Photoluminescent Peptide Nanotubes

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Bioinspired fabrication of nanomaterials is coming into the spotlight recently as an alternative to conventional nanofabrication methods such as photolithography. Peptide-based nanofabrication is an attractive method for synthesizing novel nanomaterials because of the capacity of peptides for molecular recognition and functional flexibility as well as their environmentally friendly processes without harsh chemical substances.[1–3] Among various peptide molecules and their derivatives forming nanostructures, diphenylalanine (Phe-Phe, FF) is one of the simplest building-block peptides that can readily form nanotubes in aqueous solutions at ambient conditions by a self-assembly process.[4–8] While FF peptide nanotubes show high chemical/thermal stability[6,7] and mechanical strength,[8] additional properties are critically required for optical, electrical, and biological applications.

In this communication, we first report the development of novel photoluminescent peptide-nanotube materials that were readily prepared by an in situ incorporation of photosensitizers and/or lanthanide ions, such as terbium (Tb) and europium (Eu), into the FF nanotubes through a self-assembly process (Fig. 1a). We found that FF nanotubes acted not only as a host matrix for lanthanide complexes, but also as an antenna (or photosensitizer) for luminescent lanthanide complexes. In particular, the incorporation of lanthanide ions together with photosensitizers into FF nanotubes resulted in significant enhancement of the photoluminescence of lanthanide ions. We confirmed the incorporation of lanthanide ions and photosensitizers into the FF nanotubes by multiple analyses, such as fluorescence quenching of FF, a shift of the phosphorescence peak of photosensitizer molecules, electron and optical microscopy images of the FF nanotube complexes, and qualitative analysis with energy-dispersive X-ray spectroscopy (EDXS). In addition to the analyses, we could also fabricate FF nanotubes with various luminescent colors, such as red, green, blue, cyan, purple, and so forth, through variation in the composition of lanthanide complexes.

We investigated the basic optical properties of FF, such as absorbance and fluorescence spectra, before incorporating lanthanide ions into FF nanotubes (see Fig. S1 in Supporting Information). The absorbance spectrum of FF nanotubes reveals that they are almost transparent to visible (380–750 nm) and near-UV light regions (300–380 nm), while they strongly absorb light in the middle-UV spectral region (200–300 nm, Fig. S1a in Supporting Information). FF nanotubes presented two strong absorption peaks at 222 and 260 nm, which should result from the π–π^* electronic transition of the phenyl group in FF.[9] Additionally, a weak absorption peak located at 290 nm, of which molar absorptivity was about 50 M^{-1} cm^{-1}, was attributed to n–π^* electronic transition of the carbonyl group in FF. When we further investigated fluorescence properties, a weak blue emission from FF nanotubes was observed at around 370 nm (Fig. S1b). Both the absorbance and the fluorescence excitation spectra (Fig. S1b in Supporting Information, inset) of FF nanotubes presented a peak at around 290nm, which implies that

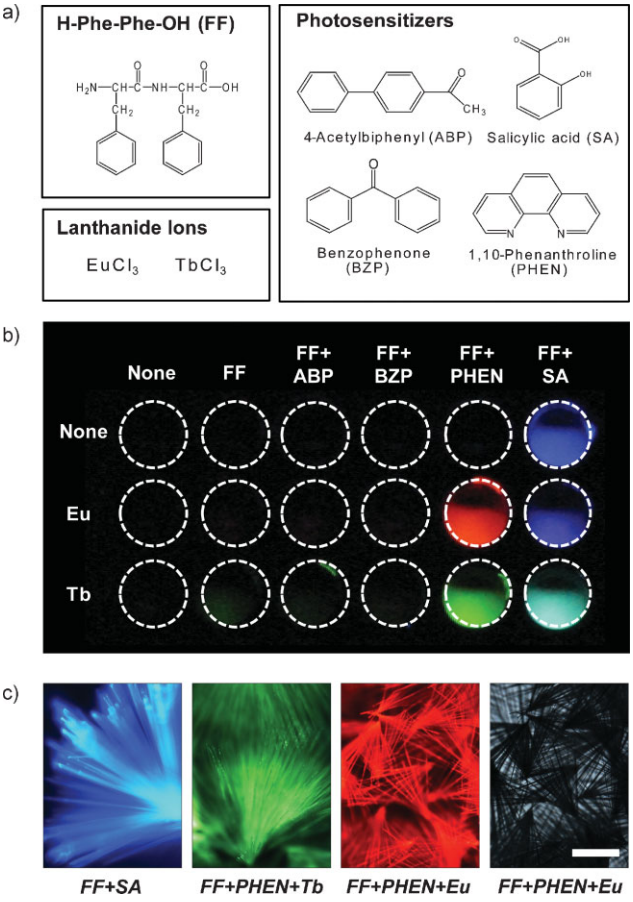

Figure 1. a) Various materials used in the present study, such as diphenylalanine (FF), photosensitizers, and lanthanide ions. b) Influence of FF nanotubes and photosensitizers on the photoluminescence of lanthanide ions (Eu and Tb). The photoluminescent properties of lanthanide ions and photosensitizers were compared in the absence or presence of FF nanotubes. Here, four different photosensitizers were tested: ABP, BZP, PHEN, and SA. The concentration of FF, photosensitizers, and lanthanide ions was kept constant at 32, 1, and 1 mM, respectively, in all the samples. The photograph was taken by excitation at 254 nm of each sample solution (200 μL) loaded into wells of a 96-well microplate. c) Optical microscopy images of FF-nanotube complex with or without UV excitation (the last image). Scale bar: 50 μm. Comparing the latter two images, it can be observed that the emission color emanates from the FF nanotubes.

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the n–π^* electronic transition of the carbonyl group is responsible for the fluorescence of FF.[9,10]

On the basis of the optical properties of FF nanotubes, we studied photoluminescence of lanthanide ions in the absence or presence of FF nanotubes and/or photosensitizers (Fig. 1). Here, we tested the effect of four different photosensitizer molecules – 4-acetylbiphenyl (ABP), benzophenone (BZP), 1,10-phenanthroline (PHEN), and salicylic acid (SA) – on the photoluminescent properties of lanthanide–peptide nanotube complexes (Fig. 1a). The photograph shown in Figure 1b summarizes at a glance the effect of FF nanotubes and/or photosensitizers on the photoluminescent properties of lanthanide ions. Under UV excitation with a filtered 254 nm UV lamp, the characteristic emission color of lanthanide ions was observed in the presence of the FF nanotubes, while no emission was observed in their absence (i.e., lanthanide alone). It has been previously reported that peptides or proteins having aromatic amino acids, such as phenylalanine, tyrosine, and tryptophan, enhance the photoluminescence of lanthanide ions by the energy transfer mechanism.[11,12] Thus, increased light emission from lanthanide ions in the present study should be due to the increase in the effective absorption cross-section of the ions by energy transfer from the FF nanotubes to lanthanide ions, the so-called antenna or photosensitizing effect.[13] The photoluminescence of FF nanotubes with lanthanide ions was significantly enhanced by the introduction of PHEN or SA, while ABP or BZP had a negligible sensitizing effect. In particular, we could observe a remarkably increased phosphorescence of SA in the presence of FF nanotubes. When we analyzed the samples with an optical microscope, characteristic luminescent colors of lanthanide ions were observed along with FF nanotubes (Fig. 1c). Comparison between the images of FF-nanotube complexes with or without UV excitation clearly showed the emission color emanating from the FF nanotubes (the latter two images in Fig. 1c), indicating that lanthanide ions and photosensitizer molecules were incorporated into FF nanotubes without clustering.

In order to investigate the influence of incorporated lanthanide ions and photosensitizer molecules on the structure of FF nanotubes, we analyzed samples with powder X-ray diffraction (XRD) analysis (Fig. 2a) and electron microscopy (Fig. 2b). According to the results, the presence of photosensitizer molecules and/or lanthanide ions had a negligible effect on the crystal structure of peptide nanotubes. All the peptide-nanotube complexes show the characteristic six-fold symmetry of FF nanotubes.[14] In addition, structures of FF nanotubes were almost similar to each other according to electron microscopy images (Fig. 2b), not affected by the presence of photosensitizers and/or lanthanide ions. We further confirmed the presence of lanthanide ions incorporated into FF peptide nanotubes by EDXS (Fig. S2 in the Supporting Information). The concentration of lanthanide ions incorporated into peptide nanotubes was about 0.3 to 0.4 at. % on average. Considering that lanthanide ions are hard cations,[15–17] the most probable binding sites would be the anionic carboxylate groups on the FF peptides; this needs to be confirmed by further study of the molecular arrangement of FF near lanthanide ions.

In order to investigate the mechanism for enhanced photoluminescence of lanthanide ions by FF nanotubes, we studied the photoluminescent spectra of lanthanide–photosensitizer–FF nanotube hybrid materials in detail. Here, we focused on Tb photoluminescence, because of the relatively weak photoluminescence of Eu compared with that of Tb, and overlapping of the Eu emission peak with a beam diffracted from FF nanotubes. Each sample was excited at wavelengths ranging from 250 to 340 nm with a 10 nm interval (see Fig. S3 in the Supporting Information). Before investigating the photoluminescence spectra of lanthanide ion–photosensitizer–FF nanotube hybrid materials, we observed the influence of each component (i.e., FF nanotubes, ABP, BZP, PHEN, and SA) on the lanthanide photoluminescence. According to the results, no characteristic emission peak was observed when Tb ions were present alone because of their low absorbance (Fig. S3a).[16] But the addition of FF nanotubes (FF+Tb, Fig. 3 and S3b), PHEN (PHEN+Tb, Fig. S3g), or SA (SA+Tb, Fig. 3 and S3i) highly enhanced the photoluminescence of Tb, while ABP (ABP+Tb, Fig. S3c) and BZP (BZP+Tb, Fig. S3e) had negligible sensitizing effect. Interesting results were obtained when the FF nanotubes were used as a host matrix for both lanthanide ions and photosensitizer molecules. The introduction of FF nanotubes into the solution containing Tb and photosensitizer molecules led to the quenching of FF fluorescence and a remarkably enhanced photoluminescence of Tb ions at the same time (Fig. S3c–j, left vs. right panels), which is additional evidence for the incorporation of Tb and photosensitizers into FF nanotubes and for the energy transfer from FF nanotubes to Tb ions via photosensitizers. According to the literature,[18,19] the energy transfer between two molecules could occur within a very short range (less than several

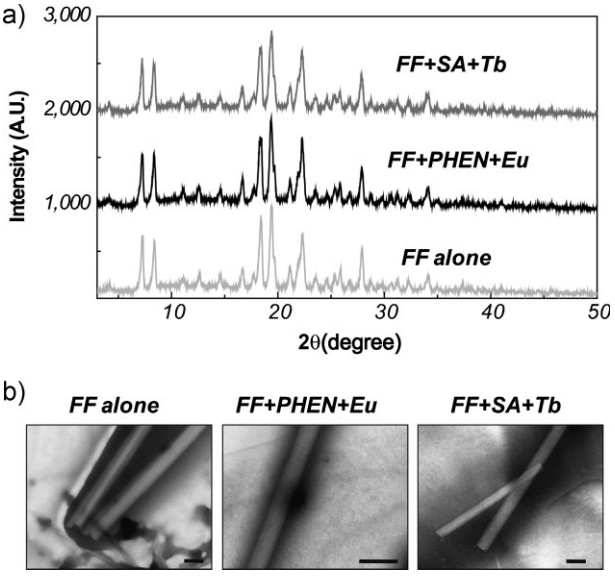

Figure 2. Powder X-ray diffractograms and electron microscopy images of photoluminescent peptide nanotubes. a) Powder X-ray diffractograms of FF nanotubes alone (FF alone), Eu–PHEN–FF nanotube complexes (FF+PHEN+Eu), and Tb–SA–FF nanotube complexes (FF+SA+Tb). The presence of other components, such as photosensitizer molecules and lanthanide ions, had a negligible effect on the structure of self-assembled FF nanotubes. All the diffractograms show the characteristic six-fold symmetry of FF nanotubes reported previously by Gorbitz [14]. b) Transmission electron microscopy images (scale bar: 100 nm) of peptide nanotubes alone or their complexes.

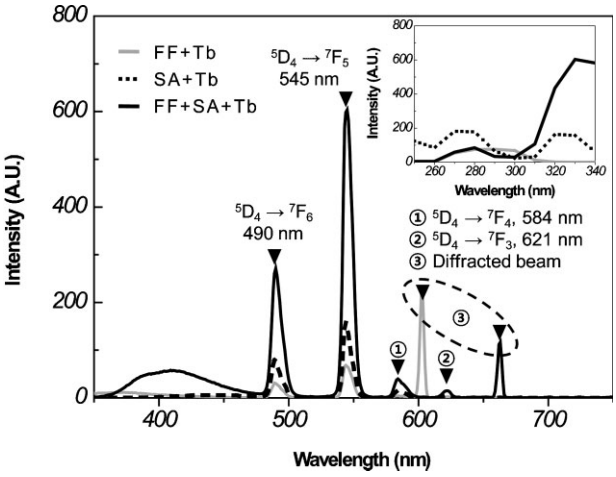

Figure 3. Enhanced photoluminescence of Tb ions by FF nanotubes and/or SA. Enhanced photoluminescence of Tb ions by FF nanotubes alone (FF+Tb, grey solid line), SA alone (SA+Tb, black dashed line), and FF nanotubes with SA (FF+SA+Tb, black solid line). The intensity of Tb luminescence was significantly enhanced when Tb ions were incorporated with SA into the FF nanotubes. Emission spectra of FF+Tb, SA+Tb, and FF+SA+Tb were measured under excitation at 300, 330, and 330 nm, respectively. Inset: Excitation spectra of FF+Tb, SA+Tb, and FF+SA+Tb were measured for emission corresponding to the $^5D_4 \rightarrow {}^7F_6$ transition of Tb ions.

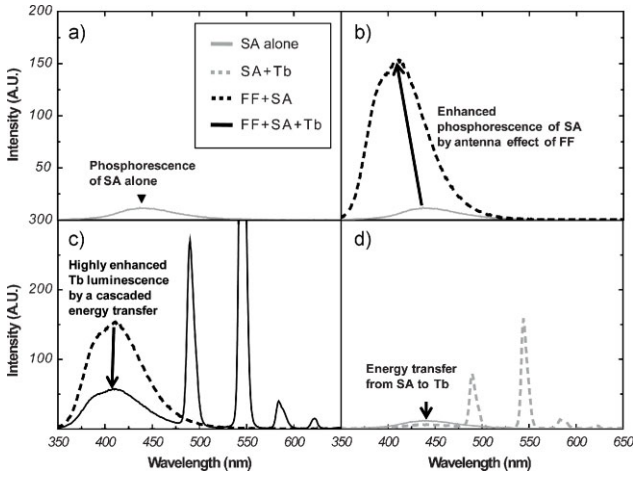

Figure 4. Emission spectra showing the cascaded energy transfer from FF nanotubes to Tb via SA. All spectra were obtained with excitation at 330 nm. Photoluminescent spectrum of a) SA alone (grey solid line), b) SA–FF nanotube complexes (black dashed line), c) Tb–SA–FF nanotube complexes (black solid line), and d) Tb–SA complexes (grey dashed line). Photoluminescent spectrum of SA was significantly enhanced by FF nanotubes (a), indicating the energy transfer from FF nanotubes to SA (b). When Tb ions were additionally present in the solution, the blue emission from SA was quenched, and intense characteristic peaks of Tb were observed by a cascaded energy transfer from FF to Tb via SA (c).

nanometers), and excited lanthanide ions readily undergo nonradiative decay when exposed to solvent molecules.

Figure 3 shows in detail highly enhanced Tb photoluminescence by incorporation of Tb ions together with SA into FF nanotubes (FF+SA+Tb). The position of characteristic emission peaks of Tb remained almost unchanged throughout the samples. The emission peaks at 490, 545, 584, and 621 nm for Tb ions with FF nanotubes and/or SA correspond to transitions from the $^5D_4$ state of Tb to ^7F_J ($J = 6$, 5, 4, 3) states, respectively. Note that additional peaks at 600 and 660 nm originated from the scattering and diffraction of the excitation beam, with wavelength of 300 and 330 nm, respectively. When we calculated the integrated peak area corresponding to the $^5D_4$–$^7F_6$ transition in order to compare the relative number of photons emitted from Tb ions in each case, the integrated area for $^5D_4$–$^7F_6$ transition of Tb for FF+SA+Tb was more than twice as large as the simple algebraic sum of those for FF+Tb or SA+Tb, indicating that the photoluminescence of Tb was synergistically enhanced by FF and SA. Excitation behavior of Tb for FF+SA+Tb was also significantly different from that of FF+Tb and SA+Tb (Fig. 3, inset).

In the following experiments, we analyzed photoluminescent spectra of each component upon step-by-step addition of other components in order to trace a path of energy transfer between them. According to our results (Fig. 4a and b), the phosphorescence of SA was significantly enhanced when it was incorporated into FF nanotubes. The phosphorescence of SA was increased more than twelve times, most likely a result of the energy transfer from FF nanotubes to SA. Since the absorbance spectrum of SA–FF-nanotube complexes (FF+SA) was different from a simple superposition of the spectra of each component (see Fig. S4 in the Supporting Information), it was concluded that the enhanced phosphorescence of SA can be attributed not only to the increased absorbance upon addition of FF nanotubes, but also to the strong interaction between them. In addition, we could observe a blue-shift in SA phosphorescence (Fig. 4b, 450 → ~410 nm) and absorbance (Fig. S4, Supporting Information) spectra in the presence of FF nanotubes, which indicates that SA was incorporated into FF nanotubes by a hydrophobic interaction, such as π–π. Note that many organic dyes were reported to show a similar behavior when surrounded by hydrophobic environments.[20,21] When Tb ions were further introduced into the system formerly composed of FF and SA, a decrease of SA phosphorescence and a remarkable increase of Tb photoluminescence were simultaneously observed, demonstrating energy transfer from SA to Tb (Fig. 4c). A comparison between the photoluminescence spectra of SA+Tb (Fig. 4d) and FF+SA+Tb (Fig. 4c) complexes clearly shows the synergistic effect of FF and SA on the increased photoluminescence of Tb ions.

Based on these results, we propose that an increased absorption cross-section and a cascaded energy transfer from FF nanotubes to lanthanide ions (Tb) via photosensitizers (SA) may lead to significant enhancement of Tb photoluminescence, as illustrated in Figure 5. According to the literature,[13,22] the energy-transfer efficiency between lanthanide ions and nearby molecules depends strongly on the size of the energy gap between the lowest triplet state of the ligand and the resonance energy level of lanthanide ions; the larger the energy gap, the lower the energy-transfer efficiency. Therefore, we suggest that the introduction of a proper photosensitizer molecule, with an excited triplet state of intermediate energy level between FF nanotubes and lanthanide ions, into the nanotubes should significantly enhance the photoluminescent properties of lanthanide ions by a cascaded energy transfer between them.

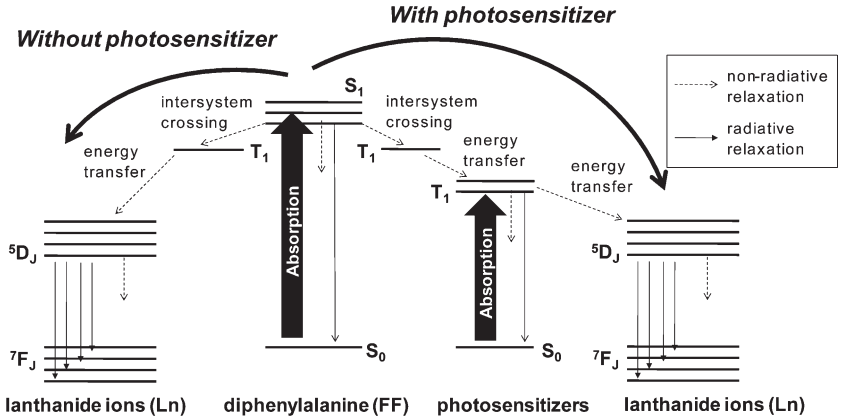

Figure 5. Possible mechanism for the enhanced photoluminescence of lanthanide ions upon incorporation into FF nanotubes with or without photosensitizers.

Our hypothesis is further supported by recent reports about the energy transfer in layer-by-layer quantum-dot structures.[23] Franzl et al. fabricated polyelectrolyte–quantum dot multilayer films by layer-by-layer deposition, where the size of quantum dots and thus their electronic energy gap also varied monotonically across the layers to prepare the funnel-like energy-level profile. They observed a super-efficient cascaded energy transfer between the layers of quantum dots.

For the further development of photoluminescent peptide nanotubes in various colors, relative intensity of three prime colors (i.e., red from Eu, green from Tb, and blue from SA) was controlled by changing the composition of peptide nanotubes. The composition of lanthanide ions and photosensitizers incorporated into FF nanotubes was indirectly controlled by varying their concentration in the precursor solution (Fig. 6a). We were able to obtain peptide-nanotube complexes in red, green, blue, pink, violet, and cyan luminescent color (see Fig. S5 in the Supporting Information). Simultaneous emission of red, green, and blue colors from FF-nanotube-based hybrid materials indicates that lanthanide ions and photosensitizer molecules are incorporated in a well-dispersed manner, not in the form of clusters. Note that when more than two kinds of phosphors were present in proximity to each other, only the emission from the phosphor with the lowest excited state energy (red emission of Eu, in the present study) would be observed, according to Kasha's rule.[24,25] In order to show the color tunability of our photoluminescent peptide nanotubes, we determined the coordinates of our luminescent peptide-nanotube complexes with various compositions in the Commission Internationale de L'Eclairage (CIE) chromaticity diagram, and investigated the relationship between the composition of peptide nanotubes and their luminescent color by regression analysis (Fig. 6b). According to the results, our photoluminescent peptide nanotubes covered almost the entire visible range, as illustrated in the CIE *x*–*y* chromaticity diagrams, and their luminescent color could be readily tuned by changing the composition of peptide nanotubes.

In summary, we report herein the development of novel photoluminescent peptide nanotubes synthesized by an in situ incorporation of luminescent complexes composed of photosensitizers and/or lanthanide ions into peptide nanotubes through a self-assembly process. According to our results, peptide nanotubes act as efficient photosensitizers as well as host matrices for lanthanide complexes. Through a cascaded energy-transfer mechanism, peptide nanotubes and photosensitizer molecules exhibited a high synergistic effect on the enhancement of lanthanide photoluminescence. We could further develop peptide nanotubes having various colors covering almost the entire visible range, as shown in the CIE chromaticity diagrams. Our results not only

a)

Sample	Mixture Composition (mM)					Sample					
	FF	PHEN	SA	Eu	Tb		FF	PHEN	SA	Eu	Tb
a	32	1	0	1	0	h	32	0.2	0.8	1	0
b	32	1	0	0.4	0.6	i	32	0	1	1	0
c	32	1	0	0.2	0.8	j	32	0.6	0.4	0	1
d	32	1	0	0	1	k	32	0.4	0.6	0	1
e	32	0.8	0.2	1	0	l	32	0.2	0.8	0	1
f	32	0.6	0.4	1	0	m	32	0	1	0	1
g	32	0.4	0.6	1	0						

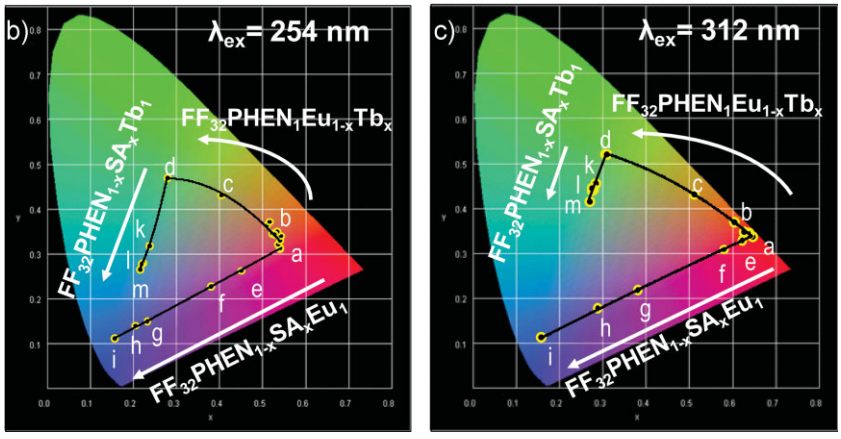

Figure 6. a) Concentration of each component in precursor solutions used to prepare photoluminescent peptide nanotubes. b,c) CIE *x*–*y* chromaticity diagrams showing the location of photoluminescent color of peptide nanotube complexes. CIE color coordinates of the samples were obtained under UV excitation at 254 nm (b) and 312 nm (c), respectively. The results show that the color of photoluminescent peptide nanotubes could be tuned by varying the composition of each component in the precursor solution.

demonstrate the utility of peptide nanotubes as a novel host matrix for luminescent complexes, but also hint at a new horizon for the application of nanotubes fabricated by peptide self-assembly.

Experimental

Materials: Diphenylalanine (FF) peptide in a lyophilized form was obtained from Bachem AG (Bubendorf, Switzerland). 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), 4-acetylbiphenyl (ABP), benzophenone (BZP), 1,10-phenanthroline (PHEN), salicylic acid (SA), $EuCl_3 \cdot 6H_2O$, and $TbCl_3 \cdot 6H_2O$ were purchased from Sigma–Aldrich (St. Louis, MO).

Preparation of Photoluminescent Peptide Nanotubes: Fresh FF solution was prepared by dissolving as-received FF in HFIP at 100 mg mL^{-1} (~320 mM). To avoid the formation of any aggregates, FF solution was always freshly prepared just before use. Stock solutions of photosensitizers and lanthanide ions were each prepared at 10 mM in methanol. Photoluminescent peptide nanotubes were readily formed by diluting concentrated FF with a methanolic solution containing photosensitizers and/or lanthanides into a final concentration of 10 mg mL^{-1}, which was followed by rigorous vortexing.

Characterization of Photoluminescent Peptide Nanotubes: Absorbance and photoluminescence spectra of each sample were obtained using a Biospec-Mini spectrophotometer (Shimadzu Co., Japan) and a RF-5301PC spectrofluorophotometer (Shimadzu Co., Japan), respectively. In order to observe photoluminescence in solutions with various combinations of each component at a glance, sample solutions were loaded in 200 μL volumes each into wells of a 96-well microplate. A photograph was taken under 254 nm UV excitation using a PowerShot G7 camera (Canon Inc., Japan). For further analysis, each sample was dried under ambient conditions on top of a glass substrate. To determine the coordinates of our luminescent peptide nanotubes on the CIE chromaticity diagram, photoluminescence spectra of each sample in a fine-powder form were obtained using a DARSA PRO 5100 PL system (Professional Scientific Instrument Co, Korea) under continuous Xe-lamp excitation (500 W) at room temperature. Optical microscopy images of luminescent peptide nanotubes were obtained using an Eclipse 80i optical microscope (Nikon, Japan) at room temperature under external UV excitation using a filtered UV lamp (with wavelength of 254 and 312 nm, respectively, with a power density of ~0.6 mW cm^{-2}, Vilber Lourmat, France). Scanning electron microscopy images were obtained using an S-4800 field-emission scanning electron microscope (Hitachi High-Technologies Co., Japan) at an acceleration voltage ranging from 1 to 3 kV after Pt-coating using a SCD005 Pt-coater (Bal-Tec AG., Liechtenstein). For analysis with transmission electron microscopy, samples were prepared by placing a drop of solution containing peptide-nanotube complexes on top of formvar–carbon-coated Cu grids for 60 s, and negatively stained with 1% (w/v) phosphotungstic acid for 60 s. The structure of photoluminescent peptide complexes was analyzed using a D/MAX-IIIC powder X-ray diffractometer (Rigaku Co., Japan) equipped with Ni filter under the following conditions: scan speed: 3 ° min^{-1}; Cu Kα radiation, $\lambda = 1.5418$ Å; scan range: 2 °–60 °.

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