.336, 0.327) which is close to those of international pure white light (0.333, 0.333) was obtained (Figure 5). In addition, the emission intensity of the white light is reaction time-dependent.

Figure 4: Emission spectra of the doped LMOCP excited at 273 nm. (a–h) (Tb, Eu, Gd%): (a) (1.01, 22.52, 76.47), (b) (2.34, 3.91, 93.75), (c) (1.015, 2.075, 96.91), (d) (1.515, 1.275, 97.21), (e) (0.015, 1.075, 98.91), (f) (0.1, 0.5, 99.4), (g) (0.15, 0.85, 99.0), and (h) (0.1, 0.9, 99.0).

Figure 5: Emission spectra of LMOCP4 with the excitation wavelength of 273 nm (4) (left) and its corresponding CIE chromaticity diagram (right). Inset is the photograph of the solution and a solid powder sample of LMOCP 4 under the UV lamp.

We checked its fluorescence peak variation at 617 nm with the reaction time. As shown in Figure S6, when the reaction time is 4 h, the luminescence intensity at 617 nm of AMP/Tb_{0.1}Eu_{0.9}Gd_{99.0}-CIP reached the maximum. Furthermore, LMOCP 4 exhibits a high relative quantum yield of 36.5% that are comparable with that of other MOCPs of 6.5% [7], 15.3% [8], 8% [9], 7.93% [26], and 50% [10]. Additionally, the obtained LMOCP 4 also possesses long luminescence lifetime of 4.359 ms (Figure S7). These distinct photophysical properties make LMOCP 4 a kind of preminent white light materials.

3.3 Thermogravimetry (TGA)

Finally, we investigated the thermal stability of the LMOCP 4 by TGA techniques. As can be seen from Figure S8, even exceeding to 350°C, the LMOCP 4 only lost 12% of its total weight. The result indicates that the obtained white materials LMOCP 4 based on three primary color theory possess high thermal stability.

4 Conclusions

Based on the three primary colors theory, via a green synthesis method, we have successfully developed a white-light emissive nanophosphor material of AMP/Tb_{0.1}Eu_{0.9}Gd_{99.0}-CIP. When compared with other methods for preparing white-emitting materials, our strategy is simple, facile, and environment friendly. As a kind of white light emitting material, AMP/Tb_{0.1}Eu_{0.9}Gd_{99.0}-CIP possesses many advantages such as high thermostability, long fluorescence lifetime, high quantum yields, and satisfactory CIE of (0.336, 0.327). Furthermore, the similar coordination behavior of Tb³⁺,

Eu³⁺, and Gd³⁺ allows in situ doping of them together into a parent LMOCP simultaneously, which is convenient for obtaining white emitting materials. We believe that the present synthetic strategy can be extended to the development of other lanthanide-based white light emitting materials.

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References

- [1] Cho J, Park JH, Kim JK, Schubert EF. White light-emitting diodes: history, progress, and future. *Laser Photon Rev.* 2017;11(2):1600147. doi: 10.1002/lpor.201600147.
- [2] Gather MC, Kohnen A, Meerholz K. White organic light-emitting diodes. *Adv Mater.* 2011;23(2):233–48. doi: 10.1002/adma.201002636.
- [3] Lee CL, Cheng CY, Su HC. Enhancing device efficiencies of solid-state near-infrared light emitting electrochemical cells by employing a tandem device structure. *Isr J Chem.* 2014;15(3):711–20. doi: 10.1016/j.jorgel.2014.01.001.
- [4] Schubert E, Kim J. Solid-state light sources etting smart. *Science.* 2005;308(5726):12741278. doi: 10.1126/science.1108712.
- [5] Zhang B, Liu L, Xie Z. Recent advances in solution processed white organic light emitting materials and devices. *Isr J Chem.* 2014;54(7):897–917. doi: 10.1002/ijch.201400056.
- [6] Tang Q, Liu S, Liu Y, He DF, Miao J, Wang XQ, et al. Color uning and white light emission via in situ doping of luminescent

- lanthanide metal–organic frameworks. *Inorg Chem.* 2014;53(1):289–93. doi: 10.1021/ic402228g.
- [7] Li YX, Li SJ, Yan PF, Wang XY, Yao X, An GH, et al. Luminescence-colour-changing sensing of Mn^{2+} and Ag^+ ions based on a white-light-emitting lanthanide coordination polymer. *Chem Commun.* 2017;53:5067–70. doi: 10.1039/c7cc00258k.
 - [8] Wang XY, Yan PF, Li YX, An GH, Yao X, Li GM. Highly efficient white-light emission and UV-visible/NIR luminescence sensing of lanthanide metal–organic frameworks. *Cryst Growth Des.* 2017;17(4):2178–85. doi: 10.1021/acs.cgd.7b00112.
 - [9] Feng C, Sun JW, Yan PF, Li YX, Liu TQ, Sun QY, et al. Color-tunable and white-light emission of one-dimensional l-di-2-thenoyltartaric acid mixed-lanthanide coordination polymers. *Dalton Trans.* 2015;10(44):4640–7. doi: 10.1039/C4DT03457K.
 - [10] Cai H, Xu LL, Lai HY, Liu JL, Seik W, Li D. A highly emissive and stable zinc(II) metal–organic framework as a host–guest chemopaletta for approaching white-light-emission. *Chem Commun.* 2017;53:7917–20. doi: 10.1039/c7cc03350h.
 - [11] Li Y, Rizzo A, Cingolani R, Gigli G. White-light-emitting diodes using semiconductor nanocrystals. *Microchim Acta.* 2008;160(3):1. doi: 10.1007/s00604-008-0953-x.
 - [12] Fanizza E, Urso C, Pinto V. Single white light emitting hybrid nanoarchitectures based on functionalized quantum dots. *J Mater Chem.* 2014;2(27):5286. doi: 10.1039/c4tc00623b.
 - [13] Li LW. Review of magnetic properties and magnetocaloric effect in the intermetallic compounds of rare earth with low boiling point metals. *Chin Phys B.* 2016;25(3):037502. doi: 10.1088/1674-1056/25/3/037502.
 - [14] Sapra S, Mayilo S, Klar TA, Rogach AL, Feldmann J. Cover Picture: bright white-light emission from semiconductor nanocrystals: by chance and by design. *Adv Mater.* 2007;19:569. doi: 10.1002/adma.200790014.
 - [15] Mazzeo M, Vitale V, Della SF, Marco A. Bright white organic light-emitting devices from a single active molecular material. *Adv Mater.* 2005;17(1):34–9. doi: 10.1002/adma.200400670.
 - [16] Chien C, Huang H, Chen TM. Novel yellow-emitting $\text{Sr}_8\text{MgLn}(\text{PO}_4)_7\text{:Eu}^{2+}$ ($\text{Ln} = \text{Y, La}$) phosphors for applications in white LEDs with excellent color rendering index. *Inorg Chem.* 2011;42(35):5725–30. doi: 10.1002/inorg.201135008.
 - [17] Peng D, Wang LL, Jae SY. Luminescence properties and energy transfer behavior of single-component $\text{NaY(WO}_4)_2\text{:Tm}^{3+}/\text{Dy}^{3+}/\text{Eu}^{3+}$ phosphors for ultraviolet-excited white light-emitting diodes. *J Alloys Compd.* 2016;673:426. doi: 10.1016/j.jallcom.2016.02.245.
 - [18] Shen CY, Yang Y, Jin SZ, Ming JZ, Feng HJ, Xu ZH. White light-emitting diodes using blue and yellow-orange-emitting phosphors. *Optik.* 2010;121(16):1487–91. doi: 10.1016/j.ijleo.2009.02.003.
 - [19] Zhao YW, Zhang FQ, Zhang XM. Single component lanthanide hybrids based on metal–organic framework for near-ultraviolet white light LED. *ACS Appl Mater Interfaces.* 2016;8:24123. doi: 10.1021/acsami.6b07724.
 - [20] Fen Z, Wanjun T. $\text{Ca}_8\text{NaY(PO}_4)_6\text{F}_2\text{:Eu}^{2+}, \text{Mn}^{2+}$: a potential color-tunable phosphor for white LEDs applications. *Appl Phys A Mater.* 2014;118(3):945–51. doi: 10.1007/s00339-014-8840-2.
 - [21] Richardson FS. Terbium(III) and europium(III) ions as luminescent probes and stains for biomolecular systems. *Chem Rev.* 1982;82(5):541–52. doi: 10.1021/cr00051a004.
 - [22] Eliseeva S, Jean C. Lanthanide luminescence for functional materials and bio-sciences. *Chem Soc Rev.* 2010;39:189. doi: 10.1039/b905604c.
 - [23] Li H. Synthesis and luminescence properties of orange-red-emitting $\text{M}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ ($\text{M} = \text{Ca, Sr, Ba}$) light-emitting diode conversion phosphors by a simple nitridation of MSi_2 . *Int J Appl Ceram Technol.* 2009;6(4):459–64. doi: 10.1111/j.1744-7402.2009.02370x.
 - [24] Tang YS, Hu SF, Lin CC, Bagkar NC. Thermally stable luminescence of $\text{KSrPO}_4\text{:Eu}^{2+}$ phosphor for white light UV light-emitting diodes. *Appl Phys Lett.* 2007;90(15):151108. doi: 10.1063/1.2721846.
 - [25] Guo N, You H, Song Y, Yang M. White-light emission from a single-emitting-component $\text{Ca}_9\text{Gd(PO}_4)_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ phosphor with tunable luminescent properties for near-UV light-emitting diodes. *J Mater Chem.* 2010;20(41):9061. doi: 10.1039/c0jm01860k.
 - [26] Han Y, Yan P, Sun J, An G, Yao X, Li Y, et al. Luminescence and white-light emitting luminescent sensor of tetrafluoro-terephthalate-lanthanide metal–organic frameworks. *Dalton Trans.* 2017;14(46):4642–53. doi: 10.1039/C7DT00215G.
 - [27] Qiu Z, Shu J, Liu J, Tang D. Dual-channel photoelectrochemical ratiometric aptasensor with up-converting nanocrystals using spatial-resolved technique on homemade 3D printed device. *Anal Chem.* 2019;91(2):1260–8. doi: 10.1021/acs.analchem.8b05455.
 - [28] Luo Z, Qi Q, Zhang L, Zeng R, Su L, Tang D. Branched polyethylenimine-modified upconversion nanohybrid-mediated photoelectrochemical immunoassay with synergistic effect of dual-purpose copper ions. *Anal Chem.* 2019;91(6):4149–56. doi: 10.1021/acs.analchem.8b05959.
 - [29] Qiu Z, Shu J, Tang D. Near-infrared-to-ultraviolet light-mediated photoelectrochemical aptasensing platform for cancer biomarker based on core–shell $\text{NaYF}_4\text{:Yb, Tm@TiO}_2$ upconversion microrods. *Anal Chem.* 2018;90(1):1021–28. doi: 10.1021/acs.analchem.7b04479.
 - [30] Spokoiny AM, Kim D, Sumrein A, Mirkin CA. Infinite coordination polymer nano- and microparticle structures. *Chem Soc Rev.* 2009;38(5):1218–27. doi: 10.1039/b807085g.
 - [31] Binnemans, Koen. Lanthanide-based luminescent hybrid materials. *Chem Rev.* 2009;109(9):4283–374. doi: 10.1021/cr8003983.
 - [32] Ma X, Li X, Cha Y, Jin LP. Highly thermostable one-dimensional lanthanide(III) coordination polymers constructed from benzimidazole-5,6-dicarboxylic acid and 1,10-phenanthroline: synthesis, structure, and tunable white-light emission. *Cryst Growth Des.* 2016;12(11):5227–32. doi: 10.1021/cg300932a.
 - [33] Tang Q, Liu S, Liu Y, He DF, Miao XQ, Ji YJ, et al. Color tuning and white light emission via *in situ* doping of luminescent lanthanide metal–organic frameworks. *Inorg Chem.* 2014;53(1):289–93. doi: 10.1021/ic402228g.
 - [34] Shen HS, Liu BX, Liu DS, Zhu X, Wei XH, Yu LM, et al. Lanthanide coordination polymer-based biosensor for citrate detection in urine. *Anal Methods.* 2019;11(10):1405–9. doi: 10.1039/c8ay02694g.
 - [35] Tan HL, Ma CJ, Chen LL, Xu FG, Chen SH, Wang L. Nanoscaled lanthanide/nucleotide coordination polymer for detection of an anthrax biomarker. *Sens Actuators B.* 2014;190:621–6. doi: 10.1016/j.snb.2013.09.024.

- [36] Liu BX, Huang YK, Zhu X, Hao YQ, Ding YJ, Wei W, et al. Smart lanthanide coordination polymer fluorescence probe for mercury(II) determination. *Anal Chim Acta*. 2016;912:139–45. doi: 10.1016/j.aca.2016.01.044.
- [37] Liu BX, Huang YK, Shen Q, Zhu X, Hao YQ, Qu P, et al. Turn-on fluorescence detection of ciprofloxacin in tablets based on lanthanide coordination polymer nanoparticles. *RSC Adv*. 2016;6(103):100743–47. doi: 10.1039/c6ra20357d.
- [38] Curman D, Zivec P, Leban I, Turel I, Polishchuk A, Klikac KD, et al. Spectral properties of Eu(III) compound with antibacterial agent ciprofloxacin (cfqH) crystal structure of [Eu(cfqH)(cfq)(H₂O)₄]Cl₄·55H₂O. 2008;27(5):1489–96. doi: 10.1016/j.poly.2008.01.014.
- [39] Tan HL, Zhang L, Ma CJ, Song YH, Xu FG, Chen SH, et al. Terbium-based coordination polymer nanoparticles for detection of ciprofloxacin in tablets and biological fluids. *ACS Appl Mater Interfaces*. 2013;5(22):11791–6. doi: 10.1021/am403442q.
- [40] Bu'nzli, J-CG. Lanthanide luminescence for biomedical analyses and imaging. *Chem Rev*. 2010;110(5):2729–55. doi: 10.1021/cr900362e.
- [41] Binnemans, K. Lanthanide-based luminescent hybrid materials. *Chem Rev*. 2009;109(9):4283–374. doi: 10.1021/cr8003983.