

Supporting Information

Systematic tuning of the emission colors and redox potential of Eu(II)-containing cryptates by changing N/O ratio of cryptands

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Methods

General methods: ^1H NMR spectra were recorded on Bruker 400MHz NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were performed in negative ion mode on Bruker Apex IV Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were conducted on a VARIO elemental analyzer from Elementar Analysensysteme GmbH.

Photophysical Measurements: UV-visible absorption spectra were measured by a Shimadzu UV-3600Plus UV-VIS-NIR spectrometer. Excitation and emission spectra were recorded on Edinburgh FLS980 fluorescence spectrophotometer. Luminescence decay lifetimes were obtained on a single photon counting spectrometer from Edinburgh FLS980 with laser lamp as the excitation source. The data were analyzed by tail fit of the decay profile using a software package provided by Edinburgh Instruments. Absolute photoluminescence (PL) quantum yields were measured using Hamamatsu C9920-02 PL quantum yield measurement system with integrating sphere for all the complexes. All measurements were performed at room temperature.

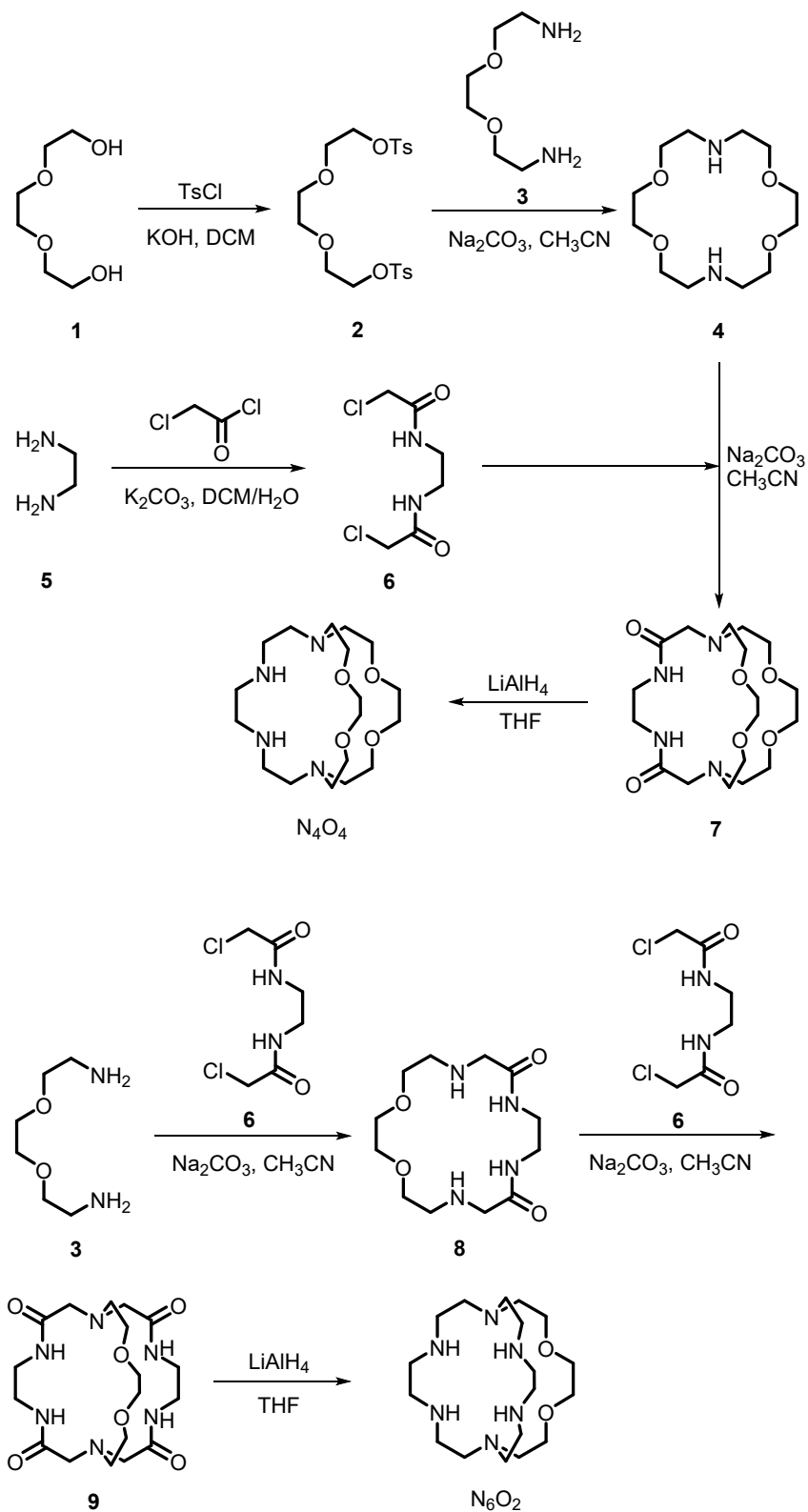
Single Crystal Structure Measurements: The single crystal X-ray diffraction (XRD) data were collected on a Rigaku Mercury CCD diffractometer. The radiation used in the XRD analysis is the graphite-monochromated Mo $K\alpha$ emission line ($\lambda = 0.71069 \text{ \AA}$). XRD data were collected by using the CrystalClear software. Structural refinements were conducted with SHELXL-2014 software.

Cyclic Voltammetry Measurement: Cyclic voltammetry was carried out in methanol solution (10^{-3} M) at room temperature with a CHI600C voltametric analyzer in a glovebox. Tetrabutylammonium hexafluorophosphate (TBAPF_6 , 0.1 M) was as the supporting electrolyte. The conventional three-electrode configuration included a platinum working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl wire pseudo-reference electrode. The scan rate is 100 mV s^{-1} .

Experimental Section

Synthesis of ligands

The detailed synthetic routes of N_4O_4 and N_6O_2 cryptates are shown in **Scheme S1**.



Scheme S1 Detailed synthetic routes of N_4O_4 and N_6O_2 .

Synthesis of 4,7,13,16-tetraoxa-1,10,21,24-tetraazabicyclo[8.8.8]hexacosane (N₄O₄):

1,8-ditosyl-3,6-dioxaoctane (**2**): Triethylene glycol (**1**) (22.50 g, 149.8 mmol) and *p*-toluenesulfonyl chloride (60.00 g, 314.7 mmol) were mixed in 250 mL dichloromethane and cooled to 0 °C. While stirring, KOH (67.30 g, 1.20 mol) was added in portion. After addition, the ice bath was removed, and the mixture was stirred at room temperature overnight. Water (200 mL) was added, and the mixture was extracted with dichloromethane (100 mL×2). The combined dichloromethane extract was dried over Na₂SO₄, evaporated and dried under vacuum to obtain a white solid. Yield: 87% (60.04 g). ¹H NMR (400 MHz, CDCl₃): δ 7.82-7.76 (d, 4H), 7.37-7.31 (d, 4H), 4.17-4.11 (t, 4H), 3.68-3.63 (t, 4H), 3.53 (s, 4H), 2.44 (s, 6H).

1,4,10,13-tetraoxa-7,16-diazacyooctadecane (**4**): 1,2-bis(2-aminoethoxy)ethane (**3**) (2.00 g, 13.5 mmol), **2** (6.19 g, 13.5 mmol) and Na₂CO₃ (14.31 g, 13.5 mmol) were mixed in 300 mL acetonitrile and heated to reflux under nitrogen atmosphere for three days. After cooling, the mixture was filtrated to remove the insoluble substance. The filtrate was evaporated to obtain a yellowish solid. The solid was sublimed under ~ 8 Pa at 120 °C to obtain a white solid. Yield: 17% (0.61 g). ¹H NMR (400 MHz, CDCl₃): δ 3.64-3.56 (m, -CH₂OCH₂CH₂OCH₂-, 16H), 2.84-2.76 (m, -NHCH₂-, 8H). ESI-MS positive: Calcd. 262.2, m/z = 263.2 (M+H⁺), 285.2 (M+Na⁺).

N,N'-bis(chloroacetyl)-1,2-ethylenediamine (**6**): To a solution of ethylenediamine (**5**) (3.61 g, 60.0 mmol) and K₂CO₃ (20.73 g, 150.0 mmol) in 45 mL dichloromethane and 35 mL water at 0 °C, the chloroacetyl chloride (13.55 g, 120.0 mmol) was added dropwise over one hour. The white precipitate was produced during the addition. After addition, the ice bath was removed, and the mixture was stirred at room temperature overnight. The mixture was filtrated. The residue was washed with methanol and dried under vacuum to obtain a white solid. Yield: 80% (10.26 g). ¹H NMR (400 MHz, CDCl₃): δ 7.10 (bs, -CONH-, 2H), 4.07 (s, -CH₂Cl, 4H), 3.54-3.50 (m, -CH₂CH₂-, 8H).

4,7,13,16-tetraoxa-1,10,21,24-tetraazabicyclo[8.8.8]hexacosane-20,25-dione (**7**): **6** (0.64 g, 3.0 mmol) and Na₂CO₃ (6.36 g, 60.0 mmol) were mixed in acetonitrile (300 mL) and heated to reflux under nitrogen atmosphere. Then **4** (0.79 g, 3.0 mmol) in

acetonitrile (50 mL) was added dropwise over one hour, and the mixture was refluxed for one day. After cooling, the mixture was filtrated to remove the insoluble substance. The filtrate was evaporated to obtain a yellowish solid. Purification of column chromatography (silica gel) by dichloromethane/methanol (v/v = 25:1) resulted in white solid. Yield: 50% (0.60 g). ¹H NMR (400 MHz, CDCl₃): δ 8.19 (bs, -CONH-, 2H), 3.63 (s, -OCH₂CH₂O-, 8H), 3.60-3.47 (m, -NCH₂CH₂O-, 8H), 3.18 (s, -NCH₂CO-, 4H), 2.90-2.78 (m, -NCH₂CH₂O-, 4H), 2.68-2.56 (m, -NCH₂CH₂O-, 4H), 1.73 (s, -NCH₂CH₂N-, 4H). ESI-MS positive: Calcd. 402.2, m/z = 425.2 (M+Na⁺).

4,7,13,16-tetraoxa-1,10,21,24-tetraazabicyclo[8.8.8]hexacosane (N₄O₄): **7** (1.00 g, 2.5 mmol) was suspended in 25 mL dry tetrahydrofuran (THF), and LiAlH₄ (0.94 g, 24.8 mmol) suspension of THF (25 mL) was added dropwise. Then the mixture was heated to reflux under nitrogen atmosphere for 4 days. After cooling, 3.0 mL water was added to quench excess LiAlH₄. The mixture was filtrated to remove insoluble substance, and the residue was washed with 100 mL THF. The filtrate was evaporated to obtain a colorless oil. The oil was sublimed under ~ 5 Pa at 120 °C to obtain a white waxy solid. Yield: 63% (0.59 g). ¹H NMR (400 MHz, CDCl₃): δ 3.73-3.63 (m, -OCH₂CH₂O-, 8H), 3.58-3.53 (t, -OCH₂CH₂N-, 8H), 2.79 (s, -NHCH₂CH₂NH-, 4H), 2.72-2.66 (m, -NCH₂CH₂NH-, 4H), 2.64-2.50 (m, -NCH₂CH₂NH-, -NCH₂CH₂O-, 12H). ESI-MS positive: Calcd. 374.3, m/z = 375.3 (M+H⁺), 397.3 (M+Na⁺).

Synthesis of 4,7-dioxa-1,10,13,16,21,24-hexaazabicyclo[8.8.8]hexacosane (N₆O₂):

1,4-dioxa-7,10,13,16-tetraazacyclooctadecane-9,14-dione (**8**): **6** (0.64 g, 3.0 mmol) and Na₂CO₃ (6.36 g, 60.0 mmol) were mixed in acetonitrile (300 mL) and heated to reflux under nitrogen atmosphere. Then **3** (0.44 g, 3.0 mmol) in acetonitrile (50 mL) was added dropwise over 30 minutes, and the mixture was refluxed for two days. After cooling, the mixture was filtrated to remove the insoluble substance. The filtrate was evaporated to obtain a yellowish solid. Purification of column chromatography (Al₂O₃) by dichloromethane/methanol (v/v = 20:1) resulted in yellowish solid. Yield: 39% (0.34 g). ¹H NMR (400 MHz, CDCl₃): δ 7.68 (bs, -CONH-, 2H), 3.64 (s, -OCH₂CH₂O-, 4H), 3.60-3.56 (m, -OCH₂CH₂NH-, 4H), 3.32 (s, -NHCH₂CO-, 4H), 2.87-2.82 (m, -

OCH₂CH₂N-, 4H), 1.96 (s, -NCH₂CH₂N-, 4H). ESI-MS positive: Calcd. 288.2, m/z = 311.2 (M+Na⁺).

4,7-dioxa-1,10,13,16,21,24-hexaazabicyclo[8.8.8]hexacosane-12,17,20,25-tetraone (**9**): **6** (1.70 g, 8.0 mmol) and Na₂CO₃ (17.0 g, 160 mmol) were mixed in acetonitrile (800 mL) and heated to reflux under nitrogen atmosphere. Then **8** (2.31 g, 8.0 mmol) in acetonitrile (50 mL) was added dropwise over one hour, and the mixture was refluxed for five days. After cooling, the mixture was filtrated to remove the insoluble substance. The filtrate was evaporated to obtain a yellowish solid. Purification of column chromatography (silica gel) by dichloromethane/methanol (v/v = 5:1) resulted in white solid. Yield: 62% (2.12 g). ¹H NMR (400 MHz, CDCl₃): δ 7.76 (bs, -CONH-, 4H), 3.69 (s, -OCH₂CH₂O-, 4H), 3.67-3.58 (m, -OCH₂CH₂N-, 4H), 3.58-3.52 (m, -NCH₂CO-, 4H), 3.31 (s, -NCH₂CO-, 4H), 2.87-2.75 (t, -OCH₂CH₂N-, 4H), 1.89 (s, -NCH₂CH₂N-, 8H). ESI-MS positive: Calcd. 428.2, m/z = 429.2 (M+H⁺), 451.2 (M+Na⁺).

4,7-dioxa-1,10,13,16,21,24-hexaazabicyclo[8.8.8]hexacosane (N₆O₂): **9** (1.00 g, 2.3 mmol) was suspended in 25 mL dry THF, and LiAlH₄ (1.77 g, 46.6 mmol) suspension of THF (25 mL) was added dropwise. Then the mixture was heated to reflux under nitrogen atmosphere for four days. After cooling, 3.5 mL water was added to quench excess LiAlH₄. The mixture was filtrated to remove insoluble substance, and the residue was washed with 100 mL THF. The filtrate was evaporated to obtain a yellowish oil. The oil was sublimed under ~ 6 Pa at 120 °C to obtain a white waxy solid. Yield: 49% (0.43 g). ¹H NMR (400 MHz, CDCl₃): δ 3.64 (s, -OCH₂CH₂O-, 4H), 3.50-3.45 (m, -OCH₂CH₂N-, 4H), 2.80-2.75 (m, -NHCH₂CH₂NH-, 8H), 2.74-2.69 (m, -NCH₂CH₂NH-, 8H), 2.64-2.59 (m, -NCH₂CH₂O-, 4H), 2.54-2.48 (m, -NCH₂CH₂NH-, 8H). ESI-MS positive: Calcd. 372.3, m/z = 373.3 (M+H⁺), 379.3 (M+Li⁺).

Synthesis of Eu(II) complexes

EuBr₂-N₂O₆: EuBr₂ (75 mg, 0.24 mmol) was dissolved in 4 mL THF and 1 mL MeOH in a round-bottom flask under magnetic stirring. N₂O₆ (100 mg, 0.27 mmol) was dissolved in 5 mL THF, which was slowly added to the EuBr₂ solution. After stirring overnight, white solid formed. The solid was filtered, washed with THF and dried.

Yield: 83% (138 mg). Elemental analysis (%) Calcd for $C_{18}H_{36}Br_2EuN_2O_6$: C, 31.41; N, 4.07; H, 5.27. Found: C, 31.53; N, 4.04; H 5.13.

EuI₂-N₂O₆: EuI₂ (100 mg, 0.25 mmol) was dissolved in 5 mL THF in a round-bottom flask under magnetic stirring. N₂O₆ (93 mg, 0.25 mmol) was dissolved in 5 mL THF, which was slowly added to the EuI₂ solution. White solid formed during addition. After stirring overnight, the solid was filtered, washed with THF and dried. Yield: 85% (164 mg). Elemental analysis (%) Calcd for $C_{18}H_{36}EuI_2N_2O_6$: C, 27.64; N, 3.58; H, 4.64. Found: C, 27.71; N, 3.55; H 4.41.

EuBr₂-N₄O₄: Similar to that of EuBr₂-N₂O₆, instead of EuBr₂ (73 mg, 0.23 mmol), N₄O₄ (96 mg, 0.26 mmol) were used. Pale yellowish green solid was obtained. Yield: 73% (116 mg). Elemental analysis (%) Calcd for $C_{18}H_{38}Br_2EuN_4O_4$: C, 31.50; N, 8.16; H, 5.58. Found: C, 31.56; N, 8.12; H 5.69.

EuI₂-N₄O₄: Similar to that of EuI₂-N₂O₆, instead of EuI₂ (120 mg, 0.29 mmol), N₄O₄ (110 mg, 0.29 mmol) were used. Pale yellowish green solid was obtained. Yield: 89% (206 mg). Elemental analysis (%) Calcd for $C_{18}H_{38}EuI_2N_4O_4$: C, 27.71; N, 7.18; H, 4.91. Found: C, 28.10; N, 6.91; H 4.96.

EuBr₂-N₆O₂: Similar to that of EuBr₂-N₂O₆, instead of EuBr₂ (81 mg, 0.26 mmol), N₆O₂ (106 mg, 0.28 mmol) were used. Pale green solid was obtained. Yield: 61% (108 mg). Elemental analysis (%) Calcd for $C_{18}H_{40}Br_2EuN_6O_2$: C, 31.59; N, 12.28; H, 5.89. Found: C, 31.57; N, 12.58; H 5.91.

EuI₂-N₆O₂: Similar to that of EuI₂-N₂O₆, instead of EuI₂ (98 mg, 0.24 mmol), N₆O₂ (90 mg, 0.24 mmol) were used. Pale green solid was obtained. Yield: 87% (163 mg). Elemental analysis (%) Calcd for $C_{18}H_{40}EuI_2N_6O_2$: C, 27.78; N, 10.80; H, 5.18. Found: C, 28.17; N, 10.83; H 5.42.

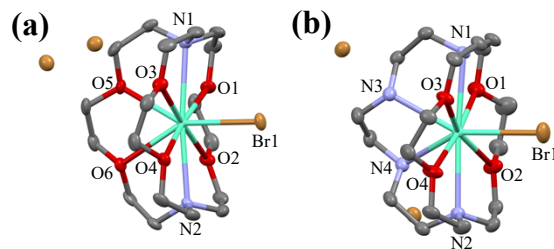


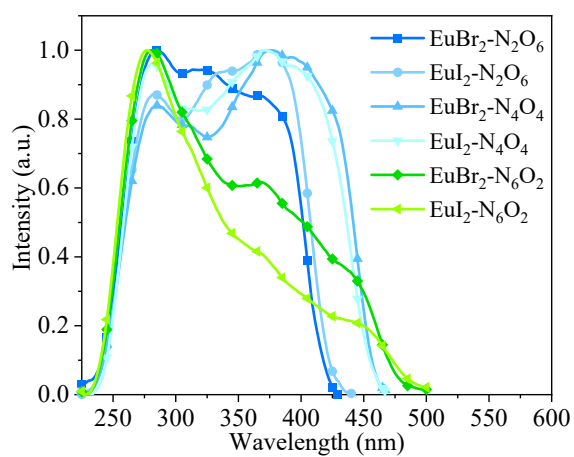
Fig. S1 Ellipsoid drawings of the crystal structures of (a) $\text{EuBr}_2\text{-N}_2\text{O}_6$ and (b) $\text{EuBr}_2\text{-N}_4\text{O}_4$. The coordinated nitrogen, oxygen and bromide atoms are labeled as N1-N2, O1-O6, Br1 ($\text{EuBr}_2\text{-N}_2\text{O}_6$) and N1-N4, O1-O4, Br1 ($\text{EuBr}_2\text{-N}_4\text{O}_4$) for the data in Table S2.

Table S1 Crystallographic data for $\text{EuBr}_2\text{-N}_2\text{O}_6$ and $\text{EuBr}_2\text{-N}_4\text{O}_4$.

Compound	$\text{EuBr}_2\text{-N}_2\text{O}_6$	$\text{EuBr}_2\text{-N}_4\text{O}_4$
chemical formula	$\text{C}_{18}\text{H}_{36}\text{Br}_2\text{EuN}_2\text{O}_6$	$\text{C}_{18}\text{H}_{38}\text{Br}_2\text{EuN}_4\text{O}_4$
formula weight	688.27	686.30
crystal size (mm)	$0.18 \times 0.16 \times 0.09$	$0.12 \times 0.06 \times 0.04$
temperature (K)	179.99(10)	180.00(10)
radiation	0.71073	0.71073
crystal system	Orthorhombic	Monoclinic
space group	P 21212	C 2/c
a (Å)	13.6795(3)	26.7964(7)
b (Å)	17.7174(3)	13.3338(3)
c (Å)	9.9143(2)	17.1779(4)
α (°)	90	90
β (°)	90	126.811(2)
γ (°)	90	90
V (Å ³)	2402.88(8)	4913.9(2)
Z	4	8
ρ (calc) (g/cm ³)	1.903	1.855
F (000)	1356	2712
absorp. coeff. (mm ⁻¹)	5.970	5.835
θ range (deg)	2.3600 to 29.2230	2.3600 to 29.3200
reflns collected	11809	31540
indep. reflns	5554	6298
Refns obs. [$I > 2\sigma(I)$]	5294	5267
data/restr/paras	5554/0/263	6298/0/263
GOF	1.010	1.030
R_1/wR_2 [$I > 2\sigma(I)$]	0.0196/0.0382	0.0342/0.0780
R_1/wR_2 (all data)	0.0218/0.0387	0.0453/0.0816

Table S2 Selected bond lengths of $\text{EuBr}_2\text{-N}_2\text{O}_6$ and $\text{EuBr}_2\text{-N}_4\text{O}_4$.

bond	$\text{EuBr}_2\text{-N}_2\text{O}_6$	$\text{EuBr}_2\text{-N}_4\text{O}_4$
Eu-N1	2.821	2.795
Eu-N2	2.843	2.825
Eu-N3	-	2.726
Eu-N4	-	2.721
Eu-O1	2.692	2.819
Eu-O2	2.724	2.694
Eu-O3	2.693	2.738
Eu-O4	2.671	2.697
Eu-O5	2.594	-
Eu-O6	2.744	-
Eu-Br	3.008	3.070

**Fig. S2** Excitation spectra of the Eu(II) complexes in solid powder.

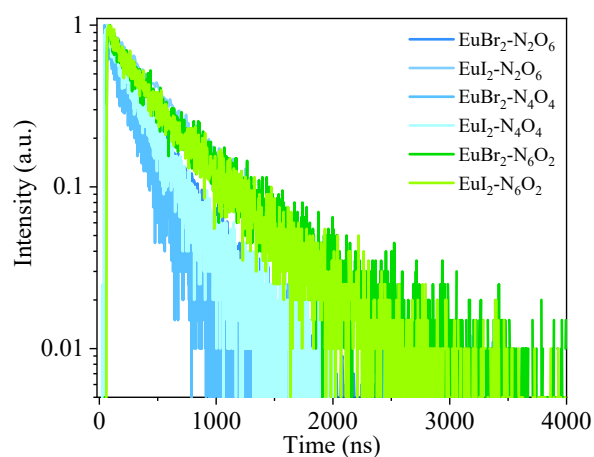


Fig. S3 Transient PL decays of the Eu(II) complexes in solid powder.

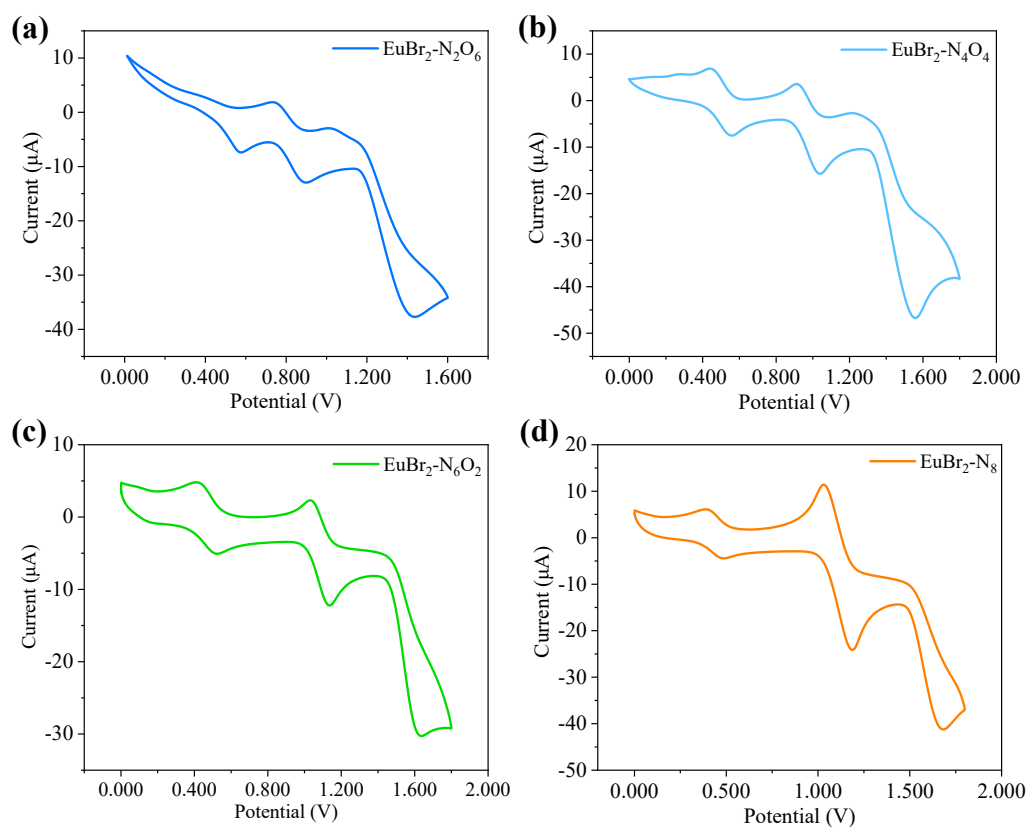


Fig. S4 Cyclic voltammograms of (a) $\text{EuBr}_2\text{-N}_2\text{O}_6$, (b) $\text{EuBr}_2\text{-N}_4\text{O}_4$, (c) $\text{EuBr}_2\text{-N}_6\text{O}_2$, (d) $\text{EuBr}_2\text{-N}_8$ recorder in methanol with ferrocene as an internal standard.

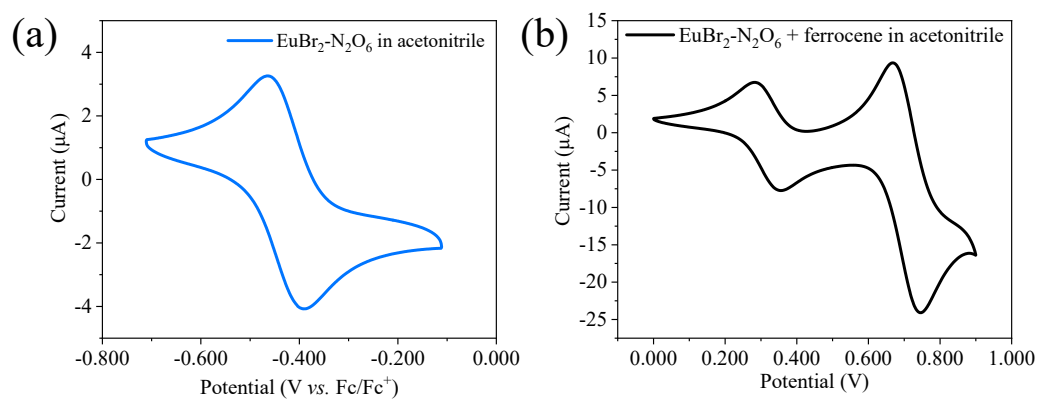


Fig. S5 Cyclic voltammograms of $\text{EuBr}_2\text{-N}_2\text{O}_6$ (a) and $\text{EuBr}_2\text{-N}_2\text{O}_6$ with ferrocene as an internal standard (b) recorder in acetonitrile.

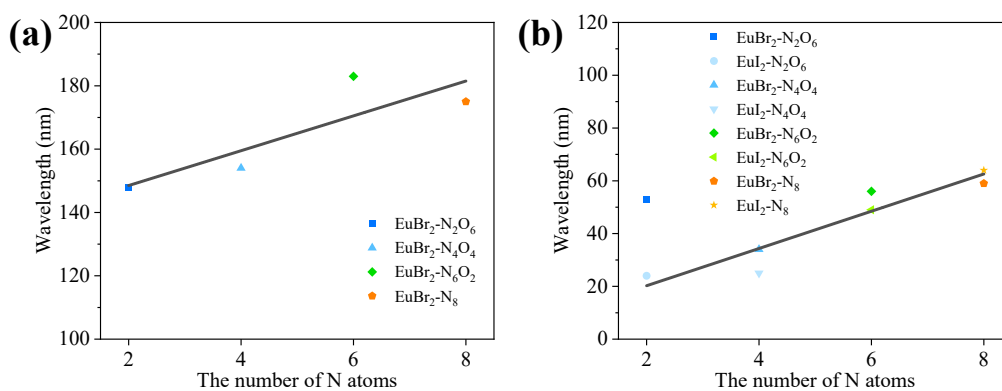


Fig. S6 The Stokes shifts (a) and red shift values of emission (b) for Eu(II) complexes.