

Supporting Information

**A Typical Metal Ion-Responsive Color-Tunable Emitting Insulated  $\pi$ -Conjugated Polymer Film**

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## 1. General Comments

### 1.1 Materials

Unless otherwise noted, manipulations were performed under argon atmosphere using standard Schlenk-type glassware in a dual-manifold Schlenk line. Unless otherwise stated, commercially available chemicals were used as received. Reaction solvents were degassed either through freeze-pump-thaw (three times) or argon bubbling, before use.

### 1.2 Experimental Equipment and Procedures

#### NMR spectroscopy

$^1\text{H}$  NMR (400 MHz, or 500 MHz) and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz, or 125 MHz) spectra were measured with either a JEOL ECX-400 spectrometer or a Bruker AVANCE-500 spectrometer. The  $^1\text{H}$  NMR chemical shifts are reported relative to tetramethylsilane (TMS) (0.00 ppm) or residual protonated solvents (7.26 ppm for  $\text{CHCl}_3$  or 5.32 ppm for  $\text{CH}_2\text{Cl}_2$ ). The  $^{13}\text{C}$  NMR chemical shifts are reported relative to TMS (0.00 ppm) or deuterated solvents (77.0 ppm for  $\text{CDCl}_3$  or 53.5 ppm for  $\text{CD}_2\text{Cl}_2$ ).

#### Analytical size-exclusion chromatography (Analytical SEC)

Analytical SEC was performed with a GL-Science GL-7400 HPLC System equipped with Shodex KF-801, -802, -802.5, -803, -804 columns, a GL-7410 HPLC pump, a GL-7400 UV detector, and a GL-7454 RI detector using THF as the eluent at a flow rate of  $0.6\text{ mL min}^{-1}$ . Average molecular weights of polymers were estimated with polystyrenes as calibration standards.

#### Preparative recycling size-exclusion chromatography (Preparative SEC)

Preparative recycling SEC was performed with one of the HPLC systems described below, using  $\text{CHCl}_3$  as the eluent at a flow rate of  $14\text{ mL min}^{-1}$ .

- JAI LC9140 System equipped with JAIGEL-2.5H and -3H columns, a JAI UV DETECTOR 310, and a JAI RI DETECTOR RI-5
- SHIMADZU LC-20AP System equipped with a Shodex K-4003L column, a SHIMADZU SPD-20A, and a SHIMADZU RID-10A

#### Mass Spectroscopy (MS)

High-resolution matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) as a matrix and NaTFA as a cationization reagent on Thermo Fisher Scientific LTQ orbitrap XL.

### Absorption spectroscopy

Absorption spectra were measured with SHIMADZU UV-2600 spectrophotometer. For solution measurements, concentrations of  $10^{-5}$  M (calculated for repeat units in the polymers) solutions were used.

### Emission spectroscopy

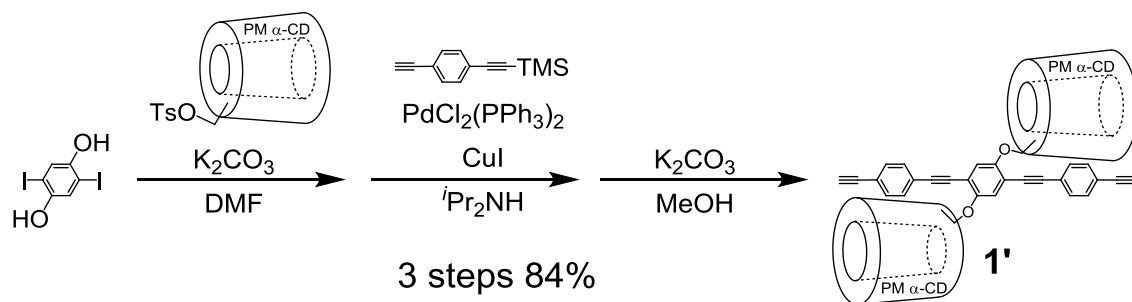
Emission spectra were measured with HITACHI F-7000 fluorescence spectrophotometer. For solution measurements, concentrations of  $10^{-5}$  M (calculated for repeat units in the polymers) solutions were used. For the film measurements, drop-casted films prepared by the procedure described in section 2.6 were used.

### Photoluminescence quantum yield measurement

Absolute photoluminescence quantum yields were measured with the HAMAMATSU Photonics C11347-11 Absolute PL quantum yields measurement system, using an integrating sphere to collect all the emitted light.<sup>2</sup> For solution measurements, concentrations of  $10^{-5}$  M (calculated for repeat units in the polymers) were used. For the film measurements, drop-casted films prepared by the procedure described in section 2.6 were used. The excitation wavelengths were scanned in the 350-400 nm range.

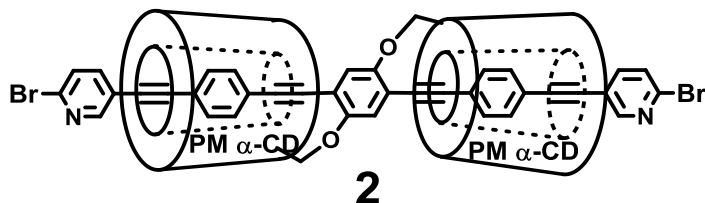
## 2. Synthetic Procedures and NMR Spectra

### 2.1 Synthesis of molecule 1'



Molecule 1' was synthesized according to the modified procedures of our previous work.<sup>1</sup>

## 2.2 Synthesis of insulated monomer **2**



Under an argon atmosphere, **1** (500 mg, 18.2  $\mu\text{mol}$ ) was dissolved in a mixture of MeOH (50 mL) and H<sub>2</sub>O (25 mL). The resulting solution was stirred at 50 °C for 30 min and cooled to 35 °C. Then, NEt<sub>3</sub> (2 mL), Cs<sub>2</sub>CO<sub>3</sub> (297 mg, 910  $\mu\text{mol}$ ), TPPTS (20.7 mg, 36.4  $\mu\text{mol}$ ), and Pd(OAc)<sub>2</sub> (2.1 mg, 9.1  $\mu\text{mol}$ ) were added. Following additional stirring at 35 °C for 30 min, the solution was cooled to 15 °C, and CuI (0.4 mg, 1.8  $\mu\text{mol}$ ) and 2-bromo-5-iodopyridine (1.04 g, 3.64 mmol) were then added. The suspension was stirred at 15 °C for 36 h, quenched with NH<sub>4</sub>Cl<sub>(aq)</sub>, and extracted with CHCl<sub>3</sub>. Following evaporation, the residue was purified by preparative SEC (eluent: CHCl<sub>3</sub>) to yield a pale yellow solid **2** (351 mg, 11.5  $\mu\text{mol}$ , 63%).

### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, r.t.)

$\delta$ : 8.41 (2H, d,  $J = 2.1$  Hz), 8.11 (4H, d,  $J = 8.2$  Hz), 7.71 (4H, d,  $J = 8.2$  Hz), 7.56 (2H, dd,  $J = 8.2, 2.4$  Hz), 7.49 (2H, d,  $J = 8.2$  Hz), 7.47 (2H, s), 5.09-4.56 (14H, m), 4.22-2.78 (172H, m).

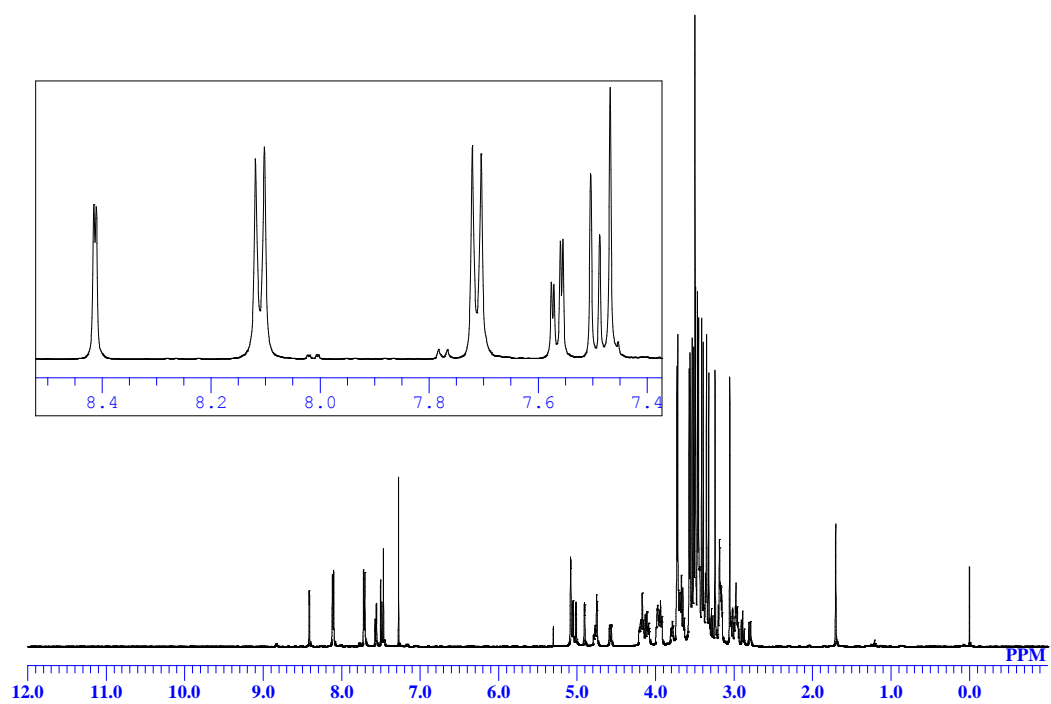
### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, r.t.)

$\delta$ : 158.81, 152.34, 141.62, 140.40, 133.13, 131.63, 127.80, 126.37, 123.38, 122.18, 119.12, 118.65, 101.31, 100.80, 100.42, 100.19, 99.98, 97.86, 96.05, 92.81, 88.19, 87.18, 83.10, 82.90, 82.79, 82.62, 82.60, 82.44, 82.13, 81.93, 81.88, 81.76, 81.43, 81.36, 81.35, 81.29, 81.20, 81.02, 80.76, 77.61, 77.25, 72.82, 72.56, 72.14, 71.87, 71.70, 71.67, 71.19, 71.16, 71.14, 70.84, 70.29, 62.03, 61.92, 61.87, 61.67, 61.47, 61.40, 59.22, 59.04, 58.97, 58.82, 58.60, 58.59, 58.13, 57.82, 57.68, 57.60, 57.46.

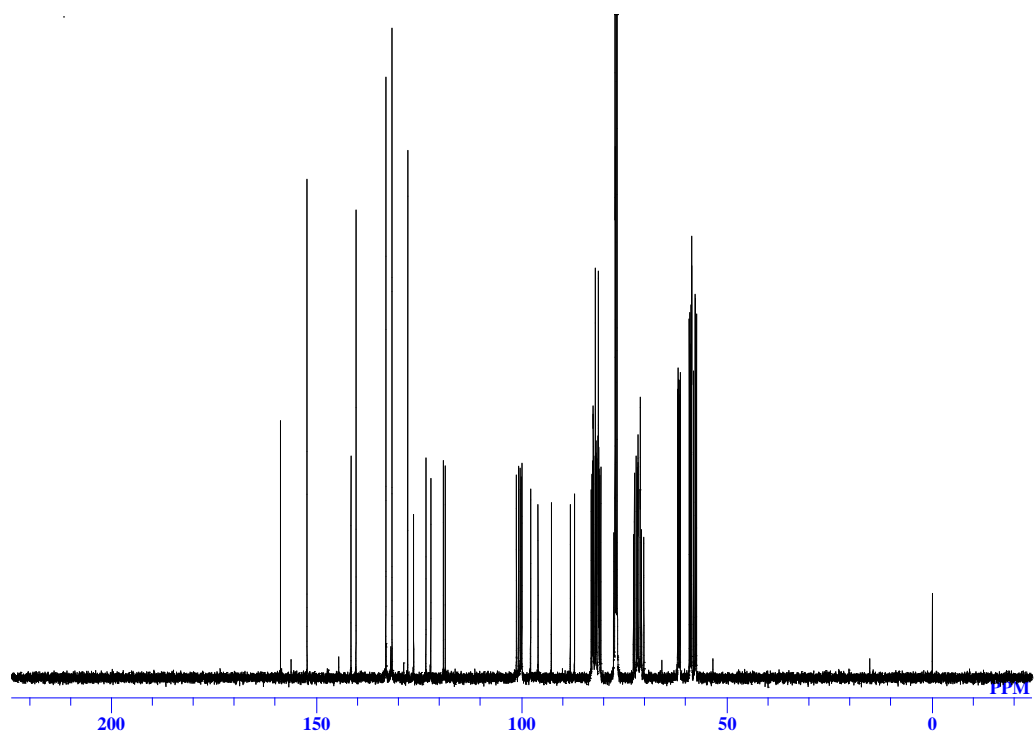
### High-Resolution MALDI TOF-MS

calcd for C<sub>142</sub>H<sub>202</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>60</sub>Na [**2**+Na<sup>+</sup>]: 3076.108; found: 3076.109 ( $m/z$ , monoisotopic mass)

$^1\text{H}$  NMR spectrum of **2**



$^{13}\text{C}$  NMR spectrum of **2**



## ROESY NMR spectrum of **2**

The 2D-ROESY NMR spectrum of **2** was acquired in CDCl<sub>3</sub>. Strong nuclear Overhauser enhancements (NOEs) between the aromatic protons of the axial oligo(phenylene ethynylene) (H<sub>a</sub>, H<sub>b</sub> and H<sub>c</sub>) and inner protons of the cyclodextrins (H<sub>3</sub> and H<sub>5</sub>) were observed (Figure S1). These experimental results indicated that the rotaxane structure was constructed between PM  $\alpha$ -CDs and phenylene ethynylene as hosts and guest, respectively.

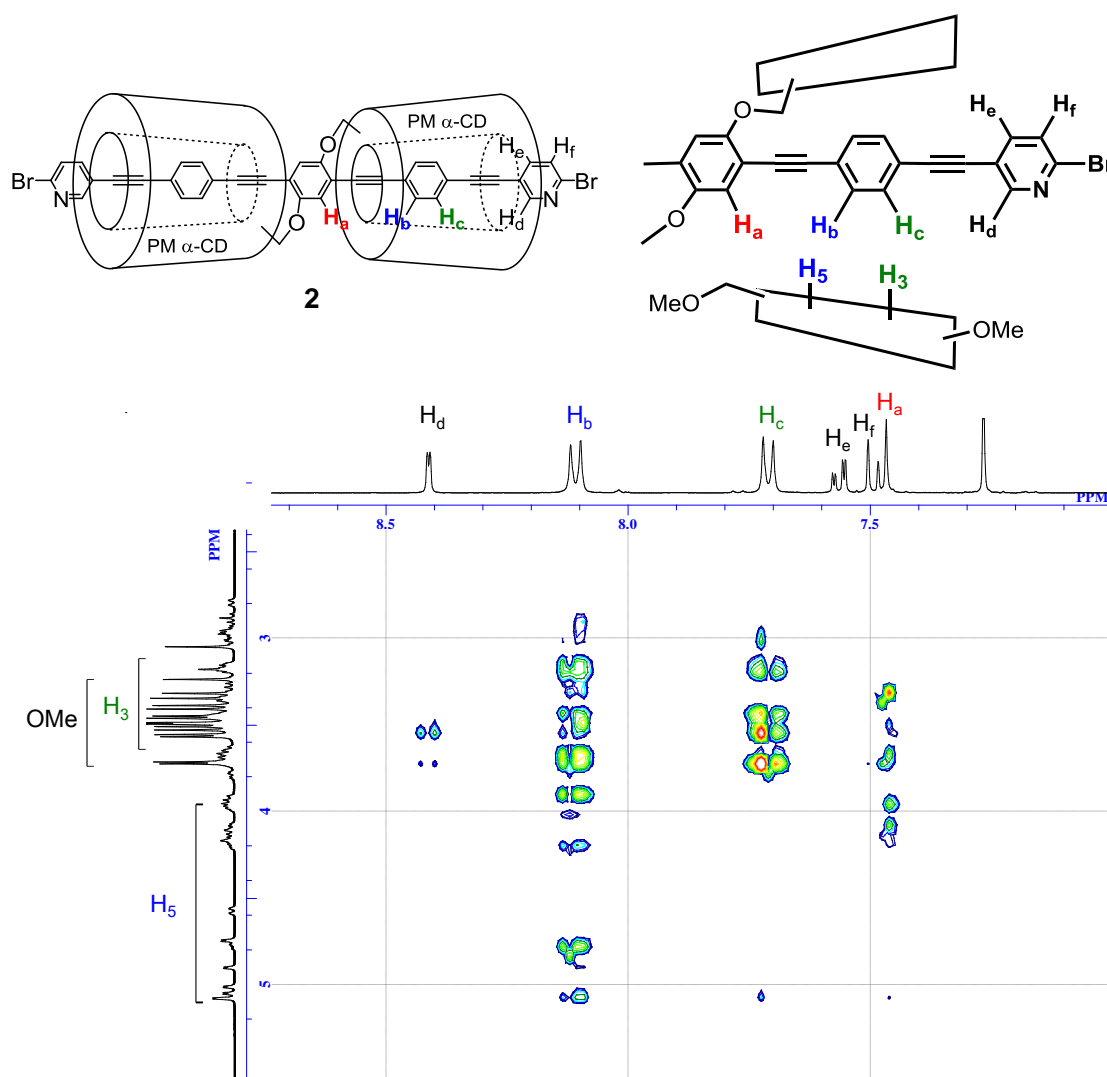
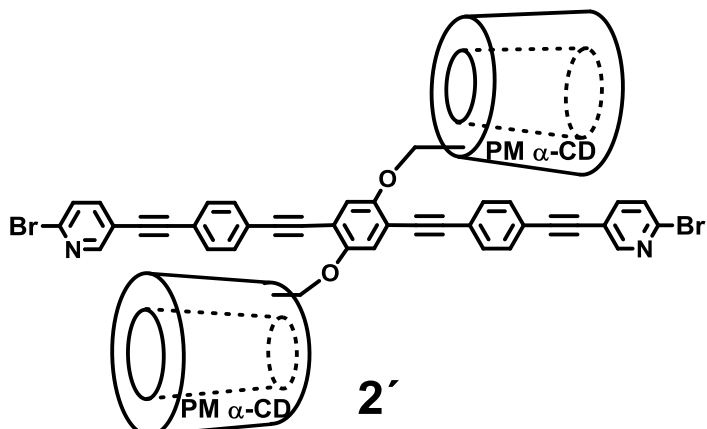


Figure S1. Partial ROESY NMR spectrum of **2** (400 MHz, CDCl<sub>3</sub>) showing the NOEs between aromatic protons of the axial oligo(phenylene ethynylene) and inner protons of cyclodextrins.

### 2.3 Synthesis of uninsulated monomer 2'



Under argon atmosphere, **1** (1.00 g, 364  $\mu$ mol), 2-bromo-5-iodo-pyridine (2.07 g, 7.28  $\mu$ mol) were dissolved in  $^i$ Pr<sub>2</sub>NH and then cooled to 0 °C. Following addition of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (25.6 mg, 36.4  $\mu$ mol), and CuI (3.5 mg, 18  $\mu$ mol), the mixture was then stirred at 0 °C for 22 h. Following evaporation, the residue was purified by preparative SEC (eluent: CHCl<sub>3</sub>) to yield a yellow solid **2'** (983 mg, 306  $\mu$ mol, 84%).

#### <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, r.t.)

$\delta$ : 8.53 (2H, d,  $J$  = 2.1 Hz), 7.67 (2H, dd,  $J$  = 8.2, 2.1 Hz), 7.57 (4H, d,  $J$  = 8.2 Hz), 7.52-7.50 (6H, m), 7.08 (2H, s), 5.17-4.79 (14H, m), 4.25-3.04 (172H, m).

#### <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, r.t.)

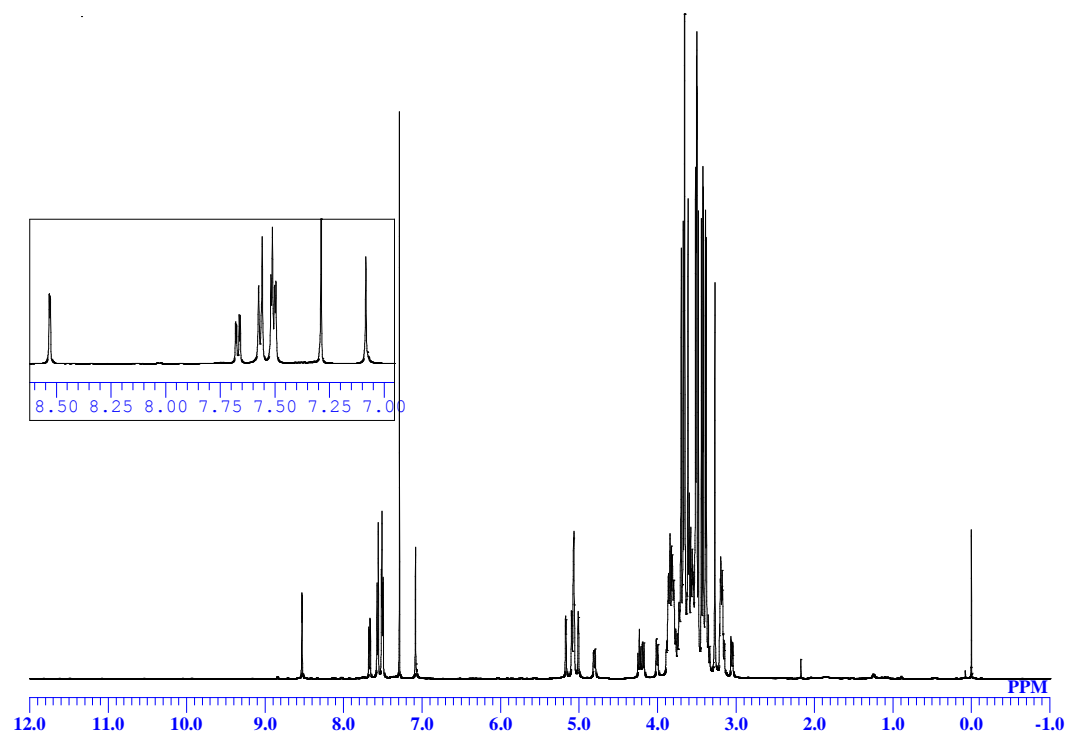
$\delta$ : 153.56, 152.37, 141.36, 140.50, 131.67, 131.59, 127.76, 123.89, 122.09, 119.45, 116.79, 113.89, 100.52, 100.30, 100.18, 100.14, 100.05, 99.52, 94.68, 93.48, 88.65, 86.78, 83.11, 82.56, 82.52, 82.46, 82.40, 82.32, 82.28, 82.22, 82.21, 82.15, 82.13, 81.80, 81.26, 81.25, 81.21 (several peaks overlapped), 81.12, 77.24, 72.30, 71.72, 71.58, 71.53, 71.52, 71.47, 71.30, 71.29, 71.22, 71.11, 70.96, 68.16, 61.91, 61.85, 61.82, 61.80 (several peaks overlapped), 61.75, 59.24, 59.09 (several peaks overlapped), 59.03, 58.26, 57.97, 57.92, 57.87, 57.83, 57.40

#### High-Resolution MALDI TOF-MS

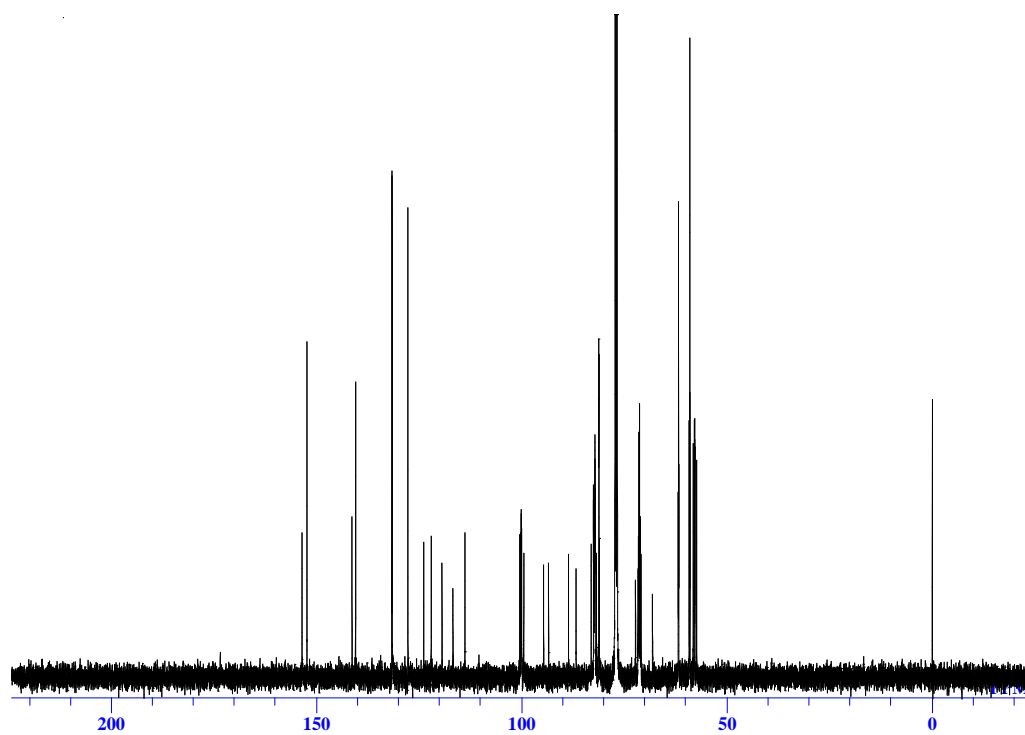
calcd for C<sub>142</sub>H<sub>202</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>60</sub>Na [**2'**+Na<sup>+</sup>]: 3076.108; found: 3076.108 ( $m/z$ , monoisotopic mass)



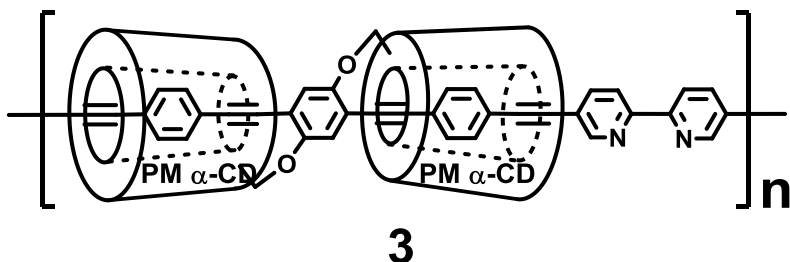
$^1\text{H}$  NMR spectrum of **2'**



$^{13}\text{C}$  NMR spectrum of **2'**



## 2.4 Synthesis of insulated polymer **3**



Under an argon atmosphere, **2** (351 mg, 115  $\mu$ mol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (13.3 mg, 11.5  $\mu$ mol) were dissolved in toluene (5 mL), after which Sn<sup>2+</sup>Bu<sub>6</sub> (58  $\mu$ L, 0.12 mmol) was added. The mixture was stirred at 115 °C in a closed flask for 48 h. After cooling, the reaction mixture was poured into Et<sub>2</sub>O. The precipitated solid was collected and fractionated by preparative SEC (using JAIGEL-3H column with CHCl<sub>3</sub> as the eluent) to obtain the desired high molecular weight fraction ( $M_n = 5.3 \times 10^4$ ,  $M_w = 1.1 \times 10^5$ ), yielding a yellow filmy solid **3** (169 mg, 58.7  $\mu$ mol, 51%).

For the coordination experiments or optical analyses, polymer **3** was washed by HNO<sub>3(aq)</sub> to remove metallic residues. 1 M HNO<sub>3(aq)</sub> and MeCN (1/1) were added to the fractionated polymer **3** to give a ratio of 0.5 mL / mg. After stirring at room temperature for several minutes, the product was extracted with CHCl<sub>3</sub>. The organic layer was then poured into NH<sub>3(aq)</sub> and extracted again with CHCl<sub>3</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated, dried in vacuo, and used for subsequent experiments.

### <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, r.t.)

$\delta$ : 8.77 (1H, s), 8.58 (1H, bs), 8.12 (2H, bs), 7.96 (1H, bs), 7.76 (2H, bs), 7.45 (1H, s), 5.07-4.59 (14H, m), 4.15-2.77 (172H, m).

$^1\text{H}$  NMR spectrum of **3**

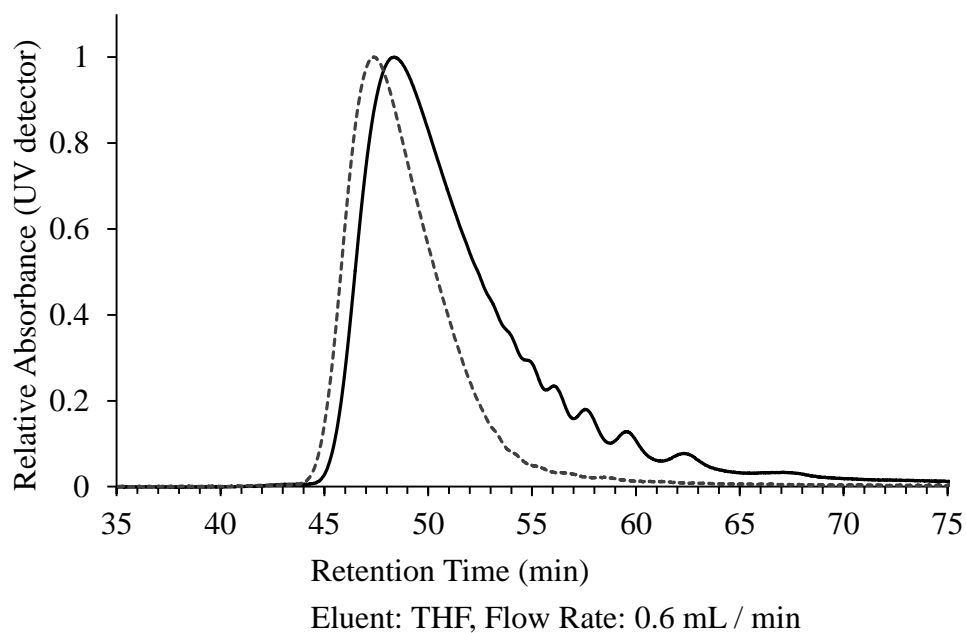
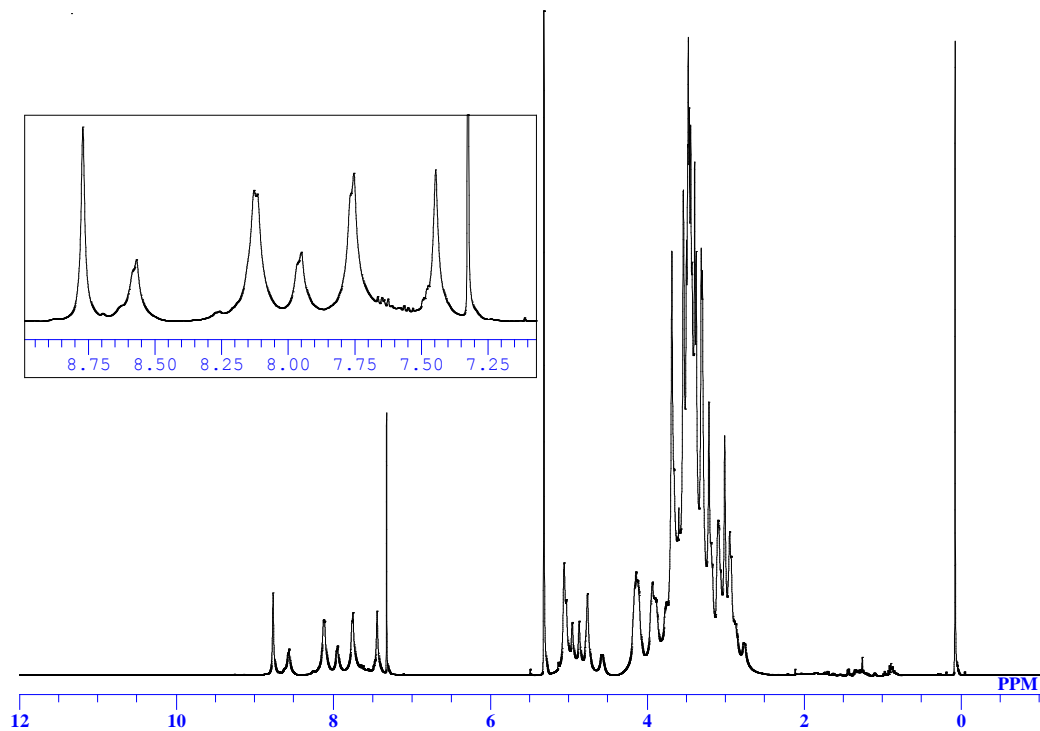
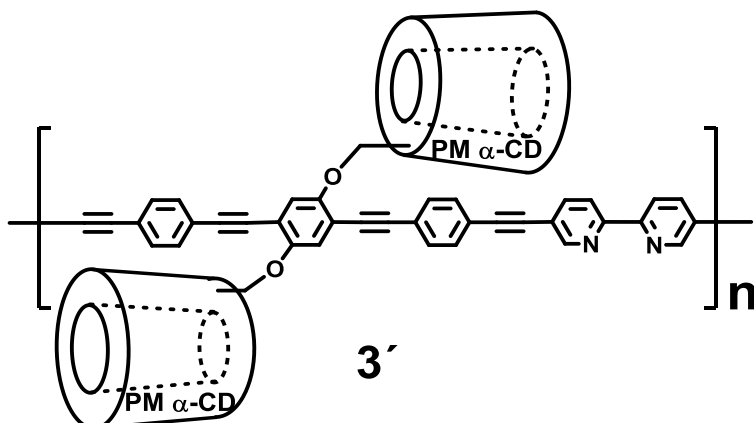


Figure S2. Analytical SEC chromatogram of **3**. Solid line indicates the elution curve of the reaction mixture. Dashed line indicates the elution curve of the fractionated polymer ( $M_n = 5.3 \times 10^4$ ,  $M_w = 1.1 \times 10^5$ )

## 2.5 Synthesis of uninsulated polymer **3'**



Under argon atmosphere, **2'** (144 mg, 47.1  $\mu\text{mol}$ ) and  $\text{Pd}(\text{PPh}_3)_4$  (6.1 mg, 5.3  $\mu\text{mol}$ ) were dissolved in toluene (10 mL) after which  $\text{Sn}_2^{\text{n}}\text{Bu}_6$  (24  $\mu\text{L}$ , 47  $\mu\text{mol}$ ) addition. The mixture was stirred at 115  $^\circ\text{C}$  in a closed flask for 72 h. After cooling, the reaction mixture was poured into  $\text{Et}_2\text{O}$ . The precipitated solid was collected and fractionated by preparative SEC (using JAIGEL-3H column with  $\text{CHCl}_3$  as the eluent) to obtain the desired high molecular weight region ( $M_n = 4.9 \times 10^4$ ,  $M_w = 1.0 \times 10^5$ ), yielding a filmy solid **3'** (16.1 mg, 5.7  $\mu\text{mol}$ , 12%).

For the coordination experiments or optical analyses, polymer **3'** was washed by  $\text{HNO}_{3(\text{aq})}$  to remove metallic residues. 1 M  $\text{HNO}_{3(\text{aq})}$  and MeCN (1/1) were added to the fractionated polymer **3** to give a ratio of 0.5 mL / mg. After stirring at room temperature for several minutes, the product was extracted with  $\text{CHCl}_3$ . The organic layer was then poured into  $\text{NH}_{3(\text{aq})}$  and extracted again with  $\text{CHCl}_3$ . The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , evaporated, dried in vacuo, and used for subsequent experiments.

### $^1\text{H}$ NMR (500 MHz, $\text{CD}_2\text{Cl}_2$ , r.t.)

$\delta$ : 8.83 (2H, s), 8.69-8.59 (2H, bs), 8.09-8.00 (2H, bs), 7.64-7.39 (8H, bs), 7.05 (s, 2H), 5.09-4.75 (14H, m), 4.20-2.85 (172H, m).

$^1\text{H}$  NMR spectrum of **3'**

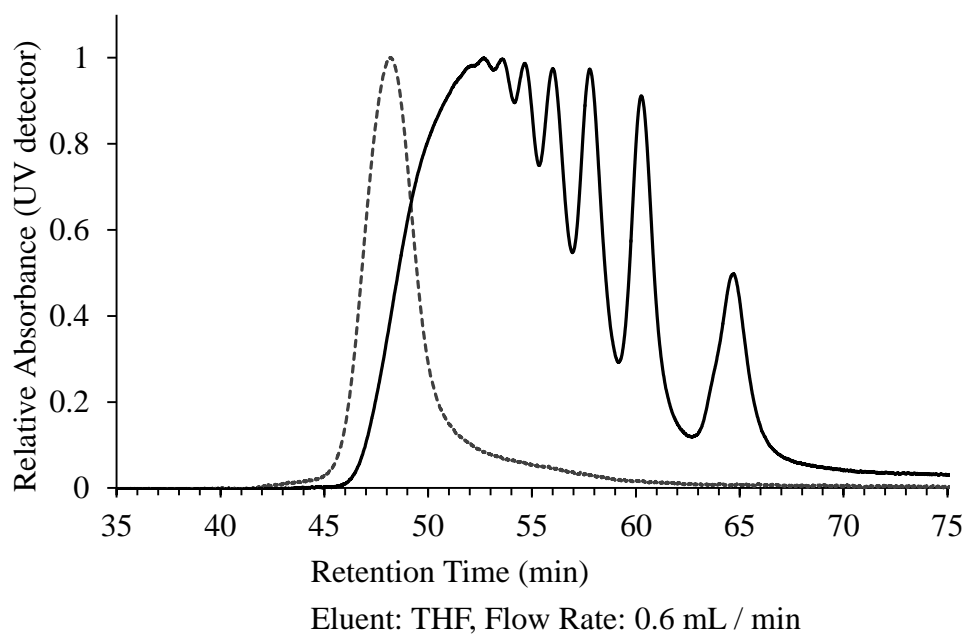
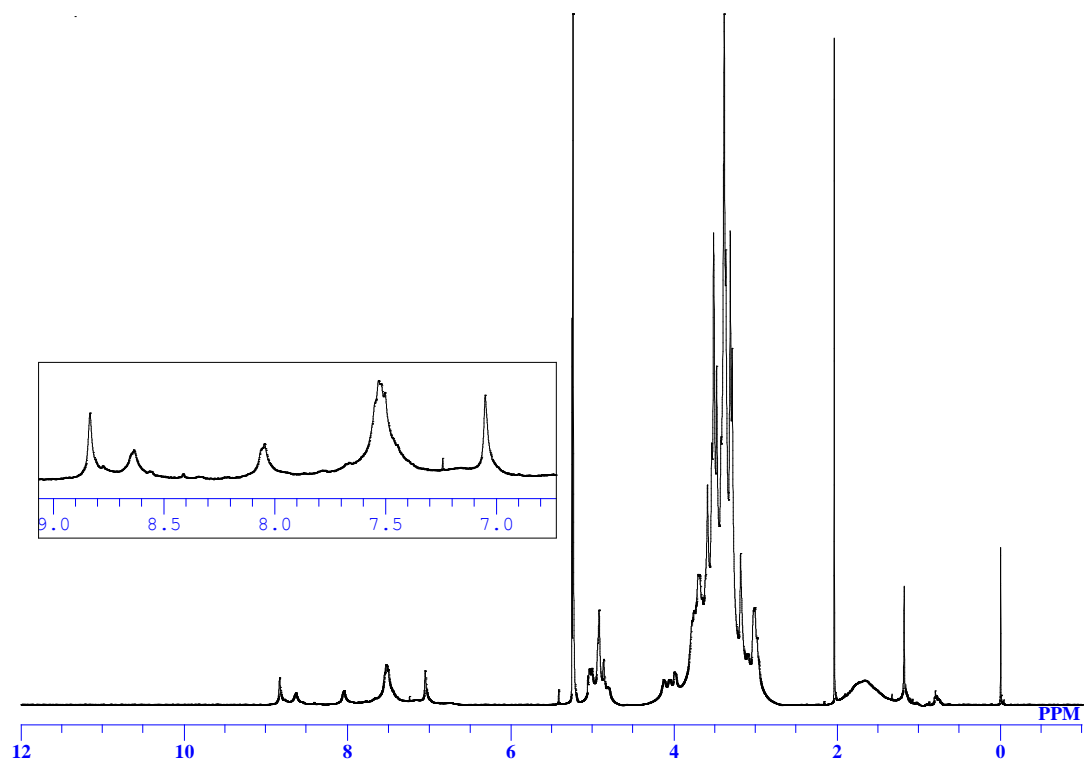


Figure S3. Analytical SEC chromatogram of **3'**. Solid line indicates the elution curve of the reaction mixture. Dashed line indicates the elution curve of the fractionated polymer ( $M_n = 4.9 \times 10^4$ ,  $M_w = 1.0 \times 10^5$ )

## 2.6 Preparation of metalated polymers 3-M or 3'-M

### Preparation of metalated polymers for the analyses in solution

In a glass vial, 1.0 mL of  $10^{-4}$  M  $\text{CHCl}_3$  solution of polymer **3** or **3'** was mixed with 3.0 equiv (bipyridine units) of anhydrous metal salt ( $\text{ZnCl}_2$ ,  $\text{InCl}_3$ , or  $\text{SnCl}_4$ ). In the case of  $\text{CdCl}_2$  or  $\text{GaCl}_3$ , 100 equiv of metal salt was used because the complex of metals are unstable in highly dilute solutions. After stirring for several hours at room temperature, 300  $\mu\text{L}$  of the resulting solution was diluted to yield a 3.0 mL  $\text{CHCl}_3$  solution ( $10^{-5}$  M for the bipyridine units) for use in absorption or fluorescence spectroscopy.

### Preparation of samples for the analyses in the films

In a glass vial, 1.0 mL of  $10^{-4}$  M  $\text{CHCl}_3$  solution of polymer **3** or **3'** was mixed with 1.0 equiv (for bipyridine units) of anhydrous metal salt ( $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{GaCl}_3$ ,  $\text{InCl}_3$ , or  $\text{SnCl}_4$ ). After stirring for several hours at room temperature, films of the polymers were prepared by drop-casting 30  $\mu\text{L}$  of the solution ( $10^{-4}$  M for the bipyridine units) onto silanized  $\text{SiO}_2$  plates (1 cm  $\times$  1 cm). After drop-casted, the films were dried in vacuo at room temperature for 3 hours. Films of metal-free polymer **3** or **3'** were also fabricated in the same procedure.

### 3. Absorption Spectra of Polymers

#### 3.1 Absorption spectra of polymer **3-M** in $\text{CHCl}_3$

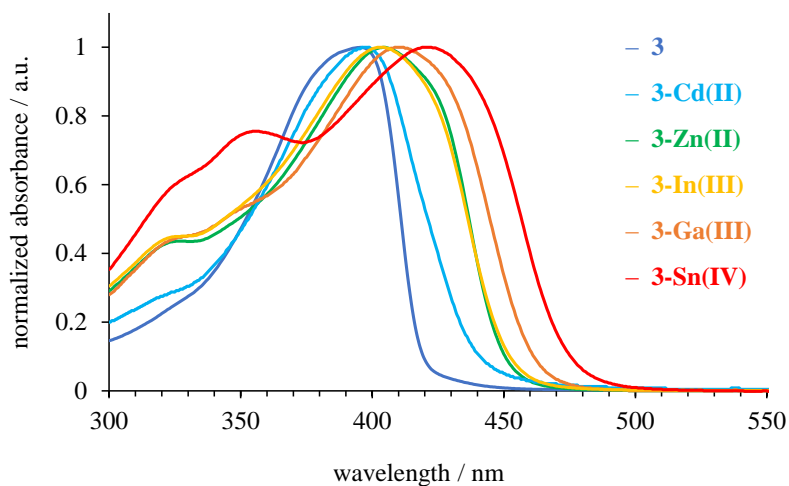


Figure S4. Absorption spectra of polymer **3-M** in  $\text{CHCl}_3$ .

#### 3.2 Absorption spectra of polymer **3'-M** in $\text{CHCl}_3$

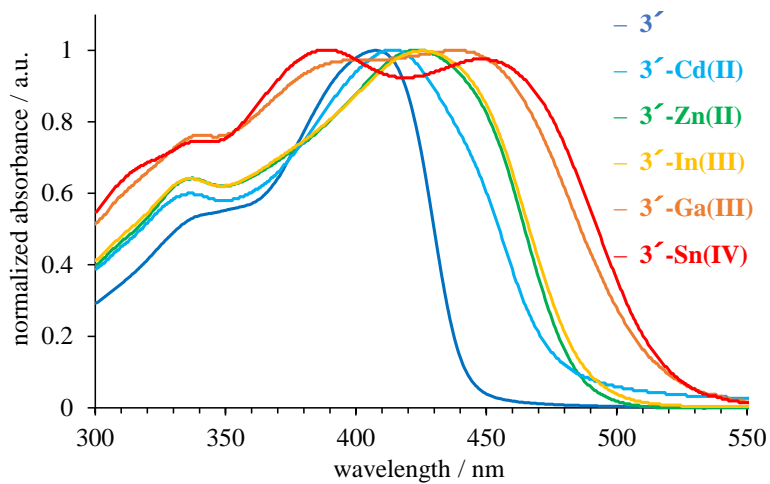
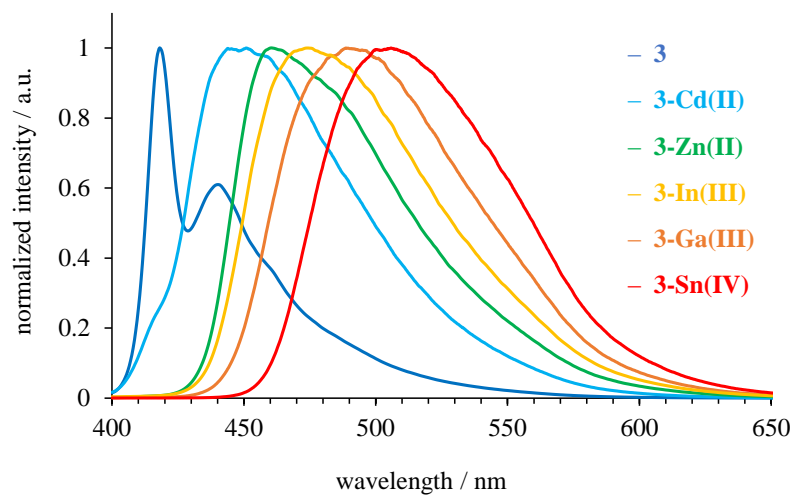


Figure S5. Absorption spectra of polymer **3'-M** in  $\text{CHCl}_3$ .

## 4. Emission Spectra and Quantum Yields of polymers in the solution

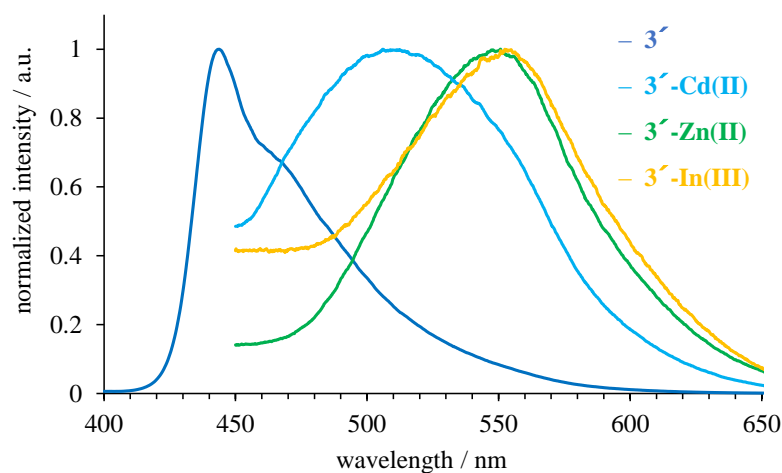
### 4.1 Emission spectra and quantum yields of polymer **3-M** in $\text{CHCl}_3$



	<b>3</b>	<b>3-Zn(II)</b>	<b>3-Cd(II)</b>	<b>3-Ga(III)</b>	<b>3-In(III)</b>	<b>3-Sn(IV)</b>
$\Phi_F$	0.58	0.68	0.58	0.61	0.62	0.47

Figure S6. Emission spectra and quantum yields of polymer **3-M** in the  $\text{CHCl}_3$  solution.

### 4.2 Emission spectra and quantum yields of polymer **3'-M** in $\text{CHCl}_3$

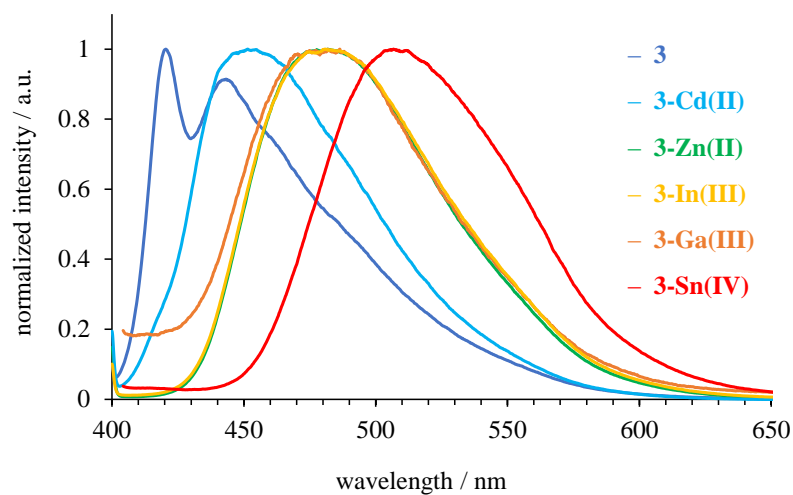


	<b>3'</b>	<b>3'-Zn(II)</b>	<b>3'-Cd(II)</b>	<b>3'-Ga(III)</b>	<b>3'-In(III)</b>	<b>3'-Sn(IV)</b>
$\Phi_F$	0.28	0.20	0.32	N.D.	0.09	N.D.

Figure S7. Emission spectra and quantum yields of polymer **3'-M** in the  $\text{CHCl}_3$  solution.



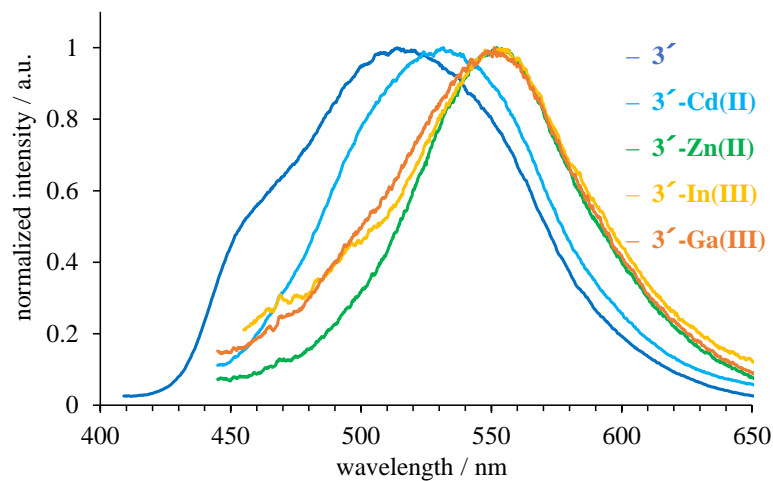
#### 4.3 Emission spectra and quantum yields of polymer **3-M** in the solid state films



	<b>3</b>	<b>3-Zn(II)</b>	<b>3-Cd(II)</b>	<b>3-Ga(III)</b>	<b>3-In(III)</b>	<b>3-Sn(IV)</b>
$\Phi_F$	0.16	0.35	0.16	0.31	0.39	0.46

Figure S8. Emission spectra and quantum yields of polymer **3-M** in the solid state films.

#### 4.4 Emission spectra and quantum yields of polymer **3'-M** in the solid state films



	<b>3'</b>	<b>3'-Zn(II)</b>	<b>3'-Cd(II)</b>	<b>3'-Ga(III)</b>	<b>3'-In(III)</b>	<b>3'-Sn(IV)</b>
$\Phi_F$	0.10	0.13	0.19	0.04	0.06	N.D.

Figure S9. Emission spectra and quantum yields of polymer **3'-M** in the solid state films.

## 5. Metalation of polymer film 3

### Procedure of the dipping experiments

The films of polymer **3** were dipped into Et<sub>2</sub>O solutions containing metal ions (Zn(II), Cd(II), In(III), Ga(III), or Sn(IV)) of known concentrations (10–3000 μM) at room temperature for 5–30 s. The emission color of the dipped moieties immediately changed into the representative colors for the metals. The films were washed by Et<sub>2</sub>O for several times to remove uncoordinated metal ions and then dried in the air. Figure S10 shows the emission spectra of the metalated films.

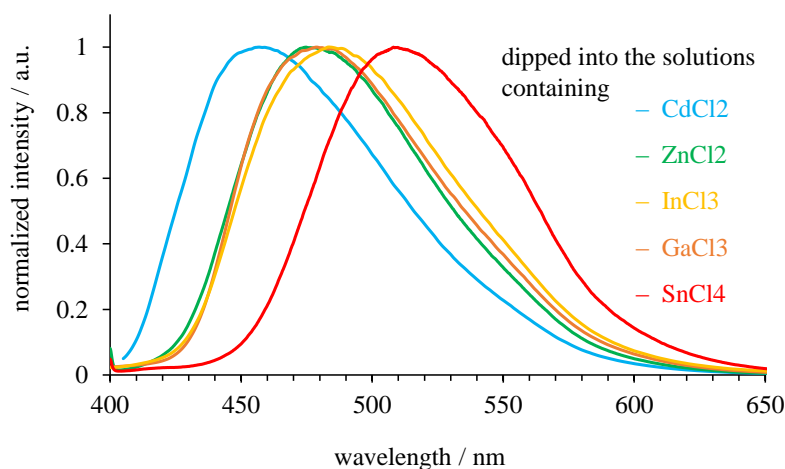


Figure S10. Emission spectra of polymer **3** after dipping into various metal-containing solutions.

### Evaluation of the coordination reversibility of polymer film 3

The coordination reversibility of polymer film **3** was examined by alternating between metalation (dipped into ZnCl<sub>2</sub>/Et<sub>2</sub>O) and demetalation steps (dipped into aq. NH<sub>3</sub>), and the emission spectra of **3-Zn(II)** were measured following each metalation step. Metal-free **3** was not measured in this experiment to reduce film damage by excitation laser irradiation. Only a slight decrease in the emission intensity of **3-Zn(II)** was observed over the 5 cycles of the metalation/demetalation process. In addition, no significant change in the spectral shapes was observed following 5 cycles. The following figures (Figure S11, S12) summarize the obtained results.

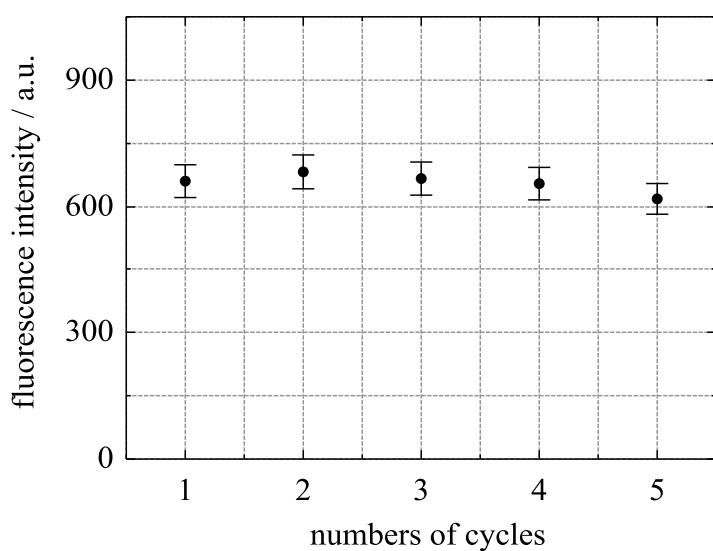
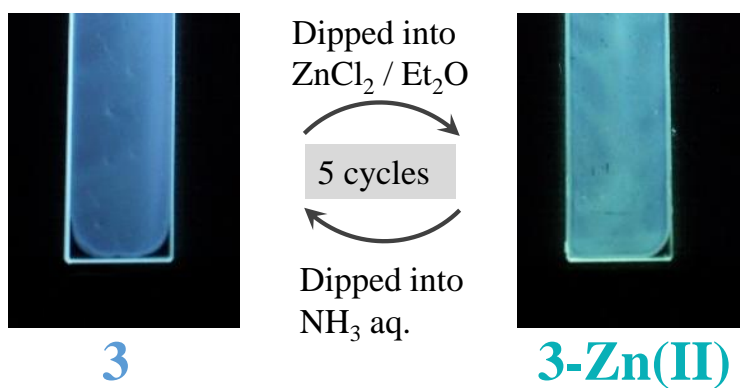


Figure S11. Variation in fluorescence intensity of **3-Zn(II)** over 5 metalation/demetalation cycles. Error bars represent 95% confidence bounds in the Gaussian fitting of 30 measurements.

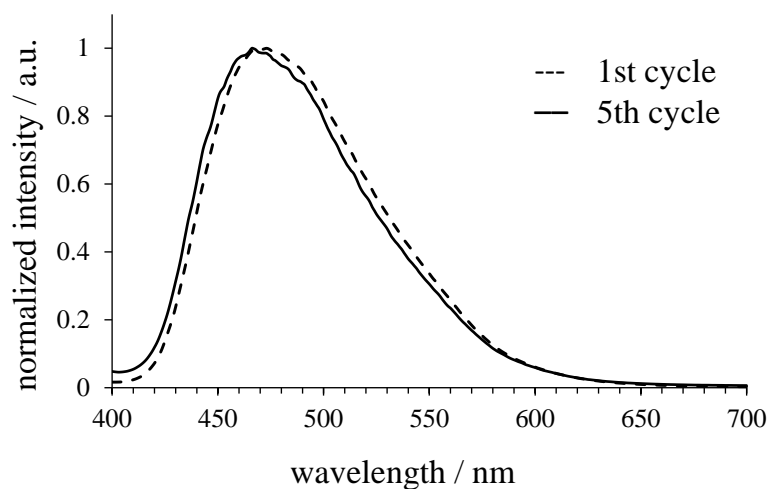


Figure S12. Normalized emission spectrum of **3-Zn(II)** film after the 1st (dashed line) and 5th (solid line) metalation/demetalation cycles (spectra were obtained following the metalation steps).

## 6. Titration study of polymer 3

### Procedure of the titration study

The  $\text{SnCl}_4$  titration experiment was started with a 3.0 mL polymer solution (in  $\text{CHCl}_3$ ) of known concentration ( $10^{-5}$  M for the bipyridine units), to which 15  $\mu\text{L}$  (0.1 equiv) aliquots of  $\text{SnCl}_4$  salt solution were added until the total amount of  $\text{SnCl}_4$  reached 1.2 equiv; after that, 30  $\mu\text{L}$  (0.2 equiv) aliquots of the  $\text{SnCl}_4$  solution were added each time. Emission (excitation: 380 nm) and absorption spectra were collected following each aliquot addition.

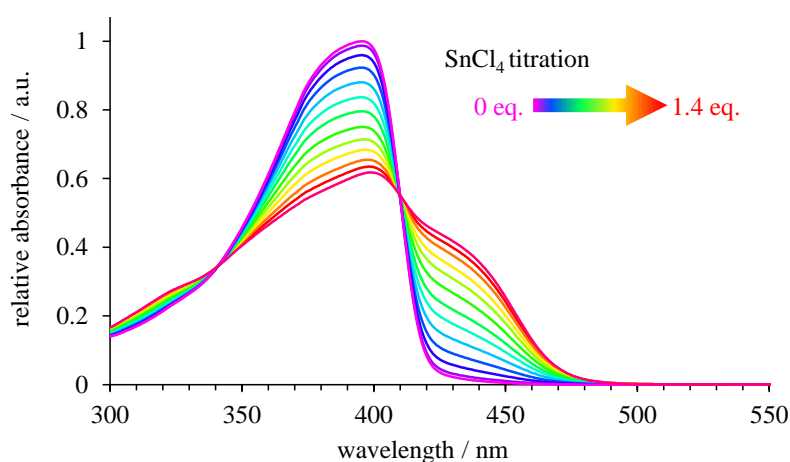


Figure S13. Absorption spectral change of polymer 3 with  $\text{SnCl}_4$  titration (solvent:  $\text{CHCl}_3$ ).

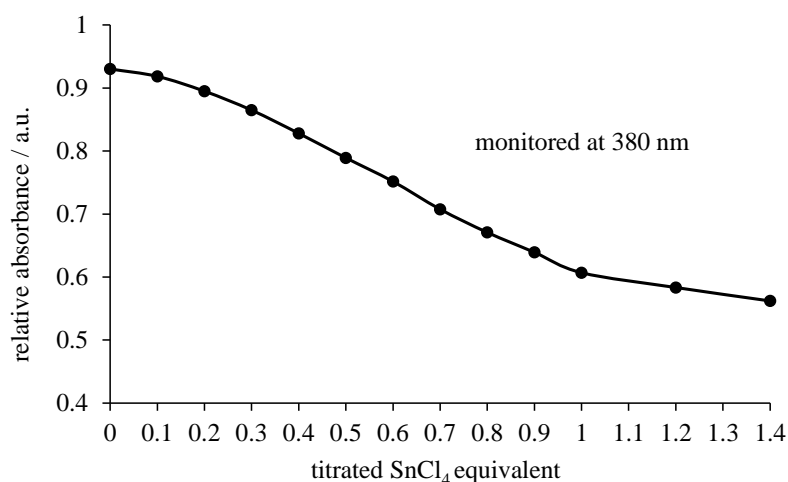


Figure S14. Absorbance change with  $\text{SnCl}_4$  titration monitored at 380 nm (emission wavelength in the emission spectroscopy).

## 7. Titration study of polymer 3'

### Procedure of the titration study

The  $\text{ZnCl}_2$  titration experiment was started with a 3.0 mL polymer solution (in  $\text{CHCl}_3$ ) of known concentration ( $10^{-5}$  M for the bipyridine units), to which 4  $\mu\text{L}$  (0.1 equiv) aliquots of  $\text{ZnCl}_2$  salt solution were added until the total amount of  $\text{ZnCl}_2$  reached 1.0 equiv; after that, 8  $\mu\text{L}$  (0.2 equiv) aliquots of the  $\text{ZnCl}_2$  solution were added each time. Emission (excitation: 380 nm) and absorption spectra were collected following each aliquot addition. The absorption data (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.4, 1.8, 2.0 equiv of  $\text{ZnCl}_2$ ) was represented in a Scatchard plot (Figure S16).  $\Delta A$  indicates the amount of absorbance change at 410 nm.  $[\text{Zn}^{2+}]$  indicates the concentration of  $\text{ZnCl}_2$ .

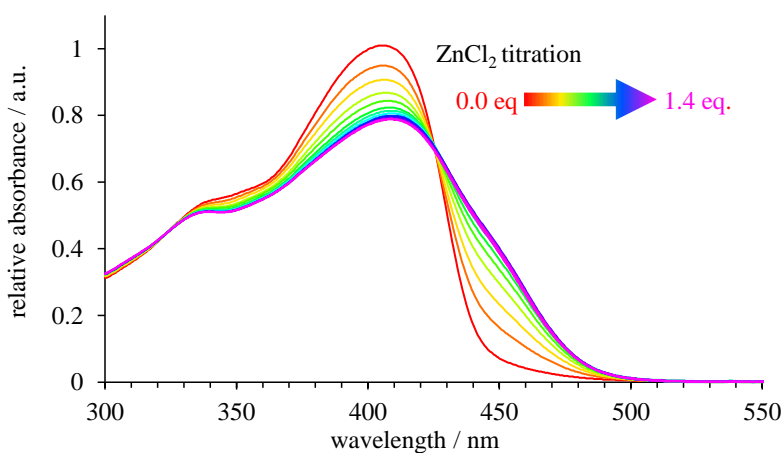


Figure S15. Absorption spectral change of polymer 3' with  $\text{ZnCl}_2$  titration (solvent:  $\text{CHCl}_3$ ).

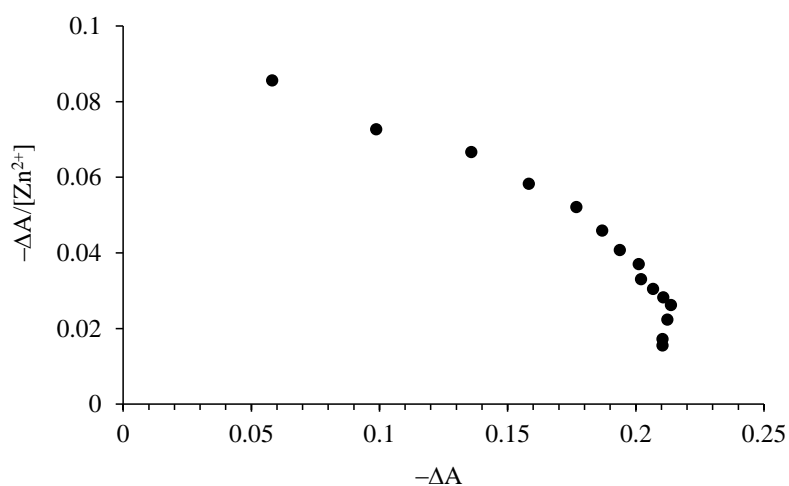


Figure S16. Scatchard plot of the absorption data shown in Figure S15.

## Abbreviation

NMR: nuclear magnetic resonance

SEC: size-exclusion chromatography

PM  $\alpha$ -CD: permethylated  $\alpha$ -cyclodextrin

TPPTS: tris(3-sulfophenyl)phosphine trisodium salt

## Reference

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