

Regulation of the switch between X-ray scintillators and photo/sonocatalysis generation of reactive oxygen species in lanthanide-titanium clusters via energy transfer pathways

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ABSTRACT: A class of orthogonal multifunctional lanthanide-titanium clusters, Ln_4Ti_9 , was obtained by reacting 4-trifluoromethylbenzoic acid, isopropyl titanate, and $\text{Ln}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$ under solvothermal conditions. These clusters can be used for the purification of colored dye wastewater and for high-performance X-ray scintillators. Specifically, the metal centers in the cluster nucleus of Ln_4Ti_9 are arranged in a near-planar manner, and the ligands are tightly wrapped around the cluster nucleus, which ensures the stability of the cluster in solution. In-depth exploration of the energy transfer pathways has demonstrated that the Eu_4Ti_9 structure possesses an efficient antenna effect and optimal energy level matching, exhibiting a bright red luminescence. Furthermore, Eu_4Ti_9 exhibits excellent X-ray scintillator performance, with a light yield of up to $11,677 \text{ photons} \cdot \text{MeV}^{-1}$ and a detection limit as low as $2.2 \mu\text{Gy} \cdot \text{s}^{-1}$, which is 2.5 times lower than the clinical standard for medical use ($5.5 \mu\text{Gy} \cdot \text{s}^{-1}$). It also shows excellent radiation stability after 36 radiation cycles and enables low-dose X-ray imaging. Under white light irradiation of $60 \text{ mW} \cdot \text{cm}^{-2}$, the rapidly generated reactive oxygen species (ROS) storm of Gd_4Ti_9 almost completely degraded methylene blue (MB), rhodamine B (RhB), and norfloxacin (NFX) in aqueous solution within 50 and 40 min, respectively, with degradation rates as high as 0.0216, 0.0592, and 0.0146 min^{-1} , respectively. This work applies a highly stable lanthanide-titanium cluster system in aqueous solution to the field of photocatalytic wastewater purification, specifically targeting colored dyes and antibiotics.

KEYWORDS: lanthanide clusters, X-ray scintillators, reactive oxygen species, photocatalytic degradation, solvothermal synthesis

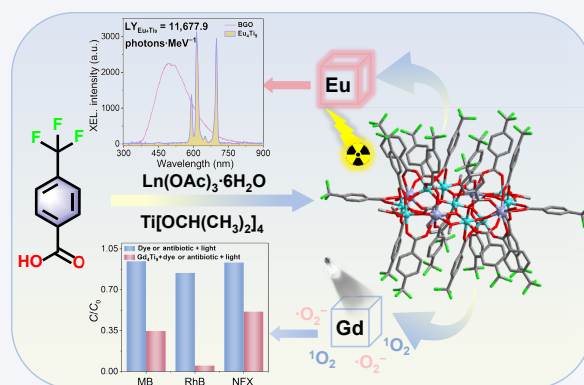
1 Introduction

Scintillators are key functional materials for radiation detection and imaging, and have been widely applied in fields such as medical imaging, nuclear detection, and high-energy physics [1–3].

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Traditional scintillators generally suffer from problems such as high manufacturing costs, difficulty in simultaneously achieving high light yield, decay rate and stability, and insufficient spectral matching [4–7]. In recent years, the research focus of scintillators has shifted from traditional inorganic and organic materials to halide perovskites, novel rare earth doped systems, lanthanide(III)-organic scintillators, and organic-inorganic hybrid scintillators [8–13]. Among them, lanthanide(III)-organic scintillators have garnered considerable interest owing to the high atomic number of lanthanide ions, their characteristic narrow-band emission, and their excellent X-ray absorption and high secondary electron

generation efficiency in X-ray scintillators [14–16]. Lanthanide(III)-organic scintillators can significantly enhance luminescence intensity through the “antenna effect” of ligands, and have a range of advantages such as high absorption, highly efficient luminescence, tunable spectrum, and designable structure [17–19]. Lanthanide-titanium clusters are a new type of luminescent material system formed by the assembly of lanthanide ions, titanium oxide cluster units, and organic ligands [20–22]. Lanthanide ions possess unique 4f electron transition characteristics and strong X-ray absorption capabilities, while titanium-oxygen clusters have stable, atomically precise structures that can serve as efficient energy transfer frameworks. The lanthanide-titanium cluster scintillator constructed by combining the two is a highly promising X-ray scintillator material [23]. However, there are still few research reports on the design and synthesis of lanthanide-titanium clusters that combine excellent X-ray luminescence efficiency, high light yield and structural stability. In 2024, Zhao et al. synthesized a europium-titanium oxide cluster (Eu-TiOC) scintillator. The inorganic titanium oxide cluster core serves as a highly efficient X-ray absorber, while the organic ligand acts as an “antenna” and bridge for energy transfer. By sensitizing the luminescence of Eu^{3+} ions through a cascaded energy transfer process, a steady-state X-ray yield of $26,816 \pm 2000$ photons $\cdot\text{MeV}^{-1}$ was obtained [23]. Therefore, the controllable construction of high-performance lanthanide-titanium cluster-based X-ray scintillators still faces enormous challenges.

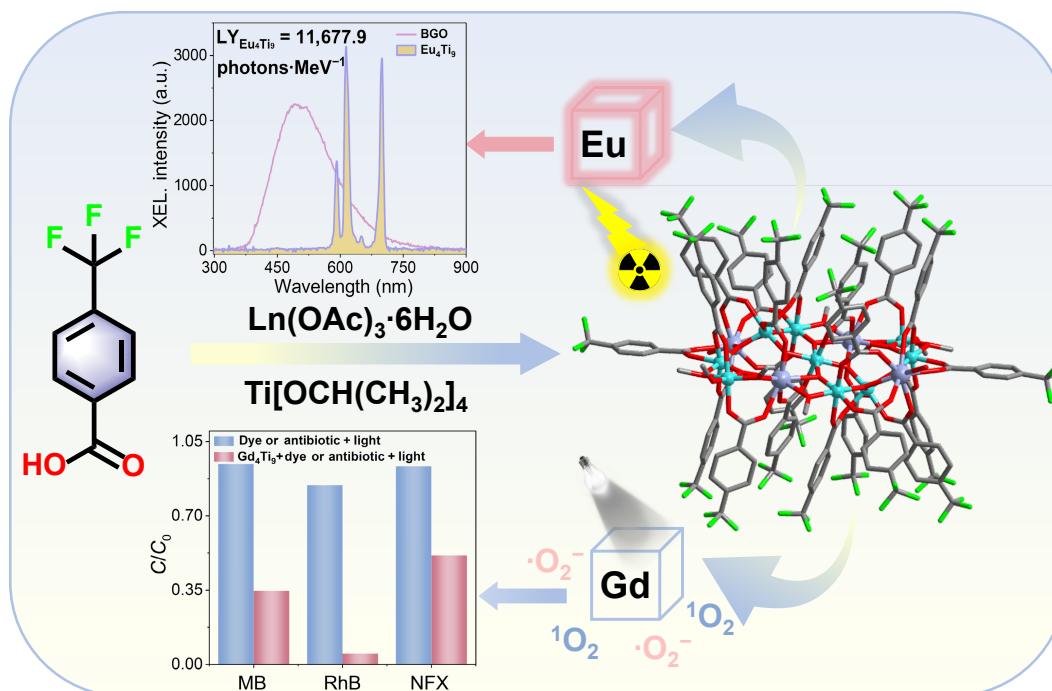
The environmental pollution caused by the long-term and excessive use of colored dyes and antibiotics and their improper discharge has gradually evolved into a major public health problem that threatens the stability of ecosystems and human health [24–27]. Organic dyes and antibiotics are generally characterized by their stable chemical structure and difficulty in natural degradation [28–31]. Photocatalytic degradation technology is widely used due to its advantages such as simple operation, high efficiency, and being environmentally friendly [32–34]. Photocatalytic degradation technology involves the excitation of photosensitizers (PSs) under light conditions, which in turn generates a large number of reactive oxygen species (ROS) with strong oxidizing capabilities. Through strong oxidation, the structure of pollutants can be efficiently and precisely destroyed, thus achieving effective decomposition of pollutants [35–39]. Traditional photosensitizers are mainly composed of organic polymers and semiconductor materials, but they generally suffer from defects such as poor stability, rapid decay of catalytic efficiency, and weak ability to generate reactive oxygen species [40, 41]. Therefore, it is necessary to design and develop novel photosensitizer systems with superior performance to further improve the efficiency and application effect of photocatalysis technology in the degradation of pollutants. Currently, research on lanthanide-titanium clusters as photosensitizers is in its rapid initial stage. On the one hand, by regulating the types of lanthanide ions, cluster nucleus size and ligand structure, energy level matching and energy transfer efficiency can be optimized; on the other hand, as heavy atoms, lanthanide atoms can boost intersystem crossing (ISC) by enhancing spin-orbit coupling, thereby improving triplet exciton yield and energy transfer efficiency [42–46]. Furthermore, the significant semiconductor properties of the Ti(IV) oxygen unit enable lanthanide-titanium clusters to possess strong light absorption and efficient charge separation capabilities, making these lanthanide-titanium clusters promising for the efficient generation of reactive oxygen species, and thus possessing potential value as photosensitizers [47–49].

Herein, lanthanide-titanium clusters with high symmetry and planar arrangement of cluster nuclei were obtained by reacting 4-trifluoromethylbenzoic acid, isopropyl titanate, and $\text{Ln}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ and Gd) under solvothermal conditions. The results of high-resolution electrospray mass spectrometry (HRESI-MS) demonstrated that the tight encapsulation of the peripheral ligands ensured the structural integrity of Eu_4Ti_5 in solution. By modulating the species of Ln ions in Ln_4Ti_5 , distinct energy transfer pathways can be realized, thereby enabling applications in X-ray scintillators and photocatalytic ROS storms (Scheme 1). Due to its high energy level matching and significant antenna effect, Eu_4Ti_5 not only exhibits bright red emission but also demonstrates excellent X-ray scintillator performance. Specifically, Eu_4Ti_5 exhibits a high light yield (11,677 photons $\cdot\text{MeV}^{-1}$) and a low detection limit (2.2 $\mu\text{Gy}\cdot\text{s}^{-1}$). In comparison with the typical dose used in medical X-ray diagnostics (5.5 $\mu\text{Gy}\cdot\text{s}^{-1}$), Eu_4Ti_5 still demonstrates certain commercial value. Furthermore, Gd_4Ti_5 can rapidly generate ROS storms under both ultrasonic and light irradiation. Notably, the excellent photocatalytic ROS storm of Gd_4Ti_5 has been successfully applied to the rapid degradation of colored dyes and antibiotics, effectively degrading various high-concentration colored dyes (MB, 0.0216 min^{-1} ; RhB, 0.0592 min^{-1}) and antibiotics (NFX, 0.0146 min^{-1}) within 50 min. This study not only opens a door to the construction of high-performance lanthanide-titanium cluster-based X-ray scintillators, but also promotes the crystal engineering progress of orthogonal multifunctional lanthanide-titanium clusters.

2 Results and discussion

2.1 Structural analysis

Under solvothermal conditions, two colorless and transparent strip-shaped crystals, Ln_4Ti_5 , were obtained by reacting 4-trifluoromethylbenzoic acid, isopropyl titanate, and $\text{Ln}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ and Gd) (Fig. 1(a)). Single-crystal X-ray diffraction (SCXRD) indicates that the Eu_4Ti_5 crystal belongs to the monoclinic C2/c space group (Tables S1 and S2 in the Electronic Supplementary Material (ESM)). Eu_4Ti_5 is composed of four Eu(III) ions, nine Ti(IV) ions, twenty ligands (L[−]) that have lost one proton, eight CH_3O^- , two H_2O , and peripheral guest molecules, with the molecular formula $[\text{Eu}_4\text{Ti}_5(\text{L})_{20}(\mu_3\text{-O})_{10}(\text{CH}_3\text{O})_8(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O} \cdot 5\text{CH}_3\text{OH}$. All deprotonated 4-trifluoromethylbenzoic acid ligands are distributed around the metal cluster nucleus, thus effectively encapsulating and protecting the cluster nucleus in space, significantly improving the stability of the Eu_4Ti_5 cluster in the solution system (Fig. 1(b)). The metal cluster core of Eu_4Ti_5 exhibits a distinct centrosymmetric configuration with Ti5 as its core (Fig. 1(c)). This structure consists of Ti atoms forming TiO_6 octahedra and Eu atoms forming EuO_8 polyhedra, which are bridged by oxygen atoms (Fig. 1(d)). The Ti(IV) ions in the Eu_4Ti_5 structure have the same coordination configuration, while the Eu(III) ions have two different coordination configurations. SHAPE calculations show that the coordination configuration of the Ti(IV) ions are Octahedron, the coordination configuration of Eu1 is Triangular dodecahedron, and the coordination configuration of Eu2 is Square antiprism (Fig. S1 and Table S3 in the ESM). The absorption peaks in the Fourier transform infrared (FT-IR) absorption spectrum of Ln_4Ti_5 are located at 3449, 1615, 1329, 1130, and 786 cm^{-1} respectively, and are attributed to the O–H stretching



Scheme 1 A schematic diagram illustrating the synthesis of Ln_4Ti_9 and its application in X-ray scintillators and the purification of wastewater from photocatalytic dyes or antibiotics.

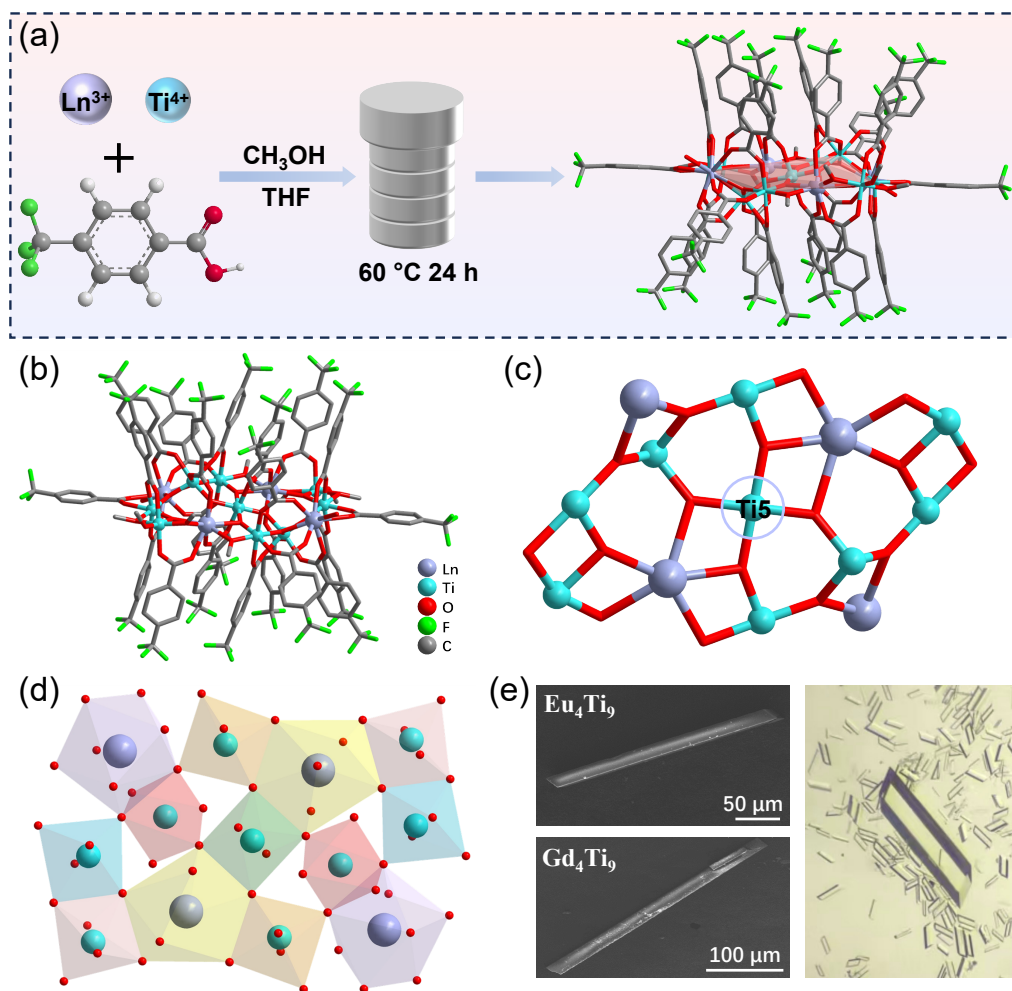


Figure 1 (a) Schematic diagram of the synthesis of Ln_4Ti_9 . (b) Structural diagram of Ln_4Ti_9 . (c) Image of the metal cluster core of Ln_4Ti_9 . (d) Image of the polyhedral core of Ln_4Ti_9 . (e) SEM images of Ln_4Ti_9 and crystal photograph of Eu_4Ti_9 .

vibrations of terminally coordinated H_2O , the $\text{C}=\text{O}$ stretching vibrations of the carboxyl groups, the $\text{C}-\text{F}$ stretching vibrations, the $\text{C}-\text{O}$ stretching vibrations, and the out-of-plane bending vibrations of the $\text{C}-\text{H}$ bonds on the benzene rings. (Fig. S2 in the ESM) [50]. At room temperature and pressure, the experimental powder X-ray diffraction (PXRD) values of Ln_4Ti_9 align closely with the simulated values, proving that they are both pure phases (Fig. S3 in the ESM). Thermogravimetric (TG) analysis showed that the guest molecules surrounding Ln_4Ti_9 contained four water molecules and five methanol molecules. When the temperature was raised to 190°C , Ln_4Ti_9 decomposed, losing the four free water molecules and five methanol molecules (Eu_4Ti_9 : theoretical value 4.11%, experimental value 4.22%; Gd_4Ti_9 : theoretical value 4.11%, experimental value 3.64%). With further increases in temperature to 530°C , Ln_4Ti_9 completely collapsed, indicating that Ln_4Ti_9 possesses excellent thermal stability (Fig. S4 in the ESM). Scanning electron microscopy (SEM) results and fluorescent photographs of the crystals confirmed that Ln_4Ti_9 consisted of distinct, regular, and very clean strip-shaped crystals (Fig. 1(e)).

To verify the stability of Eu_4Ti_9 in solution, a small amount of Eu_4Ti_9 crystal sample was dissolved in chromatographically pure DMSO, diluted with a large amount of chromatographically pure CH_3OH , and then subjected to HRESI-MS analysis [51–54]. HRESI-MS analysis showed that the detected molecular ion peak was highly consistent with the Eu_4Ti_9 main framework, indicating that Eu_4Ti_9 exhibited high stability in the above solution (Fig. 2(a)). As shown in Fig. 2(b), the assignment and fitting results of the main molecular ion peaks of Eu_4Ti_9 by HRESI-MS are as follows: $[\text{Eu}_4\text{Ti}_9(\mu_3\text{-O})_{10}(\text{L})_{18}(\text{CH}_3\text{O})_{12}\text{H}]^{2-}$ (exp. 2487.80; calc. 2487.84); $[\text{Eu}_4\text{Ti}_9(\mu_3\text{-O})_{10}(\text{L})_{18}(\text{CH}_3\text{O})_{12}(\text{C}_4\text{H}_8\text{O})(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3]^{2-}$ (exp. 2566.79; calc. 2566.40); $[\text{Eu}_4\text{Ti}_9(\mu_3\text{-O})_{10}(\text{L})_{19}(\text{CH}_3\text{O})_8(\text{OH})_3(\text{C}_4\text{H}_8\text{O})\text{H}]^{2-}$ (exp. 2581.77; calc. 2581.85); $[\text{Eu}_4\text{Ti}_9(\mu_3\text{-O})_{10}(\text{L})_{20}(\text{CH}_3\text{O})_{10}]^{2-}$ (exp. 2645.77; calc. 2645.84); $[\text{Eu}_4\text{Ti}_9(\mu_3\text{-O})_{10}(\text{L})_{20}(\text{CH}_3\text{O})_6(\text{OH})_4(\text{CH}_3\text{OH})(\text{H}_2\text{O})_3]^{2-}$ (exp. 2660.81; calc. 2660.83); $[\text{Eu}_4\text{Ti}_9(\mu_3\text{-O})_{10}(\text{C}_8\text{H}_4\text{O}_2\text{F}_3)_{20}(\text{CH}_3\text{O})_{10}(\text{CH}_3\text{OH})(\text{H}_2\text{O})_7]^{2-}$ (exp. 2724.83; calc. 2724.89). Structural analysis reveals that the outer ligand (L^-) forms a tight protective shell around the cluster nucleus of Eu_4Ti_9 , enhancing Eu_4Ti_9 's ability to resist attacks from external guest

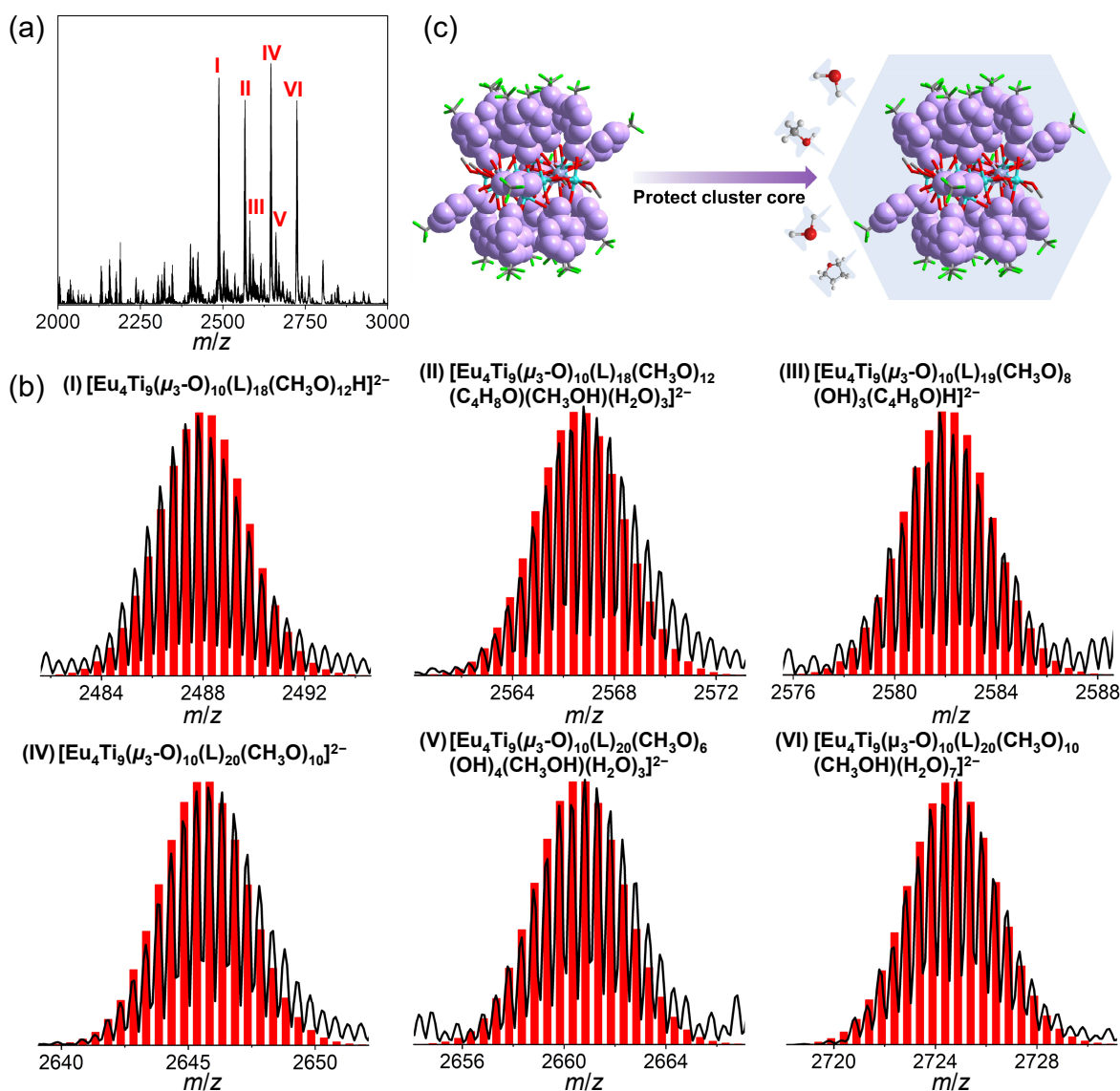


Figure 2 (a) HRESI-MS spectrum of Eu_4Ti_9 in negative ion mode. (b) Comparison of experimental (black) and simulated (red) values of the main molecular ion peaks of Eu_4Ti_9 in HRESI-MS. (c) Schematic diagram of the outer (L^-) protected cluster nucleus.

molecules (Fig. 2(c)). Furthermore, dynamic light scattering (DLS) measurements revealed that the hydrodynamic diameters of Eu_4Ti_9 and Gd_4Ti_9 were 192.8 and 180.4 nm, respectively, while their zeta potentials in a mixed solution ($V_{\text{DMSO}}/V_{\text{water}} = 1/99$) were 64.6 and 71.9 mV, respectively; this indicates that the nanoscale Ln_4Ti_9 materials exhibit high stability in aqueous solutions (Fig. S5 in the ESM).

2.2 Photophysical property analysis

The ultraviolet–visible (UV–Vis) absorption spectra of Eu_4Ti_9 and Gd_4Ti_9 are shown in Fig. S6 in the ESM, their absorption peaks are all located in the range of 250–420 nm [55]. Bright red luminescence was clearly observed in Eu_4Ti_9 crystals under 365 nm ultraviolet light illumination, and we investigated the luminescence properties of Eu_4Ti_9 in detail. The emission spectrum of Eu_4Ti_9 was measured under 394 nm excitation; its characteristic emission peaks are primarily distributed at 591, 615, 650, and 698 nm, which can be attributed to the $^3\text{D}_0 \rightarrow ^7\text{F}_1$, $^3\text{D}_0 \rightarrow ^7\text{F}_2$, $^3\text{D}_0 \rightarrow ^7\text{F}_3$, and $^3\text{D}_0 \rightarrow ^7\text{F}_4$ energy level transitions of $\text{Eu}(\text{III})$ ions, respectively (Fig. 3(a)) [56–58]. Within the excitation range of 360–420 nm, the excitation–emission dependent three-dimensional spectrum of Eu_4Ti_9 showed the optimal excitation and emission peaks, and the emission peak wavelength did not shift significantly with the change of excitation

wavelength, indicating that the luminescence behavior of Eu_4Ti_9 is not dependent on the excitation wavelength (Fig. 3(b)). The solid-state luminescence lifetime of Eu_4Ti_9 is 1066.5 μs (Fig. S7(a) in the ESM), and the solid-state quantum yield is 10.18% (Fig. 3(c) and Fig. S7(b) in the ESM). Typically, increasing temperature does not significantly alter the rate of radiative transitions (luminescence), but it greatly enhances nonradiative processes associated with excited-state energy consumption, thereby reducing luminescence efficiency. To further investigate the effect of increased ambient temperature on the photoluminescence intensity of Eu_4Ti_9 , we measured the emission spectrum of Eu_4Ti_9 under the optimal excitation wavelength within the temperature range of 80–350 K (Fig. 3(d)). As the temperature rises, the emission peak intensity of Eu_4Ti_9 decreases sharply (Figs. 3(e) and 3(f)). The above results indicate that the characteristic emission peak of Eu_4Ti_9 exhibits significant thermal quenching capability. The thermal quenching of Eu_4Ti_9 can be attributed to the presence of coordinated H_2O and CH_3OH molecules in the Eu_4Ti_9 structure, increased temperature intensifies the vibration amplitude and frequency of the high-frequency vibrational group $-\text{OH}$ in these molecules, significantly enhancing non-radiative transitions and leading to a weakening of radiative transitions [59].

To further investigate the energy transfer pathways and

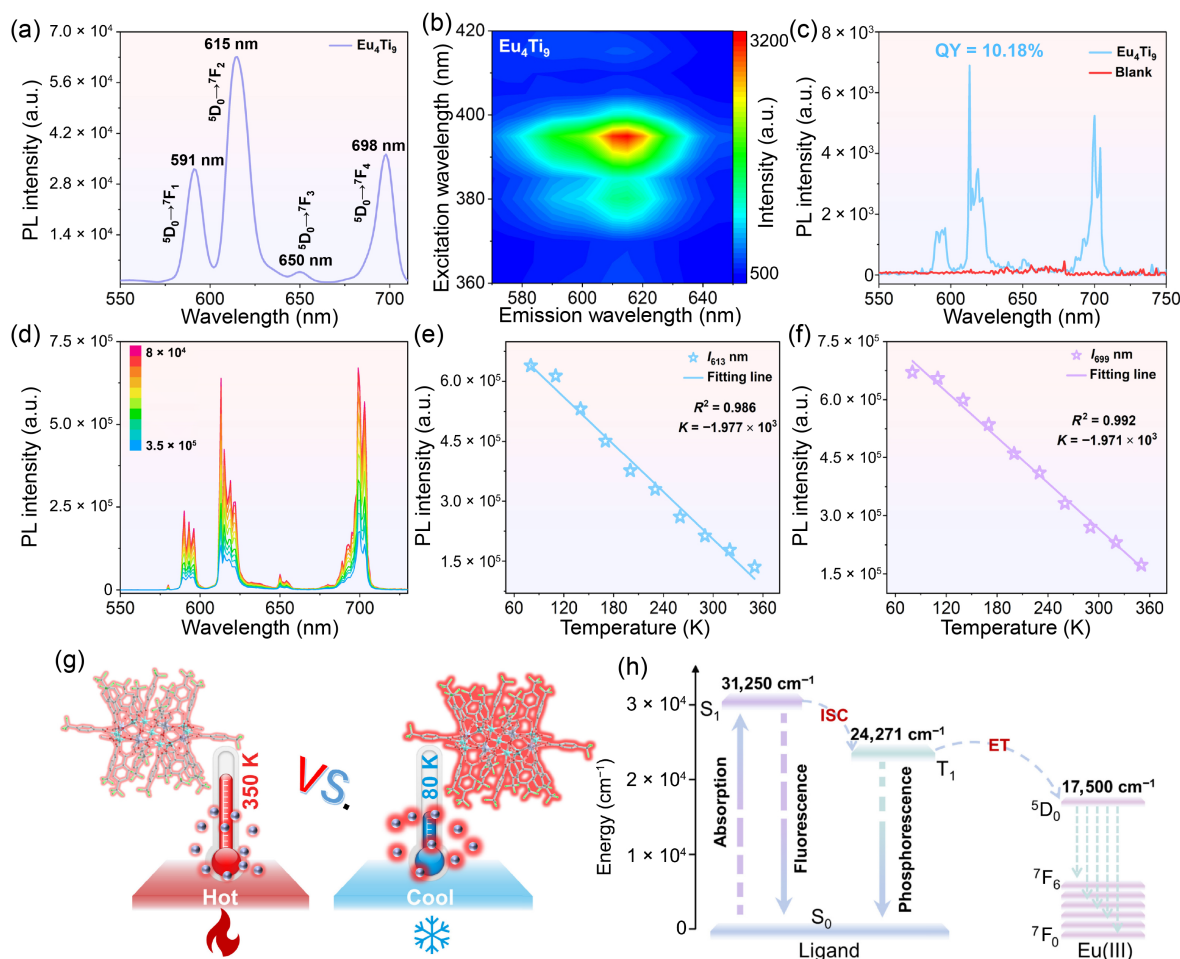


Figure 3 (a) Emission spectrum and energy level distribution of Eu_4Ti_9 (inset: photograph of Eu_4Ti_9 under 365 nm ultraviolet light). (b) Transient mode three-dimensional photoluminescence spectrum of Eu_4Ti_9 . (c) Quantum yield of Eu_4Ti_9 . (d), (e), and (f) The temperature-dependent emission spectra of Eu_4Ti_9 in the temperature range of 80–350 K, along with the relationship between its emission peak intensity ratio and temperature. (g) A schematic diagram showing the change in luminescence of Eu_4Ti_9 with temperature. (h) Jablonsky energy level diagram for Eu_4Ti_9 .

luminescence mechanism of Eu_4Ti_9 , we plotted the *Jablonski* energy level diagram (Fig. 3(h)). Analysis of the *Jablonski* energy level diagram shows that after the ligand is excited, the electron jumps to the S_1 state, then undergoes an intersystem crossing (ISC) process to reach the T_1 state, and then transfers energy to reach the emission energy level of the Eu(III) ion [60]. The UV-Vis absorption spectrum of the solid ligand was recorded, from which the S_1 energy level was estimated to be $31,250\text{ cm}^{-1}$ (Fig. S8(a) in the ESM). Since the energy levels of the ligand and the Gd(III) ion do not match, the T_1 energy level of the organic ligand was determined by fitting the phosphorescence spectrum of Gd_4Ti_9 measured at 77 K under liquid-nitrogen conditions (Fig. S8(b) in the ESM) [61]. The energy level of the $^3\text{D}_0$ of the Eu(III) ion is known to be 17500 cm^{-1} [62]. According to *Reinholdt's* rule, an efficient ISC process can occur when the energy difference between S_1 and T_1 is greater than 5000 cm^{-1} [63]. According to *Latva's* rule, an efficient ET process can occur with the $^3\text{D}_0$ energy level of the Eu(III) ion when the energy difference between T_1 and $^3\text{D}_0$ is in the range of 2000 to 5000 cm^{-1} [64]. In Eu_4Ti_9 , the energy difference between S_1 and T_1 is 6979 cm^{-1} , and the energy difference between T_1 and $^3\text{D}_0$ is 6771 cm^{-1} . Obviously, Eu_4Ti_9 has efficient ISC and ET processes, indicating that the ligand can act as an efficient antenna to sensitize the characteristic red emission of Eu(III) ions.

2.3 Eu_4Ti_9 X-ray scintillator

Lanthanide ions (such as Eu^{3+} and Tb^{3+}) possess large X-ray absorption cross-sections, characteristic narrow-band emission, and long fluorescence lifetimes, making them ideal luminescent centers [65, 66]. Titanium oxide units possess strong ultraviolet X-ray absorption capabilities and excellent chemical stability, making them suitable as efficient energy absorption and transfer media. The lanthanide-titanium cluster formed by precise assembly of the two can achieve efficient synergy of "X-ray absorption-energy transfer-characteristic luminescence". Therefore, we investigated the X-ray emission (XEL) performance of Eu_4Ti_9 . The X-ray absorption coefficients of Eu_4Ti_9 and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) within the photon energy range of 1–108 keV were calculated using the XCOM database. The consequence indicate that Eu_4Ti_9 possesses good X-ray absorption ability (Fig. 4(a)). To assess the light yield of the Eu_4Ti_9 scintillator, the relative light yield of the Eu_4Ti_9 scintillator was calculated to be $11,677\text{ photons}\cdot\text{MeV}^{-1}$ using the BGO scintillator ($10,000\text{ photons}\cdot\text{MeV}^{-1}$) as a reference standard (Fig. 4(c)) [67]. The X-ray emission spectrum of the scintillator showed characteristic emission peaks of Eu^{3+} ions at 591, 613, 650, and 698 nm, attributable to the $^3\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 1-4$) transition of Eu^{3+} . Furthermore, the detection limit and radiation stability of the scintillator are indicators for evaluating its performance. The X-ray dose response of the Eu_4Ti_9 scintillator was assessed by recording the XEL intensity as a function of X-ray dose rate in the range of $17.37\text{--}278\text{ }\mu\text{Gy}\cdot\text{s}^{-1}$. The XEL intensity of the Eu_4Ti_9 scintillator showed a linear relationship with the X-ray dose rate. The limit of detection (LOD) of Eu_4Ti_9 was $2.223\text{ }\mu\text{Gy}\cdot\text{s}^{-1}$, which is below the limit of detection for X-ray medical diagnostics ($5.5\text{ }\mu\text{Gy}\cdot\text{s}^{-1}$) (Figs. 4(d) and 4(e)) [68]. Meanwhile, Eu_4Ti_9 decayed to 99% of its initial intensity after 36 radiation cycles, indicating that Eu_4Ti_9 exhibits excellent stability under radiation (Fig. 4(f)). The XEL performance of Eu_4Ti_9 primarily stems from the following mechanism: First, X-ray photons interact with Eu^{3+} ions and the TiO core in Eu_4Ti_9 , generating high-energy electrons through Compton scattering and the photoelectric effect. Subsequently,

outer-shell electrons fill the vacancies during the relaxation process and emit low-energy secondary photons via fluorescence radiation. These secondary photons couple with Eu_4Ti_9 , simultaneously generating singlet excitons (S_1) and triplet excitons (T_1), with a generation ratio of approximately 1:3. The lowest excited triplet state (T_1) energy level of the ligand is highly matched with the $^3\text{D}_0$ excited state energy level of the Eu^{3+} ion. Therefore, ligand triplet excitons can efficiently transfer their energy to Eu^{3+} ions via the antenna effect, thereby generating the characteristic emission of Eu^{3+} (Fig. 4(g)) [69, 70]. Based on the excellent scintillation performance of Eu_4Ti_9 , X-ray imaging experiments were subsequently performed (Fig. 4(h)). Using springs, metal rings, and metal blades as test objects, the resulting images exhibit complete contours and sharp details, forcefully confirmed the imaging performance of the Eu_4Ti_9 scintillator (Fig. 4(i) and Fig. S9 in the ESM). Lanthanide ions typically exhibit characteristic narrow-band emission, which limits their photoluminescence quantum yield and overall light yield to some extent. In contrast, BGO scintillators, thanks to their wide emission band and high material density, can achieve a light yield of approximately $10,000\text{ photons}\cdot\text{MeV}^{-1}$. Although the relative light yield of Eu_4Ti_9 scintillator is $11,677\text{ photons}\cdot\text{MeV}^{-1}$, only comparable to that of BGO, it still demonstrates certain potential commercial application value.

2.4 ROS generation capacity of Gd_4Ti_9

The lowest excited state energy of Gd(III) ions in Gd_4Ti_9 is relatively high, which does not match the T_1 state energy level of the ligand. Therefore, Gd(III) ions cannot accept the T_1 state energy of the ligand, resulting in the T_1 state of the ligand having a longer time to interact with oxygen molecules and produce ROS. Furthermore, Gd(III) ions can significantly promote the ISC process from the S_1 state to the T_1 state through spin-orbit coupling and stabilize the exciton in the T_1 state, thereby generating more ROS (Fig. 5(a)) [71, 72]. To verify this hypothesis, we used NaOH-activated DCFH (2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA), which is converted to DCFH after activation) as a ROS indicator, which can react rapidly with ROS and emit bright green fluorescence [73, 74]. Under the same power density ($1.75\text{ W}\cdot\text{cm}^{-2}$) and ultrasound duration, Gd_4Ti_9 is capable of significantly enhancing the fluorescence signal of the DCFH indicator, achieving an enhancement factor of up to 35-fold; Under the same power density, the DCFH control group exhibited virtually no discernible fluorescence enhancement, indicating that Gd_4Ti_9 has excellent ROS generation ability under ultrasound conditions (Figs. S10(a)–S10(c) in the ESM). To further elucidate the specific types of ROS produced by Gd_4Ti_9 under ultrasonic irradiation, we selected dihydrorhodamine 123 (DHR 123) as a specific indicator to monitor its capability to produce $\cdot\text{O}_2^-$ [75]. Under ultrasound conditions, with increasing ultrasound time, the characteristic fluorescence of DHR 123 in the Gd_4Ti_9 experimental group gradually increased, with a fluorescence enhancement factor as high as 122 times. In contrast, the DHR 123 control group exhibited only a minimal fluorescence increase, with an enhancement factor of approximately 10, which is considered negligible, confirming the outstanding $\cdot\text{O}_2^-$ generation capability of Gd_4Ti_9 (Figs. S10(d)–S19(f) in the ESM). Subsequently, we monitored the production of $^1\text{O}_2$ using ABDA [76]. In the presence of Gd_4Ti_9 , the characteristic absorbance of ABDA exhibited a pronounced decline with increasing sonication time. Under sonication conditions, the ABDA degradation rate (k) of the Gd_4Ti_9 experimental group was

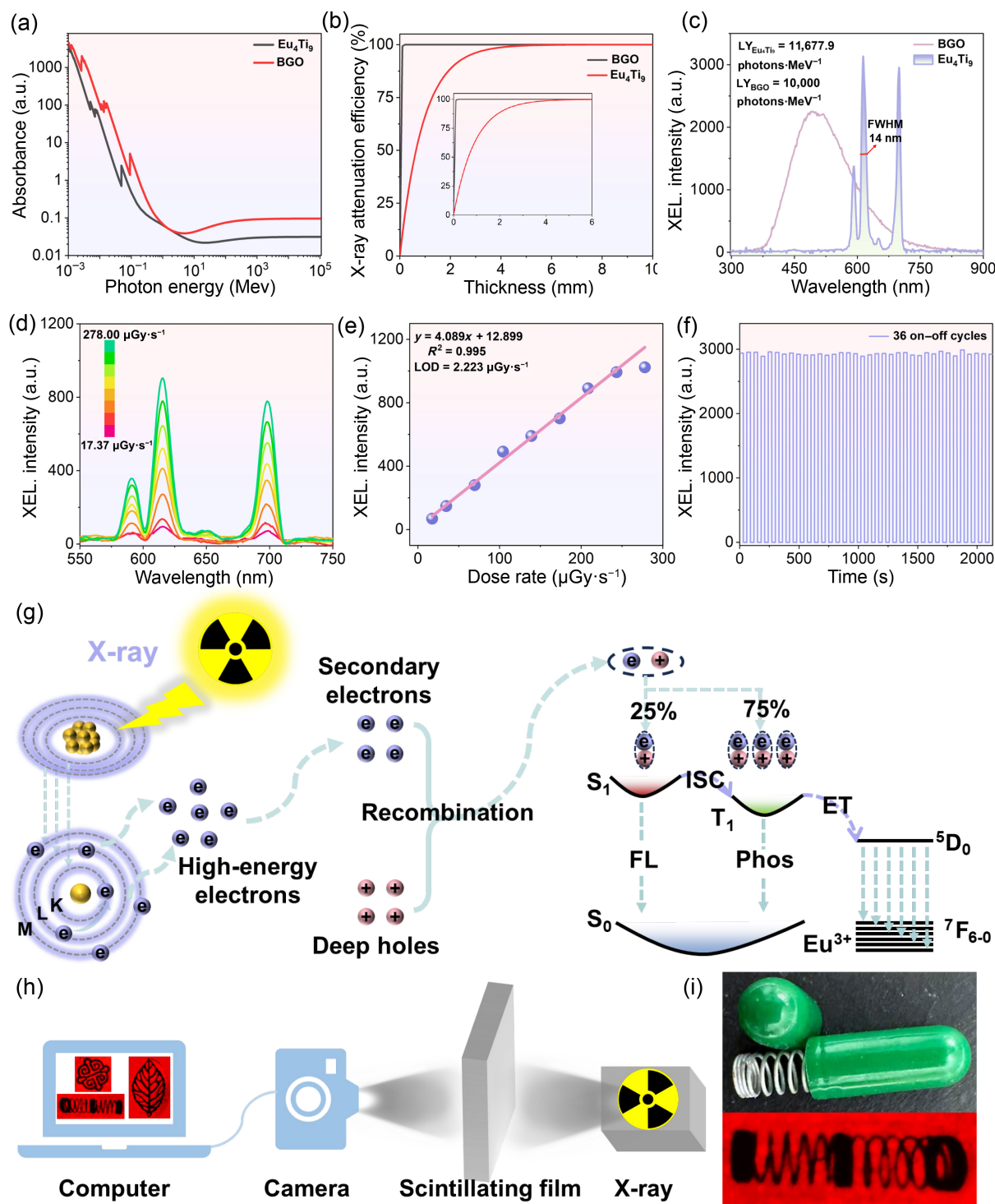


Figure 4 (a) Absorption coefficients of Eu_4Ti_3 and BGO scintillators as a function of photon energy. (b) Relationship between X-ray attenuation efficiency and thickness of Eu_4Ti_3 and BGO at 20 keV X-ray photon energy. (c) X-ray excited emission intensity spectra of Eu_4Ti_3 and BGO. (d) X-ray excited emission intensity spectra of Eu_4Ti_3 at different radiation doses. (e) The linear relationship of X-ray excited luminescence intensity of Eu_4Ti_3 at various radiation doses. (f) Stability of Eu_4Ti_3 under repeated X-ray irradiation. (g) Schematic diagram of Eu_4Ti_3 scintillation mechanism. (h) Schematic diagram of Eu_4Ti_3 scintillator X-ray imaging process. (i) Application of Eu_4Ti_3 scintillator in actual X-ray imaging.

$4.5 \times 10^{-4} \text{ s}^{-1}$, much higher than that of the ABDA control group, confirming the excellent O_2 generation capacity of Gd_4Ti_3 (Figs. S10(g)–S10(j) in the ESM). The above experimental results demonstrate that Gd_4Ti_3 exhibits exceptional capacity to generate both type I and II ROS under sonication conditions. 4T1 cells were

selected, and the MTT assay was employed to assess the effects of varying concentrations of Gd_4Ti_3 on 4T1 cell viability. Under sonication at $1.75 \text{ W}\cdot\text{cm}^{-2}$, Gd_4Ti_3 at a concentration of $100 \mu\text{g}\cdot\text{mL}^{-1}$ had a significant killing effect on 4T1 cells, with cell viability as low as 15.16% (Fig. S10(k) in the ESM).

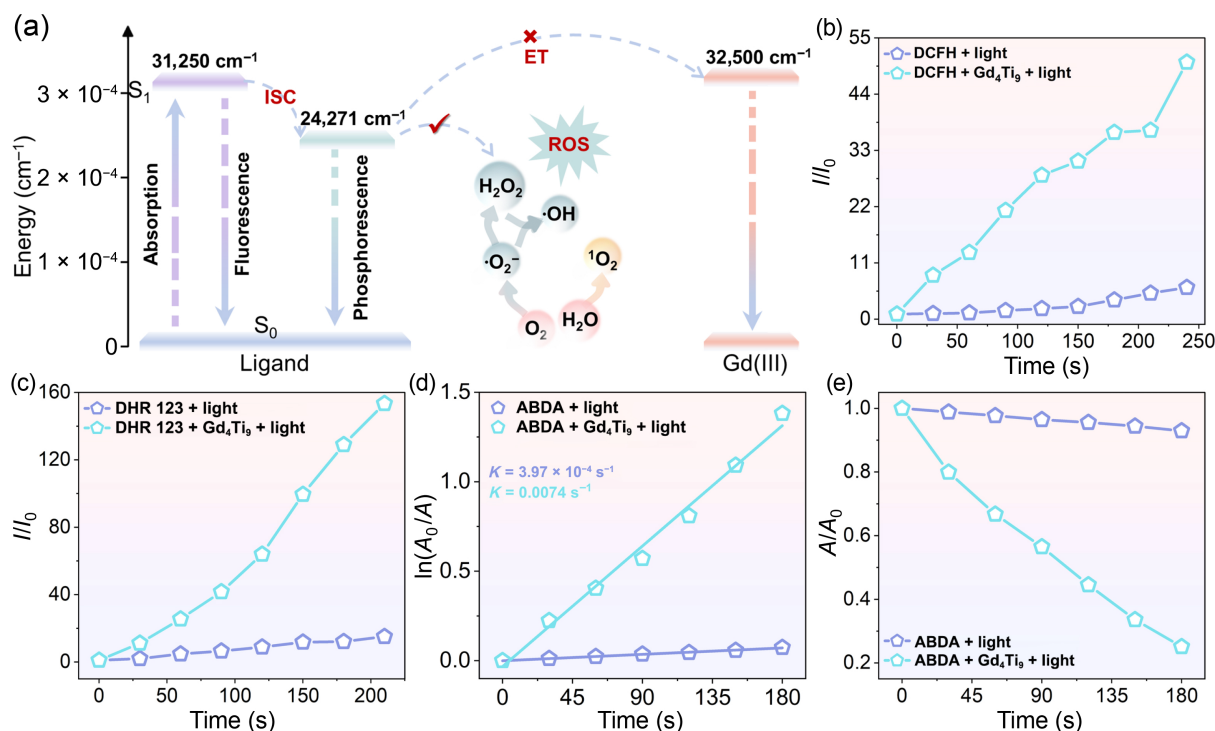


Figure 5 (a) Schematic diagram of ROS generation. (b) Monitoring ROS generated by Gd₄Ti₉ under illumination (xenon lamp, 60 mW·cm⁻²) with DCFH as an indicator. (c) Monitoring ·O₂⁻ generated by Gd₄Ti₉ under illumination (xenon lamp, 60 mW·cm⁻²) with DHR 123 as an indicator. (d) and (e) Monitoring ¹O₂ generated by Gd₄Ti₉ under illumination (xenon lamp, 60 mW·cm⁻²) with ABDA as an indicator.

Subsequently, we investigated the photoinduced ROS generation capability of Gd₄Ti₉. DCFH-DA was employed as a general indicator for ROS to assess the generation of ROS by Gd₄Ti₉ under photoirradiation conditions. Under the same irradiation power (xenon lamp, 60 mW·cm⁻²) and time, the green fluorescence of the experimental group containing DCFH with Gd₄Ti₉ was significantly enhanced, with an enhancement factor of 50 times. The green fluorescence enhancement factor of the control group containing only DCFH was smaller, indicating that Gd₄Ti₉ is capable of efficiently generating large quantities of ROS under photoirradiation (Fig. 5(b), and Figs. S11(a) and S11(b) in the ESM). Subsequently, the types of ROS generated by Gd₄Ti₉ after illumination were explored using specific ROS indicators. Under the same white light irradiation, the green fluorescence of the DHR 123 solution containing Gd₄Ti₉ increased rapidly, with an enhancement factor of 153 times, confirming that Gd₄Ti₉ has excellent ability to generate type I ROS·O₂⁻ (Fig. 5(c), and Figs. S11(c) and S11(d) in the ESM). Furthermore, the characteristic absorbance of the ABDA solution containing Gd₄Ti₉ decreased rapidly with increasing light irradiation time, demonstrating that Gd₄Ti₉ possesses the capability to produce ¹O₂ (type II ROS) (Figs. 5(d) and 5(e), and Figs. S11(e) and S11(f) in the ESM). Electron paramagnetic resonance (EPR) was further utilized to re-investigate the ROS generation capability and species of Gd₄Ti₉ (Fig. S12 in the ESM). Solutions of the spin traps TEMP (2,2,6,6-tetramethylpiperidine) and DMPO (5,5-dimethyl-1-pyrroline-N-oxide) containing Gd₄Ti₉ exhibited no distinct characteristic signals under dark conditions. Under light irradiation, the EPR spectra of the aforementioned solutions distinctly exhibited characteristic signal peaks corresponding to TEMP·¹O₂ and DMPO·O₂⁻, thereby further confirming that Gd₄Ti₉ possesses excellent light-driven ROS generation capability. Clearly, these results indicate that Gd₄Ti₉ can

effectively generate large quantities of type I (·O₂⁻) and type II (¹O₂) under low-power photoirradiation.

2.5 Photocatalytic degradation of organic dyes and antibiotics by Gd₄Ti₉

With the rapid development of modern industry, the number of dyes used is enormous. Some of these dyes are discharged into water bodies with wastewater during production and application, forming highly chromatic, highly toxic, and difficult-to-degrade organic pollutants, posing a potential threat to the growth of plants and animals, human health, and even the ecological environment. Traditional methods for treating organic dye pollutants include physical adsorption and biochemical treatment. Although these methods can remove some pollutants to a certain extent, they generally suffer from low treatment efficiency, high cost, and the potential to cause secondary pollution [77, 78]. Lanthanide-titanium clusters effectively regulate the band structure and electronic structure of materials by combining lanthanide ions (such as Eu³⁺/Gd³⁺) with titanium oxide clusters, and can efficiently generate reactive oxygen species under light irradiation. Given the capacity of Gd₄Ti₉ to produce substantial amounts of type I and type II ROS upon photoirradiation, we investigated its application in the photocatalytic degradation of various organic dyes and antibiotics (Fig. 6(a)). We selected two high-concentration organic dyes: methylene blue (MB, 0.2 mg·mL⁻¹) and rhodamine B (RhB, 0.2 mg·mL⁻¹) for photocatalytic degradation experiments. Gd₄Ti₉ (0.2 mg·mL⁻¹) was introduced into each dye solution, and 40 mL of aqueous solutions containing the dyes were irradiated using a xenon lamp with a power density of 60 mW·cm⁻². The solutions were removed at (MB: 0, 5, 10, 15, 20, 30, 40, and 50 min; RhB: 0, 10, 20, 30, 40, and 50 min) for UV-Vis absorption spectroscopy. With increasing illumination time, the intensities of the

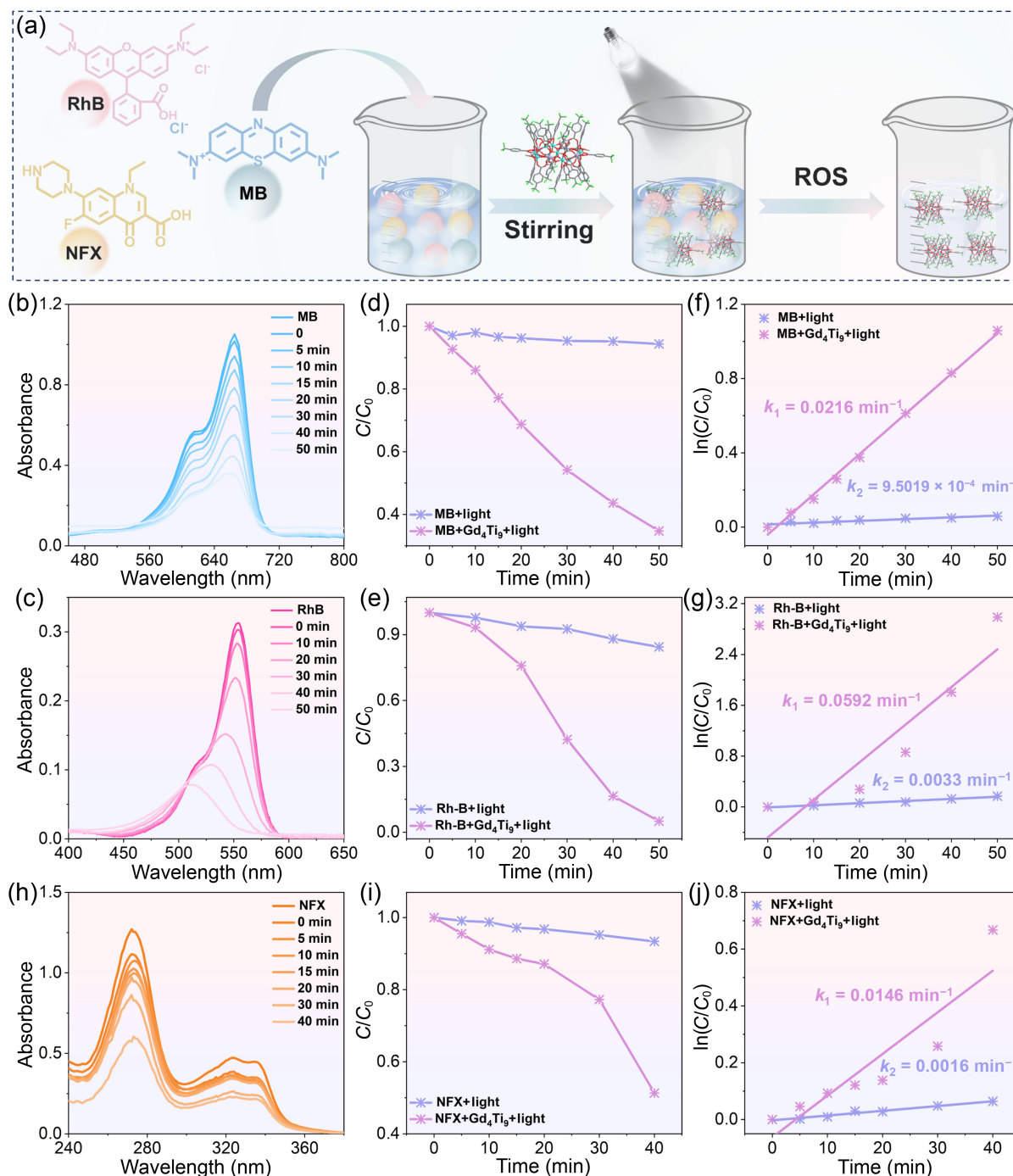


Figure 6 (a) Schematic illustration of the photocatalytic degradation process by Gd_4Ti_9 . UV-Vis absorption spectra of aqueous solutions containing (b) MB, (c) RhB, and (h) NFX under different irradiation times. Degradation curves and degradation kinetic fitting diagrams of Gd_4Ti_9 on aqueous solutions of ((d) and (f)) MB, ((e) and (g)) RhB, and ((i) and (j)) NFX under different irradiation times.

characteristic absorption peaks at 665 nm for MB and 554 nm for RhB gradually decreased (Figs. 6(b)–6(e)). After irradiation for 50 min at the same light power, there were no significant changes in the aqueous solutions of MB and RhB without the addition of Gd_4Ti_9 , indicating that Gd_4Ti_9 has a significant photocatalytic degradation effect on MB and RhB (Figs. S13(a) and S13(b) in the ESM). Based on the first-order kinetic equation $\ln(C/C_0) = kt$, the rate constants k for the photocatalytic degradation of MB and RhB by Gd_4Ti_9 were determined to be 0.0216 and 0.0592 min^{-1} , respectively. However, at the same power density, the degradation

rate constants k of the control group aqueous solution containing only MB and RhB after 50 min of illumination were 0.0009 and 0.0033 min^{-1} , respectively (Figs. 6(f) and 6(g)). Clearly, adding Gd_4Ti_9 to aqueous solutions of MB and RhB increased the photocatalytic degradation rate k by 24-fold and 18-fold, respectively, demonstrating the superior degradation efficacy of Gd_4Ti_9 on colored dyes.

Furthermore, we investigated the reusability of Gd_4Ti_9 in photocatalytic applications by subjecting an aqueous MB solution to multiple cycles of photocatalytic degradation testing. The results

demonstrated that, after five cycles, the catalytic activity of Gd_4Ti_9 remained virtually unchanged (Fig. S14 in the ESM). To evaluate the stability of Gd_4Ti_9 following the degradation reaction, samples that had been immersed in an aqueous solution of organic pollutants for 12 h were recovered via filtration and subjected to FTIR analysis. The FTIR results demonstrate that the positions of the major characteristic absorption peaks remained consistent before and after the reaction, exhibiting no significant changes; this indicates that the framework of Gd_4Ti_9 remained intact (Fig. S15 in the ESM). The aforementioned results demonstrate that Gd_4Ti_9 possesses excellent structural stability and can be utilized as a photosensitizer material for the treatment of organic pollutants. Compared to most conventional photosensitizers currently in use (such as TiO_2 , TiO_2 -supported composites, material of institute lavoisier-101 (Fe), and zeolitic imidazolate framework-8), zero-dimensional Gd_4Ti_9 clusters not only exhibit outstanding dispersibility and semiconductor properties but also effectively increase the number of active sites in contact with substrate molecules, thereby holding promise for opening up new horizons in the development of novel, more efficient photosensitizers [79–81]. However, wastewater generated during daily life and industrial production often contains two or more organic dyes. Consequently, Gd_4Ti_9 ($0.2 \text{ mg}\cdot\text{mL}^{-1}$) was added to an aqueous solution of mixed dyes (MB and RhB, both at a concentration of $0.1 \text{ mg}\cdot\text{mL}^{-1}$); the solution was then irradiated using a xenon lamp with a power density of $60 \text{ mW}\cdot\text{cm}^{-2}$, and samples were withdrawn at various time intervals for UV–Vis analysis. The experimental results indicate that, as the irradiation time increases, the intensities of the characteristic absorption peaks for both MB and RhB gradually decrease; the degradation rates k of MB and RhB in the mixed dye solution by Gd_4Ti_9 are 0.02068 and 0.00756 min^{-1} , respectively. In contrast, under identical irradiation conditions, the absorption intensities of MB and RhB in the mixed dye solution—without the addition of Gd_4Ti_9 —showed no significant change; their respective degradation rates k were 7.56×10^{-4} and $1.92 \times 10^{-4} \text{ min}^{-1}$ (Fig. S16 in the ESM). These results demonstrate that Gd_4Ti_9 continues to exhibit excellent photocatalytic degradation performance within a mixed organic dye system.

Besides, the large amount of ROS generated by Gd_4Ti_9 can be effectively utilized for the degradation of complex antibiotic molecules. With the rapid development of the pharmaceutical and animal husbandry industries, the overuse of antibiotics and their disorderly discharge have intensified, not only causing prominent antibiotic pollution problems in the environment, but also promoting the emergence and spread of drug-resistant “superbugs”. Photocatalysis technology has significant advantages in antibiotic degradation, including low cost, high efficiency, and environmental friendliness, and has gradually become a research hotspot in this field [82, 83]. To investigate the potential of Gd_4Ti_9 in photocatalytic degradation of antibiotics, $0.2 \text{ mg}\cdot\text{mL}^{-1}$ of Gd_4Ti_9 was added into an aqueous solution of norfloxacin (NFX, 10 mM) under xenon lamp irradiation at $60 \text{ mW}\cdot\text{cm}^{-2}$. As the irradiation time increased, the absorbance value of NFX gradually decreased (Figs. 6(h) and 6(i)). The degradation rate constant k of Gd_4Ti_9 for NFX was 0.0146 min^{-1} , while the constant k of the control group solution containing only NFX was 0.0016 min^{-1} after the same irradiation time (Fig. 6(j) and Fig. S13(c) in the ESM). Clearly, adding Gd_4Ti_9 to the NFX aqueous solution increased the k by 9.1 times. These experimental results demonstrate that Gd_4Ti_9 exhibits excellent photodynamic degradation effects on antibiotics in aqueous solution.

3 Conclusions

In summary, lanthanide-titanium clusters Ln_4Ti_9 , with symmetry centers and near-planar arrangement of the cluster nuclei, have been successfully applied in high-performance X-ray scintillators and photocatalytic wastewater purification. The densely packed organic ligand 4-trifluoromethylbenzoic acid surrounding the cluster nucleus provides a protective shell, ensuring the stability of the cluster in solution, and this has been confirmed by HRESI-MS combined with crystallography. Furthermore, the energy transfer pathway demonstrates that the organic ligand 4-trifluoromethylbenzoic acid has a high energy level match with the Eu(III) ion, exhibiting a highly efficient antenna effect. Therefore, Eu_4Ti_9 exhibits outstanding X-ray scintillator performance, with a light yield of $11,677 \text{ photons}\cdot\text{MeV}^{-1}$ and a detection limit of $2.2 \text{ }\mu\text{Gy}\cdot\text{s}^{-1}$, which is below the clinical requirement for commercial medical applications ($5.5 \text{ }\mu\text{Gy}\cdot\text{s}^{-1}$). It is worth noting that only the lanthanide ions were altered, the antenna effect was turned off, and the heavy atom effect was coordinated to promote the ISC process between the S_1 and T_1 states through spin-orbit coupling, which significantly enhanced the ROS storm of Gd_4Ti_9 under ultrasonic and light irradiation conditions. The ROS storm activated by Gd_4Ti_9 under low-power light irradiation showed significant degradation effects on MB, RhB, and NFX, respectively. This work not only expands the range of novel lanthanide-titanium cluster photosensitizers that can be used for the purification of wastewater containing colored dyes or antibiotics, but also opens up new horizons for the controllable synthesis of orthogonal multifunctional lanthanide-titanium cluster-based X-ray scintillators.

Electronic Supplementary Material: Supplementary material (experimental details, characterization data—comprising crystallographic details, FTIR, PXRD, TG, UV–Vis absorption spectra, decay curves, quantum yields, X-ray imaging images, and degradation of indicators, dyes, and antibiotics) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908961>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

R.-Y. L.: Data curation, formal analysis, methodology, validation, visualization, writing – original draft, software, experimental design. L.-L. Z. and W.-Y. L.: Data curation, methodology, validation, visualization. C.-K. W., F. Y., D.-X. C., and Y.-J. Z. Data curation, validation, software. H.-H. Z.: Project administration, methodology, resources, supervision. H.-L. W. and Z.-H. Z.: Project administration, funding acquisition, writing – review & editing, visualization, methodology, investigation, formal analysis, funding acquisition. All the authors have approved the final manuscript.

Use of AI statement

None.

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