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Ce³⁺-Sensitized GdPO₄:Tb³⁺ Nanorods: An Investigation on Energy Transfer, Luminescence Switching, and Quantum Yield

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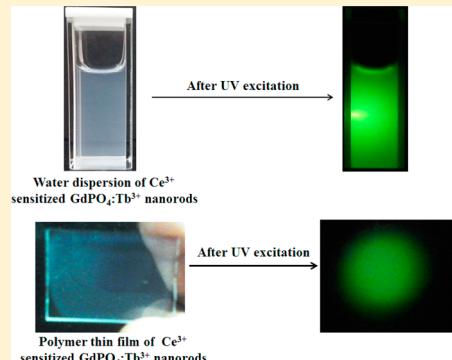
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 Supporting Information

ABSTRACT: Herein we report the enhanced green emission from Tb³⁺-doped GdPO₄ nanorods sensitized with Ce³⁺. The increase in the rate of nonradiative transition processes in sensitizer due to efficient energy transfer to activator is realized from steady-state and dynamic luminescence studies. Luminescence quenching due to cross relaxation is least significant up to 20 at. % Ce³⁺ and 7 at. % Tb³⁺ concentration. The quantum yield of the sample with maximum luminescence, i.e., GdPO₄:Tb³⁺ (5 at. %)/Ce³⁺ (7 at. %), is found to be 28%. Also, samples are readily redispersible in water and could be easily incorporated in polymer-based films that show strong green light emission under UV excitation. The luminescence switching (ON and OFF) behavior is examined using alternately an oxidizing agent (KMnO₄) and then a reducing agent (ascorbic acid) through a redox reaction (Ce³⁺/Ce⁴⁺). Both GdPO₄:Tb³⁺ and GdPO₄:Tb³⁺/Ce³⁺ are observed to be paramagnetic.

KEYWORDS: photoluminescence, energy transfer, redispersion, polymer film, magnetic behavior, optical switching



During the past decades, remarkable progress has been made in exploring varieties of physical, chemical, and biological applications of nanomaterials.^{1–7} Among many of the nanomaterials, luminescent nanoparticles are potentially useful for versatile applications including display and lighting devices, lasers, optical amplifiers, catalysis, and bioimaging.^{6–10} In particular, nanoparticles doped with lanthanide ions are significant for technological applications in the field of optoelectronics, sensing, and bioimaging due to a large Stokes shift.^{11–17} Generally the nanoparticles have lower luminescence quantum yields and shorter fluorescence lifetime than their bulk counterparts due to their large number of defects present on the surface, such as unsaturated bonds, surface-adsorbed ions/molecules (H₂O, CO₃²⁻), impurities, ligands, and an inhomogeneous distribution of lanthanide (Ln) ions. Owing to the presence of these defects on the surface of the nanoparticles, luminescence contributed by the inhomogeneous Ln³⁺ ions present on the surface of the particles is weakened. Thus, they act as the quencher in luminescence.^{18–24} Wang et al.¹⁸ systematically have shown the quenching of Ln³⁺ luminescence in the smaller nanoparticles (~10 nm) compared to the bigger size particles (~25 nm) due to the presence of more surface defects on smaller nanoparticles. These surface defects can be minimized by forming core–shell structures or annealing.^{18,19,25} In our recent study on GdPO₄:Eu³⁺ nanorods,¹⁹ the luminescence intensity of the sample increases with annealing at 500 and 900 °C, which is due to the removal of water in the lattice, as predicted by the thermogravimetric analysis and increase in crystallinity. This improvement in the crystallinity or reduction in the surface defect per gram of

sample with annealing helps in the enhancement of the luminescence of the Ln³⁺ (Ln = Eu). For example, the presence of water over the surface of the nanoparticles can quench luminescence intensity of the Ln³⁺ because the second or third overtones of the fundamental frequency of water (O–H ≈ 3600 cm⁻¹) can match the energy gap between excited and ground states of Ln³⁺, and thus, multiphonon relaxation occurs leading to a more nonradiative rate than radiative rate. However, lanthanide-doped rare-earth (RE) oxide nanoparticles possess several advantages. These include lower screen loading in display devices, high screen resolution, stable dispersion due to functionalized surface, easy encapsulation on porous materials such as silica, and easy processing for polymer-based film.^{17,20,26}

ABO₄ (A = RE, B = P, Mo, V)-type rare-earth oxides including phosphates,^{27–29} molybdates,³⁰ and vanadates^{31–33} are suitable host materials for lanthanide activators where the efficient energy transfer to excited states of activators is possible for the enhancement of the luminescence. In this prospect, the gadolinium ion (Gd³⁺), having a large absorption cross section due to the ⁸S_{7/2}→⁶I_{11/2} transition in the ultraviolet (UV) region, has the advantage of energy transfer from Gd³⁺ to activator ions (Tb³⁺, Eu³⁺, Sm³⁺, etc.). Adding a sensitizer such as Ce and Bi becomes important for further enhancement in luminescence efficiency by an effective energy transfer process through the sensitizer. In particular, sensitization with Ce³⁺ in GdPO₄:Tb³⁺ (termed GdPO₄:Tb³⁺/Ce³⁺) plays a crucial role in

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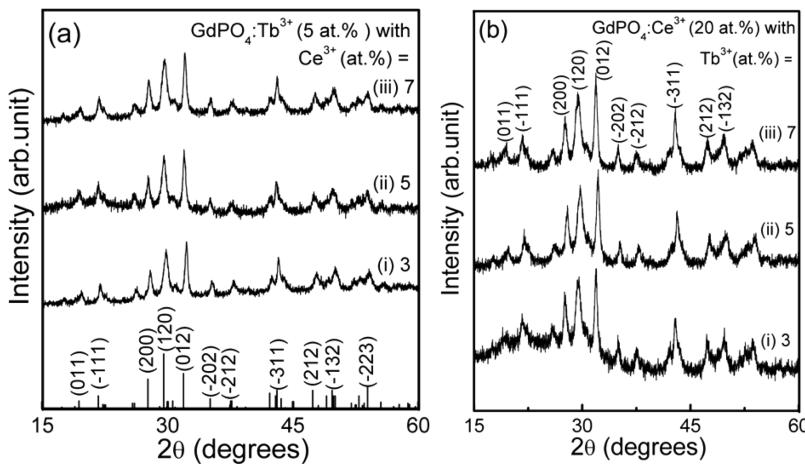


Figure 1. XRD patterns of as-synthesized GdPO_4 samples doped with (a) fixed 5 at. % Tb^{3+} and different Ce^{3+} at. % concentrations and (b) fixed 20 at. % Ce^{3+} and different Tb^{3+} at. % concentrations.

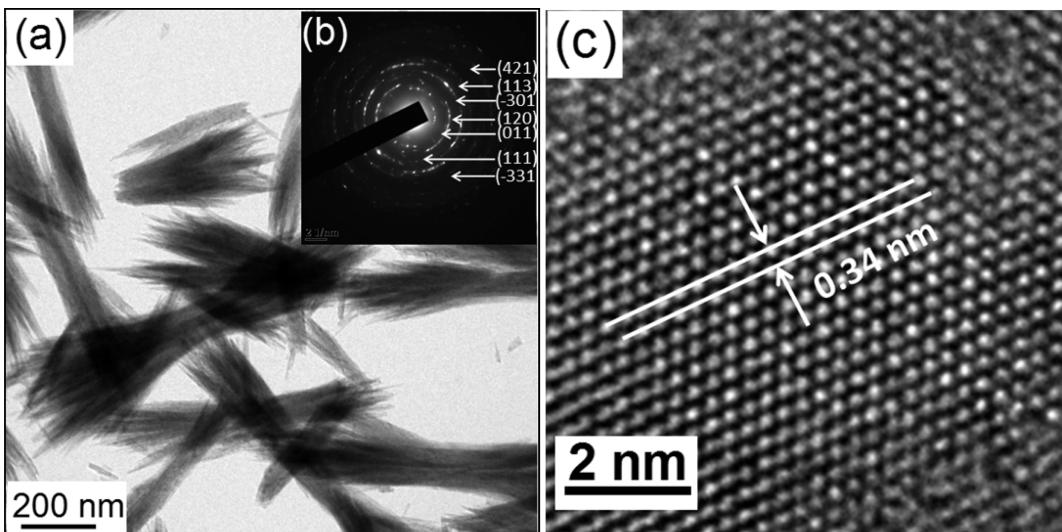


Figure 2. (a) TEM image of as-synthesized $\text{GdPO}_4:\text{Tb}^{3+}$ (5 at. %)/ Ce^{3+} (5 at. %) nanorods, (b) its SAED pattern, and (c) HRTEM image showing its lattice spacing.

the enhancement of Tb^{3+} emission.^{34,35} Therefore it is important to study the energy transfer process and its dependence on the concentration of Ce^{3+} and Tb^{3+} . Based on the energy transfer from Ce^{3+} to Tb^{3+} , a luminescence switching mechanism is possible, which gathers attention for applications including chemical sensing.³⁶ In the process, the sequential quenching of green emission of $\text{GdPO}_4:\text{Tb}^{3+}/\text{Ce}^{3+}$ in the presence of an oxidant (such as KMnO_4) occurs due to oxidation of $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$, leading to no energy transfer to Tb^{3+} (OFF state), and then luminescence can be recovered again by adding a reducing agent (ON state).

In addition, the Gd^{3+} ion has the highest seven unpaired electrons ($^8\text{S}_{7/2}$) in the 4f energy level with zero angular momentum under spin-orbit coupling. These electrons solely yield the S state electron magnetic moment. Thus, the Gd^{3+} ion can efficiently induce longitudinal relaxation of a water proton. So, the Gd^{3+} ion is known to be the best metal ion for a T_1 (longitudinal relaxation) contrast agent in magnetic resonance imaging (MRI). In view of this, there have been recent reports of Gd-chelates, GdPO_4 , Gd_2O_3 , NaGdF_4 , etc., nanoparticles for an MRI contrast agent, which is a powerful and noninvasive medical diagnostic technique.^{10,37–39}

In this investigation, photoluminescence (PL) studies of $\text{GdPO}_4:\text{Tb}^{3+}/\text{Ce}^{3+}$ have been undertaken to confirm the occurrence of efficient energy transfer from Ce^{3+} to Tb^{3+} . We also have investigated the energy transfer process and its efficiency with the variation of Ce^{3+} and Tb^{3+} with steady-state luminescence and decay lifetime. The luminescence switching behavior and its correlation with energy transfer efficiency have been investigated with respect to the concentration of Ce^{3+} and Tb^{3+} ions. We have also looked into quantum yield, its redispersible nature in polar solvents, the formation of films with a polymer matrix, and the magnetic behaviors.

RESULTS AND DISCUSSION

XRD, FTIR, and Microstructure Studies. The X-ray diffraction (XRD) patterns of as-synthesized GdPO_4 doped with different concentrations of Ce^{3+} and Tb^{3+} are shown in Figure 1. The patterns of as-synthesized samples unambiguously match with the monoclinic phase of GdPO_4 (JCPDS-32-0386). Similar patterns in all the samples indicate the homogeneous solid solution among GdPO_4 , TbPO_4 , and CePO_4 . This is due to the similar ionic radii of Gd^{3+} (1.107 Å), Tb^{3+} (1.095 Å), and Ce^{3+} (1.196 Å) in a nine-coordination

system,⁴⁰ which makes GdPO₄ a suitable matrix for incorporation of lanthanide ions. Not much difference in intensities is observed at 2θ (deg) = 29.51 and 31.89 because of the multiplicity of the planes (120) and (012) in the monoclinic structure.¹⁹ The asymmetry in intensities observed between the most intense peaks may be ascribed to the anisotropic growth of the GdPO₄ nanoparticles in the rod shape (seen in the TEM image).

The Fourier transform infrared (FTIR) spectrum of 5 at. % Tb³⁺-doped GdPO₄ nanoparticles is shown in Figure S1 (Supporting Information). Prominent bands are observed at 551, 569, 625, 881, 996, 1008, 1083, 1438, 1654, 2881, 2953, and 3321 cm⁻¹. Based on the (PO₄)³⁻ group symmetry, band regions are defined as ν_1 , ν_2 , ν_3 , and ν_4 respectively.¹⁹ The band regions ν_1 and ν_2 are Raman-active modes, whereas ν_3 and ν_4 are IR-active modes and correspond to the stretching and bending vibrations of the (PO₄)³⁻ group. The ν_4 region can be assigned at 551, 569, and 625 cm⁻¹ and ν_3 at 881, 996, 1008, and 1083 cm⁻¹. Bands at 1654 and 3382 cm⁻¹ correspond to bending and stretching vibrations of the O–H group of the ethylene glycol (EG) molecule.⁴¹ The broad band at 3382 cm⁻¹ is different from the free O–H stretching frequency (3650 cm⁻¹), indicating the presence of a hydrogen bond in EG molecules. The wagging vibration at 1266 cm⁻¹, twisting vibration at 1155 cm⁻¹, and rocking vibration at 899 cm⁻¹ due to the presence of CH₂ from EG have been merged with the vibrational bands of (PO₄)³⁻.¹⁹ The peaks at 2881 and 2953 cm⁻¹ correspond to the stretching vibrations of the CH₂ group from EG.⁴¹

The field emission scanning electron microscopy (FESEM) image of the GdPO₄:Tb³⁺ (5 at. %)/Ce³⁺ (5 at. %) nanorods is shown in Figure S2a (Supporting Information). The image clearly shows the bundle of nanorods of approximately 15–20 nm in diameter and 600–700 nm in length. Further the self-assembly of these nanorods was observed in the transmission electron microscopy (TEM) image shown in Figure 2a. The individual nanorods appear to be assembled forming broom-like nanostructures. The presence of Ce, Tb, Gd, and P is confirmed from energy-dispersive analysis of X-rays (EDAX) (Figure S2b in the Supporting Information). Figure 2b shows the selected area electron diffraction (SAED) pattern. The pattern shows that the samples are in the crystalline form. The calculated *d*-spacing of 0.30 nm from the high resolution TEM image (Figure 2c) can be matched with the plane (120) of GdPO₄.

Magnetic Study. The magnetization (*M*) versus applied magnetic field (*H*) plots of undoped and Tb³⁺/Ce³⁺-doped GdPO₄ nanorods are shown in Figure S3 (Supporting Information). All the samples show purely paramagnetic behavior, with a high paramagnetic moment due to possession of a higher number of unpaired electrons (7) in the half-filled 4f⁷ outermost orbital of the Gd³⁺ ion. The zero field cooling (ZFC) and field cooling (FC) measurements of undoped and 5 at. % Tb³⁺-doped GdPO₄ nanoparticles at 500 Oe in the range of 330 to 5 K (Figures S4 and S5 in the Supporting Information) show typical Curie behavior with high moment, reaffirming the paramagnetic behavior. Thus, these lumino-magnetic nanoparticles with both luminescence and magnetic properties will be a potential multifunctional candidate for simultaneous applications in bioimaging and MRI.^{10,16,34} The paramagnetic contribution coming from the half-filled 4f⁷ of the Gd³⁺ ion is calculated from the Curie equation,⁴²

$$\mu = \sqrt{\frac{3k_B CA}{N_A}} \quad (1)$$

where k_B is the Boltzmann constant, C is the Curie constant, A is the atomic or molecular weight, and N_A is Avogadro's number. The estimated moment (in terms of Bohr magneton, μ_B) associated per atom of Gd³⁺ is found to be 5.9 μ_B , which is ~75% of the theoretical value (7.9 μ_B). Here, the orbital contribution is neglected.

Photoluminescence (PL) Study. Excitation spectra of 5 at. % Tb³⁺-doped GdPO₄ sensitized with different Ce³⁺ (3, 5, and 7 at. %) concentrations monitored at 544 nm emission are shown in Figure S6 (Supporting Information). The excitation spectra consist of three main absorption peaks at 250, 280, and 315 nm in the range of 200 to 320 nm. The first and second peaks are associated with the spin-allowed 4f–5d transitions in Ce³⁺ from the ²F_{5/2} ground state of 4f to two different excited state levels of 5d, whereas the third one is related to the 4f–4f transition of Ce³⁺.^{35,43} The excitation peaks observed at ⁷F₆→⁵G₅ (355 nm), ⁷F₆→⁵L₁₀ (373 nm), and ⁷F₆→⁵G₆ (380 nm) are related to the f–f transition absorptions of Tb³⁺ (inset of Figure S6).³⁵ The presence of a peak arising from the ⁸S_{7/2}→⁶I_{11/2} transition of the Gd³⁺ ion at ~278 nm is not observed separately because it is merged with spin-allowed 4f–5d transitions in Ce³⁺. The presence of such strong absorption compared to the f–f transitions, which are of spin-forbidden nature, indicates the occurrence of strong energy transfer from Ce³⁺/Gd³⁺ to the excited energy states of Tb³⁺ (discussed later).

PL emission spectra of GdPO₄:Tb³⁺ (5 at. %)/Ce³⁺ (5 at. %) under excitation at 250, 280, and 355 nm (Figure S7 in the Supporting Information) show the emission bands at 490 (⁵D₄→⁷F₆), 544 (⁵D₄→⁷F₅), 585 (⁵D₄→⁷F₄), and 620 (⁵D₄→⁷F₃) nm.³⁵ Among these, the green emission at 544 nm is the strongest. The broad emission observed at 350 nm after excitation with 250 and 280 nm is due to radiative transitions from the d-level excited states of Ce³⁺ to its f-level ground states. The emission intensity area excited at 280 nm is nearly 15 times more compared to that at 355 nm excitation under similar conditions. This shows the strong energy transfer from the Ce³⁺ ions' absorption to the excited states of Tb³⁺ ions. This is clearly evident from the overlapping of the broad Ce³⁺ emission with f–f absorption bands of Tb³⁺ (see Figure S8 in the Supporting Information). It is well known that according to Föster–Dexter energy transfer theory, the transfer of energy between two fluorophors occurs if these are within a critical distance (~20 Å) and the donor's emission and the acceptor's absorption bands overlap.^{44,45} The schematic representation of energy transfer taking place in GdPO₄:Tb³⁺/Ce³⁺ is shown in Figure S9 (Supporting Information). To investigate the effect of Ce³⁺ concentration, emissions of GdPO₄:Tb³⁺ (5 at. %) sensitized with different Ce³⁺ concentrations excited at 280 nm are shown in Figure 3. It is observed that the intensity of Tb³⁺ emission increases with the increase of Ce³⁺ concentration up to 7 at. % and then decreases. The decrease in the Tb³⁺ emission with the increase of Ce³⁺ concentration (above 7 at. %) might be due to the following reasons. There may be critical concentrations of Ce³⁺ with respect to Gd³⁺ for a particular host (here it is GdPO₄), where the absorption cross-section near 250–290 nm (absorption level of Ce³⁺/Gd³⁺) will be maximum. In this, there is a high probability of energy transfer to Tb³⁺. When the amount of Ce³⁺ increases, simultaneously

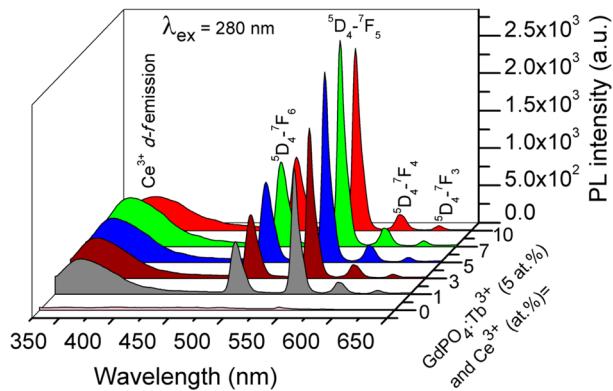


Figure 3. Emission spectra of $\text{GdPO}_4\text{:Tb}^{3+}$ (5 at. %) sensitized with different Ce^{3+} concentrations excited at 280 nm.

the amount of Gd^{3+} decreases in the system ($\text{Gd}_{1-x-y}\text{Ce}_x\text{Tb}_{y=0.05}\text{PO}_4$). Thus, there will be net effect from Ce^{3+} and Gd^{3+} in the absorption as well as emission processes. At 10 at. % Ce^{3+} , a decrease in emission intensity of $\text{Ce}^{3+}/\text{Tb}^{3+}$ may be due to the net effect from $\text{Ce}^{3+}/\text{Gd}^{3+}$ or dipole-quadrupole interactions among the Ce^{3+} ions.

To further explore the energy transfer processes and their efficiency from the Ce^{3+} emission to the Tb^{3+} excited states, we have investigated the emissions of different Tb^{3+} concentrations sensitized with Ce^{3+} (20 at. %). 20 at. % Ce^{3+} has been chosen to accommodate higher concentration of Tb^{3+} ions in the host GdPO_4 for energy transfer study. Figure 4 shows the

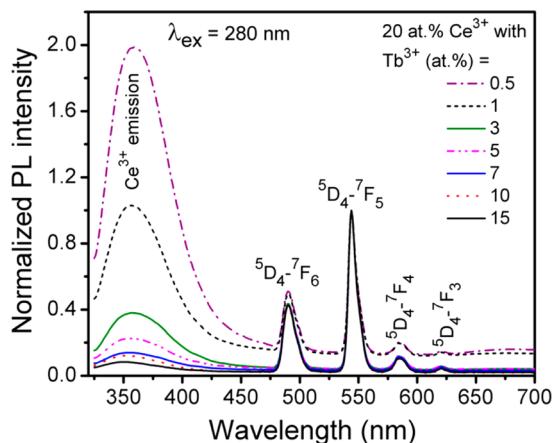


Figure 4. Normalized (at $\lambda = 544$ nm) emission spectra of Ce^{3+} -sensitized $\text{GdPO}_4\text{:Tb}^{3+}$ (5 at. %) samples under 280 nm excitation.

normalized (at $\lambda = 544$ nm) emission spectra of Ce^{3+} -sensitized $\text{GdPO}_4\text{:Tb}^{3+}$ samples after excitation at 280 nm. From the spectra, it is clearly evident that the intensity of the broad emission peak of the Ce^{3+} ions (320 to 420 nm) gradually decreases with an increase in the Tb^{3+} concentration. This gradual decrease in Ce^{3+} emission intensity indicates an increase in energy transfer efficiency with the increase in Tb^{3+} concentration. This happens because electrons from Ce^{3+} emission find more and more Tb^{3+} ions in the system for resonance-type energy transfer.

PL Decay and Quantum Yield Studies. Figure 5 shows the PL decay of the 20 at. % Ce^{3+} -sensitized $\text{GdPO}_4\text{:Tb}^{3+}$ samples with monitoring emission at 544 nm and excitation at 280 nm. In this case, the excitation of Tb^{3+} occurs through

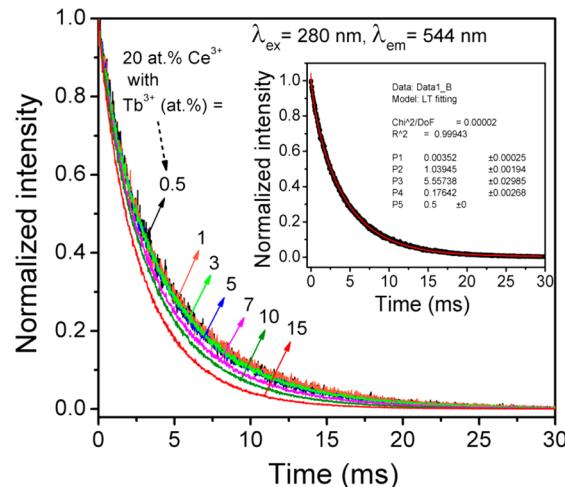


Figure 5. Luminescence decay of the 20 at. % Ce^{3+} and different Tb^{3+} concentrations doped GdPO_4 samples ($\lambda_{\text{ex}} = 280$ nm and $\lambda_{\text{em}} = 544$ nm). Inset: Typical fitting of $\text{GdPO}_4\text{:Tb}^{3+}/\text{Ce}^{3+}$ (both are 5 at. %) nanorod.

resonance energy transfer from Ce^{3+} emission to Tb^{3+} . Thus the decay does not occur immediately after excitation. In such cases, the decay process follows the form⁴⁵

$$I(t) = I_0 \exp[(-t/\tau) - (2bt^{1/2})] \quad (2)$$

where b is quencher concentration and τ is diffusion coefficient dependent. Assuming resonance energy transfer occurs in three dimensions, t has the powers of 1/2. On the basis of the above equation, the luminescence decay times of Tb^{3+} in 20 at. % Ce^{3+} -sensitized $\text{GdPO}_4\text{:Tb}^{3+}$ have been calculated and are presented in Table 1. The inset of Figure 5 shows the typical

Table 1. Decay Lifetime Values of Tb^{3+} and Ce^{3+} in Different Tb^{3+} Concentrations and Fixed 20 at. % Ce^{3+} -Doped GdPO_4

sl. no.	Tb^{3+} (at. %)	lifetime τ and goodness of fit R^2			
		Tb^{3+} (ms)	R^2	Ce^{3+} (ns)	R^2
1	0.5	6.6	0.99	10	0.99
2	1	6.8	0.99	9	0.98
3	3	5.6	0.99	8	0.98
4	5	5.7	0.99	8	0.98
5	7	5.1	0.99	6	0.98
6	10	4.5	0.99	5	0.98
7	15	3.7	0.99	4	0.98

fitting of Tb^{3+} decay in $\text{GdPO}_4\text{:Tb}^{3+}$ (5 at. %)/ Ce^{3+} (5 at. %) sample. The maximum lifetime (6.8 ms) of Tb^{3+} is found at $\text{GdPO}_4\text{:Tb}^{3+}$ (1 at. %)/ Ce^{3+} (20 at. %), which is comparatively longer than earlier reported,⁴⁶ which might be due to a decrease in nonradiative transition probabilities. The lifetime value decreases with an increase in concentration. This is ascribed to the increase in contribution of nonradiative transition probabilities as the lifetime depends on $(k_r + k_{nr})^{-1}$, where k_r and k_{nr} are the respective radiative and nonradiative transition probabilities. The increase in k_{nr} is due to concentration quenching, which is a typical property of lanthanide ions. Figure 6 shows the PL decay curve of Ce^{3+} emission (355 nm) excited at 280 nm. The lifetime value of Ce^{3+} in $\text{GdPO}_4\text{:Tb}^{3+}/\text{Ce}^{3+}$ is found to be in the range of 4–10 ns, which is much shorter than the Ce^{3+} lifetime (10–150 ns) in $\text{Ca}_2\text{Al}_3\text{O}_6\text{F:Ce}^{3+}/\text{Tb}^{3+}$ reported by Xia et al.⁴⁷ The lifetime of 20 at. % Ce^{3+}

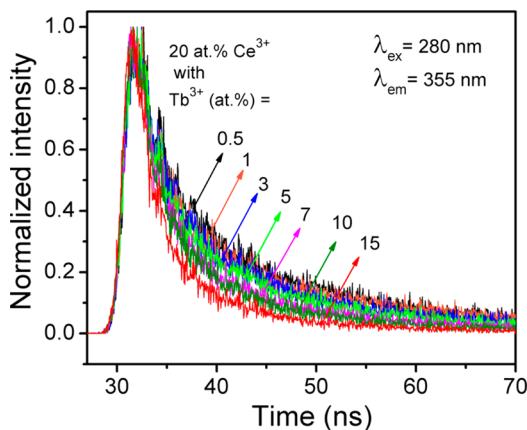


Figure 6. Luminescence decay of Ce^{3+} emission in 20 at. % Ce^{3+} and different Tb^{3+} concentrations doped GdPO_4 samples ($\lambda_{\text{ex}} = 280 \text{ nm}$ and $\lambda_{\text{em}} = 355 \text{ nm}$).

doped GdPO_4 without any Tb^{3+} was found to be 50 ns (Figure S10 in the Supporting Information). The shorter lifetime is an indication of nonradiative energy transfer from Ce^{3+} emission to excited states of Tb^{3+} . From Table 1, it is clearly observed that the lifetime decreases with an increase in Tb^{3+} concentration. This is due to the increase in nonradiative resonance energy transfer to the higher excited states of Tb^{3+} (mentioned earlier). This confirms the increase in the energy transfer efficiency with the increase in Tb^{3+} ions in the system. The quantum yield of $\text{GdPO}_4:\text{Tb}^{3+}(5 \text{ at. \%})/\text{Ce}^{3+}(7 \text{ at. \%})$, henceforth termed $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$, dispersed in water was measured using a BaSO_4 -coated integrated sphere, and it is found to be 28%.

CIE, Redispersion, and Polymer Film Formation. For the understanding of color tone of the light emission from the samples, the color coordinates (x, y) are given in a CIE chromaticity diagram (labeled with numericals) in Figure 7. The details of the coordinates are presented in Table S1 (Supporting Information). From the coordinates, it is observed

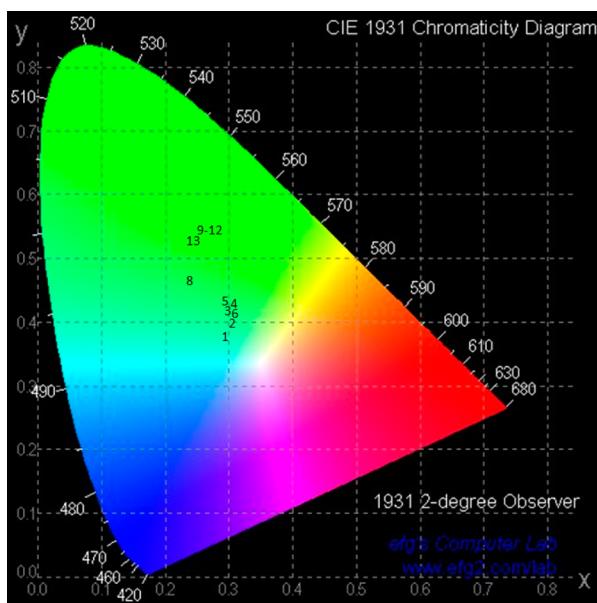
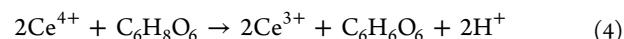
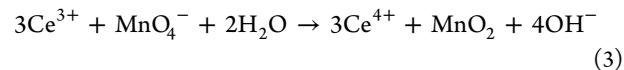


Figure 7. CIE color coordinates (x, y numbered with numericals) in CIE chromaticity diagram (1993).

that the color of the samples is tuned from greenish-blue to proper green. The emission colors of the samples are moved toward greenish-blue if the Tb^{3+} concentration decreases in $\text{GdPO}_4:\text{Ce}^{3+}$ (20 at. %)-doped samples. The presence of greenish-blue emission is understandable, as the violet-blue color originating from Ce^{3+} emission is mixed with green color from Tb^{3+} .

As-prepared samples are redispersible in polar solvents such as ethanol, methanol, and water. Redispersion is due to the presence of an O–H group adsorbed/bonded on the surface of the particles, which comes from the capping agent ethylene glycol. EG simultaneously plays the role of solvent and capping agent. The O–H group of EG can form a hydrogen bond with polar solvents. The presence of an O–H group on the surface of the particles was confirmed in the FTIR study. Further, about 5 mg of particles is dispersed in 5 mL of water and mixed with 10 mL of 4 wt.% polyvinyl alcohol (PVA) solution. After thoroughly mixing in an ultrasonic bath, the mixture was treated with 1 mL of a 0.1 M solution of borax, which helps in cross-linking between PVA molecules. Then the polymer composite film was prepared by spreading the above viscous solution over the glass slide, and a film with a thickness of ~1 mm is formed after drying. Both the dispersed sample and polymer film show strong green emission with UV light irradiation (280 nm), which is shown in Figure 8. More efficient light emission is also evident for Ce^{3+} -sensitized $\text{GdPO}_4:\text{Tb}^{3+}$, as the green color is more intense (Figure 8b) than that for $\text{GdPO}_4:\text{Tb}^{3+}$ (Figure 8a). Such dispersed samples may be useful for tagging with bioentities in imaging. Also, such polymer-based films will pave a new dimension toward development of flexible light-emitting display devices.

Luminescence Switching. A luminescence ON-OFF study of $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$ nanorods was done by subsequent addition of oxidizing agent (potassium permanganate, KMnO_4) and reducing agent (ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$) and is shown in Figure 9. Based on the following equations,



one MnO_4^- ion can oxidize three Ce^{3+} ions, whereas one $\text{C}_6\text{H}_8\text{O}_6$ can reduce two Ce^{4+} ions. At the initial stage, 20 mg of $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$ was dispersed in 1 mL of EG, and this contains $\sim 3.4 \times 10^{19}$ Ce^{3+} ions. These Ce^{3+} ions can be completely oxidized to Ce^{4+} with the addition 0.3 mg of KMnO_4 . The charge transfer from Ce^{3+} to Ce^{4+} occurs; thereby energy transfer from Ce^{3+} to Tb^{3+} is cut off when excited through Ce^{3+} (278 nm, i.e., allowed transition from $4f^1$ to $5d^0$ transition). The Ce^{4+} state is a full cell ion having the electronic configuration $[\text{Xe}]4f^05d^06s^0$. Hence, no $4f-4f$ electronic transitions can occur because of the empty $4f$ level. Eventually, no emission from Tb^{3+} should occur. But, the coexistence of Ce^{3+} with Ce^{4+} cannot be ignored, which is the case more often than not. Again, the luminescence can be restored by addition of ascorbic acid (0.35 mg) because of the reduction process from Ce^{4+} to Ce^{3+} . This process is like the ON-OFF cycle. It can be repeated five times. However, the emission intensity decreases with the number of cycles due to the decrease of active ions (Ce^{3+} and Tb^{3+}) per 1 mL of the system and also the extent of increase of quenchers arises from KMnO_4 , MnO_2 , or $\text{C}_6\text{H}_8\text{O}_6$. Thus, this system can be used as a luminescence switch through redox reaction. Further, this has been confirmed

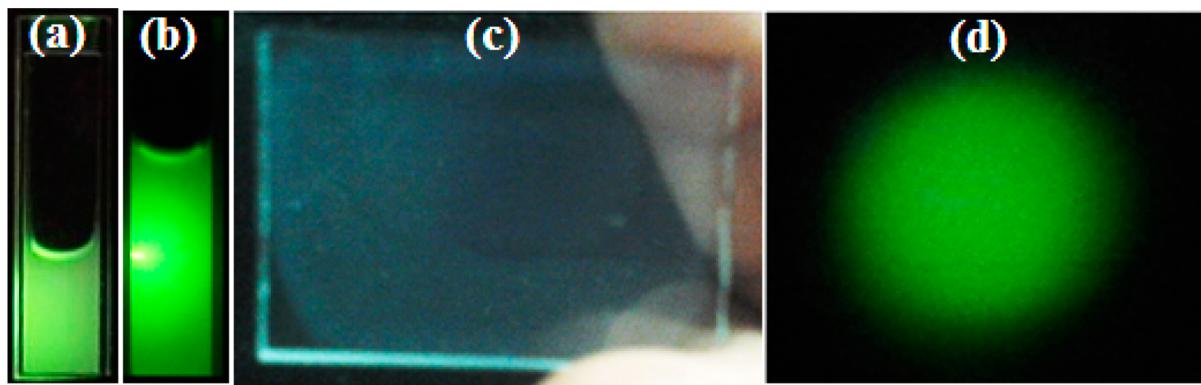


Figure 8. Photographs: (a) $\text{GdPO}_4:\text{Tb}^{3+}$ (5 at. %) and (b) $\text{GdPO}_4:\text{Tb}^{3+}$ (5 at. %)/ Ce^{3+} (7 at. %) dispersed in water under UV excitation; PVA polymer thin films (c) without and (d) with UV excitation.

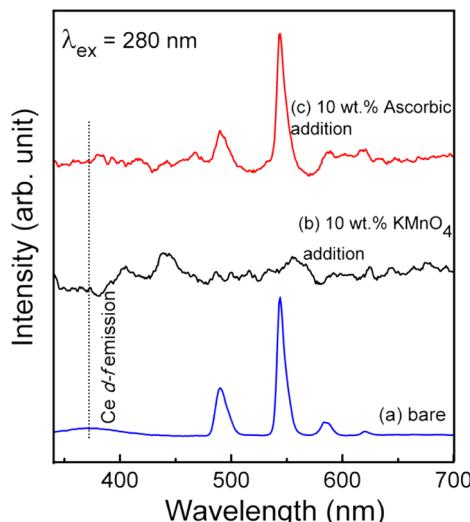


Figure 9. PL emission of (a) bare, (b) oxidized with KMnO_4 , and (c) reduced with ascorbic acid 7 at. % Ce^{3+} -sensitized $\text{GdPO}_4:\text{Tb}^{3+}$ (5 at. %).

with the quantum yield measurement with three cycles of ON/OFF. The respective quantum yields after first, second, and third cycles (1 cycle = one OFF to ON state) are found to be 22%, 18%, and 10%, respectively.

The second protocol for the switching behavior was carried out using water as the medium for dispersion. The detailed study is given in the Supporting Information. After the alternate addition of KMnO_4 and ascorbic acid, the precipitate was removed by centrifugation followed by washing. Here, the powders obtained from the precipitate were recorded for luminescence. This reduces the effect from the extra byproducts (KMnO_4 , MnO_2 , K^+ , $\text{C}_6\text{H}_8\text{O}_6$, $\text{C}_6\text{H}_6\text{O}_6$, etc.) coming out during the experiment, and these byproducts are a source of quencher in the luminescence observed in the first protocol.

Figure 10 shows PL emission spectra of the $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$ nanorods after it was given a partial oxidizing treatment by the KMnO_4 solution with varying concentrations between 0.02 and 0.3 mM. The excitation wavelength (λ_{ex}) is fixed at 280 nm. The treatment time was kept fixed at 2 h. It has been observed that with increasing the concentration of KMnO_4 , the PL intensity gradually decreases due to an increase in the oxidation rate and more Ce^{3+} ions are converted to Ce^{4+} , resulting in the lowering of energy transfer from Ce^{3+} to Tb^{3+} . This is also confirmed from the significant

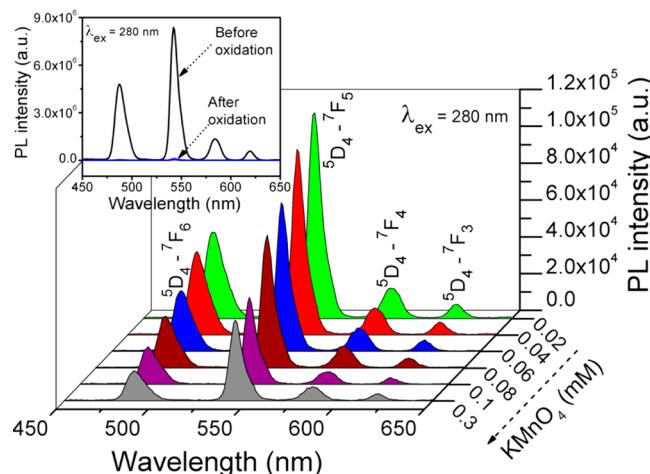


Figure 10. PL emission spectra ($\lambda_{\text{ex}} = 280$ nm) of $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$ after oxidizing with KMnO_4 solution (0.02–0.3 mM). The treatment time was kept fixed for 2 h. Inset: Comparison of PL emission spectra of the sample before and after oxidation treatment.

decrease in the intensity of Ce^{3+} (d–f) emission (Figure S11a in the Supporting Information). In addition, a slight blue shift is observed in the emission peak (the strongest one, i.e., ${}^5\text{D}_4 - {}^7\text{F}_5$). This may be due to the change in the stoichiometry after the formation of Ce^{4+} . It has been observed even at a higher concentration of KMnO_4 (0.3 mM) that the luminescence is not quenched completely. This is indicated by all Ce^{3+} ions not being converted to Ce^{4+} . Hence it is more likely to be a surface phenomenon.⁴⁸ However, the luminescence is almost quenched in the oxidized sample in comparison to the unoxidized one (inset of Figure 10). In our opinion, there are surface and core/lattice Ce^{3+} ions in a particle. When a sufficient amount of KMnO_4 solution is added to particles in order to convert all Ce^{3+} to Ce^{4+} ions, the system can be taken as heterogeneous (i.e., particles/solid + solution). The following may be expected: (1) oxidation from Ce^{3+} present on the surface of the particle to Ce^{4+} occurs at an initial stage and (2) oxidation of Ce^{3+} in the lattice/core to Ce^{4+} occurs after a longer duration. However, we observed that there are still emission peaks corresponding to Tb^{3+} after the oxidation reaction, but their intensity is significantly decreased as compared to unoxidized ones. This means that most Ce^{3+} ions are converted to Ce^{4+} ions and some Ce^{3+} ions are still remain in the core/lattice.

Figure 11 shows the PL emission spectra of a heavily oxidized $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$ sample (0.1 mM KMnO_4) after

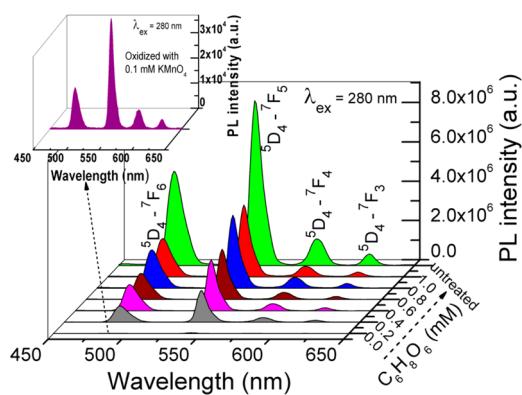


Figure 11. PL emission spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of heavily oxidized $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$ (oxidized with 0.1 mM KMnO_4) after reducing with ascorbic acid solution (0–1 mM). A PL emission spectrum of untreated sample is included for comparison. Inset: Magnified graph of a selected plot marked with an arrow. The treatment time was kept fixed at 2 h.

partial reduction by ascorbic acid solution at different concentrations between 0 and 1 mM. A PL emission spectrum of untreated/unoxidized sample is included for comparison. It has been observed that luminescence is recovered with the increase in concentration of $\text{C}_6\text{H}_8\text{O}_6$ from 0.2 mM to 1 mM, resulting in the gradual increase of luminescent intensity. This is due to the reverse effect of the oxidation, resulting in the recovery of the Ce^{3+} state from the Ce^{4+} state, which is reflected in the Ce^{3+} (d–f) emission (Figure S11b in the Supporting Information). Here also, complete recovery is not observed as that of the untreated sample because complete reduction is not possible. This is related to surface phenomena. Another possibility arises from the quenchers, such as KMnO_4 , $\text{C}_6\text{H}_8\text{O}_6$, or OH , associated during the reaction, which might not be removed from the sample completely.

Figure 12 shows the emission spectra of the sample after repeated cycles of switching for five cycles. Oxidation (X) is followed by reduction (R) in the sequence X1-R1-X2-R2-X3-R3-X4-R4-X5-R5. The concentration of the oxidant and reductant were 0.1 and 1.0 mM, respectively. The duration of oxidation or reduction is kept fixed at 10 min each, followed by a centrifugation time of 5 min after each cycle. It is observed

that the luminescence intensity decreases gradually in the oxidation cycle, while the recovery in the reduction cycle is prominent up to the second cycle, followed by a decrease. The recovery is substantial up to the fifth cycle of the experiment.

The time response of the luminescence switching was evaluated for the sample in the oxidation treatment with the KMnO_4 solutions (0.02–0.1 mM). The plot of integrated PL intensity versus time is shown in Figure 13. The integrated PL

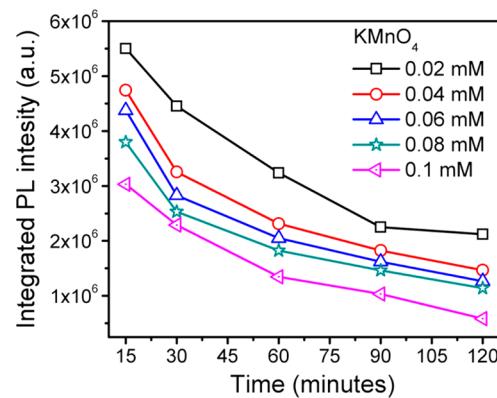


Figure 13. Time dependence of the integrated PL intensity for the oxidized sample with KMnO_4 solution with varying concentrations between 0.02 and 0.1 mM. The integrated PL intensity was calculated as the area between 450 and 650 nm in the emission spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$).

intensity for the Tb^{3+} emissions was calculated by estimating the area under the emission spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) between wavelengths of 450 and 650 nm. Gradual luminescence quenching is observed with time for all of the concentrations. However, complete quenching is not observed in any case even at higher concentrations of KMnO_4 . This oxidation reaction takes place predominantly at the surface of the particles.

CONCLUSIONS

Enhanced luminescence of Ce^{3+} -sensitized GdPO_4 nanorods activated with Tb^{3+} was successfully investigated for the energy transfer mechanism. Efficient energy transfer is observed up to 20 at. % Ce^{3+} content without noticeable cross relaxation among them. The nanorods are readily redispersible in polar solvents. They could be easily incorporated in polymer-based films for promising flexible display devices. The extent of luminescence switching in Ce^{3+} -sensitized $\text{GdPO}_4:\text{Tb}^{3+}$, which

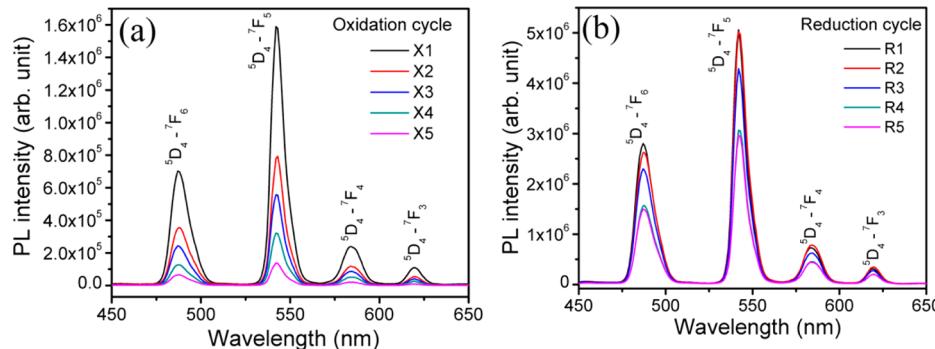
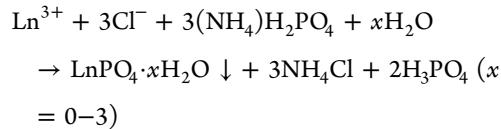


Figure 12. PL emission spectra ($\lambda_{\text{ex}} = 280 \text{ nm}$) of $\text{Gd}_{0.88}\text{Ce}_{0.07}\text{Tb}_{0.05}\text{PO}_4$ after repeated switching for five cycles. Oxidation (X) is followed by reduction (R) in the sequence X1-R1-X2-R2-X3-R3-X4-R4-X5-R5. The concentration of the oxidant and reductant were 0.1 and 1.0 mM, respectively. The duration of oxidation and reduction is 10 min each, followed by centrifugation for 5 min after each cycle.

occurs due to conversion of Ce³⁺ to Ce⁴⁺ and vice versa, depends on the concentration of oxidizing agent (KMnO₄) and reducing agent (ascorbic acid) as well as on the times scale. The optical switching in GdPO₄:Ce³⁺/Tb³⁺ is more likely to be a surface phenomenon. The luminescence quantum yield for Gd_{0.88}Ce_{0.07}Tb_{0.05}PO₄ is found to be 28%. Tb^{3+}/Ce³⁺-doped GdPO₄ samples are highly paramagnetic and show a strong luminescent property, which could be potentially useful for simultaneous optical and MR imaging.}

EXPERIMENTAL SECTION

Synthesis of Ce³⁺-Sensitized GdPO₄:Tb³⁺ Nanorods. Analytical grade reagents were used as reactants without further purification. Gd₂O₃ (Aldrich, 99.99%), Tb(NO₃)₃·6H₂O (Alfa Aesar, 99.99%), Ce(NO₃)₃·6H₂O (Aldrich, 99.99%), and NH₄H₂PO₄ (Aldrich, 99.999%) were used as precursors. EG and hydrochloric acid (HCl) were used as received. For the synthesis of GdPO₄:Tb^{3+}/Ce³⁺, a simple polyol method using EG was adopted following earlier reports.¹⁹ In a typical synthesis procedure for GdPO₄:Tb³⁺ (5 at. %)/Ce³⁺ (5 at. %) nanorods, 350 mg of Gd₂O₃, 49 mg of Tb(NO₃)₃·6H₂O, and 47 mg of Ce(NO₃)₃·6H₂O were dissolved in 1 mL of 1 M HCl in a 100 mL round-bottom flask. The excess acid was removed by evaporating the solution through successive addition of water (5 mL). Then 250 mg of (NH₄)H₂PO₄ was added to the resulting transparent solution along with 50 mL of EG. The solution was heated at 150 °C for 2 h. The resulting white precipitates were washed with a mixture of water and ethanol and collected by centrifugation. The chemical equation for the formation of LnPO₄ (Ln = Gd, Eu, Ce) is}



Characterization Techniques. The identification and purity of the phase was confirmed by XRD using a PANalytical diffractometer (X'pert PRO) with Cu K α radiation ($\lambda = 1.5405$ Å) and a Ni filter. FTIR spectra were recorded in Magna550, Nicolet Instruments Corporation, USA, by KBr pellet technique. FESEM and TEM images were recorded in JEOL JEM-7600F and JEOL JEM-2100F instruments, respectively. Magnetic measurements were carried out in a magnetic properties measurement system (MPMS, Quantum Design, USA).

The luminescence spectra were recorded at room temperature with a Hitachi F-4500 fluorescence spectrometer having a 150 W Xe lamp as the excitation source. Luminescence lifetime measurements for Tb³⁺ and Ce³⁺ transitions were carried out using a 100 W μ s flash and nanosecond lamp attached to an Edinburgh Instruments (FLS920) apparatus equipped with a 450 W xenon arc lamp having a Peltier element cooled red-sensitive Hamamatsu R955 PMT. Instrumental response function was recorded using Teflon after excitation at 280 nm, and its lifetime is found to be less than 1 ns. For steady state PL measurement, a 50 mg amount of the powder sample was mixed with 1 mL of methanol and pasted over the quartz slide (1 cm × 1 cm) and dried in the ambient condition. All fittings to the decay data were carried out above 55–100 μ s due to a delay in time response. For PL decay measurement, a 5 mg amount of the particles was dispersed in 200 μ L of methanol and pasted over the quartz slide. Then it was dried at room

temperature and put in the sample holder of the instrument. Excitation and emission of Tb³⁺ were monitored at 280 and 545 nm. Similarly, for Ce³⁺, the monitoring excitation and emission were at 280 and 355 nm, respectively. The PL spectra of the luminescence switching experiment were recorded in a Horiba Jobin-Yvon Spex Fluorolog-3 fluorimeter. Quantum yields of the samples were measured using a BaSO₄-coated integrating sphere of diameter 15 cm in FLS920, which is based on the absolute method. For quantum yield measurement, a 1 mg amount of the as-prepared sample was dispersed in 1 mL of water. Excitation at 280 nm and emission at 544 nm were fixed. The slit widths for excitation and emission were fixed at 3 and 0.7 nm, respectively. The iris was kept at 90%. The data were recorded with a step size of 0.1 nm and dwell time of 0.3 s. The instrument was calibrated using rhodamine B standard dye with a quantum yield of 31% in water.⁴⁹

ASSOCIATED CONTENT

S Supporting Information

FTIR spectrum, FESEM image, EDX spectrum, M–H plot, ZFC-FC plot, PL emission and excitation spectra, scheme for energy transfer process in GdPO₄:Tb^{3+}/Ce³⁺, luminescence decay, CIE coordinates, and protocol for redox experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.}

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Notes

The authors declare no competing financial interest.

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REFERENCES

- Yan, R.; Gargas, D.; Yang, P. Nanowire photonics. *Nat. Photonics* **2009**, *3*, 569–576.
- Ariga, K.; Vinu, A.; Yamauchi, Y.; Ji, Q. M.; Hill, J. P. Nanoarchitectonics for mesoporous materials. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 1–32.
- Zhu, M.; Nie, G.; Meng, H.; Xia, T.; Nel, A.; Zhao, Y. Physicochemical properties determine nanomaterial cellular uptake, transport, and fate. *Acc. Chem. Res.* **2013**, *46*, 622–631.
- Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Carbon nanomaterials for electronics, optoelectronics, photovoltaics, and sensing. *Chem. Soc. Rev.* **2013**, *42*, 2824–2860.
- Kumar, S.; Daverey, A.; Sahu, N. K.; Bahadur, D. In vitro evaluation of PEGylated mesoporous MgFe₂O₄ magnetic nano-assemblies (MMNs) for chemo-thermal therapy. *J. Mater. Chem. B* **2013**, *1*, 3652–3660.
- Shields, A. J. Semiconductor quantum light sources. *Nat. Photonics* **2007**, *1*, 215–223.
- Jüstel, T.; Nikol, H.; Ronda, C. New developments in the field of luminescent materials for lighting and displays. *Angew. Chem., Int. Ed.* **1998**, *37*, 3085–3103.

- (8) Gautam, A.; van Veggel, F. C. J. M. Blue electroluminescence from Eu²⁺-doped GaN@SiO₂ nanostructures tuned to industrial standards. *Chem. Mater.* **2011**, *23*, 4817–4823.
- (9) Singh, N. S.; Sahu, N. K.; Bahadur, D. Multicolor tuning and white light emission from lanthanide doped YPVO₄ nanorods: energy transfer studies. *J. Mater. Chem. C* **2014**, *2*, 548–555.
- (10) Park, J. Y.; Baek, M. J.; Choi, E. S.; Woo, S.; Kim, J. H.; Kim, T. J.; Jung, J. C.; Chae, K. S.; Chang, Y.; Lee, G. H. Paramagnetic ultrasmall gadolinium oxide nanoparticles as advanced *T*₁ MRI contrast agent: account for large longitudinal relaxivity, optimal particle diameter, and *in vivo* *T*₁ MR images. *ACS Nano* **2009**, *3*, 3663–3669.
- (11) Wang, G.; Peng, Q.; Li, Y. Lanthanide-doped nanocrystals: synthesis, optical-magnetic properties, and applications. *Acc. Chem. Res.* **2011**, *44*, 322–332.
- (12) Escribano, P.; Julián-López, B.; Planelles-Aragó, J.; Cordoncillo, E.; Vian, B.; Sanchez, C. Photonic and nanobiophotonic properties of luminescent lanthanide-doped hybrid organic-inorganic materials. *J. Mater. Chem.* **2008**, *18*, 23–40.
- (13) Xu, L.; Dong, B.; Wang, Y.; Bai, X.; Chen, J.; Liu, Q.; Song, H. Porous In₂O₃:RE (RE = Gd, Tb, Dy, Ho, Er, Tm, Yb) nanotubes: electrospinning preparation and room gas-sensing properties. *J. Phys. Chem. C* **2010**, *114*, 9089–9095.
- (14) Zhang, F.; Wong, S. S. Ambient large-scale template-mediated synthesis of high-aspect ratio single-crystalline, chemically doped rare-earth phosphate nanowires for bioimaging. *ACS Nano* **2010**, *4*, 99–112.
- (15) Petoral, R. M., Jr.; Söderlind, F.; Klasson, A.; Suska, A.; Fortin, M. A.; Abrikossova, N.; Selegård, L.; Käll, P.-O.; Engström, M.; Uvdal, K. Synthesis and characterization of Tb³⁺-doped Gd₂O₃ nanocrystals: a bifunctional material with combined fluorescent labeling and MRI contrast agent properties. *J. Phys. Chem. C* **2009**, *113*, 6913–6920.
- (16) Rodriguez-Liviano, S.; Becerro, A. I.; Alcántara, D.; Grazú, V.; de la Fuente, J. M.; Ocaña, M. Synthesis and properties of multifunctional tetragonal Eu:GdPO₄ nanocubes for optical and magnetic resonance imaging applications. *Inorg. Chem.* **2013**, *52*, 647–654.
- (17) Singh, N. S.; Kulkarni, H.; Pradhan, L.; Bahadur, D. A multifunctional biphasic suspension of mesoporous silica encapsulated with YVO₄:Eu³⁺ and Fe₃O₄ nanoparticles: synergistic effect towards cancer therapy and imaging. *Nanotechnology* **2013**, *24*, 065101 (1–11).
- (18) Wang, F.; Wang, J.; Liu, X. Direct evidence of a surface quenching effect on size-dependent luminescence of upconversion nanoparticles. *Angew. Chem., Int. Ed.* **2010**, *49*, 7456–7460.
- (19) Sahu, N. K.; Ningthoujam, R. S.; Bahadur, D. Disappearance and recovery of luminescence in GdPO₄:Eu³⁺ nanorods: propose to water/OH⁻ release under near infrared and gamma irradiations. *J. Appl. Phys.* **2012**, *112*, 014306 (1–12).
- (20) Boyer, J. C.; Manseau, M. P.; Murray, J. I.; van Veggel, F. C. J. M. Surface modification of upconverting NaYF₄ nanoparticles with PEG-phosphate ligands for NIR (800 nm) biolabeling within the biological window. *Langmuir* **2010**, *26*, 1157–1164.
- (21) Yin, A.; Zhang, Y.; Sun, L.; Yan, C. Colloidal synthesis and blue based multicolor upconversion emissions of size and composition controlled monodisperse hexagonal NaYF₄: Yb,Tm nanocrystals. *Nanoscale* **2010**, *2*, 953–959.
- (22) Huignard, A.; Buissette, V.; Franville, A.-C.; Gacoin, T.; Boilot, J.-P. Emission processes in YVO₄:Eu nanoparticles. *J. Phys. Chem. B* **2003**, *107*, 6754–6759.
- (23) Bai, X.; Song, H.; Pan, G.; Liu, Z.; Lu, S.; Di, W.; Ren, X.; Lei, Y.; Dai, Q.; Fan, L. Luminescent enhancement in europium-doped yttria nanotubes coated with yttria. *Appl. Phys. Lett.* **2006**, *88*, 143104 (1–3).
- (24) Loitongbam, R. S.; Singh, N. S.; Singh, W. R.; Ningthoujam, R. S. Observation of exceptional strong emission transitions ³D_j (*j* = 1–3) to ⁷F_j (*j* = 1–3): multicolor from single Eu³⁺ ion doped La₂O₃ nanoparticles. *J. Lumin.* **2013**, *134*, 14–23.
- (25) Vetrone, F.; Naccache, R.; Mahalingam, V.; Morgan, C. G.; Capobianco, J. A. The active-core/active-shell approach: a strategy to enhance the upconversion luminescence in lanthanide-doped nanoparticles. *Adv. Funct. Mater.* **2009**, *19*, 2924–2929.
- (26) Singh, N. S.; Ningthoujam, R. S.; Phaomei, G.; Singh, S. D.; Vinu, A.; Vatsa, R. K. Re-dispersion and film formation of GdVO₄: Ln³⁺ (Ln³⁺ = Dy³⁺, Eu³⁺, Sm³⁺, Tm³⁺) nanoparticles: particle size and luminescence studies. *Dalton Trans.* **2012**, *41*, 4404–4412.
- (27) Luwang, M. N.; Ningthoujam, R. S.; Jagannath; Srivastava, S. K.; Vatsa, R. K. Effects of Ce³⁺ codoping and annealing on phase transformation and luminescence of Eu³⁺-Doped YPO₄ nanorods: D₂O solvent effect. *J. Am. Chem. Soc.* **2010**, *132*, 2759–2768.
- (28) Yang, M.; You, H.; Liu, K.; Zheng, Y.; Guo, N.; Zhang, H. Low-temperature coprecipitation synthesis and luminescent properties of LaPO₄:Ln³⁺ (Ln³⁺ = Ce³⁺, Tb³⁺) nanowires and LaPO₄:Ce³⁺, Tb³⁺/LaPO₄ core/shell nanowires. *Inorg. Chem.* **2010**, *49*, 4996–5002.
- (29) Wu, C.-C.; Chen, K.-B.; Lee, C.-S.; Chen, T.-M.; Cheng, B.-M. Synthesis and VUV photoluminescence characterization of (Y,Gd)-(V,P)O₄:Eu³⁺ as a potential red-emitting PDP phosphor. *Chem. Mater.* **2007**, *19*, 3278–3285.
- (30) Parchur, A. K.; Ningthoujam, R. S. Preparation and structure refinement of Eu³⁺ doped CaMoO₄ nanoparticles. *Dalton Trans.* **2011**, *40*, 7590–7594.
- (31) Lisiecki, R.; Solarz, P.; Dominiak-Dzik, G.; Ryba-Romanowski, W.; Sobczyk, M.; Cerny, P.; Sulc, J.; Jelinkova, H.; Urata, Y.; Higuchi, M. Comparative optical study of thulium-doped YVO₄, GdVO₄, and LuVO₄ single crystals. *Phys. Rev. B* **2006**, *74*, 035103 (1–14).
- (32) Chen, D.; Yu, Y.; Huang, P.; Lin, H.; Shan, Z.; Zeng, L.; Yang, A.; Wang, Y. Color-tunable luminescence for Bi³⁺/Ln³⁺:YVO₄ (Ln = Eu, Sm, Dy, Ho) nanophosphors excitable by near-ultraviolet light. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7775–7778.
- (33) Singh, N. S.; Ningthoujam, R. S.; Luwang, M. N.; Singh, S. D.; Vatsa, R. K. Luminescence, lifetime and quantum yield studies of YVO₄:Ln³⁺ (Ln³⁺ = Dy³⁺, Eu³⁺) nanoparticles: concentration and annealing effects. *Chem. Phys. Lett.* **2009**, *480*, 237–242.
- (34) Ren, W.; Tian, G.; Zhou, L.; Yin, W.; Yan, L.; Jin, S.; Zu, Y.; Li, S.; Gu, Z.; Zhao, Y. Lanthanide ion-doped GdPO₄ nanorods with dual-modal bio-optical and magnetic resonance imaging properties. *Nanoscale* **2012**, *4*, 3754–3760.
- (35) Phaomei, G.; Ningthoujam, R. S.; Singh, W. R.; Loitongbam, R. S.; Singh, N. S.; Rath, A.; Juluri, R. R.; Vatsa, R. K. Luminescence switching behavior through redox reaction in Ce³⁺ co-doped LaPO₄:Tb³⁺ nanorods: re-dispersible and polymer film. *Dalton Trans.* **2011**, *40*, 11571–11580.
- (36) Wang, L.; Zhou, C. L.; Chen, H. Q.; Chen, J. G.; Fu, J.; Ling, B. Determination of formaldehyde in aqueous solutions by a novel fluorescence energy transfer system. *Analyst* **2010**, *135*, 2139–2143.
- (37) Caravan, P.; Ellison, J. J.; McMurry, T. J.; Lauffer, R. B. Gadolinium(III) chelates as MRI contrast agents: structure, dynamics, and applications. *Chem. Rev.* **1999**, *99*, 2293–2352.
- (38) Johnson, N. J. J.; Oakden, W.; Stanisz, G. J.; Prosser, R. S.; van Veggel, F. C. J. M. Size-tunable, ultrasmall NaGdF₄ nanoparticles: insights into their T₁ MRI contrast enhancement. *Chem. Mater.* **2011**, *23*, 3714–3722.
- (39) Cheung, E. N. M.; Alvares, R. D. A.; Oakden, W.; Chaudhary, R.; Hill, M. L.; Pichaandi, J.; Mo, G. C. H.; Yip, C.; Macdonald, P. M.; Stanisz, G. J.; van Veggel, F. C. J. M.; Prosser, R. S. Polymer-stabilized lanthanide fluoride nanoparticle aggregates as contrast agents for magnetic resonance imaging and computed tomography. *Chem. Mater.* **2010**, *22*, 4728–4739.
- (40) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. A* **1976**, *32*, 751–767.
- (41) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, USA, 1986.
- (42) Sudhakar, N.; Ningthoujam, R. S.; Rajeev, K. P.; Nigam, A. K.; Weissmüller, J.; Gajbhiye, N. S. Effect of La, B doping on the electrical resistivity and magnetic susceptibility of nanocrystalline vanadium nitride. *J. Appl. Phys.* **2004**, *96*, 688–695.

- (43) Ningthoujam, R. S. *Enhancement of Photoluminescence by Rare Earth Ions Doping in Semiconductor Inorganic*; Rai, S. B., Dwivedi, Y., Eds.; Nova Science Publishers Inc.: USA, 2012.
- (44) Dexter, D. L. A theory of sensitized luminescence in solids. *J. Chem. Phys.* **1953**, *21*, 836–850.
- (45) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum Publishers: New York, 1999; p 131.
- (46) Yaiphaba, N.; Ningthoujam, R. S.; Singh, N. R.; Vatsa, R. K. Luminescence properties of redispersible Tb^{3+} -doped GdPO_4 nanoparticles prepared by an ethylene glycol route. *Eur. J. Inorg. Chem.* **2010**, *18*, 2682–2687.
- (47) Xia, Z. G.; Liu, R. S. Tunable blue-green color emission and energy transfer of $\text{Ca}_2\text{Al}_3\text{O}_6\text{F:Ce}^{3+},\text{Tb}^{3+}$ phosphors for near-UV white LEDs. *J. Phys. Chem. C* **2012**, *116*, 15604–15609.
- (48) Kitsuda, M.; Fujihara, S. Quantitative luminescence switching in $\text{CePO}_4:\text{Tb}$ by redox reactions. *J. Phys. Chem. C* **2011**, *115*, 8808–8815.
- (49) Melhuish, W. H. Modified technique for determining the wavelength-sensitivity curve of a spectrofluorimeter. *Appl. Opt.* **1975**, *14*, 26–27.