Supporting Information

A vapoluminescent Eu-based metallo-supramolecular polymer

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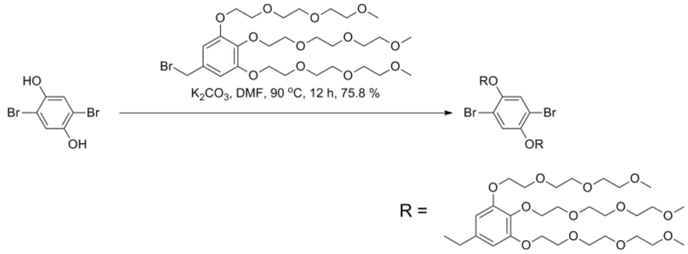
Contents

1. Experimental section

1.1 General

Unless otherwise noted, all reagents were reagent grade and were used without purification. Dehydrated methanol, ethanol, DMF and DMSO were used as reaction solvent. Methanol for UV-vis and luminescence measurement were spectro analysis. These solvents were purchased from Wako or Kanto Chemical Co. Inc. and used as received. De-ionized H_2O was used in the experiment where required. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a JEOL AL 300/BZ instrument. Chemical shifts were given relative to TMS. Mass spectra (MS) were measured by using AXIMA-CFR, Shimadzu/Kratos TOF Mass spectrometer. High resolution mass spectra (HRMS) were measured by using Shimadzu LCMS-IT-TOF spectrometer. UV-vis spectra were recorded using a Shimadzu UV-2550 UV-visible spectrophotometer. Luminescence experiments at room temperature were performed in Methanol using a Shimadzu RF-5300 PC spectrofluorophotometer. The concentrations of polyEu for the luminescence measurements were typically 1×10^{-6} M. The molecular weights of polyEu was determined by SEC-viscometry-RALLS (size exclusion chromatography-viscometry-right angle light scattering) on Viscotek 270 Dual Detector instrument using polyethylene glycol as standard in methanol solvent (flow rate 1 mL / min). The quantum yields were measured on a Hamamatsu C9920-03 Absolute PL Quantum Yield Measurement System. The thickness of polymer films was measured by micrometer (Mitutoyo). Flash column chromatographic separations were performed on silica gel 60 N (neutral, 40-100 μM), S2 Kanto Chemical Co. Inc. 3,4,5-tris(2-(2-(2-methoxy-ethoxy)ethoxy)ethoxy)benzylbromide was prepared according to the literature.[S1] 4'-(4-bromophenyl)-2,2':6',2"-terpyridine-6,6"-dicarbonitrile was prepared according to the previous report.[S2] Films for UV-vis and luminescence analysis were prepared by spin-casting the MeOH solution of the polyEu (20 μM) on a glass substrate and dried in *vacuo*.

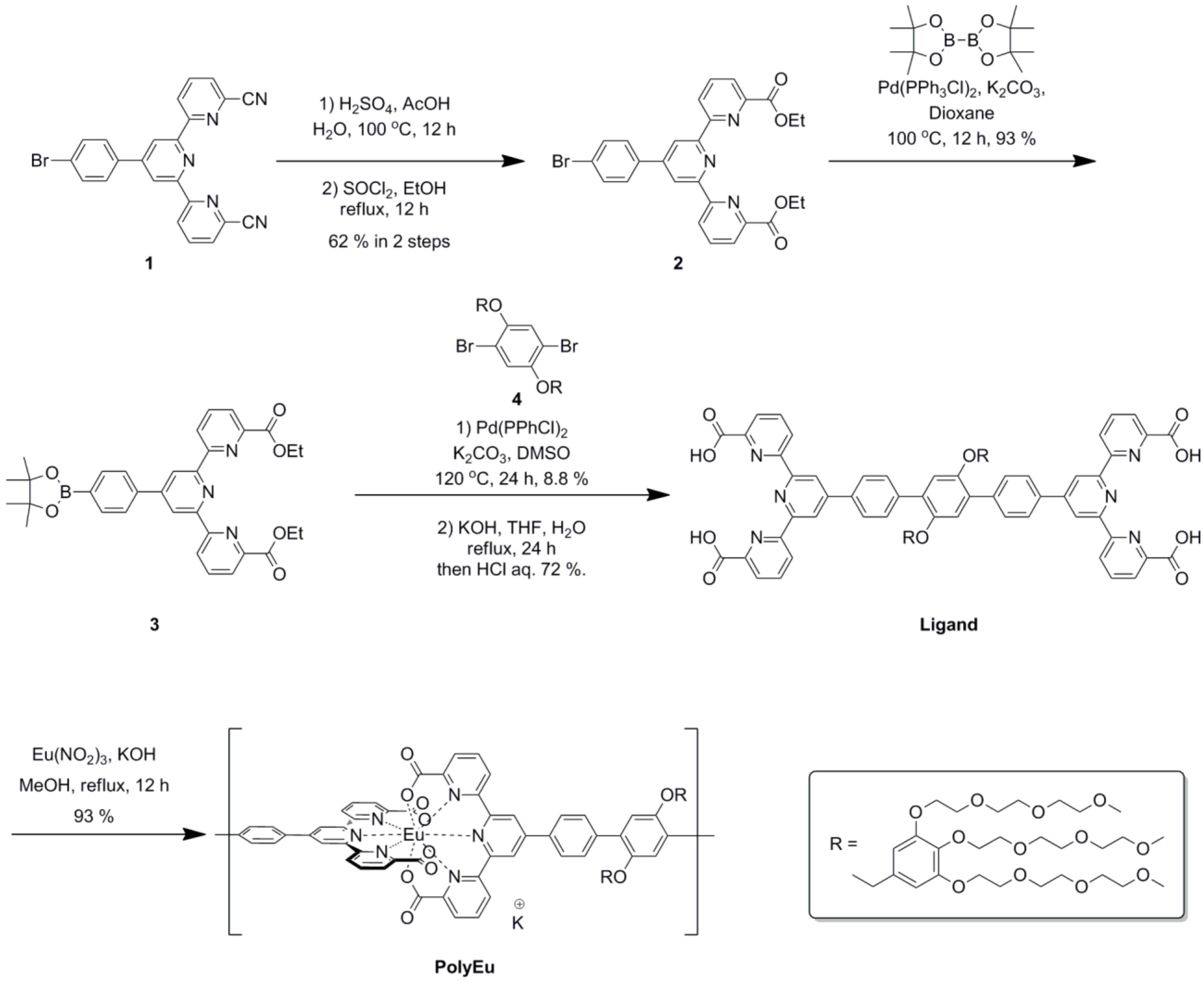
1.2 Material



Scheme S1 Synthesis of spacer unit.

2,5-bis(3,4,5-tris (2-(2-(2-methoxy-ethoxy)ethoxy)ethoxy)benzyloxy)-1,4-dibromobenzen

To a 20 mL of DMF solution of 3,4,5-tris(2-(2-(2-methoxy-ethoxy)ethoxy)ethoxy)benzylbromide (1.22g, 1.86 mmol) was added 2,5-dibromohydroquinone (0.249g, 0.93 mmol), and potassium carbonate (0.514 g, 3.72 mmol). The reaction mixture was refluxed under the nitrogen atmosphere for 12 h. After the resulting mixture was cooled at room temperature, the catalyst was removed by the filtration and washed with chloroform. The filtrate was washed with H_2O. The separated organic layer was dried over $MgSO_4$, filtrated, concentrated, and purified by column chromatography on silica gel (eluent : CH_2Cl_2 : MeOH = 9 : 1) to give 2,5-bis(3,4,5-tris(2-(2-(2-methoxy-ethoxy) ethoxy)ethoxy)benzyloxy)-1,4-dibromobenzen as brown oil(1.08 g, 75.8 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ = 7.13 (s, 2H), 6.70 (s, 2H), 4.96 (s, 4H), 4.15 (m, 12H), 3.90-3.51 (m, 72H), 3.37 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ =152.8, 150.0, 138.3, 131.5, 119.4, 111.7, 106.9, 72.6, 72.3, 71.9, 70.8, 70.7, 70.5, 69.7, 68.9, 59.0; MALDI-TOF-MASS m/z Calcd for $C_{62}H_{100}Br_2O_{26}Na^+$ [M+Na] 1443; found 1443.



Scheme S2 Synthesis of **ligand** and **polyEu**..

Diethnyl-4'-(4-bromophenyl)-2,2':6',2''-terpyridine-6,6''-dicarboxylate **2**

After a mixture of 4'-(4-bromophenyl)-2,2':6',2''-terpyridine-6,6''-dicarbonitrile **1** (8.77 g, 20.0 mmol), conc. H_2SO_4 (90 mL), acetic acid (90 mL) and H_2O (20 mL) was stirred at 100 ℃ for 12 h, the solution was added to 800 mL of ice water. The precipitate was filtered, washed with water and acetonitrile and dried. To a 600 mL of ethanol in ice bath was added dropwise 24 g of thionyl chloride. After stirring the solution for 15 min at ambient temperature, we added the above precipitate, and the mixture was refluxed for 12 h. After the solvent was evaporated, 1000 mL of chloroform was added, and the solution was washed with 5 % aqueous $NaHCO_3$. The separated organic layer was then dried over $MgSO_4$, filtered, concentrated and purified by column chromatography on silica gel (eluent : CH_2Cl_2 : MeOH = 99 : 1) to give dimethnyl-4'-(4-bromophenyl)-2,2': 6',2''-terpyridine-6,6''-dicarboxylate as white solid (5.01 g, 47.1 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ = 8.81 (d, 2H, *J* = 7.8 Hz), 8.80 (s, 2H), 8.16 (d, 2H, *J* = 7.8 MHz), 8.01 (t, 2H, *J* = 7.8 MHz), 7.76 (d, 2H, *J* = 8.8 Hz), 7.66 (d, 2H, *J* = 8.8 Hz), 4.52 (q, 4H, *J* = 7.1 Hz), 1.49 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ = 165.2, 156.2, 155.2, 149.5, 147.9, 137.8, 137.3, 132.1, 129.0, 125.1, 124.4, 123.6, 119.6, 61.9, 14.3; MALDI-TOF-MASS m/z Calcd for $C_{27}H_{25}BrN_3O_4$ [M+3H] 534; found 534.

Diethnyl-4'-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaboryl)phenyl)-2,2':6',2''-terpyridine-6,6''-dicarboxylate **3**

To a 40 mL of DMSO solution of dimethnyl-4'-(4-bromophenyl)-2,2':6',2''-terpyridine-6,6''-dicarboxylate **2** (5.32 g, 10.0 mmol) was added bispinacolatodiboron (2.79 g, 11.0 mmol), potassium acetate (4.91 g, 50.0 mmol) and $PdCl_2(PPh_3)_2$ (702 mg, 1.0 mmol). The reaction mixture was stirred at 120 ℃ under nitrogen atmosphere for 12 h. After the resulting mixture was cooled at room temperature, the catalyst was removed by the filtration and washed with chloroform. The filtrate was washed with H_2O. The separated organic layer was dried over $MgSO_4$, filtrated, concentrated, and purified by column chromatography on silica gel (eluent : CH_2Cl_2) to give diethnyl-4'-(4-(4,4,5,5- tetramethyl-1,3,2-dioxaboryl)phenyl)-2,2':6',2''-terpyridine-6,6''-dicarboxylate as white solid (5.21 g, 89.9 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ = 8.87 (s, 2H), 8.83 (d, 2H, *J* = 7.8 Hz), 8.17 (d, 2H, *J* = 7.8 MHz), 8.01 (t, 2H, *J* = 7.8 MHz), 7.98 (d, 2H, *J* = 8.2 Hz), 7.92 (d, 2H, *J* = 8.2 Hz), 4.52 (q, 4H, *J* = 7.1 Hz), 1.49 (t, 6H, *J* = 7.1 Hz), 1.39 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ = 165.4, 156.3, 155.2, 150.5, 147.9, 140.9, 137.8, 135.4, 126.7, 125.0, 124.4, 120.0, 84.0, 61.9, 24.9, 14.3; MALDI-TOF-MASS m/z Calcd for $C_{33}H_{35}BN_3O_6$ [M+H] 580; found 580.

Ligand synthesis

To a 2 mL of DMSO solution of diethnyl-4'-(4-(4,4,5,5- tetramethyl-1,3,2-dioxaboryl) phenyl)-2,2':6',2"-terpyridine-6,6"-dicarboxylate (127 mg, 0.22 mmol) was added 2,5-bis(3,4,5-tris (2-(2-(2-methoxy -ethoxy)ethoxy)ethoxy)benzyloxy)-1,4-dibromobenzen (142 mg, 0.10 mmol), potassium carbonate (69.1 mg, 0.50 mmol) and $PdCl_2(PPh_3)_2$ (7.02 mg, 10 mol). The mixture solution was stirred at 120 ℃ under nitrogen atmosphere for 24 h. After the resulting mixture was cooled at room temperature, the catalyst was removed by the filtration and washed with chloroform. The filtrate was washed with H_2O. The separated organic layer was dried over $MgSO_4$, filtrated, concentrated, and purified by column chromatography on silica gel (eluent : CH_2Cl_2) and preparative GPC to give viscous solid (38.1 mg, 8.8 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ = 8.93 (s, 4H), 8.87 (d, 4H, *J* = 7.9 Hz), 8.19 (d, 4H, *J* = 7.9 MHz), 8.04 (t, 4H, *J* = 7.9 MHz), 8.03 (d, 2H, *J* = 8.2 Hz), 7.84 (d, 2H, *J* = 8.2 Hz), 7.21 (s, 2H), 6.57 (s, 4H), 5.02 (s, 4H), 4.54 (q, 8H, *J* = 7.1 Hz), 4.07 (m, 12H), 3.79-3.40 (m, 60H) 3.34 (s, 6H), 1.50 (t, 12H, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) = 165.3, 156.3, 155.3, 152.6, 150.4, 150.2, 148.0, 139.2, 137.8, 137.0, 132.5, 131.2, 130.3, 127.1, 125.1, 124.4, 119.7, 117.2, 106.1, 72.3, 71.9, 71.8, 70.6, 70.5, 70.4, 69.6, 68.7, 61.9, 58.9, 14.4. To a 5 mL of THF-H2O (v/v = 1 : 1) mixture solution of above viscous solid (170 mg, 79 μmol) was added sodium hydroxide (12.6 mg, 314 μmol). The mixture solution was refluxed for 12 h. The resulting mixture was cooled at room temperature and neutralized with 1 M aqueous HCl. THF was removed under reduced pressure. The aqueous layer was extracted with chloroform. The separated organic layer was dried over $MgSO_4$, filtered, concentrated and purified by preparative GPC to give monomer as yellowish-white solid(117mg, 71.8%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) = 8.95 (d, 4H, *J* = 7.9 Hz), 8.82 (s, 4H), , 8.34 (d, 4H, *J* = 7.9 Hz), 8.17 (t, 4H, *J* = 7.9 Hz), 7.99 (d, 2H, *J* = 8.2 Hz), 7.86 (d, 2H, *J* = 8.2 Hz), 7.20 (s, 2H), 6.60 (s, 4H), 5.04 (s, 4H), 4.11 (m, 12H), 3.83-3.40 (m, 60H) 3.34 (s, 6H), 3.21 (s, 12H) ; ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ = 164.7, 155.1, 154.4, 152.6, 150.6, 150.2, 146.5, 139.3, 138.8, 137.8, 136.6, 132.4, 130.6, 130.3, 127.0, 125.1, 124.3, 119.6, 116.8, 106.5, 72.2, 71.8, 70.6, 70.4, 70.3, 69.5, 68.7, 58.9, 58.8,58.7; HRMS : found m/z: 2075.8353 [M + Na]; $C_{108}H_{128}N_6O_{34}$ Na requires 2075.8364.

Polymer synthesis

An equimolar amount of ligand and $Eu(NO_2)_3$ was refluxed in an argon saturated absolute methanol for 24 h. After the reaction mixture was cooled at room temperature, the reaction solvent was added to the n-Hexane/chloroform mixture (v / v = 1:1) , The precipitate was filtered, washed with water and chloroform and dried. The film was collected and dried further in *vacuo* overnight to give the corresponding **polyEu** as yellow solid (93.2%). IR (KBr) : 2924, 2855, 1199cm^{-1}

Reference

S1. Daou, T. J.; Pourroy, G.; Greneche, J. M.; Bertin, A.; Felder-Flesch D.; Begin-Colin, S. *Dalton Trans.* **2009**, 4442.

S2. Han, F. S.; Higuchi, M.; Kurth, D. G. *Org. Lett.* **2007**, *9*, 559.

2. Molecular weight measurement

PolyEu (c =1.0 mg/ mL) shows high average molecular weight (Mn = 7.8 × 10^4, Mw/Mn = 1.7), when 20 μL of methanol solution was injected. The molecular weights were obtained by automatic program calculation taking account of RI and RALLS factor into consideration. The representative figure of **polyEu** for molecular weight is shown in Fig. S1.

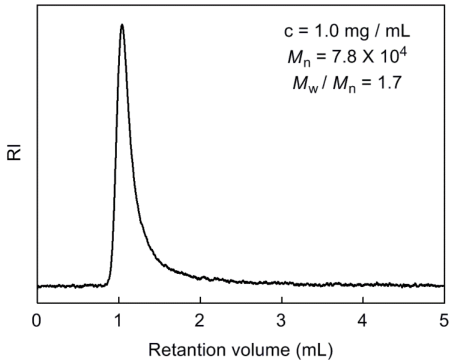


Fig. S1 Molecular weight of polyEu in the methanol solution at room temperature.

3. Supplementary X-ray diffraction profile

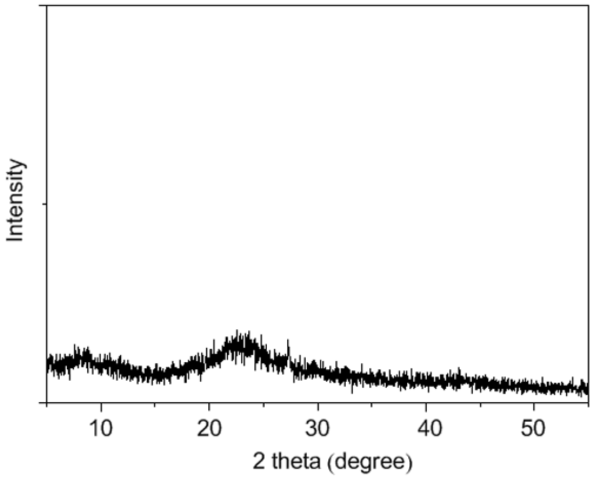


Fig. S2 Powder X-ray diffraction profile of **polyEu**.

4. Photophysical properties of polyEu and ligand

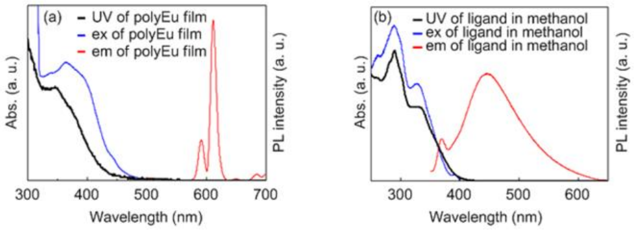


Fig. S3 (a) Photophysical properties of **polyEu** film on a glass substrate at room temperature. (b) Photophysical properties of **ligand** in methanol at room temperature. UV = absorption profile, ex = excitation profile, and em = emission profile.

5. Quantum yield measurement

Table S1 Quantum yield of **polyEu** and **ligand** in a solid state. [a]

Compound	λ_{exc} (nm)	Φ_{FL}
Ligand	340	0.021
PolyEu	365	0.24

a) Sample coated quartz glasses were measured on a Hamamatsu C9920-03 Absolute PL Quantum Yield Measurement System.

6. Supplementary IR spectrum

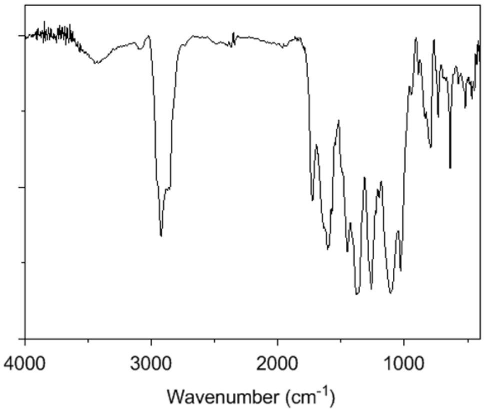


Fig. S4 IR spectra of **polyEu**.

7. Supplementary fluorescence spectra

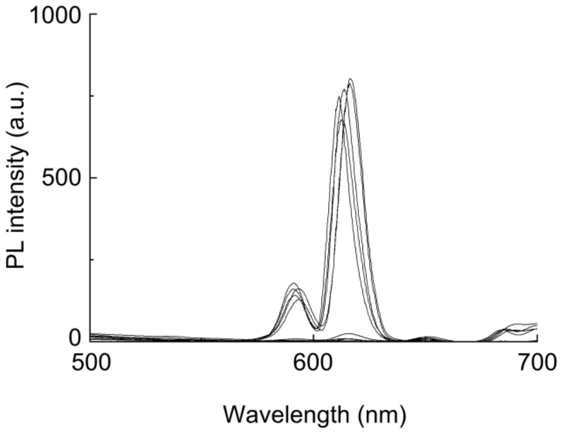


Fig. S5 Spectral changes during the alternative addition of HCl-Et_3N of photoluminescence spectra of **polyEu** film.

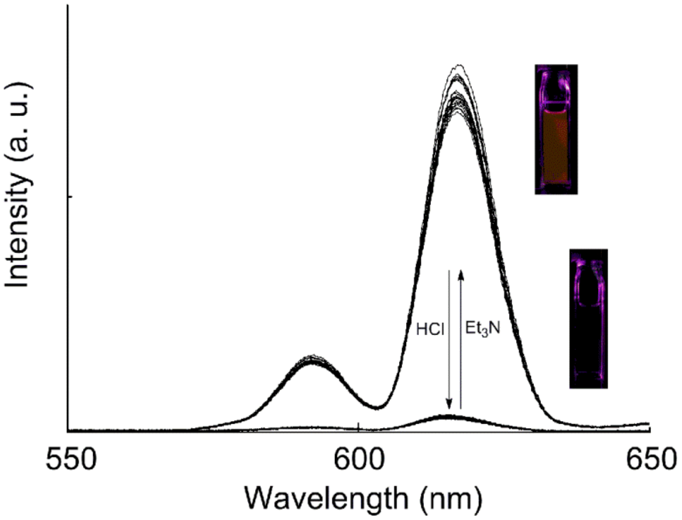


Fig. S6 Spectral changes during the alternative addition of HCl–Et_3N of photoluminescence spectra of **polyEu** in methanol solution.

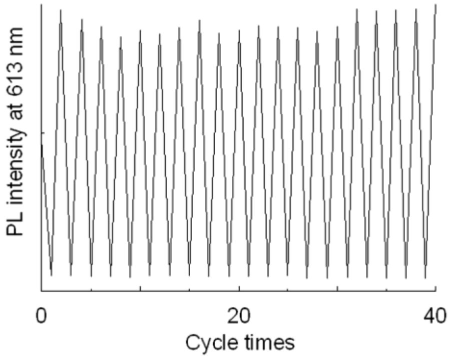


Fig. S7 Responses of luminescence intensity at 613 nm of **polyEu** in a methanol solution during the alternative addition of HCl–Et_3N.

8. Memory effect of polyEu

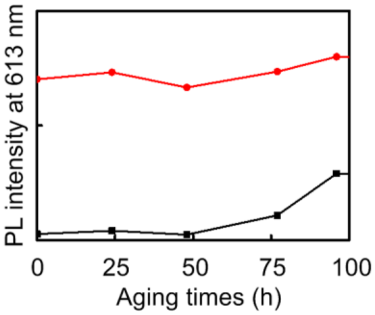


Fig. S8 Optical memory aging times of luminescent intensity for the **polyEu** film on a glass substrate after exposure to acid and base vapor.

9. Supplementary UV-vis spectra

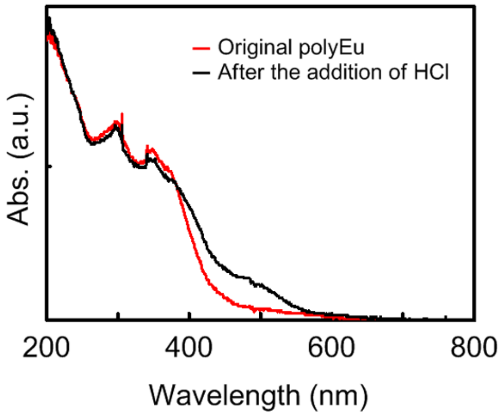


Fig. S9 UV–vis spectra of a **polyEu** film before (red) and after (black) exposure to HCl gas.

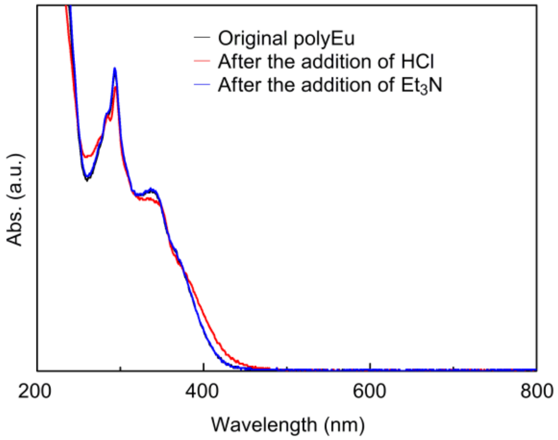


Fig. S10 Spectral changes before and after the addition of HCl–Et_3N of UV–vis spectra of **polyEu** in methanol solution.

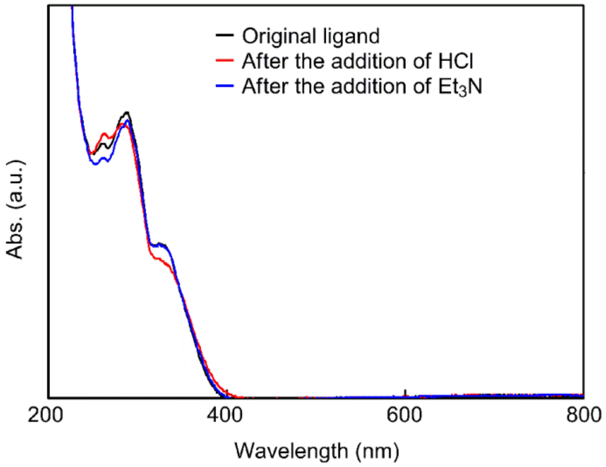


Fig. S11 Spectral changes before and after the addition of HCl–Et_3N of UV–vis spectra of **ligand** in methanol solution.

10. Photoluminescence display device

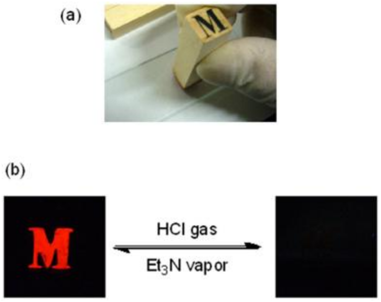


Fig. S12 Printing of a luminescent image onto a glass substrate by polyEu (a). The photographs were taken at room temperature under a 365 nm light.