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Luminescent Vesicular Nanointerface: A Highly Selective and Sensitive "Turn-On" Sensor for Guanosine Triphosphate

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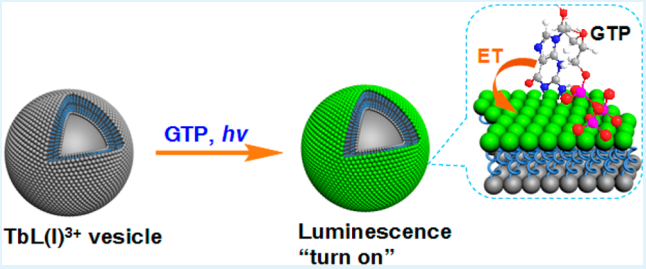
Supporting Information

ABSTRACT: A novel amphiphilic Tb^{3+} complex (TbL^{3+}(**I**)) consisting of a +3 charged head and a hydrophobic alkyl chain has been developed. It spontaneously self-assembles in water and forms stable vesicles at neutral pH. TbL^{3+}(**I**) has no aromatic groups (functioning as an antenna), and its intrinsic luminescence is thus minimized. These features lead to the self-assembling TbL^{3+}(**I**) receptor molecules demonstrating an increased luminescence intensity upon binding of nucleotides. Upon addition of guanosine triphosphate (GTP), the luminescence from Tb^{3+} was notably promoted (127-fold), as the light energy absorbed by the guanine group of GTP was efficiently transferred to the Tb^{3+} center. In the case of guanosine diphosphate (GDP) and guanosine monophosphate (GMP), respectively, 78-fold and 43-fold increases in luminescence intensity were observed. This enhancement was less significant than that observed for GTP, due to fewer negative charges on GDP and GMP. No other nucleotides or the tested nonphosphorylated nucleosides affected the luminescence intensity to any notable extent. In marked contrast, all tested nucleotides, including guanine nucleotides, barely promoted the luminescence of molecularly dispersed receptors, TbL^{3+}(**II**), indicating that the confinement and organization of molecules in a nanointerface play vital roles in improving the performance of a sensing system. This Tb^{3+} complex nanointerface is successfully used for monitoring the GTP-to-GDP conversion.



KEYWORDS: *nanointerface, molecular recognition, luminescent probes, terbium complex, nucleotides*

INTRODUCTION

The structure and functions of biomembranes are impressively exhibited in living organisms. In such cases, cell signaling is triggered by molecular recognition events on biological bilayer membranes, in which receptor proteins are embedded in the phospholipid matrix to form dynamically supramolecular assemblies and specifically bind the receptor ligands. The ligand−receptor interactions activate the signal transduction pathway and induce an amplification of the cell's response.[1,2] In this process, the preorganized supramolecular assemblies convert and amplify molecular information into other easily measured signals and play vital roles in cell signaling. Inspired by the versatile functions of biomembranes, chemists have focused on this research field, and remarkable progress has been achieved with synthetic bilayers.[3−11] However, most of this research still depends on natural surfactants or their related synthetic analogues, which form bilayer membranes integrating synthetic functional molecules.[5−11] It remains a challenge to develop signal-responsive nanointerfaces with excellent performance which could receive and convert biomolecular information efficiently into physicochemical outputs.

In this work, we have fabricated a luminescent vesicular nanointerface composed of an amphiphilic Tb^{3+} complex as a "turn on" luminescence probe, which could recognize not only the different types of nucleotides but also the closely related phosphorylated guanosines. To improve the sensing performance, the complex TbL^{3+}(**I**) (Figure 1) was designed on the basis of the following considerations: (1) The cyclen (1,4,7,10-tetraazacyclododecane) derivative was introduced into the ligand since it can form a very stable equivalent +3 charged lanthanide complex,[12] thereby enabling electrostatic attraction with, and differentiation of, the nucleotides. (2) Tb^{3+} was chosen for its desirable emission characteristics, such as a long luminescence lifetime, large Stokes shift, and narrow emission bands, etc.[13] These complexes have no aromatic moieties that could function as an antenna, and their intrinsic luminescence is thus minimized. When antenna molecules bind to TbL^{3+}(**I**) through the phosphate group, the emission from Tb^{3+} significantly increases. Such a mechanism may enable the detection of phosphorylated guanosines (purine nucleobase as the antenna) by an increased luminescence intensity. (3) To endow TbL^{3+}(**I**) with a self-assembly property, a hydrophobic alkyl chain was incorporated into the ligand.

GTP is a nucleotide involved in RNA synthesis as well as the citric acid cycle, and it acts as an energy source for protein synthesis.[14] Although fluorescent and colorimetric sensors for

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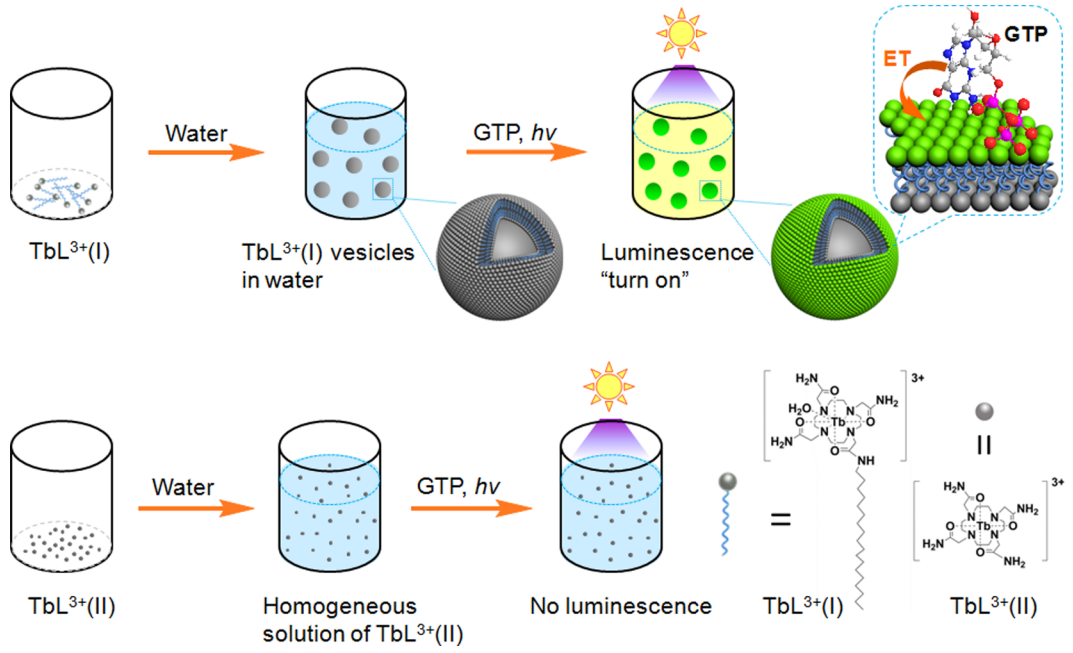

Figure 1. Self-assembly behavior of TbL^{3+}(**I**) and TbL^{3+}(**II**) complexes in H_2O and with binding to GTP molecules.

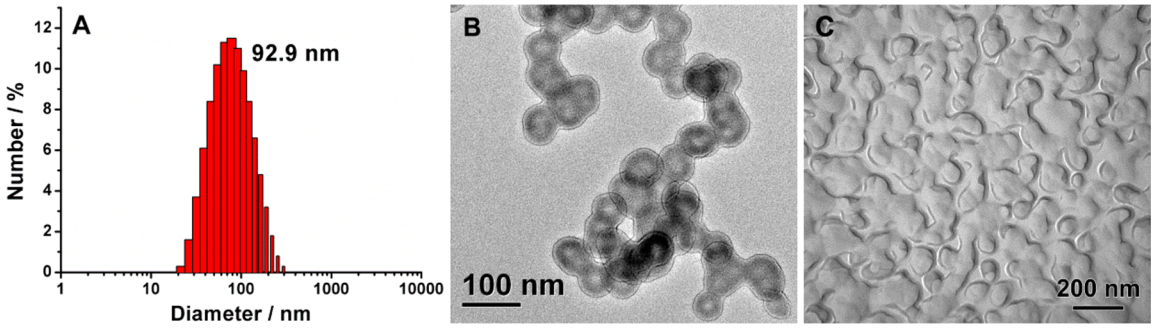

Figure 2. Particle size distribution (A), TEM image (B), and FF-TEM image (C) of TbL^{3+}(**I**). The concentration of TbL^{3+}(**I**) was 100 μM in 10 mM HEPES buffer (pH 7.0).

GTP have been extensively developed,[15−24] their ability to self-assemble into stimulus-responsive nanointerfaces is limited. Moreover, their ability to efficiently recognize nucleotides is not very strong. The confinement and organization of molecules in a nanointerface provides an attractive strategy toward this issue. The multi-interaction between preorganized receptors and biomolecules with multiple binding sites would impart the sensing system high selectivity and sensitivity for the adaptation of aligned receptors. These distinctive properties give the nanointerface an inherent capability to convert and boost molecular signals.

RESULTS AND DISCUSSION

Ligand **I** and complex TbL^{3+}(**I**) were synthesized and purified according to the method presented in the Supporting Information (Figure S1). To study the self-assembly properties of TbL^{3+}(**I**), the surface tension (γ) was measured as a function of the concentration of TbL^{3+}(**I**). This enabled determination of its critical aggregation concentration (CAC) in HEPES buffer (10 mM, pH 7.0).[25,26] There were two linear segments in the γ versus C curve and a sudden reduction in the slope, implying that the CAC is 47 μM (Figure S2, Supporting Information). However, the γ value of molecularly dispersed TbL^{3+}(**II**)[27] remained almost unchanged over the whole concentration range. The aggregation behavior of TbL^{3+}(**I**) in water was then investigated using dynamic light scattering (DLS), transmission electron microscopy (TEM), and freeze-fracture transmission electron microscopy (FF-TEM). The DLS experiment was conducted in a 100 μM aqueous solution of TbL^{3+}(**I**), and TbL^{3+}(**I**) was seen to form spherical nanoparticles with an average diameter of 92.9 nm (Figure 2A). These structures are typical of bilayer vesicles and were verified by TEM and FF-TEM observations (Figure 2B,C, diameter range 50−100 nm). The diameter of the vesicles was identical with the findings from the DLS measurement. Critical packing parameter (cpp) calculation data also supported the results from the above-mentioned experiments. The cpp value of TbL^{3+}(**I**) was 0.84, corresponding to a vesicle structure ($1/2 < cpp < 1$; see the Supporting Information for details).[28] Apparently, TbL^{3+}(**I**) spontaneously formed stable vesicles in H_2O.

The photophysical characteristics of TbL^{3+}(**I**) vesicles were studied in HEPES buffer (10 mM, pH 7.0). Addition of GTP to the aqueous dispersion of TbL^{3+}(**I**) gave bright green luminescence under UV irradiation (Figure S4, Supporting Information). In the emission spectrum, luminescence peaks were observed at 495 nm ($^5D_4 \rightarrow {}^7F_6$), 545 nm ($^5D_4 \rightarrow {}^7F_5$),

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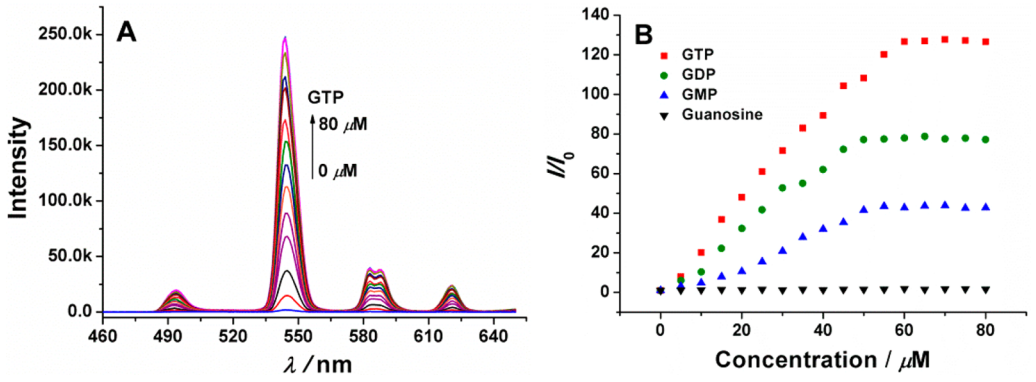

Figure 3. Luminescence spectra of TbL^{3+}(**I**) in the absence and presence of GTP (A). I/I_0 evolution of TbL^{3+}(**I**) with increasing concentration of biomolecules (B). The concentration of TbL^{3+}(**I**) was 100 μM in 10 mM HEPES buffer (pH 7.0), and λ_{ex} = 255 nm.

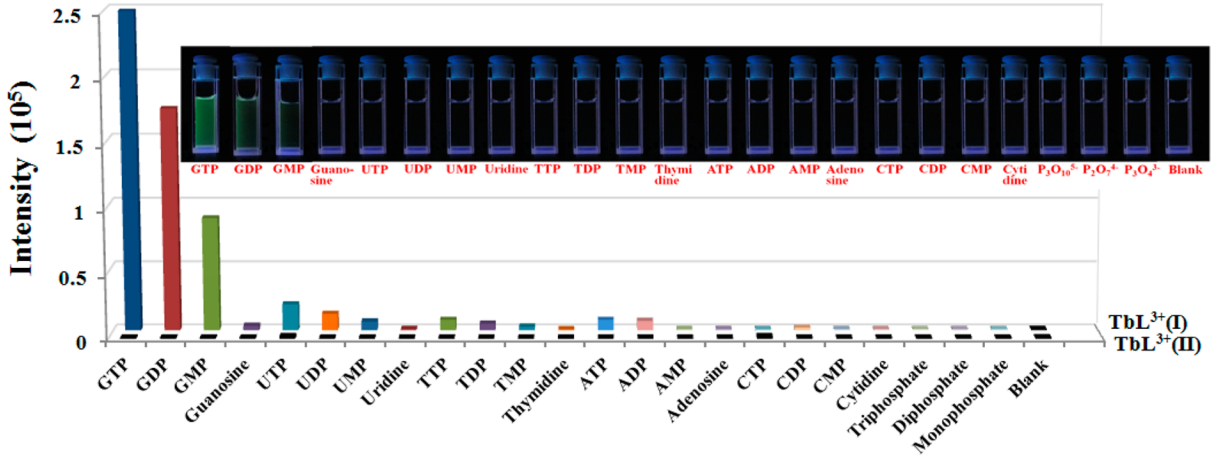

Figure 4. Luminescence response of TbL^{3+}(**I**) and TbL^{3+}(**II**) to various biomolecules. The concentration of TbL^{3+}(**I**) and TbL^{3+}(**II**) was 100 μM in HEPES buffer (10 mM, pH 7.0). The concentration of anions was 60 μM. λ_{ex} = 255 nm. Inset: photographs of the aqueous solutions of TbL^{3+}(**I**) in the presence and absence of various biomolecules under a 254 nm ultraviolet lamp.

586 nm ($^5D_4 \rightarrow {}^7F_4$), and 621 nm ($^5D_4 \rightarrow {}^7F_3$), with the 545 nm band demonstrating the highest intensity. These bands are characteristic of the Tb^{3+} ion.[29,30] As neither GTP nor TbL^{3+}(**I**) alone gives any luminescence under the same conditions (Figure S4), the observed luminescence was sensitized by the binding GTP molecules. This was proved by the excitation spectrum monitored at 545 nm, which showed a peak assigned to the guanine unit at 272 nm. The ability of TbL^{3+}(**I**) vesicles to interact with nucleotides and their effect on the luminescence properties of TbL^{3+}(**I**) were further investigated. Very interestingly, the successive additions of GTP in buffer resulted in a regular enhancement in luminescence intensity as displayed in Figure 3A. A 127-fold increase was observed when GTP was added beyond a concentration of ~60 μM (Figure 3B), which leads to an efficient detection of GTP through a "turn-on" luminescence. Moreover, an 8-fold enhancement in luminescence intensity was obtained even at a GTP concentration of 5 μM, which represents the most efficient detection of GTP currently.[15−24] A concentration of 60 μM represents 0.6 molecular equivalent of the total concentration of TbL^{3+}(**I**). In view of the fact that GTP binds only to TbL^{3+}(**I**) receptors that are aligned on the outer layer of vesicles, the molar composition on the vesicle surface was assessed as $TbL^{3+}(\mathbf{I})_{\text{vesicle surface}}$/GTP ≈ 1/1. The binding of GTP to TbL^{3+}(**I**) vesicles was also supported by changes in the ζ potential (Figure S5, Supporting Information). The ζ potential measured for TbL^{3+}(**I**) vesicles (ζ = +50.6 mV) showed a marked decrease with increasing concentration of GTP and presented a slow and gradual decline above a GTP concentration of ~69 μM, reaching a lowest ζ value of −3.01 mV. This threshold almost coincided with that obtained in the luminescence studies (Figure 3B) and supports the idea that GTP molecules were bound on the outer surface of the vesicle. Although such a quantitative binding of GTP could reduce the surface charge of TbL^{3+}(**I**) vesicles, the morphology of these vesicles was still kept after introduction of GTP to the TbL^{3+}(**I**) solution, as proved by DLS measurements and TEM analysis (Figure S6, Supporting Information). For GDP and GMP, an increase in the luminescence intensity was also seen, although the enhancement was less significant than that observed for GTP. Approximately 78- and 43-fold enhancements were obtained for GDP and GMP (Figure 3B), respectively, at a nucleotide concentration of ~60 μM, which is congruent with the fewer negative charges on GDP and GMP. The apparent binding constant (K_a) obtained for the combination of GTP/TbL^{3+}(**I**) (4.18×10^3 M^{-1}) revealed effective interactions between GTP and TbL^{3+}(**I**) aligned on the surface of vesicles and was larger than that obtained for GDP/TbL^{3+}(**I**) (3.37×10^3 M^{-1}). It was also proved that nonionic guanosine had almost no effect on the emission intensity of TbL^{3+}(**I**) (Figure 3B). These results indicate that the positive charge of the probe enabled electrostatic attraction and differentiation of the

nucleotides. In contrast, the influence of inorganic triphosphate and diphosphate anions on the luminescence intensity of TbL^{3+}(**I**) was negligible (Figure 4). Apparently, both the affinity of TbL^{3+}(**I**) for its substrate and the ability of the substrate to sensitize the luminescence of TbL^{3+}(**I**) played important roles in the selectivity of the assay.

To verify the specificity of the current vesicular receptors to guanine nucleotides, other nucleotides such as ATP, ADP, AMP, UTP, UDP, UMP, TTP, TDP, TMP, CTP, CDP, and CMP were added to the aqueous TbL^{3+}(**I**) vesicles. However, no significant changes in the emission intensity of TbL^{3+}(**I**) vesicles were observed upon addition of these nucleotides (Figure 4), which illustrates that the luminescence of TbL^{3+}(**I**) vesicles was selectively amplified by the series of guanine nucleotides, attributed to the unique energy transfer between the guanine-containing nucleotides and Tb^{3+} due to the different electronic properties of the bases.[31,32] In marked contrast, all tested nucleotides, including guanine nucleotides, hardly promoted the luminescence of molecularly dispersed TbL^{3+}(**II**) (Figures 4 and 5), which powerfully supports the

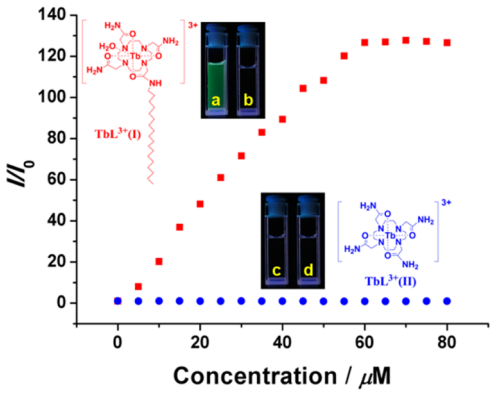

Figure 5. I/I_0 evolution of TbL^{3+}(**I**) and TbL^{3+}(**II**) as a function of the concentration of GTP. Inset: photographs of the aqueous solutions of (a) TbL^{3+}(**I**) + GTP, (b) TbL^{3+}(**I**), (c) TbL^{3+}(**II**) + GTP, and (d) TbL^{3+}(**II**), respectively, under a 254 nm ultraviolet lamp. The concentration of TbL^{3+}(**I**) and TbL^{3+}(**II**) was 100 μM in 10 mM HEPES buffer (pH 7.0), and λ_{ex} = 255 nm.

idea that the interface plays a vital role in improving the performance of the sensing system. The confinement and organization of molecules in a membrane gives rise to high local concentrations that are very unusual in homogeneous solutions,[5] which could greatly promote the efficiency of the energy transfer between the substrate and the acceptor on the membrane.

To understand the manner of the interactions between TbL^{3+}(**I**) and GTP, the number of H_2O molecules coordinating to Tb^{3+} was estimated according to the details described in the Supporting Information. The experiment results show that about one H_2O molecule coordinates to TbL^{3+}(**I**) in aqueous solution. The q value (number of H_2O molecules) has almost no change after the addition of GTP. Obviously, no ligand exchange occurred with the coordination water during the binding of GTP to the Tb^{3+} complex.[3,33]

To monitor the GTP-to-GDP conversion, the luminescence emission spectra of TbL^{3+}(**I**) in the presence of varying GTP/GDP ratios were recorded (Figure 6). As the GTP/GDP ratio decreased, the luminescence intensity of terbium at 545 nm declined. It can thus be employed for the continuous

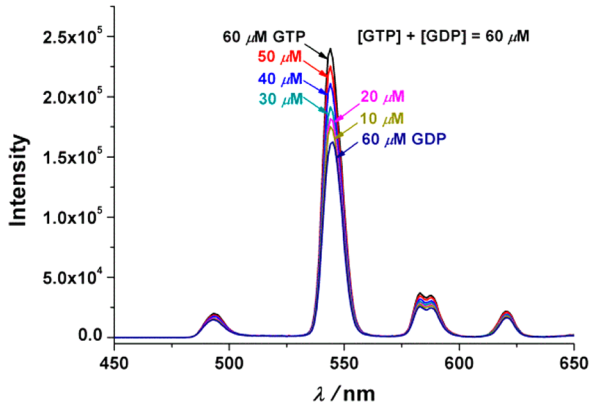

Figure 6. Ratiometric determination of GTP-to-GDP conversion: luminescence spectra of TbL^{3+}(**I**) in the presence of varying GTP/GDP ratios. The concentration of TbL^{3+}(**I**) was 100 μM in 10 mM HEPES buffer (pH 7.0). [GTP] + [GDP] = 60 μM, and λ_{ex} = 255 nm.

monitoring of some important biological processes, i.e., signal transduction, citric acid cycle, etc.

CONCLUSION

We have here presented a luminescent nanointerface composed of an amphiphilic Tb^{3+} complex as a novel sensing system. The fascinating functional feature of this vesicular nanointerface is that it can selectively and sensitively convert and amplify biomolecular information to the turn-on luminescence through an energy transfer between the Tb^{3+} complex on the outer vesicle surface and the substrate. The luminescence from Tb^{3+} was notably promoted by GTP, followed by GDP and GMP, whereas almost no enhancement was observed for other nucleotides and the nonphosphorylated nucleosides. In marked contrast, all tested nucleotides, including guanine nucleotides, only barely promoted the luminescence of molecularly dispersed receptors, TbL^{3+}(**II**), which reveals that the confinement and organization of molecules in a nanointerface endows the nanointerface with excellent sensing performance. A nanointerface self-assembled with low molecular mass receptors would be a new strategy to convert molecular information efficiently to physicochemical signals.

EXPERIMENTAL SECTION

Materials. All chemicals were purchased and used as received. All solvents were purified according to literature procedures. Water was purified with the Direct-Q system (Millipore Co.).

Characterization. Luminescence spectra were obtained on a time-correlated single-photon-counting fluorescence spectrometer (Edinburgh Instruments Ltd. FLS 920). The luminescence lifetime was measured by the above fluorescence spectrometer with a μF900 lamp as the excitation source. The particle size distribution and ζ potential determination were performed on a Malvern Zetasizer Nano-ZS90. TEM images were observed by a JEOL JEM-2010 (acceleration voltage 120 kV). The TEM grid was prepared according to the previously reported method and analyzed without staining.[3] For the FF-TEM analysis, the fracturing and replication were carried out in a freeze-fracture apparatus (Hitachi HU-5JB, Japan) at −170 °C. Pt/C was deposited at an angle of 45° to shadow the replicas, and C was deposited at an angle of 90° to consolidate the replicas. The resultant replicas were examined in a Hitachi H-7650 transmission electron microscope (acceleration voltage 80 kV).

■ ASSOCIATED CONTENT

Supporting Information

Synthesis of ligand **I** and $[TbL(\mathbf{I})]Cl_3$, determination of CAC for $[TbL(\mathbf{I})]Cl_3$, calculation of the cpp value, photophysical characteristics of $TbL^{3+}(\mathbf{I})$, profile of the ζ potential evolution, TEM analysis and DLS measurements for GTP/$TbL^{3+}(\mathbf{I})$ vesicles, and determination of the number of coordinated waters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

GTP = guanosine triphosphate
GDP = guanosine diphosphate
GMP = guanosine monophosphate
ATP = adenosine triphosphate
ADP = adenosine diphosphate
AMP = adenosine monophosphate
UTP = uridine triphosphate
UDP = uridine diphosphate
UMP = uridine monophosphate
TTP = thymidine triphosphate
TDP = thymidine diphosphate
TMP = thymidine monophosphate
CTP = cytidine triphosphate
CDP = cytidine diphosphate
CMP = cytidine monophosphate

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