

## Supporting Information

# Highly Active Aggregate Catalysts for the Synthesis of High-Molecular-Weight Polyesters via Copolymerization of Epoxides and Cyclic Anhydrides

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## 1. Materials

All the chemicals including 4-chloro-benzaldehyde, 4-methyl-benzaldehyde, 4-hydroxy-benzaldehyde, propionic acid, methacryloylchloride, triethylamine, diethyl aluminum chloride ( $\text{AlEt}_2\text{Cl}$ ) are commercially available and could be used without further purification. Pyrrole to be redistilled before use. Azobisisobutyronitrile (AIBN) and hexaphenyldiphosphazanium chloride (PPNCl) to be recrystallized before use. Propylene oxide (PO), 1-butene oxide (BO), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and trichloromethane ( $\text{CHCl}_3$ ) were distilled from calcium hydride under a nitrogen atmosphere before use. Phthalic anhydride (PA) was purified by stirring in ethyl acetate (EA) with  $\text{CaH}_2$ , concentrated to dryness, and sublimated under reduced pressure. if not mentioned. All manipulations involving air- and/or water-sensitive compounds were carried out using the Schlenk technique under a dry nitrogen atmosphere.

## 2. Characterization Methods

**NMR:**  $^1\text{H}$  NMR spectra were recorded on a Bruker ARX-300 and ARX-400 spectrometer at ambient temperature in deuterated chloroform ( $\text{CDCl}_3$ ) or dimethylsulfoxide (DMSO) with tetramethylsilane (TMS) as the internal reference. Chemical shifts were reported in ppm from the internal standard, tetramethylsilane (0 ppm) for  $^1\text{H}$  NMR, solvent proton shifts (ppm):  $\text{CDCl}_3$ , 7.26 (s); DMSO- $d_6$ , 2.50 (s).

**MALDI-TOF-MS:** Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was carried out on a Bruker auto flex III Mass spectrometer. The samples were dissolved in  $\text{CDCl}_3$  at a concentration of 10 mg  $\text{mL}^{-1}$ . The matrix was Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB).

**Gel Permeation Chromatography (GPC):** The molecular weight and its distribution of the polycarbonate-ether products were determined by gel permeation chromatography at 35 °C against polystyrene standard on Waters 410 GPC instrument with dichloromethane as eluent, where the flow rate was set at 1.0  $\text{mL min}^{-1}$ .

**UV-vis:** The UV-vis characterizations were carried out on a HITACHI U-4100 Spectrophotometer with high-temperature and high-pressure resistant cuvettes.

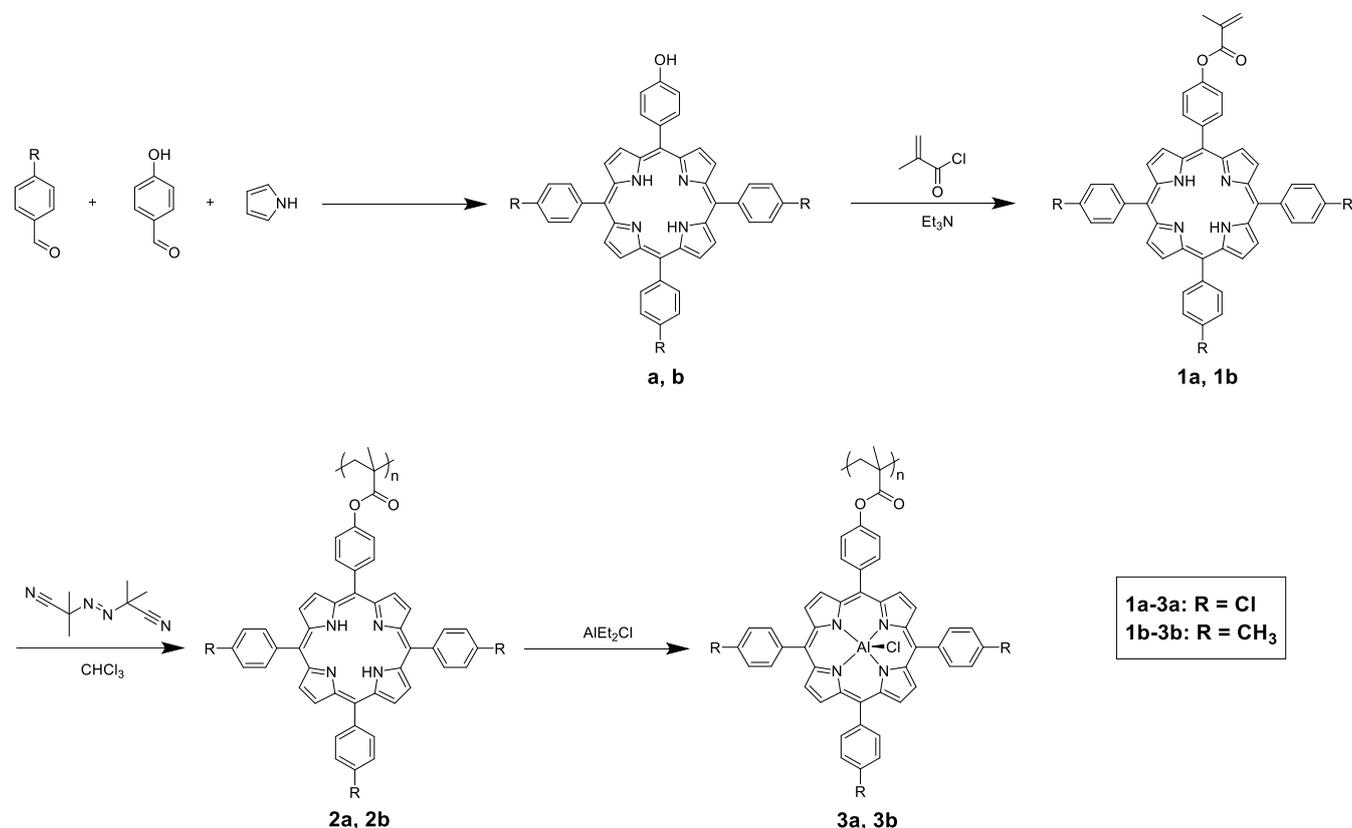
**Differential Scanning Calorimetry (DSC):** DSC analysis was performed on a Perkin-Elmer DSC-7 instrument under  $\text{N}_2$  atmosphere. The sample was first heated from -10 °C to 200 °C at 10 °C  $\text{min}^{-1}$  and then rapidly quenched to -10 °C, followed by a second heating process to obtain the glass transition temperature ( $T_g$ ).

**Thermogravimetric Analyses (TGA):** TGA was measured on a Mettler Toledo TGA-2 instrument under an  $\text{N}_2$  atmosphere with a heating rate of 10 °C  $\text{min}^{-1}$  from 40 °C temperature to 800 °C.

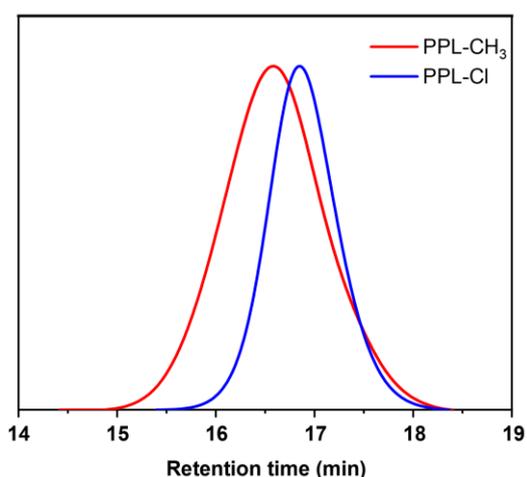
**Tensile Performance:** Tensile testing was evaluated in a screw-driven universal testing machine (Z1010, Zwick Co., Germany) equipped with a 10 KN electronic load cell and mechanical grips. The test was conducted at 20 °C using a cross-head rate of 5 mm/min according to the ASTM standard.

### 3. Experimental Procedures

#### 3.1 Synthesis and Characterization of Polymeric Aluminum Porphyrin Catalysts



**Scheme S1.** Synthetic route of polymeric aluminum porphyrin catalysts based on radical polymerization of methacrylic-based porphyrins.



Ligand Series	$M_n$ (kg/mol)	$\mathcal{D}$	DP
PPL-CH <sub>3</sub>	4200	1.3	5.6
PPL-Cl	5100	1.5	6.3

**Figure S1.** Gel permeation chromatography (GPC) characterization of polymeric porphyrin precursor (compound 2a-2b). The molecular weight ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) of polymeric porphyrin catalyst ligands were determined by GPC at 35 °C in polystyrene standard on Agilent PL GPC220 instrument with THF as the eluent, where the flow rate was set at 1.0 mL min<sup>-1</sup>. The degree of polymerization (DP) is calculated as: DP =  $M_n$ /(Mass of per porphyrin unit).

### 3.1.1 General Procedure of Methacrylic-Based Porphyrin

Scheme S1 showed a step-wise synthesis procedure of the porphyrin monomer. The unsymmetrical porphyrins were prepared by a “one-pot” reaction of pyrrole, substituted benzaldehyde, and 4-hydroxy-benzaldehyde using propionic acid as solvent followed by achromatic graphical separation. After the acylation reaction, the porphyrin monomer was obtained. The details are in the following:

### 3.1.2 Synthesis of Compounds a, b

Compounds **a** and **b** were synthesized according to the previous literature<sup>1,2</sup>. In a flask, 4-hydroxy-benzaldehyde (13.24 g, 0.11 mmol) and substituted benzaldehyde (0.32 mmol) were dissolved in propionic acid (500 mL) and then heated to 135 °C for 0.5 h. Then pyrrole (30 mL, 0.43 mmol) which was previously distilled was added dropwise to the solution under nitrogen. And the mixture was refluxed for 2 h at 165 °C. After cooling to room temperature, 500 mL methanol was added to the flask and the mixture was stored overnight in a refrigerator. The purple solid was filtered off and washed with methanol and hot water. The crude product was purified on a silica gel column with dichloromethane /methanol (95:5 v/v) as eluent and the yield was 4%-6%.

#### 5,10,15-tri(4-chlorophenyl)-20-[4-(hydroxy)phenyl]-porphyrin (**a**)

Yield was 6%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.88 (d, J = 18.2 Hz, 8H), 8.12 (dd, J = 21.2, 8.2 Hz, 8H), 7.83-7.70 (m, 6H), 7.24 (d, J = 8.3 Hz, 2H), -2.83 (s, 2H).

#### 5,10,15-tri(4-methylphenyl)-20-[4-(hydroxy)phenyl]-porphyrin (**b**)

Yield was 5%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.88 (s, 8H), 8.10 (dd, J = 13.4, 8.0 Hz, 8H), 7.57 (d, J = 7.6 Hz, 6H), 7.22-7.13 (m, 2H), 2.73 (s, 9H), -2.74 (s, 2H).

### 3.1.3 Synthesis of Compounds 1a, 1b

Briefly, **a** or **b** (2.3 mmol) and triethylamine (0.25 g, 0.6 mmol) were dissolved in the anhydrous CH<sub>2</sub>Cl<sub>2</sub> under nitrogen. Then, in an ice-water bath, methacryloyl chloride (0.26 g, 2.5 mmol) was added dropwise into the solution at 0 °C and the mixture was stirred for 12 h at 50 °C. After evaporating THF, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and then washed with brine three times and then dried with MgSO<sub>4</sub>. The crude product was purified on a silica gel column with dichloromethane as the eluent and the yield was 80%-92%.

#### 5,10,15-tri(4-chlorophenyl)-20-[4-(methacryloyloxy)phenyl]-porphyrin (**1a**)

Yield was 87%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.89 (d, J = 16.4 Hz, 8H), 8.32-8.08 (m, 8H), 7.86-7.68 (m, 6H), 7.54 (dd, J = 18.3, 8.4 Hz, 2H), 6.58 (s, 1H), 5.93 (s, 1H), 2.24 (t, J = 1.1 Hz, 3H), -2.84 (s, 2H).

#### 5,10,15-tri(4-methylphenyl)-20-[4-(methacryloyloxy)phenyl]-porphyrin (**1b**)

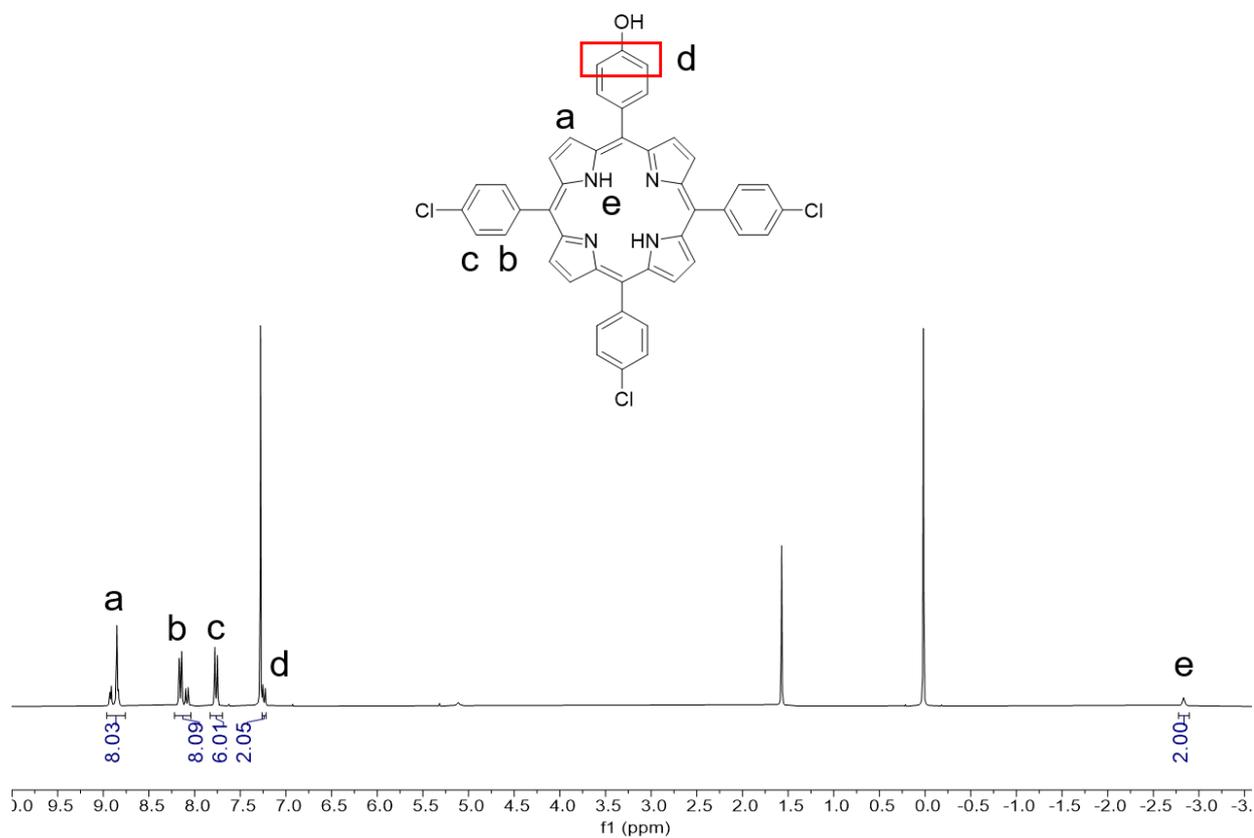
Yield was 87%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.88 (s, 8H), 8.18 (dd, J = 41.0, 7.8 Hz, 8H), 7.57 (t, J = 7.9 Hz, 8H), 6.57 (s, 1H), 5.92 (s, 1H), 2.73 (s, 9H), 2.23 (d, J = 7.9 Hz, 3H), -2.75 (s, 2H).

### 3.1.4 Synthesis of Compounds 2a, 2b

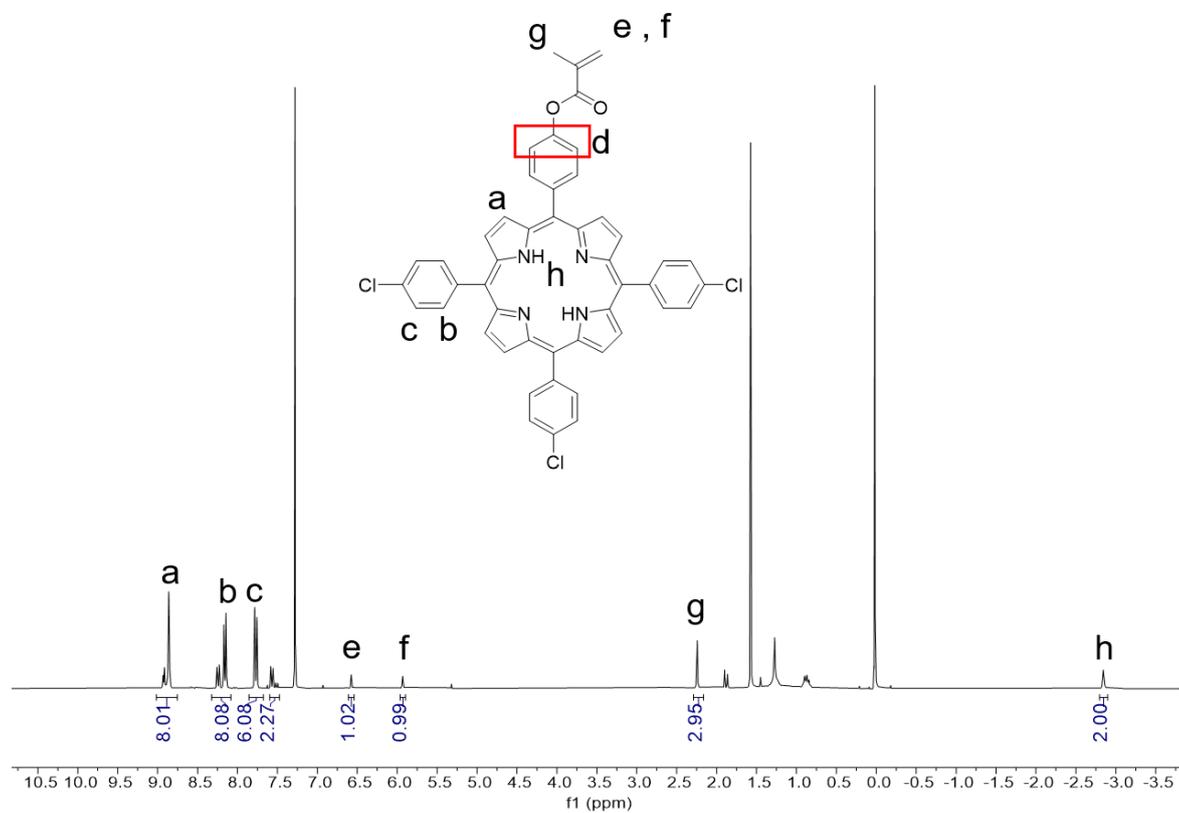
The porphyrin oligomer was synthesized by radical polymerization. In a 50 mL Schlenk flask, compounds **1a** or **1b** (0.6 mmol), and AIBN (0.67 mg, 0.04 mmol) were dissolved in CHCl<sub>3</sub> (20 mL). The solution was degassed by three freeze-evacuate-thaw cycles. The polymerization was carried out at 75 °C for 36-48 h and then quenched by liquid nitrogen. The mixture was centrifuged in cold diethyl ether 3 times and the precipitation was dried under vacuum. Finally, the obtained oligomer was characterized by <sup>1</sup>H NMR and UV-vis spectra.

### 3.1.5 Synthesis and Characterizations of Metallic Polymeric Porphyrin (complexes 3a, 3b)

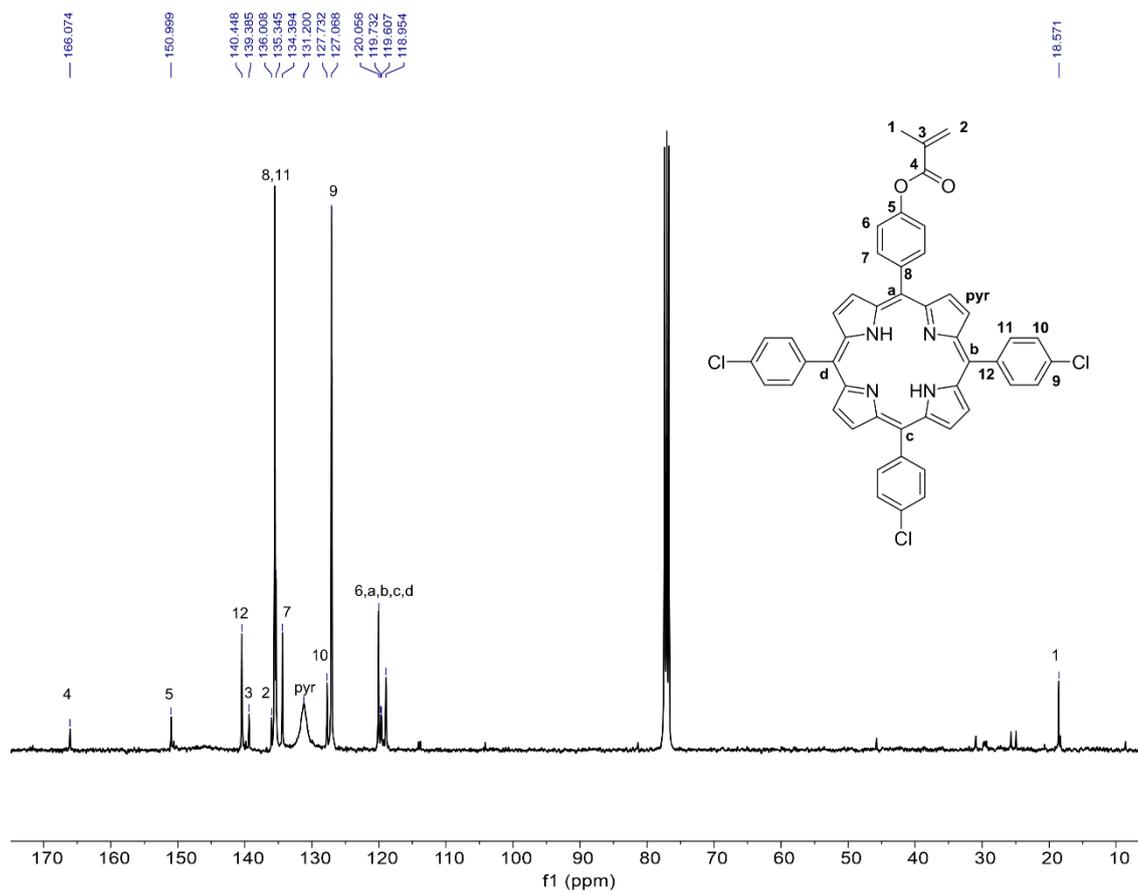
A solution of polymeric porphyrin (1.0 mmol porphyrin repeating unit) in 20 mL dry dichloromethane was degassed with a stream of nitrogen for 5 min in an ice bath. After 1.3 mmol  $\text{AlEt}_2\text{Cl}$  (2 M in hexane) was added slowly, the reaction solution was heated to room temperature and stirred for 3 h. The mixture was concentrated using a rotary evaporator to produce a residue that was purified by column chromatography (neutral alumina, dichloromethane/methanol v/v = 10:1) and poly-Al was obtained as a purple solid. Yield about 95%. After the metallization, the prepared catalyst would be heated to 70 °C in the vacuum oven for 48 h to obtain a dry catalyst. The disappearance of proton signals assigned to ring hydrogen indicated the complete coordination between Al(III) ion and porphyrin.



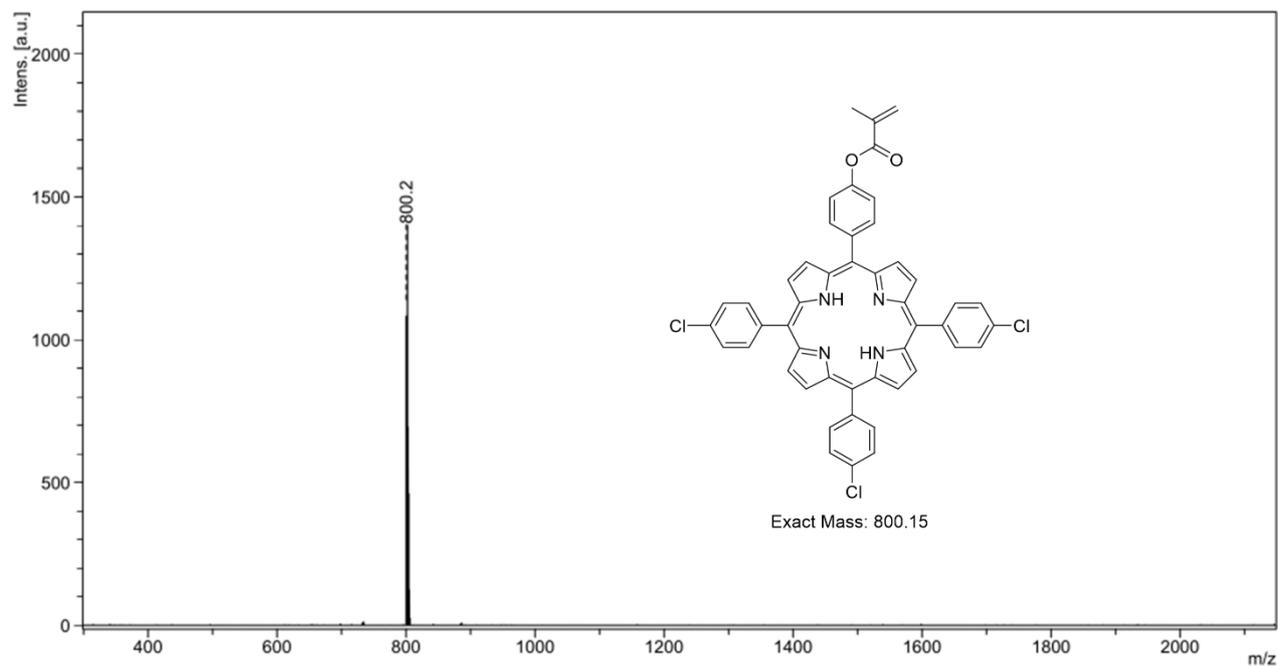
**Figure S2.** <sup>1</sup>H NMR spectrum of compound **a** (CDCl<sub>3</sub> at 25 °C, 300 MHz).



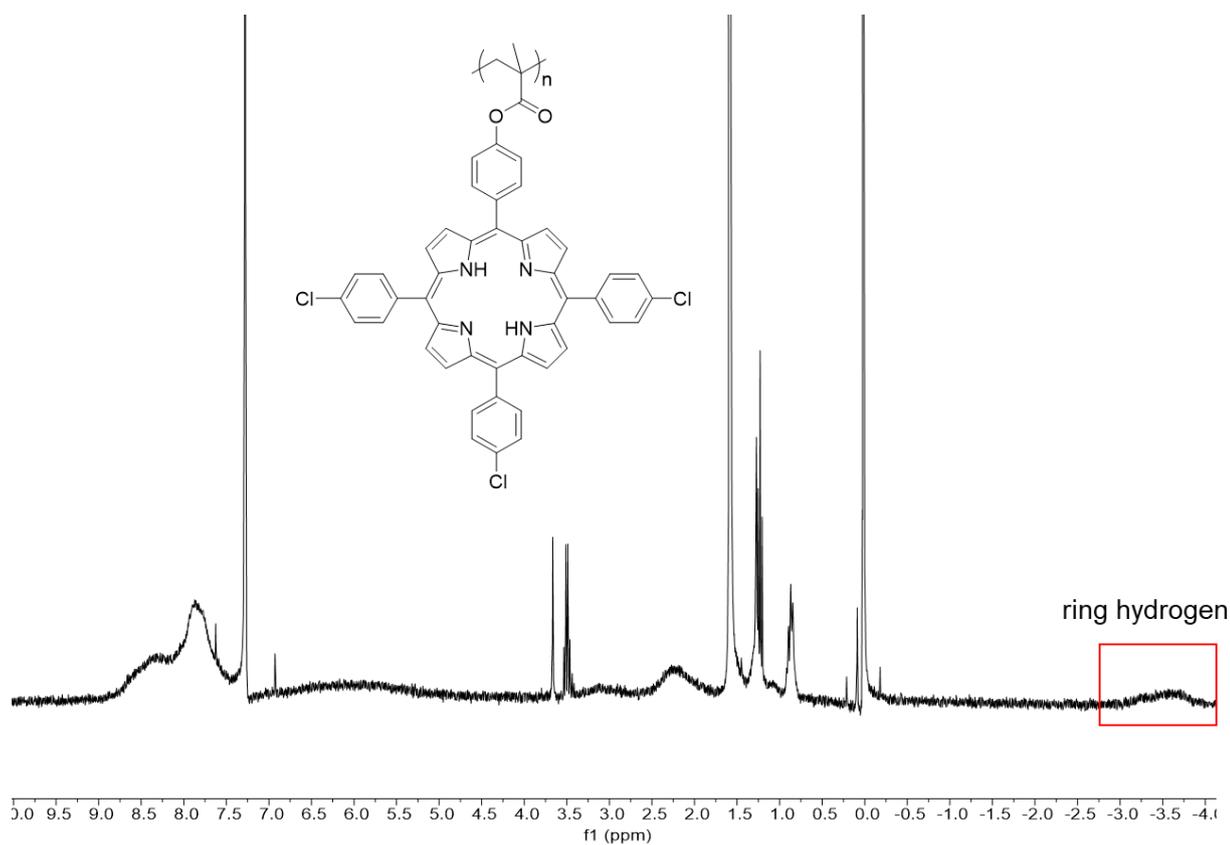
**Figure S3.** <sup>1</sup>H NMR spectrum of compound **1a** (CDCl<sub>3</sub> at 25 °C, 300 MHz).



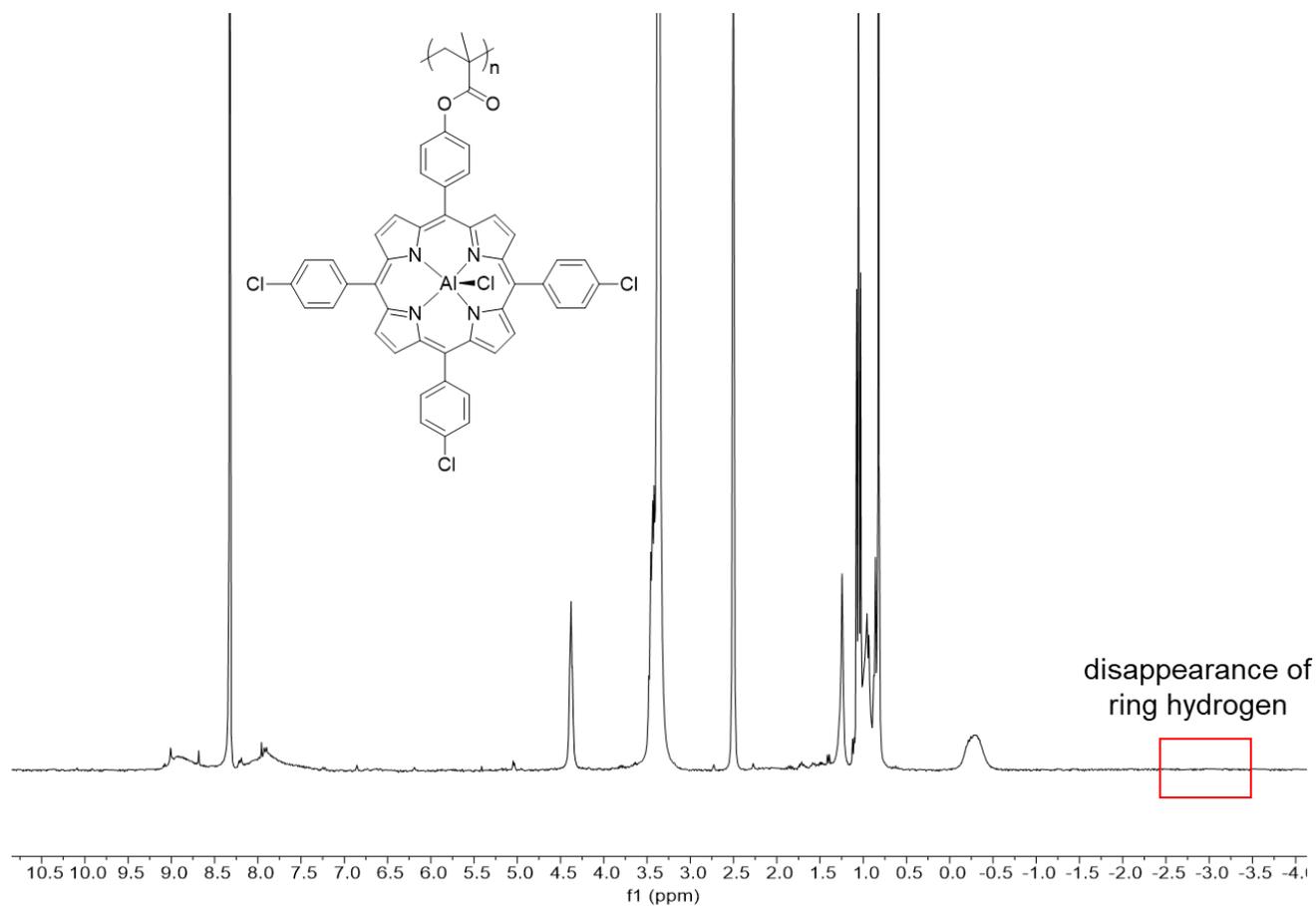
**Figure S4.**  $^{13}\text{C}$  NMR spectrum of compound **1a** ( $\text{CDCl}_3$  at 25 °C, 400 MHz).



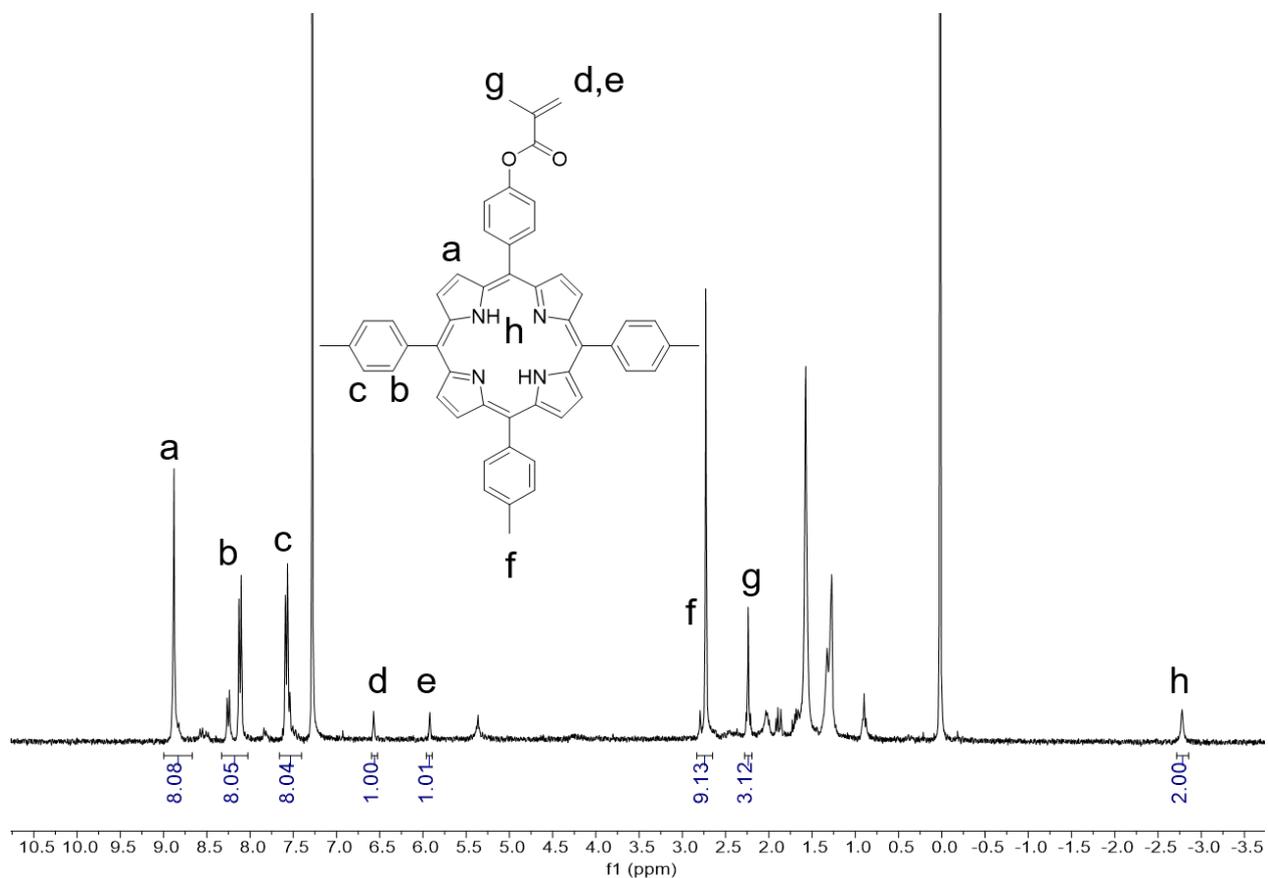
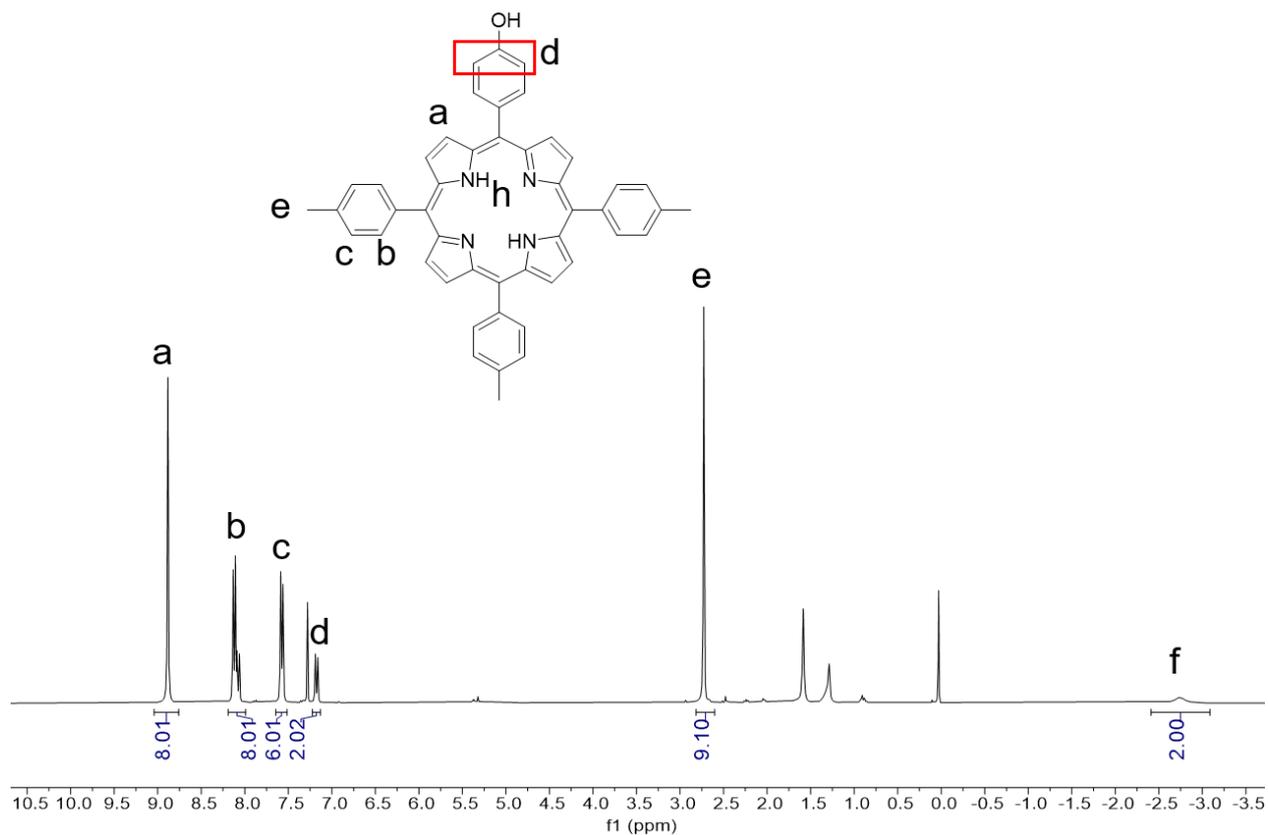
**Figure S5.** MALDI-TOF Mass spectrum of compound **1a**.

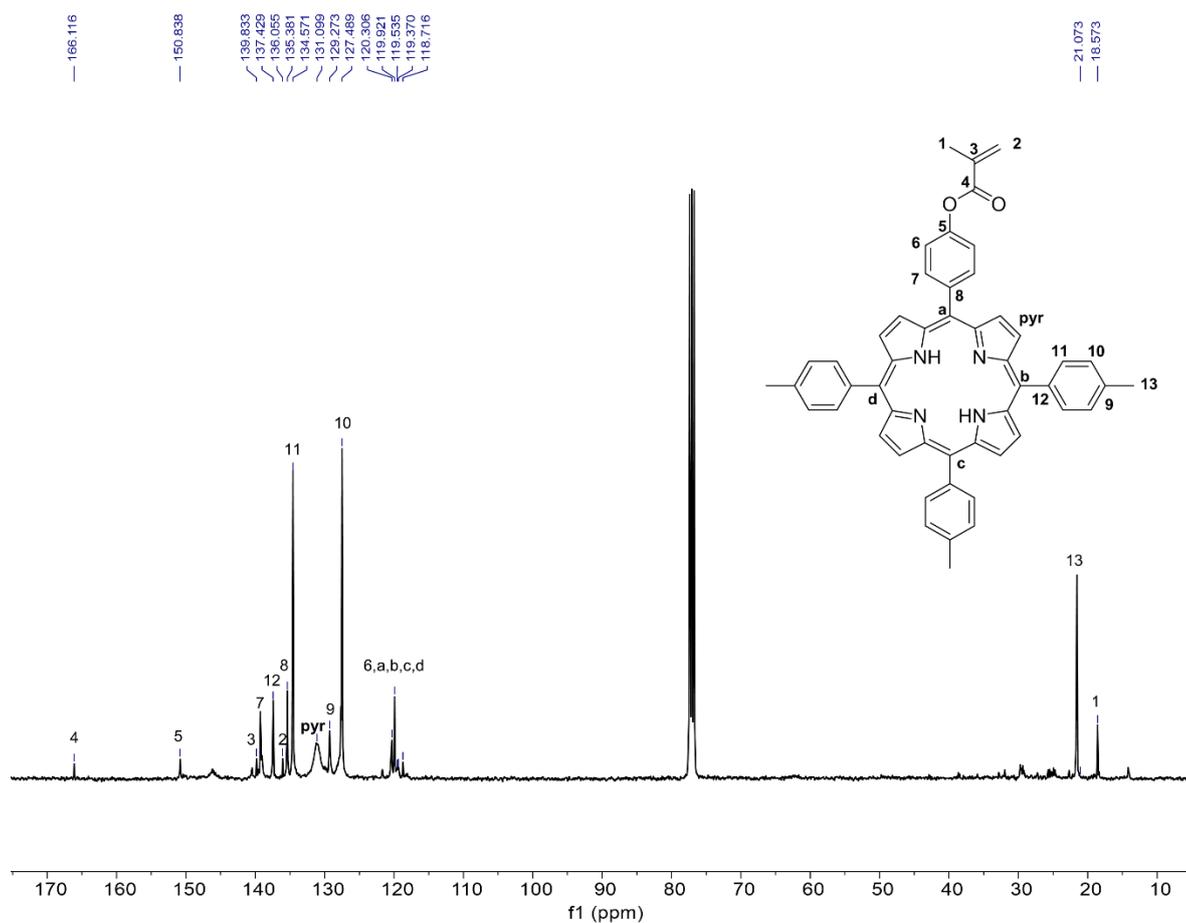


**Figure S6.**  $^1\text{H}$  NMR spectrum of compound **2a** ( $\text{CDCl}_3$  at 25  $^\circ\text{C}$ , 300 MHz).

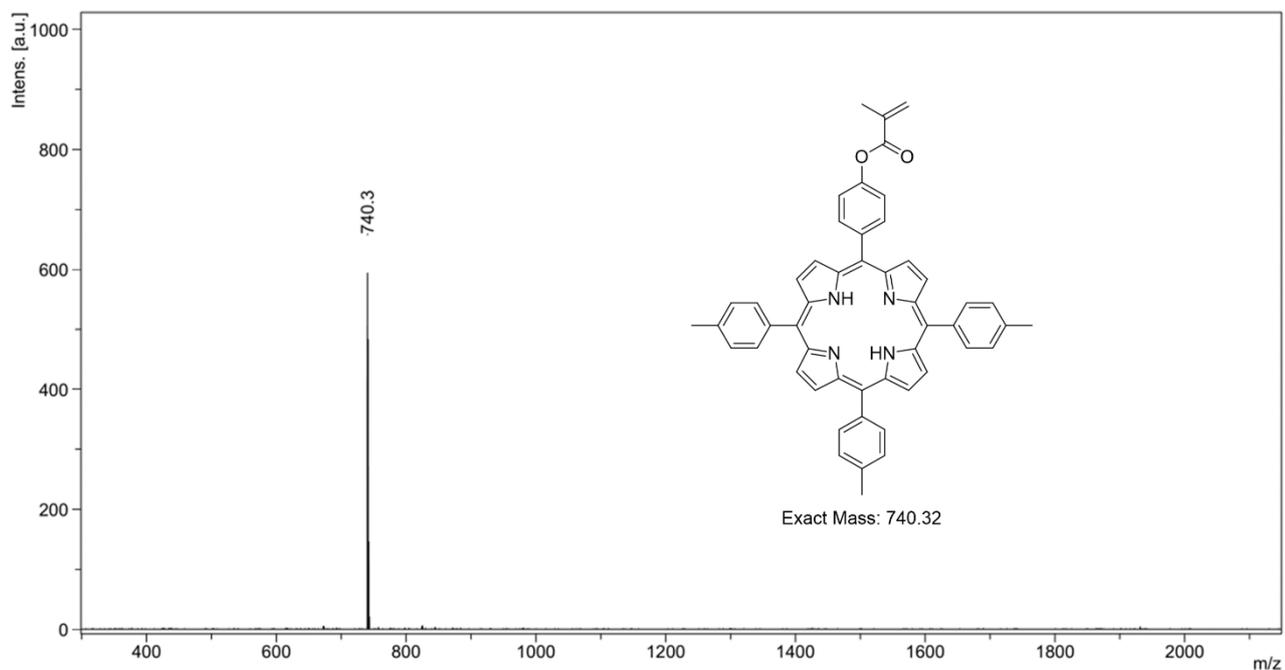


**Figure S7.**  $^1\text{H}$  NMR spectrum of complex **3a** ( $\text{DMSO-d}_6$  at 25  $^\circ\text{C}$ , 300 MHz).

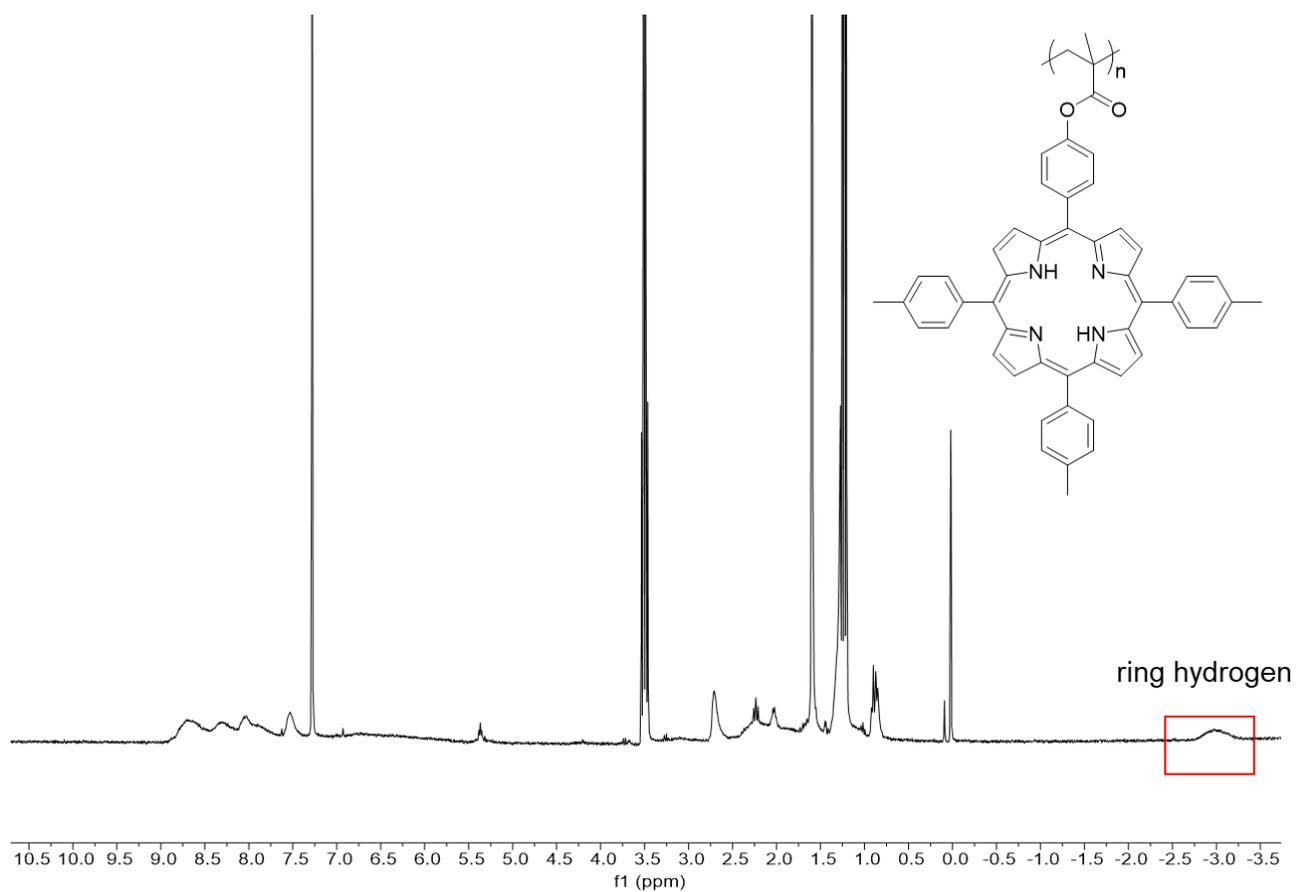




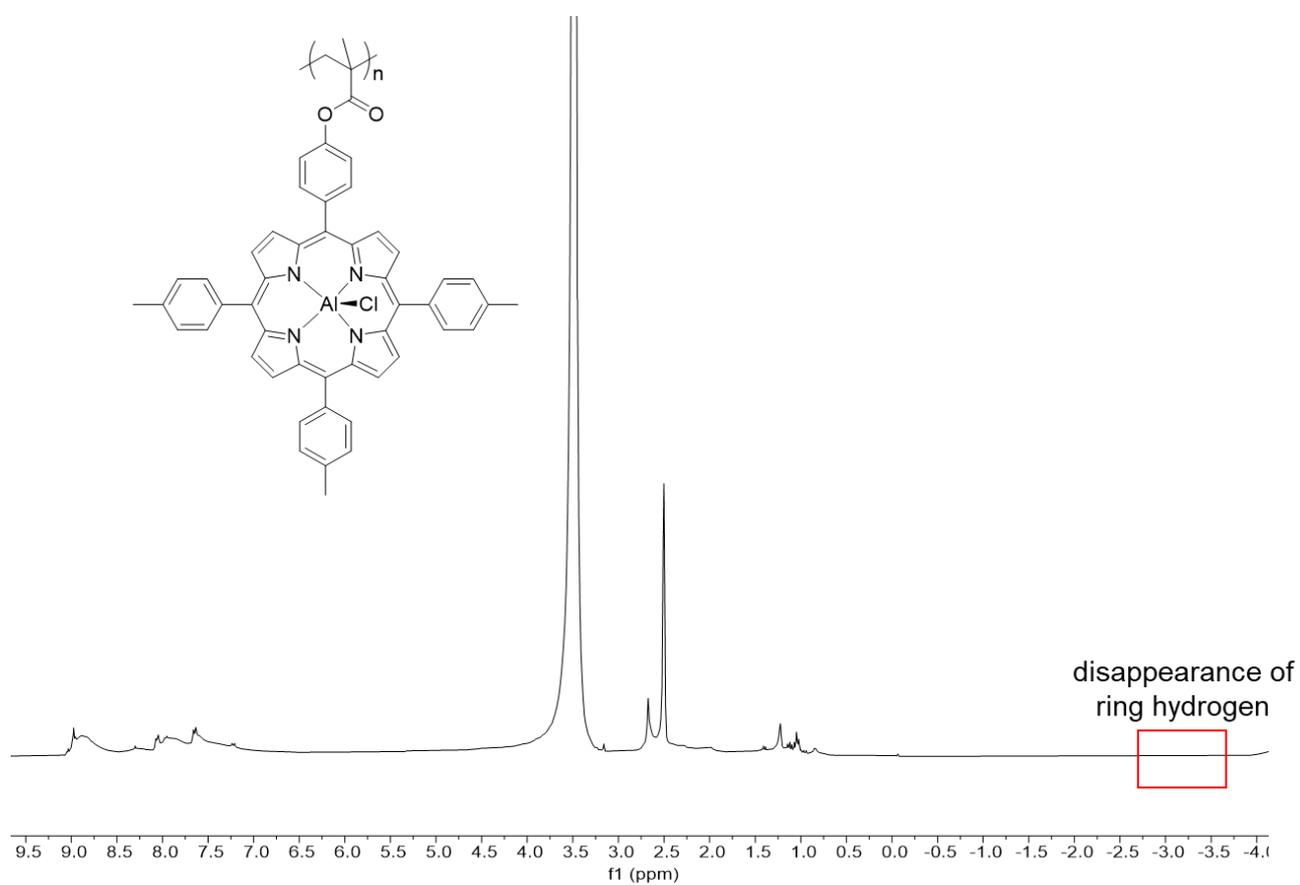
**Figure S10.**  $^{13}\text{C}$  NMR spectrum of compound **1b** ( $\text{CDCl}_3$  at 25 °C, 400 MHz).



**Figure S11.** MALDI-TOF Mass spectrum of compound **1b**.

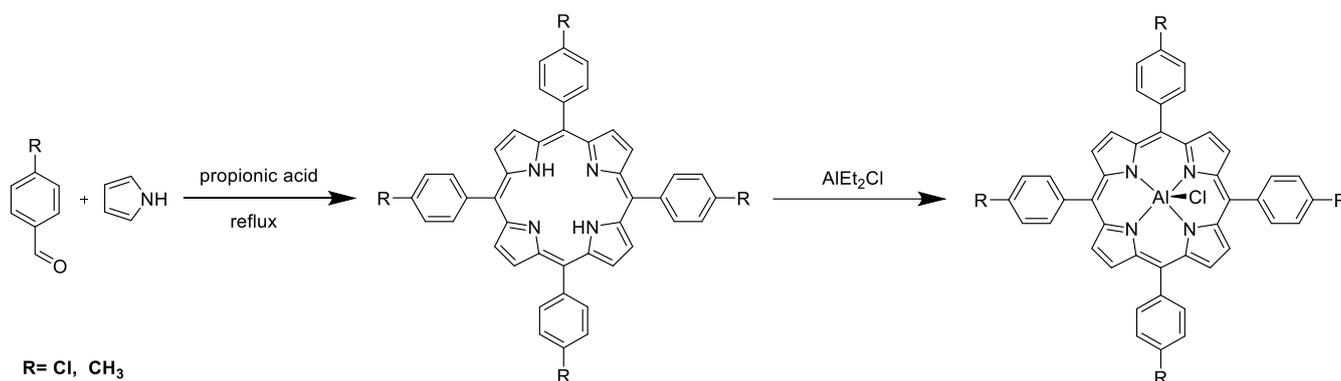


**Figure S12.**  $^1\text{H}$  NMR spectrum of compound **2b** ( $\text{CDCl}_3$  at  $25^\circ\text{C}$ , 300 MHz).



**Figure S13.**  $^1\text{H}$  NMR spectrum of compound **3b** ( $\text{DMSO-d}_6$  at  $25^\circ\text{C}$ , 300 MHz)

### 3.2 Synthesis of Mononuclear Aluminum Porphyrin Catalyst (MonoAl)



Scheme S2. Synthetic route of MonoAl series.

#### 3.2.1 General Procedure for Mononuclear Porphyrin Preparation

Porphyrin synthesis was performed according to an appropriate variation of a literature procedure. Under air, a three-neck 1000 mL round-bottom flask fitted with two pressure-equalizing dropping funnels was charged with propionic acid (500 mL). Equimolar equivalents of freshly distilled pyrrole and the appropriately substituted benzaldehyde were added via syringe into the two dropping funnels, respectively, and the main reaction vessel was heated to 160 °C. The contents of the dropping funnels were added to the refluxing acid dropwise for 0.25 h and the resulting mixture was allowed to reflux for a further 1 h. Upon cooling the mixture to room temperature for 24 h, the mixture was filtered affording a purple crystalline solid. This precipitate was washed sequentially with water (ca. 20 mL) and a minimum of cold methanol (ca. 10 mL) and allowed to dry under air. The solid was purified by column chromatography (neutral alumina, dichloromethane/petroleum ether, V/V = 1/1) to afford a bright purple crystalline solid and the yield was 20%-25%.

##### Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin

4-chlorobenzaldehyde, 0.2 mol; pyrrole, 0.2 mol; yield 23.1%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.84 (s, 8H), 8.22-8.02 (m, 8H), 7.83-7.64 (m, 8H), -2.85 (s, 2H).

##### Synthesis of 5,10,15,20-tetrakis(4-methylphenyl)porphyrin

4-methylbenzaldehyde, 0.2 mol; pyrrole, 0.2 mol; yield 25%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.87 (s, 8H), 8.12 (d, J = 7.9 Hz, 8H), 7.57 (d, J = 7.7 Hz, 8H), 2.73 (s, 12H), -2.78 (s, 2H).

#### 3.2.2 General Procedure for Mononuclear Aluminum Porphyrin Complex

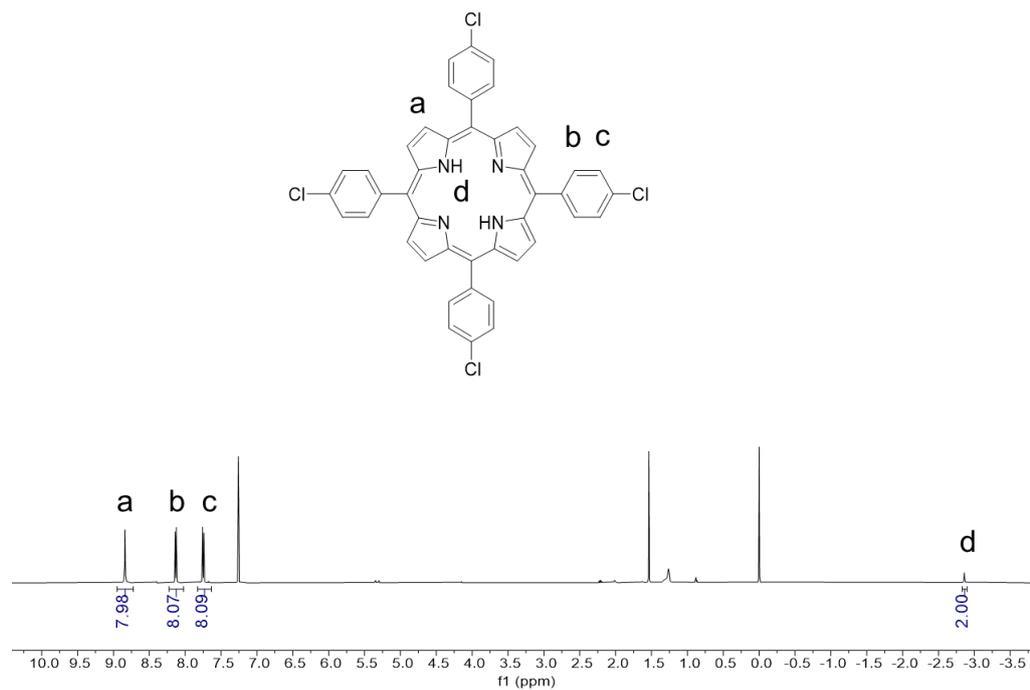
Aluminum porphyrin complex synthesis was performed according to an appropriate variation of a literature procedure<sup>1</sup>. A solution of porphyrin ligands (1.0 mmol) in 20 mL dry dichloromethane was degassed with a stream of argon for 5 min in an ice bath. After 1.1 mmol of diethylaluminum chloride (Et<sub>2</sub>AlCl) was added slowly, the reaction solution was heated to room temperature and stirred for 2 h. The mixture was concentrated using a rotary evaporator, and the concentrate was purified by column chromatography (neutral alumina, dichloromethane/ methanol, V/V = 10/1). Finally, the aluminum porphyrin complex was obtained as a purple solid.

##### Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin aluminum chloride

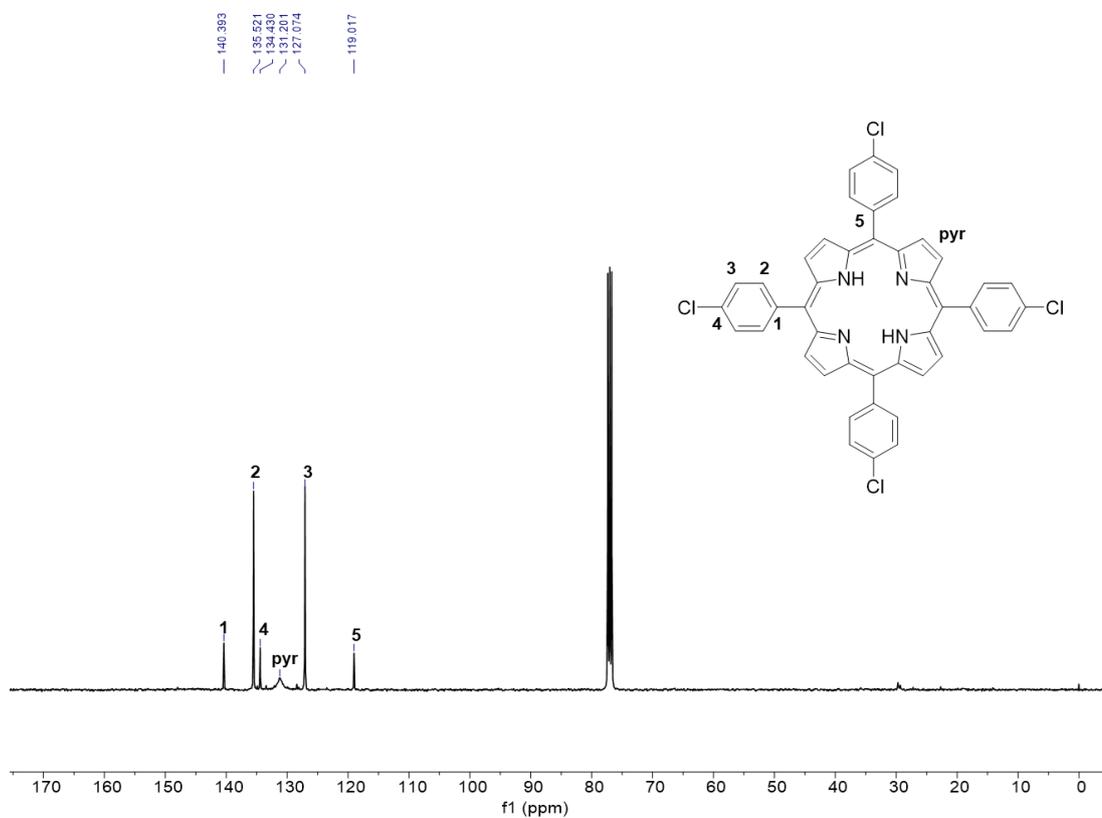
5,10,15,20-tetrakis(4-chlorophenyl)porphyrin, 1.0 mmol; yield 97%. <sup>1</sup>H NMR (300 MHz, DMSO) δ (ppm): 9.03 (s, 8H), 8.20 (d, 8H), 7.94 (d, 8H).

##### Synthesis of 5,10,15,20-tetrakis(4-methylphenyl)porphyrin aluminum chloride

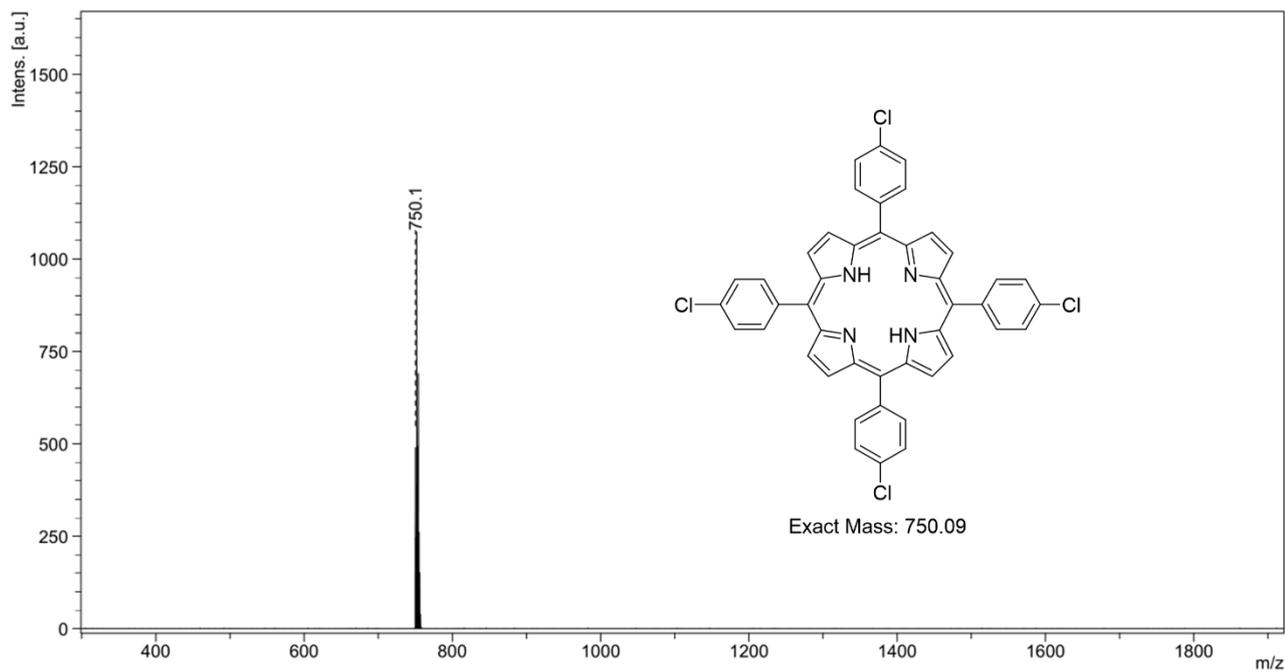
5,10,15,20-tetrakis(4-methylphenyl)porphyrin, 1.0 mmol; yield 98%. <sup>1</sup>H NMR (300 MHz, DMSO) δ (ppm): 8.86 (s, 8H), 8.13 (d, J = 7.9 Hz, 8H), 7.58 (d, J = 7.7 Hz, 8H), 2.75 (s, 12H).



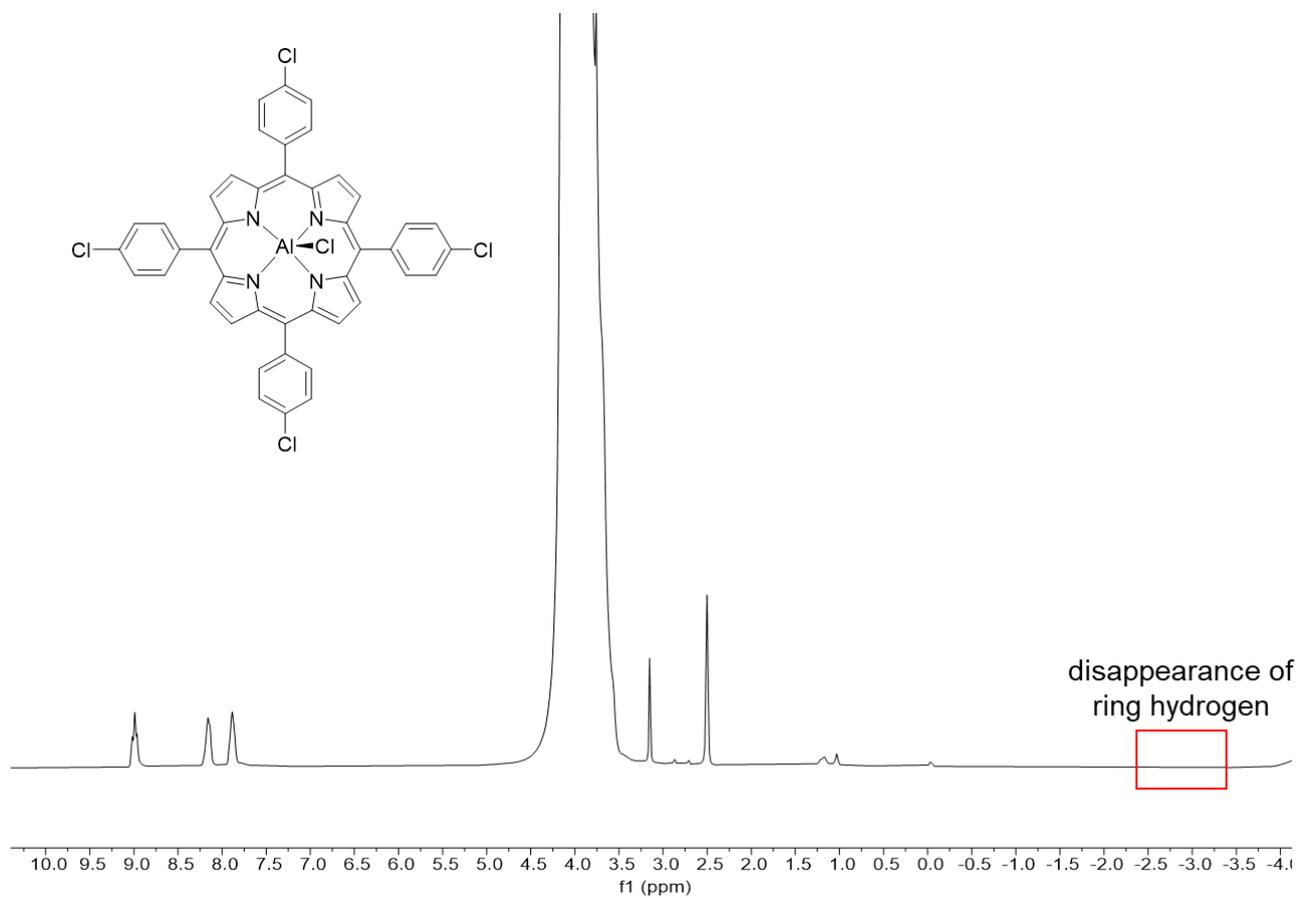
**Figure S14.** <sup>1</sup>H NMR spectrum of 5,10,15,20-tetra(4-chlorophenyl)porphyrin (CDCl<sub>3</sub> at 25 °C, 300 MHz)



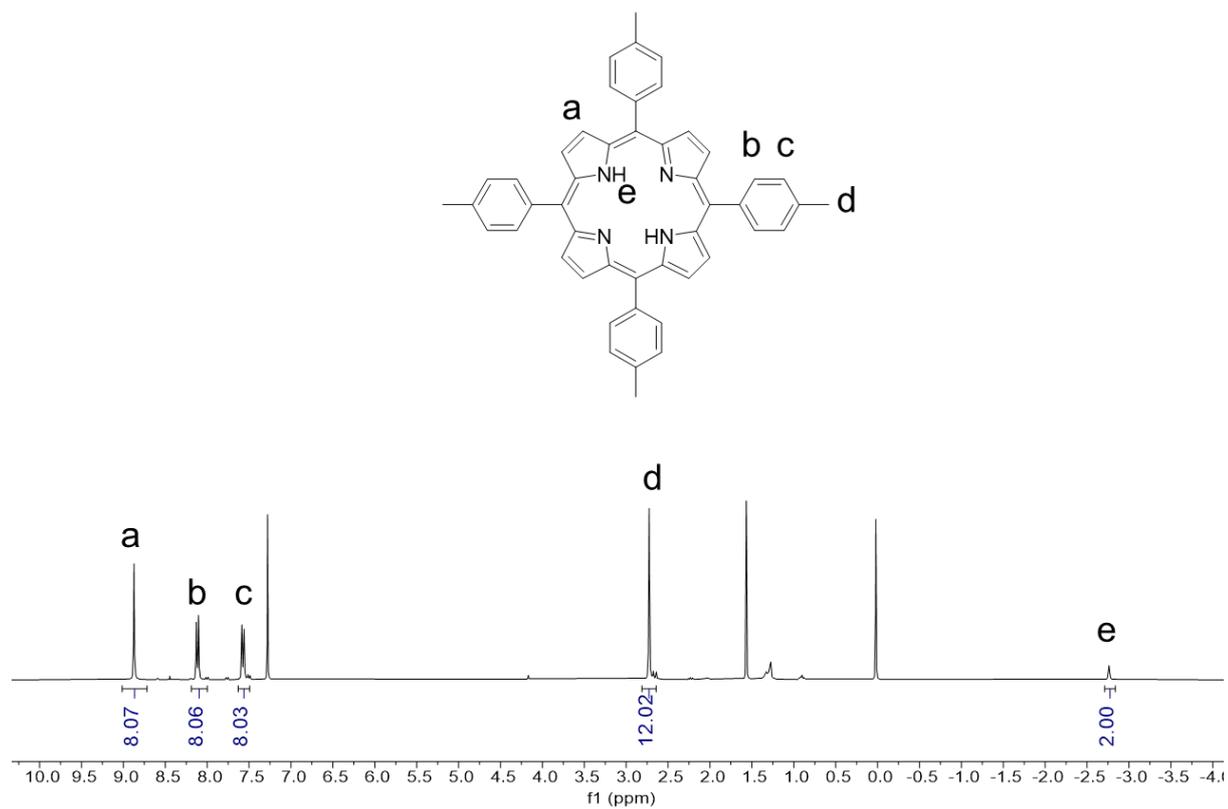
**Figure S15.** <sup>13</sup>C NMR spectrum of 5,10,15,20-tetra(4-chlorophenyl)porphyrin (CDCl<sub>3</sub> at 25 °C, 400 MHz).



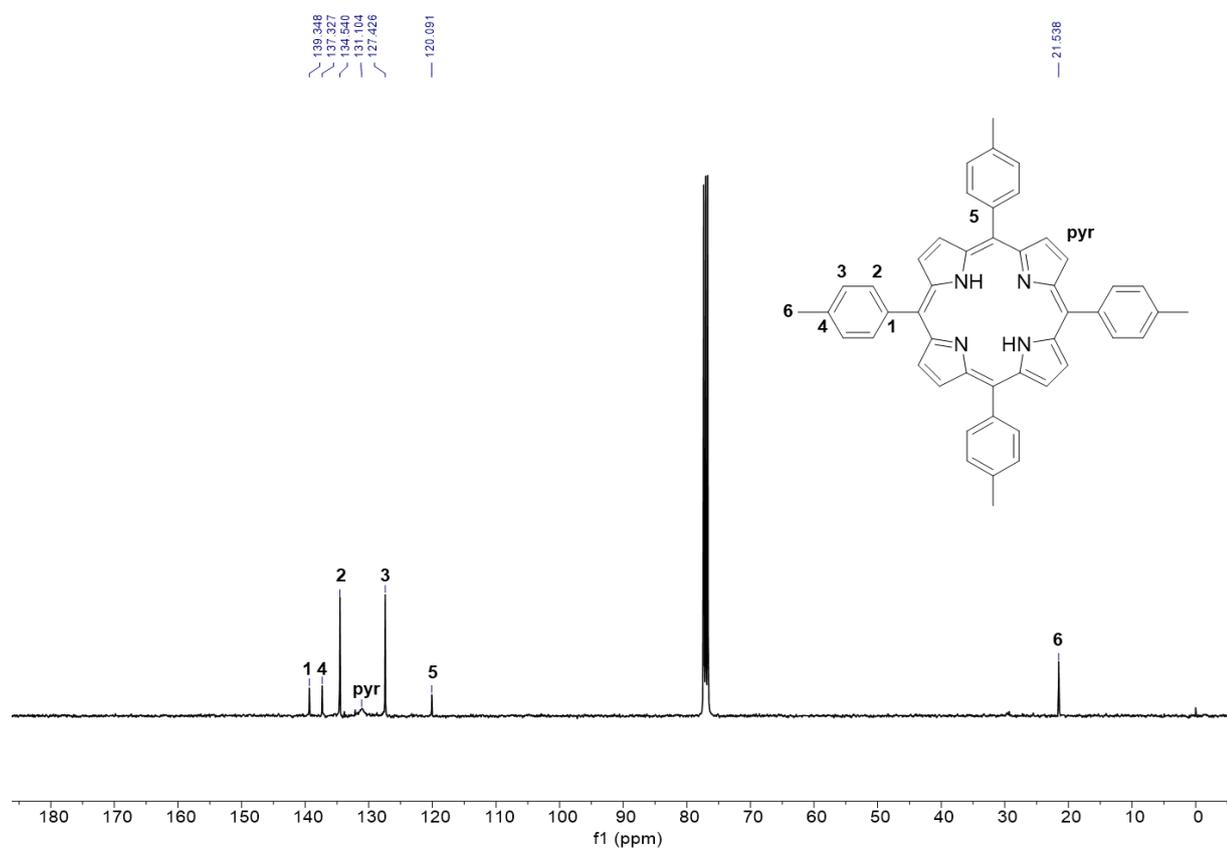
**Figure S16.** MALDI-TOF Mass spectrum of 5,10,15,20-tetra(4-chlorophenyl)porphyrin.



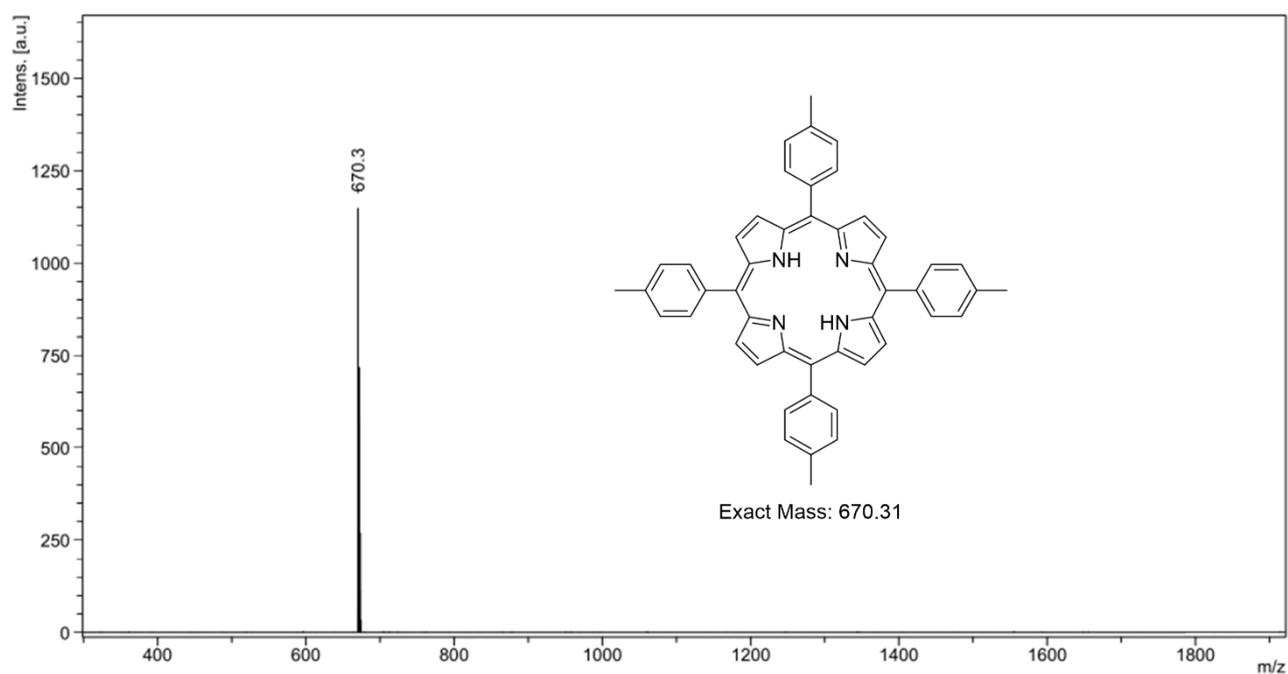
**Figure S17.**  $^1\text{H}$  NMR spectrum of MonoAl-Cl (DMSO- $d_6$  at 25 °C, 300 MHz).



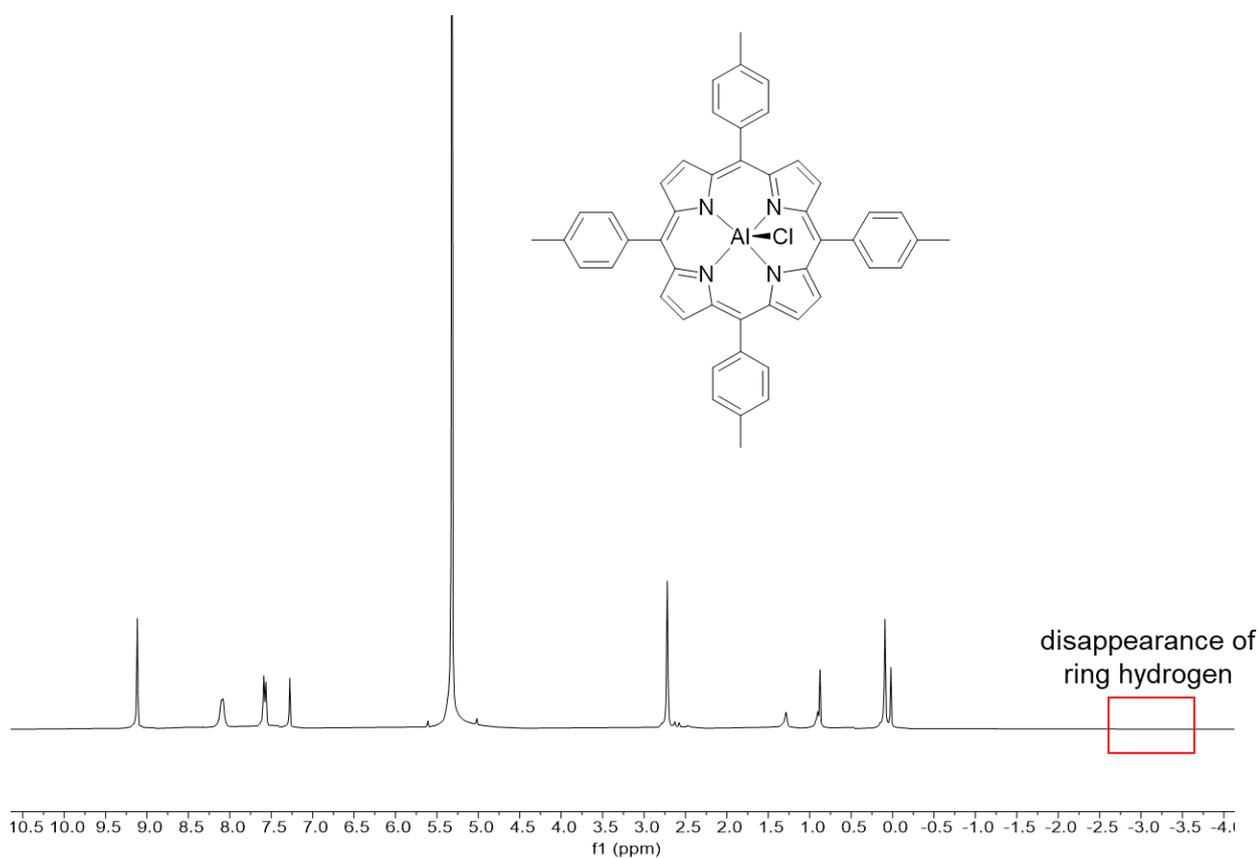
**Figure S18.** <sup>1</sup>H NMR spectrum of 5,10,15,20-tetra(4-methylphenyl)porphyrin (CDCl<sub>3</sub> at 25 °C, 300 MHz).



**Figure S19.** <sup>13</sup>C NMR spectrum of 5,10,15,20-tetra(4-methylphenyl)porphyrin (CDCl<sub>3</sub> at 25 °C, 400 MHz).



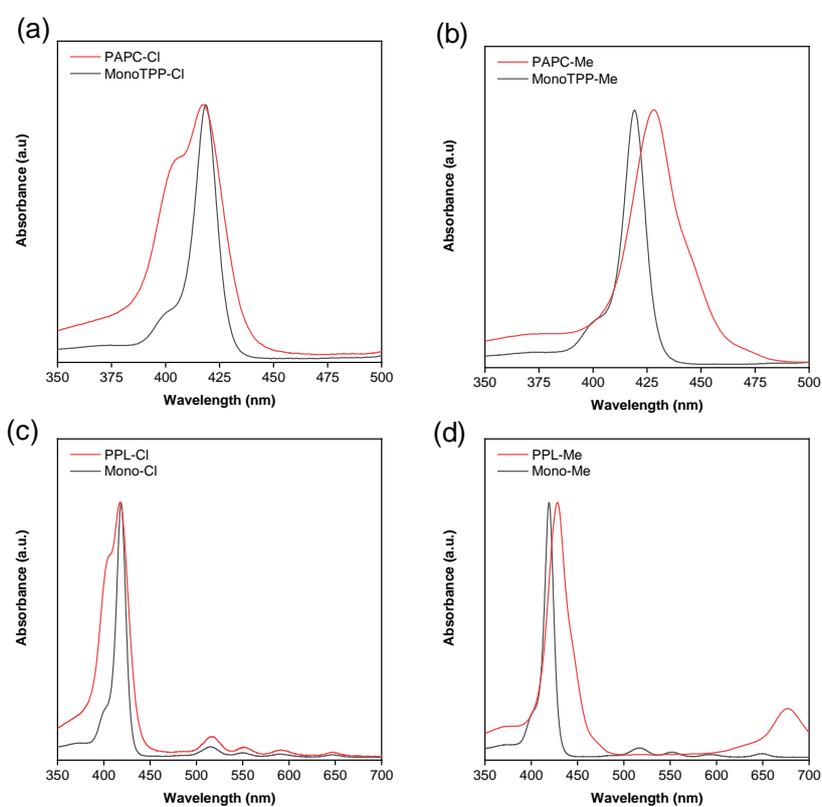
**Figure S20.** MALDI-TOF Mass spectrum of 5,10,15,20-tetra(4-methylphenyl)porphyrin.



**Figure S21.**  $^1\text{H}$  NMR spectrum of MonoAl-Me (DMSO- $d_6$  at 25 °C, 300 MHz).

	H-aggregates	J-aggregates
Geometric Arrangement	face-to-face 	edge-to-edge 
UV/Vis absorption spectra	The Soret Band will be blue-shifted, expanded or split	The Soret band will be red-shifted and narrowed, while the Q band will be red-shifted and the signal will be enhanced

**Figure S22.** The structure and UV/vis character of different aggregation types. Reproduced with permission from ref<sup>3</sup>.



**Figure S23.** The UV-vis spectra of monomeric porphyrins and polymeric porphyrins in  $\text{CHCl}_3$ .

## 4. Copolymerization Studies

### 4.1 Representative Procedure for the Copolymerization Reaction of PA and Epoxides

In a glove box, the required catalyst, co-catalyst, epoxides, and PA were charged into a pre-dried pressure-resistant reaction flask equipped with a magnetic stir bar. The reaction flasks were then taken out of the glove box at the required temperature for the required time. The polymerization was terminated by cooling the reaction flasks. Then, a small aliquot of the copolymerization mixture was taken out for  $^1\text{H}$  NMR spectroscopy. The remained crude mixture was dissolved in  $\text{CH}_2\text{Cl}_2$ , then precipitated in methanol three times to remove residual monomers and yield polymers, which could be used for further characterization.

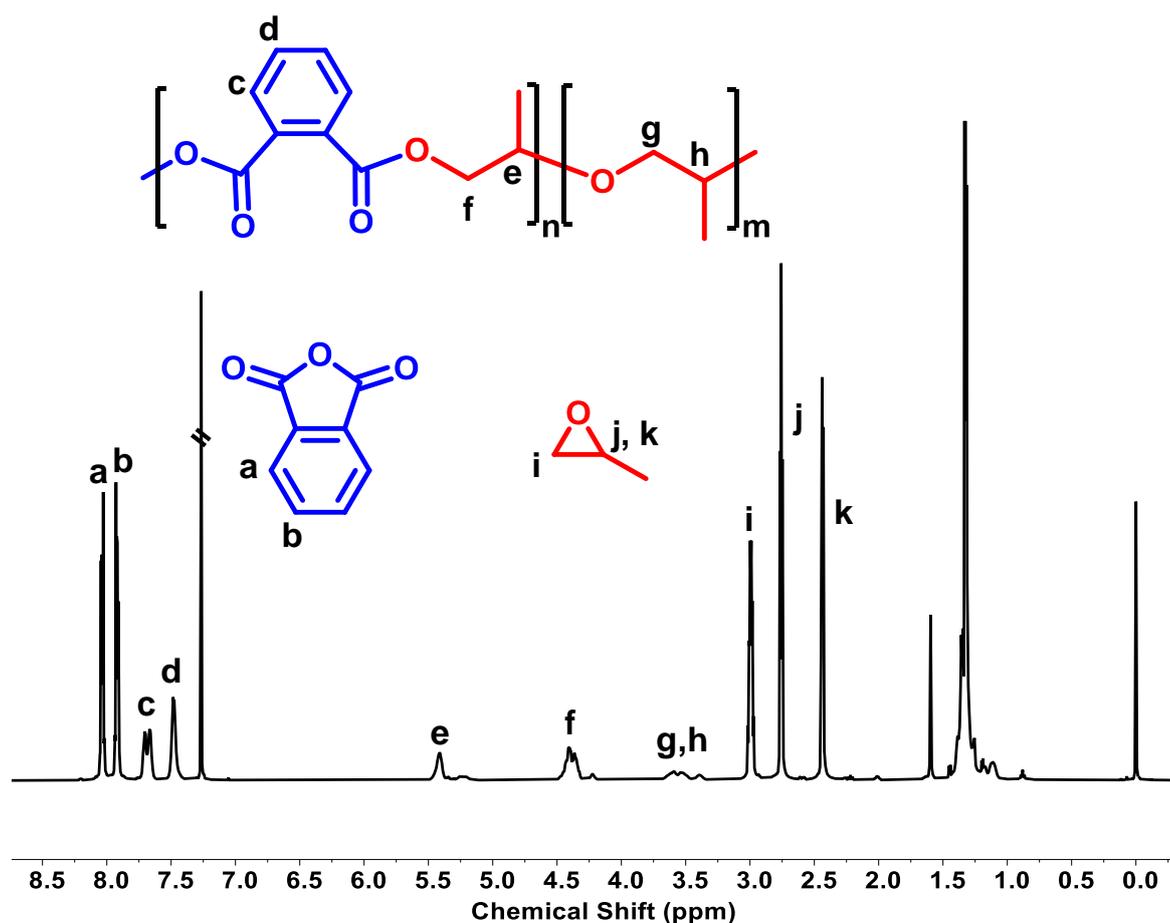
### 4.2 Studies of PA and Epoxide Copolymerization

**Table S1. Copolymerization of PA and Epoxides**

Entry <sup>a</sup>	Catalyst	Epoxide	[PA]/[Al]/PPNCl <sup>b</sup>	T (°C)	t (min)	Conv. of PA (%) <sup>c</sup>	Poly ester (%) <sup>c</sup>	TOF (h <sup>-1</sup> ) <sup>d</sup>	$M_{n, \text{theo.}}$ (kg/mol) <sup>e</sup>	$M_n$ (kg/mol) <sup>f</sup>	$\mathcal{D}$ <sup>f</sup>
1	MonoAl-Me	PO	2000/1/1	125	120	41	99	410	168.9	7.5	1.2
2	PAPC-Cl	BO	2000/1/1	125	5	22	98	5300	96.8	31.2	1.3
3	PAPC-Cl	BO	2000/1/1	125	10	45	99	5400	198.0	45.5	1.2
4	PAPC-Cl	BO	2000/1/1	125	15	65	98	5200	286.0	59.6	1.5
5	PAPC-Cl	BO	2000/1/1	125	20	83	98	5000	365.2	65.2	1.5
6	PAPC-Cl	BO	30000/1/1	125	360	45	98	2300	2970.0	75.6	1.2
7	PAPC-Cl	BO	30000/1/1	125	600	56	98	1700	3696.0	98.3	1.3
8	PAPC-Cl	PO	30000/1/1	125	600	70	81	2100	4326.0	135.1	1.5

<sup>a</sup>. The bulk copolymerizations were carried out with the ratio of [Epoxide]/[PA] = 5:1. For entries 1-5, 5 mL of epoxide was used; For entries 6-8, 20 mL of epoxide was used. <sup>b</sup>. [PA]/[Al]/[PPNCl] means the feed molar ratio of PA, aluminum porphyrin units, and PPNCl. <sup>c</sup>. Conv. of PA (%) is the conversion of the PA, and polyester (%) is the percentage of ester linkage in the polymer, which were both determined by  $^1\text{H}$  NMR spectroscopy. <sup>d</sup>. TOF = turnover frequency. <sup>e</sup>.  $M_{n, \text{theo.}} = (M_{\text{PO}}$  or  $M_{\text{BO}} + M_{\text{PA}}) \times ([\text{PA}]/[\text{Al}]) \times \text{Conv.}$  <sup>f</sup>. The molecular weight and polymer dispersity index ( $\mathcal{D}$ ) of polymers were determined by gel permeation chromatography in  $\text{CH}_2\text{Cl}_2$  at 35 °C, calibrated with polystyrene as standards.

### 4.3 Characterization of Polymers of PA/Epoxy Copolymerization.



The calculation of **polyester content (%)** is based on the chemical shift of -CH- and -CH<sub>2</sub>-  
 Polyester: δ = 5.5-5.0, 4.5-4.1 ppm  
 Polyether (PPO): δ = 3.7-3.0 ppm

The calculation of **conversion of PA (%)** is based on the chemical shift of -CH- on the benzene ring  
 Mono PA: δ = 8.1-7.9 ppm  
 Converted PA: δ = 7.8-7.4 ppm

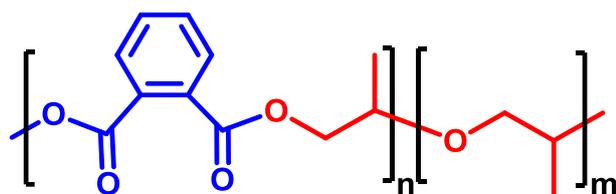
$$\text{Polyester \%} = \frac{\text{Polyester}}{\text{Polyester} + \text{Polyether}} = \frac{A_{5.5-5.0} + A_{4.5-4.1}}{A_{5.5-5.0} + A_{4.5-4.1} + A_{3.7-3.0}}$$

$$\text{Conv of PA} = \frac{\text{Converted PA}}{\text{Converted PA} + \text{Mono PA}} = \frac{A_{7.8-7.4}}{A_{8.1-7.9} + A_{7.8-7.4}}$$

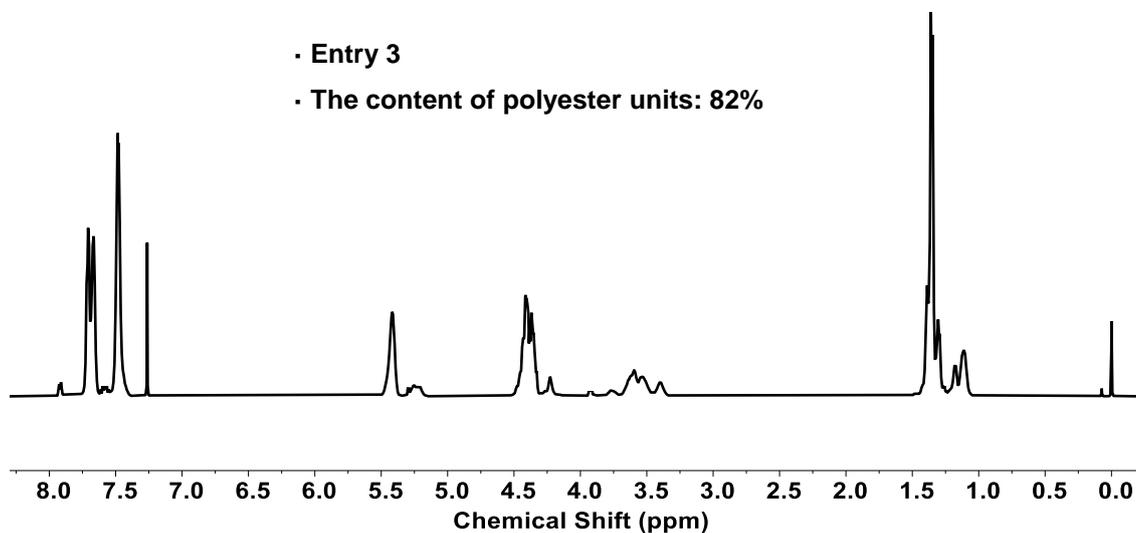
$$\text{TON} = \text{Conv. of PA} * (\text{PA}/[\text{Al}])$$

$$\text{TOF} = \text{TON}/\text{Time}(\text{h})$$

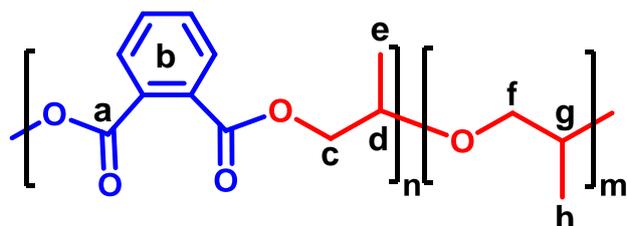
**Figure S24.** A typical <sup>1</sup>H NMR characterization and the calculation methods of all parameters for PA/PO copolymerization (CDCl<sub>3</sub> at 25 °C, 400 MHz).



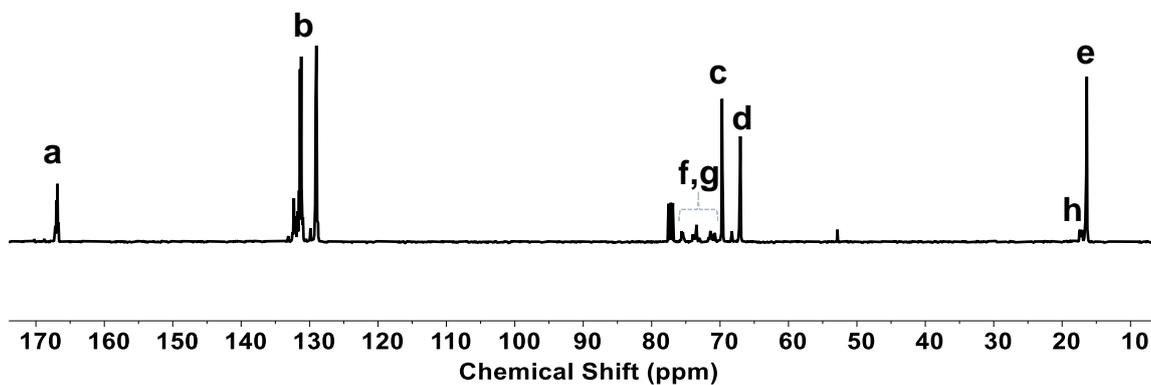
- Entry 3
- The content of polyester units: 82%



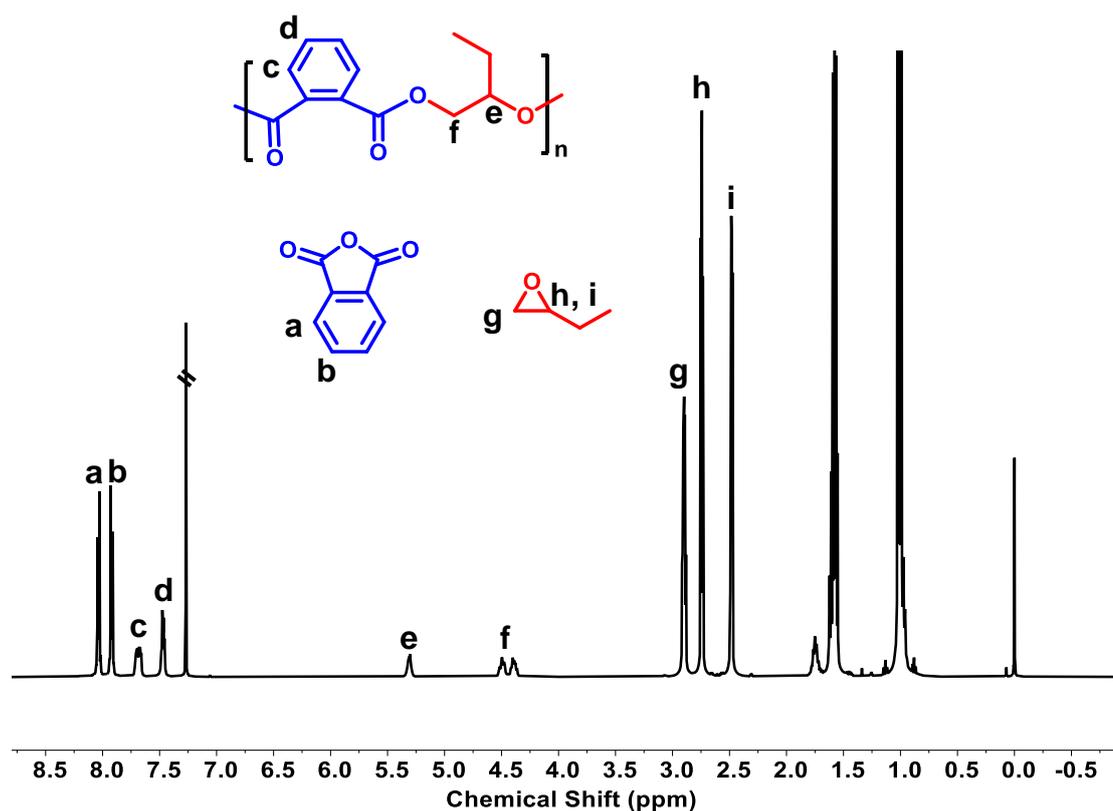
**Figure S25.**  $^1\text{H}$  NMR spectra of purified polymers of Entry 3 for PA/PO copolymerization ( $\text{CDCl}_3$  at  $25^\circ\text{C}$ , 400 MHz).



- Entry 3
- The content of polyester units: 82%



**Figure S26.**  $^{13}\text{C}$  NMR spectra of purified polymers of Entry 3 for PA/PO copolymerization ( $\text{CDCl}_3$  at  $25^\circ\text{C}$ , 400 MHz).



The calculation of **polyester content (%)** is based on the chemical shift of -CH- and -CH<sub>2</sub>-  
 Polyester:  $\delta = 5.4-5.2, 4.6-4.2$  ppm  
 Polyether (PBO):  $\delta = 3.8-3.4$  ppm

The calculation of **conversion of PA (%)** is based on the chemical shift of -CH- on the benzene ring  
 Mono PA:  $\delta = 8.1-7.9$  ppm  
 Converted PA:  $\delta = 7.8-7.4$  ppm

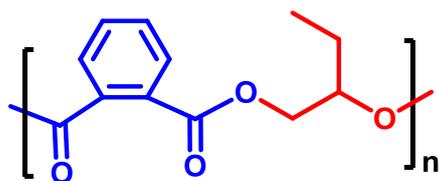
$$\text{Polyester \%} = \frac{\text{Polyester}}{\text{Polyester} + \text{Polyether}} = \frac{A_{5.4-5.2} + A_{4.6-4.2}}{A_{5.4-5.2} + A_{4.6-4.2} + A_{3.8-3.4}}$$

$$\text{Conv of PA} = \frac{\text{Converted PA}}{\text{Converted PA} + \text{Mono PA}} = \frac{A_{7.8-7.4}}{A_{8.1-7.9} + A_{7.8-7.4}}$$

$$\text{TON} = \text{Conv. of PA} * (\text{PA}/[\text{Al}])$$

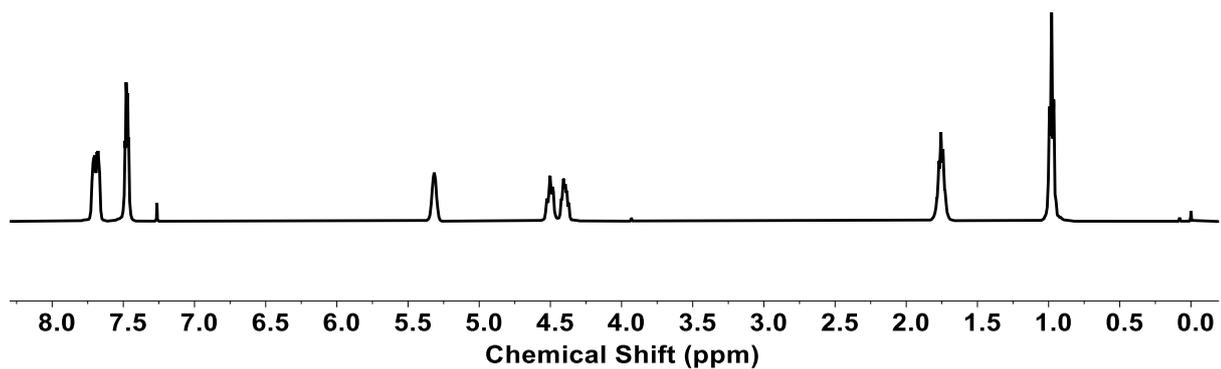
$$\text{TOF} = \text{TON}/\text{Time}(\text{h})$$

**Figure S27.** A typical <sup>1</sup>H NMR characterization and the calculation methods of all parameters for PA/BO copolymerization (CDCl<sub>3</sub> at 25 °C, 400 MHz).

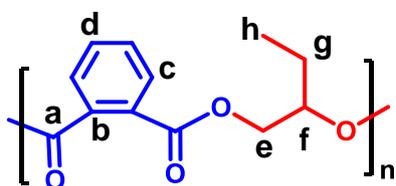


· Entry 6

· The content of polyester units: 99%

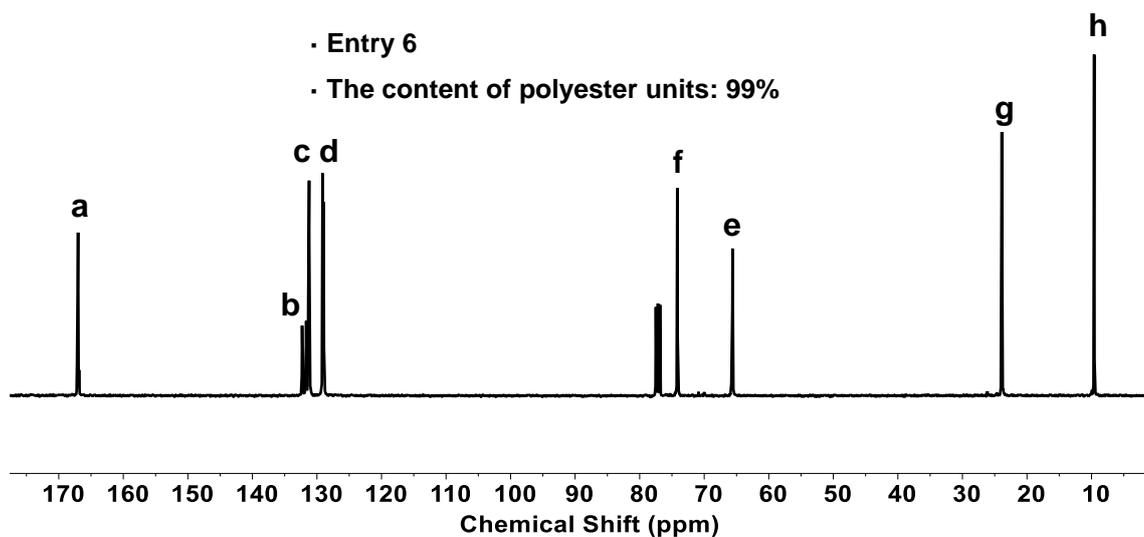


**Figure S28.**  $^1\text{H}$  NMR spectra of purified polymers of Entry 6 for PA/BO copolymerization ( $\text{CDCl}_3$  at 25 °C, 400 MHz).

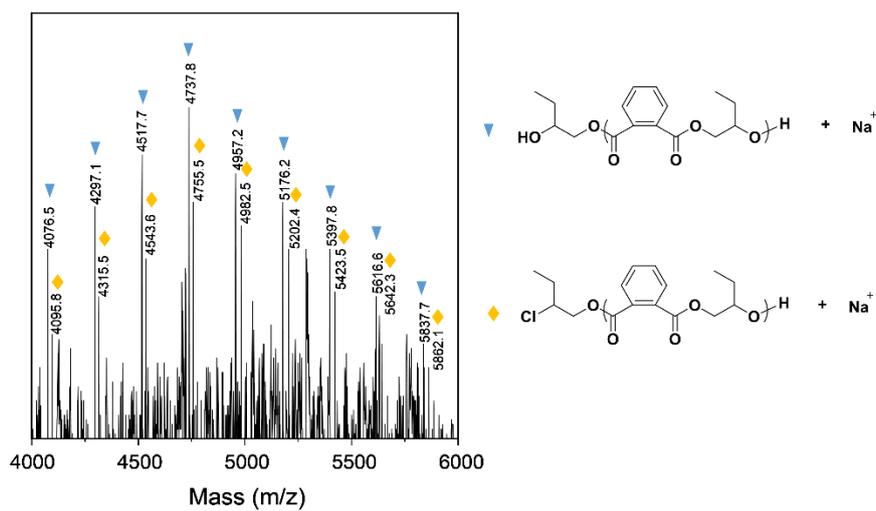


· Entry 6

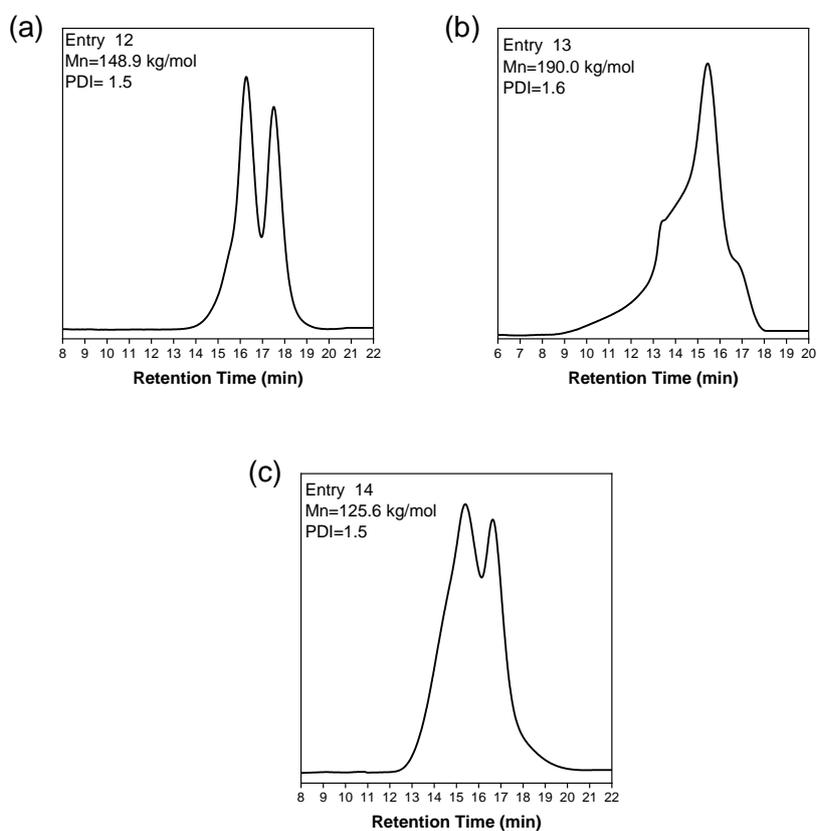
· The content of polyester units: 99%



**Figure S29.**  $^{13}\text{C}$  NMR spectra of purified polymers of Entry 6 for PA/BO copolymerization ( $\text{CDCl}_3$  at 25 °C, 400 MHz).

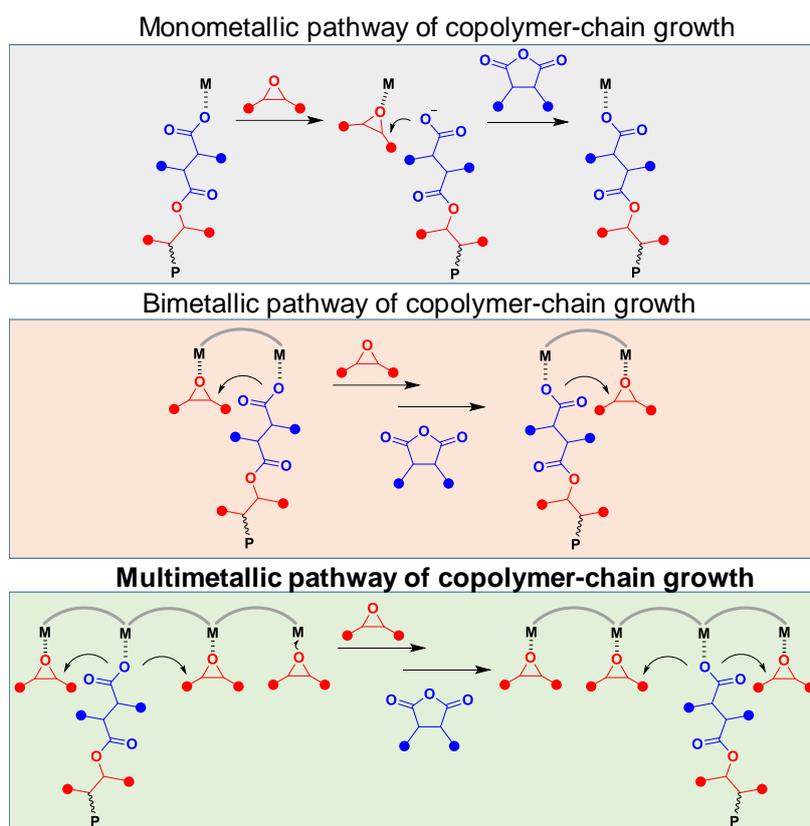


**Figure S30.** The MALDI-TOF spectrum results of poly(BO-alt-PA) from Table 1, Entry 5.



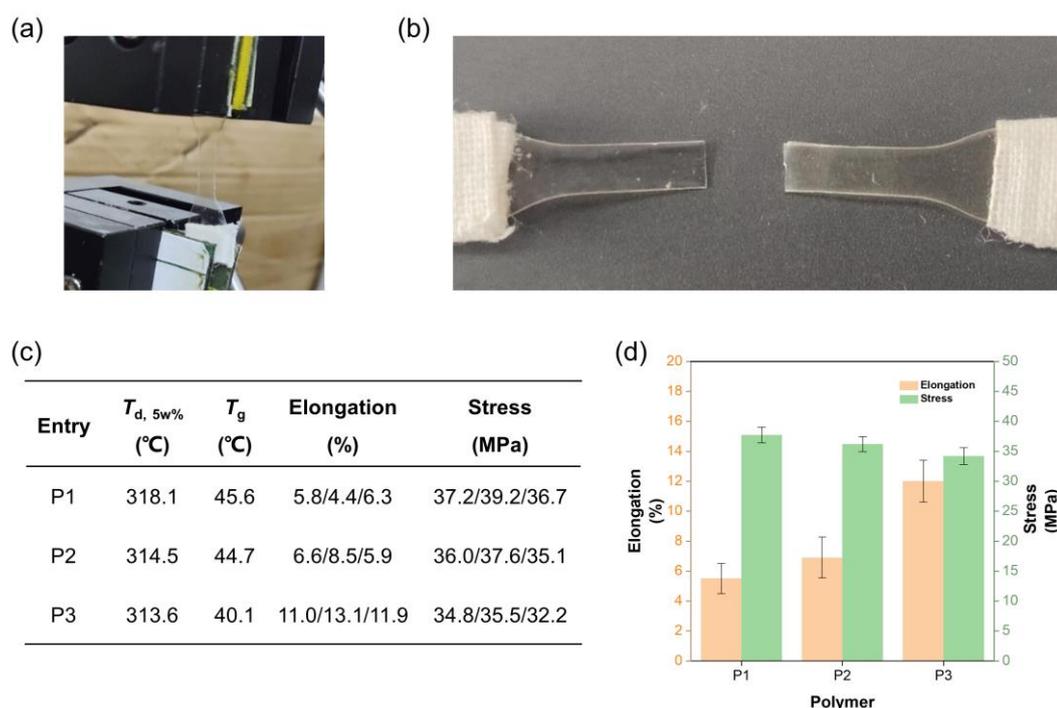
**Figure S31.** The GPC results of polymers in Entries 12-14, Table 1.

## 4.4 Polymerization Mechanisms



**Figure S32.** Monometallic, bimetallic, and multimetallic pathways copolymer-chain growth.

## 4.5 Material Properties



**Figure S33.** (a) and (b) The tensile testing of P3, from Entry 14, Table 1. (c) Material properties for P1-P3. The tensile data of each sample was tested three times and listed in the table. (d) Tensile data for P1-P3 specimens was reported as mean and standard deviation.

## 5. References

- (1) Lindsey, J. S.; Woodford, J. N. A Simple Method for Preparing Magnesium Porphyrins. *Inorg. Chem.* **1995**, *34* (5), 1063-1069.
- (2) Cao, H.; Qin, Y. S.; Zhuo, C. W.; Wang, X. H.; Wang, F. S. Homogeneous Metallic Oligomer Catalyst with Multisite Intramolecular Cooperativity for the Synthesis of CO<sub>2</sub>-Based Polymers. *ACS Catal.* **2019**, *9* (9), 8669-8676.
- (3) Ribó, J. M.; Crusats, J.; Farrera, J. A.; Valero, M. L. Aggregation in Water Solutions of Tetrasodium Diprotonated Meso-tetrakis(4-sulfonatophenyl)porphyrin. *J. Chem. Soc., Chem. Commun.* **1994**, (6), 681-682.