

Magnetic Assembly of Eu-Doped NaYF₄ Nanorods for Field-Responsive Linearly and Circularly Polarized Luminescence

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Cite This: *ACS Nano* 2024, 18, 5122–5131



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ABSTRACT: Colloidal assembly has emerged as an effective avenue for achieving polarized light emission. Here, we showcase the efficacy and versatility of the magnetic colloidal assembly in enabling both linearly and circularly polarized luminescence. Colloidal europium-doped NaYF₄ nanorods with surface-bound Fe₃O₄ nanoparticles are magnetically assembled into linear or chiral superstructures using corresponding fields created in permanent magnets. In a uniform magnetic field generated by opposing poles, the assemblies exhibit photoluminescence with intensity tunable in response to the magnetic field direction, which is higher when the nanorods are perpendicular to light propagation than when they are parallel. The obtained superstructures display strong linearly polarized luminescence when the nanorods are aligned vertically, exhibiting a high degree of polarization up to 0.61. In a quadrupole chiral field generated by permanent magnets, the assemblies emit left-handed or right-handed polarized light depending on the position of the sample placement, attaining a *g*-factor of 0.04. Furthermore, the superstructures immobilized in a hydrogel film are found to retain their chirality, exhibiting opposite chiroptical responses depending on the sample orientation. The magnetic colloidal assembly approach facilitates the convenient and efficient generation of polarized light emissions from nonmagnetic luminescent materials, thus creating opportunities for tailoring light behavior in developing innovative optoelectronic devices.

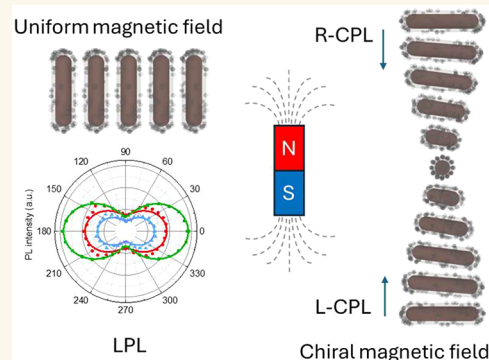
KEYWORDS: self-assembly, magnetic field, chirality, circularly polarized luminescence, linearly polarized luminescence

INTRODUCTION

Light polarization has important applications for display,¹ imaging,² sensing,³ actuation,⁴ and information storage.^{5,6} The polarization state of light can assume various forms—linear, circular, or elliptical—and contribute depending on the direction in which the electric field oscillates. Theoretically, the light emitted by any phosphor contains a certain amount of polarized light, including linearly and circularly polarized light. By assembling the phosphors into a well-aligned orientation or specific configurations, the polarization of emitted light could be greatly magnified.^{7,8} Various self-assembly methods have been reported to transform the unpolarized emission into linear or circular polarization using anisotropic alignment or chirality transfer between chiral templates and luminescent phosphors.^{9,10} For example, lanthanide-doped NaYF₄ upconversion nanorods were aligned on silicon substrates by a shear force-driven method, producing superstructures showing linearly polarized luminescence (LPL) with a high degree of polarization.¹¹ In addition, perovskite- and lanthanide-doped upconversion nanoparticles (NPs) were coassembled with

chiral organic nanotube templates to exhibit circularly polarized luminescence (CPL).^{12,13}

As a nontemplate approach, magnetic assembly has been widely employed for organizing nanoscale building blocks into diverse superstructures with controllable symmetries and phases.^{14–16} It features many advantages, including instantaneous and reversible action, contactless operation, and the directional nature of magnetic interactions.^{1,17–20} Recent studies have further revealed that the magnetic field can be configured as uniform or chiral depending on the spatial arrangement of magnets, enabling the creation of chiral superstructures through the magnetic assembly approach.^{21–23} Applying this approach to luminescent nanostructures is



Received: December 8, 2023

Revised: January 25, 2024

Accepted: January 29, 2024

Published: February 1, 2024



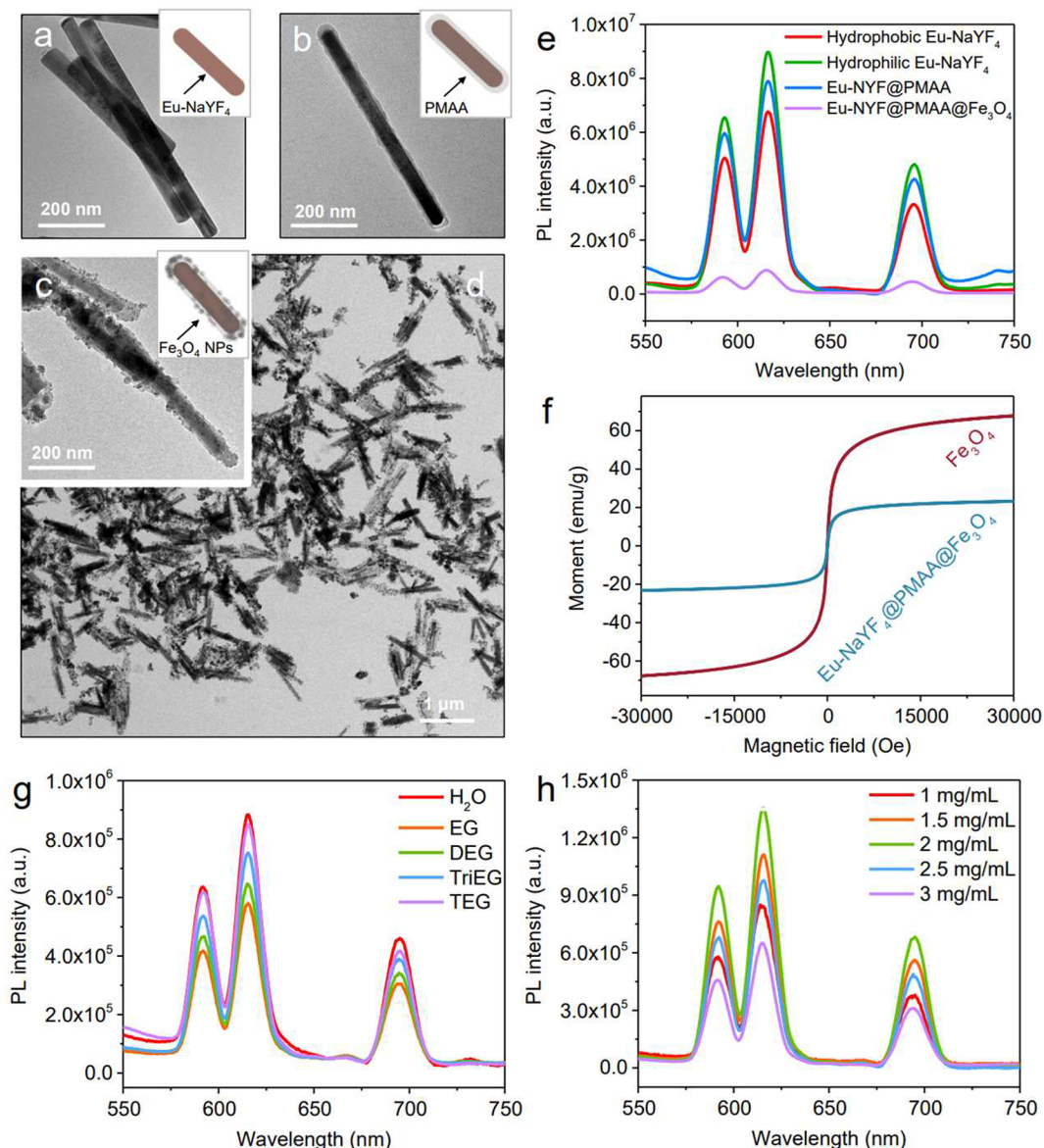


Figure 1. (a–d) TEM images of Eu-NaYF₄ nanorods: (a) after transferring into the aqueous phase by TMAH treatment; (b) after PMAA coating; (c, d) after surface decoration with Fe₃O₄ nanoparticles at different magnifications. (e) PL spectra of Eu-NaYF₄ nanorods throughout the surface treatment process in a concentration of 1 mg/mL. (f) The magnetic hysteresis curve of Fe₃O₄ nanoparticles and Eu-NaYF₄@PMAA@Fe₃O₄ composite nanorods. (g) PL spectra of composite nanorods dispersed in different solvents, with a Eu-NaYF₄ concentration of 1 mg/mL. (h) PL spectra of composite nanorods dispersed in TEG in different concentrations. The insets in (a–c) are schematic illustrations of the corresponding nanostructures.

therefore expected to produce superstructures featuring polarized emission with dynamic tunability offered by the convenient manipulation of the strength and direction of the magnetic field.

In this study, we demonstrate the successful magnetic assembly of inorganic fluorescent nanorods into superstructures capable of producing linearly and circularly polarized luminescence. Lanthanide-doped NaYF₄ was chosen as the fluorescent component due to its high stability, narrow emission band, long emission lifetime, and the capacity for polarization-dependent luminescence enabled by the anisotropic crystalline environment surrounding the emitter.²⁴ It was synthesized in the form of colloidal nanorods, which were then made magnetically responsive by coating their surfaces with a thin layer of Fe₃O₄ nanoparticles. We show that the

fluorescence intensity and polarization properties of the assemblies can be controlled by the direction and chirality of the applied magnetic field, leading to tunable linearly or circularly polarized luminescence. Notably, the degree of polarization reached up to 0.61 for LPL, while the luminescence dissymmetry factor, g_{lum} , attained values of up to 0.04 for CPL. Moreover, we demonstrate that the chiral superstructures can be fixed in hydrogel films to exhibit an unusual chiroptical inversion property upon flipping the samples.

RESULTS AND DISCUSSION

The europium (Eu)-doped NaYF₄ (Eu-NaYF₄) nanorods (NRs) were prepared by a hydrothermal method using oleic acid as a capping ligand,¹¹ featuring a hydrophobic surface and

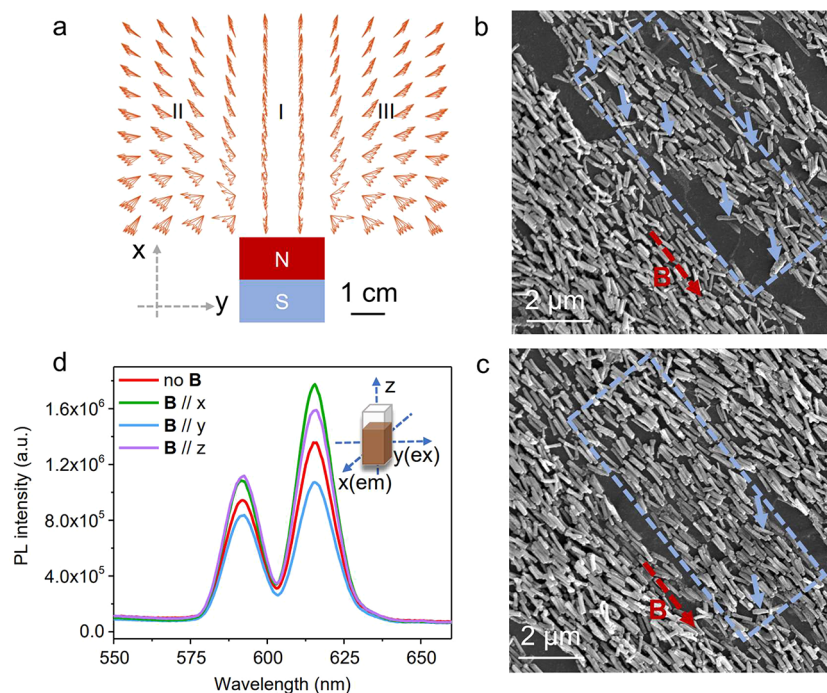


Figure 2. (a) Simulation of the chiral field distribution from a cubic permanent magnet. (b) The alignment of the composite nanorods under a chiral magnetic field. (c) The alignment of the composite nanorods under a uniform magnetic field. (d) PL spectra of composite nanorods (2 mg/mL in TEG) under magnetic fields of different directions or no magnetic field.

an average length of 530 nm and aspect ratio of 10 (Figure 1a). Under optimal excitation at 394 nm, the Eu-NaYF₄ nanorods showed strong photoluminescence (PL) at 591, 614, and 694 nm, corresponding to the energy transition of ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, and ⁵D₀ → ⁷F₄ in Eu³⁺, respectively (Figure S1). The hydrophobic Eu-NaYF₄ NRs were transferred to the aqueous phase by being treated with a commonly used phase transfer agent, tetramethylammonium hydroxide (TMAH), which could replace the original oleic acid ligands.^{25,26} Magnetic Fe₃O₄ NPs with an average size of around 8.7 nm (Figure S2), prepared through co-precipitating the Fe(III) and Fe(II) in the presence of OH⁻,²⁷ were incorporated onto the surface of Eu-NaYF₄ NRs to enable the magnetic response of the composite nanorods to external fields.^{28–33} Poly(methacrylic acid) (PMAA) containing carboxylic groups was used as a coupling agent, first coating the NaYF₄ NRs with a thickness of around 10 nm (Figure 1b) and then binding to Fe₃O₄ NPs through a strong coordination between COO⁻ and Fe(II)/Fe(III).³⁴ After free Fe₃O₄ NPs were removed by repeated centrifugation at a proper speed (see details in the Supporting Information), a thin layer of Fe₃O₄ NPs was retained on the nanorod surface, as shown in Figure 1c. Low-magnification TEM images of Eu-NaYF₄@PMAA and Eu-NaYF₄@PMAA@Fe₃O₄ structures are shown in Figure S3 and Figure 1d, respectively, indicating no serious agglomeration throughout the surface treatment process.

The absorption spectra and PL intensity were monitored throughout the surface treatment and coating process at a Eu-NaYF₄ concentration of 1 mg/mL, as shown in Figure S4a and Figure 1e, respectively. After phase transfer, the PL intensity increased, likely due to both the removal of oleic acid layers on the NaYF₄ nanorod surface, which could inhibit the emission,^{35,36} and the stronger optical absorption (Figure S4a). This is consistent with a recent report on the influence of oleic acid removal on the optical properties of lanthanide-

doped nanocrystals.³⁷ After PMAA coating, the PL intensity slightly decreased due to the absorption of light by the polymer layer. After Fe₃O₄ coating in a thin layer, the PL intensity significantly decreased because of the intensive absorption of visible light by Fe₃O₄ NPs (Figure S4b). The presence of a dense coating of Fe₃O₄ nanoparticles led to a more pronounced reduction in PL intensity, as illustrated in Figure S5. Thanks to the initial strong PL of Eu-NaYF₄, the composite nanorods could emit PL with sufficient intensity for further investigations. Magnetic hysteresis measurements were conducted on Fe₃O₄ nanoparticles and Eu-NaYF₄@PMAA@Fe₃O₄ composite nanorods (Figure 1f). Both samples exhibited S-shaped curves with minimal hysteresis loops, indicating their superparamagnetic nature and confirming their suitability for colloidal assembly under the magnetic field. However, upon exposure to a magnetic field for an extended period, the composite nanorods in the aqueous dispersion eventually aggregate, leading to significant PL quenching (Figure S6).

To bolster the colloidal stability of the assemblies within magnetic fields, we employed polyols as solvents due to their higher viscosities compared with water (Table S1). Indeed, the magnetic separation of the composite nanorods from the dispersion took the longest time in tetraethylene glycol (TEG) due to its highest viscosity among all polyols. Figure 1g evaluates the PL intensities of Eu-NaYF₄@PMAA@Fe₃O₄ nanorods with the concentration of 1 mg/mL of Eu-NaYF₄ in these polyols. Compared with water, the polyol solvents could quench the PL to a certain degree due to abundant OH groups.³⁸ From EG to diethylene glycol (DEG), triethylene glycol (TriEG), and TEG, PL increased largely because of the reduced chelating effect of the two OH groups as the carbon chain elongated.³⁹ Thus, TEG was selected as the solvent in this study due to its minimum PL quenching and highest viscosity.

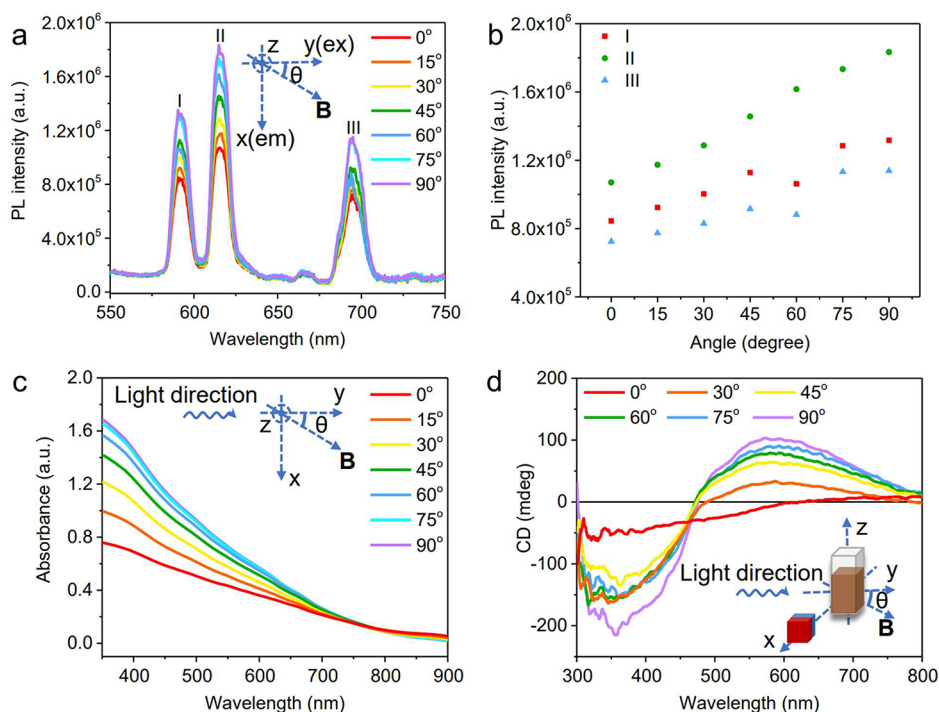


Figure 3. (a) PL spectra of composite nanorods (2 mg/mL in TEG) under magnetic fields of changing directions within the x - y plane. (b) Dependence of PL intensity of peaks (I), (II) and (III) on field direction. (c) Absorption spectra of 1 mg/mL composite nanorods under magnetic fields of changing directions within the x - y plane. (d) CD spectra of the sample under magnetic fields of changing directions within the x - y plane.

We compared PL values at various concentrations of composite nanorods in TEG to ascertain the optimal concentrations, as shown in Figure 1h. The highest PL intensity was obtained at a concentration of around 2 mg/mL Eu-NaYF₄, which resulted from the interplay between Eu-NaYF₄ emission and Fe₃O₄ absorption. While the PL was weak when the phosphor concentration was below 2 mg/mL, a higher nanorod concentration would result in stronger magnetic interactions, consequently accelerating particle agglomeration and leading to PL quenching. Therefore, TEG dispersions of the composite nanorods at 2 mg/mL Eu-NaYF₄ concentrations were chosen for further studies.

It was recently discovered that a cubic permanent magnet can generate a quadrupole chiral magnetic field due to constant field rotation.²³ Figure 2a shows the simulated magnetic field distribution of a cubic magnet, with region I corresponding to a uniform magnetic field and regions II and III exhibiting left-handed and right-handed chirality, respectively. We have recently shown that the chirality of the magnetic field can be transferred to nonmagnetic species by attaching them to magnetic nanoparticles and then assembling the nanocomposites within the field.⁴⁰ As a result, the assembly of composite nanorods in uniform or chiral magnetic fields is expected to produce linear or left-/right-handed chiral superstructures, depending on their spatial location within the field. We assessed the alignment of the composite nanorods under both a chiral (Figure 2b) and a uniform magnetic field (Figure 2c). While most nanorods follow the field direction, there are a small number of unaligned nanorods in both samples, as indicated by the solid arrows. The extent of alignment was estimated to be 0.94 and 0.96 under a chiral and uniform magnetic field, respectively, by quantifying the nanorods aligned parallel to the magnetic field direction and

dividing this count by the total number of nanorods within the marked squares.

The alignment of Eu-NaYF₄@PMAA@Fe₃O₄ composite nanorods in solution could be precisely controlled by tuning the direction of the external magnetic field (Figure S7). We observed simultaneous changes in the PL intensity in response to an external magnetic field. As shown in Figure 2d, in the 90° setup of PL measurement (with the detector at 90° to the excitation source), the PL intensity of the assemblies varied with the magnetic field direction. When the nanorods were aligned parallel to the detector direction (x -axis) or the vertical direction (z -axis), the PL intensity of the assemblies was stronger than that when they were along the excitation direction (y -axis) or in random orientation without the magnetic field.

To investigate this angle-dependent emission behavior, the angle (θ) between the magnetic field direction and the y -axis was delicately changed in the x - y plane from 0° (along y) to 90° (along x). As shown in Figure 3a and Figure 3b, the PL intensity increased gradually when the magnetic field direction changed from 0° to 90°. To explain the angle-dependent PL, absorption spectra were measured in the corresponding magnetic field directions (Figure 3c). It could be seen that the absorbance of the Fe₃O₄-coated Eu-NaYF₄ nanorods increased gradually from 0° to 90°, in a way similar to the PL changes. This orientation-dependent absorption could only be attributed to the anisotropic shape of Eu-NaYF₄ nanorods since the Fe₃O₄ NPs exhibit no angle-dependent absorption, as shown in Figure S8. When the composite nanorods were aligned along the x -axis (perpendicular to the propagation of excitation light), a larger absorption cross section led to stronger absorption and photoluminescence.

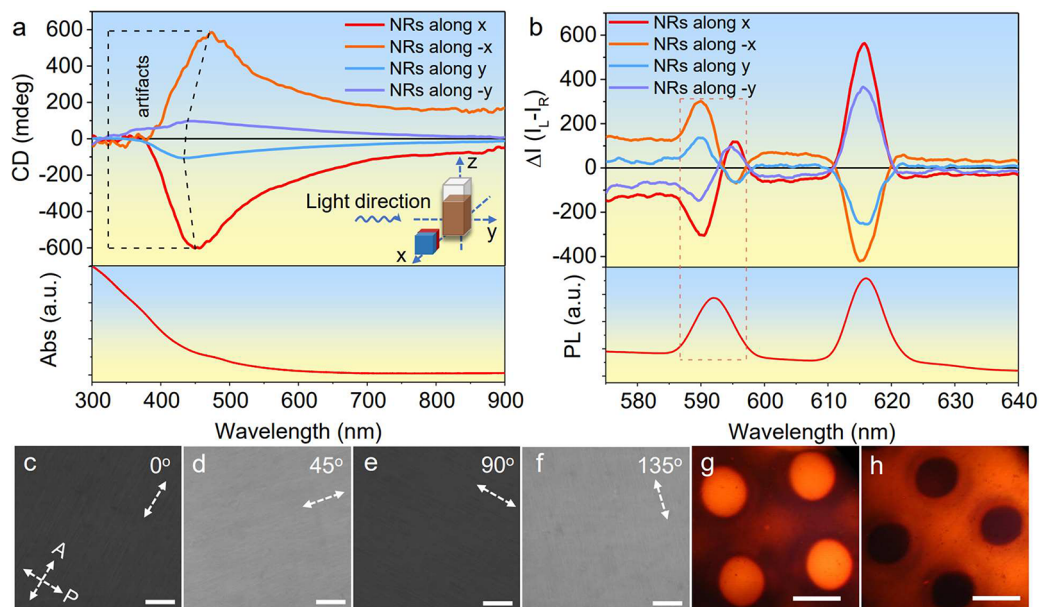


Figure 4. Chiroptical properties of Eu-NaYF₄@PMAA@Fe₃O₄ nanorods magnetically assembled in a hydrogel. The distance between the hydrogel and magnet is 1 cm, creating a magnetic field of 35 mT. (a, b) CD (a) and CPL (b) spectra of the hydrogel measured by flipping the sample. (c–f) Polarized light microscope images of a hydrogel thin film containing the magnetically assembled nanorods observed between a polarizer (P) and analyzer (A) in 90°. The relative orientations between the nanorods and polarizer/analyzer were labeled as dashed lines. (g, h) Polarized light microscope images of a hydrogel thin film with a circle lattice pattern fabricated by the lithography method. The thin films were observed on a rotating sample stage sandwiched between the crossed polarizer and analyzer.

It is worth noting that unlike those with large sizes (usually above 100 nm) and high local concentrations,⁴¹ the Fe₃O₄ NPs in this study did not display observable angle-dependent absorption, likely due to their small sizes (below 10 nm on average) and low concentrations (which were estimated to be below 0.03 mg/mL via Beer's law by subtracting the absorbance of Eu-NaYF₄@PMAA from that of Eu-NaYF₄@PMAA@Fe₃O₄ (Figure S4c)).

When a chiral magnetic field was used, the self-assembly of Eu-NaYF₄@PMAA@Fe₃O₄ nanorods in TEG solution produced a strong circular dichroism (CD) signal due to the formation of chiral superstructures. Furthermore, the CD signal of the assembled superstructures also showed an angular dependence in magnetic fields of different directions. The experimental setup of the CD measurement under different magnetic field directions is shown in Figure S9. As shown in Figure 3d, the CD signal gradually increased when the magnetic field was rotated from 0° to 90°. According to Rosenfeld's theory, the CD chiroptical signal can be expressed by a single parameter R , which is equal to the dot product of electronic transition dipole moment μ and magnetic transition dipole moment \mathbf{m} ($R = \mu \cdot \mathbf{m} = \mu m \cos \varphi$).^{42,43} The rotation of the magnetic field could possibly result in the change of φ , which is the angle between μ and \mathbf{m} since the electron spin could produce an induced magnetic field.

To investigate their chiroptical properties further, we fixed the magnetically assembled chiral nanorod superstructures in a polyacrylamide (PAM) hydrogel through photopolymerization within a cuvette.¹ Consistent with the solution case, a strong CD signal was observed when the nanorods were parallel to the x -axis (perpendicular to light propagation; Figure 4a). Notably, the peak at around 430 nm is caused by an artifact due to detector saturation under this wavelength (Figure S10). Interestingly, the CD signal of the hydrogel turned to an opposite sign but at the same magnitude when the sample was

flipped over by 180° (Figure 4a), indicating an opposite chirality. A similar chiral property was reported in an organic thin film.⁴⁴ According to a recent theoretical study,⁴⁵ such CD inversion phenomenon upon sample flipping could be explained by the linear dichroism (LD) and linear birefringence (LB) effect (LDLB effect, $CD_{\text{obs}} \approx CD + 1/2(LD \cdot LB - LD' \cdot LB')$, in which CD_{obs} represents the observed CD signal and the prime sign means a 45° axis rotation. The sign of the second part of the formula will be reversed if the sample is flipped. When the LDLB effect is dominant in certain circumstances, such as samples with strong linear dichroism and linear birefringence, the sign of the total CD signal could also be inverted by flipping over the samples. Additionally, the hydrogel displayed preferential absorption of either left-handed or right-handed circularly polarized light, contingent on its location within the left-handed or right-handed chiral magnetic field, yielding opposing CD spectra (Figure S11a).

As expected, this photoluminescent hydrogel with chirality exhibited obvious CPL and, more interestingly, inverted CPL when the sample was rotated by 180° (Figure 4b) regardless of whether the nanorods were along the x - or y -axis. The CPL signals with inverted handedness indicate orientation-dependent circularly polarized emission, consistent with a chiral superstructure generated by the magnetic field. Corresponding to the opposite CD signal in Figure S11a, the chiral superstructure immobilized in the magnetic field with the opposite chirality also demonstrated inverted circularly polarized light emission (Figure S11b). It is worthwhile to note that when the nanorods were parallel to the x -axis, stronger CPL was observed with g_{lum} (defined as $2(I_L - I_R)/(I_L + I_R)$) up to 0.04 along the x -axis and 0.01 along the y -axis (Figure S12), consistent with the distinct chirality signals in different directions. Furthermore, from 587 to 597 nm, bisignate signals in the CPL spectra were observed, as labeled by the dashed-square region in Figure 4b. Although a

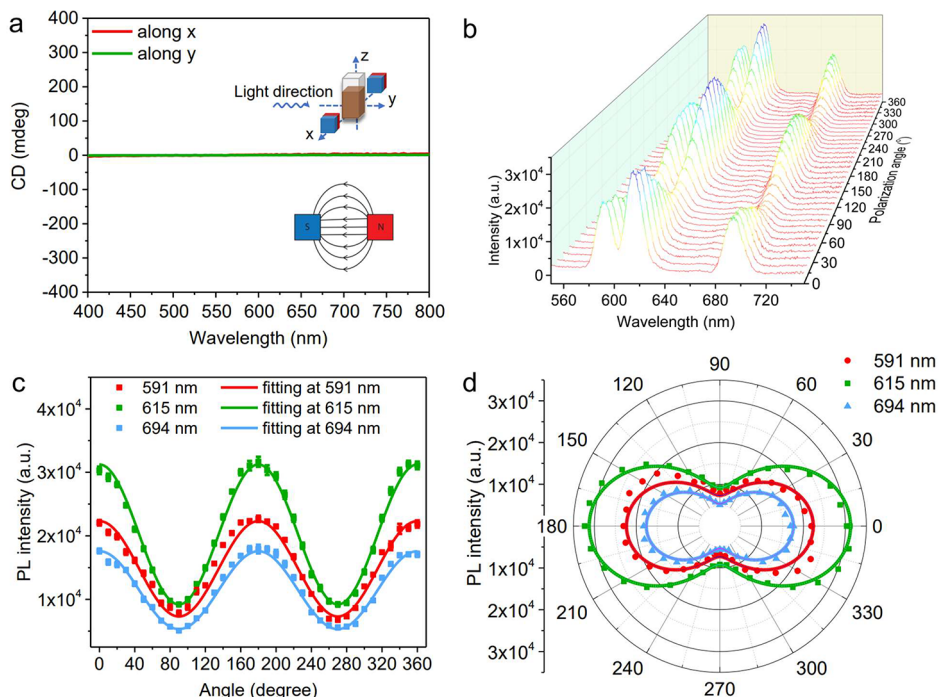


Figure 5. LPL of $\text{Eu-NaYF}_4@PMAA@Fe_3O_4$ nanorods assembled in a linear magnetic field. (a) CD spectra of the superstructures assembled in TEG along the x -axis and y -axis in a uniform magnetic field. (b) PL spectra of the linear superstructures measured at different angles of the analyzer. (c) Change of peak intensity with polarization angle of the superstructures assembled in TEG in a uniform magnetic field. (d) Polar plot of the superstructures assembled in TEG in a uniform magnetic field.

maximum of three transitions should be observed for the crystal field splitting of the $^5D_0 \rightarrow ^7F_1$ transition,^{46,47} only two transitions are resolved at 590 and 595 nm. The intensity of CD and CPL signals was proved to be contingent on the strength of the magnetic field. When a smaller magnet (4 mm) with a weaker intrinsic magnetic field strength (3 mT) was employed, the CD and CPL signals were considerably lower compared to the use of a 1 in. magnet (Figure S13).

Linear dichroism and linear birefringence are believed to play an important role in both the CD and CPL inversion upon sample overturn.⁴⁸ We measured the LD spectra of chiral superstructures assembled in a PAM hydrogel in a cuvette (Figure S14a) and a PAM hydrogel thin film (Figure S14b) based on $LD = A_{\parallel} - A_{\perp}$, where A_{\parallel} and A_{\perp} represent the absorbance when the polarizer is parallel and perpendicular to the orientation of nanorods, respectively.⁴⁹ The LD values of chiral superstructures are significant, albeit slightly smaller than those of linear superstructures.

The significant linear birefringence of nanorod assemblies was studied by aligning them under a chiral magnetic field followed by fixation in a PAM hydrogel thin film (0.5 mm in thickness). The thin film fabrication process was explained in detail in the Supporting Information and schematically illustrated in Figure S15a. Similar nonreciprocal chirality was observed with the hydrogel thin film prepared under a chiral magnetic field. The handedness was found to be opposite when the film was measured from the front and back faces (Figure S16). The hydrogel thin film was observed under a polarized light microscope with two crossed polarizers and a rotating sample stage between them. It was found that the film brightness varied as the rotation angle changed. When the nanorods were 45° or 135° to the polarizer (P)/analyzer (A), the brightness was the highest, indicating the highest light transmission through the film (Figure 4d,f). When the

nanorods were perpendicular or parallel to the polarizer/analyzer (0° or 90°), the brightness became the lowest (Figure 4c,e). A lattice pattern of circles can be incorporated into the chiral hydrogel thin film by using a lithography method (Figure S15b). The nanorods aligned inside and outside the circle areas are in 45° due to the 45-degree rotation of the magnetic field during UV-curing of these regions. Similarly, the circles became bright (nanorods inside the circles are 45° or 135° to the polarizer/analyzer) and dark (nanorods were perpendicular or parallel to the polarizer/analyzer) alternately under the polarized microscope when the film was rotated, as shown in Figure 4g,h. These results are clear evidence of linear birefringence in the chiral hydrogel film,¹⁵ which was sufficiently significant to allow the total CD and CPL inversion with sample reversal.

Since linear birefringence is the difference between its ordinary and extraordinary refractive indices (Δn),⁵⁰ we used the equation $I = I_0 \sin^2(2\alpha) \sin^2(\pi\Delta nL/\lambda)$ to estimate the Δn of thin films observed under a polarizing microscope, where I_0 is the intensity of light passing through the first polarizer; I is the intensity of light passing through the second polarizer; α is the angle between the transmission axes of the polarizer and the long axis of the thin film; L is the sample thickness; λ is the wavelength of incident light; and Δn is the linear birefringence.¹⁵ The linear birefringence of the chiral and linear thin film was estimated to be 0.04 and 0.17, respectively.

To gain a deeper insight into the disparity in chiroptical signals arising from the magnetic assembly in different orientations, we conducted theoretical simulations of the magnetic field distribution on a 1 in. permanent cubic magnet, as illustrated in Figure S17a. Given that the incident light is directed along the y -axis, as shown in Figure 4a for the CD measurement, we compared the magnetic field distribution in the x - z and y - z planes, as depicted in Figures S17b and S17c,

respectively. Our analysis revealed a significant change in the field direction within the x - z plane, while only minimal changes in the field direction were observed in the y - z plane. Therefore, aligning the nanorods along the x -axis as opposed to the y -axis induced a greater rotation in response to the magnetic field, consequently resulting in a higher degree of chirality.²³

The nanorods were aligned in a uniform magnetic field to obtain linear superstructures. Figure 5a shows that the linear superstructures aligned along either the x -axis or y -axis had no CD response due to the unidirectional alignment of the nanorods in the uniform field of opposing magnets (shown in the insets of Figure 5a). Besides, no CPL signal was detected from the linear superstructure (Figure S18). The alignment of nanorods under chiral and uniform magnetic fields was compared through observations of hydrogel thin films using an optical microscope. We can observe twisting or crossing conformations within the chiral superstructure (Figure S19a), whereas the linear superstructure (Figure S19b) exhibits a more uniform alignment. To measure the LPL of the linear superstructure, we aligned the nanorods vertically by changing the magnetic field direction to the z -direction, while the polarization direction of the polarizer was also fixed vertically. By rotating the analyzer on the detection side, the angle between the nanorod c -axis and the electric field vector was changed, thereby allowing LPL measurement (see the setup scheme in Figure S20).⁵¹ Figures 5b and 5c show the PL intensity of the assemblies in TEG solution reached the maximum when the analyzer was parallel to the polarizer as well as the nanorods (0° , 180° , 360° , denoted as I_{VV}) and minimum at perpendicular positions (90° , 270° , denoted as I_{VH}). The solid fitting curves in Figure 5c indicate that the PL intensity changes with polarization angle, in good agreement with the Malus law ($I(\theta) = (I_{VV} - I_{VH}) \cos^2 \theta + I_{VH}$).⁵² The degree of polarization (DOP) calculated as $(I_{VV} - I_{VH}) / (I_{VV} + I_{VH})$ was 0.50 for the peak at 591 nm, 0.54 for the peak at 615 nm, and 0.54 for the peak at 694 nm. A higher DOP up to 0.61 for the peak at 615 nm was obtained by fixing the nanorods in the PAM hydrogel under a uniform magnetic field (Figures S21 and S22a). The values of luminescence anisotropy (R) at different wavelengths calculated from $(I_{VV} - I_{VH}) / (I_{VV} + 2I_{VH})$ are listed in Table S2. Consistent with the DOP, the highest R (0.51) was achieved at 615 nm for the assembly in the PAM hydrogel. The polar plots of the magnetic self-assembly in TEG solution and the PAM hydrogel are illustrated in Figures 5d and S22b, respectively, in which the solid curves represent the fitted PL intensities of the three PL peaks at different analyzer angles. Detailed information related to the LPL of self-assembly in TEG solution and the PAM hydrogel is shown in Table S3. The DOP obtained in our magnetic assemblies was found to be higher than the NaYF₄ nanorods self-assembled using a shear-driven method.¹¹

CONCLUSION

In summary, we showcase the convenience and efficacy of the magnetic assembly approach in creating superstructures displaying CPL and LPL. By decorating the surface of fluorescent Eu-doped NaYF₄ nanorods with Fe₃O₄ nanoparticles, we demonstrate their successful assembly into linear and chiral superstructures in the corresponding fields of cubic permanent magnets. A uniform magnetic field created by two magnets with opposing polarities induces the unidirectional alignment of the nanorods, leading to LPL with a DOP up to

0.61 and, more importantly, a dynamically tunable emission intensity that can be controlled by the magnetic field direction. On the other hand, a quadrupolar chiral magnetic field of a cubic magnet assembles achiral nanorods into superstructures with high chirality, showing a distinct chirality signal depending on the relative spatial arrangement of the nanorods and the light propagation. The chiral superstructures exhibit left- or right-handed CPL with g_{lum} up to 0.04. Furthermore, a hydrogel film containing the as-assembled nanorods features the ability to inverse its chiroptical signals, including both CD and CPL, upon sample flipping, thanks to the significant linear birefringence of the nanorod assemblies. The magnetic assembly approach operates without the need for templates and exhibits versatile applicability across diverse luminescent materials. It enables instant and remote initiation, positioning it as a promising avenue for developing optoelectronic devices that capitalize on the advantages of polarized emission.

METHODS

Eu-NaYF₄ Nanorod (β Phase) Synthesis. The nanorods were prepared by following a hydrothermal process reported previously.⁵³ A typical synthesis started by mixing 700 mg of NaOH with 8 mL of oleic acid and then 12.7 mL of ethanol. The mixture was stirred vigorously for 30 min to obtain a white, viscous colloidal solution, followed by the dropwise addition of an aqueous NaF solution (12.45 mL, 0.58 M) to produce a clear solution. Then, a 1.5 mL aqueous solution containing 80 mol % Y(NO₃)₃·6H₂O and 20 mol % Eu(NO₃)₃·6H₂O (1.2 mmol in total) was added to the system quickly. A white suspension was produced after stirring for 20 min, which was transferred into a 50 mL Teflon-lined autoclave and heated at 230 °C for 12 h. The reaction led to the formation of nanorods, which were collected by centrifugation, cleaned with ethanol three times, and dried in a vacuum oven at 60 °C for 3 h. The as-prepared nanorods were sonicated in a 10% TMAH solution for 30 min to remove the hydrophobic ligands of oleic acid. After that, the nanorods were collected by centrifugation and redispersed in water/ethanol (v:v = 1:1), and the process was repeated another time. Finally, the nanorods were dried in a vacuum oven at 60 °C for 3 h.

Surface Modification with γ -Methacryloxypropyltrimethoxysilane (MPS). A 250 mg amount of ligand-free nanorods was dispersed in 20 mL of ethanol in a round-bottomed flask, into which 5 mL of deionized water, 300 μ L of ammonia solution (30 wt %), and 200 mg of MPS were added in sequence. The mixture was heated to 60 °C and kept at that temperature for 6 h. After that, the nanorods were collected by centrifugation and washed with ethanol and water three times.

PMAA Coating. The PMAA coating was achieved by a precipitation polymerization process.³⁴ The MPS-modified nanorods were dispersed into 20 mL of acetonitrile in a single-neck round-bottom flask, followed by the addition of 25 mg of *N,N'*-methylenebis(acrylamide) (MBA) as the cross-linking agent, 2.5 mg of 2,2'-azobis(2-methylpropionitrile) (AIBN) as the initiator, and 100 μ L of MAA as the monomer. The mixture was heated at 90 °C in an oil bath for 1 h, evaporating 10 mL of acetonitrile. The PMAA-coated nanorods were washed three times by centrifugation at 4000 rpm and ethanol redispersion to remove any free PMAA particles.

Fe₃O₄ Decoration. Fe₃O₄ nanoparticles were coated by a simple co-precipitation method. The PMAA-coated NaYF₄ nanorods were dispersed in 20 mL of deionized water. Then 0.8 mmol of anhydrous FeCl₃ and 0.4 mmol of anhydrous FeCl₂ were added. The mixture was heated to 95 °C, followed by the quick injection of 5 mL of 1 M NaOH aqueous solution. The reaction was kept at this temperature for 30 min. The excess Fe₃O₄ nanoparticles were removed by repeated centrifugation at 3500 rpm up to 5 times until the supernatant became clear and transparent. Then, the precipitate was redispersed in 10 mL of water as a stock solution in a nominal concentration of 25 mg/mL for Eu-NaYF₄.

Preparation of Poly(acrylamide) Hydrogel. A 250 mg amount of acrylamide, 14 mg of MBA, and 3 μL of the initiator 2-hydroxy-2-methylpropiophenone were added into 1 mL of ethylene glycol. Then, the solution was cured under UV light for 5 min to produce the PAM hydrogel. The Eu-NaYF₄@PMAA@Fe₃O₄ in different concentrations was added into the pregel solution to obtain composite hydrogels after UV curing. The thickness of the hydrogel films was determined by curing the pregel solution within a narrow space defined by two glass substrates and two PDMS spacers (0.5 mm in thickness). During UV curing, a permanent magnet was placed beside the hydrogel solution at varying distances of 1–3 cm to induce linear or chiral self-assembly. Patterns were generated in the hydrogel thin film by covering the pregel solution film with a photomask. After being cured for \sim 5 min, the photomask was removed. The magnetic field was rotated 45°, followed by curing of the film for another 5 min.

Optical Characterizations. The UV–vis spectra were measured on a Cary-60 spectrometer or an Ocean Optics FLAME spectrometer with optic fibers. The PL spectra were measured on a Horiba QM-400 spectrometer. The CD spectra were measured on a Jasco J-815 spectrometer equipped with a built-in light source, photochromator, photoelastic modulator, and detector, with a beam size of 1.5 mm and a wavelength range of 200–900 nm. The angle-dependent CD of the solution was measured by rotating the magnet within the CD spectrometer. CPL was measured on an Olis Solo UV–vis spectrometer with a 380 nm LED light source, 0.25 nm step size, 1 s integration time, and 13 nm emission bandpass. A total of 100 scans were collected and averaged to produce the final data. Linear dichroism was obtained based on $LD = A_{\parallel} - A_{\perp}$, where A_{\parallel} and A_{\perp} represent the absorbance when the polarizer was parallel and perpendicular to the orientation of nanorods, respectively. The composite nanorods were aligned vertically under a chiral or uniform magnetic field, followed by the absorbance measurement with the polarizer parallel and perpendicular to the nanorods. The linear dichroism spectra were obtained by subtracting the spectrum with the perpendicular polarizer from that with the parallel polarizer.

Microscopy Characterization. Transmission electron microscopy was carried out on a Talos 120C system. Optical microscopy was performed on a Zeiss Axio microscope and a Keyence BZ-X710 microscope. The optical images with different magnetic field directions were taken by placing a magnet under the sample stage. Vertical and parallel magnetic fields could be created when the magnet was below or away from the sample. The polarized microscope images were taken by rotating the sample between the crossed polarizer and analyzer.

Magnetic Field Strength Measurement. The magnetic field strength was measured by using an HT20 Tesla meter.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.3c12344>.

Simulation methods of the magnetic field distribution; excitation and emission of Eu-NaYF₄; TEM image, size distribution, and absorption spectra of Fe₃O₄ NPs; TEM images of Eu-NaYF₄@PMAA at lower magnifications; absorption spectra of Eu-NaYF₄ throughout the surface treatment; TEM image and PL intensity with a thick layer of Fe₃O₄ NPs; PL quenching due to magnetic separation; viscosity and magnetic separation time using different polyol solvents; optical images of magnetic responses of Eu-NaYF₄@PMAA@Fe₃O₄ nanorods; absorption spectra of Fe₃O₄ NPs under a magnetic field with different directions; scheme of the experiment setup for CD measurements; high tension voltage of CD measurement; CD and CPL spectra of the assembly in a left-handed or right-handed magnetic field and using a smaller magnet; g_{lum} of the PAM hydrogel; the scheme

of hydrogel thin film preparation; linear dichroism spectra of composite nanorods aligned in PAM hydrogels; fabrication of PAM hydrogel thin film and lithography processes; the CD signal of hydrogel thin film; the simulation results of the magnetic field distribution; dark-field optical microscope images of Eu-NaYF₄@PMAA@Fe₃O₄ nanorod superstructure aligned in helical and uniform magnetic fields; CPL spectra of linear superstructures; experimental setup of LPL measurement; LPL of Eu-NaYF₄@PMAA@Fe₃O₄ aligned in a PAM hydrogel; PL intensity and polar plot of the hydrogel containing the magnetic composite nanorods; table showing the LPL information on the solution and hydrogel (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the U.S. National Science Foundation (No. CHE-2203972). Z.W. thanks Mr. Zuyang Ye for his help with hydrogel preparation, Dr. Ningning Song for her assistance with magnetic property measurement, and Dr. Adam Berges for his help with sample characterizations.

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