

Supporting information available for

**Amide-bridged ladder poly(*p*-phenylene): synthesis by direct arylation and  $\pi$ -stacked assembly**

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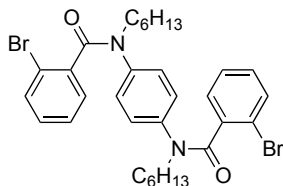
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## S1. Materials and instruments

All materials were obtained from commercial suppliers and used without purification. *N,N'*-Dihexyl-1,4-phenylenediamine<sup>1</sup> and *N*-methylphenanthridinone (Biphenyl oligomer: **1**)<sup>2</sup> were synthesized following to previous reports. <sup>1</sup>H- and <sup>13</sup>C-nuclear magnetic resonance (NMR) spectroscopies were obtained on a Bruker Avance 200 and 400 FT-NMR spectrometers using tetramethylsilane (<sup>1</sup>H-NMR,  $\delta$  0.00) and solvent residual peaks as the internal standard (<sup>1</sup>H-NMR and <sup>13</sup>C-NMR). Infrared (IR) spectra were recorded on a JASCO FT-IR 460Plus spectrophotometer in the attenuated total reflectance (ATR) method. Melting points (Mp) were determined on a Yanaco micro melting point apparatus MP-J3. High resolution electrospray ionization mass spectra (HR ESI-MS) were obtained on a Waters Synapt G2 HDMS. Elemental analyses (EA) were performed on a Elementar vario EL cube in the CHN mode. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectra were obtained on a JEOL JMS-S3000 in the spiral mode using dithranol as a matrix. Gel permeation chromatography (GPC) analyses were carried out on a Shodex 104 system using tandem LF-404 columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with an UV detector (Shimadzu SPP-20A). Number-averaged molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) were determined on the basis of a calibration curve made from standard polystyrene samples and ethylbenzene. Ultraviolet-visible (UV-vis) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650 spectrophotometer and a Shimadzu RF-5300 spectrofluorometer, respectively, using a 10 mm quartz cell. Fluorescence quantum yields (QYs) in solution were determined relative to quinine sulfate in 0.05 M H<sub>2</sub>SO<sub>4</sub> having a QY of 0.55. Thermogravimetric analyses (TGA) were performed on a Shimadzu DTG-60 in the nitrogen stream of 50 mL/min at the heating rate of 10 °C/min. Microwave-assisted reactions were performed in a Biotage microwave reactor (Initiator) using 0.5–2.0 mL microwave reaction vials.

## S2. Syntheses

### *N,N'*-Bis(2'-bromophenacyl)-*N,N'*-dihexyl-1,4-phenylenediamine (**2'**)



A pyridine solution (6 mL) of *N,N'*-dihexyl-1,4-phenylenediamine (0.40 g, 1.5 mmol), 2-bromobenzoic acid (0.65 g, 3.2 mmol), triphenylphosphine (1.0 g, 3.8 mmol), and hexachloroethane (0.90 g, 3.8 mmol) was heated to reflux under nitrogen for 18 h. After pyridine was evaporated, water and CH<sub>2</sub>Cl<sub>2</sub> were added and the mixture was vigorously stirred. An organic phase was separated and dried over MgSO<sub>4</sub>. The crude product was purified by SiO<sub>2</sub> column chromatography (hexane : ethyl acetate = 1 : 1, R<sub>f</sub> = 0.56) to obtain yellow solid in 0.76 g (82% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 0.87 (t, *J* = 6.7 Hz, 6H), 1.18–1.38 (12 H), 1.44–1.62 (4H), 3.66–4.04 (4H), 6.82–7.25 (12H). *Note*: Proton signals of the *cis-cis* isomer are only indicated. IR (ATR) 1642.1 cm<sup>-1</sup> (ν<sub>C=O</sub>).

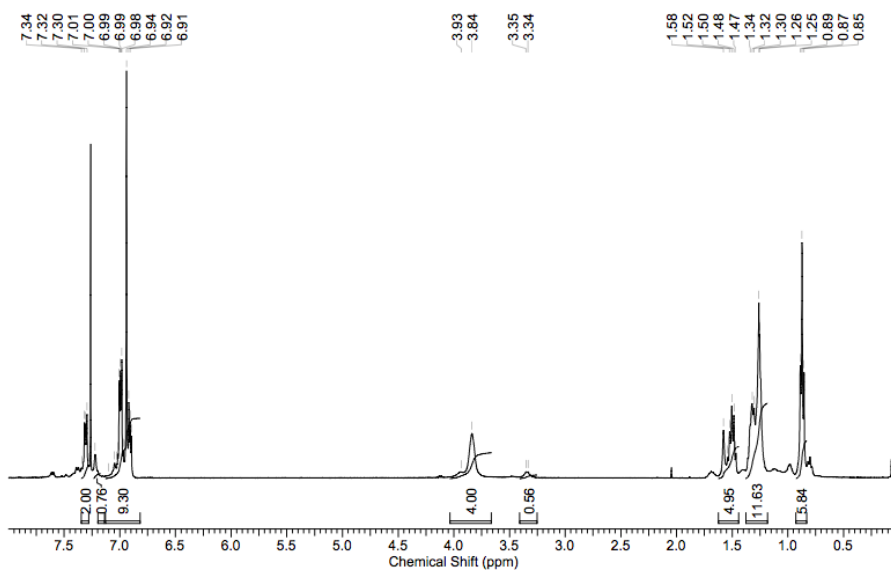
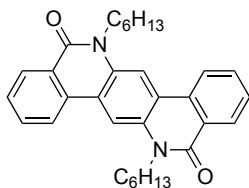


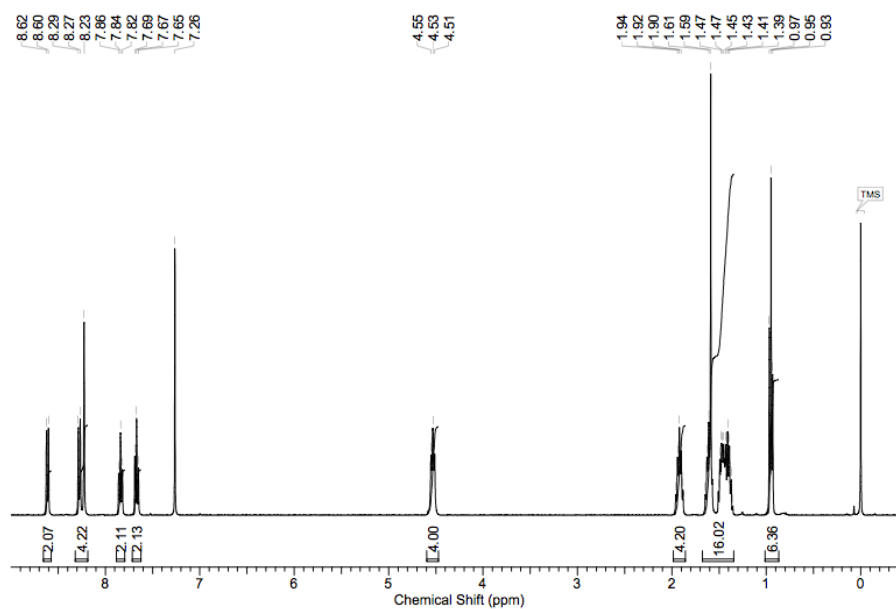
Figure S1. <sup>1</sup>H-NMR spectrum of **2'** in CDCl<sub>3</sub>.

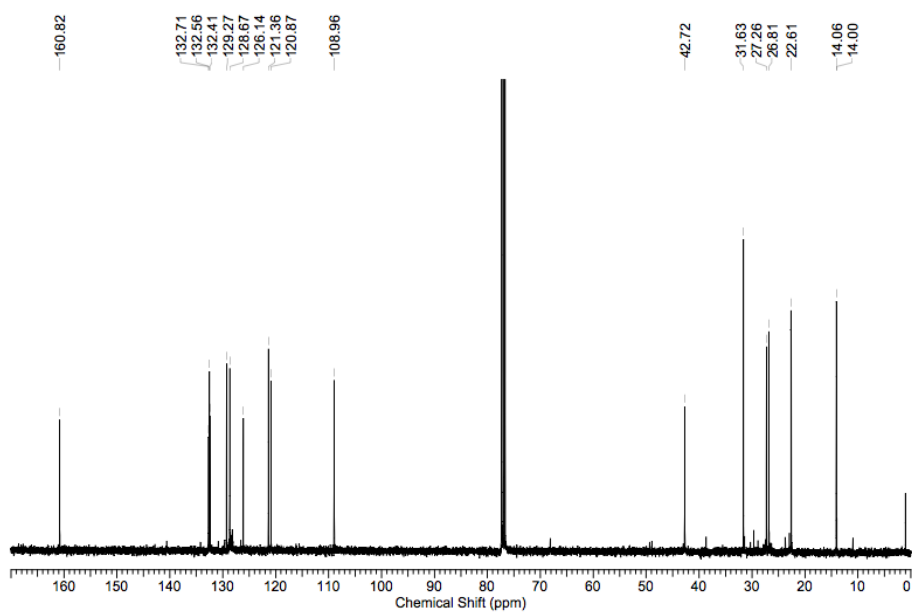
## Terphenyl oligomer (**2**)



To a DMAc solution (2 mL) of **2**<sup>†</sup> (0.20 g, 0.31 mmol) were added KOAc (0.12 g, 1.3 mmol) and Pd(OH)<sub>2</sub> 20% on carbon (wetted with ca. 50% water) (87 mg, 0.06 mmol), and the mixture was heated at 145 °C under nitrogen for 24 h. After DMAc was evaporated, CHCl<sub>3</sub> was added and passed through a Celite pad. A filtrate was washed with water and dried over MgSO<sub>4</sub>. The crude product was purified by SiO<sub>2</sub> column chromatography (CHCl<sub>3</sub> : ethyl acetate = 5 : 1, R<sub>f</sub> = 0.70) to obtain yellow solid in 0.10 g (66% yield<sup>†</sup>). Mp. 190–192 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 0.95 (t, *J* = 7.7 Hz, 6H) 1.34–1.66 (12 H), 1.92 (m, 4H), 4.53 (t, *J* = 7.7 Hz, 4H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.84 (t, *J* = 7.6 Hz, 2H), 8.23 (s, 2H), 8.28 (d, *J* = 8.1 Hz, 2H), 8.61 (d, *J* = 7.3 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) 14.1, 22.6, 26.8, 27.3, 31.6, 42.7, 109.0, 120.9, 121.4, 126.1, 128.7, 129.3, 132.4, 132.6, 132.7, 160.8. IR (ATR) 1638.2 cm<sup>-1</sup> (ν<sub>C=O</sub>). HRMS (ESI/TOF-Q) *m/z*: [**2** + Na]<sup>+</sup> Calcd for C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>NaO<sub>2</sub> 503.2674; Found: 503.2673. Anal Calcd for C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>: C, 79.96%; H, 7.55%; N, 5.83%; Found: C, 79.77%; H, 7.68%; N, 5.69%.

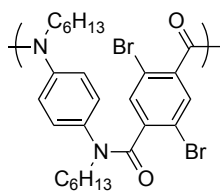
<sup>†</sup>Although the intramolecular cyclization proceeded very efficiently, the isolated yield of **2** was relatively low due to the technical problem of experimenter.



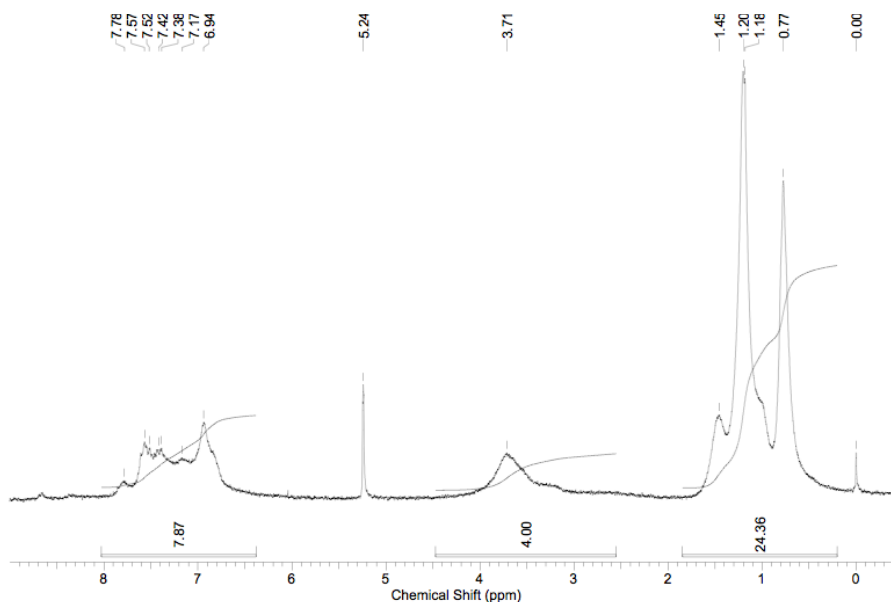


**Figure S2.**  $^1\text{H}$ -NMR (top) and  $^{13}\text{C}$ -NMR (bottom) spectra of **2** in  $\text{CDCl}_3$ .

### Precursor polymer (P')

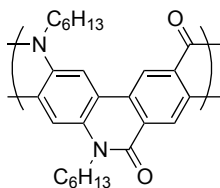


A pyridine solution (4 mL) of *N,N'*-dihexyl-1,4-phenylenediamine (0.50 g, 1.8 mmol), 2,5-dibromoterephthalic acid (0.59 g, 1.8 mmol), triphenylphosphine (1.1 g, 4.3 mmol), and hexachloroethane (1.0 g, 4.3 mmol) in a microwave vial was heated to 120 °C under nitrogen for 24 h. The solution was then poured into MeOH/conc. HCl (11/1 in volume ratio) to precipitate a polymer. The polymer was purified by the similar reprecipitation in three times and dried in vacuo to obtain **P'** in 0.11 g (11% yield). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 200 MHz) δ (ppm) 0.34–1.94 (24H), 3.71 (4H), 6.56–8.09 (8H). IR (ATR) 1645.9 cm<sup>-1</sup> (ν<sub>C=O</sub>).

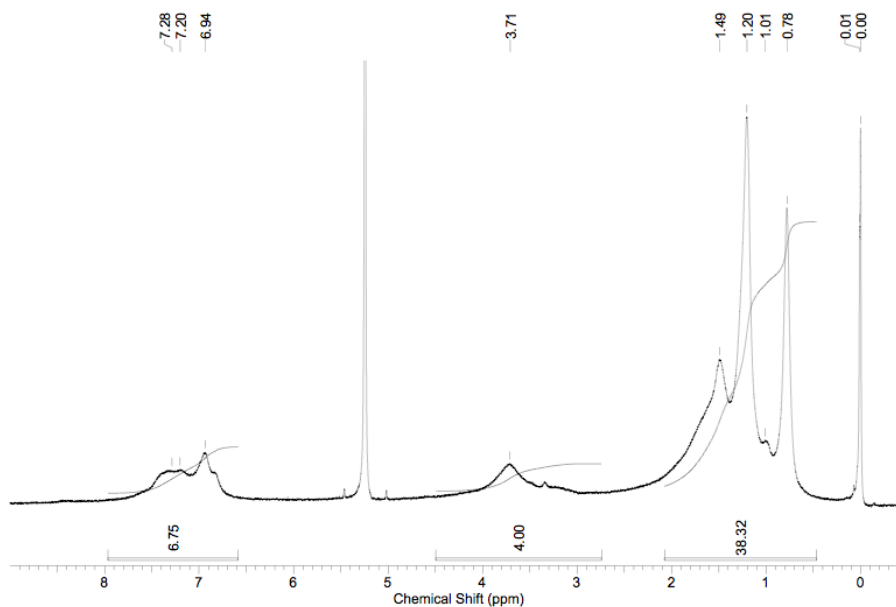


**Figure S3.** <sup>1</sup>H-NMR spectrum of **P'** in CD<sub>2</sub>Cl<sub>2</sub>.

### Ladder polymer (P)

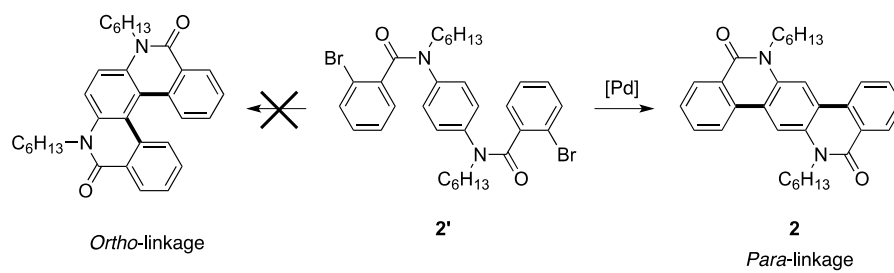


To a DMAc solution (2 mL) of **P'** (40 mg, 0.07 mmol) were added KOAc (28 mg, 0.28 mmol) and Pd(OH)<sub>2</sub> 20% on carbon (wetted with ca. 50% water) (20 mg, 14 μmol), and the mixture was heated at 145 °C under nitrogen for 24 h. After DMAc was evaporated, CHCl<sub>3</sub> was added and passed through a Celite pad. A filtrate was poured into MeOH/conc. HCl (11/1 in volume ratio) to precipitate a polymer. The polymer was purified by the similar reprecipitation in three times and dried in vacuo to obtain **P** in 10 mg (35% yield). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) δ (ppm) 0.46–2.29 (38H), 3.71 (4H), 6.55–8.10 (7H). IR (ATR) 1639.2 cm<sup>-1</sup> (ν<sub>C=O</sub>).



**Figure S4.** <sup>1</sup>H-NMR spectrum of **P** in CD<sub>2</sub>Cl<sub>2</sub>.

### S3. Model reaction



**Scheme S1.** Intramolecular direct arylation of **2'**.



## S4. MALDI-ToF mass spectrum

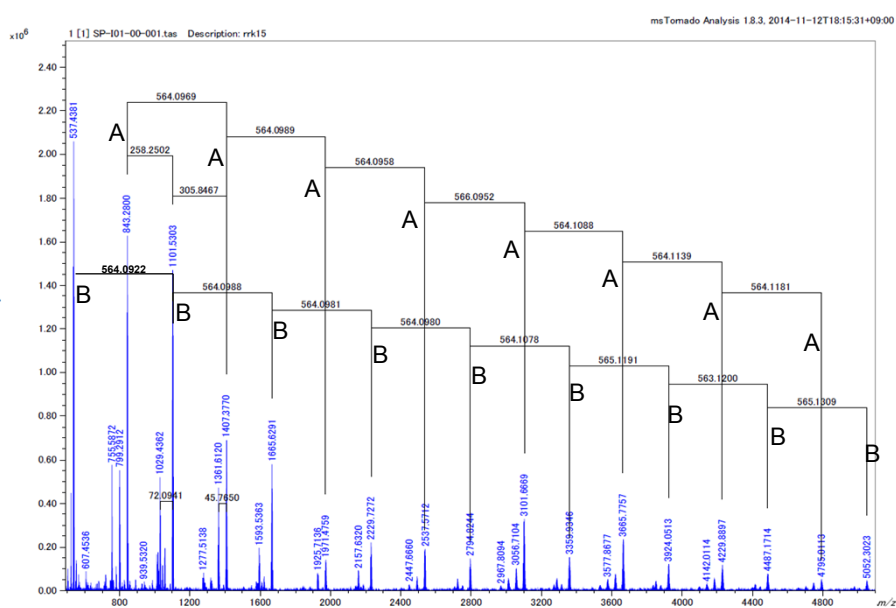
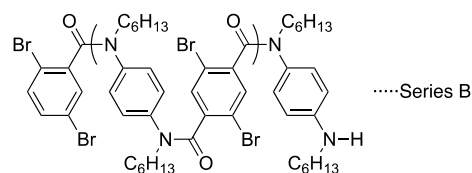
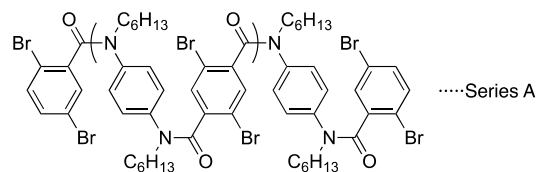
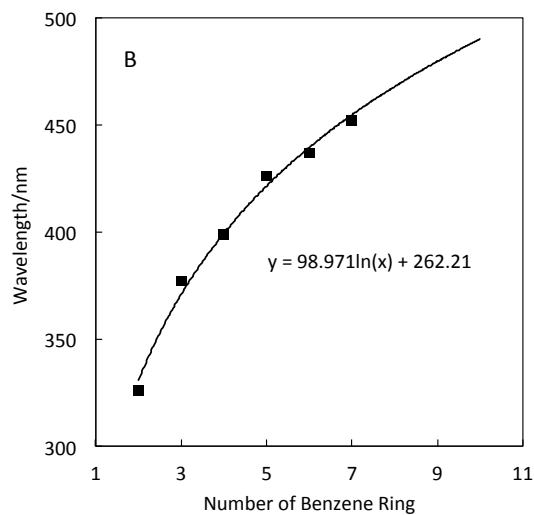
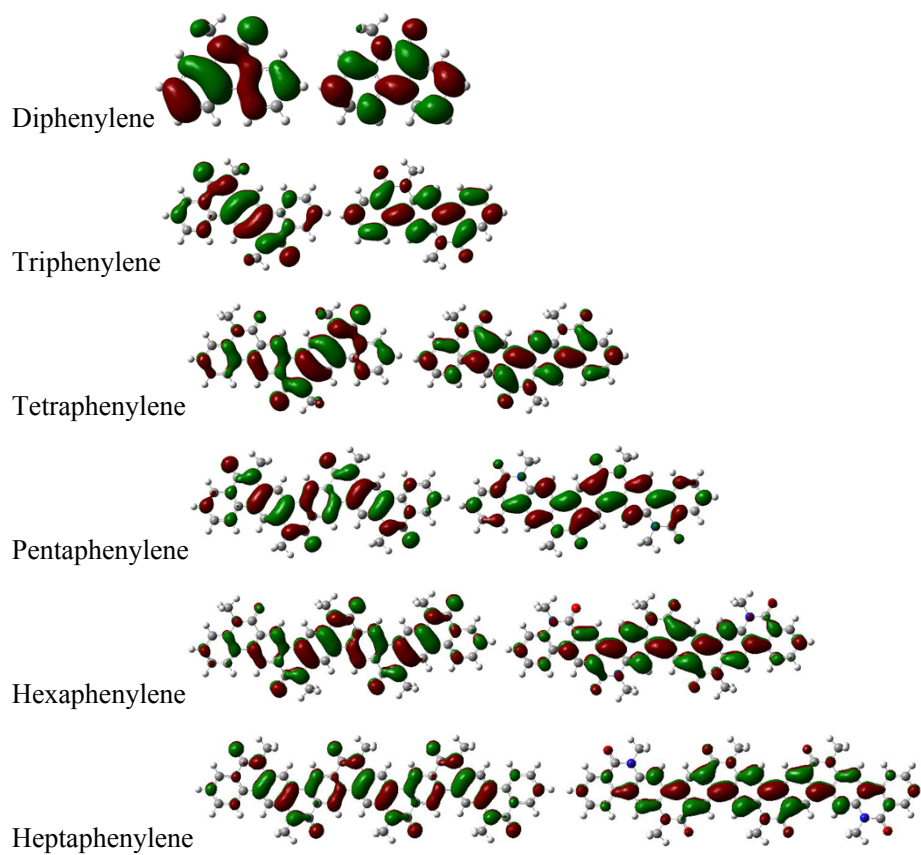


Figure S5. MALDI-ToF mass spectrum of **P'** (dithranol as a matrix, spiral mode).

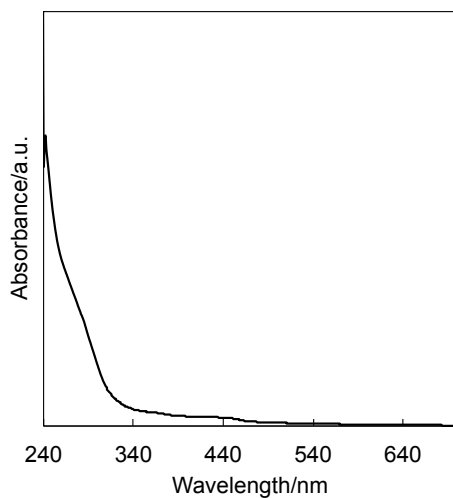
## S5. Theoretical calculation

A

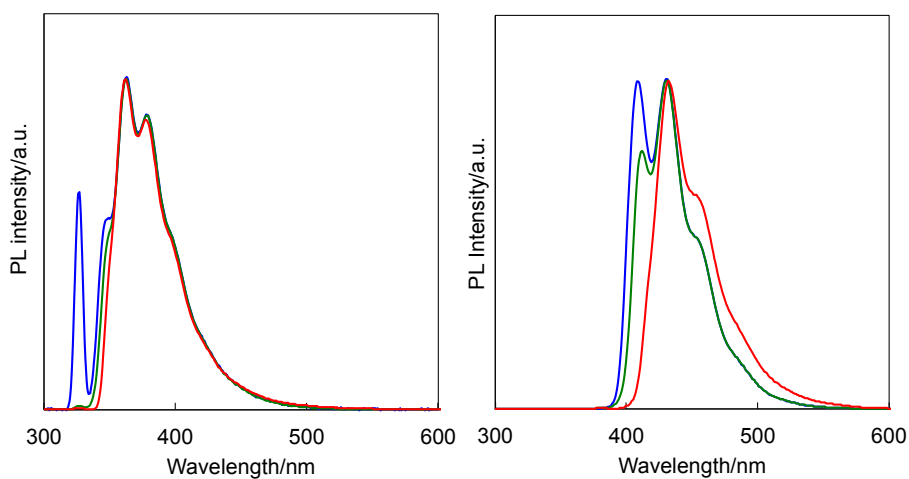


**Figure S6.** (A) HOMO and LUMO topologies for oligo(*p*-phenylene)s. (B) Relationship between theoretical absorption wavelength and number of benzene ring.

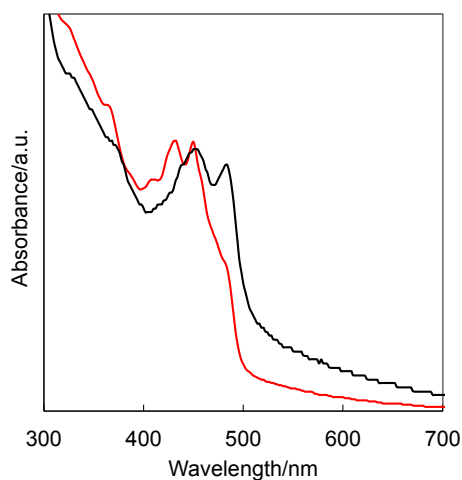
## S6. UV-vis and Fluorescence spectra



**Figure S7.** UV-vis absorption spectrum of **P\*** in  $\text{CHCl}_3$  ( $10 \mu\text{M}$ ).

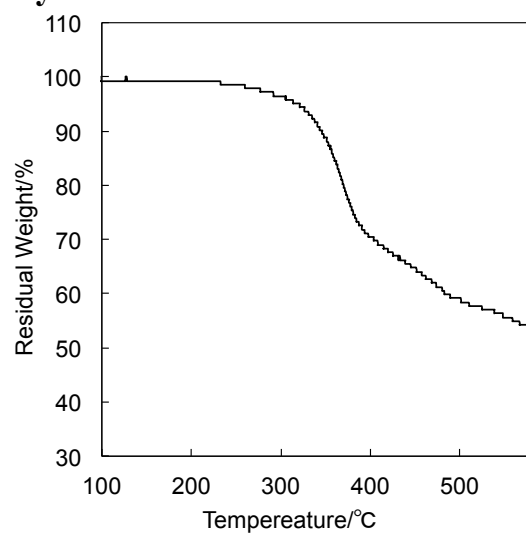


**Figure S8.** Fluorescence emission spectra of **1** (left) and **2** (right) in  $\text{CHCl}_3$  under the concentration of  $10 \mu\text{M}$  (blue line),  $100 \mu\text{M}$  (green line), and  $1000 \mu\text{M}$  (red line).



**Figure S9.** UV-vis absorption spectra of **P** in  $\text{CHCl}_3$  (red line) and spin-coated film (black line).

## S7. Thermal property

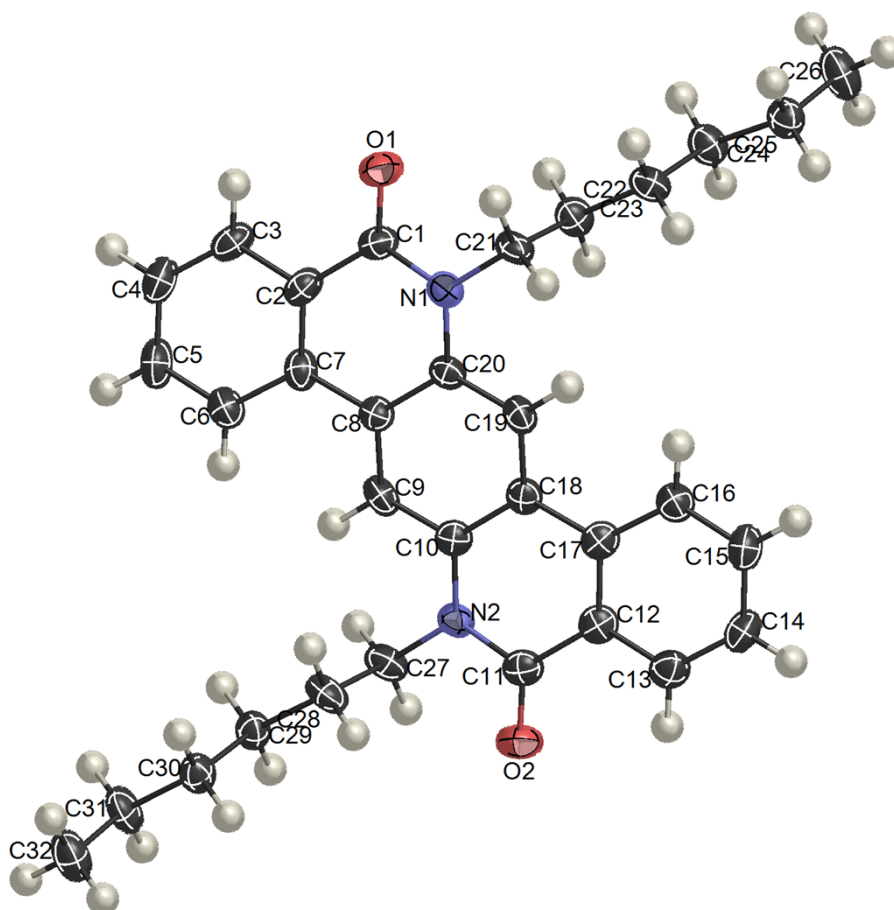


**Figure S10.** TGA curve of **P** at the heating rate of 10 °C/min.

## S8. Crystal structure

**Measurement.** Crystallographic data of **2** was collected on a CCD diffractometer with Cu K $\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation. Data collections were carried out at low temperature (173 K) using liquid nitrogen. All of the crystal structures were solved by direct methods with SHELXS-97 and refined with full-matrix least-squares SHELXL-2013.<sup>3</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at their calculated positions.

**Crystal data for 2:** C<sub>32</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>,  $M_r = 480.63$ , Orthorhombic,  $Pna2_1$ ,  $a = 30.3531(1)$ ,  $b = 5.0918(2)$ ,  $c = 16.0639(5) \text{ \AA}$ ,  $V = 2482.7(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.286 \text{ Mg m}^{-3}$ ,  $2\theta_{\text{max}} = 136.562^\circ$ ,  $T = 173 \text{ K}$ , 9251 reflections measured, 3546 unique ( $R_{\text{int}} = 0.0365$ ),  $\mu = 0.621 \text{ mm}^{-1}$ . The final  $R_1$  and  $wR_2$  were 0.0706 and 0.1849 ( $I > 2\sigma(I)$ ), 0.0862 and 0.1994 (all data). CCDC 1414494



**Figure S11.** Thermal ellipsoid model of crystal of **2**. The ellipsoids are drawn at 50% probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The labels of hydrogen atoms are omitted for clarity.

## S9. References

- 1) W. Cui and F. Wudl, *Macromolecules*, 2013, **46**, 7232–7238.
- 2) M. Parisien, D. Valette, and K. Fagnou, *J. Org. Chem.*, 2005, **70**, 7578–7584.
- 3) A short history of SHELX. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.