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Conversion of Molecular Information by Luminescent Nanointerface Self-Assembled from Amphiphilic Tb(III) Complexes

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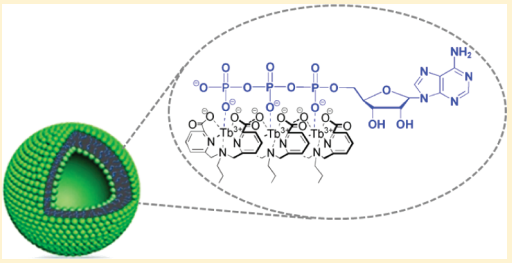
Supporting Information

ABSTRACT: A novel amphiphilic Tb^{3+} complex (**TbL**$^+$) having anionic bis(pyridine) arms and a hydrophobic alkyl chain is developed. It spontaneously self-assembles in water and gives stable vesicles that show sensitized luminescence of Tb^{3+} ions at neutral pH. This **TbL**$^+$ complex is designed to show coordinative unsaturation, i.e., water molecules occupy some of the first coordination spheres and are replaceable upon binding of phosphate ions. These features render **TbL**$^+$ self-assembling receptor molecules which show increase in the luminescence intensity upon binding of nucleotides. Upon addition of adenosine triphosphate (ATP), significant amplification of luminescent intensity was observed. On the other hand, ADP showed moderately increased luminescence and almost no enhancement was observed for AMP. Very interestingly, the increase in luminescence intensity observed for ATP and ADP showed sigmoidal dependence on the concentration of added nucleotides. It indicates positive cooperative binding of these nucleotides to **TbL**$^+$ complexes preorganized on the vesicle surface. Self-assembly of amphiphilic Tb^{3+} receptor complexes provides nanointerfaces which selectively convert and amplify molecular information of high energy phosphates linked by phosphoanhydride bonds into luminescence intensity changes.



INTRODUCTION

Biological anions such as nucleotides constitute important family of receptor ligands which play indispensable roles in storage, transformation of genetic information and in intracellular signaling. The intracellular signaling is initiated by molecular recognition events on biomembranes, where receptor proteins and lipids are dynamically self-assembled into specific supramolecular complexes successively to the binding of receptor ligands. They activate signaling pathways, leading to the amplification into cellular response.[1] The sophisticated interfacial functions of biomembranes manifest the importance of preorganized supramolecular systems which dynamically convert and amplify molecular information to the other physicochemical signals. Although synthetic molecular receptors for biological phosphate molecules has been extensively reported,[2] their integration into molecular assemblies and to construct signal-responsive nanointerfaces have met limited success.[3] It remains challenges to develop such supramolecular interfaces which are capable of receiving and converting molecular information of biological anions synergistically into physicochemical outputs. We herein report a novel supramolecular luminescent receptor for nucleotides that is self-assembled from amphiphilic lanthanide complex **TbL**$^+$ (Figure 1). The ligand $\mathbf{L}^{2-}$ is composed of bis(pyridine) anionic arms and a long alkyl chain, based on the following considerations.

1. The bis(pyridine) anionic arms are introduced in the ligand $\mathbf{L}^{2-}$ since they secure high stability constant to lanthanide ions and quantitative complexation is expected in water. Pyridine ligands also serve as antenna moieties which exert efficient energy transfer to coordinated lanthanide ions upon ultraviolet illumination.[4]
2. To impart self-assembling nature to the lanthanide complex, a hydrophobic alkyl chain is introduced to the ligand $\mathbf{L}^{2-}$. It would drive amphiphilic self-assembly of lanthanide complexes in water.
3. Stoichiometric (1:1) coordination between the dianionic ligand $\mathbf{L}^{2-}$ and trivalent lanthanide ion give a monocationic lanthanide complex. Tb^{3+} ion was selected as lanthanide ion because of its distinct emission properties with a large Stokes shift and long luminescence lifetime.[5] Coordinative unsaturation is expected for this 1:1 complex, that is, water molecules would occupy the rest of coordination spheres. The complexes are aligned regularly at the aqueous interface, and water molecules in the coordination spheres are replaceable by coordinating anions such as phosphates. As coordinating water molecules generally quench luminescence of lanthanide ions via deactivation of the excited states through O−H vibrational modes of coordinated water molecules, such replacement may allow detection of phosphate coordination by increased luminescence intensity.[6]

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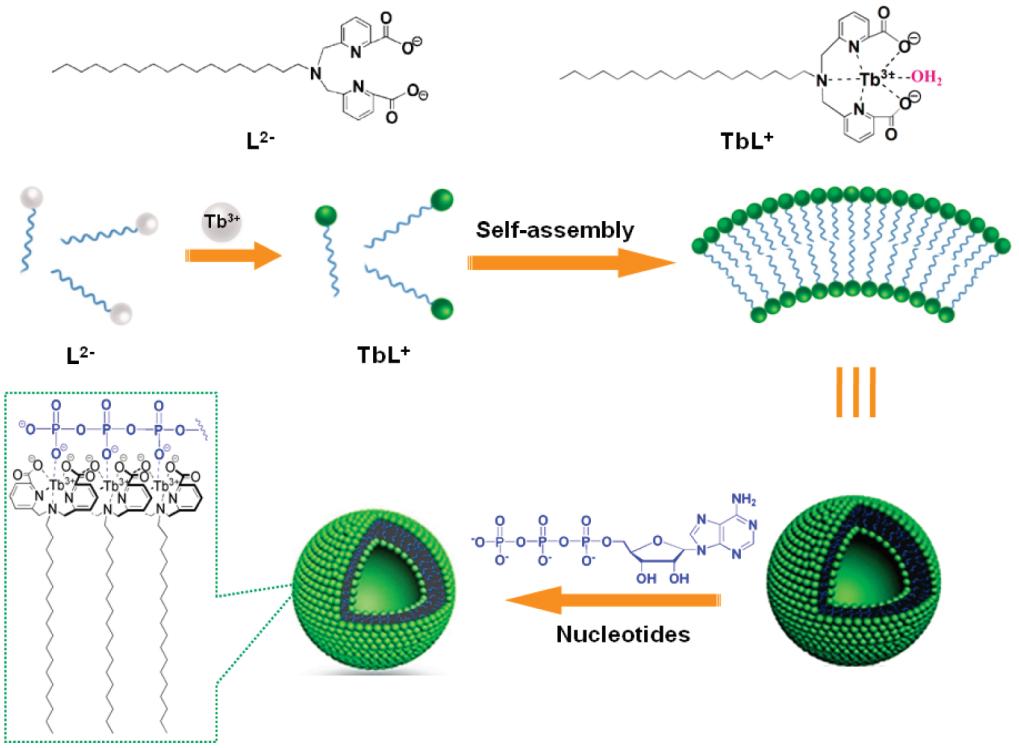

Figure 1. Schematic representation for self-assembly of amphiphilic $\mathbf{TbL}^+$ complexes in water and binding of ATP molecules.

As biological phosphate molecules, nucleotides were chosen. Nucleotides carry one or more phosphate groups which are linked in series by phosphoanhydride bonds. Rupture of these phosphoanhydride bonds releases large amounts of useful energy. Above all nucleotides, adenosine triphosphate (ATP) transfers chemical energy in hundreds of different cell reactions, rendering it the molecular unit currency of intracellular energy transfer.[7] The transformation of ATP into ADP or AMP (adenosine diphosphate or monophosphate) provides energy to power cell reactions such as protein synthesis or cell movement. It also serves as (co)substrates for signal-regulating enzymes like kinases and adenylate cyclase. Thus, they play essential roles in the storage and retrieval of biological information in the cell. Although fluorescent[8] or colorimetric[9] molecular receptors for ATP have been extensively developed, molecular self-assemblies responsive to ATP has been limited to surface monolayers with guanidinium-receptors,[10] and recent binuclear zinc(II) cyclen complex embedded in liposomes.[3f] Surface monolayer systems show changes in the surface pressure−area isotherms which reflect interactions at the air−water interface,[10] but are not suitable to rapid and qualitative sensing of guest molecules. In conventional vesicular system, on the other hand, receptor molecules do not exert self-assembling properties by themselves and they require lipid matrices to be stably dispersed in water.[3f] Such membrane-embedded molecular receptors generally do not show cooperative or synergistic responses, which provide the basis for conversion and processing of molecular information. Self-assembly of amphiphilic receptor complexes may provide a rational strategy toward this issue. The interaction between preorganized receptors and anionic guest molecules especially with multiple receptor-binding sites may lead to selectivity and cooperative interactions, as a consequence of adaptation by aligned receptors. These features would give nanointerfaces the capability to convert and amplify molecular signals.

RESULTS AND DISCUSSION

The ligand $\mathbf{L}^{2-}$ was synthesized and purified according to the procedure described in Supporting Information. Self-assembling characteristics of $\mathbf{L}^{2-}$ and its interaction with $TbCl_3$ were investigated in HEPES buffer (10 mM, pH = 7.5). Addition of Tb^{3+} ion to aqueous dispersion of $\mathbf{L}^{2-}$ gave bright green luminescence under UV irradiation (Figure S1 inset, Supporting Information). In the emission spectrum, luminescence peaks are observed at 489 ($^5D_4 \rightarrow {}^7F_6$), 545 ($^5D_4 \rightarrow {}^7F_5$), 586 ($^5D_4 \rightarrow {}^7F_4$), and 621 nm ($^5D_4 \rightarrow {}^7F_3$) with the 545 nm band having the highest intensity, which are characteristics of Tb^{3+} ion (Figure S1, Supporting Information).[11] As neither of the ligand $\mathbf{L}^{2-}$ nor Tb^{3+} ions alone reveal any luminescence under these conditions, the observed luminescence is sensitized by the coordinating ligand $\mathbf{L}^{2-}$. This is confirmed by the excitation spectrum monitored at 545 nm which displayed a peak of pyridine unit at 272 nm. The composition of the complex Tb^{3+}:$\mathbf{L}^{2-}$ was determined to be 1:1, as revealed by plotting luminescence intensity as a function of $[Tb^{3+}]/([Tb^{3+}] + [\mathbf{L}^{2-}])$ (Job's plot, Supporting Information Figure S2) and elemental analysis (Supporting Information). To investigate the self-assembling characteristics of $\mathbf{TbL}^+$, dynamic light scattering (DLS) experiments were conducted. Figure S3a (Supporting Information) shows dependence of light scattering intensity plotted as a function of $\mathbf{TbL}^+$ concentration. A flection point is observed around at 0.35 μM, which corresponds to the critical aggregation concentration (CAC) for the 1:1 complex ($\mathbf{TbL}^+$). This value is almost by 3 orders of magnitude lower than that determined for the aqueous ligand $\mathbf{L}^{2-}$ alone (0.18 mM, Figure S3b in Supporting Information). The order of CAC value obtained for aqueous $\mathbf{L}^{2-}$ is typical of micelle-forming amphiphiles, which is consistent with the molecular structure. These observations clearly indicate that the formation of $\mathbf{TbL}^+$ complex promotes self-assembly (Figure 1). Morphology of

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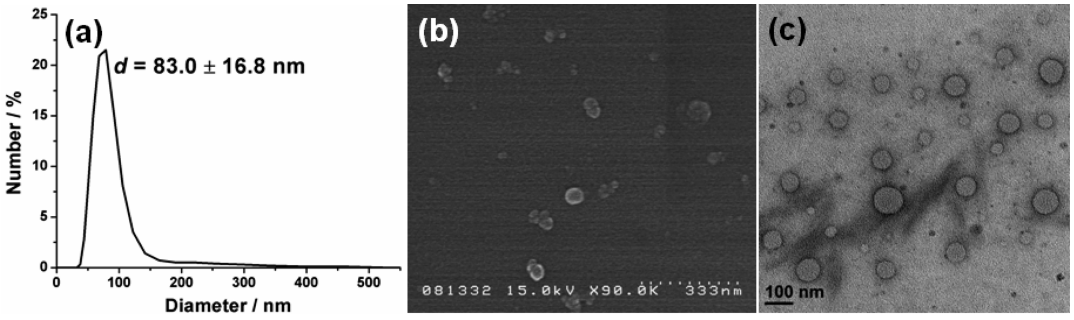

Figure 2. (a) Particle size distribution, (b) SEM image, and (c) TEM image of [TbL]Cl (50 μM): 10 mM HEPES buffer (pH = 7.5). In TEM measurement, the sample was poststained with uranyl acetate.

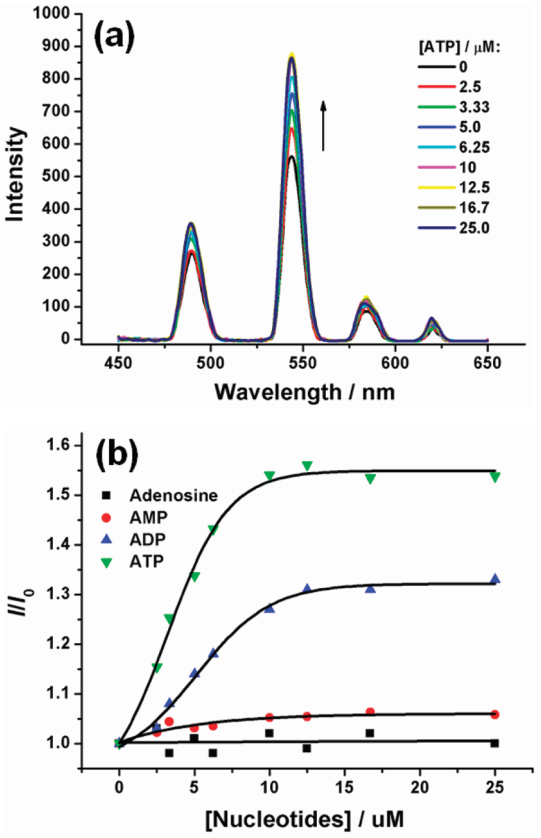

Figure 3. (a) Luminescence spectra of [TbL]Cl in the absence and presence of ATP; (b) I/I_0 evolution as a function of the concentration of biomolecules. The concentration of [TbL]Cl for all experiments is 50 μM, in 10 mM HEPES buffer (pH = 7.5), λ_{ex} = 285 nm.

these nanoparticles was subsequently observed by scanning electron microscopy (SEM), transmission and cryo-transmission electron microscopy (TEM, cryoTEM). In SEM and TEM observation, **TbL**$^+$ showed spherical nanoparticles with diameters of 50−110 nm (Figures 2b, c). These structures are characteristics of bilayer vesicles, which were also confirmed by cryo-TEM observation (Figure S4, Supporting Information). The observed diameter of vesicles is consistent with the DLS measurement (Figure 2a, average diameter, 83.0 ± 16.8 nm). It is apparent that **TbL**$^+$ spontaneously forms stable self-assemblies in water without the help of any other matrices such as surfactant micelles or lipid bilayers.

The ability of **TbL**$^+$ vesicles to interact with nucleotides and their influence on luminescence characteristics were then investigated. Very interestingly, upon addition of ATP, aqueous **TbL**$^+$ showed a significant increase in luminescence intensity as shown in Figure 3a. The increase in luminescence intensity of **TbL**$^+$ ($I/I_0 = I_{ATP+TbL}/I_{TbL}$) reached a maximum value of ∼1.54 when ATP was added beyond the concentration of ∼10 μM (Figure 3b). The concentration of 10 μM corresponds to 0.2 molecular equivalents to the total concentration of **TbL**$^+$. By considering that ATP would bind only to **TbL**$^+$ receptors self-assembled on the outer surface of aqueous vesicles, the molar composition on the vesicle surface is estimated as **TbL**$^+_{\text{vesicle surface}}$/ATP ≈ 3:1. Formation of this $[TbL^+]_3$(ATP) complex was supported by ESI-MS measurement (Figure S5, Supporting Information). The binding of ATP to **TbL**$^+$ vesicles was also confirmed by changes in zeta potential (Figure S6 in Supporting Information). The zeta potential obtained for **TbL**$^+$ vesicles (ζ, +6.89 mV) showed pronounced decrease upon the addition of ATP, and reached a lowest ζ value of −41.3 mV above the ATP concentration of ∼10 μM. This threshold coincides with that observed for the ATP-induced increase in luminescence intensity (Figure 3), which supports binding of ATP molecules on outer vesicle surfaces. The evidence for outer vesicle surface-binding model was further provided by luminescence titration experiments conducted for molecularly dispersed **TbL**$^+$ in HEPES buffer/THF (40 vol%) (Figure S12, Supporting Information). Although such a quantitative binding of ATP could reduce the surface charge of **TbL**$^+$ vesicles, morphology of these vesicles were stably maintained after the addition of ATP, as confirmed by DLS and TEM measurements (Figure S7, Supporting Information). In the case of ADP, increase in the luminescence intensity was also observed, while the enhancement is only half of that observed for ATP. The luminescence intensity attained a maximum at higher nucleotide concentration of ∼13 μM, which is consistent with the less number of negative charges on ADP. Meanwhile it is noticeable that luminescence intensity profiles in the presence of ATP and ADP (Figure 3) show sigmoidal curvature against the concentration of nucleotides, which indicate cooperative binding. The observed changes in luminescence intensity were analyzed by using the Hill equation (Figures S8 and S9, Supporting Information). The Hill coefficient (n) reflects the extent of cooperativity among multiple binding sites and those determined for ATP/**TbL**$^+$ and ADP/**TbL**$^+$ systems are 2.4 and 2.3, respectively (Table S1, Supporting Information). The n values greater than one indicate positive cooperative effect, that is, the binding of phosphate groups in ATP or ADP occur cooperatively on the surface of **TbL**$^+$ vesicles. This is further supported by the Scatchard plots constructed for the binding of ATP and ADP to aqueous **TbL**$^+$ vesicles (Figure

S10, Supporting Information). These plots possess maxima which are consistent with the positively cooperative binding.[12] The apparent binding constant (K_a) obtained for the combination of ATP/**TbL**$^+$ ($4.37 \times 10^4\ M^{-1}$) reveal strong interactions between ATP and **TbL**$^+$ complexes self-assembled on the surface of vesicles, and is larger than that observed for ADP/**TbL**$^+$ ($1.78 \times 10^4\ M^{-1}$). On the other hand, the addition of aqueous AMP caused only slight increase in the luminescence intensity of **TbL**$^+$ vesicles (Figure 3b), reflecting weak interaction without cooperativity (the Hill coefficient estimated as $n \approx 1$).

The cooperative binding of ATP and ADP and selectivity observed for ATP require preorganization of **TbL**$^+$ receptor molecules. When vesicle structures are disrupted by addition of 40 vol% THF, luminescence intensity changes I/I_0 upon addition of ATP or ADP showed only monotonous increases (Figure S12 in Supporting Information). The sigmoidal curves and selectivity observed in aqueous vesicles were lost in the HEPES/THF mixture. Thus, cooperativity and selectivity are not observed for molecularly dispersed receptors but they immerge only when receptors self-assemble to form supramolecular interfaces.

It was also confirmed that nonionic adenosine showed almost no influence on the emission intensity of **TbL**$^+$ (Figure 3b). These data indicates that the presence of tri- or diphosphate groups linked by phosphoanhydride bonds is prerequisite to the sigmoidal enhance luminescence intensity of **TbL**$^+$ vesicles. This is further supported by the effect of inorganic triphosphate and diphosphate anions on the luminescence intensity of **TbL**$^+$ (Figure S13, Supporting Information). The inorganic phosphtates enhanced luminescence intensity of **TbL**$^+$ vesicles, in the order triphosphate > diphosphate > monophosphate. It is however noticeable that the addition of ATP and ADP to **TbL**$^+$ vesicles showed slightly larger normalized luminescence intensities I/I_0 compared to those observed for inorganic phosphates [ATP (maximum I/I_0 value, 1.54), ADP (1.32), AMP (1.07); triphosphate (1.42), diphosphate (1.25), monophosphate (1.07)]. Therefore, the presence of ribose and nucleobase in ATP and ADP seems to provide additional interactions which promote their binding to the vesicular receptors. This effect was however negligible for AMP, since it showed the same degree of intensity changes as observed for monophosphate. To check specificity of the current vesicular receptors to phosphate anions, various mono- and divalent anions such as F^-, Br^-, I^-, NO^{3-}, CH_3COO^-, ClO_4^-, CO_3^{2-}, and SO_4^{2-} were added to aqueous **TbL**$^+$ vesicles (Figure S14, Supporting Information). As a result, significant changes were not observed in the emission intensity of **TbL**$^+$ vesicles upon addition of these anions. It supports that the luminescence of **TbL**$^+$ vesicles is selectively amplified for high energy phosphate anions linked in series by phosphoanhydride bonds.

As described previously, the luminescence of **TbL**$^+$ complex is quenched to a certain level by the energy transfer from excited state of Tb^{3+} to the higher O−H vibration overtones of coordinating water. In this case, the luminescence lifetime of **TbL**$^+$ complex will be increased by replacing coordinating H_2O molecules with D_2O. The number of water molecules coordinating to Tb^{3+} ion in the first coordination sphere, is represented by a q value, which can be estimated by using the eq 1.[13]

$$q = 5.0 \times (K_{H_2O} - K_{D_2O} - 0.06) \quad (1)$$

Here, K_{H_2O} and K_{D_2O} represent the rate constants of luminescence decay, which are measured in H_2O and D_2O, respectively (the decay curves are shown in Figure S15 in Supporting Information). In the case of **TbL**$^+$ complex, its luminescence lifetime in H_2O (τ = 1.16 ms) is considerably shorter than that observed in D_2O (τ = 1.72 ms), which supports the quenching mechanism described above. The q value was determined as 1.1 (Table 1), indicating that almost one water molecule is coordinated to the **TbL**$^+$ complex in water. In contrast, luminescence decay measurements for [TbL]Cl in the presence of ATP gave longer luminescence lifetimes of 2.53 ms in H_2O and 3.54 ms in D_2O, which are consistent with the observed increase in luminescence intensity. A q value of 0.26 was obtained in the presence of ATP (Table 1), and it is obvious that the number of coordinating water molecules is reduced as a consequence of the replacement by triphosphate groups (Figure 1).

Table 1. Luminescence Lifetime τ and Rate Constants k Determined for [TbL]Cl in H_2O and D_2O, in the Presence or Absence of ATP[a]

samples	τ (ms)	k (ms^{-1})	q
[TbL]Cl(H_2O)	1.16	0.86	1.11
[TbL]Cl(D_2O)	1.72	0.58	
[TbL]Cl+ATP(H_2O)	2.53	0.40	0.26
[TbL]Cl+ATP(D_2O)	3.54	0.28	

[a] q values were calculated according to the eq 1.

In conclusion, we have developed a novel amphiphilic receptor **TbL**$^+$ complex which spontaneously self-assembles in water and form stable vesicles. The aqueous vesicles of **TbL**$^+$ complexes show luminescence in water as a consequence of energy transfer from the coordinating bis(pyridine) units to Tb^{3+} ion. Upon addition of varied nucleotides, sigmoidal increase in luminescence intensity was observed for ATP, followed by ADP whereas almost no enhancement was observed for AMP. The enhanced luminescence intensity is ascribed to the displacement of coordinating water molecules by the phosphate groups, as supported by the luminescence lifetime measurements. Importantly, such sigmoidal increase of luminescence intensity has not been observed for the structurally relevant water-soluble lanthanide complexes. A water-soluble Eu^{3+} complex with bis(bipyridylcarboxylate) arms showed luminescence of Eu^{3+} ions which was quenched upon coordination with ATP.[14] The two-dimensional self-assembly of receptor complexes play essential roles in the emergence of positive cooperative binding for nucleotides carrying high energy phosphate anions linked by phosphoanhydride bonds. The binding of **TbL**$^+$ complexes to each phosphate unit linked by phosphoanhydride bonds occur cooperatively, probably by adaptively changing their molecular orientation in the bilayer. They demonstrate synergistic interactions between highly organized receptors (**TbL**$^+$complex) at the membrane surface. Self-assembly of receptor molecules to form nanointerfaces thus open a new strategy to the recognition, conversion and amplification of molecular information. Together with adaptive self-assemblies formed in water from nucleotides and lanthanide ions,[5] we envisage these coordination nanointerfaces a wide range of applications including sensing and diagnostics.

EXPERIMENTAL SECTION

Materials. 6-Chloromethylpyridine-2-carboxylic acid ethyl ester was synthesized according to the reported method.[15] All the other chemicals were purchased and used as received. All solvents used are of analytical grade and used after purification by standard literature methods. Water was purified with Direct-Q system (Millipore Co.).

Characterization. Luminescence spectra were measured by using a PerkinElmer LS 55 fluorescence spectrometer. Luminescence decay curves were obtained by a streak camera (Hamamatsu, C4334) with a Nd:YAG laser (λ = 266 nm, LOTIS TII, LS-2132) as an excitation source. UV−vis absorption spectra were conducted on a JASCO V-550 spectrometer; DLS and Zeta potential measurements were conducted on the Malvern Zeta sizer Nano-ZS. ESI-MS spectrum was obtained for aqueous mixtures of [TbL]Cl and ATP by using a JMS-T100CS MS. Pure water was used as solvent to avoid any disturbance of HEPES salt to the ESI-MS measurement. In addition, 40% of THF was added to the mixture to reduce high surface energy of water. SEM and TEM were performed by Hitachi S-5000 (acceleration voltage, 10 KV) and JEOL JEM-2010 (acceleration voltage, 120 KV) respectively. For SEM and TEM measurement, the sample solution was drop coated on carbon-meshed copper grid. After 1 min, the excess solution was removed by using a filtration paper and the resultant grid was dried in vacuum. In TEM measurement, the grid was poststained with uranyl acetate. For SEM measurement, the sample was coated with Pt on HITACHI E-1030 ion sputter. In cryo-transmission electron microscopy (cryo-TEM) observation, the sample aqueous solution was drop cast onto a holey carbon TEM grid, held with a pair of forceps. Excess liquid was blotted a way by using a filter paper and the samples were plunged into cryo preparation chamber containing liquid nitrogen. The vitrified samples were transferred to the JEOL JEM-2010. The sample was observed at the acceleration voltage of 120 kv under working temperature below −170 °C.

■ ASSOCIATED CONTENT

Supporting Information. Synthesis of ligand, synthesis of [TbL]Cl, luminescence of **TbL**$^+$ complex and its composition, determination of CAC for [TbL]Cl, Cryo-TEM image of [TbL]Cl, the profile of zeta potential evolution, ESI-MS spectrum of [TbL]Cl/ATP, nucleotides binding studies, TEM and DLS measurement for ATP/**TbL**$^+$ vesicle, and luminescence lifetime measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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