Electronic Supplementary Information

K^+-induced in situ self-assembly of near-infrared luminescent membrane material armored with bigger Yb (III) complex crystallites

Wanmin Chen,[a] Xiaoliang Tang,[a] Wei Dou,[a] Zhenghua Ju,[a] Benhua Xu,[a] Wenxuan Xu[a] and Weisheng Liu*[a]*

[a] *Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province and State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Special Function Materials and Structure Design, Ministry of Education, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China.*

*Corresponding author. E-mail: tangxiaol@lzu.edu.cn, liuws@lzu.edu.cn

Fax: +86-931-8912582; Tel: +86-931-8915151

1. Materials and Instrumentations

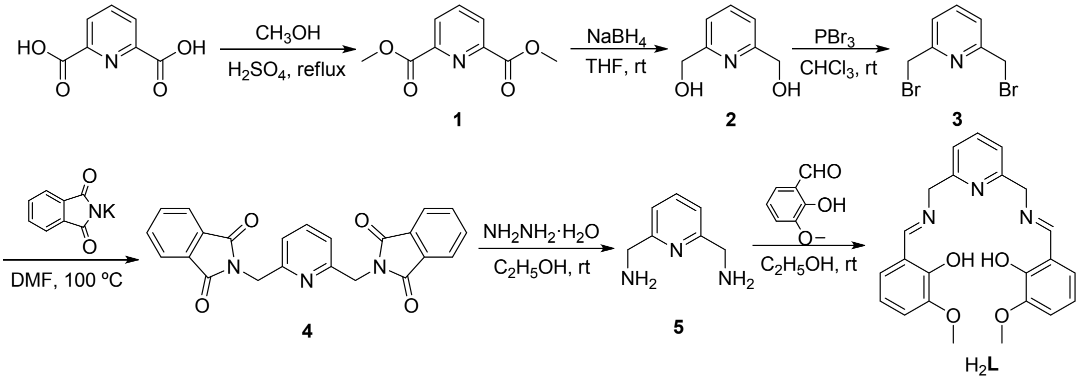
All reagents and solvents were obtained commercially and used in this work without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JNM-ECS-400 MHz spectrometer and referenced to the solvent signals. Mass spectra (ESI) were performed on a Bruker Daltonics Esquire6000 mass spectrometer. Elemental analyses (C, H, N) were performed on a Vario EL elemental analyzer. The steady-state near-infraed luminescence spectra and lifetime measurements were performed on Edinburgh Instrument FLS920 fluorescence spectrometer, with a 450W Xe arc lamp as the steady-state excitation source and a 100W μF 920H lamp as excitation source for lifetime measurement. The absolute quantum yields were determined by an absolute method using an integrating sphere (150 mm diameter, $BaSO_4$ coating) on Edinburgh Instrument FLS920, and by using the following equation:[1]

$$QY = \frac{\varepsilon}{\alpha} = \frac{L_s}{E_b - E_s}$$

Where QY is the quantum yield, ε is the number of photons emitted by the sample, α is the number of photons absorbed by the sample; L_s is the luminescence emission spectrum of the sample, collected using integrating sphere; E_b is the spectrum of the light in the absence of sample in the sphere, collected using integrating sphere; E_s is the spectrum of the light used to excite the sample, collected using the integrating sphere. Each sample was measured at least three times and the final value of quantum yield corresponds to the arithmetic mean value. Estimated experimental error for quantum yields determination is less than 10%. (Note that the probably errors for quantum yield determined by the absolute method arise from four main sources: the standard lamp and calibration, the detection system, the excitation system used to generate photoluminescence, and the sample itself. If the sample shows significant overlap of absorption and luminescence spectra, the reabsorption of photoluminescence takes place and can affect the precision of a quantum yield determination.[2])

IR spectra of all complexes were recorded in KBr pellets, and IR spectra of the sulfonated poly(ether ether ketone) (SPEEK) and Yb^{3+} complex-coated SPEEK membranes were characterized by attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectroscopy on a NEXUS 670 in the region 400−4000 cm^{-1}. UV-vis diffuse reflection spectra (DRS) were measured on the Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Powder X-ray diffraction (PXRD) data were recorded by using Cu Kα radiation with a wavelength of 1.5405 Å at 40 kV and 40 mA from an X'Pert PRO MPD diffractometer (PANalytical, Almelo, the Netherlands). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI-5702 multi-functional spectrometer using Al Kα radiation. The morphology of films was investigated using a scanning electron microscope (SEM), Hitachi S-4800, Japan. All measurements were carried out at room temperature.

2. Synthesis of Ligand



Scheme S1. Preparation of ligand H_2**L**.

The synthetic route is shown above. Compound **1** was first prepared according to the literatures.[3] The synthesis of compound **2** was improved to increase the extraction quantity in organic solvent.

2,6-Bis(hydroxymethyl)pyridine (2). To pyridine-2,6-dicarboxylic acid dimethyl ester (5.00 g 25.64 mmol) in THF (50 mL) was slowly added $NaBH_4$ (4.21g, 111 mmol) in portions over 5 min in an ice bath, the solution was then stirred at room temperature for 12 h. After evaporation of the solvent, the residue was dissolved in 30 mL water, adjusted to pH 3 with 2 M HCl, and then adjusted to pH 9 with saturated aqueous Na_2CO_3 solution. Evaporation of the solvent, the residual solid was extracted with ethanol (4 × 50 mL). The combined extraction solvent was evaporated to dryness in vacuo, and the white raw product was further purified by silica gel column chromatography using ethanol as the eluent to afford **2** (2.92 g, yield 82.0 %). m.p. 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.78 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 4.0 Hz, 2H), 5.40 (t, J = 6.0 Hz, 2H), 4.50 (d, J = 4.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 160.67, 136.81, 118.09, 64.13. ESI mass spectrum *m/z*: calcd for $C_7H_9NO_2$ 139.2; found: 140.3 $[M+H]^+$.

2,6-Bis(bromomethyl)pyridine (3). 2,6-Bis(hydroxymethyl)pyridine (5.00 g, 35.93 mmol) was dissolved in absolute $CHCl_3$ (60 mL) and cooled to 0 °C. Then PBr_3 (3.38 mL, 35.93 mmol) was added dropwise to the solution. The mixture was warmed slowly to room temperature and further refluxed for 18 h. Subsequently, it was allowed to cool to room temperature before water (50 mL) was added. The organic layer was extracted, and the aqueous solution was extracted with $CHCl_3$ (3 × 50 mL). The organic layers were combined, washed with brine (40 mL), dried with $MgSO_4$, filtered, and the solvent was removed in vacuo to obtain white powder **3** (4.20 g, yield 44.1 %). m.p. 83–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.72 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 4.0 Hz, 2H), 4.55 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 156.81, 138.39, 123.03, 33.51. ESI mass spectrum *m/z*: calcd for $C_7H_7NBr_2$ 264.9; found: 265.8 $[M+H]^+$.

2,6-bis(aminomethyl)pyridine) (5). A mixture of **3** (4.00 g, 15.09mmol) and potassium phthalimide (5.59 g, 30.18 mmol) in DMF (30 mL) was stirred and heated at 100 °C for 48 h. After cooling, it was poured into 60 mL crushed ice and allowed to stand for 1 h. The precipitate was filtered off, washed with water, and then dried in vacuo for 24 h. Colorless 2,6-bis(phthalimidomethyl)pyridine **4** was obtained without further purified (5.50 g, yield 91.7 %).

2,6-bis(phthalimidomethyl)pyridine **4** (4.30 g, 10.82 mmol) was suspended in absolute ethanol (80 mL), and $N_2H_4 \cdot H_2O$ solution (1.11g, 22 mmol, 99 %) was added. The reaction mixture was then heated at reflux for 22 h. After cooling, the mixture was acidified with 6 N HCl to pH~1 and refluxed for 1 h again. The precipitate was filtered off, washed with water, and the filtrate was then concentrated almost to dryness. A 50% KOH solution (5 mL) was added (up to pH = 14), and the aqueous layer was extracted with $CHCl_3$ (3 × 100 mL). The organic layers were combined, dried with $MgSO_4$, filtered, and the solvent was removed in vacuo to obtain pale yellow oil **5** (0.95g, 64.2 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.62 (t, *J* = 6.0 Hz, 1H), 7.14 (d, *J* = 4.0 Hz, 2H), 3.97 (s, 4H), 1.87 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 161.68, 137.13, 119.34, 47.98. ESI mass spectrum *m/z*: calcd for $C_7H_{11}N_3$ 137.2; found: 138.0 $[M+H]^+$.

Synthesis of ligand (H_2L). To a solution of the 2,6-bis(aminomethyl)pyridine (0.91 g, 6.64mmol) in ethanol (15 mL) was added 2-hydroxy-3-methoxybenzaldehyde (2.22g ,14.61mmol) in ethanol (10 mL). This mixture was then stirred and allowed to stand for 4 h. The yellow precipitate was filtered out and washed with ether, and dried in vacuo to obtain yellow ligand. Yield: 2.45 g (91.1%). m.p. 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.53 (s, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 2H), 6.94(td, *J* = 8.0 Hz, *J* = 4.0 Hz, 4H), 6.84 (t, *J* = 8.0 Hz, 4H), 4.96 (s, 4H), 3.92(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 162.37, 156.83, 150.77, 143.80, 128.86, 109.24, 108.37, 108.77, 108.37, 100.00, 97.61, 44.89, 12.52. ESI mass spectrum *m/z*: calcd for $C_{23}H_{23}N_3O_4$ 405.2, found: 406.1 $[M+H]^+$.

3. Synthesis of Complexes

[LiYbL$(NO_3)_2(CH_3OH)$]·CH_3OH (1). A mixture of $LiOH·H_2O$ (4.2 mg, 0.1 mmol) and H_2**L** (20.3 mg, 0.05 mmol) in methanol (5 mL) was stirred for 5 min to obtain a transparent yellow solution. Then a solution of $Yb(NO_3)_3·6H_2O$ (22.3 mg, 0.05 mmol) in methanol (2 mL) was added to the mixture, which was stirred for 10 min at room temperature and filtered immediately. The crystals suitable for X-ray analysis were obtained by slow evaporation of methanol of the complex within two weeks at room temperature in air. The yellow complex crystals were collected and washed with methanol, then dried under vacuum 4 h to afford **1**, 47 % yield. Elemental analysis (%) found (calcd) for **1** $C_{25}H_{29}N_5O_{12}LiYb$: C 38.87 (38.92), H 3.75 (3.79), N 9.10 (9.08). IR (KBr, cm^{-1}): 3434 (br), 3058(w), 2898(w), 2833(w), 1632(vs), 1579(vs), 1552(m), 1471(m), 1454(m), 1411(m), 1384(m), 1319(m), 1240(m), 1222(m), 1170(m), 1109(w), 1083(vs), 1041(m), 1017(m), 976(m), 954(w), 859(s), 816(w), 786(s), 743(s), 655(w), 630(w).

[NaYbL(NO$_3$)$_2$(CH$_3$OH)]·CH$_3$OH (2). Complex **2** was prepared in the same way as complex **1** except that NaOH (4.0 mg, 0.1 mmol) was used instead of LiOH. The yellow complex crystals were collected and dried to afford **2**, 48 % yield. Elemental analysis (%) found (calcd) for **2** $C_{25}H_{29}N_5O_{12}NaYb$: C 38.01 (38.13), H 3.70 (3.71), N 8.80 (8.89). IR (KBr, cm^{-1}): 3411(br), 2944(w), 2905(w), 2842(w), 2801(w), 1625(vs), 1577(vs), 1556(vs), 1471(m), 1412(w), 1384(m), 1320(m), 1286(m), 1240(m), 1222(s), 1173(m), 1110(m), 1082(m), 1041(m), 1015(m), 977(m), 959(w), 861(m), 816(m), 786(s), 746(s), 648(w), 635(s).

[KYbL(NO$_3$)$_2$]$_n$ (3). Complex **3** was prepared in the same way as complex **1** except that KOH (5.6 mg, 0.1 mmol) was used instead of LiOH. The crystals suitable for X-ray analysis were obtained by slow evaporation of methanol within three days. The yellow complex crystals were collected and dried to afford **3**, 60 % yield. Elemental analysis (%) found (calcd) for **3** $C_{23}H_{21}N_5O_{10}KYb$: C 37.29 (37.35), H 2.81 (2.86), N 9.40 (9.47). IR (KBr, cm^{-1}): 3434(br), 2912(w), 2891(w), 2836(w), 1632(vs), 1577(m), 1553(m), 1470(s), 1452(s), 1410(w), 1382(m), 1322(vs), 1238(m), 1220(s), 1165(m), 1109(w), 1084(m), 1041(m), 1014(w), 976(w), 942(w), 861(m), 818(w), 790(m), 749(s), 655(w), 629(w).

[Rb$_4$Yb$_4$L$_4$(NO$_3$)$_8$] (4a) and **[Rb$_2$Yb$_4$L$_4$(NO$_3$)$_6$] (4b).** Complexes **4a** and **4b** were prepared in the same way as complex **1** except that RbOH (12 mg, 0.1 mmol) was used instead of LiOH. Two kinds of structures are coexisted in the same condition and could not be separated accurately. The yellow crystals were collected and dried to afford a mixture of **4a** and **4b**, 41 % total yield. Elemental analysis (%) calcd for **4a** $C_{23}H_{21}N_5O_{10}RbYb$: C 35.15, H 2.69, N 8.91 and for **4b** $C_{46}H_{42}N_9O_{17}RbYb_2$: C 37.88, H 3.03, N 8.76, found: C 36.32, H 2.90, N 8.85. IR (KBr, cm^{-1}): 3423(br), 2924(w), 2886(w), 2834(w), 1 630(vs), 1578(m), 1551(m), 1472(s), 1451(s), 1410(w), 1384(m), 1313(s), 1240(m), 1220(m), 1169(m), 1108(w), 1083(m), 1039(m), 1015(w), 974(w), 959(w), 861(m), 816(w), 785(m), 742(s), 654(w),629(w).

4. Single-Crystal X-ray Diffraction Analysis

Single–crystal X-ray diffraction measurements were carried out on a Bruker SMART APEX-II CCD diffractometer with graphite monochromated Mo Kα (λ= 0.71073 Å) radiation. Multi-scan absorption correction was applied with the SADABS program. Unit cell dimensions were obtained with least-squares refinements, and all structures were solved by direct methods using SHELXS-97. Metal atoms in each complex were located from *E*-maps. The non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were introduced at calculated positions and not refined (riding model). The details of the crystal parameters, data collections and refinement for all complexes are summarized in Table S1. Selected bond lengths and angles for all complexes are given in Table S2.

Table S1 Crystal Data and Structural Refinement Parameters for Complexes **1-4**.

	1	**2**	**3**	**4a**	**4b**
Formula	$C_{25}H_{29}N_5O_{12}LiYb$	$C_{25}H_{29}N_5O_{12}NaYb$	$C_{23}H_{21}N_5O_{10}KYb$	$C_{92}H_{84}N_{20}O_{40}Rb_4Yb_4$	$C_{46}H_{42}N_9O_{17}RbYb_2$
Formula Weight	771.51	787.56	739.59	3143.83	1424.44
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$C2/c$	*P***Error!**	$C2/c$
a (Å)	10.5784(6)	10.5784(6)	19.9224(8)	12.2689(10)	18.668(18)
b (Å)	17.3413(10)	17.3413(10)	14.1721(6)	13.8207(11)	17.375(17)
c (Å)	16.6413(9)	16.6413(9)	10.3924(4)	16.0314(15)	16.785(17)
α (°)	90.00	90.00	90.00	89.063(4)	90.00
β (°)	104.996(3)	104.996(3)	111.833(2)	84.408(5)	102.485(11)
γ (°)	90.00	90.00	90.00	88.521(4)	90.00
Z	4	4	4	1	4
Volume (Å^3)	2948.8(3)	2948.8(3)	2723.75(19)	2704.3(4)	5310(9)
D_{calcd} (g/cm^3)	1.738	1.774	1.804	1.930	1.782
μ (mm^{-1})	3.241	3.257	3.649	5.310	4.488
F(000)	1532	1564	1452	1524	2776
Temperature	296(2)	296(2)	293 (2)	296(2)	296(2)
Crystal Size (mm)	0.23 × 0.21 × 0.18	0.23 × 0.20 × 0.19	0.19 × 0.19 × 0.18	0.11 × 0.07 × 0.06	0.18 × 0.13 × 0.12
Reflections Collected	15172	15434	7126	13891	18991
Independent Ref. (R_{int})	5475 (0.0353)	5478 (0.0349)	2540 (0.0229)	9441 (0.0582)	4620 (0.0740)
Final R indices [I>2.0σ (I)]	R_1 = 0.0297 wR_2 = 0.0638	R_1 = 0.0292 wR_2 = 0.0599	R_1 = 0.0202 wR_2 = 0.0525	R_1 = 0.0666 wR_2 = 0.1275	R_1 = 0.0430 wR_2 = 0.0862

R indices (all date)	R_1 = 0.0466	R_1 = 0.0434	R_1 =0.0225	R_1 = 0.1492	R_1 = 0.0945
	wR_2 = 0.0710	wR_2 = 0.0649	wR_2 = 0.0540	wR_2 = 0.1465	wR_2 = 0.1016
GOF	1.017	1.015	1.006	1.004	1.010

Table S2 Selected Bond Lengths (Å) and Angles (°) for All Complexes.

Complex **1**

Yb(1)—O(2)	2.197 (3)	Yb(1)—N(2)	2.450 (3)	Li(1)—O(3)	2.051 (8)
Yb(1)—O(3)	2.224 (3)	Yb(1)—N(1)	2.472 (3)	Li(1)—O(8)	2.054 (9)
Yb(1)—O(11)	2.329 (3)	Yb(1)—O(5)	2.518 (10)	Li(1)—O(1)	2.135 (8)
Yb(1)—O(6)	2.395 (14)	Li(1)—O(2)	2.043 (8)	Li(1)—O(4)	2.174 (8)
Yb(1)—N(3)	2.441 (4)				
O(2)—Yb(1)—O(3)	72.52 (10)	N(3)—Yb(1)—N(1)	136.40 (12)	N(2)—Yb(1)—O(5)	107.9 (4)
O(2)—Yb(1)—O(11)	87.34 (12)	N(2)—Yb(1)—N(1)	68.22 (12)	N(1)—Yb(1)—O(5)	122.4 (2)
O(3)—Yb(1)—O(11)	83.39 (11)	O(2)—Yb(1)—O(5)	98.0 (5)	O(2)—Li(1)—O(3)	79.4 (3)
O(2)—Yb(1)—O(6)	95.6 (5)	O(3)—Yb(1)—O(5)	75.8 (3)	O(2)—Li(1)—O(8)	115.4 (4)
O(3)—Yb(1)—O(6)	123.2 (4)	O(11)—Yb(1)—O(5)	155.7 (2)	O(3)—Li(1)—O(8)	110.4 (4)
O(11)—Yb(1)—O(6)	152.9 (3)	O(6)—Yb(1)—O(5)	50.4 (4)	O(2)—Li(1)—O(1)	76.2 (3)
O(2)—Yb(1)—N(3)	148.03 (12)	N(3)—Yb(1)—O(5)	75.4 (4)	O(3)—Li(1)—O(1)	144.3 (4)
O(3)—Yb(1)—N(3)	75.55 (11)	O(6)—Yb(1)—N(2)	80.2 (5)	O(8)—Li(1)—O(1)	103.5 (4)
O(11)—Yb(1)—N(3)	87.59 (12)	N(3)—Yb(1)—N(2)	68.36 (12)	O(2)—Li(1)—O(4)	142.6 (4)
O(6)—Yb(1)—N(3)	103.0 (5)	O(2)—Yb(1)—N(1)	73.78 (11)	O(3)—Li(1)—O(4)	75.9 (3)
O(2)—Yb(1)—N(2)	141.36 (12)	O(3)—Yb(1)—N(1)	143.66 (11)	O(8)—Li(1)—O(4)	99.4 (3)
O(3)—Yb(1)—N(2)	140.96 (11)	O(11)—Yb(1)—N(1)	81.84 (11)	O(1)—Li(1)—O(4)	109.7 (4)
O(11)—Yb(1)—N(2)	80.77 (11)	O(6)—Yb(1)—N(1)	73.3 (3)		

Complex **2**

Yb(1)—O(2)	2.185 (3)	Yb(1)—N(3)	2.440 (4)	Na(1)—O(3)	2.332 (3)
Yb(1)—O(3)	2.217 (3)	Yb(1)—N(2)	2.466 (3)	Na(1)—O(1)	2.334 (4)
Yb(1)—O(11)	2.298 (3)	Yb(1)—N(1)	2.473 (3)	Na(1)—O(8)	2.370 (4)
Yb(1)—O(6)	2.389 (4)	Na(1)—O(4)	2.309 (3)	Na(1)—O(9)	2.592 (5)
Yb(1)—O(5)	2.431 (4)	Na(1)—O(2)	2.324 (3)		
O(2)—Yb(1)—O(3)	77.49 (10)	O(2)—Yb(1)—N(2)	140.07 (11)	O(4)—Na(1)—O(3)	69.61 (11)
O(2)—Yb(1)—O(11)	89.52 (11)	O(3)—Yb(1)—N(2)	137.49 (11)	O(2)—Na(1)—O(3)	72.56 (11)
O(3)—Yb(1)—O(11)	82.19 (11)	O(11)—Yb(1)—N(2)	79.91 (11)	O(4)—Na(1)—O(1)	118.18 (14)
O(2)—Yb(1)—O(6)	104.66 (14)	O(6)—Yb(1)—N(2)	72.68 (13)	O(2)—Na(1)—O(1)	68.35 (11)
O(3)—Yb(1)—O(6)	125.61 (12)	O(5)—Yb(1)—N(2)	116.86 (14)	O(3)—Na(1)—O(1)	130.56 (14)
O(11)—Yb(1)—O(6)	150.60 (12)	N(3)—Yb(1)—N(2)	67.19 (12)	O(4)—Na(1)—O(8)	97.49 (15)

O(2)—Yb(1)—O(5)	85.34 (15)	O(2)—Yb(1)—N(1)	73.17 (11)	O(2)—Na(1)—O(8)	123.27 (15)
O(3)—Yb(1)—O(5)	76.16 (13)	O(3)—Yb(1)—N(1)	146.12 (11)	O(3)—Na(1)—O(8)	109.41 (15)
O(11)—Yb(1)—O(5)	158.34 (13)	O(11)—Yb(1)—N(1)	81.00 (11)	O(1)—Na(1)—O(8)	116.89 (16)
O(6)—Yb(1)—O(5)	50.53 (13)	O(6)—Yb(1)—N(1)	78.80 (13)	O(4)—Na(1)—O(9)	82.77 (14)
O(2)—Yb(1)—N(3)	151.79 (12)	O(5)—Yb(1)—N(1)	117.27 (14)	O(2)—Na(1)—O(9)	142.82 (15)
O(3)—Yb(1)—N(3)	74.46 (11)	N(3)—Yb(1)—N(1)	134.34 (12)	O(3)—Na(1)—O(9)	143.22 (14)
O(11)—Yb(1)—N(3)	89.53 (12)	N(2)—Yb(1)—N(1)	67.19 (12)	O(1)—Na(1)—O(9)	83.57 (14)
O(6)—Yb(1)—N(3)	89.49 (14)	O(4)—Na(1)—O(2)	131.53 (14)	O(8)—Na(1)—O(9)	49.43 (14)
O(5)—Yb(1)—N(3)	85.23 (16)				

Complex **3**

Yb(1)—O(2)	2.1782 (19)	Yb(1)—N(2)	2.499 (3)	K(1)—O(2)	2.716 (2)
Yb(1)—O(4)	2.389 (2)	Yb(1)—O(5)	2.653 (2)	K(1)—O(3)^{ii}	2.909 (3)
Yb(1)—N(1)	2.450 (2)	K(1)—O(1)	2.710 (2)	K(1)—O(5)^{ii}	3.093 (2)
O(2)—Yb(1)—O(2)^{i}	89.25 (10)	N(1)—Yb(1)—O(5)^{i}	76.34 (8)	O(3)^{ii}—K(1)—O(5)^{ii}	42.25 (7)
O(2)—Yb(1)—O(4)	84.27 (8)	N(1)^{i}—Yb(1)—O(5)^{i}	123.83 (8)	O(3)^{iii}—K(1)—O(5)^{ii}	90.90 (8)
O(2)—Yb(1)—N(1)	75.09 (7)	N(2)—Yb(1)—O(5)^{i}	112.60 (5)	O(5)^{iii}—K(1)—O(5)^{ii}	125.30 (10)
O(4)^{i}—Yb(1)—N(1)	82.33 (9)	O(2)—Yb(1)—O(5)	73.04 (8)	O(3)^{iii}—K(1)—O(5)^{iii}	42.25 (7)
O(4)—Yb(1)—N(1)	82.05 (9)	O(2)^{i}—Yb(1)—O(5)	75.21 (8)	O(1)—K(1)—O(5)^{ii}	73.19 (6)
O(2)^{i}—Yb(1)—N(1)^{i}	75.09 (7)	O(4)—Yb(1)—O(5)	50.00 (7)	O(2)—K(1)—O(5)^{ii}	110.74 (6)
O(4)^{i}—Yb(1)—N(1)^{i}	82.04 (9)	N(1)—Yb(1)—O(5)	123.83 (8)	O(1)—K(1)—O(5)^{iii}	105.70 (7)
O(4)—Yb(1)—N(1)^{i}	82.33 (9)	N(1)^{i}—Yb(1)—O(5)	76.34 (8)	O(2)—K(1)—O(5)^{iii}	113.90 (7)
N(1)—Yb(1)—N(1)^{i}	130.71 (11)	N(2)—Yb(1)—O(5)	112.60 (5)	O(2)—K(1)—O(2)^{i}	68.57 (8)
O(2)—Yb(1)—N(2)	135.37 (5)	O(5)^{i}—Yb(1)—O(5)	134.80 (11)	O(1)—K(1)—O(3)^{ii}	105.74 (8)
O(4)—Yb(1)—N(2)	70.98 (5)	O(1)^{i}—K(1)—O(2)	124.02 (7)	O(1)—K(1)—O(3)^{iii}	72.36 (8)
N(1)—Yb(1)—N(2)	65.35 (5)	O(1)—K(1)—O(2)	58.25 (6)	O(2)—K(1)—O(3)^{iii}	114.46 (8)
O(2)—Yb(1)—O(5)^{i}	75.21 (8)	O(1)—K(1)—O(2)^{i}	124.02 (7)	O(3)^{ii}—K(1)—O(3)^{iii}	75.90 (14)

Symmetry codes: (i) −x, y, −z+1/2; (ii) −x, −y, −z+1; (iii) x, −y, z−1/2.

Complex **4a**

Yb(1)—O(2)	2.185 (8)	Yb(2)—O(18)	2.403 (9)	Rb(1)—O(20)	3.236 (12)
Yb(1)—O(3)	2.197 (8)	Yb(2)—N(6)	2.436 (9)	Rb(1)—O(19)	3.417 (12)
Yb(1)—O(9)	2.401 (9)	Yb(2)—N(4)	2.471 (10)	Rb(1)—O(11)	3.556 (10)
Yb(1)—N(1)	2.437 (11)	Yb(2)—N(5)	2.480 (9)	Rb(2)—O(6)	2.791 (8)
Yb(1)—N(3)	2.437 (9)	Yb(2)—O(15)	2.547 (10)	Rb(2)—O(14)	2.835 (9)
Yb(1)—O(12)	2.444 (10)	Yb(2)—O(20)	2.974 (12)	Rb(2)—O(8)	2.851 (8)
Yb(1)—N(2)	2.471 (9)	Rb(1)—O(4)	2.768 (9)	Rb(2)—O(20)	2.862 (10)
Yb(1)—O(14)	2.502 (10)	Rb(1)—O(2)	2.880 (8)	Rb(2)—O(7)	2.966 (8)

Yb(1)—O(11)	2.630 (9)	Rb(1)—O(1)	2.881 (9)	Rb(2)—O(5)	2.982 (9)
Yb(2)—O(7)	2.171 (7)	Rb(1)—O(3)	2.891 (8)	Rb(2)—O(13)	3.233 (12)
Yb(2)—O(6)	2.178 (8)	Rb(1)—O(10)^{i}	2.968 (11)	Rb(2)—O(1)	3.568 (9)
Yb(2)—O(17)	2.397 (9)	Rb(1)—O(11)^{i}	3.095 (9)		
O(2)—Yb(1)—O(3)	89.6 (3)	O(6)—Yb(2)—O(18)	116.8 (3)	O(3)—Rb(1)—O(20)	113.8 (3)
O(2)—Yb(1)—O(9)	126.6 (3)	O(7)—Yb(2)—N(6)	76.1 (3)	O(10)^{i}—Rb(1)—O(20)	81.3 (3)
O(3)—Yb(1)—O(9)	82.1 (3)	O(17)—Yb(2)—N(6)	79.8 (3)	O(4)—Rb(1)—O(19)	74.6 (3)
O(2)—Yb(1)—N(1)	75.7 (3)	O(18)—Yb(2)—N(6)	87.9 (3)	O(1)—Rb(1)—O(19)	101.4 (3)
O(9)—Yb(1)—N(1)	81.9 (3)	O(6)—Yb(2)—N(4)	73.9 (3)	O(3)—Rb(1)—O(19)	114.8 (3)
O(3)—Yb(1)—N(3)	75.6 (3)	O(17)—Yb(2)—N(4)	84.4 (3)	O(10)^{i}—Rb(1)—O(19)	69.6 (3)
O(9)—Yb(1)—N(3)	81.4 (3)	O(18)—Yb(2)—N(4)	79.4 (3)	O(11)^{i}—Rb(1)—O(19)	84.9 (3)
N(1)—Yb(1)—N(3)	131.7 (3)	N(6)—Yb(2)—N(4)	131.7 (3)	O(20)—Rb(1)—O(19)	37.8 (3)
O(2)—Yb(1)—O(12)	83.4 (3)	O(17)—Yb(2)—N(5)	71.6 (3)	O(4)—Rb(1)—O(11)	80.7 (3)
O(3)—Yb(1)—O(12)	127.7 (3)	O(18)—Yb(2)—N(5)	73.2 (3)	O(2)—Rb(1)—O(11)	54.8 (2)
N(1)—Yb(1)—O(12)	82.5 (3)	N(6)—Yb(2)—N(5)	65.8 (3)	O(1)—Rb(1)—O(11)	103.2 (2)
N(3)—Yb(1)—O(12)	82.6 (3)	N(4)—Yb(2)—N(5)	65.8 (3)	O(3)—Rb(1)—O(11)	50.6 (2)
O(2)—Yb(1)—N(2)	135.1 (3)	O(7)—Yb(2)—O(15)	76.2 (3)	O(11)^{i}—Rb(1)—O(11)	87.1 (2)
O(3)—Yb(1)—N(2)	135.3 (3)	O(6)—Yb(2)—O(15)	75.3 (3)	O(14)—Rb(2)—O(8)	79.5 (3)
O(9)—Yb(1)—N(2)	70.8 (3)	O(17)—Yb(2)—O(15)	51.7 (3)	O(6)—Rb(2)—O(20)	67.2 (3)
N(1)—Yb(1)—N(2)	65.8 (3)	N(6)—Yb(2)—O(15)	75.1 (3)	O(14)—Rb(2)—O(20)	117.8 (3)
N(3)—Yb(1)—N(2)	65.9 (3)	N(4)—Yb(2)—O(15)	126.4 (3)	O(8)—Rb(2)—O(20)	89.6 (3)
O(12)—Yb(1)—N(2)	69.9 (3)	N(5)—Yb(2)—O(15)	115.3 (3)	O(6)—Rb(2)—O(7)	64.2 (2)
O(2)—Yb(1)—O(14)	73.1 (3)	O(7)—Yb(2)—O(20)	67.6 (3)	O(14)—Rb(2)—O(7)	133.0 (2)
O(3)—Yb(1)—O(14)	77.2 (3)	O(6)—Yb(2)—O(20)	72.9 (3)	O(8)—Rb(2)—O(7)	54.2 (2)
N(1)—Yb(1)—O(14)	125.9 (3)	O(18)—Yb(2)—O(20)	45.7 (3)	O(20)—Rb(2)—O(7)	60.5 (3)
N(3)—Yb(1)—O(14)	74.5 (3)	N(6)—Yb(2)—O(20)	123.4 (3)	O(6)—Rb(2)—O(5)	54.0 (2)
O(12)—Yb(1)—O(14)	51.1 (3)	N(4)—Yb(2)—O(20)	77.8 (3)	O(14)—Rb(2)—O(5)	112.9 (3)
N(2)—Yb(1)—O(14)	111.6 (3)	N(5)—Yb(2)—O(20)	113.4 (3)	O(20)—Rb(2)—O(5)	116.6 (3)
O(2)—Yb(1)—O(11)	77.1 (3)	O(4)—Rb(1)—O2	120.4 (2)	O(7)—Rb(2)—O(5)	106.7 (2)
O(3)—Yb(1)—O(11)	70.9 (3)	O(4)—Rb(1)—O(1)	164.1 (3)	O(14)—Rb(2)—O(13)	41.2 (3)
O(9)—Yb(1)—O(11)	50.2 (3)	O(2)—Rb(1)—O(1)	54.5 (2)	O(8)—Rb(2)—O(13)	99.3 (3)
N(1)—Yb(1)—O(11)	75.0 (3)	O(4)—Rb(1)—O(3)	56.2 (2)	O(5)—Rb(2)—O(13)	73.5 (3)
N(3)—Yb(1)—O(11)	123.4 (3)	O(2)—Rb(1)—O(3)	64.7 (2)	O(6)—Rb(2)—O(1)	86.4 (2)
N(2)—Yb(1)—O(11)	112.3 (3)	O(1)—Rb(1)—O(3)	114.3 (2)	O(14)—Rb(2)—O(1)	82.1 (3)
O(7)—Yb(2)—O(6)	89.6 (3)	O(1)—Rb(1)—O(10)^{i}	81.4 (3)	O(8)—Rb(2)—O(1)	134.0 (3)
O(7)—Yb(2)—O(17)	126.7 (3)	O(4)—Rb(1)—O(11)^{i}	78.6 (3)	O(20)—Rb(2)—O(1)	63.0 (3)
O(6)—Yb(2)—O(17)	87.9 (3)	O(10)^{i}—Rb(1)—O(11)^{i}	41.7 (3)	O(5)—Rb(2)—O(1)	90.1 (2)
O(7)—Yb(2)—O(18)	80.9 (3)	O(1)—Rb(1)—O(20)	67.5 (3)	O(13)—Rb(2)—O(1)	93.7 (3)

Symmetry codes: (i) −x+1, −y+2, −z.

Complex **4b**

Yb(1)—O(3)	2.149 (5)	Yb(1)—O(9)	2.56 (3)	Rb(1)—O(1)	3.171 (7)
Yb(1)—O(2)	2.162 (5)	Yb(1)—O(10)	2.739 (13)	Rb(1)—O(3)	3.181 (5)
Yb(1)—O(7)	2.379 (7)	Yb(1)—N(3)	2.432 (7)	Rb(1)—O(5)	3.267 (7)
Yb(1)—N(1)	2.425 (7)	Yb(1)—N(2)	2.474 (6)	Rb(1)—O(4)	2.845 (5)
Yb(1)—O(5)	2.551 (6)	Rb(1)—O(2)	2.927 (5)		
O(3)—Yb(1)—O(2)	86.50 (19)	N(1)—Yb(1)—O(9)	80.8 (9)	O(4)—Rb(1)—O(4)^i	66.4 (2)
O(3)—Yb(1)—O(7)	86.8 (2)	N(3)—Yb(1)—O(9)	81 (2)	O(4)—Rb(1)—O(2)	107.97 (15)
O(2)—Yb(1)—O(7)	128.7 (2)	N(2)—Yb(1)—O(9)	68.2 (15)	O(4)—Rb(1)—O(2)^i	94.40 (16)
O(2)—Yb(1)—N(1)	75.7 (2)	O(3)—Yb(1)—O(10)	71.8 (3)	O(4)—Rb(1)—O(1)	122.41 (17)
O(7)—Yb(1)—N(1)	86.8 (2)	O(2)—Yb(1)—O(10)	74.3 (3)	O(4)^i—Rb(1)—O(1)	63.81 (16)
O(3)—Yb(1)—N(3)	75.1 (2)	N(1)—Yb(1)—O(10)	123.0 (3)	O(2)—Rb(1)—O(1)	51.12 (15)
O(7)—Yb(1)—N(3)	80.2 (2)	N(3)—Yb(1)—O(10)	72.0 (3)	O(2)^i—Rb(1)—O(1)	126.99 (15)
N(1)—Yb(1)—N(3)	131.2 (2)	N(2)—Yb(1)—O(10)	106.6 (3)	O(4)—Rb(1)—O(3)	51.36 (14)
O(2)—Yb(1)—N(2)	134.4 (2)	O(5)—Yb(1)—O(10)	139.4 (3)	O(4)^i—Rb(1)—O(3)	81.80 (14)
O(7)—Yb(1)—N(2)	73.9 (2)	O(9)—Yb(1)—O(10)	48.2 (3)	O(2)—Rb(1)—O(3)	57.65 (14)
N(1)—Yb(1)—N(2)	65.9 (2)	N(2)—Yb(1)—O(5)	114.1 (2)	O(2)^i—Rb(1)—O(3)	138.25 (14)
N(3)—Yb(1)—N(2)	65.4 (2)	O(3)—Yb(1)—O(9)	119.8 (4)	O(1)—Rb(1)—O(3)	94.12 (14)
O(3)—Yb(1)—O(5)	77.8 (2)	O(2)—Yb(1)—O(9)	83 (2)	O(1)—Rb(1)—O(3)^i	88.86 (13)
O(2)—Yb(1)—O(5)	77.6 (2)	O(2)—Rb(1)—O(5)	56.96 (16)	O(3)—Rb(1)—O(3)^i	125.43 (19)
O(7)—Yb(1)—O(5)	51.3 (2)	O(1)—Rb(1)—O(5)	106.82 (15)	O(2)—Rb(1)—O(5)^i	110.58 (16)
N(1)—Yb(1)—O(5)	76.3 (2)	O(1)^i—Rb(1)—O(5)	70.31 (15)	O(1)—Rb(1)—O(5)^i	70.31 (15)
N(3)—Yb(1)—O(5)	125.1 (2)	O(3)—Rb(1)—O(5)	54.76 (15)	O(4)—Rb(1)—O(5)	89.37 (16)

Symmetry codes: (i) −x+1, y, −z+3/2.

5. Coordination Geometry of the Yb^{3+}

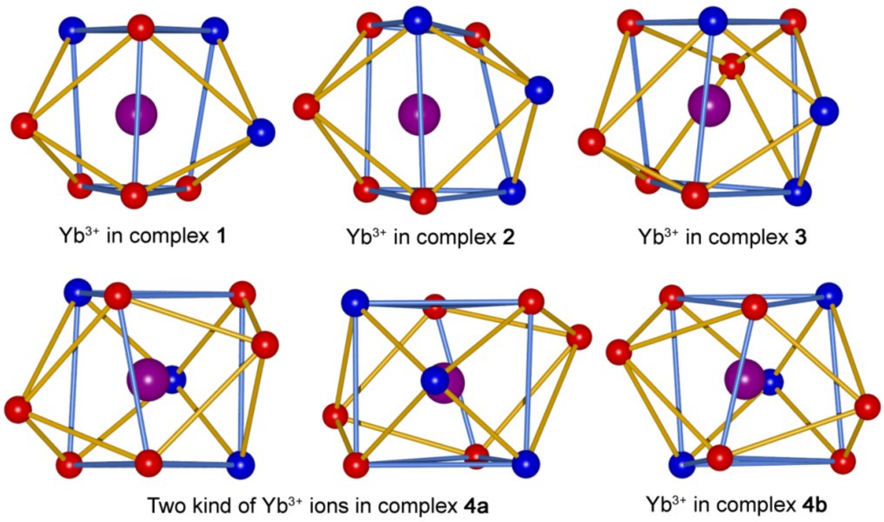


Fig. S1 Coordination polyhedron of the Yb^{3+} ion in different complexes. Coordination atom: O red, N blue, Yb violet.

6. Supramolecular Structure of Complexes

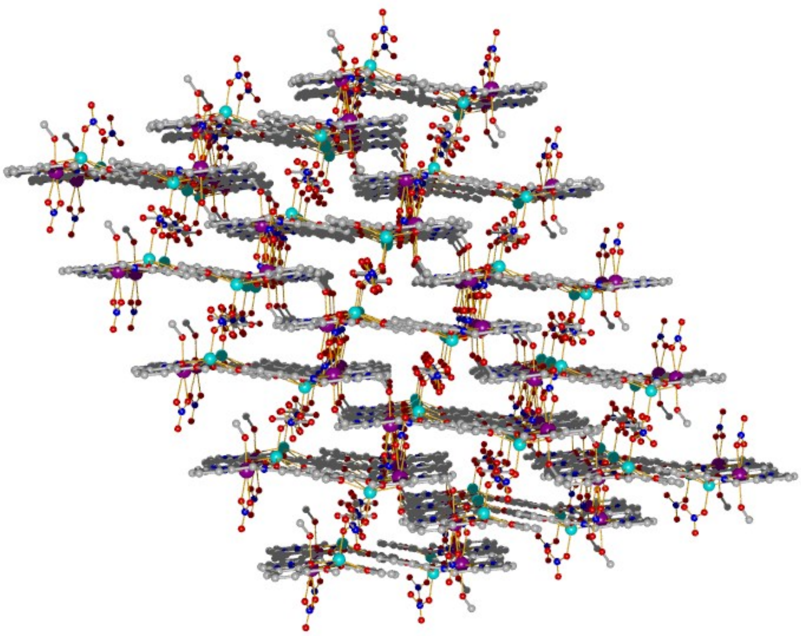


Fig. S2 Supramolecular aggregation structure of complex **1** through a series of hydrogen bonds and π–π stacking interactions. All hydrogen atoms are omitted for clarity. C gray, O red, N blue, Yb violet, Li turquoise.

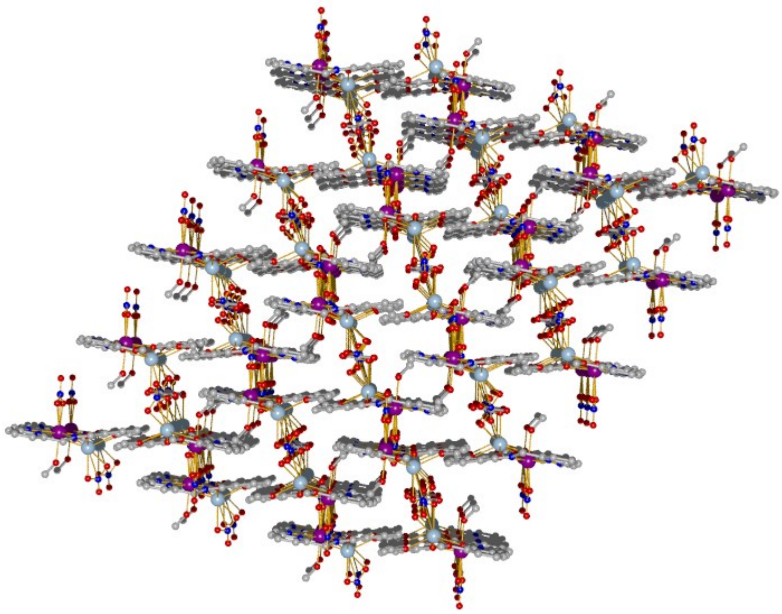


Fig. S3 Supramolecular aggregation structure of complex **2** through a series of hydrogen bonds and π–π stacking interactions. All hydrogen atoms are omitted for clarity. C gray, O red, N blue, Yb violet, Na pale blue.

7. Photophysical Properties of Complexes

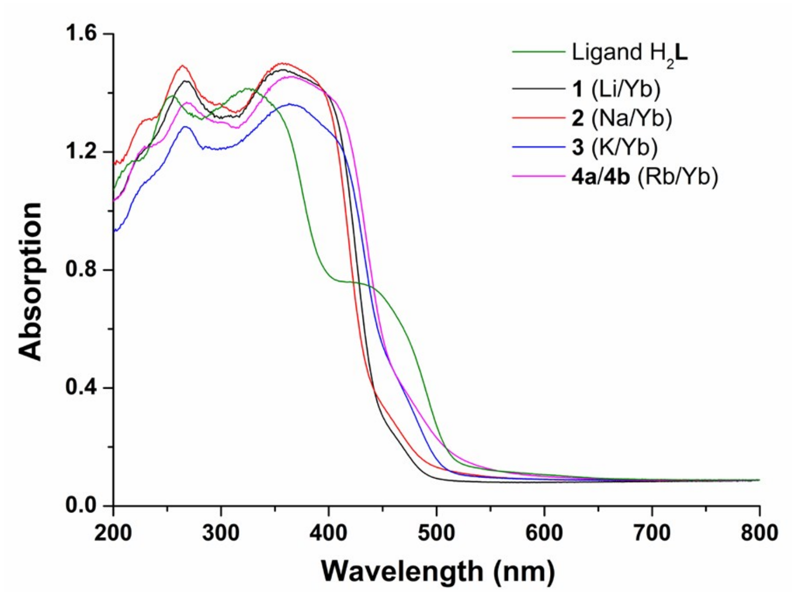


Fig. S4 UV-vis of the ligand and heteronuclear Yb^{3+} complexes in solid at room temperature.

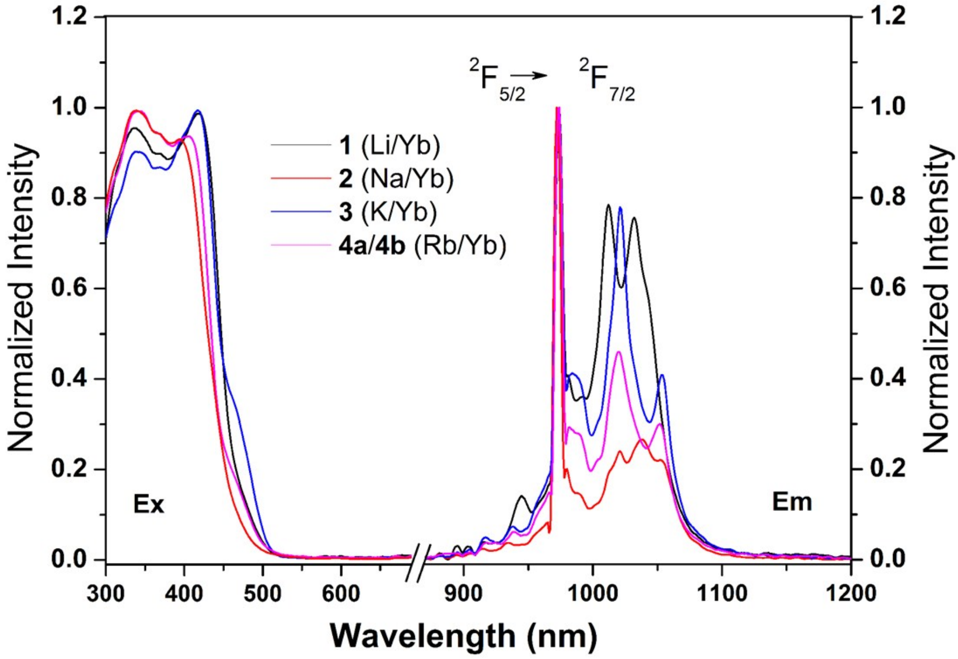


Fig. S5 The excitation and NIR emission spectra of s-f heteronuclear Yb^{3+} complexes in solid at room temperature.

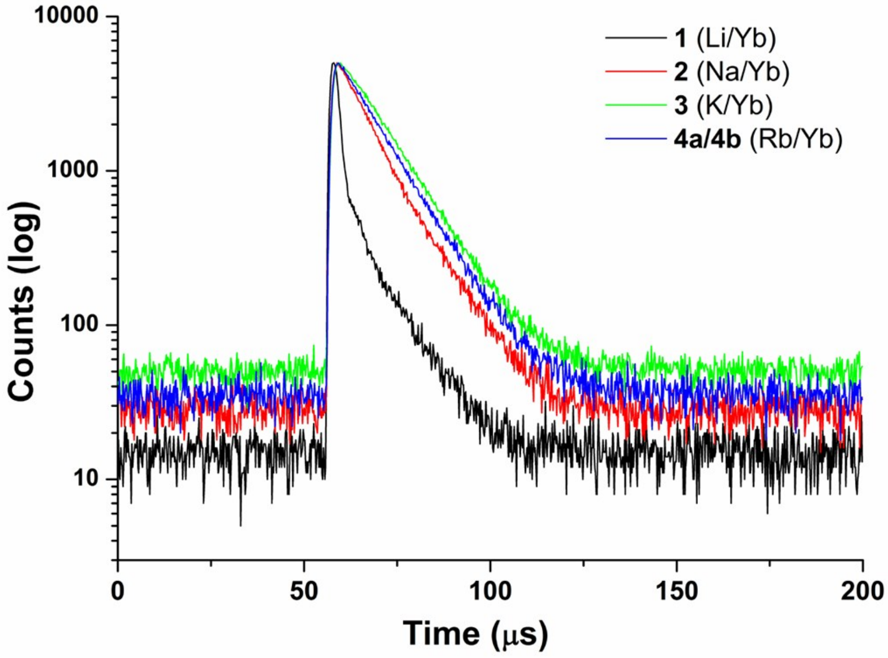


Fig. S6 The emission decay curves of s-f heteronuclear Yb^{3+} complexes in solid at 975 nm.

8. Preparation of Membrane Material

Sulfonated poly(ether ether ketone) (SPEEK) was prepared by post-sulfonation method according to the literatures.[4] The sulfonation degree up to 0.6 suitable for further application was controlled by appropriate sulfonation time, which was determined by calculating the ratio between the peak area of the proton near the sulfonic acid group and the peak area of all other aromatic protons in the ^{1}H NMR spectrum.[5]

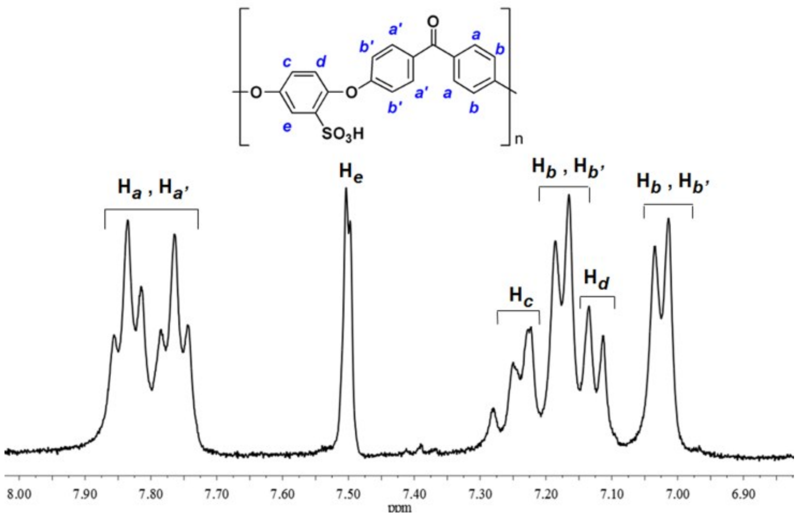


Fig. S7 ^{1}H NMR spectrum of the SPEEK dissolved in DMSO-*d*.

The presence of the sulfonic acid group could cause a down-field shift of the hydrogen (H_e) to 7.50 ppm, and the intensity of the distinct H_e signal was enhanced with an increasing of the sulfonation degree. The sulfonation degree of 60 % was determined through the calculation of the ratio between the peak area of the H_e (AH_e) and the integrated peak area of the signals corresponding to all the other aromatic hydrogens ($AH_{a,a',b,b',c,d}$) using the following equation:

$$\frac{n}{12-2n}=\frac{AH_e}{\sum AH_{a,a',b,b',c,d}}$$

where AH_e is the peak area of the H_e signal, and $\sum AH_{a,a',b,b',c,d}$ is the sum of the peak area of the signals corresponding to all the other aromatic hydrogens. The sulfonation degree can be obtained from $n \times 100$ %.

The prepared SPEEK (0.3 g) was dissolved in dimethylacetamide (6 mL) to form a 5 % (w/v) solution, which then was coated on a glass slide (8 cm × 8 cm). The polymer solution on the glass slide was roasted by infrared lamp for 5 min and further dried at 80°C for 4 h. The residual solvent in SPEEK membrane was removed in vacuo at 120°C for 24 h. The protons of the sulfonic acid on SPEEK membrane were exchanged by immersing the membrane (2 cm × 2 cm) into 1 M alkali solution (LiOH, NaOH, KOH or RbOH) for 24 h. Then, the membrane was washed with deionized water and dried. A series of treated SPEEK membrane materials coated with different alkali metal ions were immersed into the corresponding methanol solutions of complexes (0.025 mol·L^{-1} for ligand $\mathbf{L}^{2-}$) for a few hours, in each of which alkali metal ion, $\mathbf{L}^{2-}$, NO_3^- and Yb^{3+} were self-assembled on the surface of corresponding SPEEK membrane to obtain heteronuclear Yb^{3+} complex-based NIR SPEEK membrane.

9. The Characterization of Complexes and Complex-Coated SPEEK Membranes

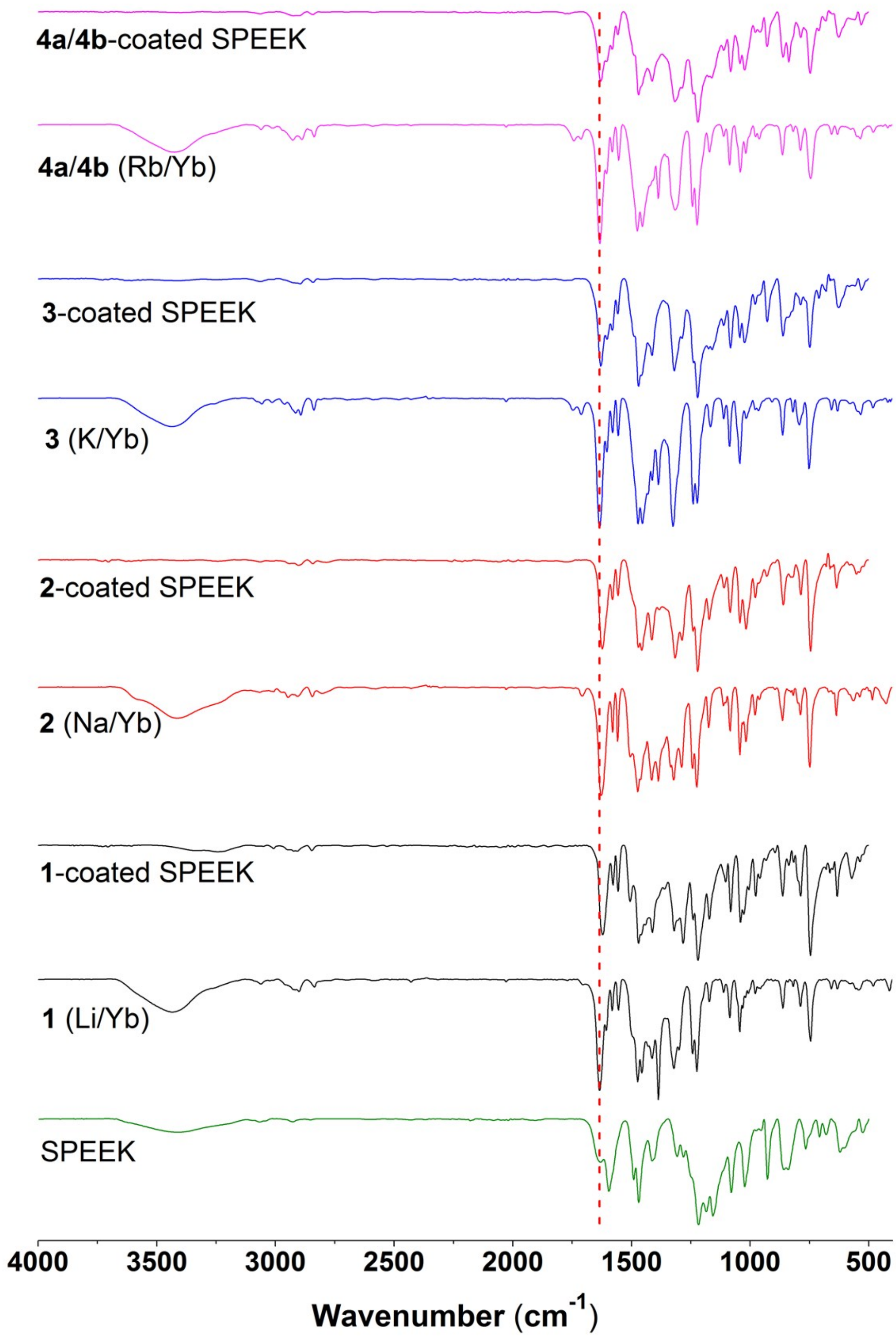


Fig. S8 FT-IR spectra of the SPEEK, complexes and Yb^{3+} complex-coated SPEEK membranes.

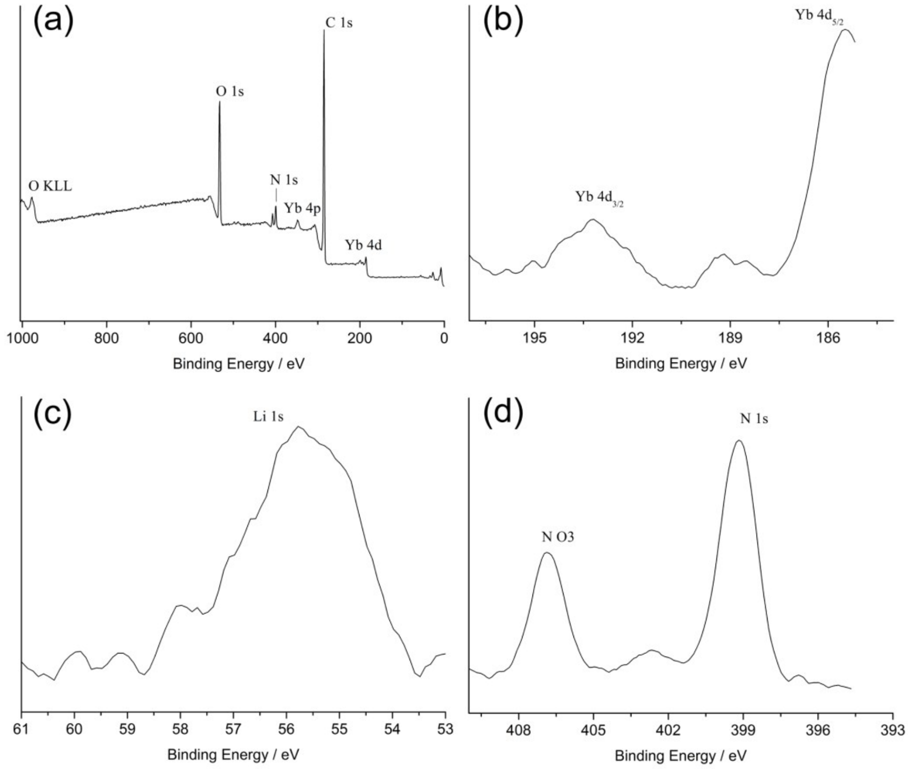


Fig. S9 (a) XPS spectrum of **1**(Li/Yb)-coated SPEEK membrane. (b) Yb 4d energy region. (c) Li 1s energy region. (d) N 1s energy region.

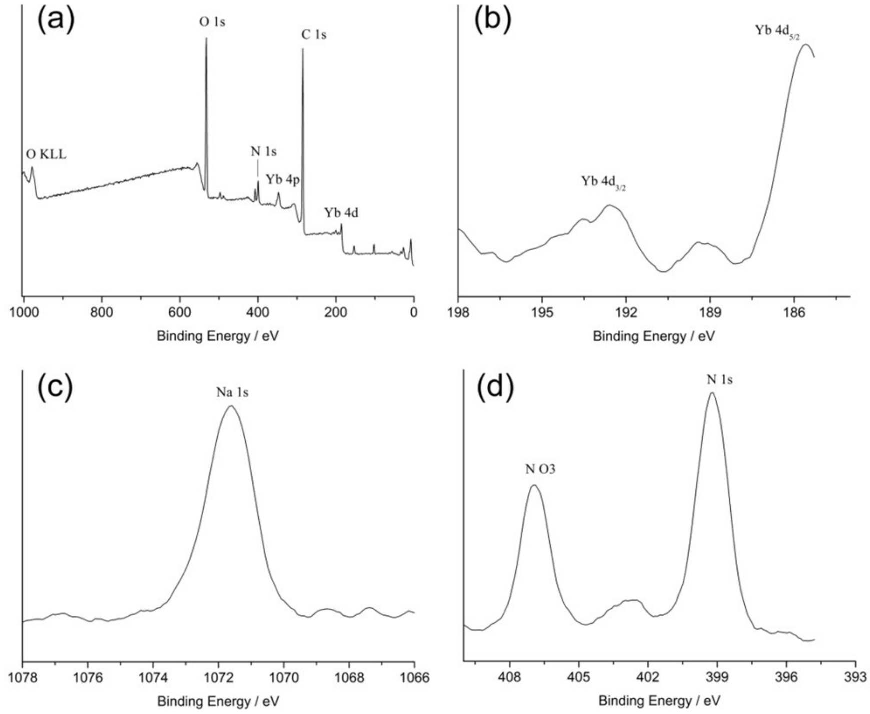


Fig. S10 (a) XPS spectrum of **2**(Na/Yb)-coated SPEEK membrane. (b) Yb 4d energy region. (c) Na 1s energy region. (d) N 1s energy region.

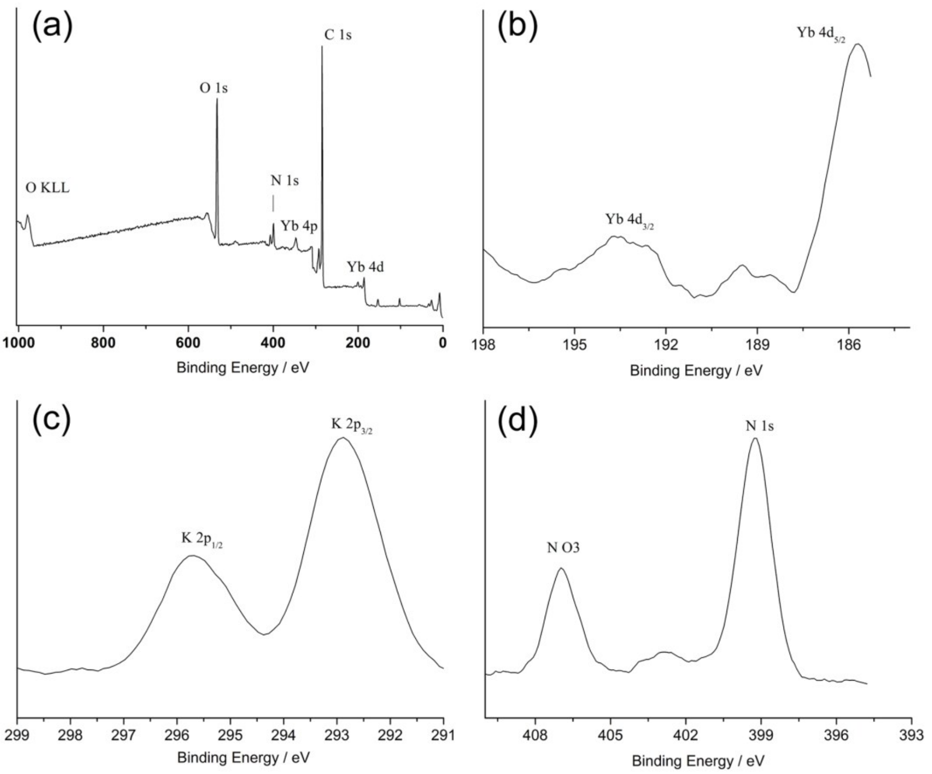


Fig. S11 (a) XPS spectrum of **3**(K/Yb)-coated SPEEK membrane. (b) Yb 4d energy region. (c) K 2p energy region. (d) N 1s energy region.

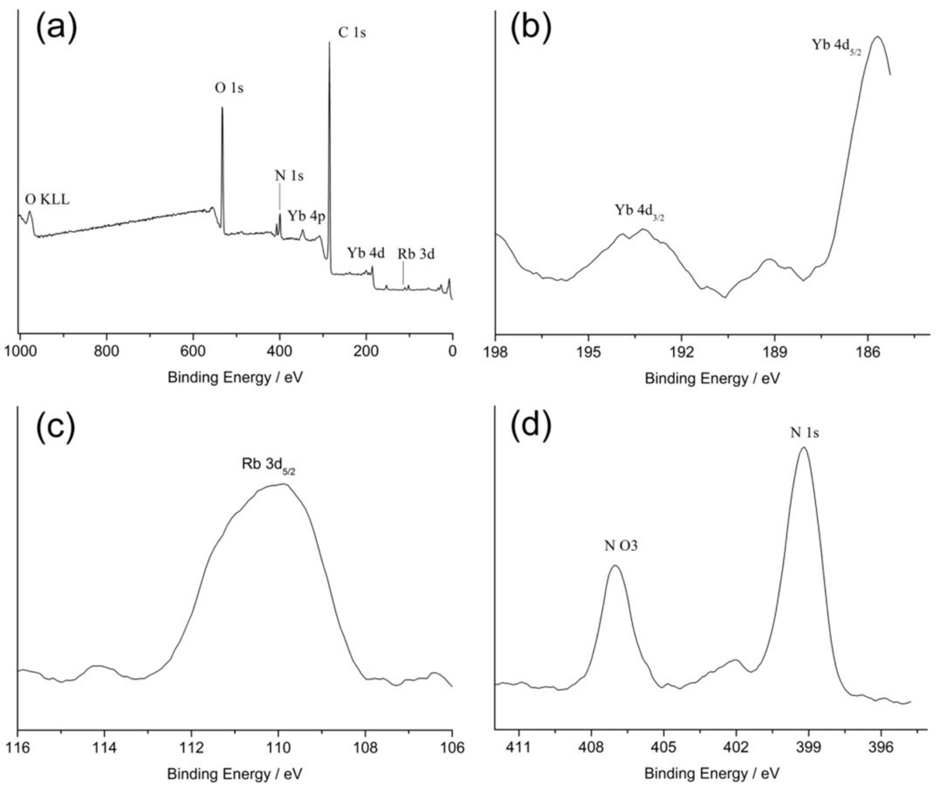


Fig. S12 (a) XPS spectrum of **4a/4b**(Rb/Yb)-coated SPEEK membrane. (b) Yb 4d energy region. (c) Rb 3d energy region. (d) N 1s energy region.

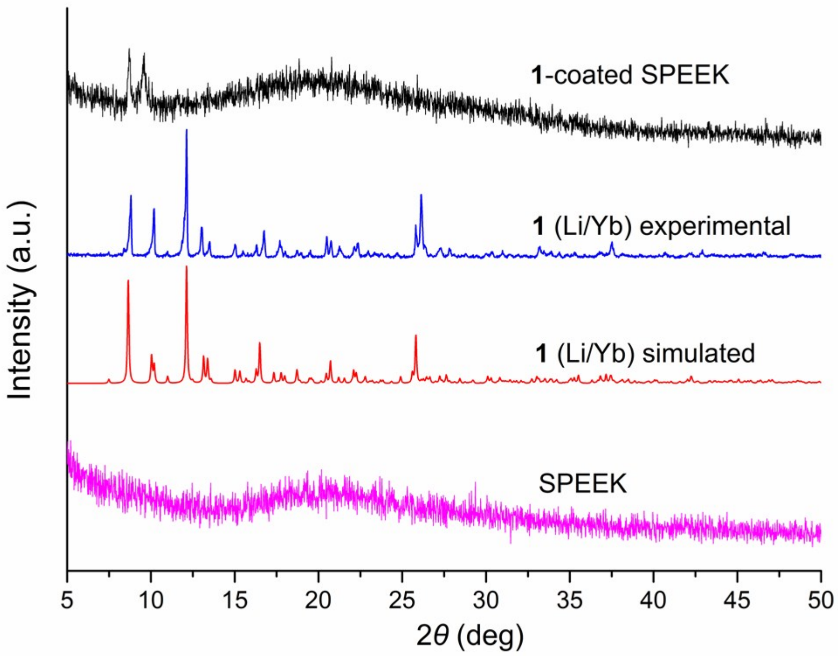


Fig. S13 PXRD patterns of the SPEEK, simulated result from crystal **1**, experimental result from complex **1** and **1**-coated SPEEK membrane.

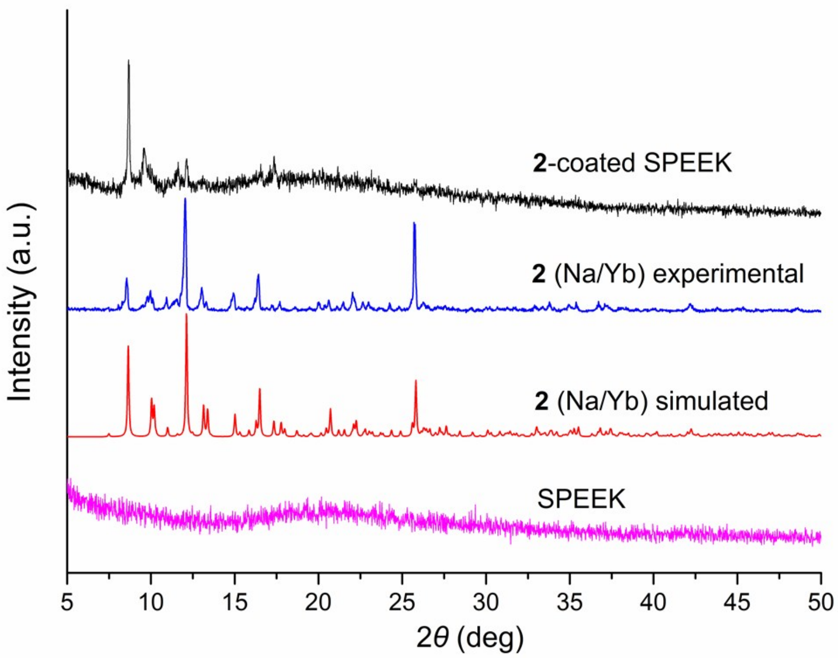


Fig. S14 PXRD patterns of the SPEEK, simulated result from crystal **2**, experimental result from complex **2** and **2**-coated SPEEK membrane.

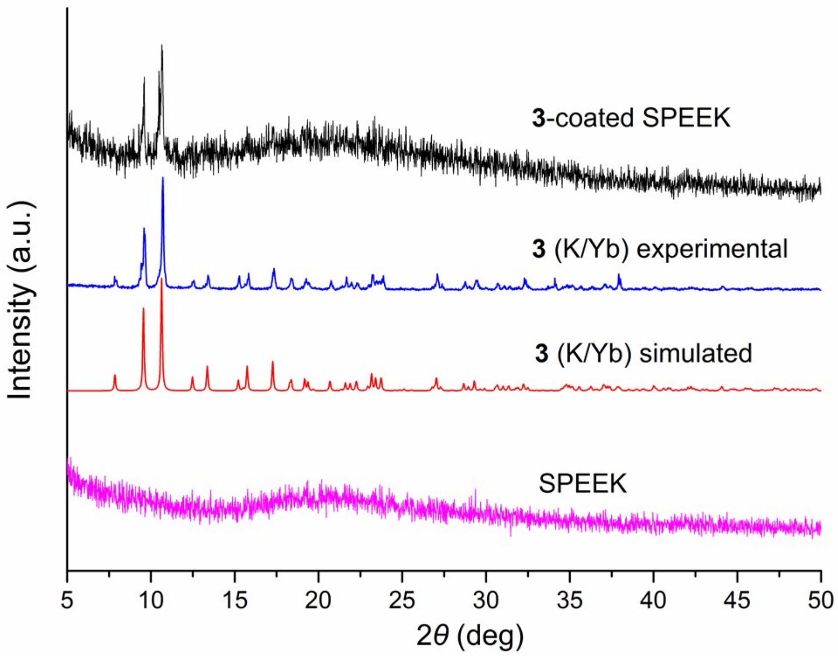


Fig. S15 PXRD patterns of the SPEEK, simulated result from crystal **3**, experimental result from complex **3** and **3**-coated SPEEK membrane.

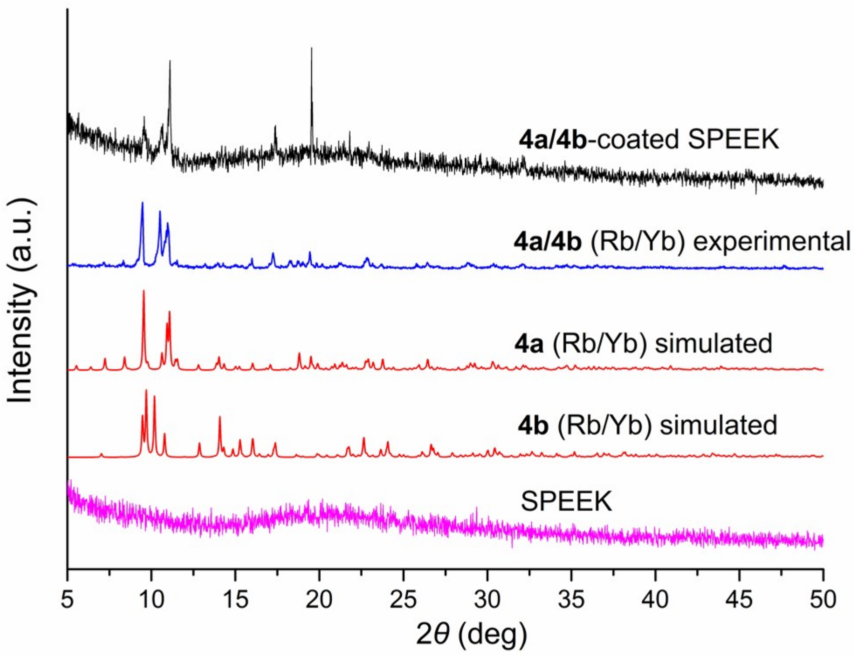


Fig. S16 PXRD patterns of the SPEEK, simulated results from crystal **4a** and **4b**, experimental result from **4a/4b** and **4a/4b**-coated SPEEK membrane.

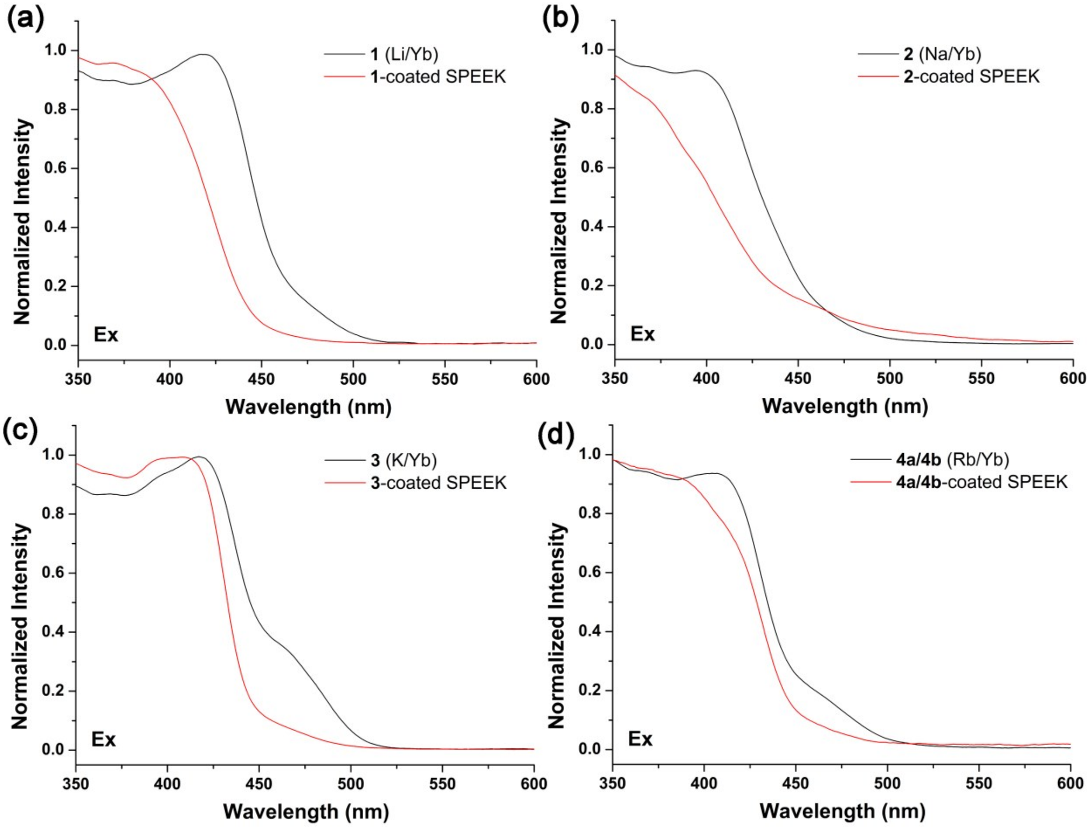


Fig. S17 The changes of excitation spectra between heteronuclear Yb^{3+} complexes and their corresponding complex-coated SPEEK membranes.

References:

(1) J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230.

(2) (a) J. Valenta, *Nanosci. Methods*, 2014, **3**, 11. (b) C. Würth, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nat. Protoc.*, 2013, **8**, 1535. (c) A. R. Johnson, S. J. Lee, J. Klein and J. Kanicki, *Rev. Sci. Instrum.*, 2007, **78**, 096101.

(3) X.-M. Shi, R.-R. Tang, G.-L. Gu and K.-L. Huang, *Spectrochim. Acta. A*, 2009, **72**, 198.

(4) P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang and S. Kaliaguine, *J. Membrane. Sci.*, 2004, **229**, 95.

(5) J. M. Song, D. W. Shin, J. Y. Sohn, Y. C. Nho, Y. M. Lee and J. Shin, *J. Membrane. Sci.*, 2013, **430**, 87.