

Photon Upconversion Through Tb³⁺-Mediated Interfacial Energy Transfer

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Substantial attention has been given to photon upconversion of lanthanide-doped nanoparticles in recent years due to their important potential applications in solid-state lasing, optical data storage, display, photovoltaics, and biological imaging.^[1] Photon upconversion via lanthanide ions is a nonlinear optical phenomenon, characterized by photon emission at short wavelengths when irradiated at long wavelengths.^[2] For these nanoparticles, upconverted emission bands spanning from ultraviolet to near-infrared spectral regions are readily accessible using infrared laser excitations.^[3] Notably, the photon upconversion mechanisms involved are mainly attributed to energy transfer upconversion and excited-state absorption,^[2a] as dominated in Yb³⁺/Er³⁺-coupled systems.^[2c] Recently, photon upconversion from a collection of lanthanide ions (e.g., Eu³⁺), which are insensitive to the infrared excitation sources, has been realized by a core-shell structure design in combination with energy migration,^[4a,b] or through a dimerized sensitizer (e.g., Yb³⁺-Mn²⁺).^[4c] However, such photon upconversion process needs the assistance of energy migratory Gd³⁺ sublattices or requires transition metal-coupled sensitizers, making it highly dependent on host materials. The five-photon upconversion process through the Yb³⁺/Tm³⁺ couple, by which the excitation energy needs to be transferred to the migrator, also poses a fundamental limitation because it requires a relatively high pump power density for an efficient energy management.

In this work, we report photon upconversion in core-shell nanocrystals through Tb³⁺-mediated interfacial energy transfer, which occurs directly from the donor Tb³⁺ in the core structure to the activator in the shell layer (Figure 1a). In our design, the conventional gadolinium host lattice is not required. We choose Tb³⁺ as the energy donor to couple with Yb³⁺ because intense two-photon upconversion emission of Tb³⁺ from ⁵D₄ → ⁷F_J (J = 0–6) transitions can be realized under 980 nm excitation as a result of cooperative sensitization upconversion

(Figures S1–S5, Supporting Information).^[5] We use Eu³⁺ as the emitter because it is known as a suitable energy acceptor to yield visible emission in Tb³⁺/Eu³⁺ codoped systems (Figure S6, Supporting Information).^[6] Optically inactive hexagonal phase NaYF₄ is used as the shell layer by virtue of its advantage in providing a host matrix with low-phonon-energy for lanthanide doping as well as its ease in chemical synthesis.^[7] A core-shell architecture is employed to spatially separate the energy donor and emitter lanthanide ions in the core and shell region, respectively,^[8] thereby enabling to minimize nonradiative decays due to energy transfer (Figure S6a, Supporting Information).^[4,6]

In a typical experiment, we first prepared hexagonal phase NaYbF₄:Tb (30 mol%) core nanocrystals, followed by shell coating with NaYF₄:Eu (30 mol%) via a coprecipitation method (Figure 1b and Figure S7, Supporting Information). Under 980 nm excitation, the resulting NaYbF₄:Tb@NaYF₄:Eu nanoparticles exhibited emissions at 590, 615, and 696 nm, corresponding to ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, and ⁵D₀ → ⁷F₄ optical transition of Eu³⁺, respectively (Figure 1c). The decay curve of Tb³⁺ at its ⁵D₄ state, measured by monitoring the emission at 546 nm, also showed a decrease in lifetime after Eu³⁺ doping in the shell layer (Figure S8, Supporting Information). In contrast, in the absence of Tb³⁺ in core the emission intensity of Eu³⁺ was markedly reduced (Figure S9a, Supporting Information), indicating the dominant pathway of interfacial energy transfer from Tb³⁺ to Eu³⁺ (Figure S10, Supporting Information). Importantly, the Eu³⁺ emission obtained in this way is much higher than a direct activation of Eu³⁺ through Yb³⁺ (Figure S9b, Supporting Information). With increasing Eu³⁺ content in the shell, the emission color can be tuned from green to yellow (Figure 1d and Figure S11, Supporting Information). Such Tb³⁺-mediated upconversion for Nd³⁺ activator was also observed in NaYbF₄:Tb@NaYF₄:Nd core-shell nanoparticles, as evident by characteristic Nd³⁺ emission recorded at 864 nm (due to ⁴F_{3/2} → ⁴I_{9/2} transition) under 980 nm excitation (Figure 1c and Figure S12, Supporting Information).^[3g] In contrast to Gd³⁺-based counterpart,^[4a,b] the present Tb³⁺ system shows a much lower dependence on excitation power benefiting from the two-photon upconversion process.^[5] It also holds advantage in obtaining stable yellow-color or intense near-infrared emission, especially at low pump powers (Figure S13, Supporting Information).

For a given energy transfer between a couple of lanthanide ions, it depends sensitively on the donor-acceptor separation.^[9] For example, the energy transfer rate is proportional to r^{-6} (where r is the average donor-acceptor separation) within the dipole-dipole interaction.^[9a] We can predict that the energy transfer from Tb³⁺ to Eu³⁺ at the core/shell interface should be spatially confined in a narrow region. This means that, for

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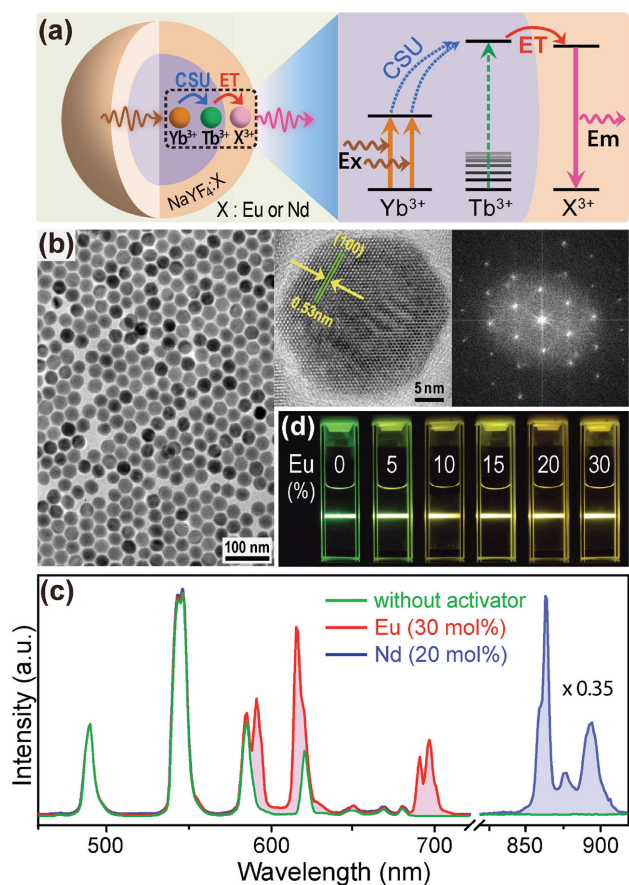


Figure 1. a) Proposed upconversion mechanism through Tb³⁺-mediated interfacial energy transfer in NaYbF₄:Tb@NaYF₄:X (X: Eu or Nd) core-shell structures. The infrared excitation energy is initially absorbed by Yb³⁺ and then transferred to Tb³⁺ by cooperative sensitization upconversion (CSU), followed by energy transfer (ET) to X³⁺ doped in the shell layer. b) Representative TEM image (left), high-resolution TEM image (middle), and corresponding Fourier transform diffraction pattern (right) of the as-synthesized NaYbF₄:Tb(30 mol%)@NaYF₄:Eu(30 mol%) nanoparticles. c) Upconversion emission spectra of NaYbF₄:Tb@NaYF₄ and NaYbF₄:Tb@NaYF₄:X (X: Eu or Nd) nanoparticles under 980 nm excitation. Note that the emission spectra are normalized to Tb³⁺ 546 nm emission. d) Emission photographs of NaYbF₄:Tb@NaYF₄:Eu_x (x = 0–30 mol%) nanocrystals.

a sizeable shell layer, the Eu³⁺ ions away from the interfacial region may not be activated by the Tb³⁺ in the core, as illustrated in **Figure 2a** (Scheme A). In our work, the shell thickness is typically fixed at around 4.5 nm, thick enough to prohibit an efficient energy transfer across the shell layer.^[4b] To validate our hypothesis, we synthesized trilayer nanoparticles of NaYbF₄:Tb@NaYF₄:Eu@NaYF₄ and NaYbF₄:Tb@NaYF₄@NaYF₄:Eu with different interlayer thickness *d* (*d* = 0, 0.6, 1.5, and 4.5 nm) as shown in **Figure 2a** (Schemes B and C) and **Figure 2b**. It was found that the emission intensity of Eu³⁺ increases with *d* for sample B (**Figure 2c**), and an emission profile similar to common NaYbF₄:Tb@NaYF₄:Eu nanoparticles was obtained when *d* reaches 1.5 nm. In contrast, sample C shows a dramatic decrease in emission intensity of Eu³⁺ with *d* (**Figure 2d**), indicating that the interfacial energy transfer is easily prohibited by growing an optically inert NaYF₄ interlayer.

These results confirmed that the Tb³⁺-mediated upconversion occurs spatially in a narrow core/shell interfacial region. More importantly, it can be concluded that the emission of Eu³⁺ in NaYbF₄:Tb@NaYF₄:Eu nanoparticles mainly originates from Eu³⁺ ions located within the 1.5 nm thick shell. When the NaYF₄ outer shell as shown in Scheme B was not adopted, we did observe a notable quenching in Eu³⁺ emission (**Figure S14**, Supporting Information). This result implies that the 4.5 nm thick shell layer of common NaYbF₄:Tb@NaYF₄:Eu nanoparticles can protect the Eu³⁺ ions contributing to photon upconversion.

Apart from the long lifetime of Tb³⁺ at its ⁵D₄ state (2.75 ms), its decay curves show single exponential (**Figure S8**, Supporting Information), indicating that all Tb³⁺ ions may have an equal probability of access to exciting the Eu³⁺ ions. Considering this effect and the weak concentration quenching effect (e.g., up to 30 mol%, **Figure S4**, Supporting Information), the energy migration through Tb³⁺ lattice at the ⁵D₄ state could help facilitate the upconversion process. To confirm the occurrence of energy migration among Tb³⁺ lattice, we designed a core-shell nanoparticle with Tb³⁺-constituted shell host (i.e., NaYbF₄:Tb@NaTbF₄:Eu). The spectral power results (**Figure 3a**) show a slight increase in Eu³⁺ emission as compared to the common NaYbF₄:Tb@NaYF₄:Eu nanoparticle (**Figure S15**, Supporting Information). This result indicates that the excitation energy transferred to the Tb³⁺ ions in the shell layer is able to migrate over a relatively long distance. As a result, additional Eu³⁺ ions located farther away from the interface can be activated. It should be noted that only the shell host matrix (NaTbF₄:Eu or NaYF₄:Eu) is changed during this process, and the effect of energy migration among Eu³⁺ ions can be excluded because of its identical concentration in the two shells (**Figure S16**, Supporting Information).^[6d]

To further study the energy migration among Tb³⁺ ions, we designed NaYbF₄:Tb@NaYF₄:Tb@NaYF₄:Eu core-shell-shell nanocrystals with Tb³⁺ doped in the 4.5 nm thick intermediate shell layer (**Figure S17**, Supporting Information). These nanoparticles exhibited characteristic emission of Eu³⁺ (**Figure 3b** and **Figure S17b**, Supporting Information), clearly confirming the occurrence of energy migration through Tb³⁺ ions at both the core/innershell interface and within the Tb³⁺-doped inner shell layer (**Figure 3c**). By comparison, no Eu³⁺ emission is recorded when an optically inert NaYF₄ inner shell layer is used (**Figure 3b**). Critically, from **Figure 3b** we observed a notable enhancement of Eu³⁺ emission in NaYbF₄:Tb@NaTbF₄@NaYF₄:Eu structure as opposed to NaYbF₄:Tb@NaYF₄:Eu and NaYbF₄:Tb@NaTbF₄:Eu structures. A high density of Tb³⁺ at the interfacial region could greatly reduce the donor-acceptor separation and thereby remarkably improve the energy transfer,^[9] as evident by the enhanced Eu³⁺ emission with increasing the Tb³⁺ content in the inner shell layer (**Figure 3d** and **Figure S17b**, Supporting Information). Taken together, these results indicate that, in addition to Gd³⁺, Tb³⁺ can act as an excellent energy migrator in promoting photon upconversion.

It is worth noting that the use of NaYbF₄:Tb as the core for the synthesis of NaYbF₄:Tb@NaYF₄:Eu core-shell nanoparticles is due to the intense emission nature of Tb³⁺ in response to 980 nm excitation. However, in a sample with lower Yb³⁺

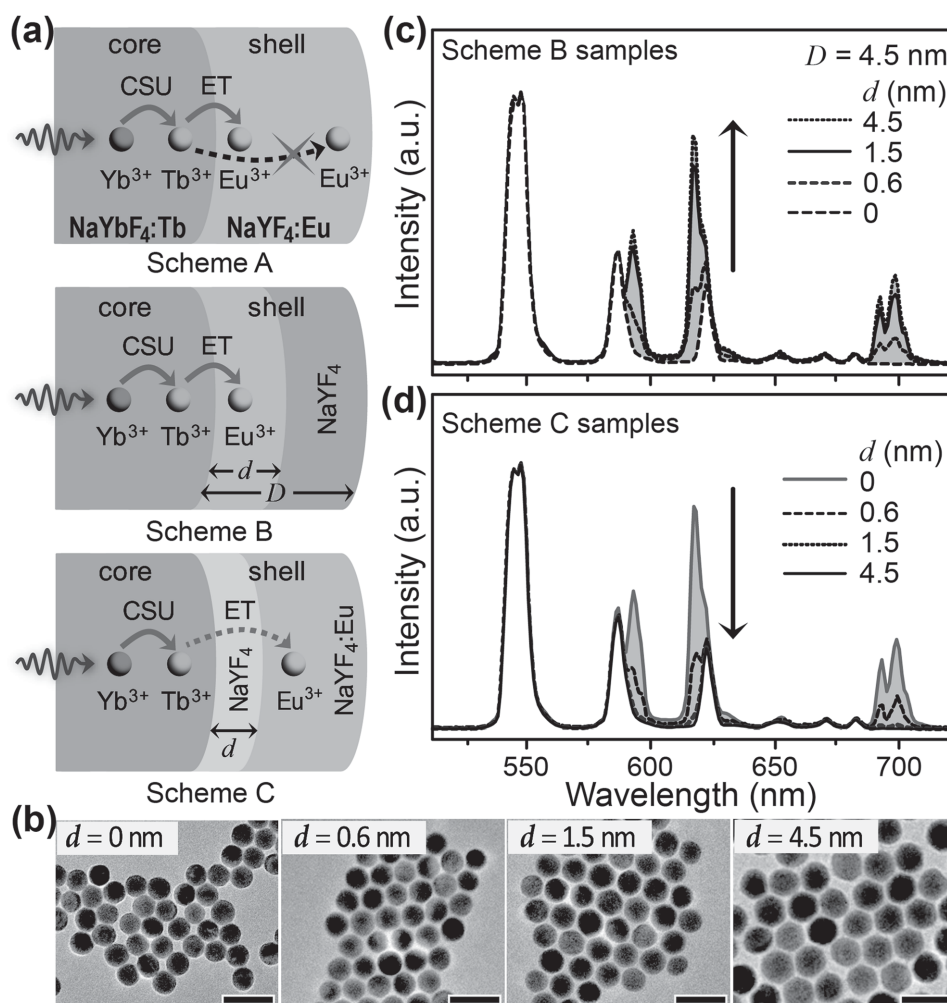


Figure 2. a) Mechanistic investigations of interfacial energy transfer from Tb³⁺ to NaYF₄:Eu (30 mol%) single-shell layer (Scheme A), and to NaYF₄:Eu (30 mol%)-NaYF₄ (Scheme B) or NaYF₄-NaYF₄:Eu (30 mol%) (Scheme C) double-shell layer. b) TEM images of the NaYbF₄:Tb core samples coated with different inner layer thickness of NaYF₄:Eu ($d = 0, 0.6, 1.5, 4.5$ nm). The scale bars are 50 nm. c) Upconversion emission spectra of NaYbF₄:Tb@NaYF₄:Eu@NaYF₄ nanoparticles with different thickness of NaYF₄:Eu inner shell layer ($d : 0-4.5$ nm). The total shell thickness (D) of NaYF₄:Eu and NaYF₄ layers is kept at 4.5 nm for all samples. When d reaches 4.5 nm, we obtained the NaYbF₄:Tb@NaYF₄:Eu core-shell sample. d) Upconversion emission spectra obtained from NaYbF₄:Tb@NaYF₄@NaYF₄:Eu nanoparticles with an optically inert NaYF₄ interlayer ($d : 0-4.5$ nm). Note that the emission spectra in (c) and (d) are normalized to Tb³⁺ 546 nm emission.

content in the core, for example, NaYF₄:Yb/Tb(20/30 mol%), intense Eu³⁺ emission was also observed upon coating of the NaYF₄:Eu shell layer (Figure S18, Supporting Information). This result suggests that the Tb³⁺-mediated upconversion depends less on the choice of the host matrix, showing potential to be applicable to other nanocrystal systems.

As an added benefit, our work shows that it is feasible to activate Tb³⁺ ions by energy migration through use of Gd³⁺ ions in a core-shell structure design.^[4a,b] The combination of Tb³⁺ and Gd³⁺ ions in a nanocrystal may offer an intriguing route toward dual-migrator systems. As a proof of principle, we designed and synthesized a core-shell-shell nanoparticle sample in form of NaGdF₄:Yb/Tm@NaGdF₄:Tb@NaYF₄:Eu containing both Gd³⁺ and Tb³⁺ migrators in the inner shell layer (Figure 4a,b), in which intense Eu³⁺ emission was observed on 980 nm excitation (Figure 4c). To confirm the pathway of energy migration,

we further synthesized a control sample with a thin layer of NaTbF₄ between the inner NaGdF₄:Tb and outer NaYF₄:Eu shell layers. In this sample, Eu³⁺ emission was observed and the lifetime of Tb³⁺ at its ⁵D₄ state decreased after addition of Eu³⁺ in the outer NaYF₄ layer (Figure 4c and Figure S19, Supporting Information). When Gd³⁺ ions in the core and inner-shell layers were replaced with optically inert Y³⁺ ions (i.e., NaYF₄:Yb/Tm@NaYF₄:Tb@NaYF₄:Eu), we did not observe any emission of Eu³⁺ or Tb³⁺ (Figure S19b, Supporting Information). These results confirm the role of dual-migratory Gd³⁺/Tb³⁺ system for activation of Eu³⁺ ions (Figure 4d).

In conclusion, we have demonstrated a new type of upconversion process in core-shell structure nanocrystals by taking advantage of Tb³⁺-mediated interfacial energy transfer. The cooperative sensitization occurring in Yb³⁺/Tb³⁺ codoped systems is shown to be an efficient approach to activating

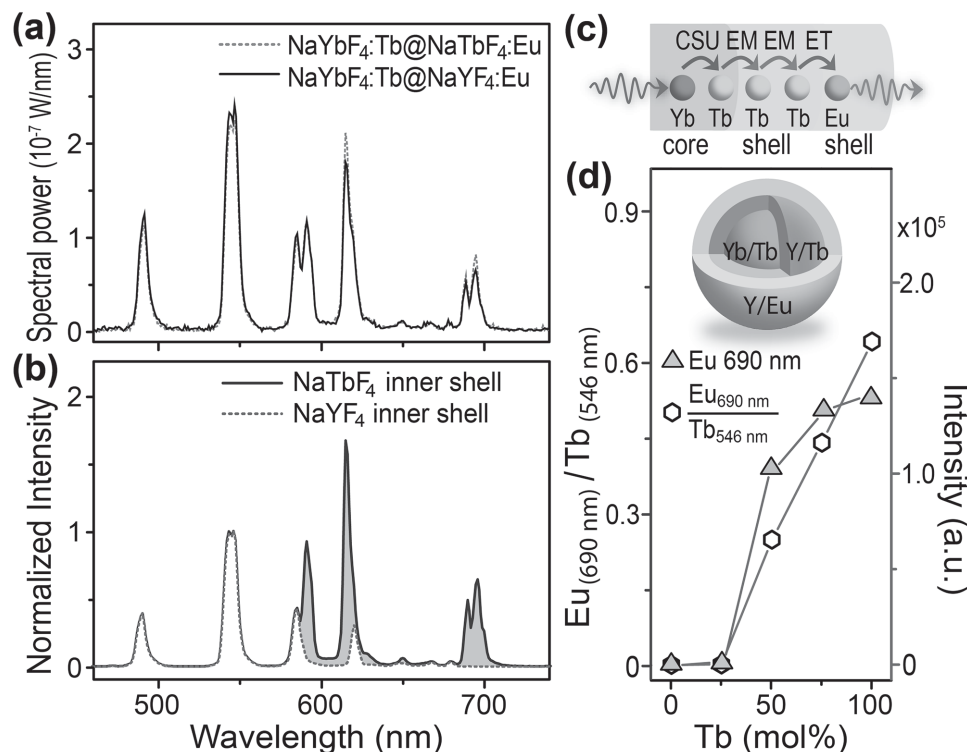


Figure 3. a) Spectral power distribution of upconversion luminescence in NaYbF₄:Tb@NaTbF₄:Eu and NaYbF₄:Tb@NaYF₄:Eu nanoparticles on 980 nm excitation (46 W cm⁻²). Note that the shell thickness of the two core-shell samples is identical (4.5 nm). b) Upconversion luminescence spectra in NaYbF₄:Tb@NaTbF₄@NaYF₄:Eu and NaYbF₄:Tb@NaYF₄@NaYF₄:Eu nanocrystals. The emission spectra were normalized to the Tb³⁺ emission at 546 nm for comparison. c) Proposed energy migration through Tb³⁺ ions in a core-shell-shell structure. d) Luminescence intensity ratio of Eu³⁺ emission at 696 nm (⁵D₀ → ⁷F₄ transition) to Tb³⁺ emission at 546 nm (⁵D₄ → ⁷F₅ transition) and absolute intensity at 696 nm recorded for NaYbF₄:Tb@NaYF₄:Eu nanoparticles with varied Tb³⁺ content in the inner shell (0, 25, 50, 75, 100 mol%).

Tb³⁺ ions on 980 nm excitation. Importantly, our results indicate that photon upconversion can be enhanced by energy migration via Tb³⁺ lattice, a fascinating optical phenomenon comparable to conventional Gd³⁺-based nanoparticle systems.

More importantly, the observation of energy migration through a dual-migrator (Gd³⁺/Tb³⁺) system may provide a new direction for research into better control of energy transfer at the nanometer length scale.

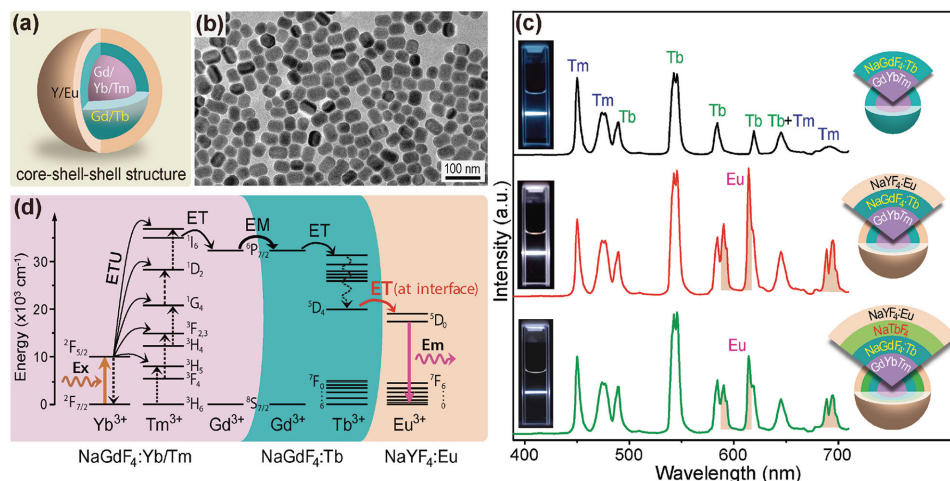


Figure 4. Energy transfer upconversion in core-shell nanocrystals through a dual-migrator (Gd³⁺ and Tb³⁺) system. a) Schematic design and b) TEM image of NaGdF₄:Yb/Tm@NaGdF₄:Tb@NaYF₄:Eu nanocrystals. c) Emission spectra of NaGdF₄:Yb/Tm@NaGdF₄:Tb, NaGdF₄:Yb/Tm@NaGdF₄:Tb@NaYF₄:Eu and NaGdF₄:Yb/Tm@NaGdF₄:Tb@NaTbF₄@NaYF₄:Eu under 980 nm excitation. Insets show the corresponding emission photographs. d) Proposed energy transfer processes responsible for the activation of Eu³⁺ through Gd³⁺- and Tb³⁺-mediated energy migration.

Experimental Section

The experimental details on the preparation of core, core-shell, and multishell nanocrystal samples, their morphology characterization, spectroscopy, lifetime, quantum yield, and spectral power measurements are provided in the Supporting Information.

Supporting Information

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

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