Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Sensing of Fluoride Ions in Aqueous Media Using a Luminescent Coordination Polymer and Liposome Composite

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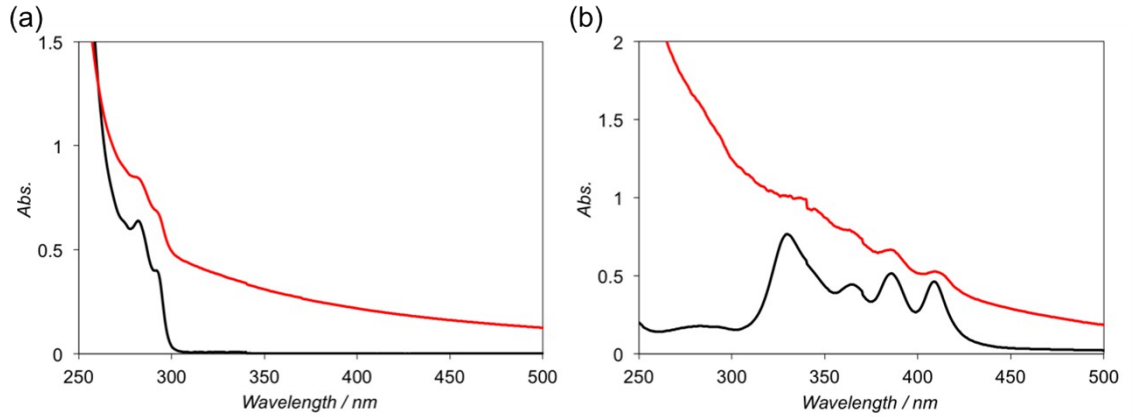

Fig. S1 UV-vis spectra of (a) BTC (black) and BTC@Lipo (red), and (b) AmB (black) and **Tb-BTC@Lipo** (red) in 20 mM HEPES pH 7.0.

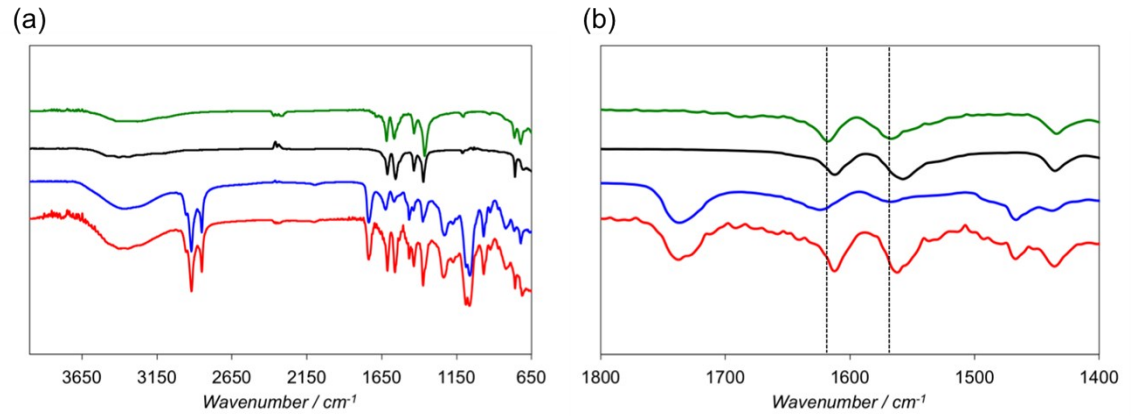

Fig. S2 (a) and (b) ATR-FTIR spectra of Na_3BTC (green), **Tb-BTC** bulk (black), BTC@Lipo (blue), and **Tb-BTC@Lipo** (red). The characteristic absorptions of the symmetric and asymmetric vibrations of coordinated carboxylate groups with peaks at 1651–1597 and 1631–1580 cm^{-1} respectively. The shift of these peaks is attributed to the coordination of Tb^{3+} ions.

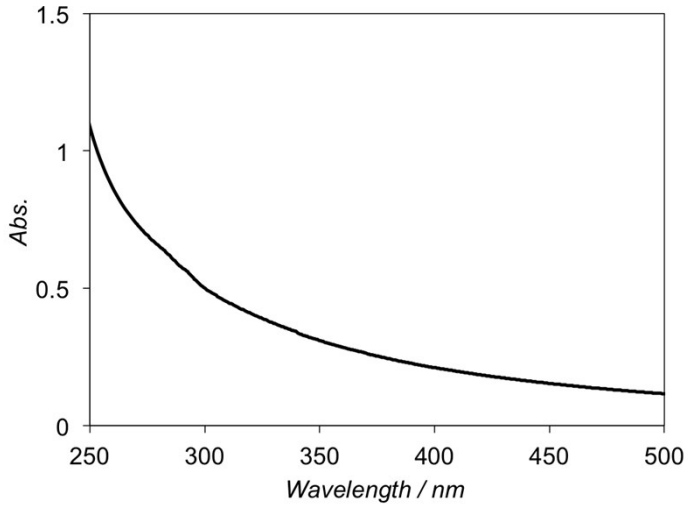

Fig. S3 UV-vis spectrum of BTC@Lipo without DOPE-PEG_{2000} ([phospholipid]=0.5 mM)

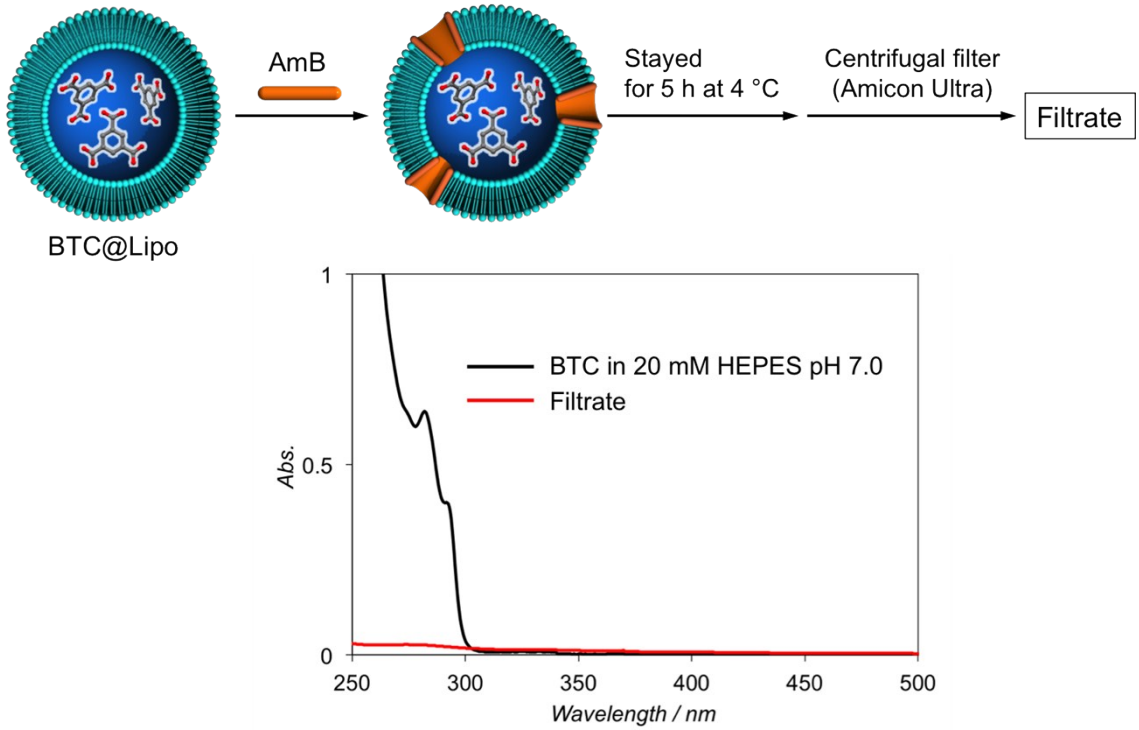

Fig. S4 BTC^{3-} ion leakage experiment. The mixture of BTC@Lipo and AmB was stayed for 5 h at 4 °C, and then BTC@Lipo including AmB was separated by centrifugal filter (Amicon Ultra). The filtrate was collected for the measurement of the UV-vis spectrum.

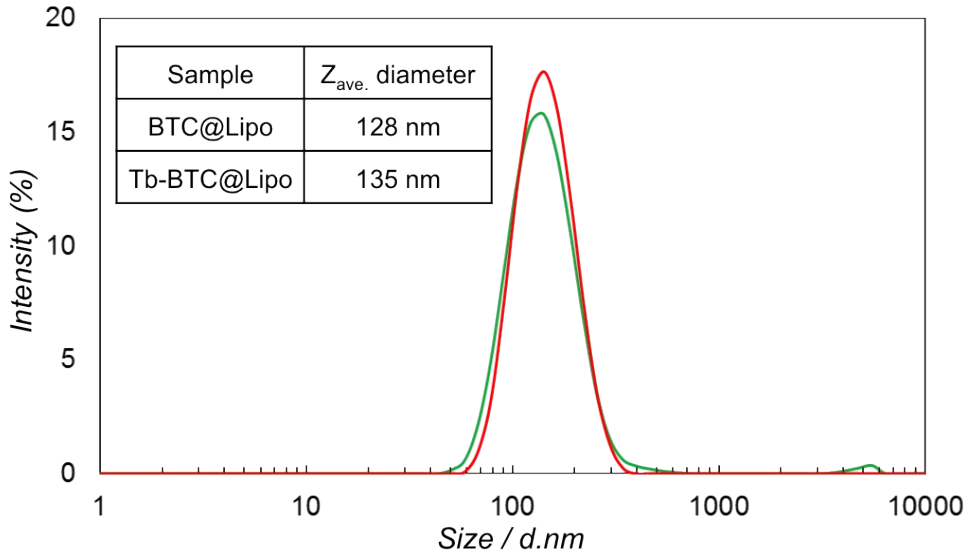

Fig. S5 Dynamic light-scattering spectra of BTC@Lipo (green) and **Tb-BTC@Lipo** (red).

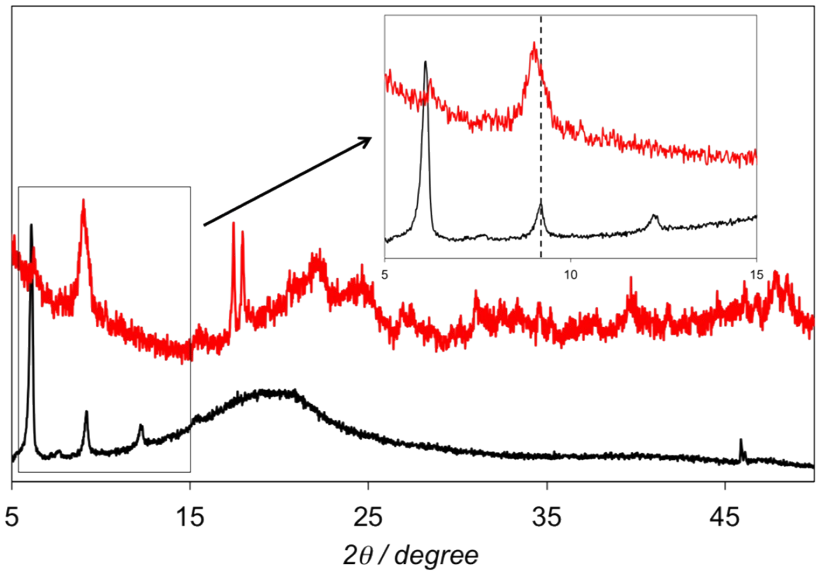

Fig. S6 PXRD patterns of **Tb-BTC@Lipo** (red), and BTC@Lipo (black).

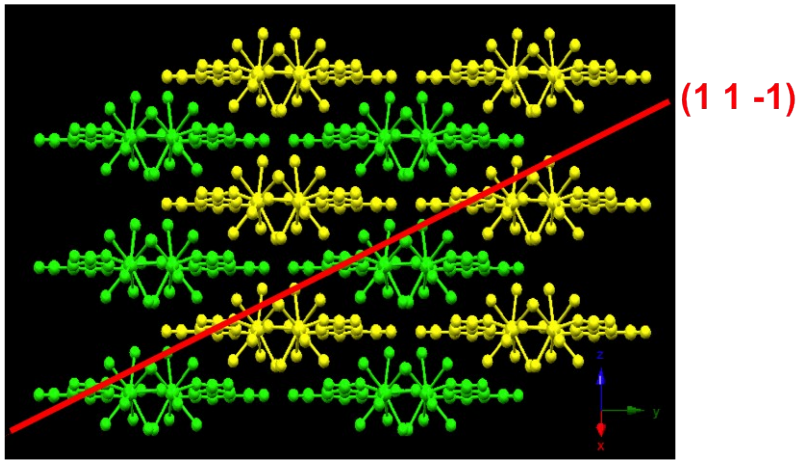

Fig. S7 Crystal Packing of [Tb(1,3,5-BTC)·6H_2O] showing (11–1) plane.

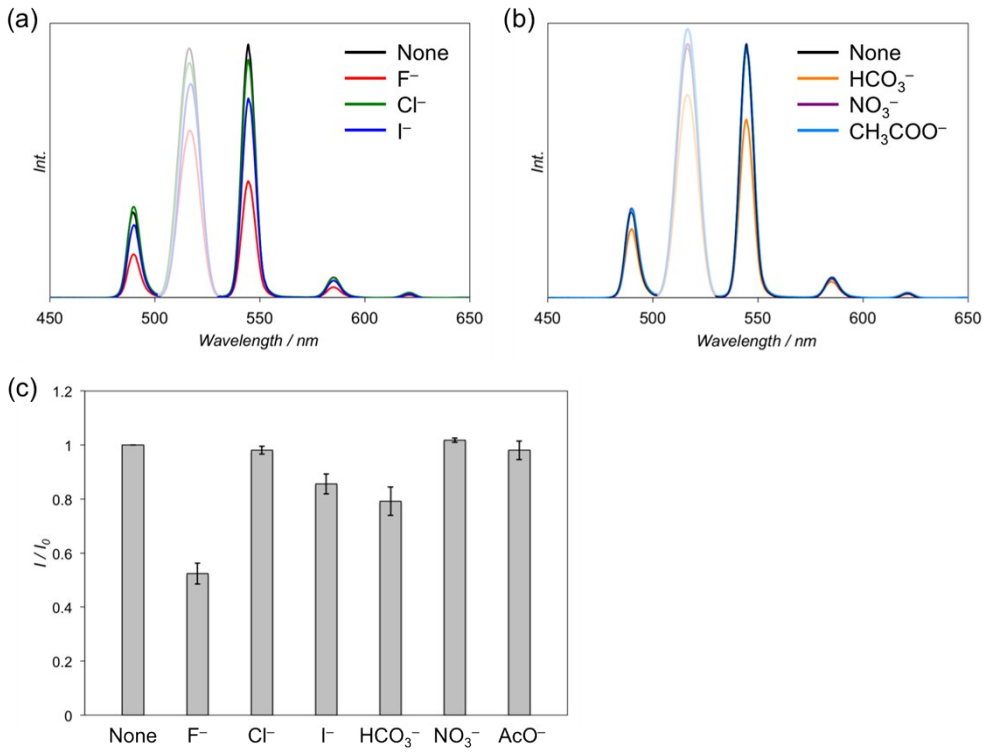

Fig. S8 Fluorescence spectra (λ_{ex} = 260 nm) after 10 h incubation of **Tb-BTC** bulk (20 mM HEPES buffer pH 7.0) at 12 °C with (a) NaF, NaCl and NaI, and (b) $NaHCO_3$, $NaNO_3$ and CH_3COONa. Reaction Conditions: [Tb] = 0.1 mM and [NaX] = 2 mM. (c) Relative fluorescence intensity at 545 nm (I/I_0). I_0 and I are the fluorescence intensities in the absence and presence of anions, respectively.

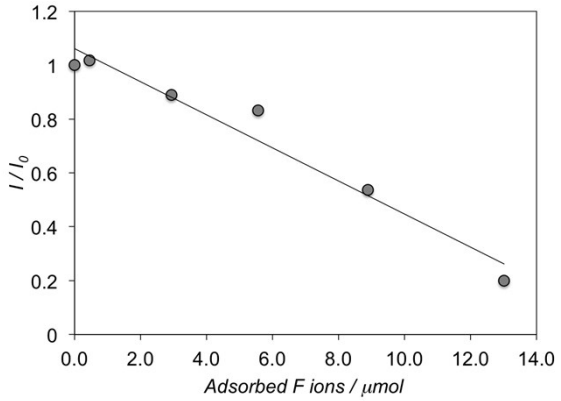

Fig. S9 Relative fluorescence intensity at 545 nm (I/I_0) of **Tb-BTC** bulk (λ_{ex} = 260 nm) *vs* adsorbed F ions (μmol). Reaction Conditions: [Tb] = 0.1 mM and [NaF] = 0 – 3 mM, incubation for 10 h at 12 °C. The adsorbed F ions were calculated from the F ion concentration in the supernatant of each sample. F ion concentration was determined using a fluoride ion monitor.

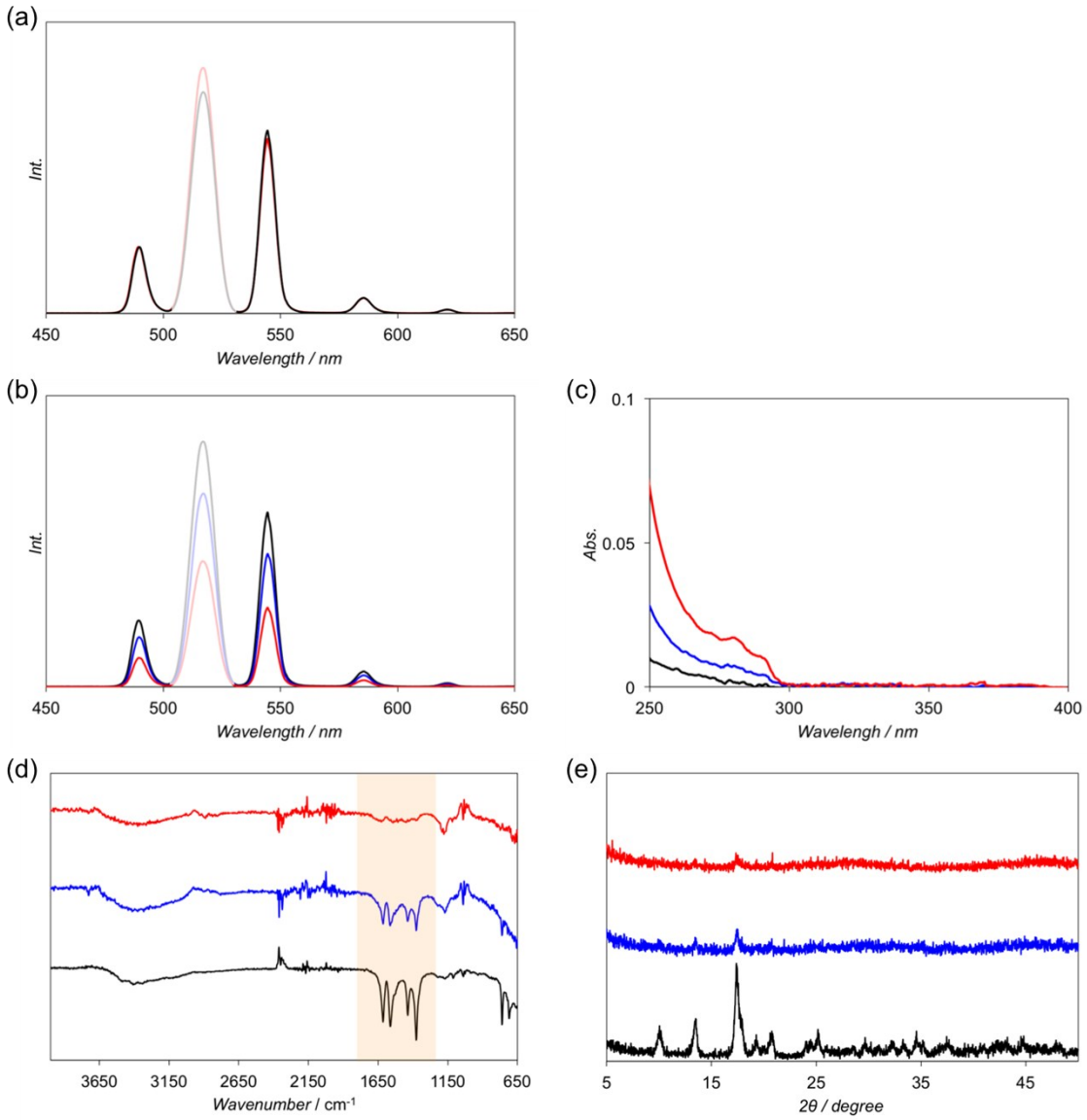

Fig. S10 (a) Fluorescence spectra (λ_{ex} = 260 nm) of **Tb-BTC** bulk before (black) and after (red) 10 h incubation at 12 °C in 20 mM HEPES buffer pH 7.0. (b) Fluorescence spectra (λ_{ex} = 260 nm), (c) UV-vis spectra, and (d) ATR-FTIR spectrum, and (e) XRPD patterns of **Tb-BTC** bulk after 10 h incubation at 12 °C in the absence and presence of NaF (20 mM HEPES buffer pH 7.0). Concentration ratio; [**Tb-BTC** bulk]:[NaF] = 1:0 (black), 1:10 (blue) and 1:20 (red).

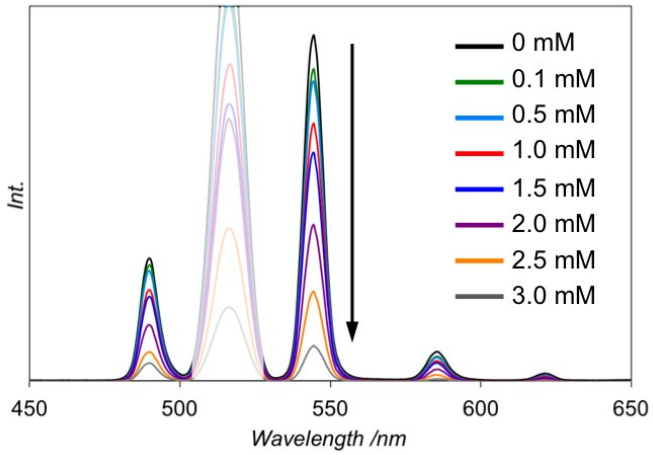

Fig. S11 Fluorescence spectra (λ_{ex} = 260 nm) of **Tb-BTC** bulk in 20 mM HEPES buffer pH 7.0 after 10 h incubation with various concentaraions of NaF at 12 °C ([Tb] = 0.1 mM).

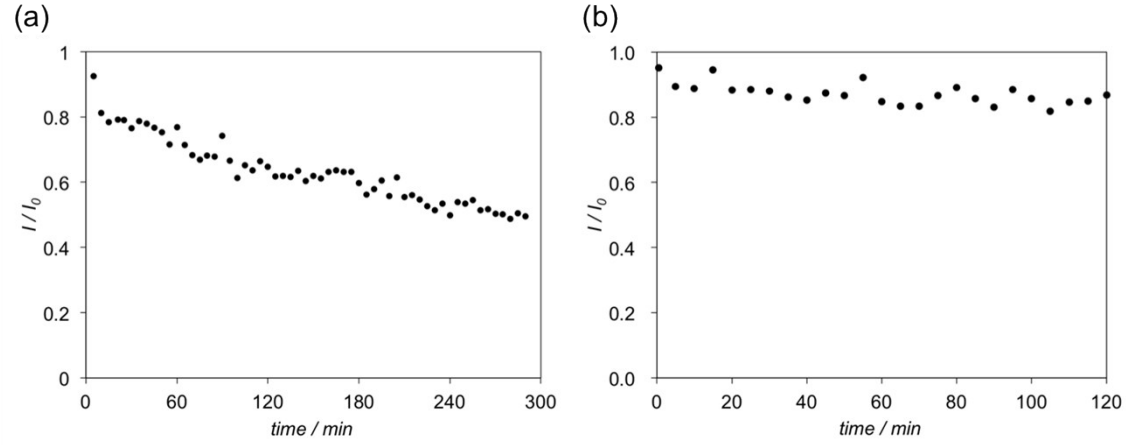

Fig. S12 Time-dependent fluorescence quenching of (a) **Tb-BTC@Lipo**, and (b) **Tb-BTC** bulk by F^- ion ([Tb] = 0.1 mM, [NaF] = 0.5 mM). Plots of the relative fluorescence intensity (I/I_0) versus time. I_0 and I are the fluorescence intensities at 545 nm in the absence and presence of NaF, respectively.

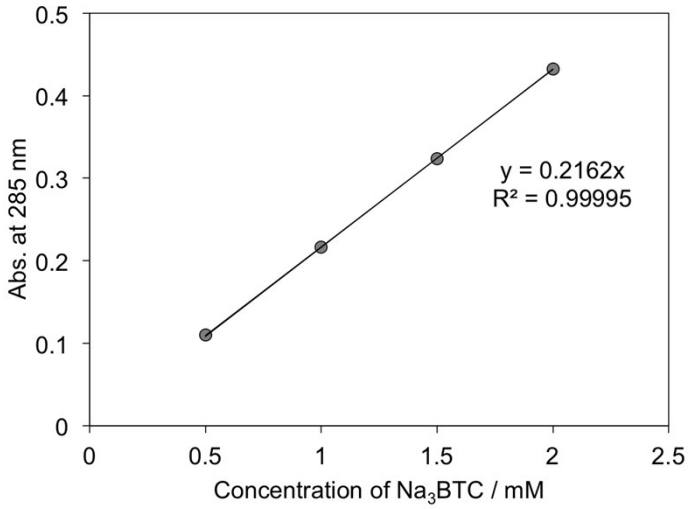

Fig. S13 Standard curve of Na_3BTC in 20 mM HEPES buffer pH 7.0.

Materials

Reagents were purchased from Wako, TCI, Nacalai Tesque and Sigma-Aldrich, and used without further purification. 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine -N-[methoxy(polyethylene glycol)- 2000] (ammonium salt) (DSPE-PEG2000), 1,2-di-(9Z-octadecenoyl)-*sn*-glycero-3-phosphocholine (DOPC), and 1,2-dihexadecanoyl-*sn*-glycero-3- phosphocholine (DPPC) were purchased from Avanti Polar Lipids.

Synthesis of sodium salt of benzene-1, 3, 5-tricarboxylate (Na_3BTC)

525 mg of H_3BTC was added to 5.0 mL of 40 mg/mL NaOHaq. The mixture was stirred until white powder was dissolved. After adding 10 mL of ethanol, the mixture was stirred for another 30 min. White powder of Na_3BTC was collected by filtration, and washed with ethanol, and dried in vacuum.

Preparation of Na_3BTC encapsulated liposome (BTC@Lipo)

8.8 mg of DOPC, 8.2 mg of DPPC, 3.7 mg of cholesterol, and 3.6 mg of DOPE-PEG (2000) were dissolved in 2.0 mL of $CHCl_3$ in a round-bottomed flask. The lipids were dried under reduced pressure to form a thin film, and placed overnight in a vacuum desiccator to remove residual solvent. The resulting lipid film was hydrated in 4.0 mL of 11.7 mg/mL Na_3BTC in 20 mM HEPES buffer (pH 7.0) at 45 °C for 6 h. The suspension was vortexed and sonicated for 10 min. After 5 cycles of freezing and thawing, the liposome suspension was extruded 10 times through a 200 nm polycarbonate membrane. The Na_3BTC encapsulated liposome was purified by a Sephacryl S400 column (Pharmacia, Uppsala, Sweden) pre-equilibrated with 20 mM HEPES buffer (pH 7.0) to remove the untrapped Na_3BTC. Encapsulation of Na_3BTC into liposome was determined by UV-vis spectrum. The total concentration of phosphorus was determined by molybdenum blue method.[1, 2]

Preparation of Na_3BTC encapsulated liposome without DOPE-PEG (2000) (BTC@Lipo without DOPE-PEG_{2000})

BTC@Lipo without DOPE-PEG_{2000} was prepared by the same procedure as BTC@Lipo, except that lipid composition was DOPC (35 mol%), DPPC (35 mol%), and cholesterol (30 mol%).

Preparation of [$Tb(BTC)(H_2O)_6$] encapsulated liposome (Tb-BTC@Lipo)

$TbCl_3 \cdot 5H_2O$ in 20 mM HEPES buffer (pH 7.0), and Amphotericin B in DMSO were added to a BTC@Lipo suspension. Final concentrations of $TbCl_3 \cdot 5H_2O$,

Amphotericin B, and phospholipid are 5 mM, 5 μM and 2 mM, respectively. The reaction mixture was placed for 12 h at 4 °C, and then purified by a Sephadex G-25 column pre-equilibrated with 20 mM HEPES buffer (pH 7.0) to remove excess Tb^{3+} ions and AmB. The formation of Tb-BTC particles within liposome was identified with ATR-FTIR spectra, emission spectra, powder X-ray diffraction and transmission electron microscopy. Concentration of Tb^{3+} ions in samples was determined by an inductively coupled plasma mass spectrometry (ICP-MS, Aglient7500).

Concentration Determination of encapsulated BTC^{3-} ions in BTC@Lipo or BTC@Lipo without DOPE-PEG_{2000}

UV-vis spectra of BTC@Lipo or BTC@Lipo without DOPE-PEG_{2000} after destruction with ethanol were measured. The concentration of BTC^{3-} ions was determined from the standard curve of Na_3BTC (absorbance at 285 nm) in 20 mM HEPES buffer pH 7.0 (Fig. S13).

Determination of Tb^{3+} concentration of Tb-BTC@Lipo by ICP-MS

250 μL concentrated nitric acid was added to 50 μL Tb-BTC@Lipo. The mixture was heated at 150 °C for 15 min. After heating, the mixture was diluted with 750 μL milli-Q for ICP-MS measurement. The concentration of total Tb^{3+} ion in samples was determined by a calibration curve using the standards.

Synthesis of $[Tb(BTC)(H_2O)_6]$ bulk

$[Tb(BTC)(H_2O)_6]$ bulk was synthesized by mixing 83 mg Na_3BTC and 112 mg $TbCl_3 \cdot 5H_2O$ in 10 mL of 20 mM HEPES buffer (pH 7.0) at 27 °C for 12 h. The resulting precipitate was collected by centrifugation, and washed several times with the buffer.

Elucidation of the mechanism for the luminescence quenching of Tb-BTC bulk with the addition of F^- ions

Tb-BTC bulk suspension was mixed with F^- ions for 10 h at 12 °C in 20 mM HEPES buffer pH 7.0 (Final concentration ratios; [Tb-BTC bulk]:[NaF] = 1:0, 1:10 and 1:20). Then, fluorescence spectrum of the mixture was measured. The mixture was separated by centrifugation into precipitate and supernatant for the measurement of UV-vis, FT-IR, powder X-ray diffraction and transmission electron microscopy. Tb^{3+} concentration of the supernatant was determined by ICP-MS.

Crystallization of [Tb(BTC)(H_2O)$_6$]

NH_3 aq. (0.5 mL, 0.2 M), THF solution of H_3BTC (1 mL, 0.1M) and MeOH solution of $Tb(NO_3)_3$•$6H_2O$ (1 mL, 0.1 M) were layered in straight tube at room temperature. The single crystals of [Tb(BTC)(H_2O)$_6$] were formed after about a week.

Crystal Structure Analysis of [Tb(BTC)(H_2O)$_6$]

Single-crystal X-ray data were recorded on a Bruker SMART APEX II ULTRA CCD Diffractometer with confocal monochromated Mo-Kα radiation. The structure was solved by a direct method and refined by full-matrix leastsquares refinement using the SHELXL-2014/6 computer program. Hydrogen atoms of BTC were positioned geometrically and refined using riding models. The hydrogen atoms of coordinated water molecules were placed from the residual density map and calculation geometrically, and refined with some restrictions. (CCDC1499450)

Table S1 Crystal parameters

Temperature	223 K
Formula	$C_9H_{15}O_{12}Tb$
F. W.	474.13
Crystal system	Monoclinic
Space group	*C c*
a / Å	11.324(3)
b / Å	17.756(4)
c / Å	7.1389(17)
α / °	90
β / °	118.871(2)
γ / °	90
V / Å^3	1257.0(5)
Z	4
D / g cm^{-3}	2.505
R	0.0263
R_W	0.0575

Physical Measurements

UV-vis spectra were recorded on a spectrophotometer JASCO V-630 BIO using a quartz cuvette. ATR-FTIR spectroscopy was performed on a JASCO FT/IR-4200. For the ATR-FTIR measurement of liposome samples, liposomes were collected by centrifuge, and dropped on a ZnSe prism. Fluorescence spectra were recorded in the range from 450 to 650 nm (λ_{ex} = 260 nm) using a spectrofluorometer JASCO FP-8200. Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku Ultima IV over an angular range of 2θ = 3-50°. For the PXRD measurement, liposome samples, which were dialyzed against Milli-Q water, were collected by centrifuge, and dropped on a silicon plate and dried in a vacuum desiccator. The size distribution of liposomes was determined by dynamic light scattering (Zetasizer Nano ZS (Malvern)). Transmission electron microscopy images of samples were recorded on a JEM-2100HCKM microscope (200 kV).

References

(1) P. S. Chen, T. Y. Toribara, H. Warner, *Anal. Chem.,* **1956**, *28*, 1756-1758.
(2) C. H. Fiske, Y. Subbarow, *J. Biol. Chem.,* **1925**, *66*, 375-400.