Supporting Information

Luminescence switch based on the acid/base induced reversibility of covalent bonds in lanthanide(III) complexes

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Experimental Section

Infrared spectra were obtained using a JASCO FT/IR–4100 spectrophotometer. Elemental analyses were conducted using a J-Science LAB JM-10 Micro Corder. UV-Vis absorption spectra were recorded on a JASCO V-630 spectrometer. Luminescence spectra were measured on a HORIBA SPEX Fluorolog-3 spectrofluorometer. Cold electrospray ionization mass spectrometry (CSI-MS) measurements were conducted using a JMS-T100CS system (JEOL).

General Procedures and Materials.

All chemicals and solvents used in syntheses were of commercial grade and used without purification. The solvents for CSI-MS and photophysical measurements were dried over appropriate drying agents. Bis(benzimidazole-2-ylmethyl)amine (H**L**) was synthesized according to literature procedures.[1]

TbLPhen. A degassed methanol solution (2.0 mL) of H**L** (0.0444 g, 0.16 mmol) and 1,10-phenanthroline-2-carbaldehyde (**Phen**; 0.0333 g, 0.16 mmol) was stirred at room temperature for 1.5 h. To this solution was added terbium(III) nitrate hexahydrate (0.0725 g, 0.16 mmol), and the mixture was stirred for 3 h. The resulting pale-brown precipitate was collected by suction filtration and recrystallized by slow vapor diffusion of diethyl ether into methanol solution. Yield: 0.035 g (24%). Anal. calc. for $C_{30}H_{25}N_{10}O_{10}Tb \cdot 3H_2O$: C, 40.10; H, 3.48; N, 15.59. Found: C, 40.39; H, 3.28; N, 15.59. IR: ν_{max} (KBr): 3404, 1625, 1508, 1454, 1384, 1292, 1115, 1087, 1038, 747 cm^{-1}.

GdLPhen. The synthetic procedure for **GdLPhen** is similar to that of **TbLPhen**, using gadolinium(III) nitrate hexahydrate (0.0720 g, 0.16 mmol) instead of terbium(III) nitrate hexahydrate. Yield: 0.062 g (43%). Anal. calc. for $C_{30}H_{25}GdN_{10}O_{10} \cdot 3H_2O$: C, 40.18; H, 3.48; N, 15.62. Found: C, 40.33; H, 3.33; N, 15.43. IR: ν_{max} (KBr) / cm^{-1}: 3358, 1625, 1517, 1452, 1384, 1291, 1114, 1087, 1029, 746.

TbLQ. A degassed methanol solution (1.0 mL) of H**L** (0.0113 g, 0.041 mmol) and 8-hydroxyquinoline-2-carbaldehyde (**Q**; 0.0072 g, 0.042 mmol) was stirred at room temperature for 1.5 h. To this solution was added a methanol solution (0.5 mL) of terbium(III) nitrate hexahydrate (0.0182 g, 0.040 mmol), and the mixture was stirred for 1 h. The resulting pale-yellow precipitate was collected by suction filtration and recrystallized by slow vapor diffusion of diethyl ether into methanol solution. Yield: 0.010

g (33 %). Anal. calc. for $C_{27}H_{23}N_8O_8Tb\cdot2.5MeOH$: C, 42.87; H, 4.02; N, 13.56. Found: C, 42.44; H, 3.78; N, 13.70. IR: ν_{max} (KBr): 3409, 1624, 1503, 1455, 1384, 1332, 1273, 1102, 745 cm^{-1}.

GdLQ. The synthetic procedure for **GdLQ** is similar to that of **TbLQ**, using gadolinium(III) nitrate hexahydrate (0.0183 g, 0.041 mmol) instead of terbium(III) nitrate hexahydrate. Yield: 0.007 g (23 %). Anal. calc. for $C_{27}H_{23}GdN_8O_8\cdot2H_2O$: C, 43.06; H, 3.86; N, 13.85. Found: C, 42.83; H, 3.87; N, 14.04. IR: ν_{max} (KBr): 3196, 1624, 1596, 1566, 1503, 1455, 1383, 1332, 1282, 1103, 743 cm^{-1}.

General procedure for the reversible exchange reaction of aldehydes

The solvents for the reversible exchange reactions—methanol and acetonitrile—were dried using activated 3Å molecular sieves and degassed by N_2 bubbling. For the exchange reactions without acid/base regulation, two solutions (0.1 mM, 10 mL), each containing one of the above Tb(III) complexes with 1 equiv. of aldehyde, were stirred at room temperature overnight. The resulting solutions were used directly for CSI-MS measurements and diluted to 0.01 mM for photophysical measurements. For the exchange reactions using acid/base regulation, two solutions (0.01 mM, 3 mL), each containing one of the above Tb(III) complexes with 1 equiv. of aldehyde, were used for photophysical measurements. The reaction mixtures in the cells were shaken for 1 min. at room temperature after every addition of acid or base (0.15 M, 0.4 μL each), then the emission spectra were recorded.

Crystallography

Suitable single crystals for X-ray crystallography were obtained by vapor diffusion of Et_2O into a CH_3OH solution of **TbLPhen** and **LnLQ** to yield [Tb(**LPhen**)(NO$_3$)$_2$](NO$_3$)·3MeOH (**TbLPhen**·3MeOH) and [Ln(**LQ**)(NO$_3$)$_2$]·MeOH·Et$_2$O (**LnLQ**·MeOH·Et$_2$O, **Ln** = Tb^{3+}, Gd^{3+}), respectively, and by vapor diffusion of Et_2O into a CH_3CN–CH_3OH solution of **GdLQ** to yield [Gd(**LPhen**)(NO$_3$)$_2$](NO$_3$)·2CH$_3$CN (**GdLPhen**·2CH$_3$CN). Data collection was performed on the Bruker SMART APEX II CCD area detector diffractometer with a graphite monochromator and MoKα radiation ($\lambda = 0.71073$ Å). Data correction was carried out at 100 K. An empirical absorption correction was applied using the SADABS-2016/2 program.[2] The structures were solved using intrinsic phasing (SHELXTL XT-2014/5) and refined by full-matrix least-squares calculations on F^2 using SHELXTL XLMP-2017/1.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the core

structure were fixed in calculated positions and refined with a riding model. The crystallographic data are listed in Table S1 and the selected bond distances and angles are summarized in Table S2. CCDC 2101776, 2101777, 2101778, and 2101779, for **TbLPhen**, **GdLPhen**, **TbLQ**, and **GdLQ**, respectively, contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.
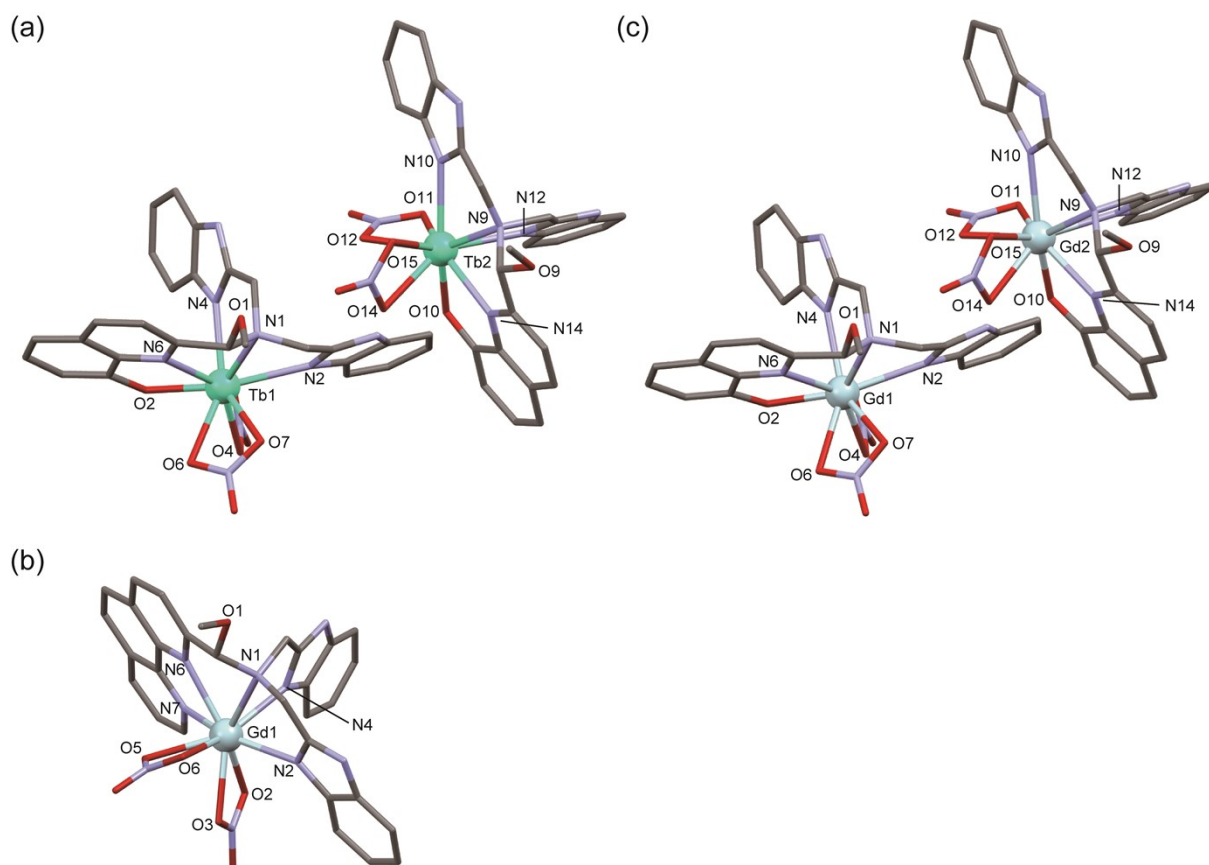
Fig. S1 Crystal structures of (a) **TbLQ** including two crystallographically independent molecules, (b) **GdLPhen**, and (c) **GdLQ**. The counter anions, solvent molecules, and hydrogen atoms were omitted for clarity.
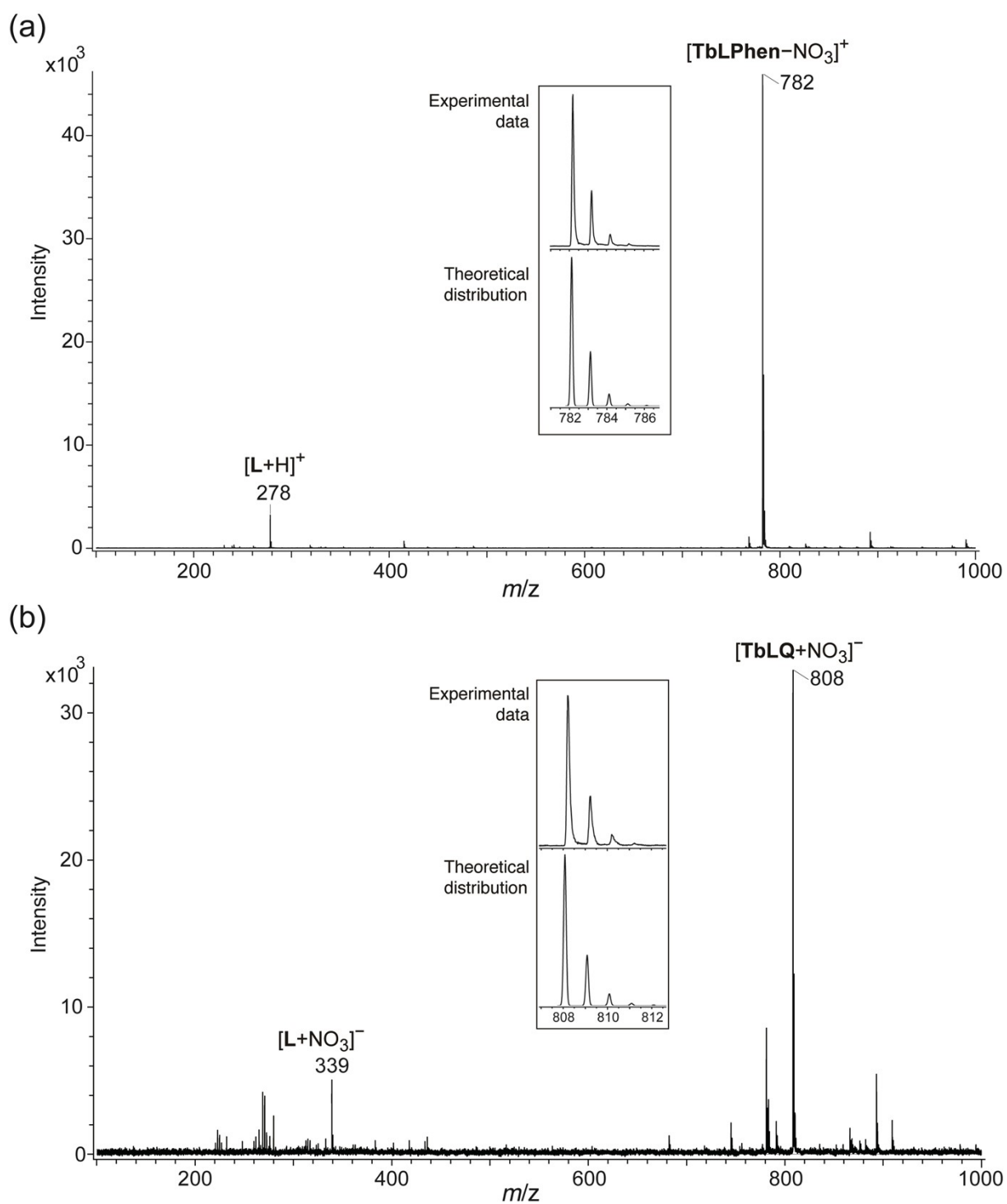
Fig. S2 CSI-MS of (a) an acetonitrile solution including 500 equiv. methanol of **TbLPhen** in the positive ion mode, and (b) an acetonitrile-methanol (99:1) solution of **TbLQ** in the negative ion mode with sample concentrations of 0.1 mM. The experimental data and theoretical distribution patterns are shown in the inset.
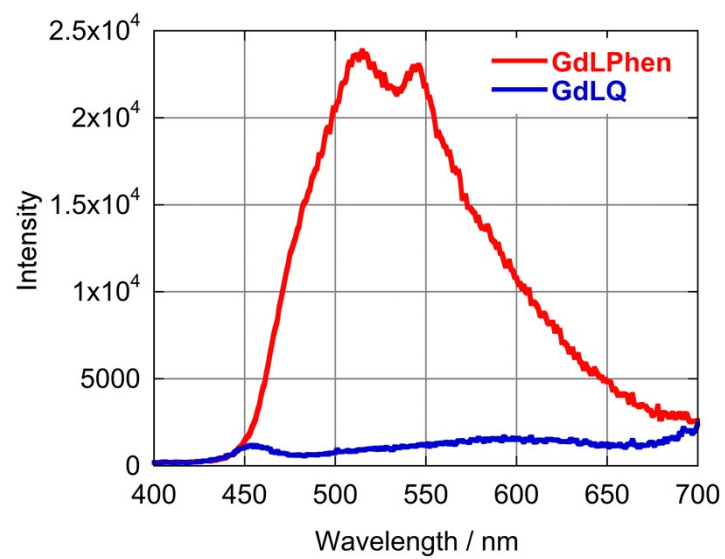
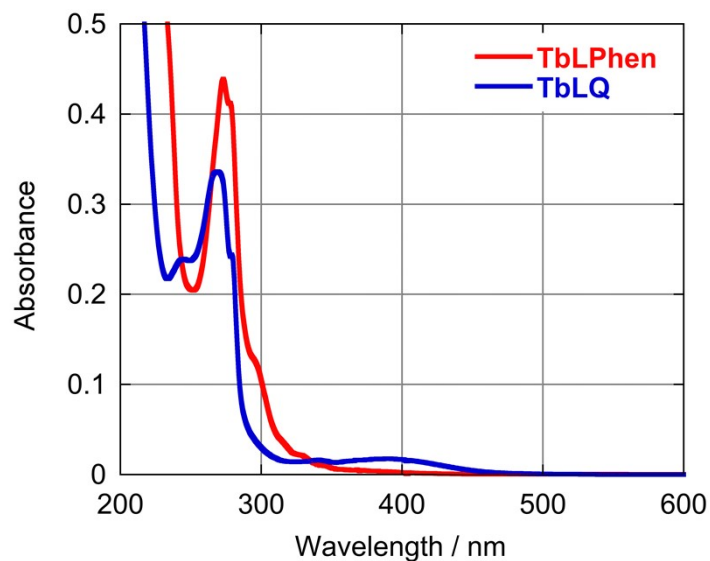**Fig. S3** Phosphorescence spectra of **GdLPhen** and **GdLQ** in the solid state at 77 K excited at 300 nm.

Fig. S4 UV-Vis absorption spectra of **TbLPhen** (an acetonitrile solution including 500 equiv. methanol, 1.0×10^{-5} M) and **TbLQ** (an acetonitrile-methanol (99:1) solution, 1.0×10^{-5} M).
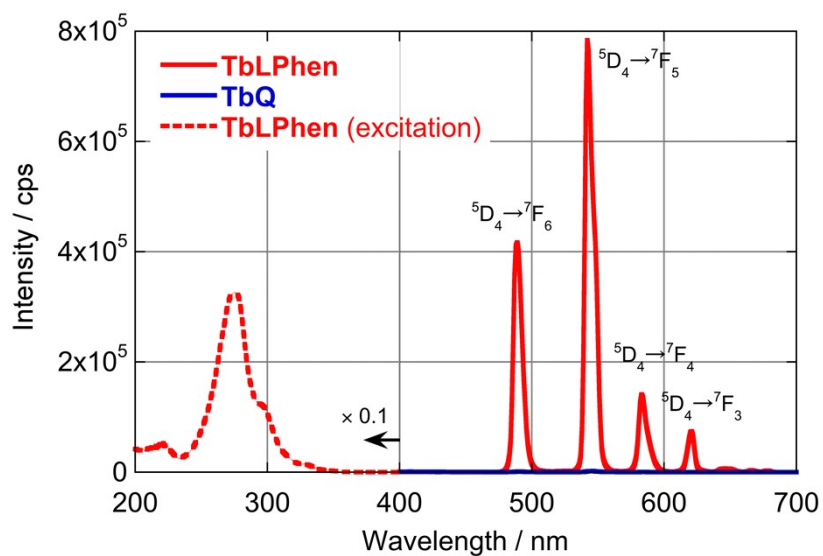

Fig. S5 Emission spectra (solid lines) of **TbLPhen** (an acetonitrile solution including 500 equiv. methanol, 1.0×10^{-5} M) and **TbLQ** (an acetonitrile-methanol (99:1) solution, 1.0×10^{-5} M) at 298 K excited at 275 nm. Excitation spectrum for **TbLPhen** (200–400 nm, dotted line) obtained by monitoring the emission wavelength at 542 nm ($^5D_4 \rightarrow {}^7F_5$).
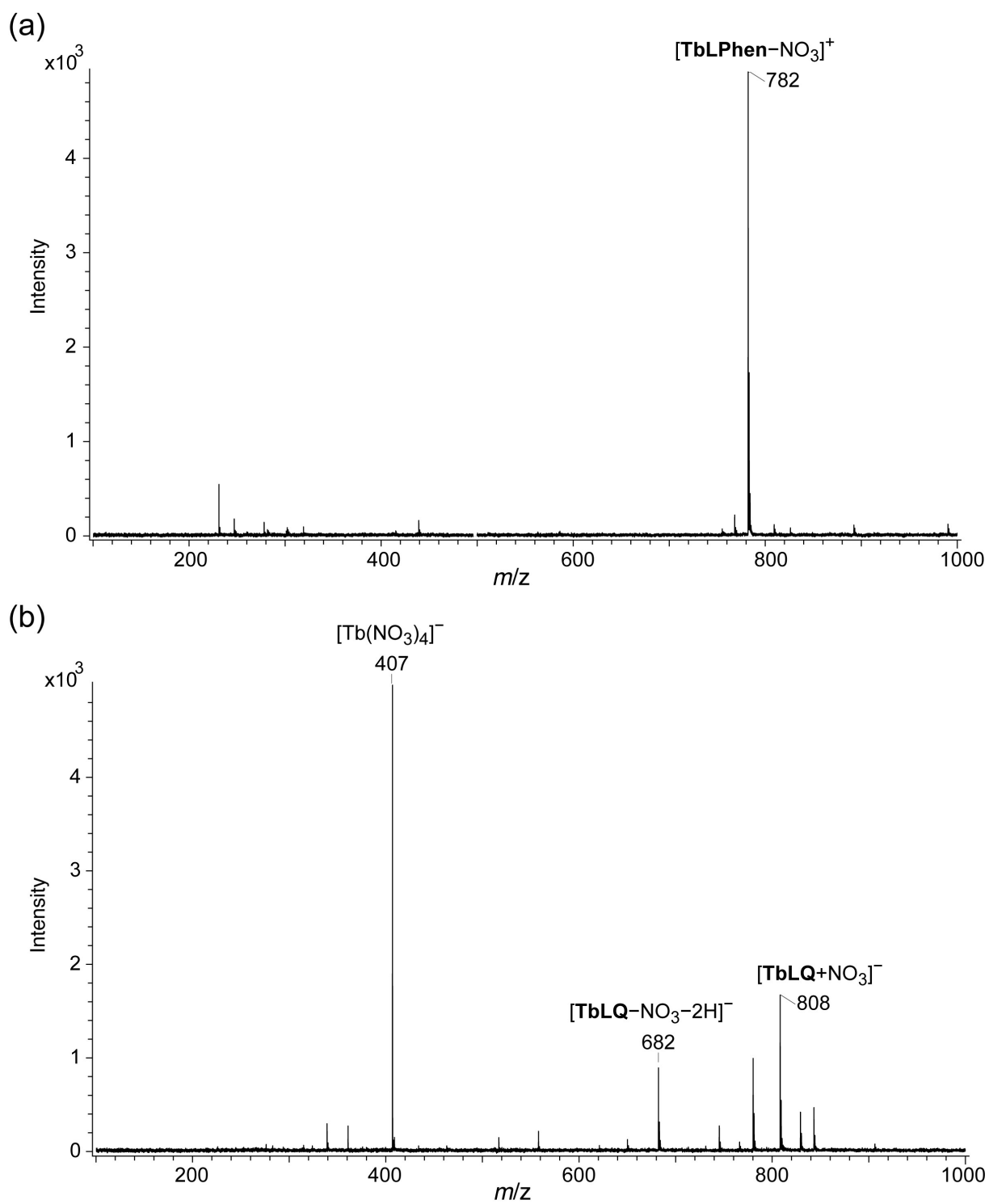
Fig. S6 CSI-MS data of **TbLPhen** : **Q** = 1 : 1 in an acetonitrile solution including 500 equiv. methanol (a) in the positive ion mode and (b) in the negative ion mode with sample concentrations of 0.1 mM.

Fig. S7 CSI-MS data of **TbLQ** : **Phen** = 1 : 1 in an acetonitrile-methanol (99:1) solution (a) in the positive ion mode and (b) in the negative ion mode with sample concentrations of 0.1 mM.

Fig. S8 CSI-MS data of a **TbLPhen** : **Q** : NaOMe = 1 : 1 : 1 acetonitrile solution including 500 equiv. methanol (a) in the positive ion mode and (b) in the negative ion mode with sample concentrations of 0.1 mM.
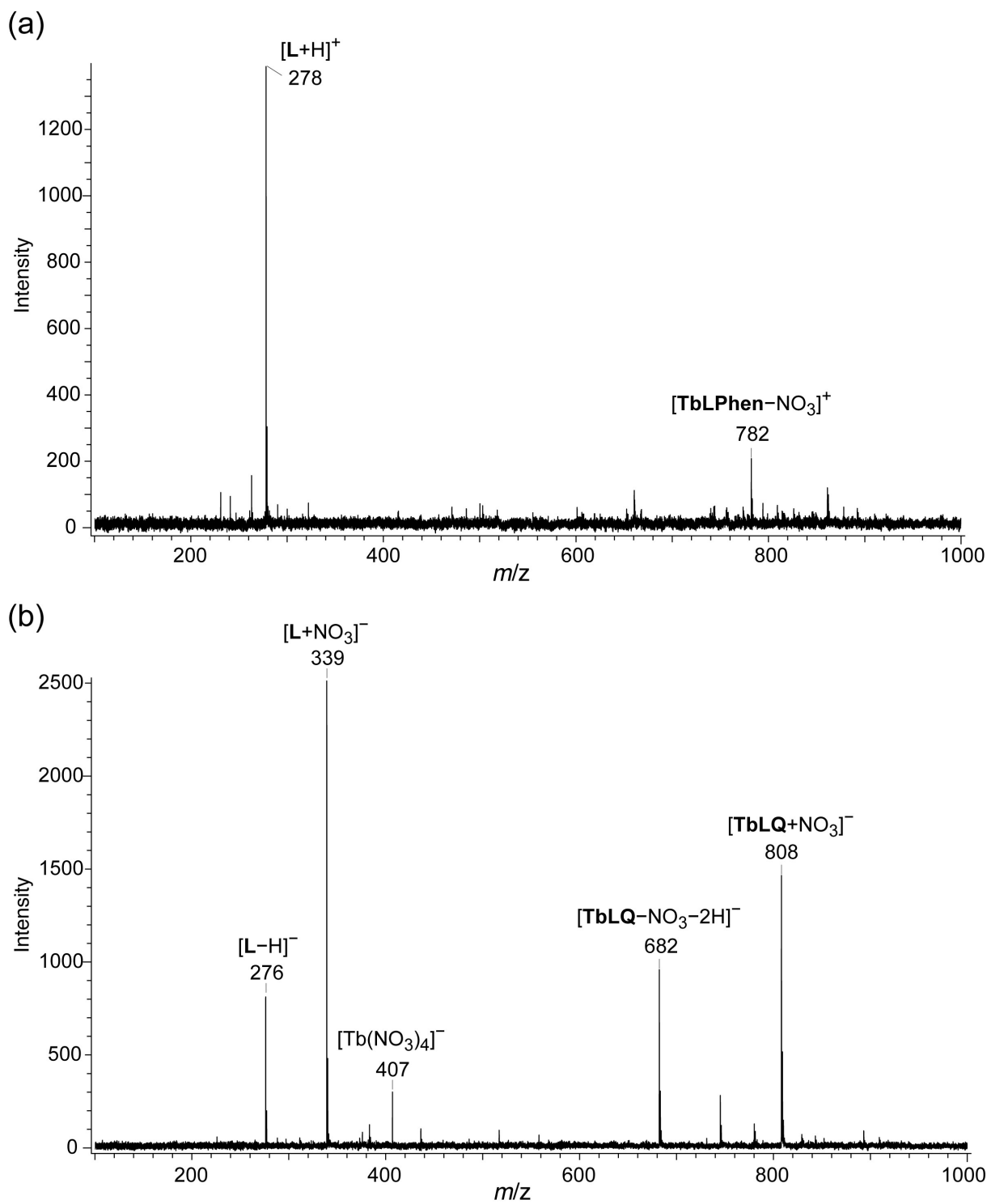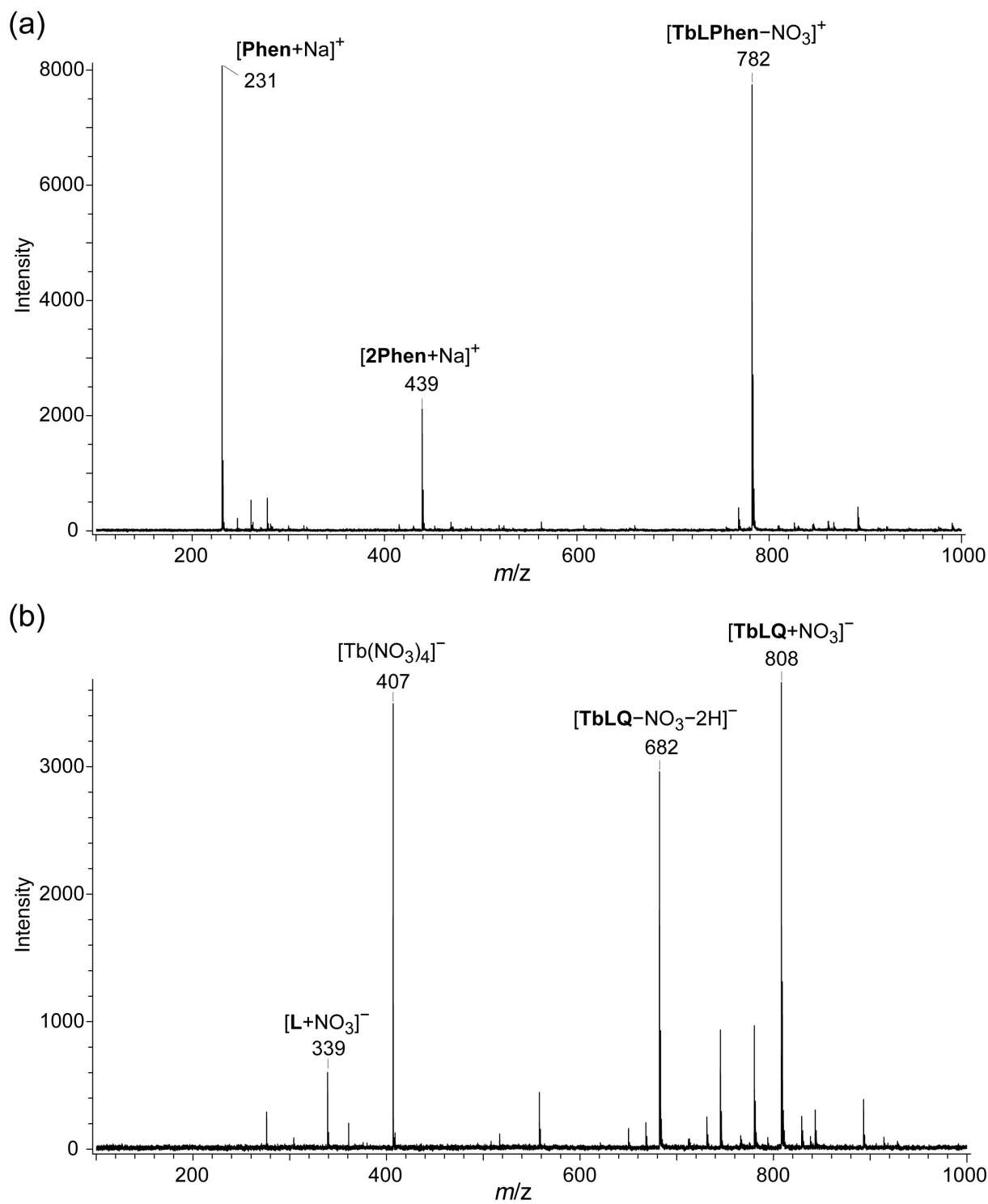
Fig. S9 CSI-MS data of a **TbLPhen** : **Q** : NaOMe : HNO_3 = 1 : 1 : 1 : 1 acetonitrile solution including 500 equiv. methanol (a) in the positive ion mode and (b) in the negative ion mode with sample concentrations of 0.1 mM.
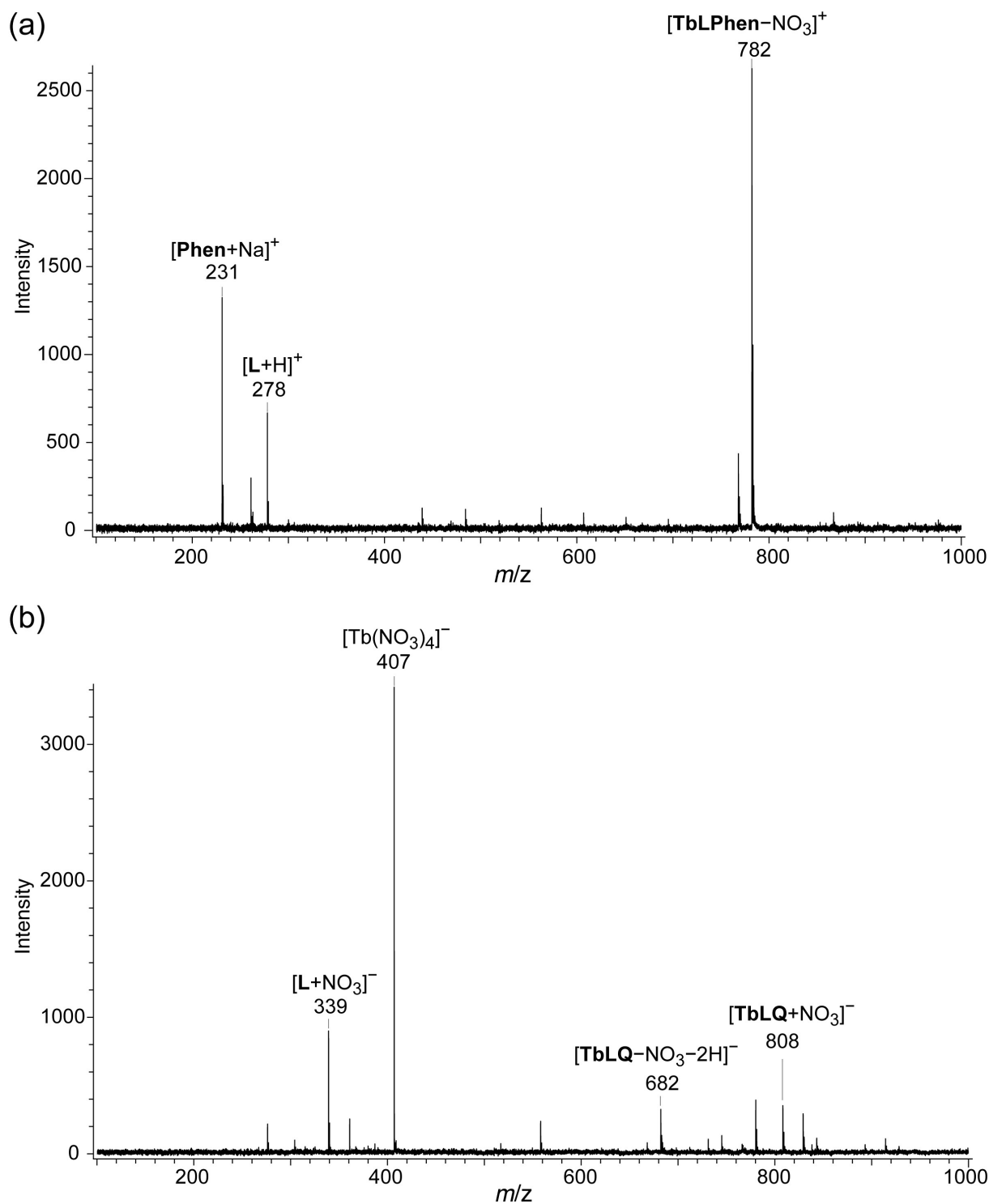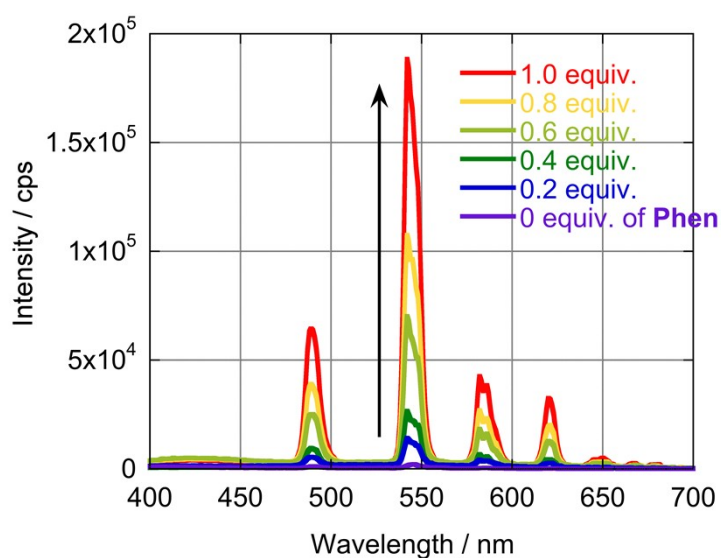
Fig. S10 Emission changes of **TbLQ** in an acetonitrile-methanol (99:1) solution upon addition of **Phen** (0.2 equiv each addition) without the addition of acid or base.
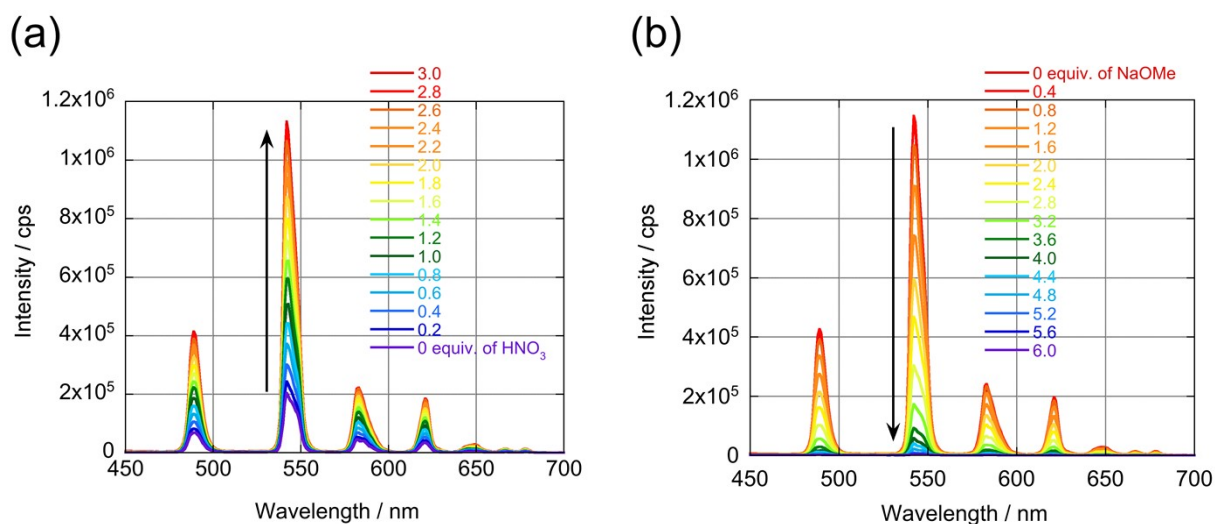

Fig. S11 Emission changes of **TbLQ** : **Phen** = 1 : 1 in an acetonitrile-methanol (99:1) solution (a) with the addition of HNO_3 and (b) with the addition of NaOMe.

Table S1 Crystal Data and Structure Refinement for *Ln***LPhen** and *Ln***LQ** (*Ln* = Tb and Gd)

	TbLPhen	GdLPhen	TbLQ	GdLQ
Empirical formula	$C_{33}H_{37}N_{10}O_{13}Tb$	$C_{34}H_{31}GdN_{12}O_{10}$	$C_{32}H_{37}N_8O_{10}Tb$	$C_{32}H_{37}GdN_8O_{10}$
Fw / g·mol^{-1}	940.64	924.96	852.61	850.94
Temperature / K	100	100	100	100
Crystal system	*triclinic*	*monoclinic*	*monoclinic*	*monoclinic*
Space group	*P*-1	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*n*
a / Å	10.264(7)	10.4520(12)	16.1224(11)	16.1612(12)
b / Å	12.525(8)	27.477(3)	25.0927(18)	25.1081(19)
c / Å	15.232(10)	12.9143(14)	18.9394(13)	18.9535(14)
α / °	82.512(10)	90	90	90
β / °	85.717(11)	106.006(2)	113.3250(10)	113.3990(10)
γ / °	87.038(10)	90	90	90
V / Å^3	1934.(2)	3565.1(7)	7035.8(8)	7058.4(9)
Z	2	4	8	8
D_{calc} / g·cm^{-3}	1.615	1.723	1.610	1.602
Reflections collected	14934	23668	54575	54658
Independent reflections (R_{int})	11081 (0.0436)	8455 (0.0550)	21063 (0.0411)	21394 (0.0368)
GOF	1.006	1.025	1.005	1.019
R_1 (I>2σ (all data))	0.0422 (0.0477)	0.0400 (0.0623)	0.0380 (0.0567)	0.0350 (0.0528)
wR_2 (I>2σ (all data))	0.1062 (0.1108)	0.0824 (0.0905)	0.0834 (0.0903)	0.0803 (0.0879)
Weighting scheme	$w = 1 / [\sigma^2(F_o^2) + (0.0523P)^2 + 0.6989P]$, where $P = (F_o^2+2F_c^2)/3$	$w = 1 / [\sigma^2(F_o^2) + (0.0358P)^2 + 1.3749P]$, where $P = (F_o^2+2F_c^2)/3$	$w = 1 / [\sigma^2(F_o^2) + (0.0325P)^2 + 11.8140P]$, where $P = (F_o^2+2F_c^2)/3$	$w = 1 / [\sigma^2(F_o^2) + (0.0380P)^2 + 4.6219P]$, where $P = (F_o^2+2F_c^2)/3$
CCDC No.	2101776	2101777	2101778	2101779

Table S2 Selected Bond Distances (Å) and Angles (°) of *Ln*LPhen and *Ln*LQ (*Ln* = Tb and Gd) with Estimated Standard Deviations in Parentheses

	TbLPhen	GdLPhen		TbLQ	GdLQ
*Ln*1-N1	2.634(3)	2.664(3)	*Ln*1-N1	2.699(2)	2.709(2)
*Ln*1-N2	2.510(3)	2.505(3)	*Ln*1-N2	2.557(3)	2.571(2)
*Ln*1-N4	2.419(3)	2.408(3)	*Ln*1-N4	2.413(3)	2.433(2)
*Ln*1-N6	2.512(3)	2.521(3)	*Ln*1-N6	2.474(3)	2.491(2)
*Ln*1-N7	2.549(3)	2.584(4)	*Ln*1-O2	2.297(2)	2.316(2)
*Ln*1-O2	2.464(3)	2.432(3)	*Ln*1-O3	2.466(2)	2.473(2)
*Ln*1-O3	2.481(3)	2.530(3)	*Ln*1-O4	2.469(2)	2.484(2)
*Ln*1-O5	2.477(3)	2.466(3)	*Ln*1-O6	2.537(2)	2.546(2)
*Ln*1-O6	2.406(3)	2.438(3)	*Ln*1-O7	2.445(2)	2.464(2)
			*Ln*2-N9	2.720(3)	2.727(2)
			*Ln*2-N10	2.537(3)	2.553(2)
			*Ln*2-N12	2.438(3)	2.460(3)
			*Ln*2-N14	2.477(3)	2.495(2)
			*Ln*2-O10	2.293(2)	2.309(2)
			*Ln*2-O11	2.479(2)	2.483(2)
			*Ln*2-O12	2.439(2)	2.454(2)
			*Ln*2-O14	2.518(3)	2.524(2)
			*Ln*2-O15	2.423(3)	2.441(3)

	TbLPhen	GdLPhen		TbLQ	GdLQ
N1-*Ln*1-N2	66.56(9)	66.07(10)	N1-*Ln*1-N2	65.36(8)	65.19(7)
N1-*Ln*1-N4	69.80(10)	68.77(11)	N1-*Ln*1-N4	68.41(8)	68.09(7)
N1-*Ln*1-N6	63.45(9)	62.75(10)	N1-*Ln*1-N6	63.03(8)	62.91(7)
N1-*Ln*1-N7	123.57(9)	121.62(10)	N1-*Ln*1-O2	127.98(8)	127.47(7)
N2-*Ln*1-N4	75.36(10)	76.40(11)	N2-*Ln*1-N4	80.77(8)	80.63(7)
			N9-*Ln*2-N10	66.42(8)	66.14(7)
			N9-*Ln*2-N12	68.02(9)	67.74(8)
			N9-*Ln*2-N14	62.15(8)	62.03(7)
			N9-*Ln*2-O10	127.06(8)	126.62(7)
			N10-*Ln*2-N12	84.31(9)	83.91(8)

References

1.	R. Cariou, J. J. Chirinos, V. C. Gibson, G. Jacobsen, A. K. Tomov, G. J. P. Britovsek, and A. J. P. White, *Dalton Trans.*, 2010, **39**, 9039–9045.

2.	G. M. Sheldrick, *SADABS, Empirical Absorpt. Correct. program, Univ. Göttingen*, 1997.

3.	G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.