

## Supporting information

### **Zinc and linkage effects of novel porphyrin-containing polyimides on resistor memory behaviors**

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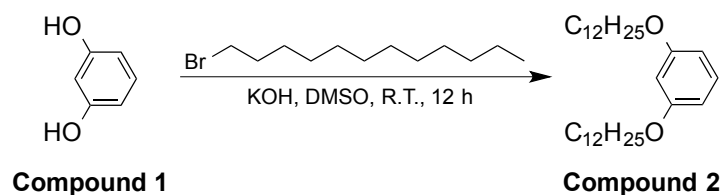
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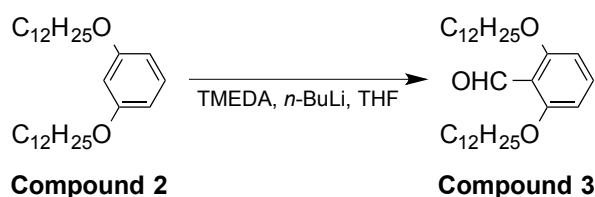
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## Synthetic procedure and characterization of compound 2-6

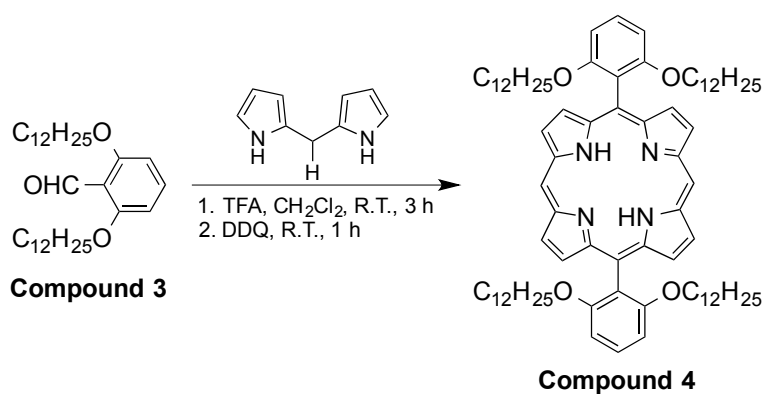


**Compound 2:** Compound 2 was synthesized according to literature condition.<sup>19a</sup> A mixture of resorcinol (compound 1, 10.0 g, 90 mmol), 1-bromododecane (86.4 mL, 360 mmol) and KOH (30.5 g, 545.4 mmol) was stirred for 12 h in analytical grade dimethyl sulfoxide (DMSO; 160 mL) at room temperature. Then, the reaction mixture was diluted with cold water (1000 mL) and extracted by hexanes (300 mL\*3). Organic layer was dried over anhydrous MgSO<sub>4</sub> and removal of solvent under reduced pressure obtained the crude pale yellowish oil. This crude product was purified by silica gel chromatography (short plug) with hexanes as eluent and removal of eluted solvent under reduced pressure followed by recrystallization obtained the titled compound 2 (33.5 g, 83 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.15 (t, J = 4 Hz, 1H), 6.47 (m, 3H), 3.93 (t, J = 6.5 Hz, 4H), 1.79 (m, 4H), 1.46 (m, 4H), 1.25-1.38 (br, 32H), 0.91 (t, J = 6.5 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.37, 129.76, 106.60, 101.36, 67.98, 31.96, 29.70, 29.68, 29.64, 29.62, 29.44, 29.39, 29.30, 26.08, 22.73, 14.17.



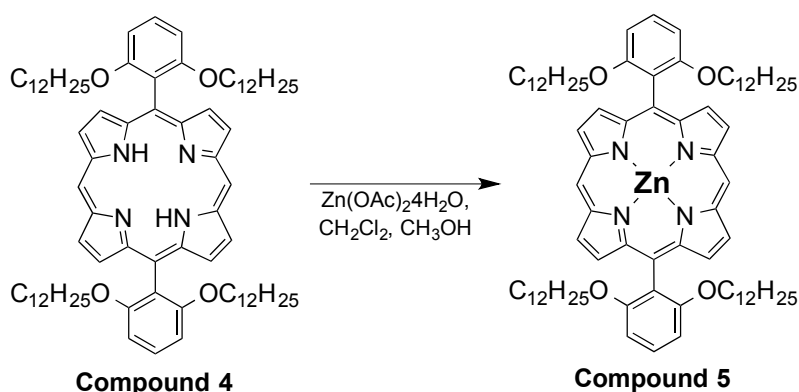
**Compound 3:** Compound 3 was synthesized according to modified literature conditions.<sup>19a</sup> Oven dried three neck 500 mL round bottom flask was equipped with 250 mL dropping funnel. Compound 2 (10.00 g, 22.38 mmol), freshly dried tetrahydrofuran (THF; 250 mL) and tetramethylethylenediamine (TMEDA; 1.04 mL, 8.90 mmol) was added to the flask. The reaction mixture was degassed by purging with N<sub>2</sub> gas prior to cool at -20 °C and after cooling 1.6 M *n*-butyllithium (1.72 g, 26.85 mmol) was added to the reaction mixture drop wise through dropping funnel for 30 min. Stirred the reaction mixture for 1.5 h and raised the reaction temperature to 0°C,

without any external aid, then added dimethylformamide (DMF; 3.44 mL, 44.78 mmol) slowly. After 30 min of stirring, saturated NH<sub>4</sub>Cl was added to the reaction mixture, followed by extraction with dichloromethane (DCM). Organic layer was dried through anhydrous MgSO<sub>4</sub>, evaporated the solvent to get pale yellowish oil. This crude compound was purified by column with DCM/hexanes = 1/4 to yield (10.61 g, 68%) pale yellow solid compound 3. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.53 (s, CHO) δ 7.35 (t, J = 10.0 Hz, 1H), 6.51 (d, J = 5.0 Hz 2H), 4.00 (t, J = 7.5 Hz, 4H), 1.80 (m, 4H), 1.44 (m, 4H), 1.25-1.38 (br, 32H), 0.87 (t, J = 5.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 189.20, 161.65, 135.55, 114.65, 104.43, 68.86, 31.94, 29.70, 29.66, 29.64, 29.59, 29.52, 29.47, 29.39, 29.07, 26.00, 22.71, 14.13.

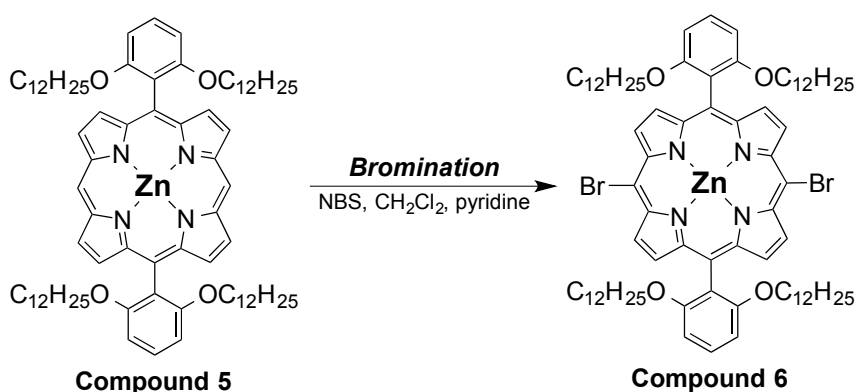


**Compound 4:** To a degassed solution of dipyrromethane (15.17 g, 35.41 mmol) and compound 3 (16.0 g, 33.72 mmol) in dry DCM (5.0 L) trifluoroacetic acid (TFA; 2.25 mL, 30.05 mmol) was added under dark environment at room temperature under nitrogen atmosphere. After the solution was stirred for 3 h, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ; 11.49 g, 50.58 mmol) was added and the reaction mixture was stirred for an additional 1 h. The mixture was basified with triethylamine (7 mL) and filtered through silica gel (to remove excess of polymer). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using DCM/hexanes = 1/2 as eluent to yield purple colored compound 4 (6.28 g, 30 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.16 (s, 2H), 9.28 (d, J = 4.5 Hz, 4H), 8.99 (d, J = 4.5 Hz, 4H), 7.72 (t, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 4H), 3.85 (t, J = 6.4 Hz, 8H), 1.31-1.23 (m, 8H), 1.23-1.09 (m, 16H), 1.07-0.98 (m, 8H), 0.98-0.84 (m, 28H), 0.78-0.68 (m, 8H), 0.63-0.53 (m, 16H), 0.51-0.42 (m, 8H), -2.99 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.10, 147.61, 144.89, 130.77, 130.40, 129.96, 119.89, 111.50, 105.23, 103.89, 68.63,

29.50, 29.44, 29.31, 29.20, 29.06, 28.68, 28.58, 25.27, 22.70, 14.15.



**Compound 5:** Compound 4 (6.28 g, 5.23 mmol) was dissolved in DCM (675 mL) and  $Zn_2 \bullet 4H_2O$  (11.5 g, 52.3 mmol) in methanol (170 mL) was added to the reaction mixture followed by stirring for 2 h at room temperature. Thin layer chromatography (TLC) showed complete absence of free base and washed the excess  $Zn_2 \bullet 4H_2O$  with water (750 mL), followed by separation of DCM layer and dried over anhydrous  $MgSO_4$ . The solvent was removed under reduced pressure and recrystallization from DCM/methanol to yield purple colored compound 5 (6.47 g, 98 %).  $^1H$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  10.30 (s, 2H), 9.52 (d,  $J = 4.4$  Hz, 4H), 9.32 (d,  $J = 4.3$  Hz, 4H), 7.94 (t,  $J = 8.4$  Hz, 2H), 7.28 (t,  $J = 7.9$  Hz, 4H), 4.09 (t,  $J = 6.3$  Hz, 8H), 1.54 (ddd,  $J = 18.1, 10.2, 4.8$  Hz, 26H), 1.37 (dt,  $J = 13.2, 6.6$  Hz, 8H), 1.32-1.12 (m, 26H), 1.05 (dd,  $J = 21.9, 15.0$  Hz, 10H), 0.79 (s, 16H), 0.65 (d,  $J = 6.2$  Hz, 6H).



**Compound 6:** Compound 6 was synthesized according modified literature conditions.<sup>19b</sup> Compound 5 (3.58 g, 2.83 mmol) was taken in two neck 3 L round bottom flask and dissolved in dry DCM (1.35 L). Pyridine (16 mL) was added to the reaction mixture and cooled at  $-5$  °C. *N*-Bromosuccinimide

(NBS; 1.26 g, 7.08 mmol) was (dissolved in DCM 250 mL) added to the reaction mixture for 2 h followed by monitored the reaction with TLC. Upon completion of the reaction quenched with acetone and solvent was removed by reduced pressure and subjected to column chromatography (silica gel) (eluent: 1/3 = DCM/hexanes) to yield compound 6 (3.62 g, 90 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.56 (dd,  $J = 4.6, 0.9$  Hz, 4H), 8.85 (dd,  $J = 4.6, 0.9$  Hz, 4H), 7.72 (t,  $J = 8.4$  Hz, 2H), 7.03 (d,  $J = 8.4$  Hz, 4H), 3.87 (t,  $J = 6.4$  Hz, 8H), 1.46 (s, 5H), 1.42 – 1.12 (m, 46H), 1.06 (dt,  $J = 13.7, 6.7$  Hz, 13H), 1.01-0.84 (m, 36H), 0.78 (d,  $J = 6.6$  Hz, 9H), 0.69-0.49 (m, 17H), 0.43 (d,  $J = 6.5$  Hz, 6H). FAB-MS:  $m/z$  calcd for  $\text{C}_{80}\text{H}_{114}\text{Br}_2\text{N}_4\text{O}_4\text{Zn} = 1420.9$ , found 1421.6  $[\text{M}+1]^+$ .

### **Fabrication and Measurement of the Memory Devices:**

The memory devices were fabricated with the configuration of ITO/PI film/Al or Au. The PI thin films were spin-cast onto the ITO substrate which was cleaned by ultrasonication with water, acetone and isopropanol each for 15 min, and the PI film thickness was adjusted to be around 50 nm. Finally, a 300-nm-thick Al or Au top electrode was thermally evaporated through the shadow mask (recorded device units of  $0.5 \times 0.5 \text{ mm}^2$  in size) at a pressure of  $10^{-7}$  torr with a uniform depositing rate of 3-5 Å/s. The electrical characterization of the memory device was performed by a Keithley 4200-SCS. ITO was used as the cathode (maintained as common), and Al or Au was set as the anode during the voltage sweep. The probe tip used 10  $\mu\text{m}$  diameter tungsten wire attached to a tinned copper shaft with a point radius  $<0.1 \mu\text{m}$  (GGB Industries, Inc.).

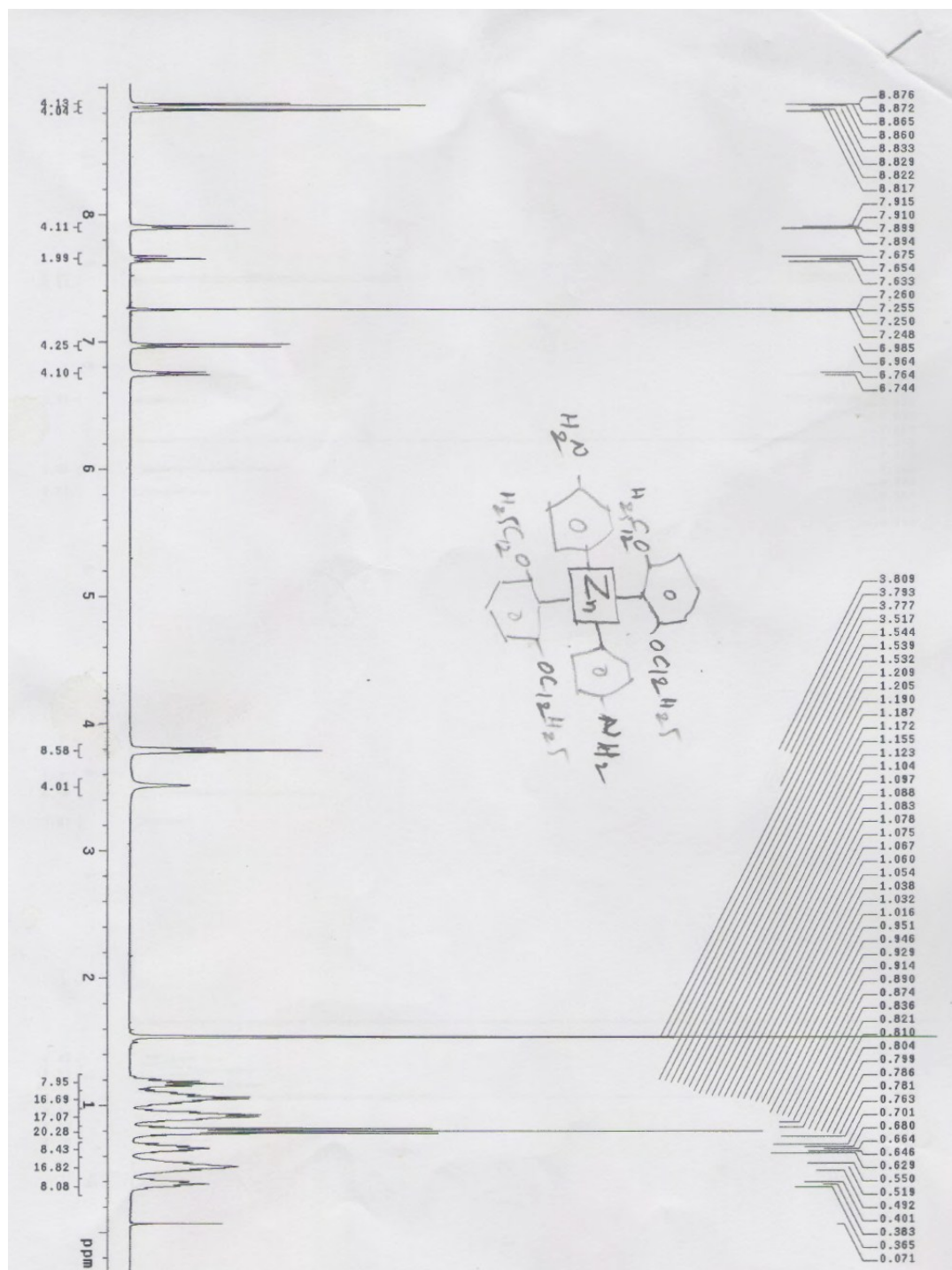
**Measurement of Basic Properties:** Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer 100 Model FT-IR spectrometer with resolution of  $1 \text{ cm}^{-1}$  and number of scans 4.  $^1\text{H}$  NMR spectrum was measured on a Bruker AC-300 MHz spectrometer in  $\text{DMSO-}d_6$ , using tetramethylsilane as an internal reference, and peak multiplicity was reported as follows: s, singlet; d, doublet; m, multiplet. The inherent viscosity was determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector, calibrating with polystyrene standards. Two Waters 5  $\mu\text{m}$  Styragel HR-2 and HR-4 columns (7.8 mm I. D.  $\times$  300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 ml/min at 40 °C. Thermogravimetric analysis (TGA) was conducted with TA SDT Q600. Experiments were carried out on approximately 3-5 mg samples heated in flowing nitrogen or air (flow rate =  $20 \text{ cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Coefficient of thermal expansion (CTE) and glass transition temperatures ( $T_g$ ) are measured on a dilatometer (TA instrument TMA Q400EM). The TMA experiments were conducted from 50 to 380 °C at a scan rate of 10 °C/min with a tensile probe under an applied constant load of 50 mN.  $T_g$  was taken as the onset temperature of probe displacement on the TMA traces. The CTE data were determined in the range of 50–180 °C by film-fiber probe with expansion mode. Cyclic voltammetry (CV) was performed with a Bioanalytical System Model CV-27 and conducted with the

use of a three-electrode cell in which ITO (polymer films area about 0.5 cm x 1.2 cm) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 100 mV/s against a Ag/AgCl reference electrode in anhydrous CH<sub>3</sub>CN, using 0.1 M of TBAP as a supporting electrolyte. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. The microstructure of the prepared films was examined by using a JOEL JEM-1230 transmission electron microscope (TEM). UV-visible absorption was recorded on UV-visible spectrophotometer (Hitachi U-4100).

# NMR and Mass spectra

NMR

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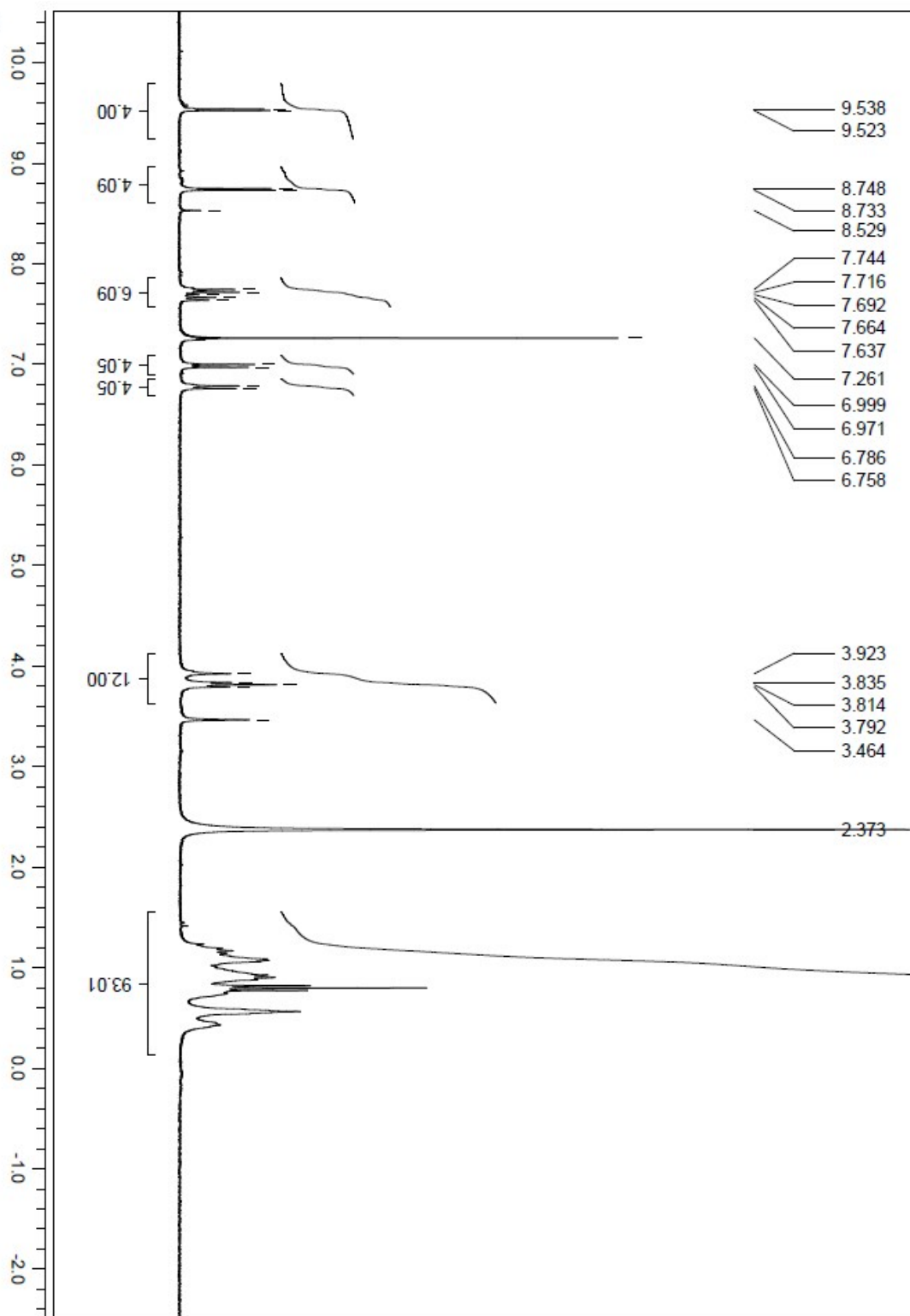






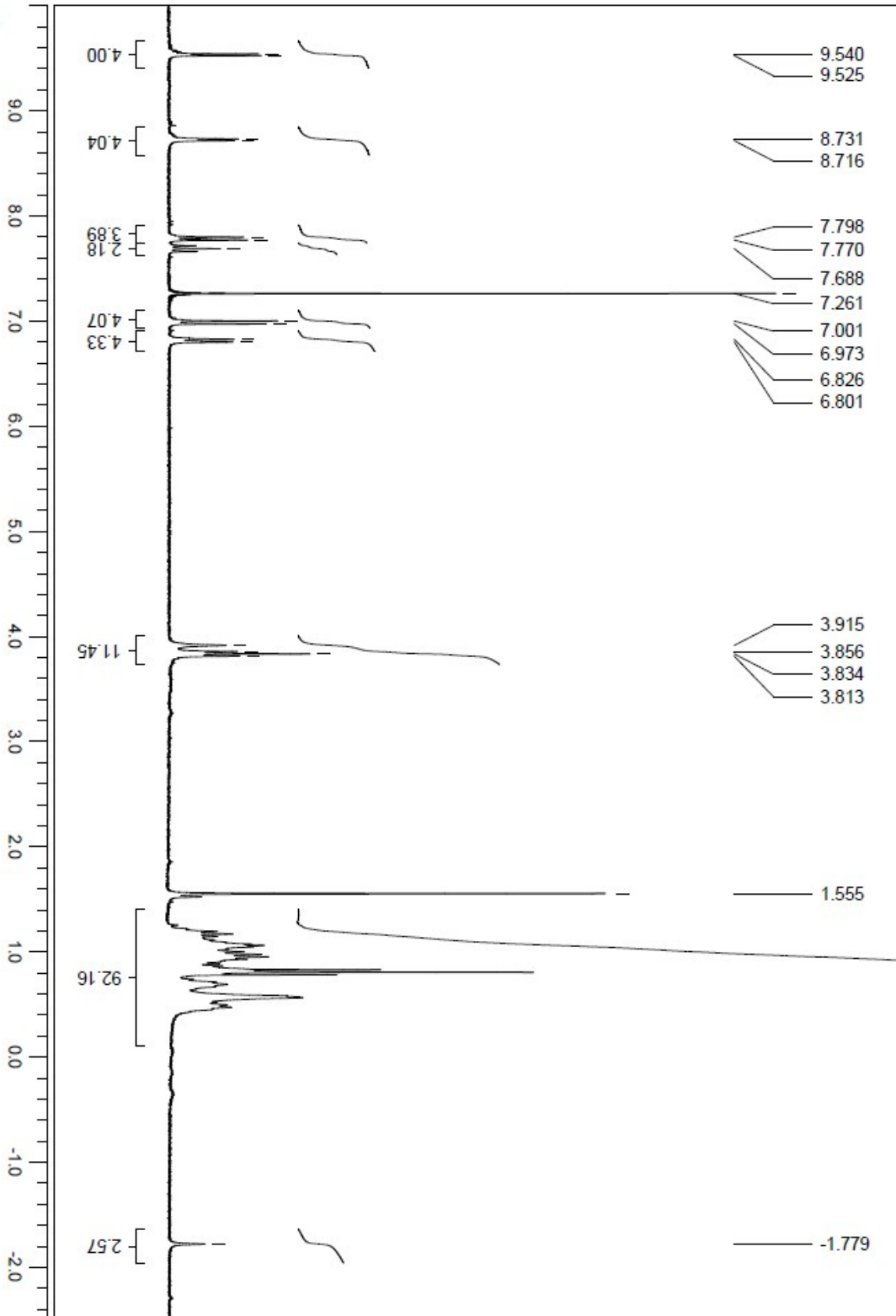
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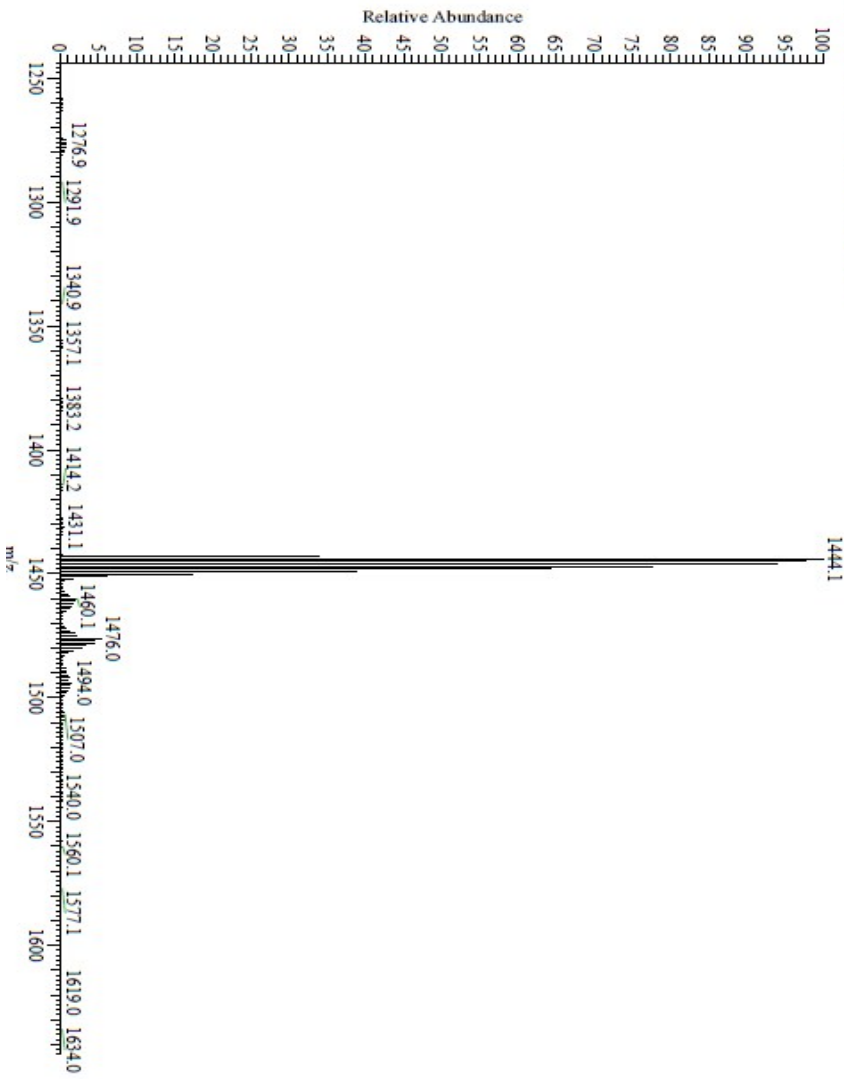
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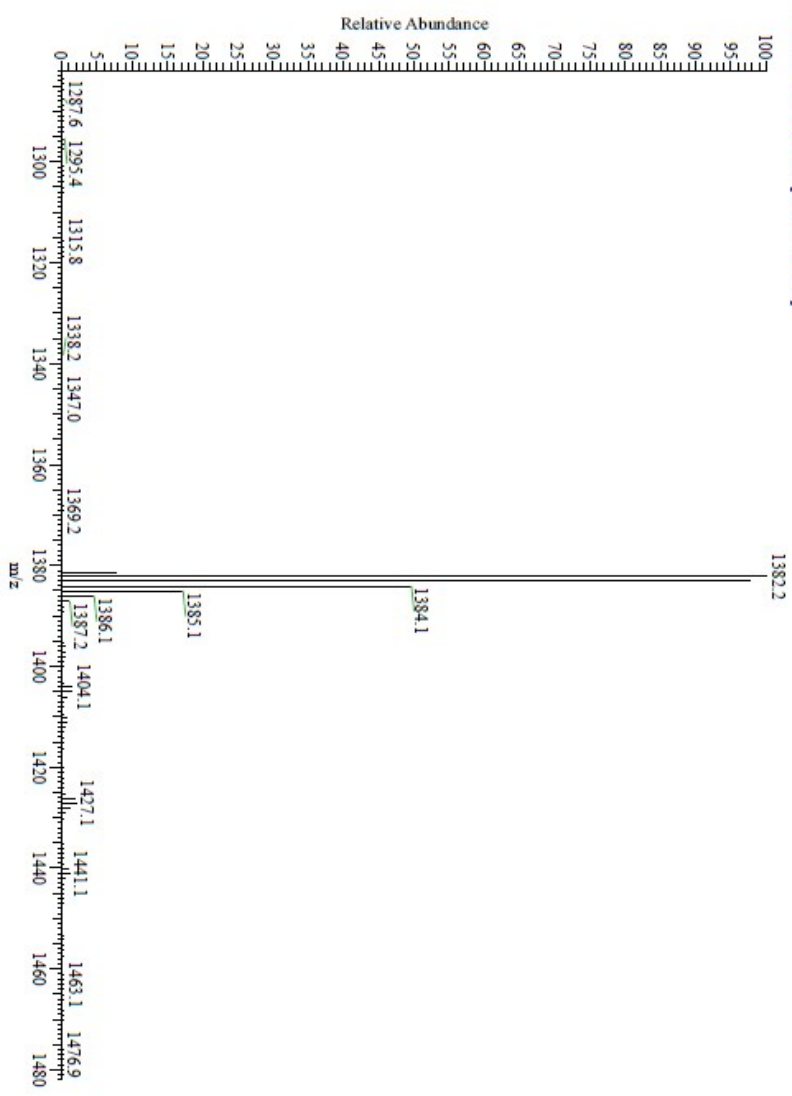


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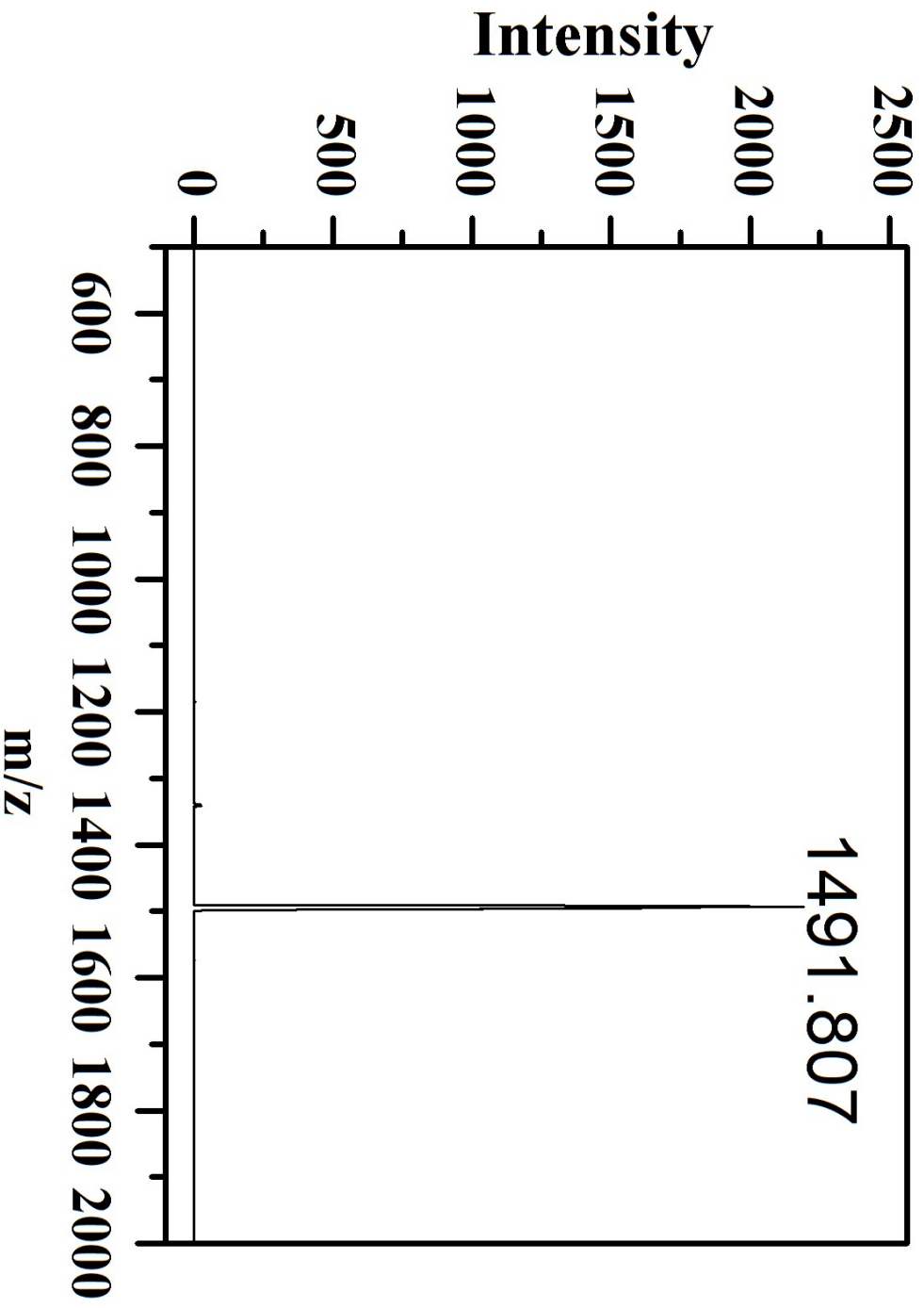
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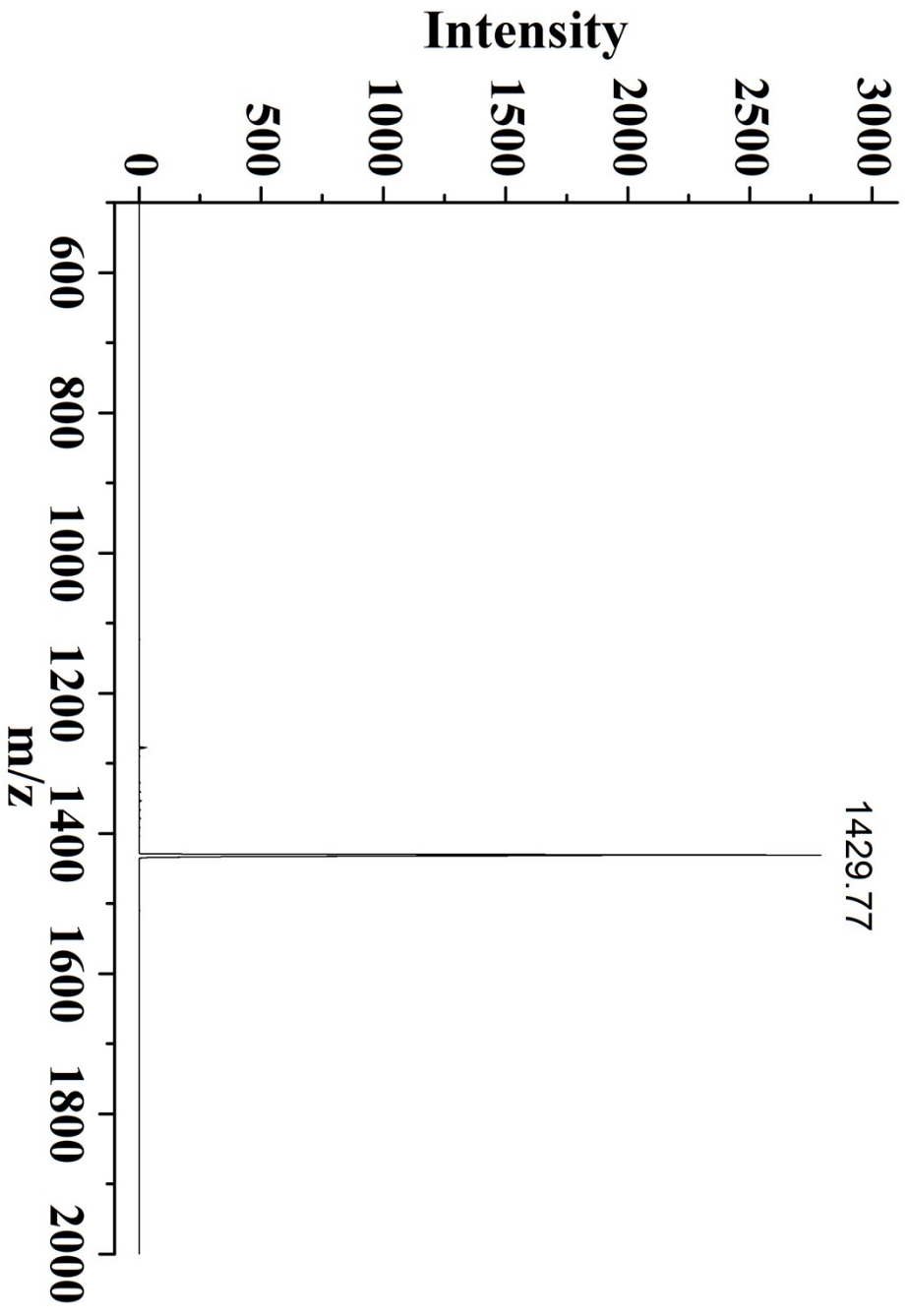
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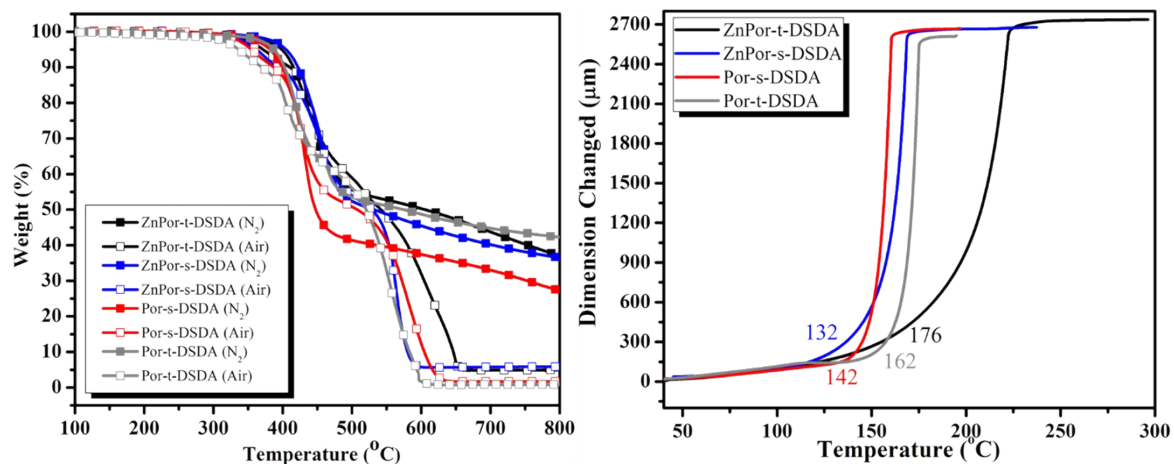
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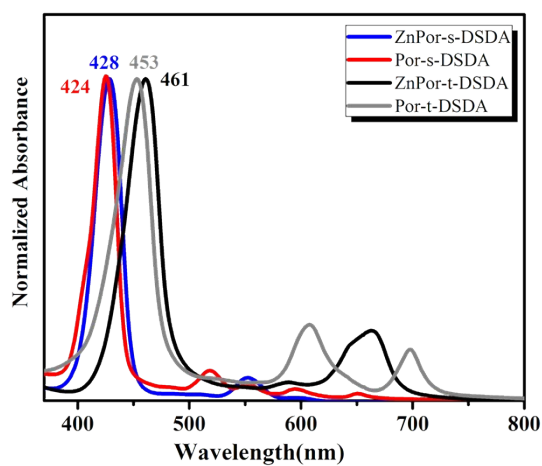
P3:







**Figure S1.** (a) TGA curve and (b) TMA curve of porphyrin-containing polyimides.



**Figure S2.** The normalized UV-Vis absorption spectra of porphyrin-containing polyimides.



**Table S1**

Polymer	Mw	Mn	PDI <sup>b, c</sup>	$\eta_{inh}^c$ (dL g <sup>-1</sup> )
ZnPor-t-DSDA	116600	48100	2.42	0.29
ZnPor-s-DSDA	202000	88000	2.29	0.71
Por-t-DSDA	90800	29400	3.08	0.25
Por-s-DSDA	152400	81000	1.88	0.43

<sup>a</sup> Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 mL/min at 40 °C. <sup>b</sup> Polydispersity index (Mw/Mn). <sup>c</sup> Measured at a polymer concentration of 0.5 g dL<sup>-1</sup> in NMP at 30 °C.

**Table S2**

Polymer	Solubility in various solvents <sup>a</sup>					
	NMP	DMAc	DMF	THF	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>
ZnPor-t-DSDA	++	++	+-	++	+-	+-
ZnPor-s-DSDA	++	+-	+-	++	++	++
Por-t-DSDA	++	++	+-	++	++	++
Por-s-DSDA	++	++	+	++	++	++

<sup>a</sup> The solubility was determined with a 1mg sample in 0.2 ml of a solvent. ++, soluble at room temperature; + soluble at heating; +-, partial soluble even on heating

**Table S3**

Polymer	T <sub>g</sub> (°C) <sup>a</sup>	CTE ( $\mu\text{m}/\text{m}^\circ\text{C}$ ) <sup>b</sup>	T <sub>d</sub> <sup>5</sup> (°C) <sup>d</sup>		T <sub>d</sub> <sup>10</sup> (°C) <sup>d</sup>		Char yield (%) <sup>d</sup>
			Air	N <sub>2</sub>	Air	N <sub>2</sub>	
ZnPor-t-DSDA	176	179	370	400	410	415	37%
ZnPor-s-DSDA	132	141	360	405	395	420	37%
Por-t-DSDA	162	205	335	385	370	400	42%
Por-s-DSDA	142	152	355	380	385	400	27%

<sup>a</sup> Glass transition temperature measured by TMA using the film/fiber mode with a constant applied load of 50 mN at a heating rate of 10 °C min<sup>-1</sup>. <sup>b</sup> Coefficient of linear thermal expansion between 50°C and 200 °C measured by TMA using the film/fiber mode with a constant applied load of 50 mN at a heating rate of 10 °C min<sup>-1</sup>. Temperature at which 5% and 10% weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C min<sup>-1</sup> and a gas flow rate of 20 cm<sup>3</sup> min<sup>-1</sup>. Char yield percentages at 800 °C under nitrogen flow.