Supporting Information
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Switching On Luminescence in Nucleotide/Lanthanide Coordination Nanoparticles via Synergistic Interactions with a Cofactor Ligand

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Switching-On Luminescence in Nucleotide-Lanthanide Coordination Nanoparticles via Synergistic Interactions with a Cofactor Ligand

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(i) Experimental

Chemicals. 2’-deoxynucleotides 5’-monophosphate (dAMP and dCMP) disodium salts were purchased from Across Organics, and terbium lanthanide ions from Wako Pure Chemical, Ltd., and used without any further purification. Water was purified with a Direct-Q system, Millipore Co (18.2 MΩ.cm).

Fluorescence spectroscopy. Luminescence measurements were recorded on a Perkin Elmer LS55 fluorescence spectrometer, with a xenon lamp as excitation source. Emission spectra were recorded with excitation wavelengths of 260 nm, 300 nm or 338 nm. Excitation spectra were recorded for the emission intensity of Tb3+ at 545 nm (λem = 200-400 nm). The bandwidth of the excitation and emission monochromators was set at 10 nm,
and the scan speed set at 240 nm/sec. Samples were investigated in water at 25 °C in 1 mm path length (1 cm path width) quartz cells for fluorescence measurements.

**UV spectroscopy.** UV absorption spectra (200-400 nm) in water were measured at 25 °C using a UV-visible spectrophotometer (Jasco V-560, Japan), equipped with a Peltier-type thermostatic cell holder, and using 1 mm path length quartz cells.

**Transmission Electron Microscopy.** A small drop of samples in water was deposited on carbon-coated copper grids. After one minute, the excess liquid was blotted with filter paper. Neither staining nor Pt vaporization were used prior to sample observation. TEM images were recorded using a JEOL JEM-2010 electron microscope operating at 120 kV and a Gatan ssCCD camera.

**(ii) Spectroscopic properties of dAMP/Tb$^{3+}$ CNPs**

Figure S1 shows the absorption (a) and luminescence (b) properties of dAMP/Tb$^{3+}$ CNPs in the absence of ancillary ligand 1. Although dAMP exhibits a large absorption band centered at 260 nm, irradiation of the complex at $\lambda_{ex} = 260$ nm does not lead to Tb$^{3+}$ emission around at 545 nm. Reciprocally, no excitation band could be detected on the excitation spectrum ($\lambda_{em} = 545$ nm).

![Figure S1](image_url)

**Figure S1.** Spectroscopic properties of dAMP (0.75 mM)/Tb$^{3+}$ (0.25 mM) in water: (a) absorption spectrum, (b) excitation (solid line, $\lambda_{em} = 545$ nm) and emission (dashed line, $\lambda_{ex} = 260$ nm) spectra.
(iii) Absorption properties of 1 and 1/Tb$^{3+}$ complex

Figure S2 represents the absorption spectrum of 1 in water, exhibiting a unique band centered at 299 nm (dashed line). Upon Tb$^{3+}$ complexation, this absorption band is split into two components with a shoulder shifted at lower energy (ca. 338 nm, solid line).

![Figure S2: Absorption spectra of 1 (dashed line) and 1/Tb$^{3+}$ complex (solid line) in water ([1] = 50 μM, [Tb$^{3+}$] = 0.25 mM).](image)

(iv) Spectroscopic properties of 1/Tb$^{3+}$ complex as a function of pH

Figure S3 shows the absorption (a) and excitation (b) properties of 1/Tb$^{3+}$ complex as a function of pH. Upon increasing pH, a bathochromic displacement of the absorption maximum from 300 nm up to 338 nm was observed. Consecutively, similar shift are observed on the excitation spectra of 1/Tb$^{3+}$ complex ($\lambda_{em}$ = 545 nm), excitation maximum shifting from 300 to 338 nm. As described in the text, the 338-nm peak is much red-shifted compared to that of free ligand 1 in the dianionic form ($\lambda_{max}$ ~ 310 nm at alkaline pH, ref. 11b). It suggests that 1 is coordinated to Tb$^{3+}$ by the N,O- or O,O-chelation mode.

![Figure S3: (a) Absorption and (b) excitation ($\lambda_{em}$ = 545 nm) spectra of 1/Tb$^{3+}$ in water as a function of pH ([1] = 50 μM, [Tb$^{3+}$] = 0.25 mM, pH = 4.4-7.4).](image)
(v) Absorption properties of the three-component complex

Figure S4 shows absorption properties of dAMP/Tb³⁺ CNPs in the absence (dotted line) and presence (solid line) of the ancillary ligand 1. The absorption spectrum of the ternary complex (dAMP+1)/Tb³⁺ shows the appearance of a band at ca. 300 and 338 nm attributed to ligand 1.

![Figure S4](image)

**Figure S4:** Absorption spectra of dAMP/Tb³⁺ (dotted line) and (dAMP+1)/Tb³⁺ CNPs (solid line) in water ([dAMP] = 0.75 mM, [1] = 50 μM, and [Tb³⁺] = 0.25 mM).

(vi) Three-component complex: Identification of excitation maxima

Figure S5 shows the excitation spectrum of (dAMP (0.75 mM) + 1 (50 μM))/ Tb³⁺ (0.25 mM) CNPs (dotted line) exhibiting a strong excitation band at 338 nm attributed to the three-component complex. In presence of an excess Tb³⁺ ([dAMP] = 0.5 mM, solid line) an additional band is observed at 300 nm. This band can be attributed to the formation of 1/Tb³⁺ complexes. This is supported by the excitation spectrum of 1/Tb³⁺ (in absence of dAMP, dashed line) that shows a unique peak at 300 nm.

![Figure S5](image)

**Figure S5:** Excitation spectra (λₑᵐ = 545 nm) of (dAMP + 1 (50 μM))/ Tb³⁺ (0.25 mM) in water. [dAMP] = 0 mM (dashed line), 0.5 mM (solid line), and 0.75 mM (dotted line).
(vii) Luminescence switch-on in dCMP-Tb\(^{3+}\) CNPs

Figure S6 represents the adaptation of the strategy described in this work to another type of nucleotide/Tb\(^{3+}\) CNPs. In this part, dAMP has been replaced by 2'-deoxycytidine 5'-monophosphate (dCMP, Figure S6a). Mixing dCMP and Tb\(^{3+}\) in water induces the formation of CNPs in few minutes,\(^3\) where irradiation of dCMP does not lead to Tb\(^{3+}\) sensitization (Figure S6b, left). To overcome this feature, ligand 1 has been added to dCMP before mixing with Tb\(^{3+}\) and CNPs formation. Irradiation of the three-component complex (dCMP+1)/Tb\(^{3+}\) within ligand 1 absorption band (\(\lambda_{ex} = 338\) nm) gave Tb\(^{3+}\) luminescence, as observed with the typical four emission bands characteristic of Tb\(^{3+}\) emission (Figure S6c, red solid line with open squares). Reciprocally, excitation spectrum of the three-component complex exhibits a large band at 338 nm, providing the identification of 1 as the group responsible for Tb\(^{3+}\) sensitization (Figure S6c, red dashed line with open squares). Moreover, as observed for (dAMP+1)/Tb\(^{3+}\) CNPs, isolation of precipitating CNPs by centrifugation provides the evidence for the successful incorporation of 1 within the dCMP/Tb\(^{3+}\) coordination network. Indeed, the luminescence switch-on upon irradiation of the sample is specific to the precipitated CNPs (Figure S6 b,d). Again, the supernatant exhibits an excitation band at ca. 300 nm, previously attributed to the formation of 1/Tb\(^{3+}\) complex, while the heteroleptic complex (dCMP+1)/Tb\(^{3+}\) in the precipitate is characterized by an excitation maximum at 338 nm (Figure S6d, dashed black and red lines respectively, and Figure S3).

![Figure S6: (a) Molecular structure of 2'-deoxycytidine 5'-monophosphate (dCMP). (b) Photographs showing the emission properties of dCMP/Tb\(^{3+}\) CNPs upon irradiation of a drop of sample at 365 nm using a handy UV lamp. From the left to the right: dCMP/Tb\(^{3+}\) in absence of the ancillary ligand, precipitate and supernatant fractions of (dCMP+1)/Tb\(^{3+}\) sample. (c) Excitation (dashed lines) and emission (solid lines) spectra of dCMP/Tb\(^{3+}\) in the absence (black lines) and presence (red lines with open squares) of 1 in water. (d) Excitation (dashed lines) and emission (solid lines) spectra of (dCMP+1)/Tb\(^{3+}\): supernatant (black lines) and precipitate fraction (red lines with open squares) in water. ([dCMP] = (0.75 mM), [1] = 50 \(\mu\)M, Tb\(^{3+}\) = (0.25 mM), \(\lambda_{em} = 545\) nm, \(\lambda_{ex} = 338\) nm).]