Supporting Information to:

Synthesis of Poly(1,10-phenanthroline-5,6-diyl)s Having a π-Stacked Helical Conformation

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Experimental Section

Measurements

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL JNM-ESC400 spectrometer using $CDCl_3$ and D_2O containing 35% DCl as a solvent using tetramethylsilane (TMS) and 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt (DSS), respectively, as the internal standard,. SEC analyses were carried out at room temperature using a chromatographic system consisting of a JASCO PU-980 intelligent HPLC pump and a JASCO UV-2070 PLUS UV detector (275 nm) equipped with a Shodex Asahipak GF-310HQ column (30 × 0.75 (i.d.) cm) (eluent DMF containing LiCl (30 mM), flow rate 0.5 mL/min). FT-IR spectra were measured using a ThermoFischer Scientific Nexus 870 spectrometer. Electronic absorption spectra were measured with a JASCO V-560 spectrophotometer. CD spectra were taken with a JASCO J-820 spectrometer. Melting points were determines on Yanaco (model MP-S3) apparatus. WAXD measurements were performed using an Ultima IV diffractometer (Protectus ADS) (Cu-Ka).

MD simulation

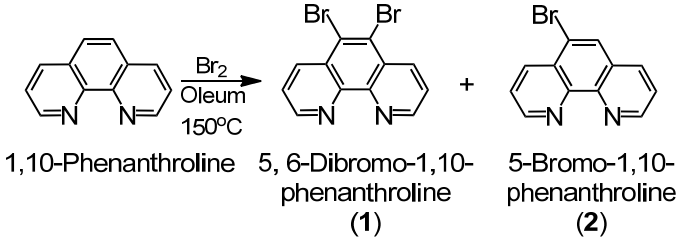
Molecular mechanics structure optimization was effected using the COMPASS[1] force field implemented in the Discover module of the Material Studio 4.2 (Accelrys) software package with the Fletcher-Reeves[2] conjugate gradient algorithm until the RMS residue went below 0.01 kcal/mol/Å. Molecular dynamic simulation was performed under a constant NVT condition in which the numbers of atoms, volume, and thermodynamic temperature were held constant. Berendsen's thermocouple[3] was used for coupling to a thermal bath. The step time was 1 fs and the decay constant was 0.1 ps. Conformations obtained through MD simulation were saved in trajectory files at every 5 or 10 ps and were optimized by MM simulation.

Materials

Reagents: The chemicals listed as follows were used without further purification; 1,10-phenanthroline monohydrate (TCI Chemicals), sulfuric acid, fuming (30%) (Wako Chemicals), bromine (Kanto Chemical), *n*-butyllithium in *n*-hexane (1.60 mol/L) (Kanto Chemical), manganese dioxide (Wako Chemicals), bis(1,5-cyclooctadiene) nickel (0) ($Ni(COD)_2$) (Kanto Chemical), 1,5-cyclooctadiene (COD) (TCI Chemicals), 2,2'-bipyridine (BPy) (Kanto Chemical), (*R*)- and (*S*)-BINAP (Kanto Chemical). Anhydrous 1,10-phenanthroline was recrystallized from benzene (m.p. 117-118^{o}C). Sparteine (Wako Chemicals) (Sp), 2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB) (TCI Chemicals), and 1-(2-pyrrolidinylmethyl)pyrrolidine (PMP) (TCI Chemicals) were dried over calcium hydride, distilled under vacuum, and store under nitrogen atmosphere. Tetrahydrofuran (THF) (Kanto Chemical) was dried over sodium and benzophenone, distilled and stored under nitrogen atmosphere. *N*,*N*-Dimethylformamide (DMF) was dried over calcium hydride, distilled under vacuum, and store under nitrogen atmosphere.

Synthesis and Structural Analysis of Compounds

5,6-Dibromo-1,10-phenanthroline (1) and **5-bromo-1,10-phenanthroline (2)** were synthesized according to the method indicated in Scheme S1.



Scheme S1. Synthesis of **1** and **2**.

5,6-Dibromo-1,10-phenanthroline (1). 1,10-Phenanthroline monohydrate (10 g, 50 mmol) was placed in a 200-mL two-neck flask with a stirring tip. A rubber septum and a condenser equipped with a tail gas absorber system (H_2O) were attached to the necks of the flask. After the addition of oleum (30%, 80 mL) with a graduated cylinder, the mixture was cooled in an ice bath. Bromine (7.8

mL, 150 mmol) was introduced through the rubber septum with a syringe. The mixture was stirred at 150°C for 72 h, and was then neutralized with aq. KOH to obtain orange precipitates. The product was purified first by Al_2O_3 column chromatography (eluent: dichloromethane containing trimethylamine (1 vol.%)), and then by recrystallization from an ethanol solution to give white crystals. Yield 9.5 g, 28 mmol, 56%. M.p. 222-223°C (lit.[4] 221-223°C). Analytical data (Figs. S1-S3): IR (KBr, cm^{-1}) 3069, 1569, 1492, 1409, 1276, 1177, 737; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, J = 4.4 Hz, 2H), 8.79 (dd, J = 8.4, 1.5 Hz, 2H), 7.74 (dd, J = 8.4, 4.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.08, 145.71, 137.21, 128.63, 125.20, 124.45; ESIMS [m/z (%)] 338.90 (M^+, 28), 360.88 (100); HRMS (ESI) calcd for $C_{12}H_6N_2Br_2 + Na^+$ 358.8790, found 358.8794.

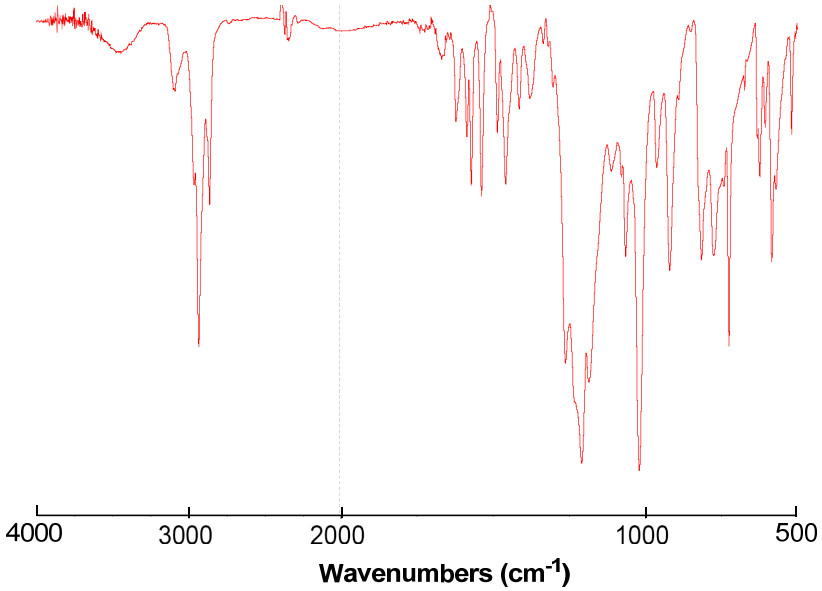


Fig. S1. FT-IR spectrum of **1.** [KBr pellet]

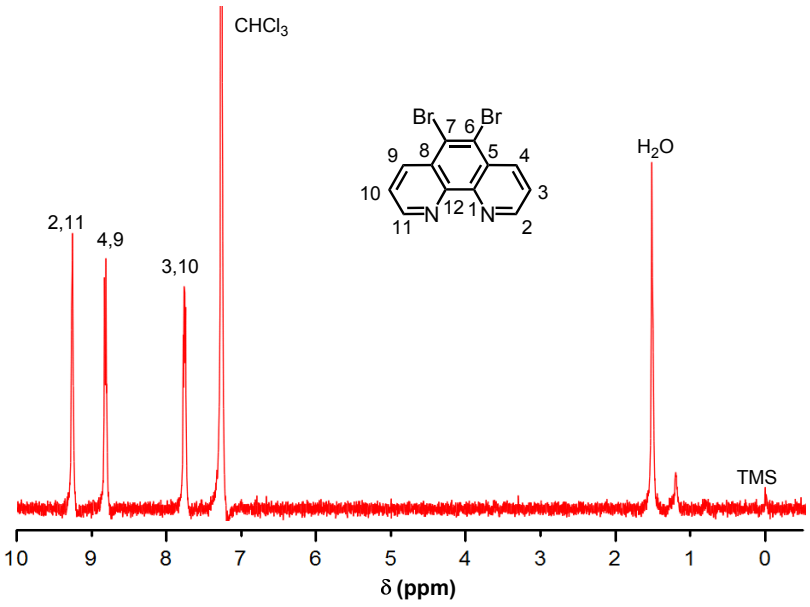


Fig. S2. ^{1}H NMR spectrum of **1**. [$CDCl_3$, 400MHz, r.t.]

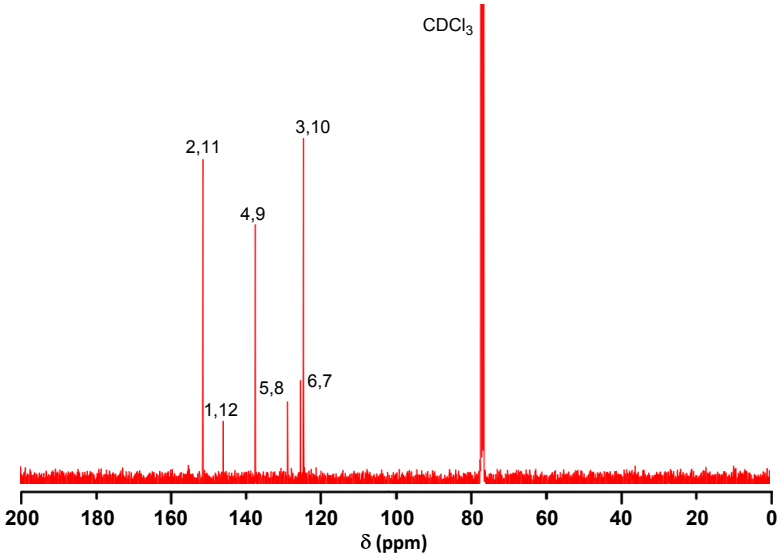


Fig. S3. ^{13}C NMR spectrum of **1**. [$CDCl_3$, 100MHz, r.t.]

5-Bromo-1,10-phenanthroline (2). 1,10-Phenanthroline monohydrate (2.6 g, 13 mmol) was placed in a 100-mL two-neck flask with a stirring tip. A rubber septum and a condenser equipped with a tail gas absorber system (H_2O) were attached to the necks of the flask. After the addition of oleum (30%, 20 mL) with a graduated cylinder, the mixture was cooled in an ice bath. Bromine (1.8 mL, 35 mmol) was introduced through the rubber septum with a syringe. The mixture was stirred at 150°C for 72 h, and was then neutralized by aq. KOH to obtain orange precipitates. The product was purified first by Al_2O_3 column chromatography (eluent: $CHCl_3$) and then by recrystallization from a *n*-hexane-dichloromethane (1/1, v/v) solution to give white crystals. Yield 1.4 g, 5 mmol, 42%. M.p. 117-118.5°C (lit.[5] 118°C). Analytical data (Figs. S4-S6): IR (KBr, cm^{-1}) 3021, 1588, 1554, 1500, 1414, 1278, 1147, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (td, J = 4.5, 1.7 Hz, 2H), 8.69 (dd, J = 8.3, 1.6 Hz, 1H), 8.20 (dd, J = 8.1, 1.6 Hz, 1H), 8.17 (s, 1H), 7.71 (ddd, J = 37.5, 8.2, 4.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.91, 150.71, 146.64, 145.66, 135.93, 135.10, 129.66, 128.81, 127.90, 123.83, 123.67, 120.80; ESIMS [m/z (%)] 258.99 (M^+, 60), 280.97 (100); HRMS (ESI) calcd for $C_{12}H_7N_2Br + Na^+$ 280.9685, found 280.9686.

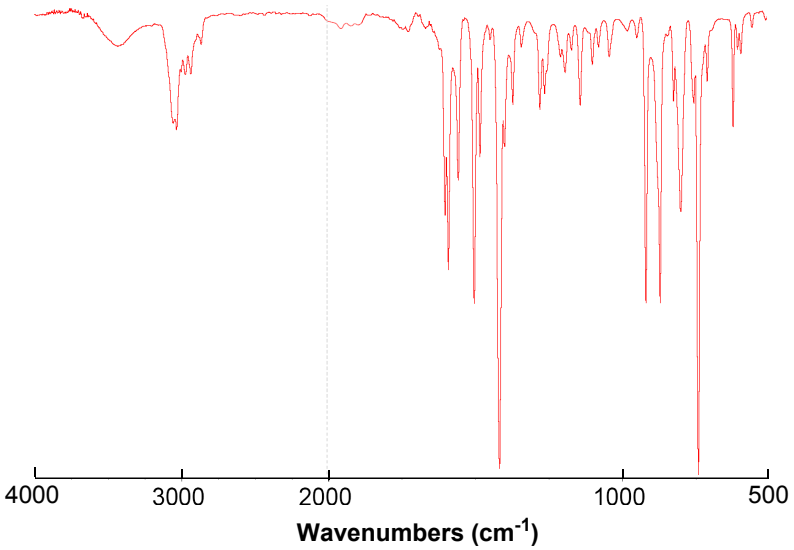


Fig. S4. FT-IR spectrum of **2.** [KBr pellet]

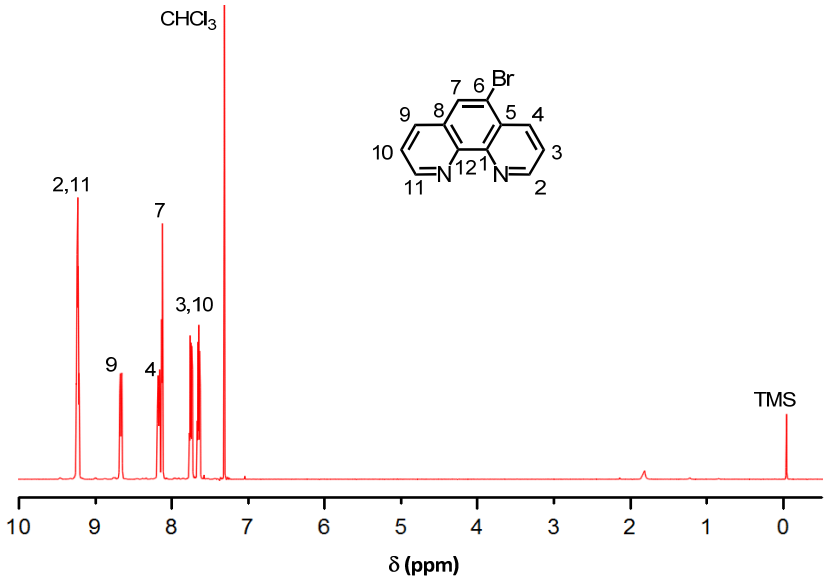


Fig. S5. ^{1}H NMR spectrum of **2**. [$CDCl_3$, 400MHz, r.t.]

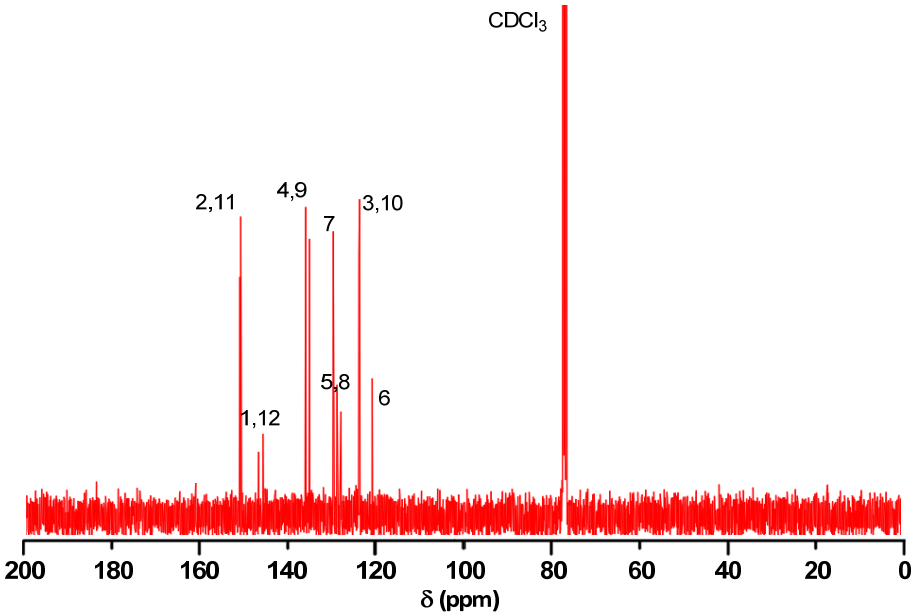


Fig. S6. ^{13}C NMR spectrum of **2**. [$CDCl_3$, 100MHz, r.t.]

2D and 1D NMR spectra of Phen with signal assignments

The assignments in Figs. S7 and S8 were performed using the HMQC, HMBC, and DEPT(45º) spectra (Figs. S9-S11). Using the 2D spectra, the assignments were conducted starting from the signals of H6 and H7 which are the signals with the weakest coupling with other protons. Alternatively, the assignments can also be performed starting from the signals of H2 and H11 next to the N atoms which appear in the lowest magnetic field (highest frequency). The signals of C1, C5, C11, and C12 were identified by the DEPT(45º) spectrum.

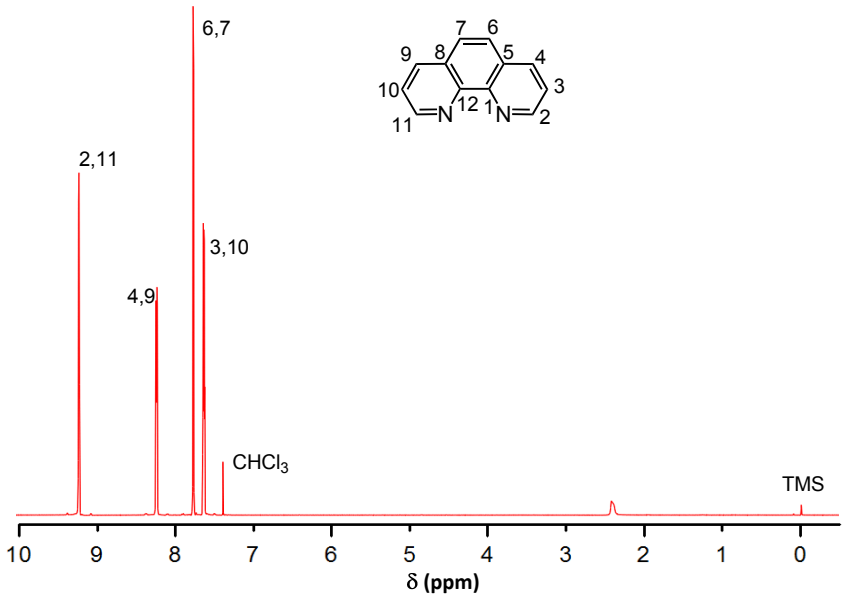


Fig. S7. ^{1}H NMR spectrum of **Phen**. [$CHCl_3$, 400 MHz, r.t.]

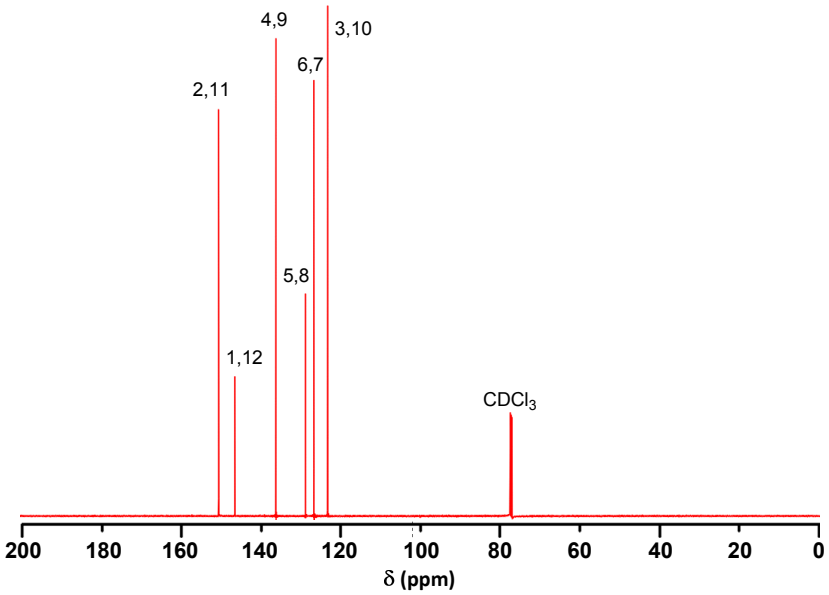


Fig. S8. ^{13}C NMR spectrum of **Phen**. [$CHCl_3$, 150 MHz, r.t.]

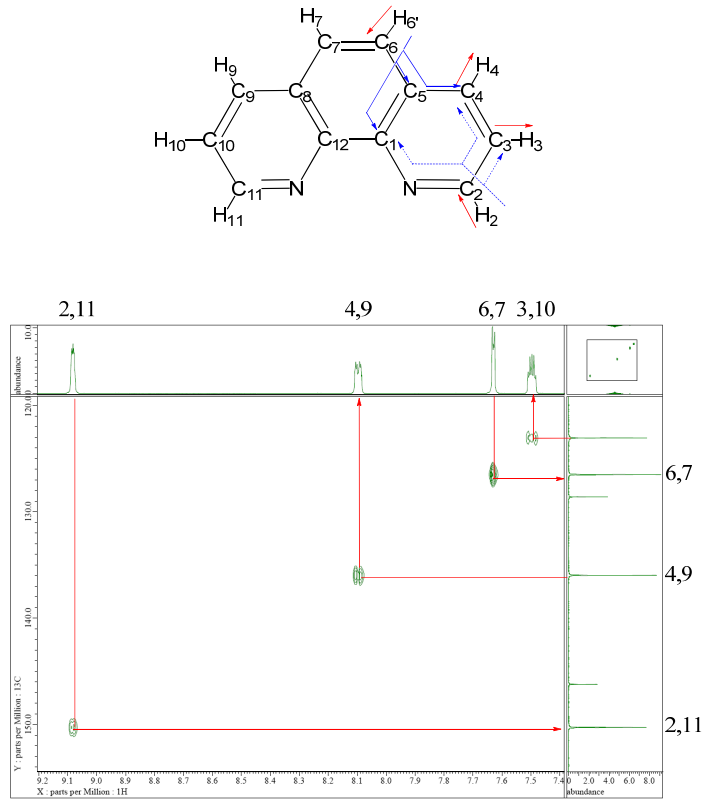


Fig. S9. ^{1}H-^{13}C HMQC NMR spectrum of **Phen**. [$CHCl_3$, 600 MHz, r.t.]
Red arrows indicate $^{1}J_{C\text{-}H}$ correlations.

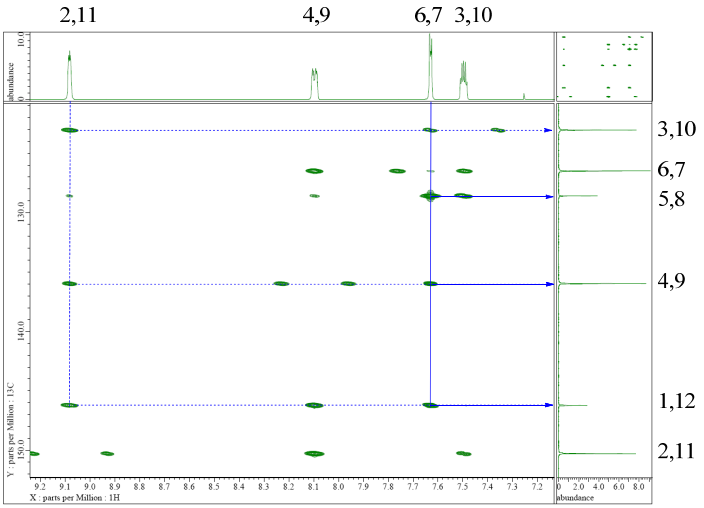


Fig. S10. ^{1}H-^{13}C HMBC NMR spectrum of **Phen**. [$CHCl_3$, 600 MHz, r.t.]
Blue arrows indicate $^{2}J_{C\text{-}H}$ and $^{3}J_{C\text{-}H}$ correlations.

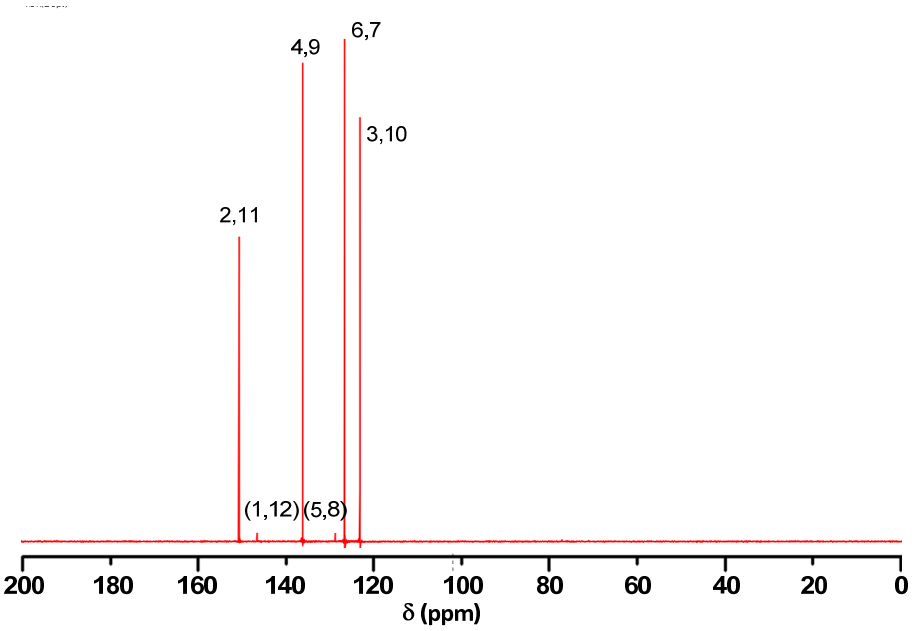
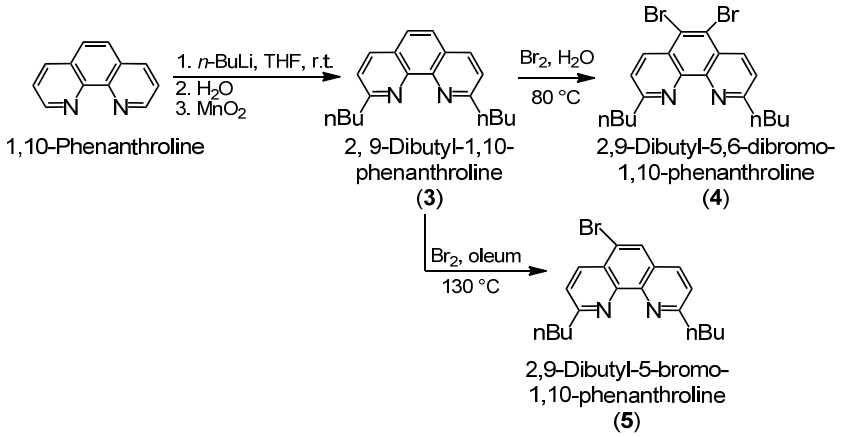


Fig. S11. DEPT(45^{o}) NMR spectrum of **Phen**. [$CHCl_3$, 150 MHz, r.t.]

2,9-Dibutyl-1,10-phenanthroline (3), **2,9-dibutyl-5,6-dibromo-1,10-phenanthroline (4),** and **2,9-dibutyl-5-bromo-1,10-phenanthroline (5)** were synthesized according to the method indicated in Scheme S2.



Scheme S2. Synthesis of **3**, **4** and **5.**

2,9-Dibutyl-1,10-phenanthroline (3). Anhydrous 1,10-phenanthroline (2.5 g, 14 mmol) was dissolved in dried THF (100 mL) in a dried 300-mL flask equipped with a three-way stopcock. A solution of *n*-butyllithium (1.59 M in *n*-hexane, 26 mL, 42 mmol) was added with a syringe to result in a dark red solution. The mixture was stirred for 18 h at room temperature, and the reaction was decomposed by adding water at 0 ^{o}C. The product was extracted with CH_2Cl_2. To the combined organic layer was added excess MnO_2 (9.56 g, 110 mmol). After the reaction mixture was stirred for 1 h, anhydrous Na_2SO_4 was added, and stirring was continued for additional 2 h at room temperature. The resulting mixture was filtered using filter paper and concentrated with a rotary evaporator. Silica gel chromatography (eluent: *n*-hexane-CH_2Cl_2 (1/1, v/v)) of the crude material afforded a yellow crystalline product. Yield 3.6 g, 12 mmol, 88%. M.p. 47-50^{o}C (lit.[6] 53-57^{o}C). Analytical data (Figs. S12-S14): IR (KBr, cm^{-1}) 3039, 2956, 2858, 1610, 1591, 1505, 1466, 1365, 1293, 1144; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2 Hz, 2H), 7.69 (s, 2H), 7.51 (d, J = 8.2 Hz, 2H), 3.33-3.08 (m, 4H), 1.91 (dt, J = 12.5, 7.8 Hz, 4H), 1.61-1.41 (m, 4H), 1.06-0.95 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.20, 145.40, 136.08, 126.98, 125.36, 122.23, 39.23, 31.80, 22.90, 14.04; ESIMS [m/z (%)] 293.20 (MH^+, 100); HRMS (ESI) calcd for $C_{20}H_{25}N_2$ 293.2012, found 293.2012.

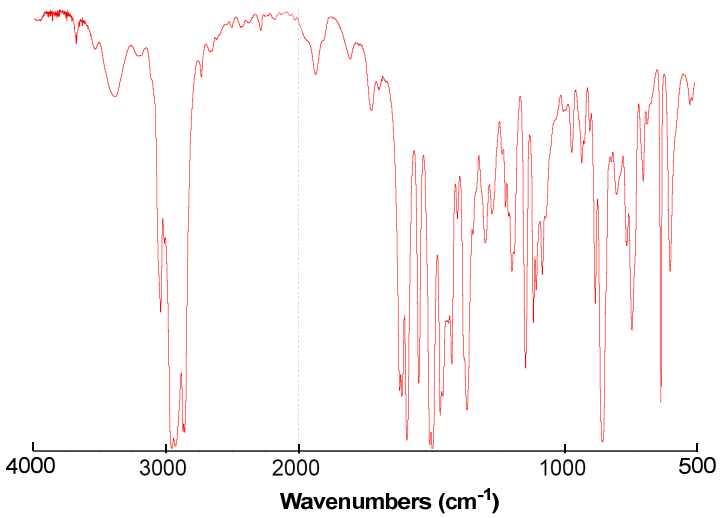


Fig. S12. FT-IR spectrum of **3.** [KBr pellet]

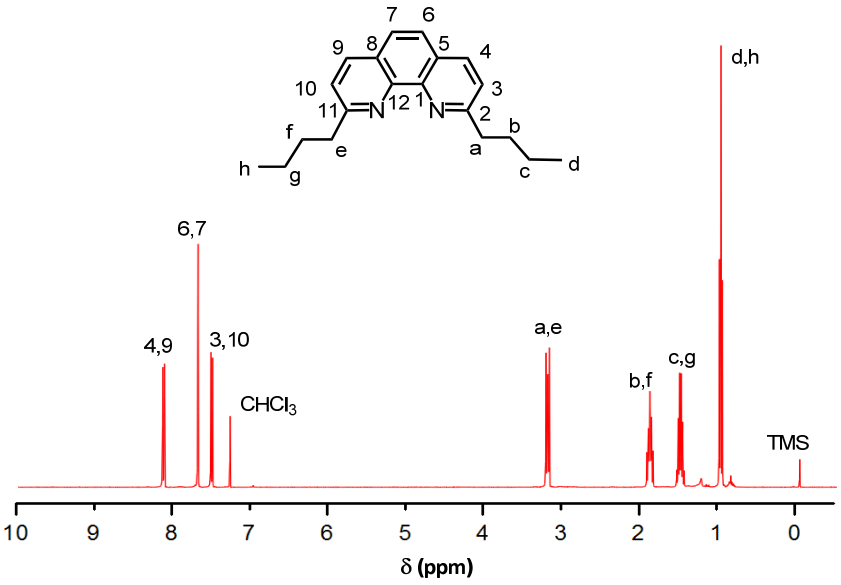


Fig. S13. ^{1}H NMR spectrum of **3**. [$CHCl_3$, 400 MHz, r.t.]

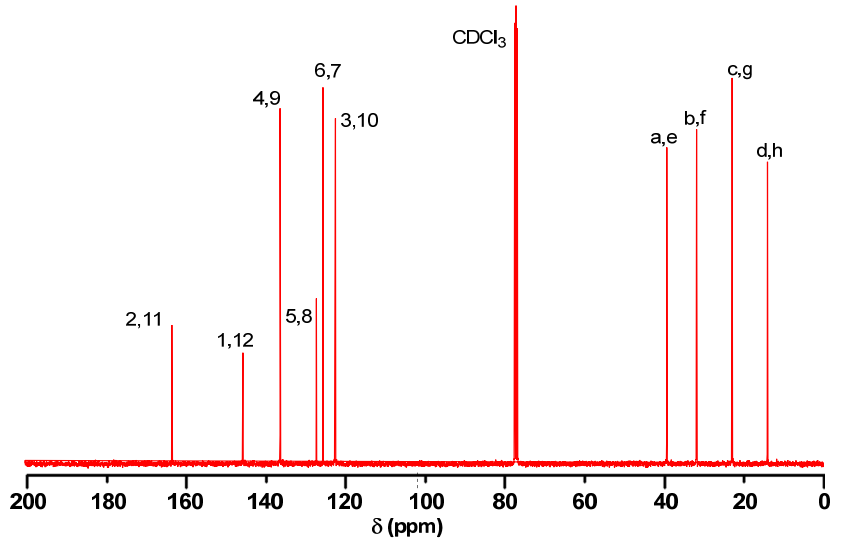


Fig. S14. ^{13}C NMR spectrum of **3**. [$CHCl_3$, 150 MHz, r.t.]

2D and 1D NMR spectra of DBPhen with signal assignments

The assignments in Figs. S13 and S14 were performed using the HMQC, HMBC, and DEPT(45º) spectra (Figs. S15-S17). Using the 2D spectra, the assignments were conducted starting from the signal of H6 and H7 which is the only singlet in the aromatic region. The signals of C1, C5, C8, C12, C2, and C11 were identified by the DEPT(45º) spectrum.

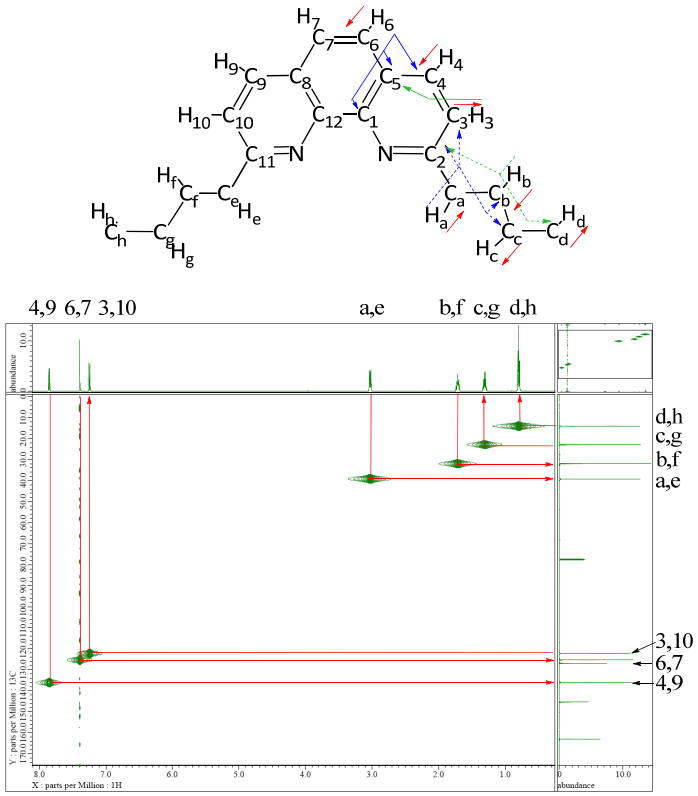


Fig. S15. ^{1}H-^{13}C HMQC NMR spectrum of **3**. [$CHCl_3$,600 MHz, r.t.]

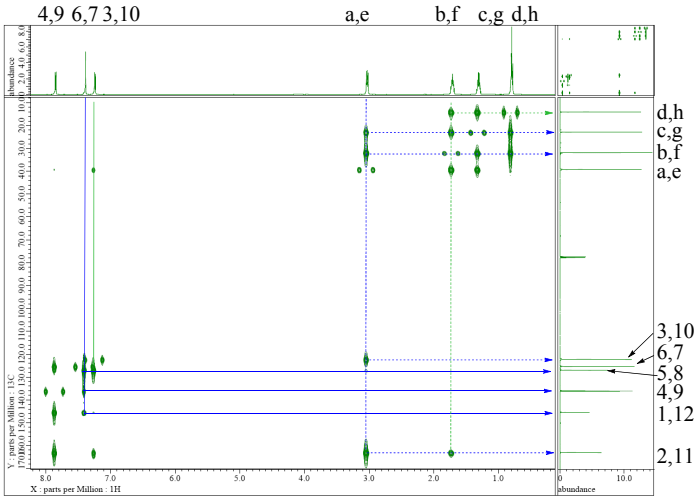


Fig. S16. ^{1}H-^{13}C HMBC NMR spectrum of **3**. [$CHCl_3$, 600 MHz, r.t.]

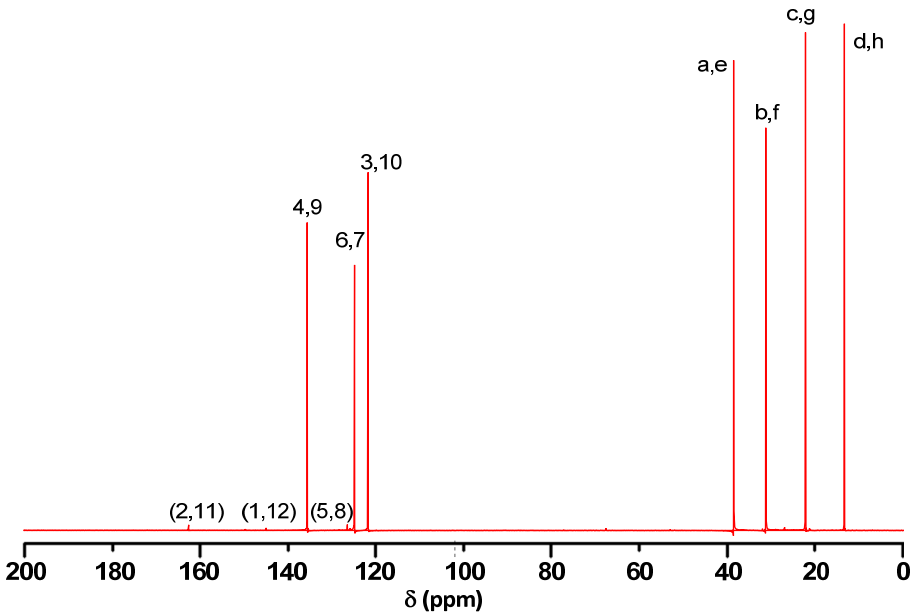


Fig. S17. DEPT(45^{o}) NMR spectrum of **3**. [$CHCl_3$, 150 MHz, r.t.]

2,9-Dibutyl-5,6-dibromo-1,10-phenanthroline (4). **3** (1.76 g, 6 mmol) was placed in a 100-mL two-neck flask with a stirring tip. A rubber septum and a condenser equipped with a tail gas absorber system (H_2O) were attached to the necks of the flask, and water (20 mL) was introduced to the system with a syringe. After bromine (10 mL, 190 mmol) was introduced through the rubber septum with a syringe, the mixture was stirred at 80°C for 24 h. The resulting dark brown mixture was treated with saturated aq. $Na_2S_2O_4$ (200 mL), and the product was extracted using $CHCl_3$. The combined brown organic phase was washed with aq. KOH (2 M, 200 mL) and water (200 mL), dried by Na_2SO_4, and concentrated using a rotary evaporator. The crude material was purified by silica gel column chromatography (eluent: *n*-hexane containing trimethylamine (5 vol.%)) to give a light brown solid. Yield 422 mg, 0.9 mmol, 16%. Analytical data (Figs. S18-S20): IR (KBr, cm^{-1}) 3039, 2957, 2871, 1590, 1540, 1482, 1367, 1294, 1152, 948, 827; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 3.27-3.15 (m, 4H), 1.97-1.86 (m, 4H), 1.53 (dp, J = 14.7, 7.3 Hz, 4H), 1.06-0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.29, 144.99, 137.22, 126.99, 123.93, 123.75, 38.80, 31.53, 22.81, 14.01; ESIMS [m/z (%)] 451.02 (MH^+, 100), 371.11 (74); HRMS (ESI) calcd for $C_{20}H_{23}N_2Br_2$ 449.0223, found 449.0226.

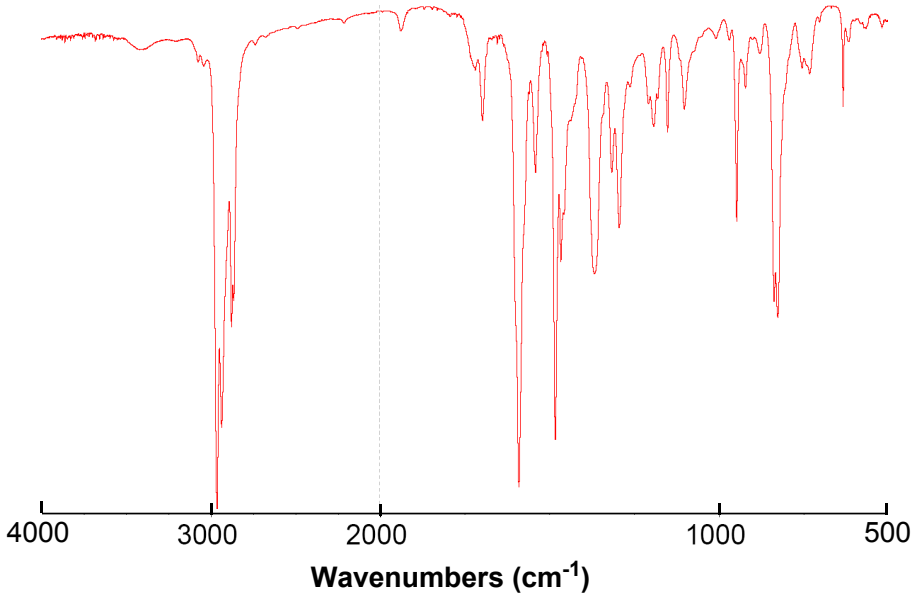


Fig. S18. FT-IR spectrum of **4**. [KBr pellet]

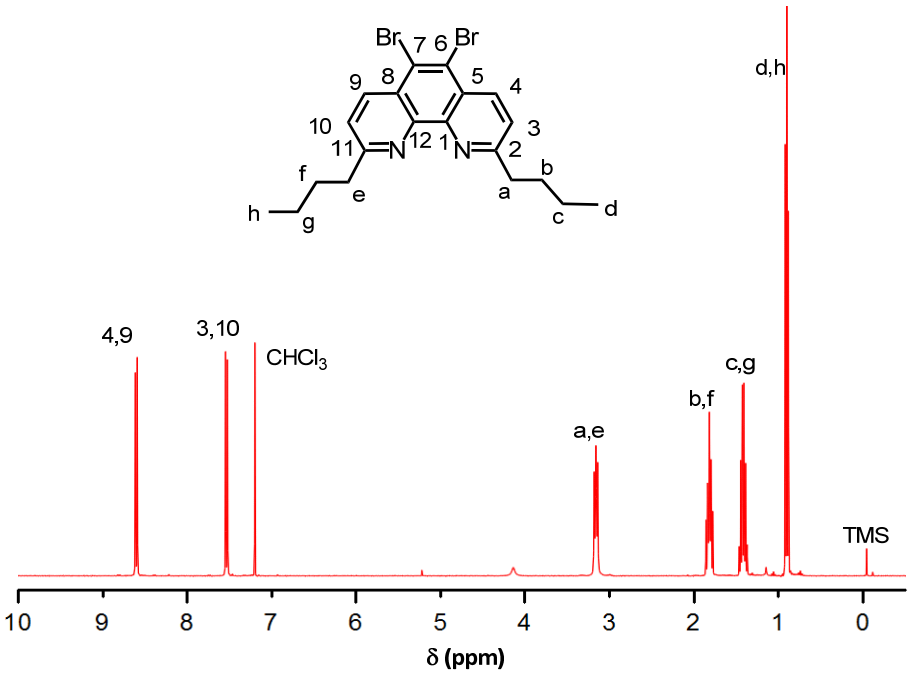


Fig.S19. ^{1}H NMR spectrum of **4**. [$CDCl_3$, 400 MHz, r.t.]

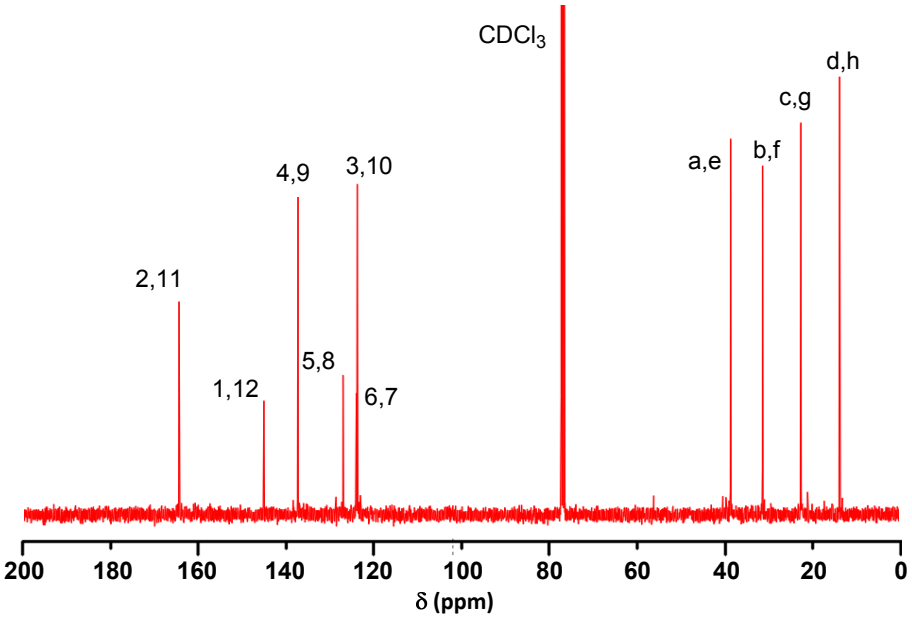


Fig. S20. ^{13}C NMR spectrum of **4**. [$CHCl_3$, 100 MHz, r.t.]

2,9-Dibutyl-5-bromo-1,10-phenanthroline (5). **3** (146 mg, 0.5 mmol) was placed in a 100-mL two-neck flask with a stirring tip. A rubber septum and a condenser equipped with a tail gas absorber system (H_2O) were attached to the necks of the flask. After oleum (30%, 0.85 mL) was introduced, the mixture was cooled in an ice bath. Bromine (0.1 mL, 2 mmol) was introduced through the rubber septum with a syringe, and the mixture was stirred at 130°C for 24 h. The resulting dark brown mixture was treated with saturated aq. $Na_2S_2O_4$ (50 mL), and the product was extracted using $CHCl_3$. The brown organic phase was washed with aq. KOH (50 mL) and water (100 mL), dried on Na_2SO_4, and concentrated using a rotary evaporator. The crude material was purified by silica gel column chromatography (eluent: *n*-hexane containing trimethylamine (2 vol.%)) to give a yellow solid. Yield 89 mg, 0.24 mmol, 47%. Analytic data (Figs. S21-S23): IR (KBr, cm^{-1}) 3043, 2956, 2871, 1604, 1544, 1495, 1380, 1292, 1146, 803; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 8.03 (s, 1H), 7.62-7.48 (m, 2H), 3.21 (ddd, J = 16.5, 8.8, 7.6 Hz, 4H), 1.97-1.84 (m, 4H), 1.59-1.45 (m, 4H), 1.05-0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.03, 163.77, 145.88, 144.82, 135.94, 135.25, 128.56, 127.27, 126.19, 123.10, 122.96, 119.62, 39.21, 38.90, 31.70, 22.86, 14.02; ESIMS [m/z (%)] 371.10 (MH^+, 100), 393.09 (35); HRMS (ESI) calcd for $C_{20}H_{24}N_2Br$ 371.1117, found 371.1116.

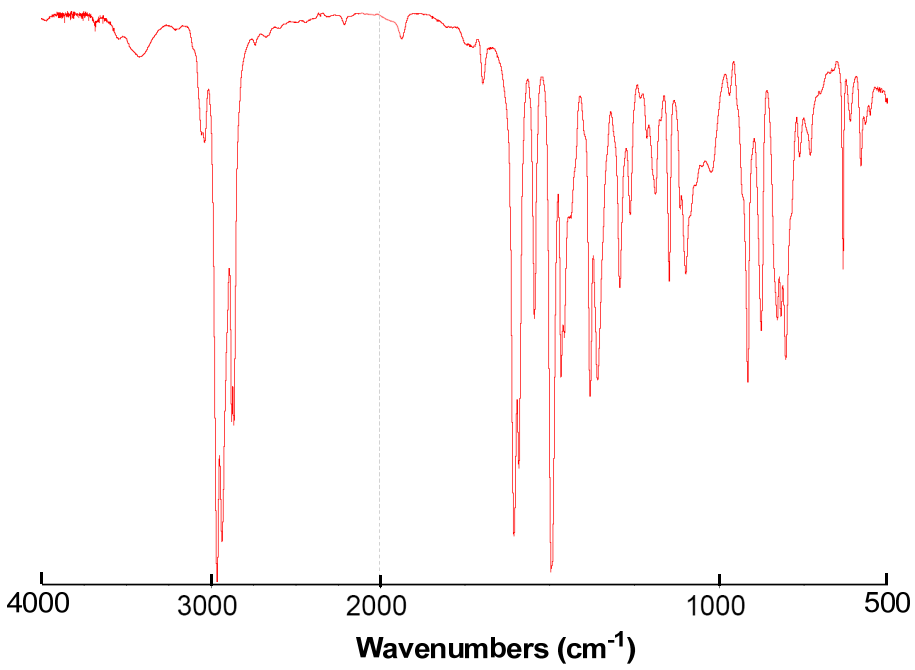


Fig. S21. FT-IR spectrum of **5**. [KBr pellet]

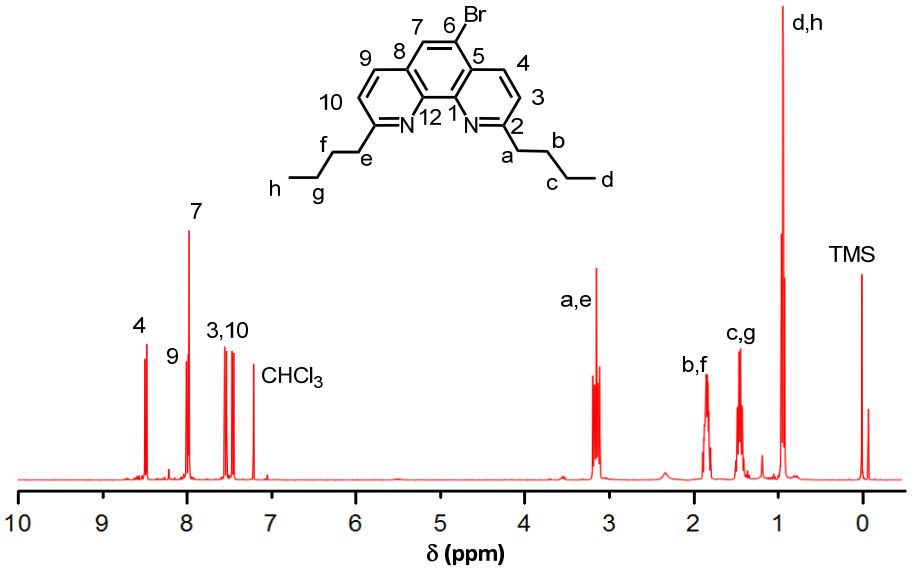


Fig.S22. ^{1}H NMR spectrum of **5**. [$CDCl_3$, 400 MHz, r.t.]

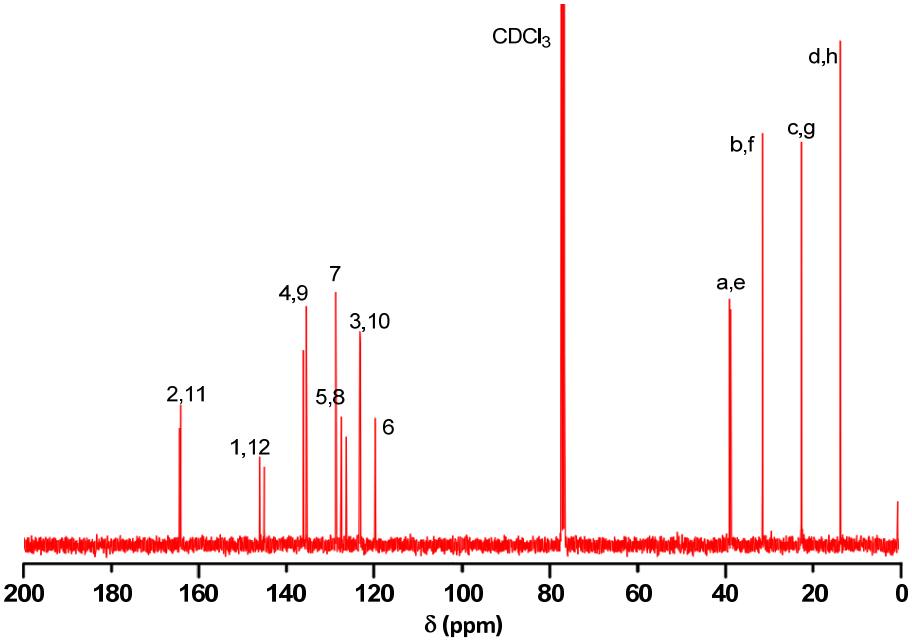
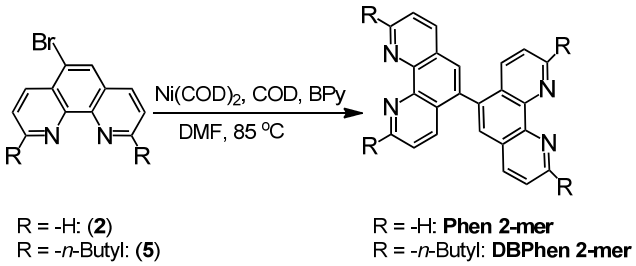


Fig.S23. ^{13}C NMR spectrum of **5**. [$CDCl_3$, 100 MHz, r.t.]

5,5'-Bi-1,10-phenanthroline (Phen dimer) and **5,5'-bi-2,9-dibutyl-1,10-phenanthroline (DBPhen dimer)** were prepared according to the method indicated in Scheme S3.



Scheme S3. Synthesis of Phen dimer and DBPhen dimer.

5,5'-Bi-1,10-phenanthroline (Phen dimer). A solution of 1,5-cyclooctadiene (0.07 mL, 0.6 mmol), 2,2'-bipyridine (86 mg, 0.6 mmol) and $Ni(COD)_2$ (186 mg, 0.6 mmol) in distilled DMF (3 mL) was placed under N_2 in a dried 20-mL flask equipped with a three-way stopcock. The mixture was heated to 85°C for 30 min to obtain a deep purple catalyst solution. **2** (129 mg, 0.5 mmol) dissolved in distilled DMF (9 mL) was introduced into the flask with a syringe with stirring. The reaction mixture was stirred at 85°C for 24 h, and **2** was completely consumed as confirmed by ^{1}H NMR. The resulted mixture was washed with aq. EDTA (pH = 9), and extracted with $CHCl_3$. The combined $CHCl_3$ layer was dried on Na_2SO_4, and concentrated using a rotary evaporator. Al_2O_3 column chromatography (eluent: $CHCl_3$) afforded a yellow solid. Yield 33 mg, 0.09 mmol, 35%.[7] Analytic data (Figs. S24-S27): IR (KBr, cm^{-1}) 3031, 2955, 1612, 1562, 1505, 1419, 1262, 1148, 743; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (dd, J = 4.3, 1.6 Hz, 2H), 9.23 (dd, J = 4.2, 1.5 Hz, 2H), 8.32 (dd, J = 8.0, 1.4 Hz, 2H), 7.95 (s, 2H), 7.81-7.71 (m, 4H), 7.48 (dd, J = 8.3, 4.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.87, 150.51, 146.18, 146.08, 136.05, 135.25, 134.48, 128.54, 128.07, 127.95, 123.57, 123.14; ESIMS [m/z (%)] 359.13 (MH^+, 100), 360.13 (25), 252.11 (10); HRMS (ESI) calcd for $C_{24}H_{14}N_4 + H^+$ 359.1291, found 359.1924.

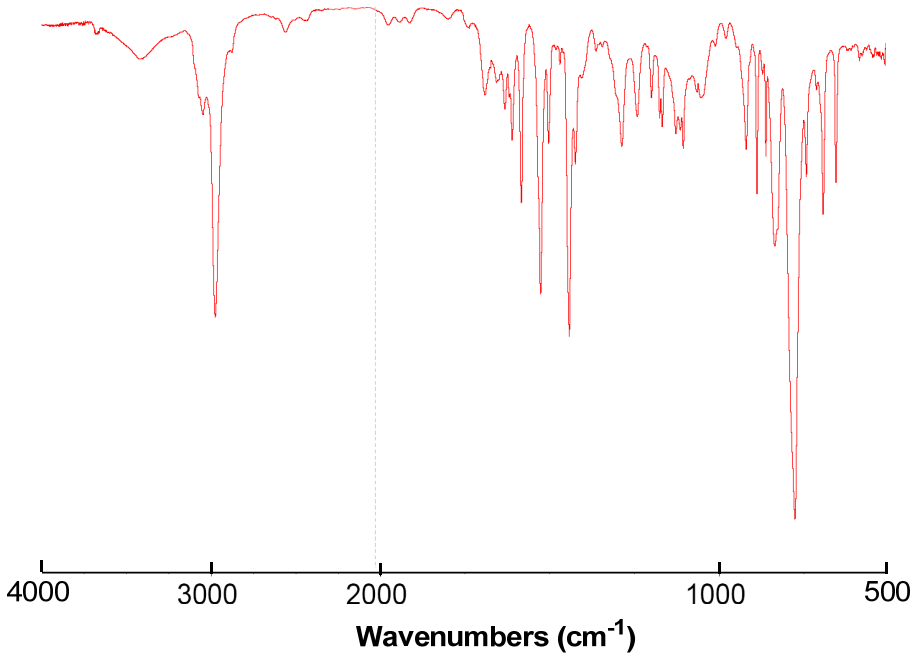


Fig. S24. FT-IR spectrum of **Phen dimer**. [KBr pellet]

2D and 1D NMR spectra of Phen dimer with signal assignments

The assignments in Figs. S25-S27 were performed using the HMQC, HMBC, and DEPT(45º) spectra (Figs. S28-S31). Using the 2D spectra, the assignments were conducted starting from the signal of H6 and H7 which is the only singlet in the aromatic region. The signals of C1, C5, C8, C12, C2, and C11 were identified by the DEPT(45º) spectrum.

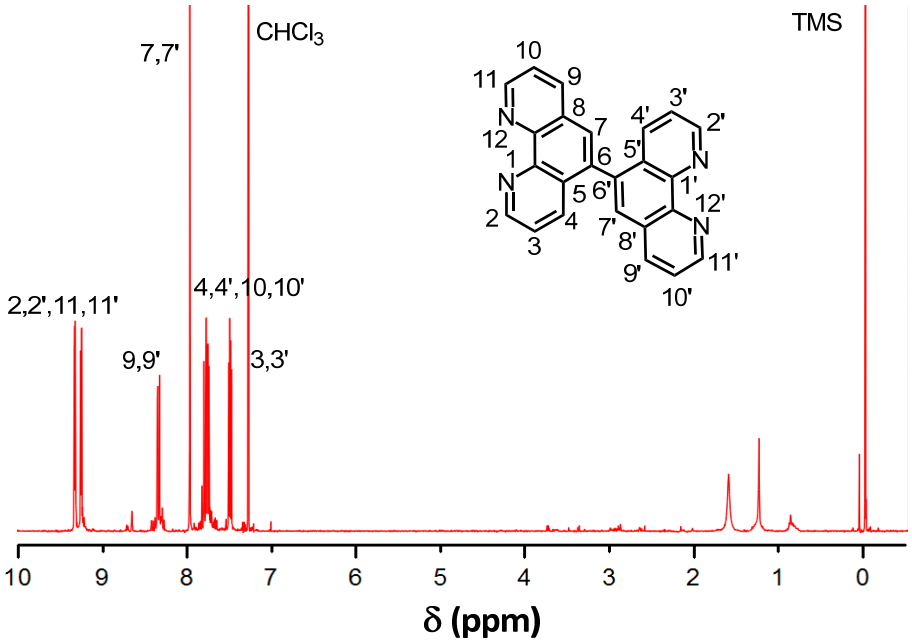


Fig. S25. ^{1}H NMR spectrum of **Phen dimer**. [$CHCl_3$, 400 MHz, r.t.]

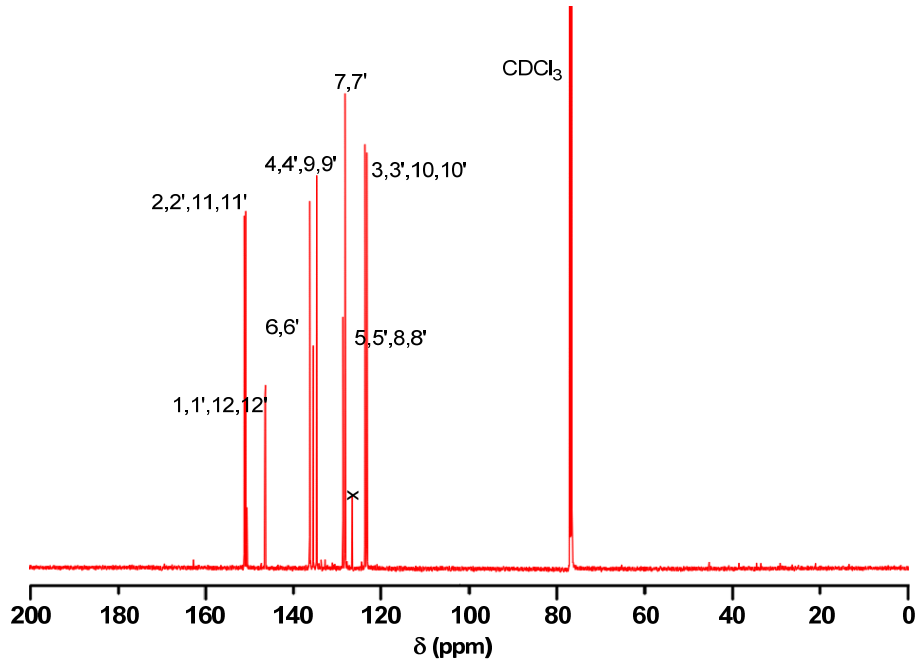


Fig.S26. ^{13}C NMR spectra of **Phen dimer**. x denotes impurities. [$CDCl_3$, 150 MHz, r.t.]

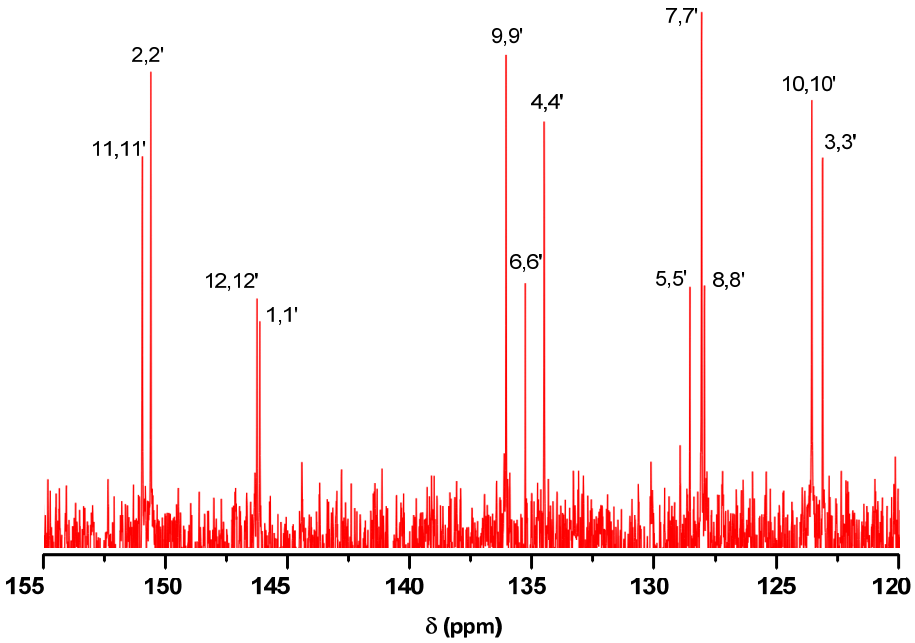


Fig.S27. ^{13}C NMR spectra of **Phen dimer** (120-155 ppm). [$CDCl_3$, 150 MHz, r.t.]

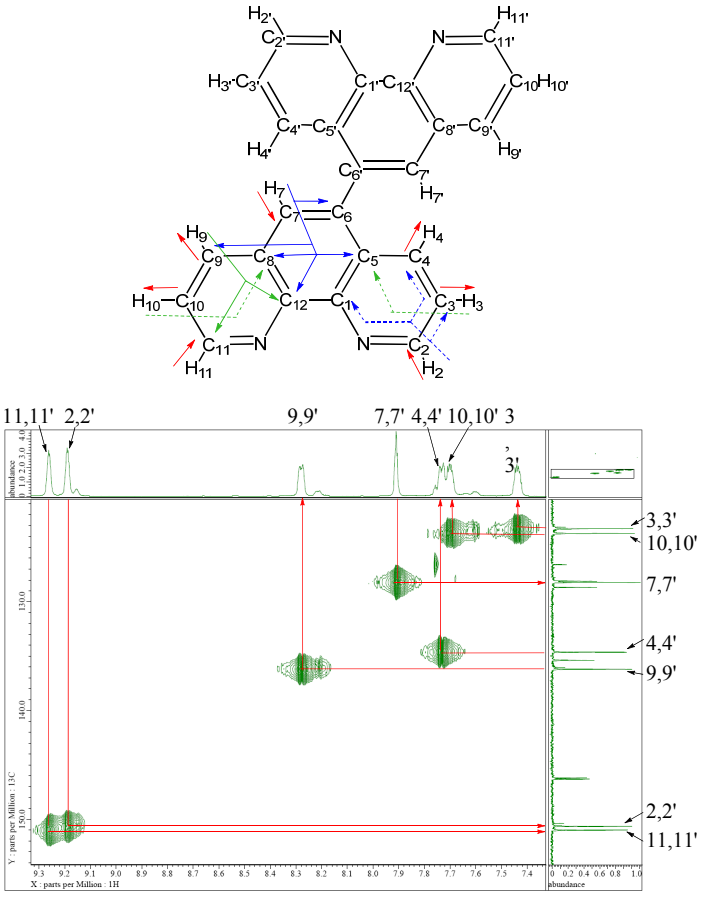


Fig. S28. ^{1}H-^{13}C HMQC NMR spectrum of **Phen dimer**. [$CHCl_3$, 600 MHz, r.t.]

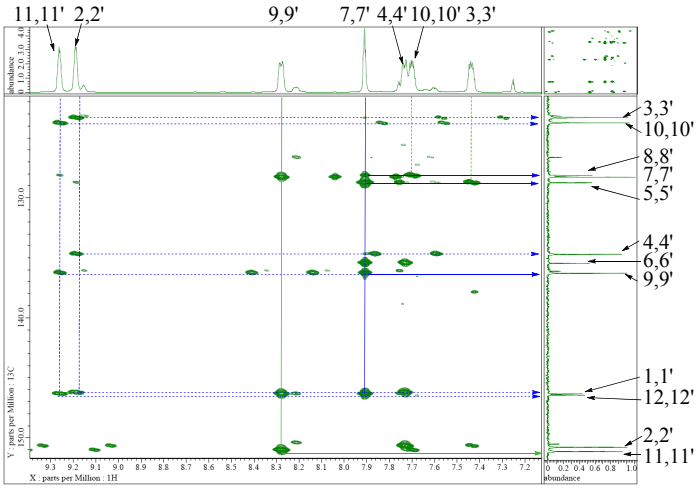


Fig. S29. ^{1}H-^{13}C HMBC NMR spectrum of **Phen dimer**. [$CHCl_3$,600 MHz, r.t.]

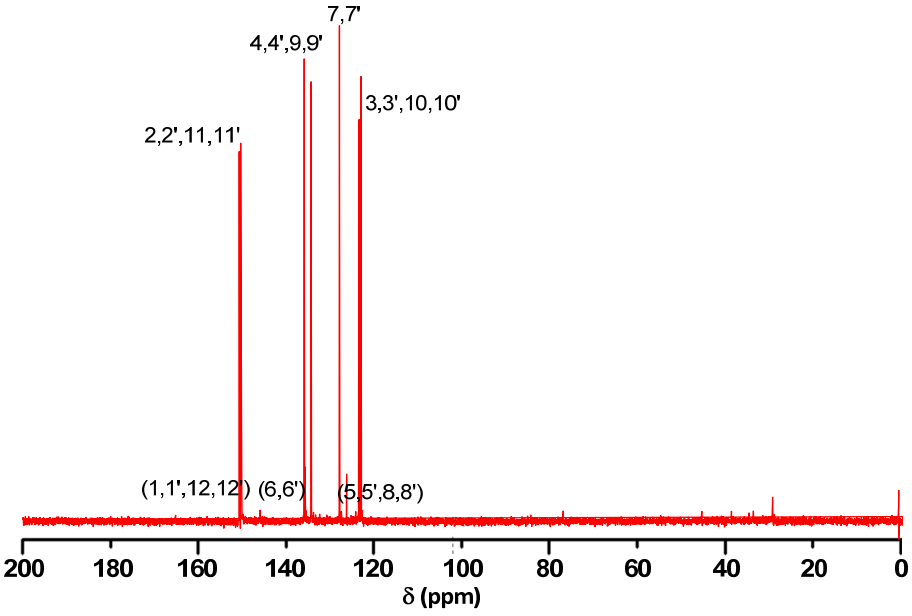


Fig. S30 . DEPT(45^{o}) NMR spectrum of **Phen dimer**. [$CHCl_3$, 150 MHz, r.t.]

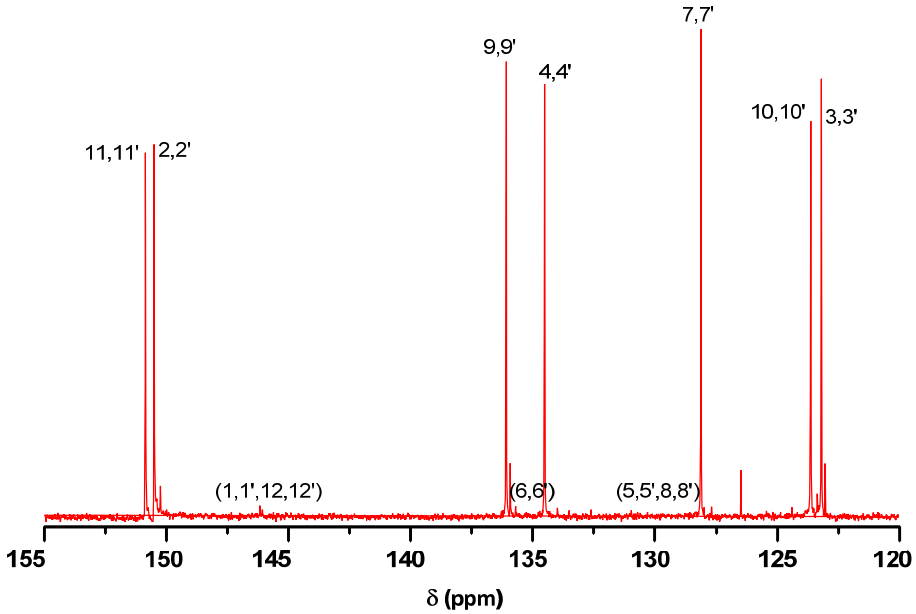


Fig. S31. DEPT(45^{o}) NMR spectrum of **Phen dimer** (120-155 ppm). [$CHCl_3$, 150 MHz, r.t.]

5,5'-Bi-2,9-dibutyl-1,10-phenanthroline (DBPhen dimer). A solution of 1,5-cyclooctadiene (0.05 mL, 0.4 mmol), 2,2'-bipyridine (63 mg, 0.4 mmol) and $Ni(COD)_2$ (110 mg, 0.4 mmol) in distilled DMF (4 mL) was placed in a dried 20-mL flask equipped with a three-way stopcock under N_2. The mixture was heated to 85°C for 30 min to obtain a deep purple catalyst solution. **5** (100 mg, 0.3 mmol) dissolved in distilled DMF (6 mL) was introduced into the flask with a syringe with stirring. The reaction mixture was stirred at 85°C for 24 h, and **5** was completely consumed as confirmed by ^{1}H NMR. The resulted mixture was washed with aq. EDTA (pH = 9), and extracted with $CHCl_3$. The combined $CHCl_3$ layer was dried on Na_2SO_4, and concentrated using a rotary evaporator. Al_2O_3 column chromatography (eluent: $CHCl_3$-*n*-hexane (25/75, v/v)) afforded a yellow solid. Yield 16 mg, 0.03 mmol, 10%. Analytic data (Figs. S32-S35): IR (KBr, cm^{-1}) 3030, 2957, 2857, 1604, 1547, 1489, 1378, 1292, 1154, 884; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 2H), 7.81 (s, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 3.25 (ddd, J = 29.5, 11.7, 4.8 Hz, 8H), 1.93 (tdd, J = 15.7, 11.0, 7.9 Hz, 8H), 1.62-1.46 (m, 8H), 1.02 (dt, J = 19.6, 7.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.78, 163.39, 145.36, 145.28, 136.23, 134.78, 134.69, 127.14, 126.93, 126.49, 122.86, 122.41, 39.31, 31.95, 22.92, 14.10; ESIMS [m/z (%)] 583.38 (M^+, 100), 584.39 (45); HRMS (ESI) calcd for $C_{40}H_{46}N_4 + H^+$ 583.3795, found 583.3799.

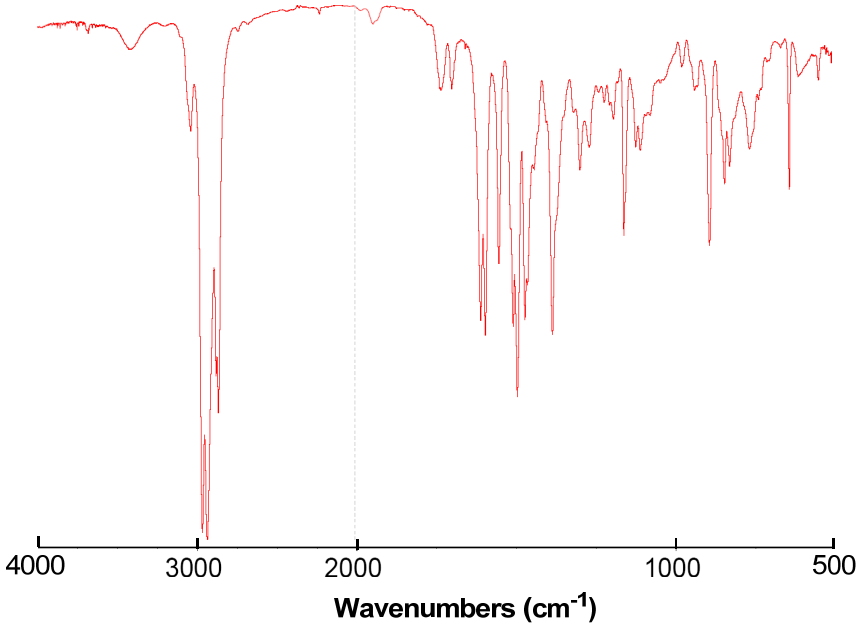


Fig. S32. FT-IR spectrum of **DBPhen dimer**. [KBr pellet]

2D and 1D NMR spectra of DBPhen dimer with signal assignments

The assignments in Figs. S33-S35 were performed using the HMQC, HMBC, and DEPT(45º) spectra (Figs. S36-S39). Using the 2D spectra, the assignments were conducted starting from the signal of H6 and H7 which is the only singlet in the aromatic region. The signals of C1, C5, C8, C6, C12, C2, C11, C1', C5', C8', C6', C12', C2', and C11' were identified by the DEPT(45º) spectrum.

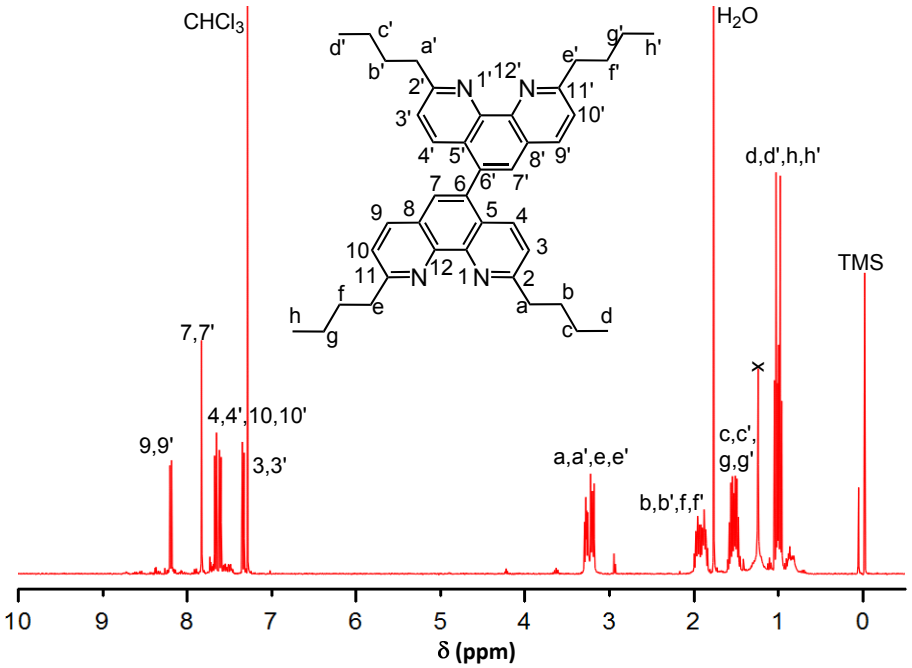


Fig.S33. ^{1}H NMR spectrum of **DBPhen dimer**. x denotes impurities. [$CDCl_3$, 400MHz, r.t.]

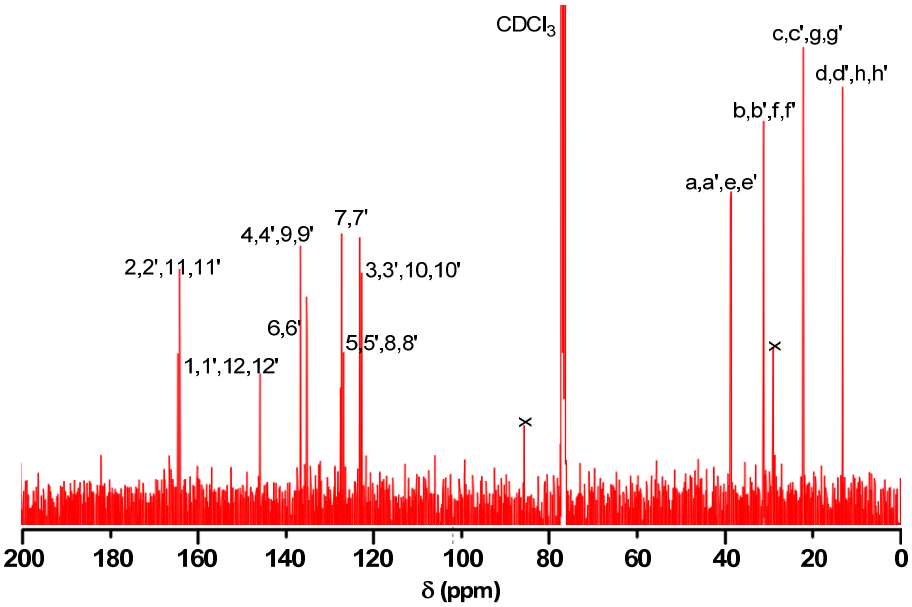


Fig.S34. ^{13}C NMR spectrum of **DBPhen dimer**. x denotes impurities. [$CDCl_3$, 150MHz, r.t.]

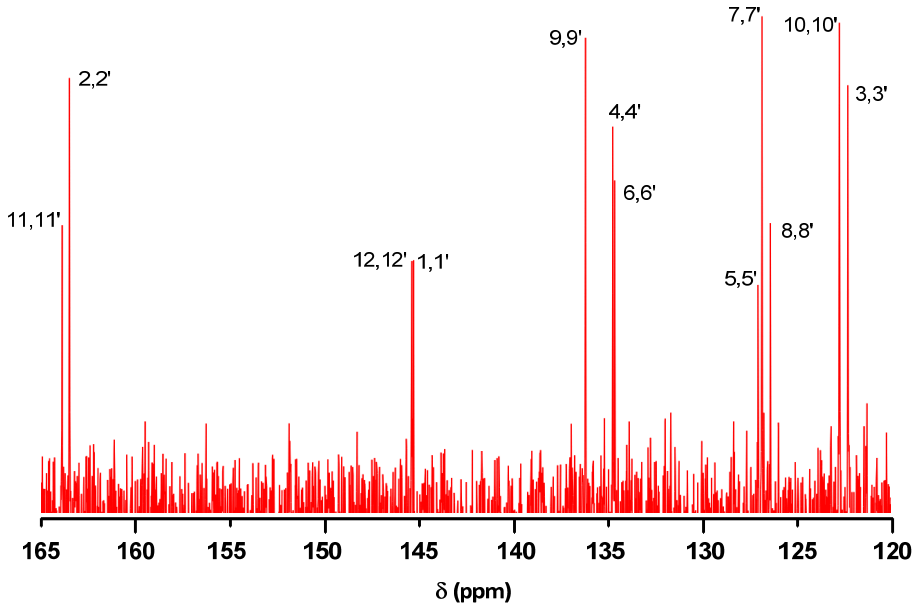


Fig.S35. ^{13}C NMR spectrum of **DBPhen dimer** (120-165 ppm). [$CDCl_3$, 150MHz, r.t.]

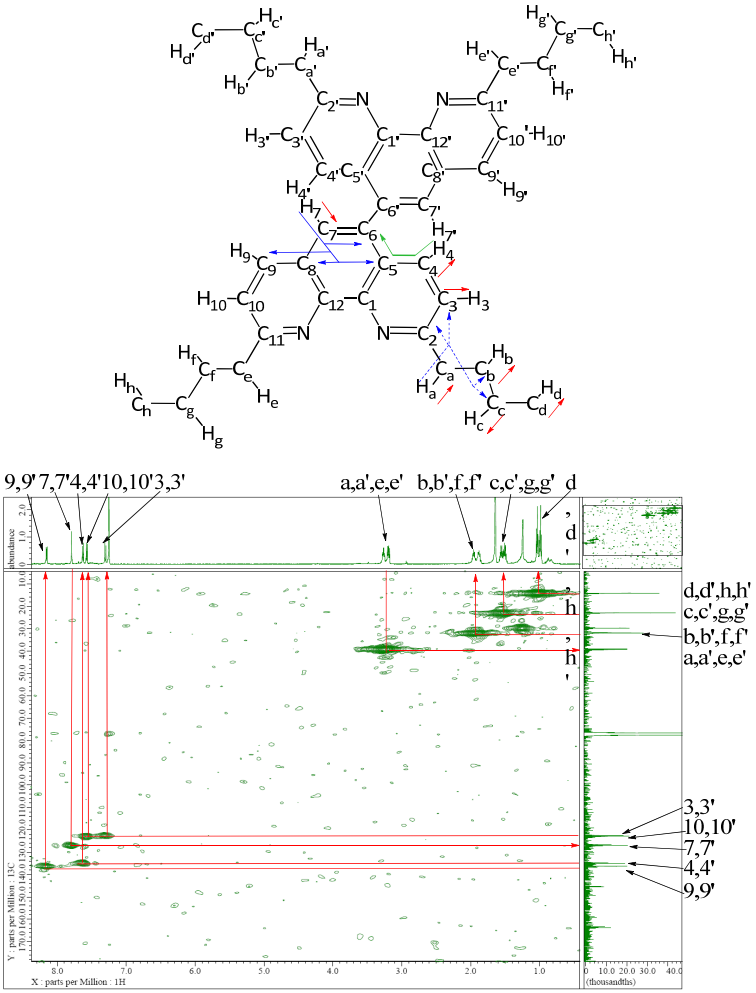


Fig. S36. ^{1}H-^{13}C HMQC NMR spectrum of **DBPhen dimer**. [$CHCl_3$,600 MHz, r.t.]

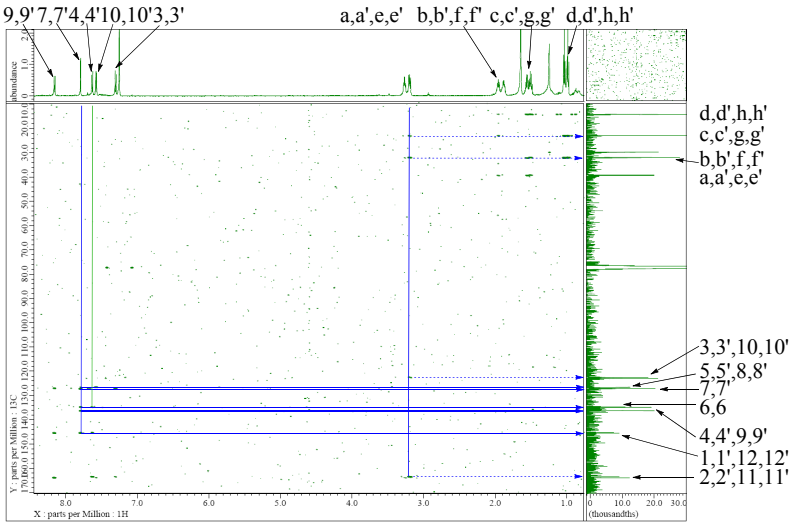


Fig. S37. ^{1}H-^{13}C HMBC NMR spectrum of **DBPhen dimer**. [$CHCl_3$,600 MHz, r.t.]

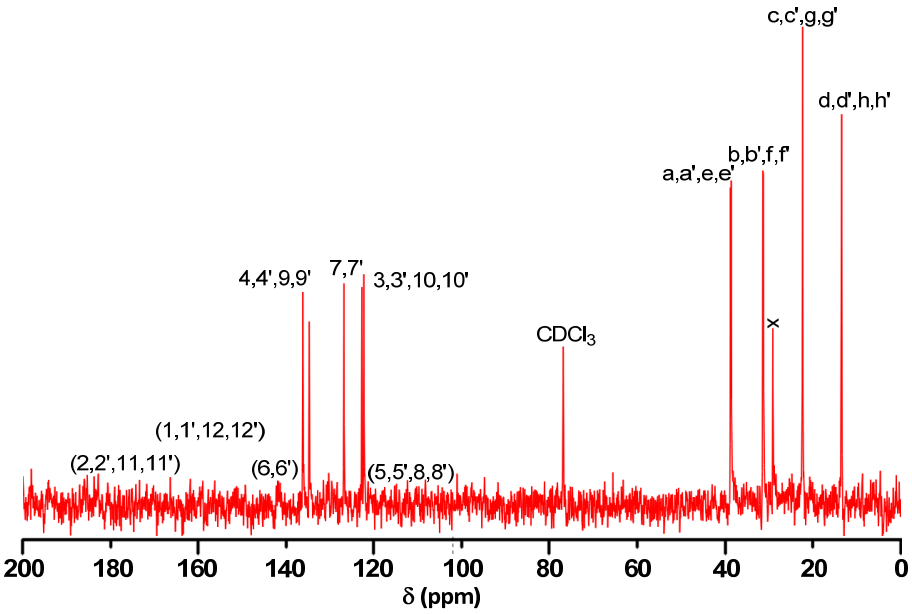


Fig. S38. DEPT(45^{o}) NMR spectrum of **DBPhen dimer**. x denotes impurities. [$CHCl_3$, 150 MHz, r.t.]

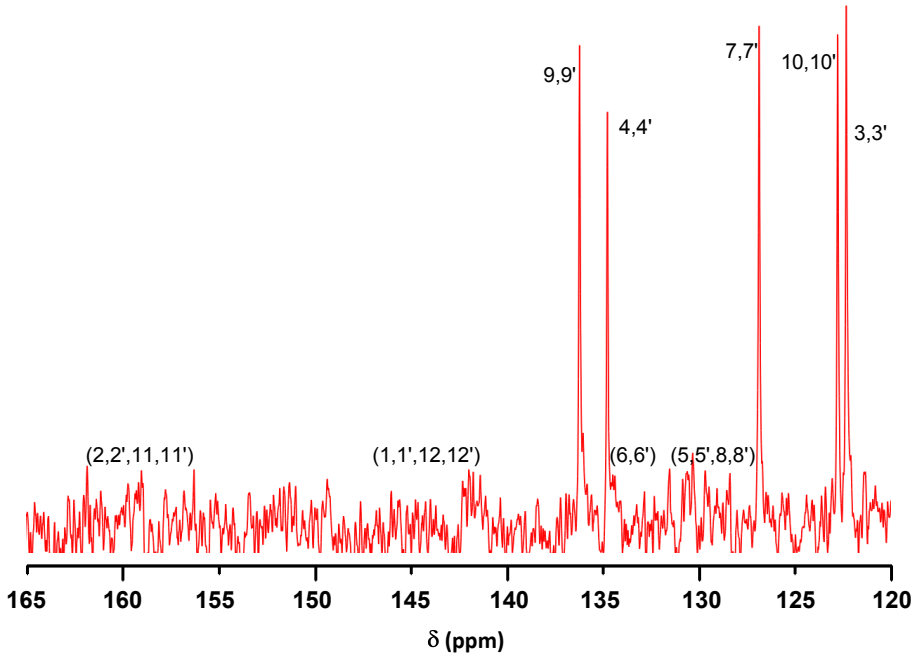


Fig. S39. DEPT(45^{o}) NMR spectrum of **DBPhen dimer** (120-165 ppm). [$CHCl_3$, 150 MHz, r.t.]

Polymerization and Polymer Analysis

As a typical procedure, polymerization of 2,9-dibutyl-5,6-dibromo-1,10-phenanthroline in entry 4 in Table 1 is described. A solution of 1,5-cyclooctadiene (0.18 mL, 1.5 mmol), 2,2'-bipyridine (236 mg, 1.5 mmol) and $Ni(COD)_2$ (420 mg, 1.5 mmol) in distilled DMF (3 mL) was placed in a dried 20-mL flask equipped with a three-way stopcock under N_2. The mixture was heated to 85°C for 30 min to obtain a deep purple catalyst solution. **4** (223 mg, 0.5 mmol) dissolved in distilled DMF (9 mL) was introduced into the flask with stirring. The polymerization reaction was carried out at 85°C for 24 h, and volatile components were removed under vacuum to yield a deep brown solid. The solid was washed with toluene (20 mL), aq. EDTA (pH = 5) (40 mL), aq. EDTA (pH = 9) (40 mL), aq. KOH (2 M) (20 mL), distilled water (100 mL), and benzene (20 mL) in this order. In washing, the solid material was soaked in these solvents at 80°C for ca. 10 min and collected with a centrifuge. The washed material was dried under vacuum to result in a dark brown powder. Yield 119 mg, 0.41 mmol, 82%. Analytical data: M_n 2700, M_w/M_n 5.32; IR (KBr, cm^{-1}) 2950, 2874, 1603, 1459, 1376; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.02, 3.23, 1.89, 1.54, 1.01; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.74, 145.27, 136.36, 134.33, 126.99, 122.98, 38.98, 31.81, 22.74, 13.95.

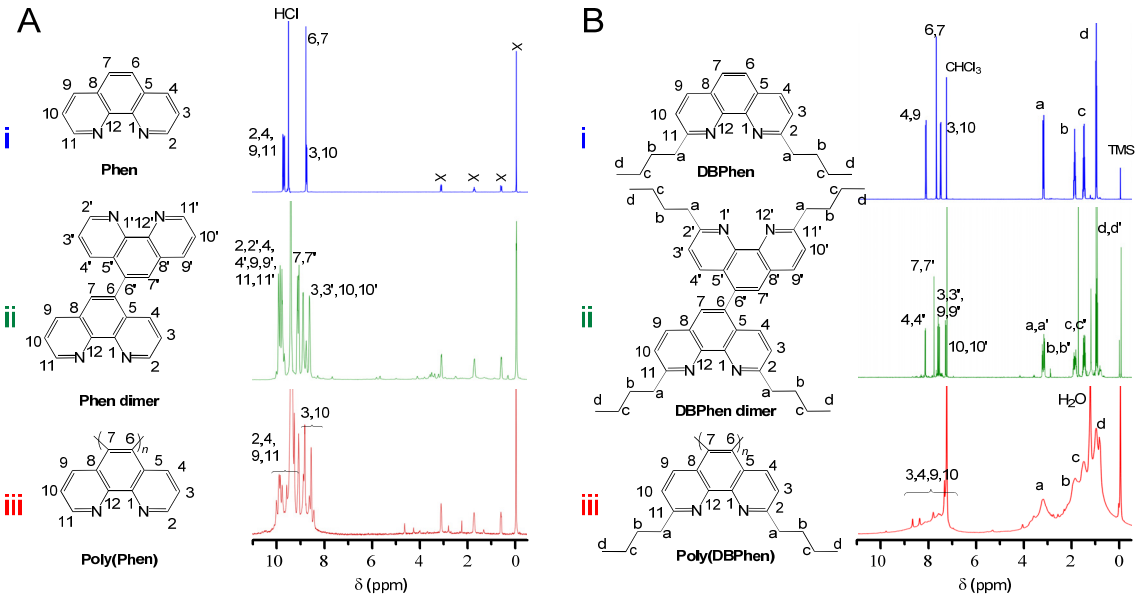


Fig. S40. 400 MHz ^1H NMR spectra of **Phen** (i), **Phen dimer** (ii) and **poly(Phen)** (entry 1 in Table 1) (iii) (panel A) and those of **DBPhen** (i), **DBPhen dimer** (ii) and **poly(DBPhen)** (entry 3 in Table 1) (iii) (panel B). The spectra in A were taken in D_2O containing 35% DCl with 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt (DDS) standard at room temperature and those in B in $CDCl_3$ at room temperature. x denotes DDS signals.

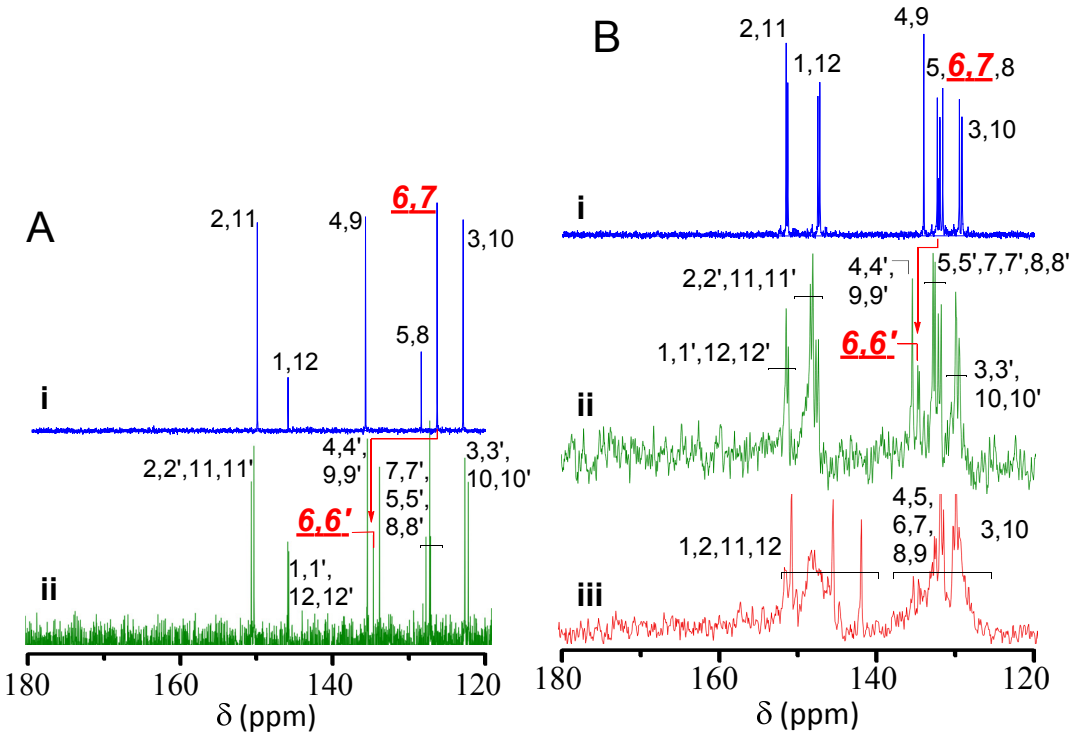


Fig. S41. 400 MHz ^{13}C NMR spectra of **Phen** (i), **Phen dimer** (ii) and **poly(Phen)** (entry 1 in Table 1) (iii) (panel A). The spectra in A were taken in $CDCl_3$ at room temperature and those in B in D_2O containing 35% DCl with 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt (DDS) standard at room temperature.

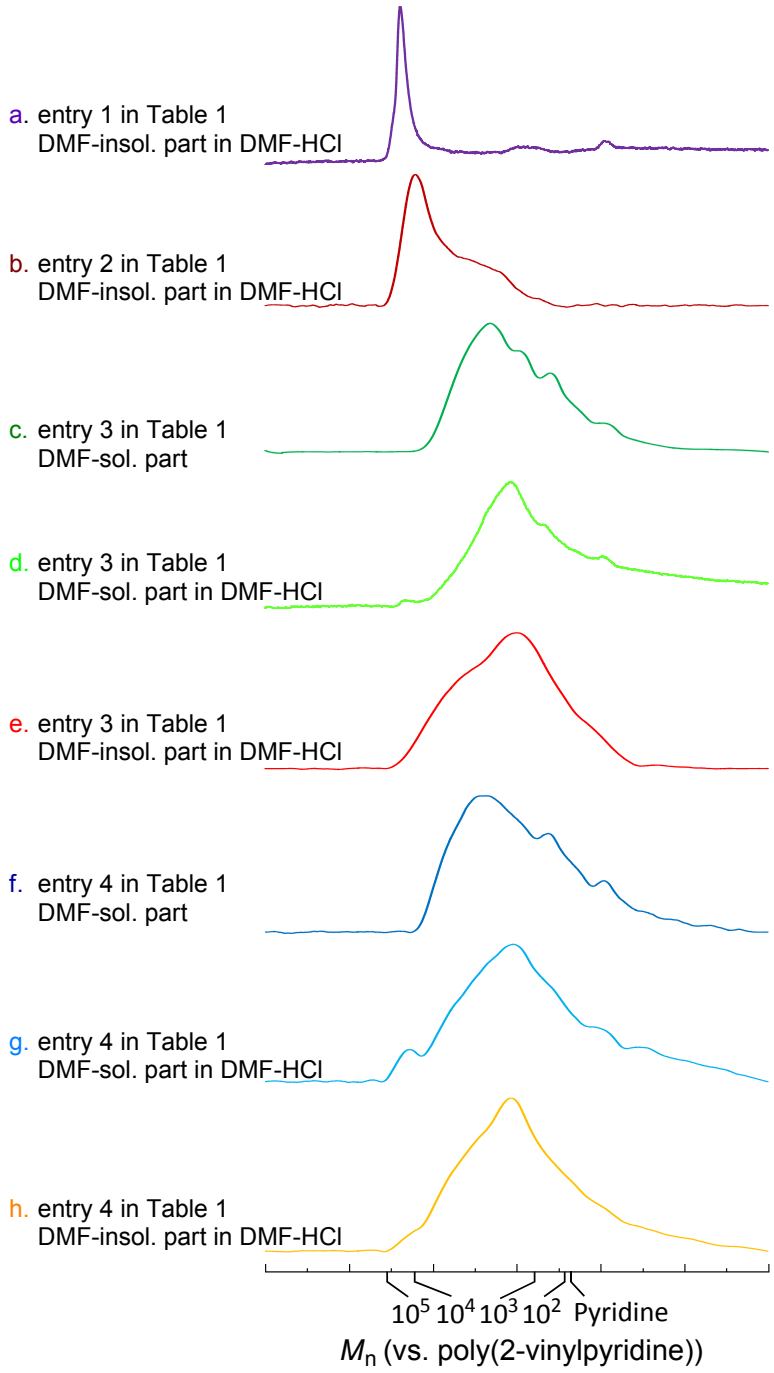


Fig. S42. SEC traces of **poly(Phen)** and **poly(DBPhen)** samples from Table 1: DMF-insoluble part in entry 1 (a), DMF-insoluble part in entry 2 (b), DMF-soluble part in entry 3 (c,d), DMF-insoluble part in entry 3 (e), DMF-soluble part in entry 3 (f,g), and DMF-insoluble part in entry 3 (h). Samples for injection were prepared in pure DMF (1 mL) for c and f and in DMF (1 mL) containing conc. aq. HCl (0.01 mL) for a, b, d, e, g, h. [column, Shodex Asahapak GF-310HQ; eluent, DMF containing LiCl (30 mM); flow rate, 0.5 mL/min; detection, absorbance at 275 nm; standard sample, poly(2-vinylpyridine) and pyridine]

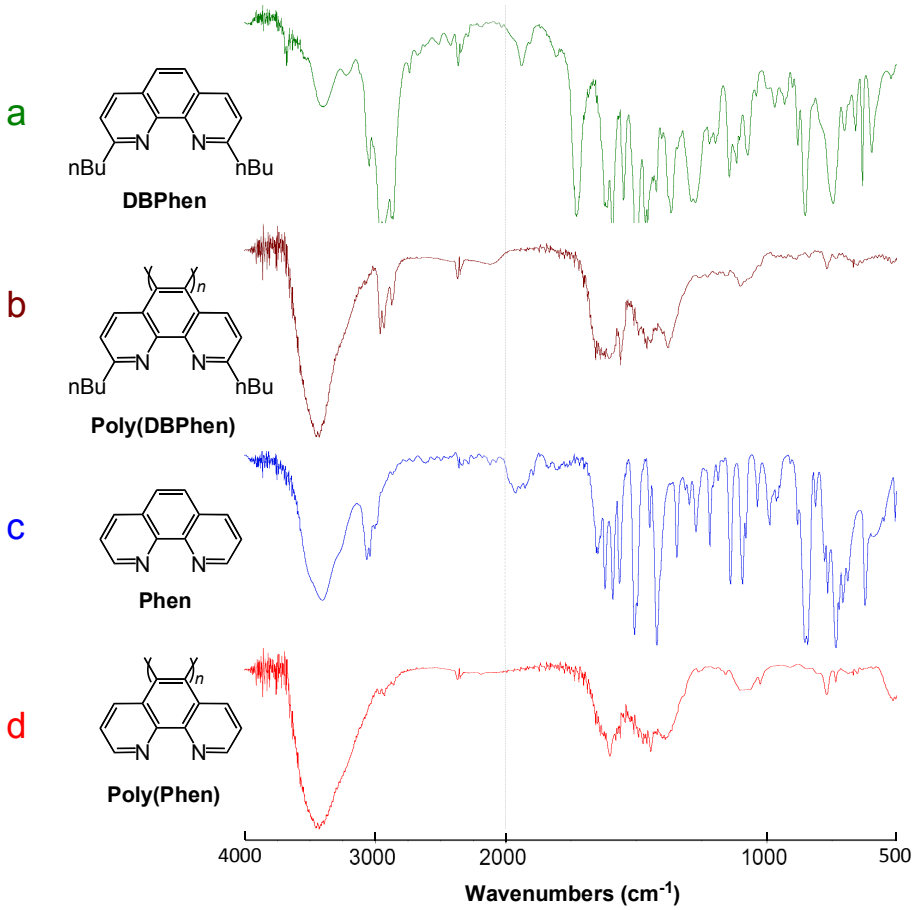


Fig. S43. FT-IR spectra of **DBPhen** (a), **poly(DBPhen)** (entry 1 in Table 1) (b) , Phen (c), and **poly(Phen)** (entry 3 in Table 1) (c). [KBr pellet]

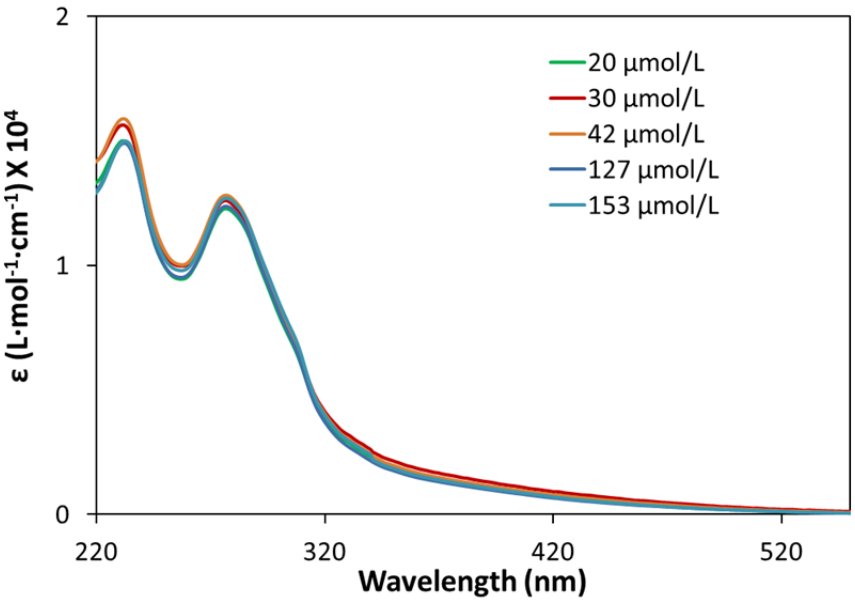


Fig. S44. UV spectra of **poly(DBPhen)** (entry 3 in Table 1) at different concentrations. [MeOH, 10-mm cell]

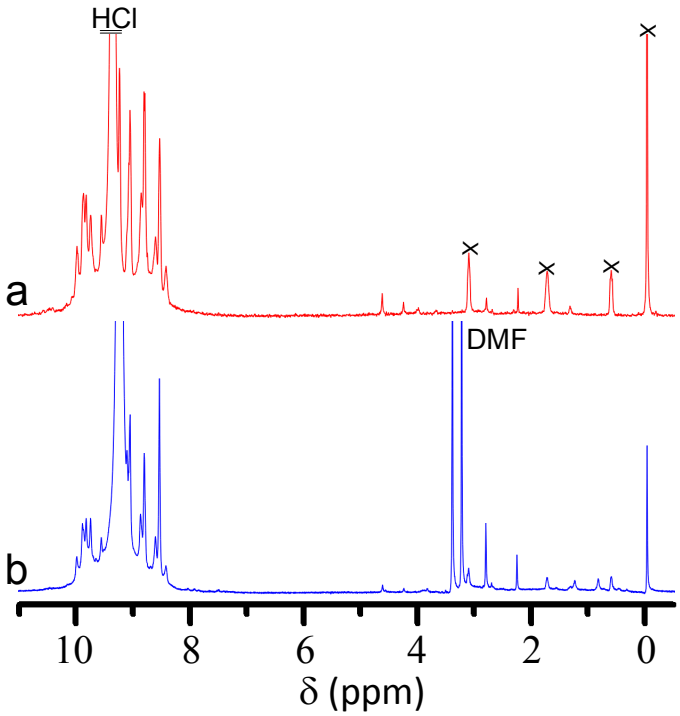


Fig. S45. 400 MHz ^{1}H NMR spectra of **poly(Phen)** (entry 1 (a), entry 2(b) in Table 1). [D_2O containing 35% DCl with 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt (DDS) standard, r.t., x denotes DDS signals]

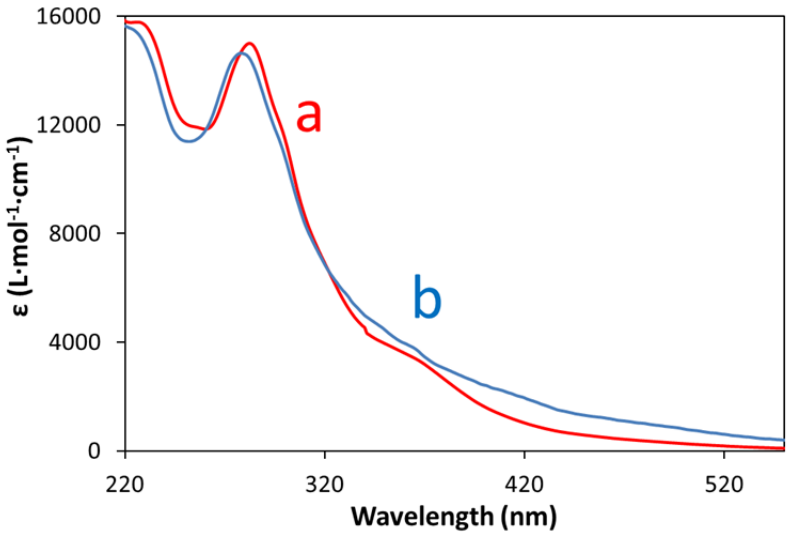
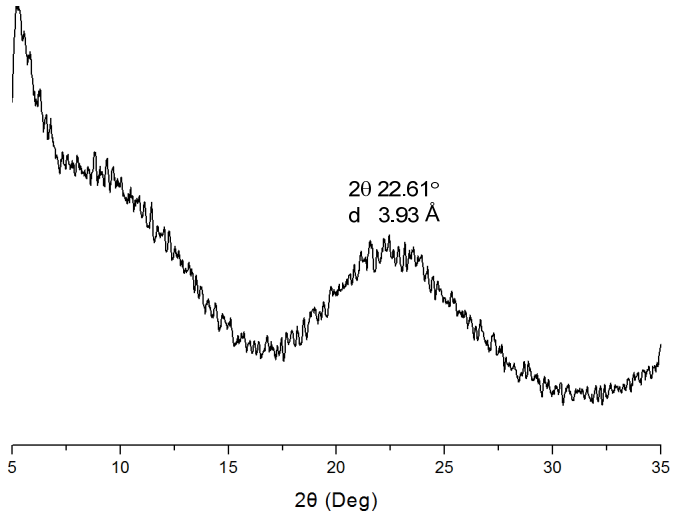


Fig. S46. UV spectra of **poly(Phen)** (entry 1 (a), entry 2(b) in table 1). [conc. aq. HCl, 0.06 mmol/L, 2 mm cell, r.t.]

A. Poly(Phen)



B. Poly(DBPhen)

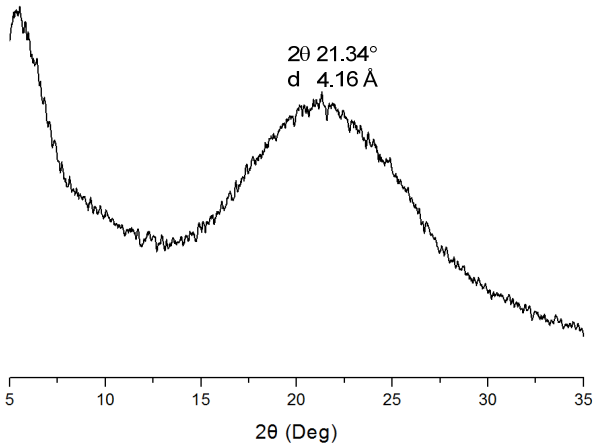
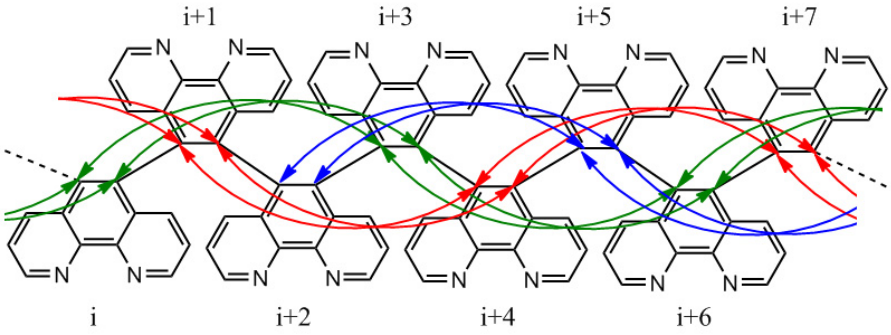
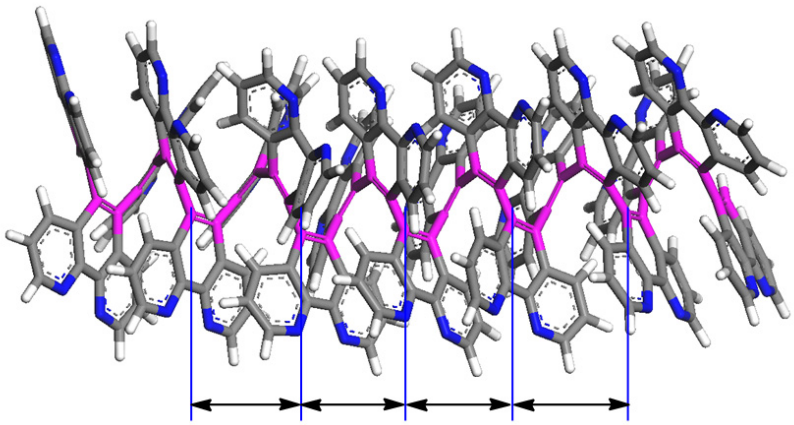


Fig. S47. WAXD profiles of **poly(Phen)** (A) and **poly(DBPhen)** (B) prepared in a larger scale under conditions similar to those in entries 1 and 3 in Table 1, respectively. [Ultima IV diffractometer (Protectus ADS), CuKa, 40 KV, 20 mA, scan speed 2 degree/min, step 0.02 degree, smoothing process was carried out in Adjacent-Averaging method with 10 points of window]

A. Poly(Phen) chain with C6-C6 intervals indicated by arrows



B. Poly(Phen) 20-mer model with turn spacing



Spacing of turns in poly(Phen) helix

Averaged spacing = 4.05 Å

Fig. S48. Schematic extended drawing of **poly(Phen)** chain with arrows pointing C6 carbons of monomeric where three units form a turn (3/1-helix) (A) and **poly(Phen)** 20-mer model with C6-C6 intervals corresponding to spacing of turns in helix. Averaged distance between the C6 carbons was 4.05 Å for **poly(Phen)** (B). On measuring the intervals, the first and second monomeric units from the initiation and termination terminals were omitted. The same analysis was performed for **poly(DBPhen)** whose averaged distance between the C6 carbons was 3.81 Å.

Asymmetric Polymerization and Chiral Polymer Analysis

As a typical procedure, polymerization of 2,9-dibutyl-5,6-dibromo-1,10-phenanthroline in entry 4 in Table S1 is described. A solution of 1,5-cyclooctadiene (0.15 mL, 1.2 mmol), (*R*)-BINAP (747 mg, 1.2 mmol) and $Ni(COD)_2$ (363 mg, 1.2 mmol) in distilled DMF (1 mL) was placed in a dried 10-mL flask equipped with a three-way stopcock under N_2. The mixture was heated to 85°C for 30 min to obtain a deep red catalyst solution. **4** (182 mg, 0.4 mmol) dissolved in distilled DMF (1 mL) was introduced into the flask with stirring. The polymerization reaction was carried out at 85°C for 24 h, and volatile components were removed under vacuum to yield a deep brown solid. The solid was washed with toluene (20 mL), aq. EDTA (pH = 5) (40 mL), aq. EDTA (pH = 9) (40 mL), aq. KOH (2 M) (20 mL), distilled water (100 mL), and benzene (20 mL) in this order. In washing, the solid material was soaked in these solvents at 80°C for ca. 10 min and collected with a centrifuge. The washed material was dried under vacuum to result in a dark brown powder. Yield 20 mg, 0.07 mmol, 17%. Analytical data: M_n 2100, M_w/M_n 3.04; IR (KBr, cm^{-1}) 2940, 2878, 1608, 1460, 1367; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.02, 3.23, 1.89, 1.54, 1.01; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.70, 145.28, 136.26, 134.93, 126.99, 122.88, 39.08, 31.60, 22.87, 14.02.

Table S1. Asymmetric polymerization of 2,9-dibutyl-5,6-dibromo-1,10-phenanthroline using $Ni(COD)_2$-COD-chiral ligand as catalyst in DMF for 24 h leading to **poly(DBPhen)**[a]

Entry	Ligand	[Monomer] (M)	Temp (°C)	Conv.[b] (%)	Yield[c] (%)	M_n[d]	M_w/M_n[d]
1	(-)-Sp	0.12	85	> 99	49	5800	2.00
2	(-)-PMP	0.12	85	> 99	63	3700	5.38
3	(+)-DDB	0.12	85	> 99	28	7900	3.14
4	*(R)*-BINAP	0.60	85	> 99	17	2100	3.04
5	*(S)*-BINAP	0.60	85	> 99	12	2700	3.26

[a] Monomer 0.2 mmol, $Ni(COD)_2$ 0.6 mmol, COD 0.6 mmol. [b]Determined by ^1H NMR analysis of crude mixture. [c]Purified by washing with toluene, aq. EDTA (pH=5), aq. EDTA (pH=9), aq. KOH (2 M), H_2O and benzene in this order. All polymers were soluble in DMF, MeOH, $CHCl_3$, and DMSO. [d]Determined by SEC using a Shodex Asahapak GF-310HQ column with DMF containing LiCl (30 mM) as eluent at a flow rate of 0.5 mL/min using poly(2-vinylpyridine) and pyridine as standard. Samples for injection were dissolved in pure DMF.

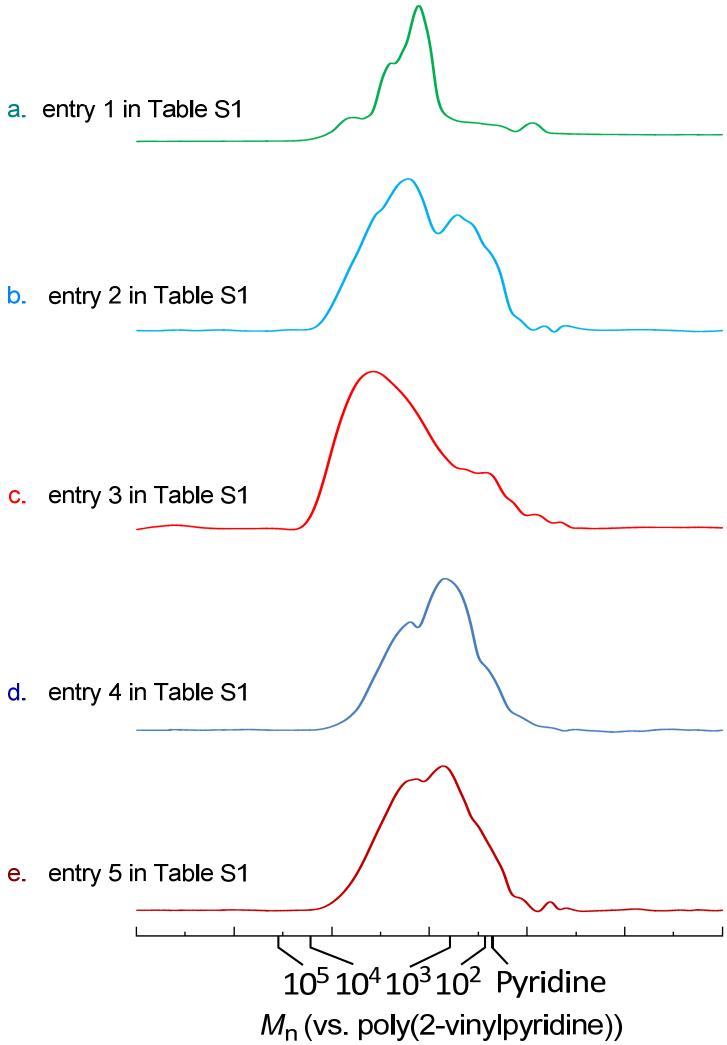


Fig. S49. SEC traces of **poly(DBPhen)** samples from Table S1: entry 1 (a), entry 2 (b), entry 3 (c), entry 4 (d) and entry 5 (e). Samples for injection were prepared in pure DMF (1 mL). [column, Shodex Asahapak GF-310HQ; eluent, DMF containing LiCl (30 mM); flow rate, 0.5 mL/min; detection, absorbance at 275 nm; standard sample, poly(2-vinylpyridine) and pyridine]

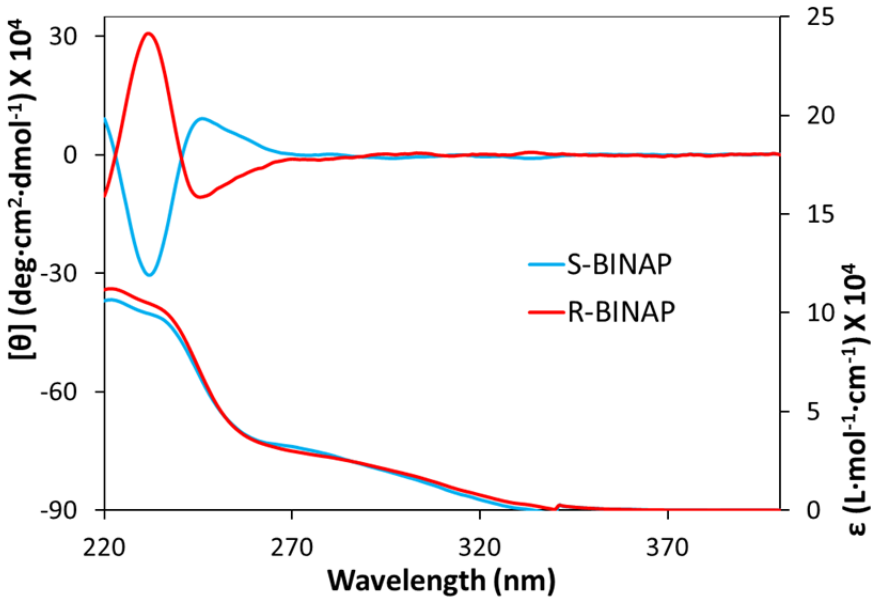


Fig. S50. UV (bottom) and CD (top) spectra of (*R*)- and (*S*)-BINAP. [MeOH, conc. 0.04 mmol/L, 1-mm cell]

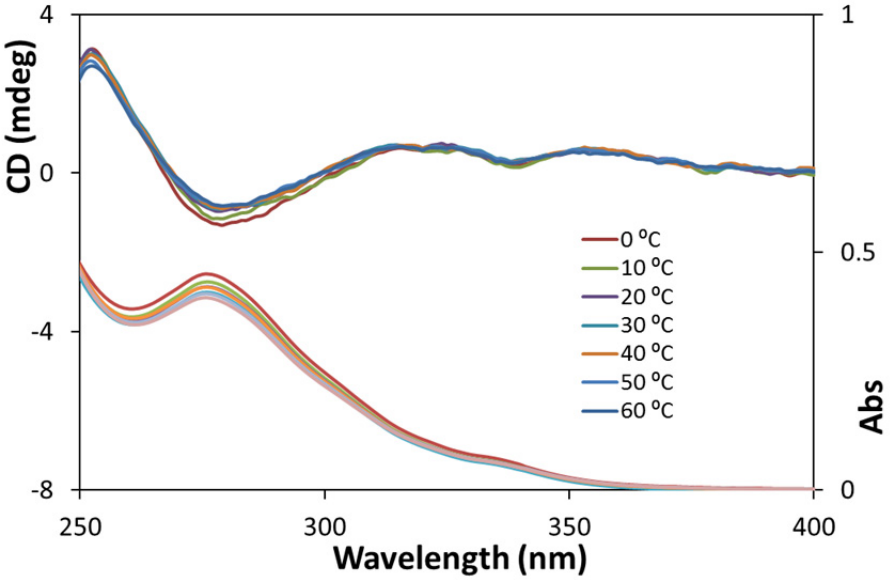


Fig. S51. UV (bottom) and CD (top) spectra of **poly(DBPhen)** (entry 4 in Table S1) measured at different temperatures. [$CHCl_3$, [conc, (residue)] 0.4 mmol/L, 1-mm cell]

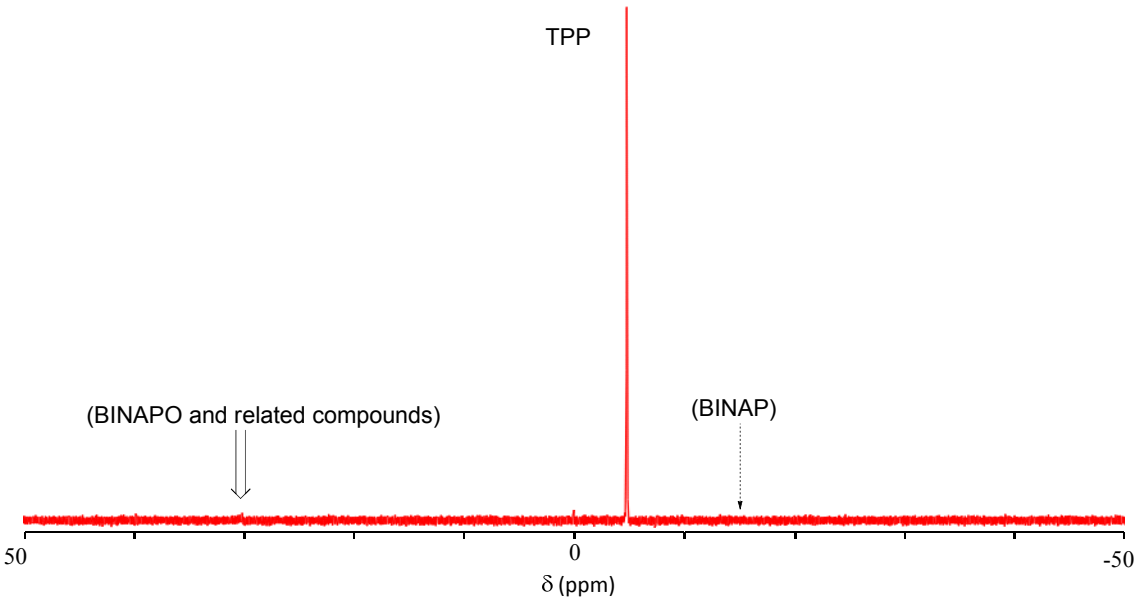


Fig. S52. ^{31}P NMR spectrum of a mixture of **poly(DBPhen)** (Entry 4) and triphenylphosphine (TPP) as an internal standard compound at [**poly(DBPhen)** (unit residue)] = 6 mmol/L and [TPP] = 42 mmol/L in $CDCl_3$. [400MHz, r.t.]

Notes: Possible impurities in **poly(DBPhen)** samples may be BINAP and 2,2'-bis(diphenylphosphoryl)-1,10-binaphthyl[8] and related P=O species.[9] The S/N ratio of the TPP signal at -6.00 ppm was ca. 306, indicating that the minimal amount of P compound residues detectable by this spectrum is 0.14 mmol/L which is 2.3 mol% of **DBPhen** unit. There are no clear signals of BINAP or any P=O species beyond this level.

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