Electronic Supplementary Information

Development of Tuneable Green-to-Red Emitting Transparent Film Based on Nafion with Tb^{III}/Eu^{III} β-Diketonate Complexes Modulated by pH and Proton Flow

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Experimental Procedures

General Information

All reagents and chemicals were obtained from commercial sources and used directly unless otherwise noted. MeOH was dried from magnesium methoxide. Nafion 117 was purchased from FURUKAWA AGENCY Co., Ltd.

Synthesis of 1: HPBA (72.5 mg, 0.30 mmol) and NaOH (12.0 mg, 0.30 mmol) in MeOH and $Tb(NO_3)_3 \cdot 6H_2O$ (45.0 mg, 0.1 mmol) in MeOH were slowly diffused in H-shaped glass tube. Pale yellow single crystals of **1** were obtained in 12.8% yield after 3 days. Elemental analysis for $C_{84}H_{68}N_{12}O_{13}Tb_2$ ($[Tb_2(PBA)_6] \cdot H_2O$): Calcd.: C, 56.96; H, 3.87; N, 9.49; Tb, 17.94. Found: C, 56.81; H, 3.74; N, 9.58; Tb, 17.94. IR (ATR): 3195, 3060, 1623, 1592, 1569, 1508, 1465, 1446, 1421, 1338, 1295, 1268, 1187, 1151, 1008, 987, 910, 759, 690 cm^{-1}. UV-Vis (in EtOH, λ_{max} / nm): 249, 273, 335.

Synthesis of 2: HPBA (72.5 mg, 0.30 mmol) and NaOH (12.0 mg, 0.30 mmol) in MeOH and $Eu(NO_3)_3 \cdot 6H_2O$ (44.6 mg, 0.1 mmol) in MeOH were slowly diffused in H-shaped glass tube. Pale yellow single crystals of **2** were obtained in 14.5% yield after 3 days. Elemental analysis for $C_{84}H_{68}N_{12}O_{13}Eu_2$ ($[Eu_2(PBA)_6] \cdot H_2O$): Calcd.: C, 57.41; H, 3.90; N, 9.56; Eu, 17.29. Found: C, 57.14; H, 3.75; N, 9.62; Eu, 17.90. IR (ATR): 3201, 3060, 1623, 1592, 1569, 1508,1465, 1448, 1421, 1338, 1295, 1267, 1189, 1151, 1006, 987, 910, 759, 690 cm^{-1}. UV-Vis (in EtOH, λ_{max} / nm): 249, 273, 335.

Preparation of 1/2@Nafion: In order to exchange inner cations of Nafion for Na^+ ions, Nafion 117 was soaked in 2 M aqueous solution of NaOH at room temperature for 24 h. The Na-form Nafion was soaked in a solution of **1** (0.89 mg, 5.0×10^{-4} mmol) and **2** (0.88 mg, 5.0×10^{-4} mmol) in EtOH (50 mL) with Britton-Robinson buffer (pH 3, 50 mL) at room temperature for 90 h. The transparent film of **1**/**2**@Nafion was washed with EtOH and dried in vacuo for 2 h.

Measurements and Characterization

IR spectra were recorded on HORIBA FT-730. Elemental analysis was carried out by Perkin-Elmer instruments Series II CHNS/O Analyzer 2400. UV-vis spectra were recorded on JASCO V-550 UV-vis Spectrophotometer. Emission spectra were recorded on SHIMADZU RF-6000 Spectrofluorophotometer

X-ray Crystallography

The single crystal X-ray diffraction data were collected by Bruker SMART APEX II Ultra with monochromated Mo-Kα radiation (λ = 0.71073 Å). Indexing was performed using APEX2 (Difference Vectors method).[1] Data integration was performed with Bruker SAINT.[2] Absorption correction was performed by multi-scan method implemented in SADABS.[3] The space group determination was performed with XPREP implemented in APEX2.[4] The structure solution was carried out using SHELXS-97 program[5] and the crystal structure was refined by full-matrix least-squares on F^2 using SHELXL-2016.[6] Hydrogen atoms were placed in geometrically calculated positions. The X-ray crystal structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1938544 and 1938545.

Table S1. Bond distances (Å) of **1**.

Tb(1)-O(4)	2.288(3)	C(3)-C(4)	1.377(6)
Tb(1)-O(6)	2.315(3)	C(9)-C(10)	1.342(7)
Tb(1)-O(1)	2.317(3)	C(9)-C(14)	1.370(7)
Tb(1)-O(3)	2.326(3)	C(10)-C(11)	1.402(7)
Tb(1)-O(2)	2.333(3)	C(11)-C(12)	1.344(8)
Tb(1)-O(5)	2.405(2)	C(12)-C(13)	1.340(9)
Tb(1)-O(5)#1	2.458(2)	C(13)-C(14)	1.384(8)
Tb(1)-N(5)	2.581(3)	C(20)-C(21)	1.428(5)
Tb(1)-Tb(1)#1	3.9771(13)	C(19)-C(18)	1.393(6)
O(1)-C(8)	1.272(4)	C(15)-C(16)	1.371(7)
O(2)-C(6)	1.273(4)	C(16)-C(17)	1.375(7)
O(5)-C(34)	1.286(4)	C(17)-C(18)	1.381(6)
O(4)-C(20)	1.251(4)	C(21)-C(22)	1.389(5)
O(3)-C(22)	1.268(4)	C(22)-C(23)	1.513(5)
O(6)-C(36)	1.283(4)	C(23)-C(24)	1.382(6)
N(2)-C(6)	1.361(5)	C(23)-C(28)	1.383(6)
N(2)-C(5)	1.398(5)	C(28)-C(27)	1.387(6)
N(1)-C(1)	1.346(5)	C(27)-C(26)	1.389(7)
N(1)-C(5)	1.348(5)	C(26)-C(25)	1.364(7)
N(4)-C(20)	1.369(5)	C(25)-C(24)	1.390(6)
N(4)-C(19)	1.401(5)	C(34)-C(35)	1.406(5)
N(3)-C(19)	1.332(5)	C(33)-C(32)	1.406(5)
N(3)-C(15)	1.355(5)	C(29)-C(30)	1.375(6)
N(6)-C(34)	1.374(4)	C(30)-C(31)	1.378(7)
N(6)-C(33)	1.393(5)	C(31)-C(32)	1.377(6)
N(5)-C(33)	1.334(5)	C(35)-C(36)#1	1.384(5)
N(5)-C(29)	1.351(5)	C(36)-C(37)	1.499(5)
C(8)-C(7)	1.372(5)	C(37)-C(38)	1.385(6)
C(8)-C(9)	1.525(5)	C(37)-C(42)	1.383(6)
C(7)-C(6)	1.417(5)	C(38)-C(39)	1.384(6)
C(5)-C(4)	1.399(5)	C(39)-C(40)	1.372(8)
C(1)-C(2)	1.369(6)	C(40)-C(41)	1.370(8)
C(2)-C(3)	1.370(6)	C(41)-C(42)	1.390(7)

#1 -x+1,-y+2,-z+2

Table S2. Bond angles (°) of **1**.

O(4)-Tb(1)-O(6)	78.81(9)	C(34)-O(5)-Tb(1)#1	122.9(2)	C(18)-C(19)-N(4)	124.8(4)
O(4)-Tb(1)-O(1)	73.67(10)	Tb(1)-O(5)-Tb(1)#1	109.76(9)	N(3)-C(15)-C(16)	123.3(4)
O(6)-Tb(1)-O(1)	77.26(10)	C(20)-O(4)-Tb(1)	134.7(2)	C(17)-C(16)-C(15)	117.8(4)
O(4)-Tb(1)-O(3)	72.21(9)	C(22)-O(3)-Tb(1)	134.0(2)	C(16)-C(17)-C(18)	120.4(5)
O(6)-Tb(1)-O(3)	135.11(9)	C(36)-O(6)-Tb(1)	128.0(2)	C(17)-C(18)-C(19)	118.2(5)
O(1)-Tb(1)-O(3)	123.98(11)	C(6)-N(2)-C(5)	128.5(3)	C(22)-C(21)-C(20)	122.7(4)
O(4)-Tb(1)-O(2)	100.88(10)	C(1)-N(1)-C(5)	118.0(3)	O(3)-C(22)-C(21)	124.0(3)
O(6)-Tb(1)-O(2)	148.08(9)	C(20)-N(4)-C(19)	127.9(3)	O(3)-C(22)-C(23)	115.5(3)
O(1)-Tb(1)-O(2)	72.19(9)	C(19)-N(3)-C(15)	118.0(4)	C(21)-C(22)-C(23)	120.5(3)
O(3)-Tb(1)-O(2)	72.31(9)	C(34)-N(6)-C(33)	130.1(3)	C(24)-C(23)-C(28)	118.5(4)
O(4)-Tb(1)-O(5)	145.42(8)	C(33)-N(5)-C(29)	117.1(3)	C(24)-C(23)-C(22)	117.9(4)
O(6)-Tb(1)-O(5)	113.95(9)	C(33)-N(5)-Tb(1)	122.9(2)	C(28)-C(23)-C(22)	123.5(4)
O(1)-Tb(1)-O(5)	139.01(9)	C(29)-N(5)-Tb(1)	115.9(3)	C(27)-C(28)-C(23)	120.5(5)
O(3)-Tb(1)-O(5)	77.23(9)	O(1)-C(8)-C(7)	124.6(3)	C(26)-C(27)-C(28)	120.3(5)
O(2)-Tb(1)-O(5)	84.59(9)	O(1)-C(8)-C(9)	114.8(3)	C(25)-C(26)-C(27)	119.5(4)
O(4)-Tb(1)-O(5)#1	85.44(9)	C(7)-C(8)-C(9)	120.6(3)	C(26)-C(25)-C(24)	120.2(5)
O(6)-Tb(1)-O(5)#1	71.21(9)	C(8)-C(7)-C(6)	123.7(4)	C(23)-C(24)-C(25)	121.0(4)
O(1)-Tb(1)-O(5)#1	144.97(8)	O(2)-C(6)-N(2)	118.3(3)	O(5)-C(34)-N(6)	119.3(3)
O(3)-Tb(1)-O(5)#1	72.97(9)	O(2)-C(6)-C(7)	124.2(4)	O(5)-C(34)-C(35)	124.4(3)
O(2)-Tb(1)-O(5)#1	140.70(8)	N(2)-C(6)-C(7)	117.5(3)	N(6)-C(34)-C(35)	116.3(3)
O(5)-Tb(1)-O(5)#1	70.24(9)	N(1)-C(5)-C(4)	121.4(4)	N(5)-C(33)-N(6)	120.9(3)
O(4)-Tb(1)-N(5)	146.97(9)	N(1)-C(5)-N(2)	112.3(3)	N(5)-C(33)-C(32)	122.7(4)
O(6)-Tb(1)-N(5)	85.53(9)	C(4)-C(5)-N(2)	126.3(4)	N(6)-C(33)-C(32)	116.4(4)
O(1)-Tb(1)-N(5)	74.60(10)	N(1)-C(1)-C(2)	123.6(4)	N(5)-C(29)-C(30)	124.1(4)
O(3)-Tb(1)-N(5)	135.40(9)	C(1)-C(2)-C(3)	118.0(4)	C(29)-C(30)-C(31)	117.6(4)
O(2)-Tb(1)-N(5)	77.74(10)	C(2)-C(3)-C(4)	120.3(4)	C(32)-C(31)-C(30)	120.3(4)
O(5)-Tb(1)-N(5)	67.61(9)	C(3)-C(4)-C(5)	118.5(4)	C(31)-C(32)-C(33)	118.0(4)
O(5)#1-Tb(1)-N(5)	116.79(9)	C(10)-C(9)-C(14)	117.7(4)	C(36)#1-C(35)-C(34)	124.9(3)
O(4)-Tb(1)-Tb(1)#1	116.66(7)	C(10)-C(9)-C(8)	118.7(4)	O(6)-C(36)-C(35)#1	124.3(3)
O(6)-Tb(1)-Tb(1)#1	92.66(7)	C(14)-C(9)-C(8)	123.4(4)	O(6)-C(36)-C(37)	115.9(3)
O(1)-Tb(1)-Tb(1)#1	164.24(8)	C(9)-C(10)-C(11)	120.9(6)	C(35)#1-C(36)-C(37)	119.8(3)
O(3)-Tb(1)-Tb(1)#1	71.66(8)	C(12)-C(11)-C(10)	120.9(6)	C(38)-C(37)-C(42)	117.7(4)
O(2)-Tb(1)-Tb(1)#1	114.91(7)	C(11)-C(12)-C(13)	118.2(5)	C(38)-C(37)-C(36)	118.9(4)
O(5)-Tb(1)-Tb(1)#1	35.56(6)	C(12)-C(13)-C(14)	121.5(6)	C(42)-C(37)-C(36)	123.4(4)
O(5)#1-Tb(1)-Tb(1)#1	34.68(5)	C(9)-C(14)-C(13)	120.5(6)	C(37)-C(38)-C(39)	121.1(4)
N(5)-Tb(1)-Tb(1)#1	92.76(7)	O(4)-C(20)-N(4)	118.6(3)	C(40)-C(39)-C(38)	120.5(5)
H(7B)-O(7)-H(7C)	107(8)	O(4)-C(20)-C(21)	124.5(3)	C(39)-C(40)-C(41)	119.3(5)
C(8)-O(1)-Tb(1)	135.3(2)	N(4)-C(20)-C(21)	116.8(3)	C(40)-C(41)-C(42)	120.3(5)
C(6)-O(2)-Tb(1)	134.8(2)	N(3)-C(19)-C(18)	122.3(4)	C(37)-C(42)-C(41)	121.1(5)
C(34)-O(5)-Tb(1)	126.7(2)	N(3)-C(19)-N(4)	112.9(3)		

#1 -x+1,-y+2,-z+2

Table S3. Hydrogen bond distances (Å) of **1**.

O(7)...O(3)	3.148(5)	N(6)...O(7)#2	2.913(5)
O(7)...O(2)	3.099(6)	N(4)...N(1)#3	3.013(5)
C(18)...O(4)	2.781(5)	N(2)...N(3)#4	3.031(5)
C(4)...O(2)	2.806(5)		

#1 -x+1,-y+2,-z+2 #2 x+1/2,-y+3/2,-z+2 #3 -x+1/2,y+1/2,z #4 -x+1/2,y-1/2,z

Table S4. Bond distances (Å) of **2**.

C(8)-O(1)	1.271(4)	C(23)-C(28)	1.385(5)
C(8)-C(7)	1.375(5)	C(28)-C(27)	1.384(5)
C(8)-C(9)	1.507(4)	C(27)-C(26)	1.374(6)
C(7)-C(6)	1.415(4)	C(26)-C(25)	1.372(6)
C(6)-O(2)	1.265(4)	C(25)-C(24)	1.393(5)
C(6)-N(2)	1.361(4)	C(34)-O(5)	1.273(4)
C(5)-N(1)	1.337(4)	C(34)-N(6)	1.376(4)
C(5)-C(4)	1.397(5)	C(34)-C(35)	1.409(4)
C(5)-N(2)	1.401(4)	C(33)-N(5)	1.336(4)
C(4)-C(3)	1.372(5)	C(33)-N(6)	1.394(4)
C(3)-C(2)	1.376(5)	C(33)-C(32)	1.396(5)
C(2)-C(1)	1.371(5)	C(29)-N(5)	1.349(4)
C(1)-N(1)	1.345(4)	C(29)-C(30)	1.371(5)
C(9)-C(10)	1.362(6)	C(30)-C(31)	1.382(6)
C(9)-C(14)	1.382(6)	C(31)-C(32)	1.376(6)
C(10)-C(11)	1.399(6)	C(35)-C(36)#1	1.385(4)
C(11)-C(12)	1.348(7)	C(36)-O(6)	1.279(4)
C(12)-C(13)	1.351(7)	C(36)-C(37)	1.500(4)
C(13)-C(14)	1.387(6)	C(37)-C(38)	1.389(5)
C(20)-O(4)	1.247(4)	C(37)-C(42)	1.390(6)
C(20)-N(4)	1.370(4)	C(38)-C(39)	1.383(5)
C(20)-C(21)	1.429(4)	C(39)-C(40)	1.374(7)
C(19)-N(3)	1.327(4)	C(40)-C(41)	1.378(7)
C(19)-C(18)	1.398(5)	C(41)-C(42)	1.391(6)
C(19)-N(4)	1.396(4)	Eu(1)-O(4)	2.325(2)
C(15)-N(3)	1.349(4)	Eu(1)-O(6)	2.328(2)
C(15)-C(16)	1.366(6)	Eu(1)-O(1)	2.334(2)
C(16)-C(17)	1.369(7)	Eu(1)-O(3)	2.343(2)
C(17)-C(18)	1.379(6)	Eu(1)-O(2)	2.354(2)
C(21)-C(22)	1.383(5)	Eu(1)-O(5)	2.435(2)
C(22)-O(3)	1.275(4)	Eu(1)-O(5)#1	2.486(2)
C(22)-C(23)	1.503(4)	Eu(1)-N(5)	2.612(3)
C(23)-C(24)	1.381(5)	Eu(1)-Eu(1)#1	3.9990(3)

#1 -x+1,-y+2,-z+1

Table S5. Bond angles (°) of **2**.

O(1)-C(8)-C(7)	124.7(3)	C(26)-C(27)-C(28)	120.5(4)	O(2)-Eu(1)-O(5)	84.31(8)
O(1)-C(8)-C(9)	114.6(3)	C(27)-C(26)-C(25)	119.9(4)	O(4)-Eu(1)-O(5)#1	85.03(8)
C(7)-C(8)-C(9)	120.7(3)	C(26)-C(25)-C(24)	119.6(4)	O(6)-Eu(1)-O(5)#1	70.61(7)
C(8)-C(7)-C(6)	123.6(3)	C(23)-C(24)-C(25)	121.1(4)	O(1)-Eu(1)-O(5)#1	145.09(7)
O(2)-C(6)-N(2)	118.4(3)	O(5)-C(34)-N(6)	119.6(3)	O(3)-Eu(1)-O(5)#1	72.60(8)
O(2)-C(6)-C(7)	124.4(3)	O(5)-C(34)-C(35)	124.8(3)	O(2)-Eu(1)-O(5)#1	140.84(7)
N(2)-C(6)-C(7)	117.2(3)	N(6)-C(34)-C(35)	115.6(3)	O(5)-Eu(1)-O(5)#1	71.31(8)
N(1)-C(5)-C(4)	122.1(3)	N(5)-C(33)-N(6)	120.4(3)	O(4)-Eu(1)-N(5)	147.75(8)
N(1)-C(5)-N(2)	112.3(3)	N(5)-C(33)-C(32)	122.8(3)	O(6)-Eu(1)-N(5)	87.22(8)
C(4)-C(5)-N(2)	125.7(3)	N(6)-C(33)-C(32)	116.8(3)	O(1)-Eu(1)-N(5)	74.66(9)
C(3)-C(4)-C(5)	118.3(3)	N(5)-C(29)-C(30)	123.6(4)	O(3)-Eu(1)-N(5)	134.80(8)
C(2)-C(3)-C(4)	120.4(4)	C(29)-C(30)-C(31)	118.3(4)	O(2)-Eu(1)-N(5)	77.27(9)
C(3)-C(2)-C(1)	117.6(3)	C(32)-C(31)-C(30)	119.6(4)	O(5)-Eu(1)-N(5)	66.96(8)
N(1)-C(1)-C(2)	123.9(3)	C(31)-C(32)-C(33)	118.3(4)	O(5)#1-Eu(1)-N(5)	117.64(8)
C(10)-C(9)-C(14)	117.7(4)	C(36)#1-C(35)-C(34)	124.5(3)	O(4)-Eu(1)-Eu(1)#1	116.52(6)
C(10)-C(9)-C(8)	118.7(3)	O(6)-C(36)-C(35)#1	124.6(3)	O(6)-Eu(1)-Eu(1)#1	92.74(5)
C(14)-C(9)-C(8)	123.4(4)	O(6)-C(36)-C(37)	116.1(3)	O(1)-Eu(1)-Eu(1)#1	164.67(7)
C(9)-C(10)-C(11)	120.6(5)	C(35)#1-C(36)-C(37)	119.2(3)	O(3)-Eu(1)-Eu(1)#1	71.33(6)
C(12)-C(11)-C(10)	121.0(5)	C(38)-C(37)-C(42)	117.9(3)	O(2)-Eu(1)-Eu(1)#1	114.94(5)
C(11)-C(12)-C(13)	119.1(4)	C(38)-C(37)-C(36)	118.4(3)	O(5)-Eu(1)-Eu(1)#1	36.09(5)
C(12)-C(13)-C(14)	120.7(5)	C(42)-C(37)-C(36)	123.7(3)	O(5)#1-Eu(1)-Eu(1)#1	35.23(5)
C(9)-C(14)-C(13)	120.8(5)	C(37)-C(38)-C(39)	121.1(4)	N(5)-Eu(1)-Eu(1)#1	92.87(6)
O(4)-C(20)-N(4)	118.6(3)	C(40)-C(39)-C(38)	119.9(4)	C(34)-N(6)-C(33)	130.6(3)
O(4)-C(20)-C(21)	124.6(3)	C(39)-C(40)-C(41)	120.5(4)	C(33)-N(5)-C(29)	117.3(3)
N(4)-C(20)-C(21)	116.8(3)	C(42)-C(41)-C(40)	119.3(5)	C(33)-N(5)-Eu(1)	123.1(2)
N(3)-C(19)-C(18)	122.2(3)	C(37)-C(42)-C(41)	121.2(5)	C(29)-N(5)-Eu(1)	115.1(2)
N(3)-C(19)-N(4)	113.1(3)	O(4)-Eu(1)-O(6)	78.86(8)	C(6)-N(2)-C(5)	128.7(3)
C(18)-C(19)-N(4)	124.7(3)	O(4)-Eu(1)-O(1)	74.06(8)	C(5)-N(1)-C(1)	117.7(3)
N(3)-C(15)-C(16)	123.3(4)	O(6)-Eu(1)-O(1)	78.02(8)	C(20)-N(4)-C(19)	128.0(3)
C(15)-C(16)-C(17)	118.0(4)	O(4)-Eu(1)-O(3)	71.44(8)	C(19)-N(3)-C(15)	118.2(3)
C(16)-C(17)-C(18)	120.5(4)	O(6)-Eu(1)-O(3)	134.07(8)	C(8)-O(1)-Eu(1)	135.7(2)
C(17)-C(18)-C(19)	117.8(4)	O(1)-Eu(1)-O(3)	123.82(9)	C(6)-O(2)-Eu(1)	135.2(2)
C(22)-C(21)-C(20)	122.9(3)	O(4)-Eu(1)-O(2)	99.97(9)	C(22)-O(3)-Eu(1)	134.2(2)
O(3)-C(22)-C(21)	124.0(3)	O(6)-Eu(1)-O(2)	148.56(7)	C(20)-O(4)-Eu(1)	134.4(2)
O(3)-C(22)-C(23)	115.3(3)	O(1)-Eu(1)-O(2)	71.60(8)	C(34)-O(5)-Eu(1)	127.61(19)
C(21)-C(22)-C(23)	120.7(3)	O(3)-Eu(1)-O(2)	72.41(8)	C(34)-O(5)-Eu(1)#1	123.09(18)
C(24)-C(23)-C(28)	118.5(3)	O(4)-Eu(1)-O(5)	145.26(7)	Eu(1)-O(5)-Eu(1)#1	108.69(8)
C(24)-C(23)-C(22)	117.9(3)	O(6)-Eu(1)-O(5)	114.69(8)	C(36)-O(6)-Eu(1)	128.2(2)
C(28)-C(23)-C(22)	123.6(3)	O(1)-Eu(1)-O(5)	138.28(8)	H(7C)-O(7)-H(7B)	112(7)
C(27)-C(28)-C(23)	120.5(4)	O(3)-Eu(1)-O(5)	77.27(8)		

#1 -x+1,-y+2,-z+1

Table S6. Hydrogen bond distances (Å) of **2**.

O(7...O(3)#2	3.142(4)	N(6)...O(7)	2.912(4)
O(7)...O(2)#2	3.094(5)	C(18)...O(4)	2.781(5)
N(4)...N(1)#3	3.012(4)	C(4)...O(2)	2.805(4)
N(2)...N(3)#4	3.030(4)		

#1 -x+1,-y+2,-z+1 #2 x+1/2,-y+3/2,-z+1 #3 -x+1/2,y+1/2,z #4 -x+1/2,y-1/2,z

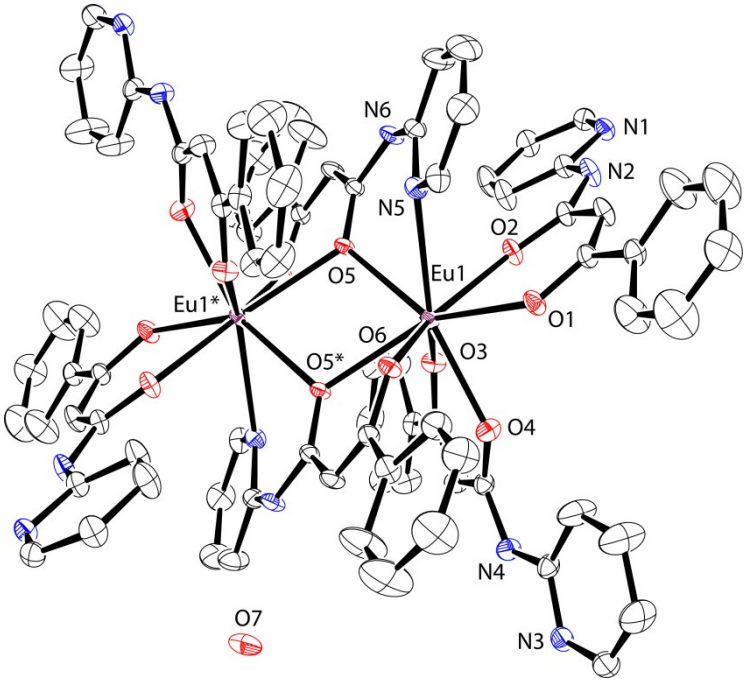

Figure S1. ORTEP image of **2** with thermal ellipsoids at the 30% probability level.

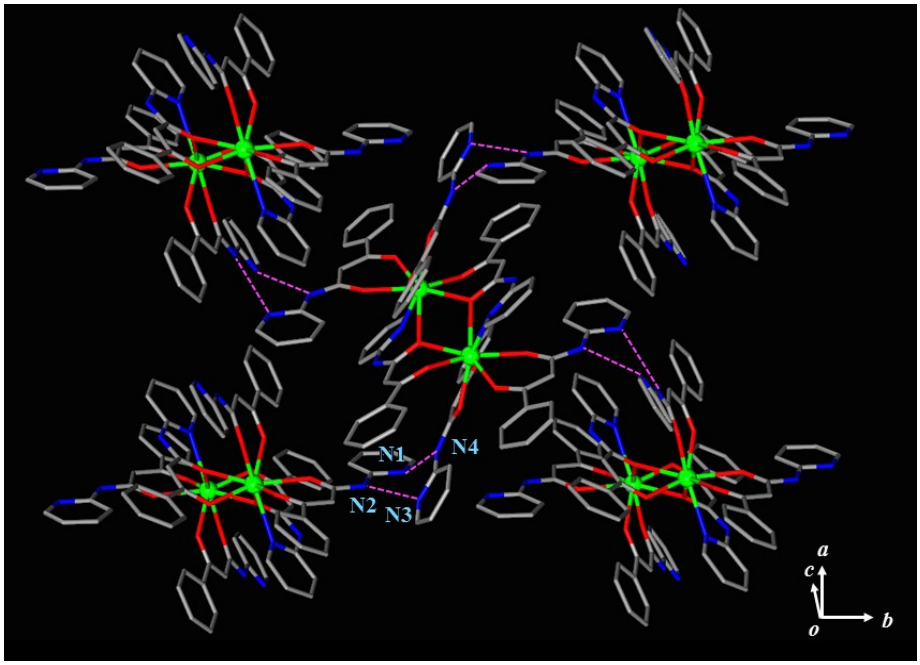

Figure S2. Intermolecular hydrogen bonds between $[Tb^{III}_2(PBA)_6]$ units.

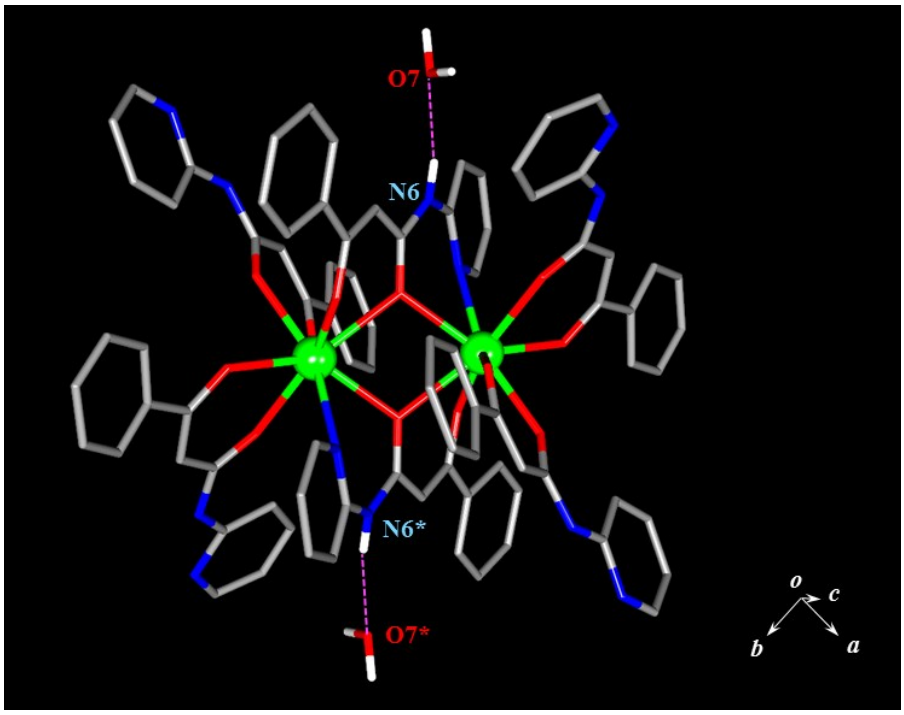

Figure S3. Intermolecular hydrogen bonds between $[Tb^{III}_2(PBA)_6]$ unit and crystallisation water molecule.

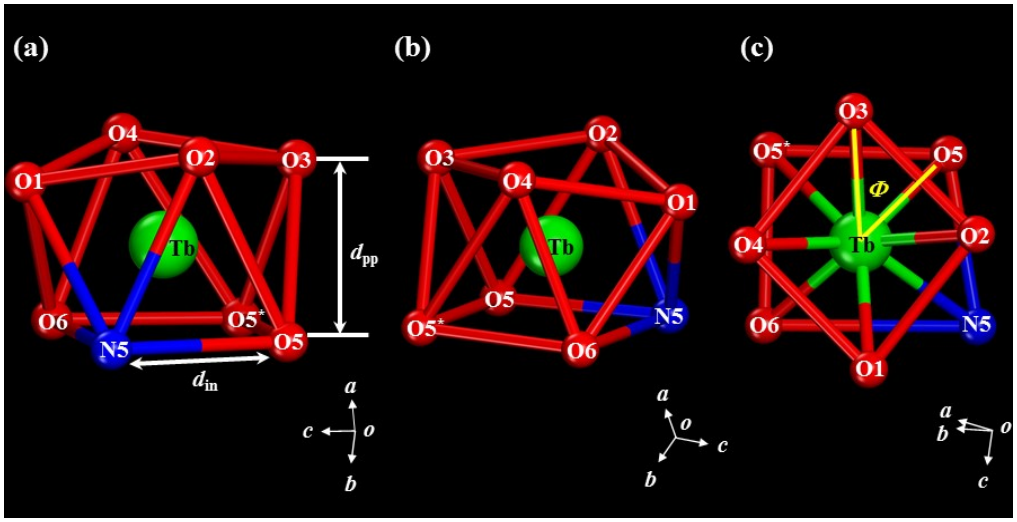

Figure S4. (a) and (b) Square antiprismatic (SAP) geometry of **1**. (c) The relevant angular parameter *Φ*.

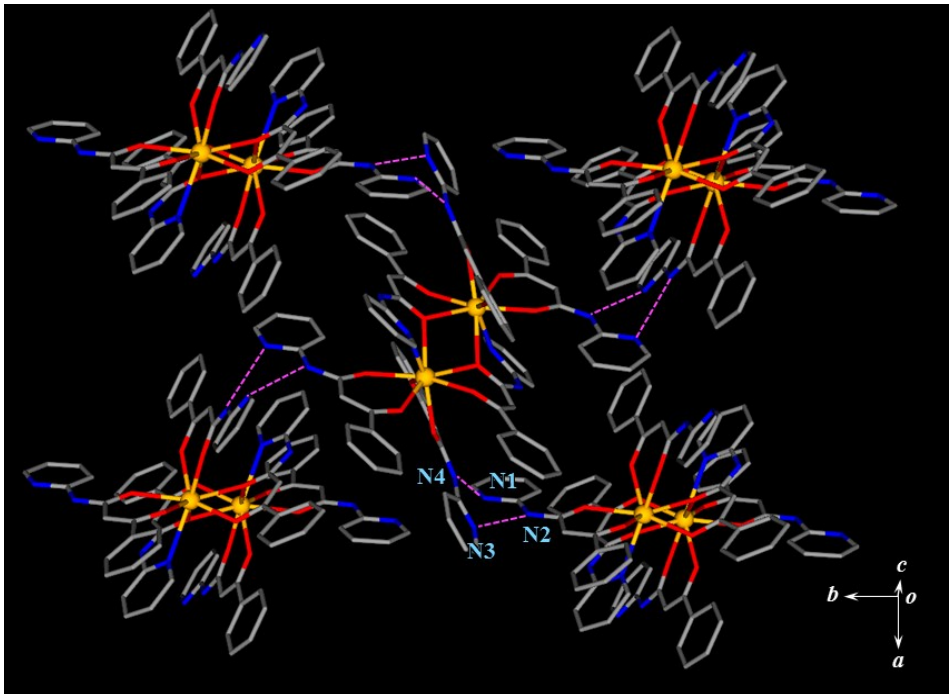

Figure S5. Intermolecular hydrogen bonds between $[Eu^{III}_2(PBA)_6]$ units.

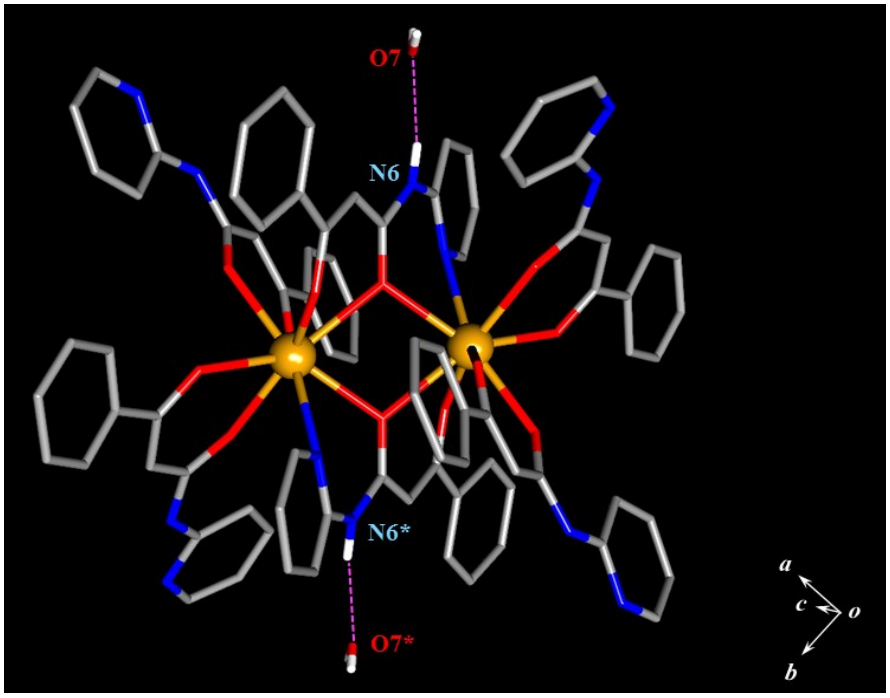

Figure S6. Intermolecular hydrogen bonds between $[Eu^{III}_2(PBA)_6]$ unit and crystallisation water molecule.

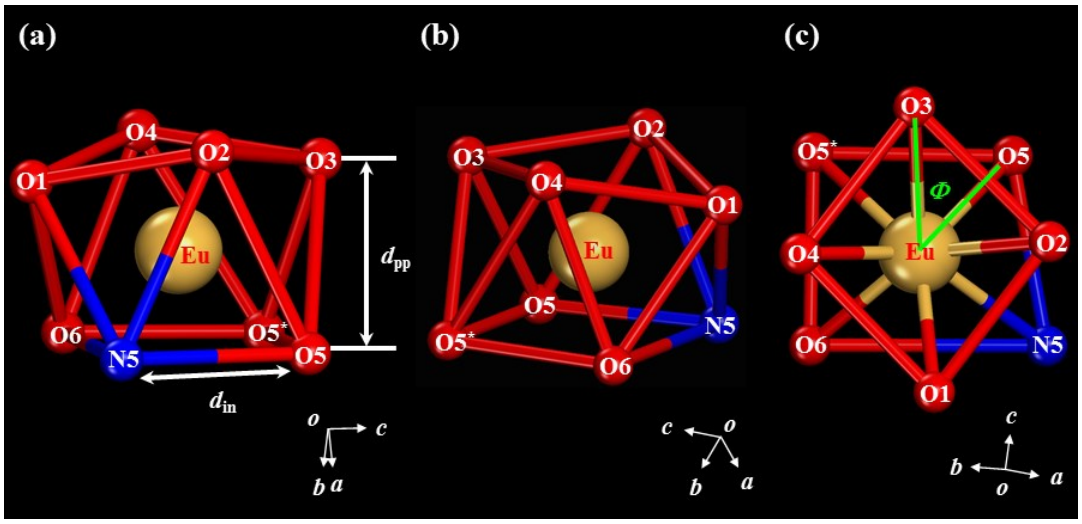

Figure S7. (a) and (b) Square antiprismatic (SAP) geometry of **2**. (c) The relevant angular parameter *Φ*.

Table S7. Selected loading weight and concentration estimated from UV-vis spectra.

Soaking Time / h	Loading Weight / mg g^{-1}(Nafion)	Concentration / μmol g^{-1} (Nafion)
10	5.87	3.31
20	8.38	4.73
30	10.82	6.11
40	12.21	6.90
50	13.25	7.49
60	14.24	8.04
70	14.74	8.33
80	15.55	8.78
90	16.08	9.08

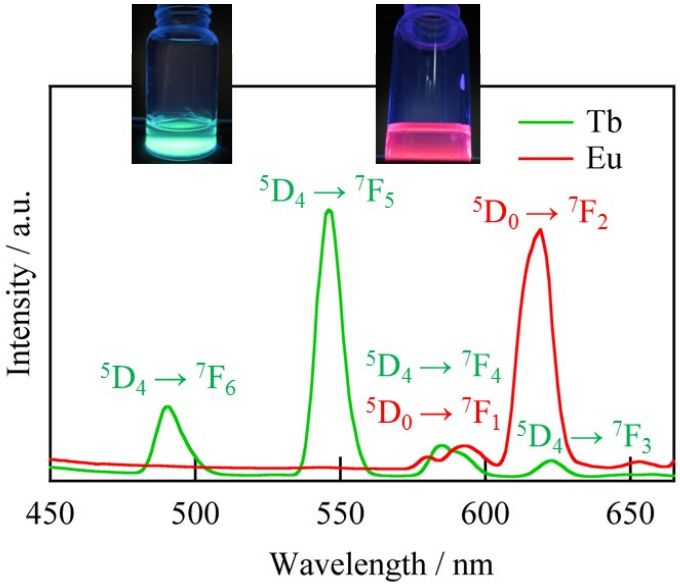

Figure S8. Emission spectra of **1** and **2** at 77 K with the pictures of luminescence in EtOH solutions under UV irradiation.

Supplemental Movie Legend

Movie S1. Control of emission colour under UV light (365 nm) by proton flow induced by external voltage of 40 V for **1**/**2**@Nafion prepared at pH 3. This is a real-time movie, and the aluminum electrodes were separated by a distance of *ca.* 1 cm in plane.

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