Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Supramolecular Aggregates with Distinct Optical Properties from PDI Oligomers of Similar Structures

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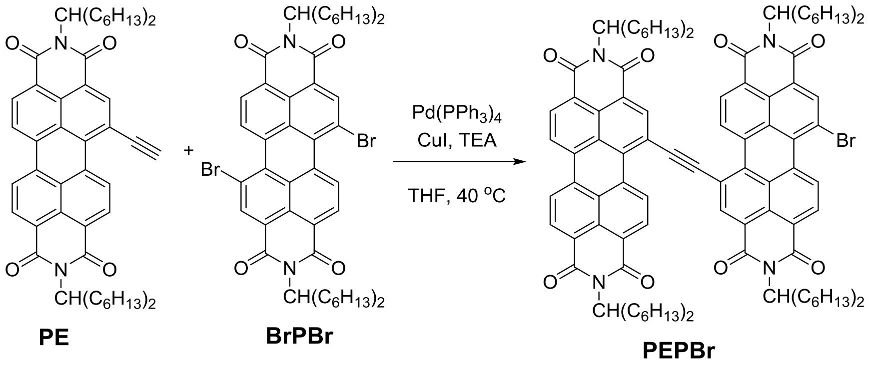
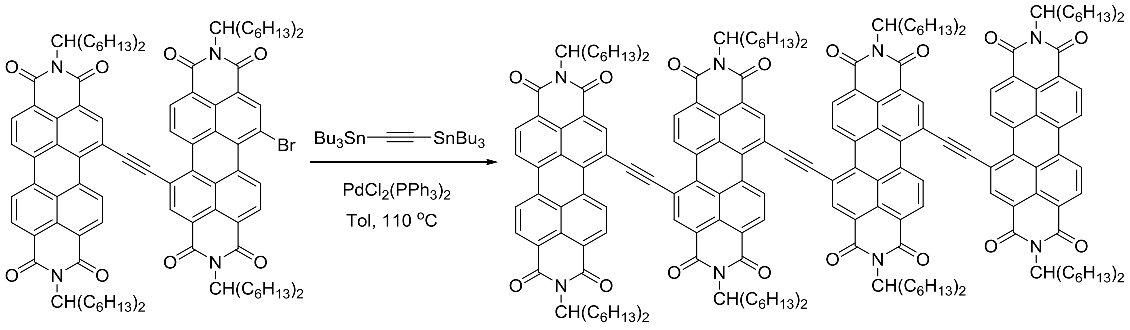
I. Synthesis procedures and characterization data

General Methods. Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen atmosphere using standard Schlenk protocols. Reagent grade tetrahydrofuran (THF) was distilled over sodium and benzophenone. Diisopropylamine ($i\mathrm{Pr}_2\mathrm{NH}$) and triethylamine (TEA) were distilled over CaH_2 prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 MHz) or a Varian 300 plus (300 MHz) using CDCl_3 as the solvent unless otherwise noted. Chemical shifts in ^{1}H and ^{13}C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm) as standards. MALDI-TOF mass spectra were recorded on an ABI 4800 Plus MALDI TOF/TOF Analyzer.

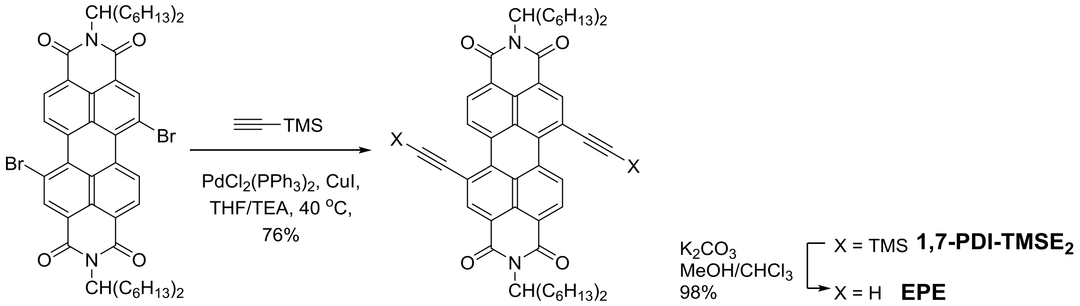


PEPBr was synthesized using similar conditions as applied for **PEPEP**.[S1] To a Schlenk tube containing **BrPBr**[S1b] (546 mg, 0.60 mmol), **PE**[S1a] (94 mg, 0.12 mmol), $\mathrm{Pd(PPh_3)_4}$ (8 mg, 0.08 mmol), and CuI (1 mg, 0.08 mmol) was added degassed THF (5 mL) and TEA (5 mL). The tube was sealed under nitrogen atmosphere and heated at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (DCM). The organic solution was sequentially washed with HCl (aq. 6 M) and sat. $\mathrm{NaHCO_3}$ (aq.), and then dried over anhydrous $\mathrm{Na_2SO_4}$. After the solvents were removed in *vacuo*, column chromatography over silica gel eluted with petroleum ether/DCM (6:1 to 3:1, v/v) afforded recovered **BrPBr** first, followed by **PEPBr** as a black solid (40%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 10.23 (d, 1H, *J* = 8.1 Hz), 9.93 (d, 1H, *J* = 7.5 Hz), 9.69 (d, 1H, *J* = 8.4 Hz), 8.98 (m, 3H), 8.65-8.76 (m, 7H), 5.15-5.22 (m, 4H), 2.20-2.27 (m, 8H), 1.85-1.87 (m, 8H), 1.10-1.40 (m, 64H), 0.78-0.89 (m, 24H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 164.7, 164.5, 164.1, 163.9, 163.5, 163.1, 162.9, 162.7, 139.1, 138.4, 137.8, 137.4, 136.9, 135.5, 135.0, 134.2, 134.0, 133.8, 133.3, 132.5, 131.9, 130.7, 129.5, 129.3, 128.9, 128.4, 128.3, 127.8, 127.7, 127.0, 124.0, 123.6, 121.6, 118.90, 118.86, 99.3, 98.0, 55.3, 55.0, 32.6, 32.5, 32.00, 31.96, 29.9, 29.5, 27.2, 27.14, 27.11, 22.83, 22.82, 22.80, 14.3, 14.2. MALDI-TOF MS: Calc'd for $C_{102}H_{121}BrN_4O_8$, 1609.8 (m/z); Found, 1609.1.



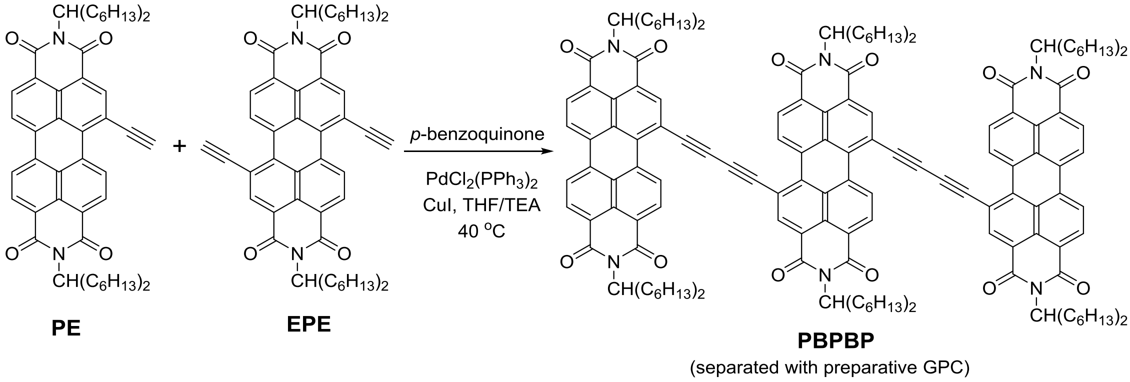
PEPBr **PEPEP**

PE(PE)$_2$P A Schlenk tube containing **PEPBr** (81 mg, 0.050 mmol), 1,2-bis(tributylstannyl)acetylene (15 mg, 0.025 mmol), and PdCl$_2$(PPh$_3$)$_2$ (1.4 mg, 0.002 mmol) was evacuated and backfilled with nitrogen for three times. After degassed toluene (1 mL) was added, the tube was sealed under nitrogen atmosphere and heated at 110 ^{o}C for 96 h. After the reaction mixture was cooled to room temperature, KF (aq.) was added and stirred for 6 h. The organic layer was then separated and diluted with chloroform and toluene, then washed with NaCl (aq.) and NH_4Cl (aq.) sequentially, before dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo*. The residue was applied to flash column chromatography over silica gel, eluted with petroleum ether/dichloromethane (2:1 to 1:1, v/v) to afford **PE(PE)$_2$P** as a black solid (29 mg, 37%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 10.29 (d, 2H, *J* = 6.3 Hz), 10.17-10.18 (m, 4H), 8.98-9.02 (m, 6H), 8.76 (m, 14H), 5.20 (m, 8H), 2.26 (m, 16H), 1.88 (m, 16H), 1.25-1.31 (m, 128H), 0.81-0.85 (m, 48H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 164.7, 164.3, 164.1, 164.0, 163.6, 163.1, 162.9, 138.4, 137.9, 137.8, 137.3, 135.6, 135.0, 134.25, 134.18, 134.1, 132.5, 132.2, 132.1, 131.9, 131.7, 131.5, 131.4, 131.2, 131.1, 129.6, 129.3, 128.8, 128.1, 127.9, 127.7, 127.2, 127.0, 124.8, 124.1, 123.8, 123.6, 123.1, 119.34, 119.28, 118.9, 99.6, 99.1, 55.34, 55.31, 55.1, 32.6, 31.99, 31.98, 29.9, 29.5, 27.20, 27.16, 22.83, 22.81, 14.27, 14.26, 14.24. MALDI-TOF MS: Calc'd for $C_{206}H_{242}N_8O_{16}Na$, 3107.8 (M + Na$^+$); Found, 3107.9.



1,7-PDI-TMSE$_2$. A Schlenk tube containing **BrPBr** (913 mg, 1.0 mmol),[S1b] CuI (10 mg, 0.060 mmol), and $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol) was evacuated and backfilled with nitrogen for three times. After degassed THF (10 mL), TEA (10 mL), and trimethylsilylacetylene (0.56 mL, 4.0 mmol) was added, the tube was sealed under nitrogen atmosphere and heated at 40 °C for 48 h. After cooled to room temperature, the reaction mixture was diluted with chloroform and washed with HCl (6 M) and $NaHCO_3$ (aq.) sequentially, before dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo*. The residue was applied to flash column chromatography over silica gel, eluted with petroleum ether/dichloromethane (5:1), to afford **1,7-PDI-TMSE$_2$** as a red solid (720 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 10.22 (d, 2H, J = 8.7 Hz), 8.82-8.85 (m, 2H), 8.66 (m, 2H), 5.17-5.19 (m, 2H), 2.23-2.28 (m, 4H), 1.81-1.87 (m, 4H), 1.23-1.33 (m, 32H), 0.80-0.85 (m, 12H), 0.39 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 164.7, 164.3, 163.6, 163.3, 138.8, 138.2, 138.1, 134.4, 134.2, 131.1, 130.4, 128.2, 127.8, 127.7, 124.1, 123.4, 122.9, 122.2, 120.0, 106.4, 106.0, 55.1, 32.6, 32.0, 29.4, 27.1, 22.8, 14.2, 0.2. MALDI-TOF MS: Calc'd for $C_{60}H_{78}N_2O_4Si_2$, 946.6 (M^+); Found, 946.7.

EPE. A solution of **1,7-PDI-TMSE$_2$** (34 mg, 0.036 mmol) in $CHCl_3$ (4 mL) was added to a solution of K_2CO_3 (16 mg, 0.12 mmol) in MeOH (4 mL). The reaction mixture was stirred at room temperature for 40 min before it was quenched with NH_4Cl (aq.), and then dried over anhydrous Na_2SO_4. After the solvents were removed *in vacuo*, **EPE** was directly used in next step without further purification.



PBPBP. A Schlenk tube containing **PE** (30 mg), **EPE** (30 mg), CuI (trace), $PdCl_2(PPh_3)_2$ (trace), and 1,4- benzoquinone (5 mg) was evacuated and backfilled with nitrogen for three times. After degassed THF (1 mL) and TEA (1 mL) were added, the tube was sealed under nitrogen atmosphere and heated at 40 ^{o}C for 16 h. After cooled to room temperature, the reaction mixture was diluted with DCM and washed with NH_4Cl (aq.) twice before dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo*. The residue was applied to flash column chromatography over silica gel eluted with petroleum ether/dichloromethane (1:2) to give a mixture of different oligomers. Subsequent separation and purification was performed with preparative recycle gel permeation chromatography eluted with chloroform to afford **PBPBP** (3 mg, 2%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 10.10 (d, 2H, *J* = 8.1 Hz), 9.98 (d, 2H, *J* = 8.1 Hz), 8.93-8.97 (m, 4H), 8.72-8.81 (m, 12H), 5.18-5.20 (m, 6H), 2.25-2.27 (m, 12H), 1.86 (m, 12H), 1.24-1.30 (m, 96H), 0.82-0.84 (m, 36H). MALDI-TOF MS: Calcd for $C_{158}H_{182}N_6O_{12}$, 2356.4 (m/z); Found, 2355.8 .

II. Optical spectra measurements

UV-Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer using the absorption mode in a 1-cm or 1-mm quartz cell depending on the concentration. Fluorescence emission spectra were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer using 1-cm quartz cuvette with a right-angle geometry. The emission spectra were not corrected for the wavelength dependency of the detector sensitivity and monochromator gratings. The temperature of the sample was controlled using a circulated liquid (water + glycol) bath with a DC-2006 temperature control unit (Ningbo SCIENTZ Biotechnology Co., Ltd, China).

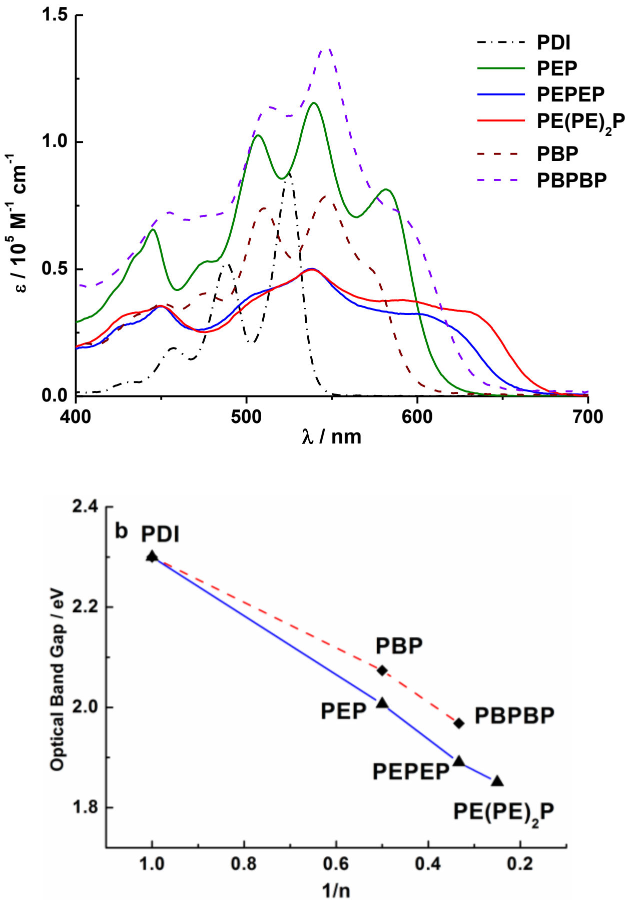


Figure S1. Absorption spectra of PDI oligomers in CH_2Cl_2.

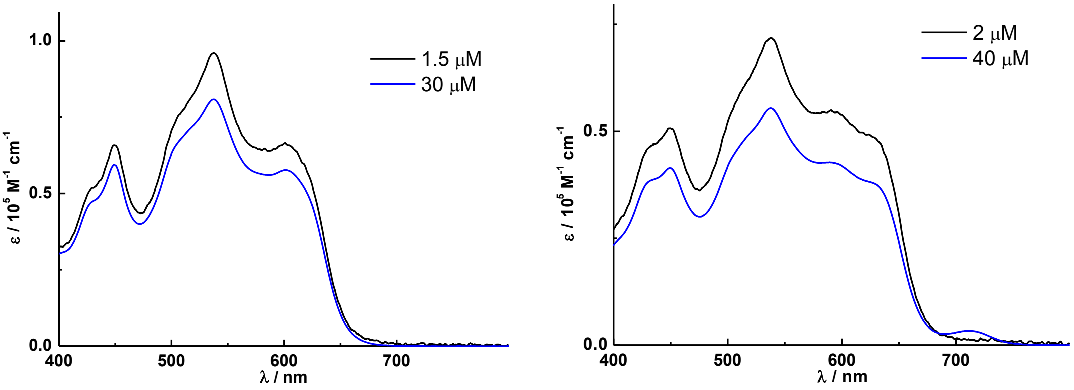


Figure S2. Absorption spectra of **PEPEP** (left) and **PE(PE)$_2$P** (right) at indicated concentrations in CH_2Cl_2 at 23 °C.

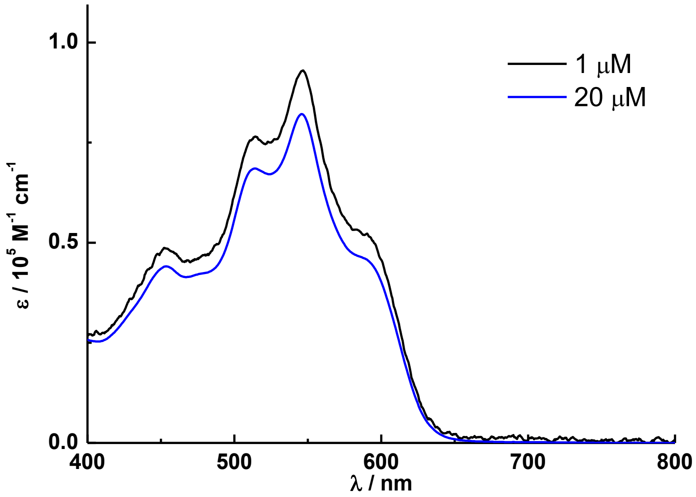


Figure S3. Absorption spectra of **PBPBP** at varied concentrations in CH_2Cl_2 at 23 °C

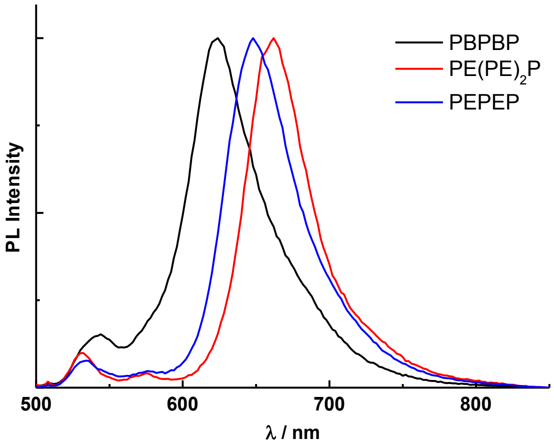


Figure S4. Normalized fluorescence emission spectra of PDI oligomers in CH_2Cl_2 (excited at 490 nm, OD < 0.1, 23 °C)

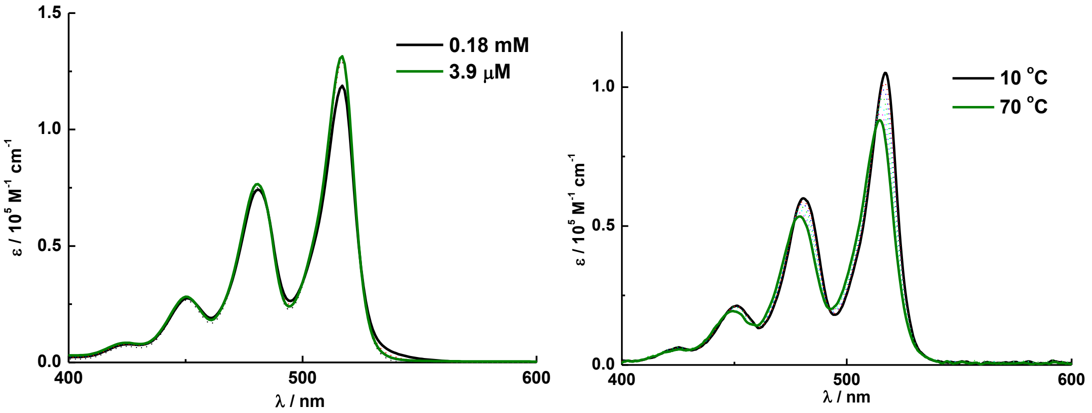


Figure S5. UV-vis absorption spectra of **PDI** in CH at varied concentrations (left, at 288 K) and temperatures (right, at 2.26 μM).

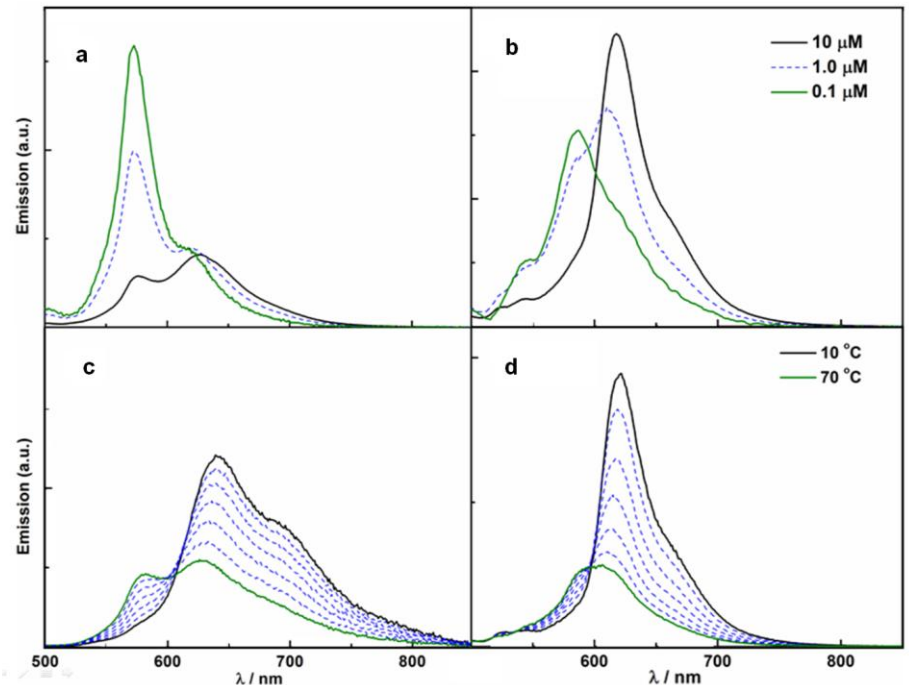


Figure S6. Fluorescence emission spectra of **PBP** (a & c) and **PEP** (b & d) in CH at varied concentrations (a and b) and temperatures (c and d, at 11 μM); the spectra were calibrated based on the optical density at the excitation wavelengths of 430 and 458 nm for **PEP** and **PBP** solutions, respectively.

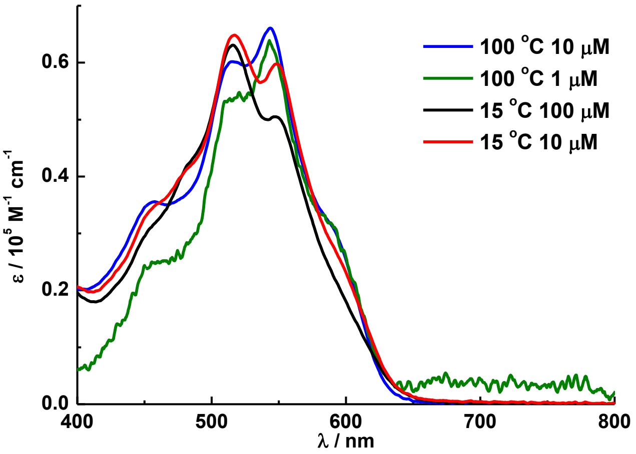


Figure S7. Absorption spectra of **PBPBP** in toluene at varied concentrations and temperatures.

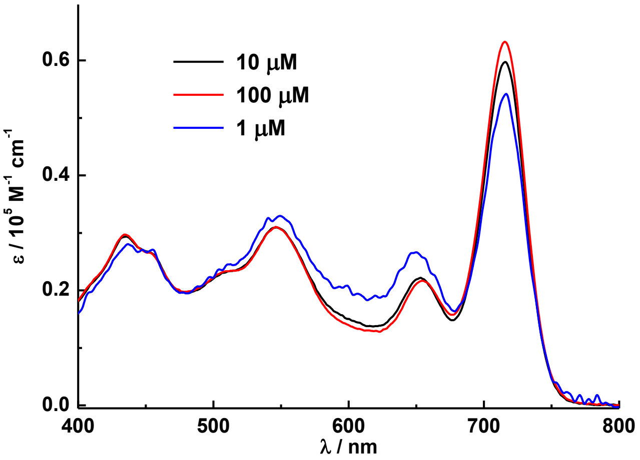


Figure S8. UV-vis absorption spectra of **PE(PE)$_2$P** in toluene at varied concentrations at 273 K.

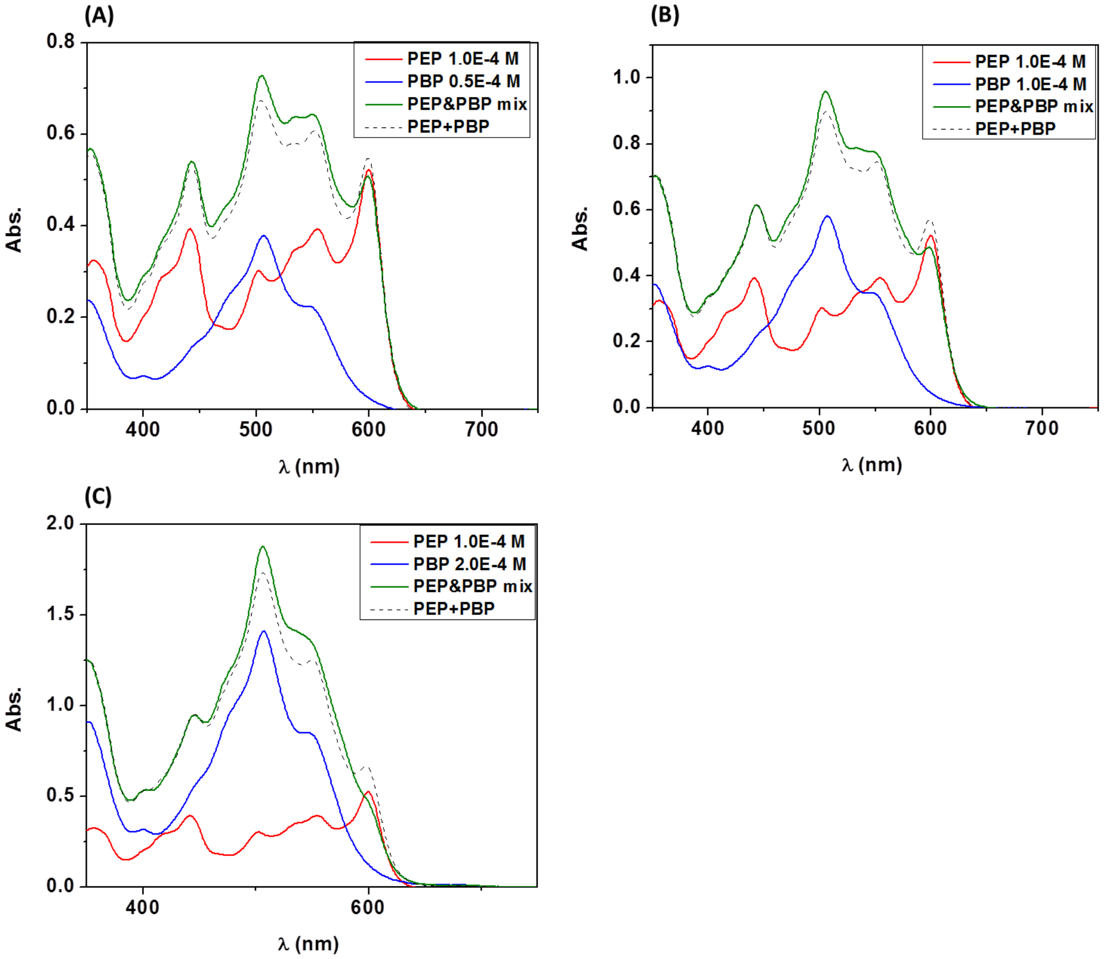


Figure S9. Comparison of absorption spectra of **PEP** (red line, 0.10 μM), **PBP** (blue line; A, 0.050 μM; B, 0.10 μM; C, 0.20 μM), and mixtures of **PEP** and **PBP** (green solid line) in CH, in comparison to summed spectra of **PEP** and **PBP** (dashed line).

III. Mathematic fitting

Apparent extinction coefficients measured in variable-concentration absorption spectra were fitted by nonlinear regression analysis to the following expression,[S2,S3]

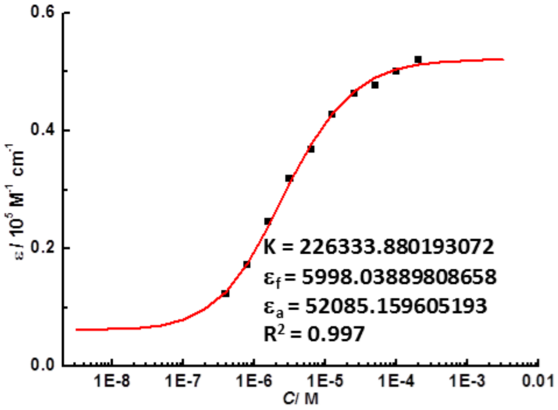
$$\varepsilon = (2Kc + 1 - (4Kc + 1)^{0.5}) / 2 / K^2 / c^2 \times (\varepsilon_m - \varepsilon_a) + \varepsilon_a \qquad \text{(S1)}$$

where ε is the apparent extinction coefficient; ε_m and ε_a are the extinction coefficient of the monomer and aggregated species, respectively; K is the binding constant, and c is the total concentration of the compounds.

In temperature dependent measurement, apparent extinction coefficients were fitted using equation (S1) with conjunction with van't Hoff equation (S2):

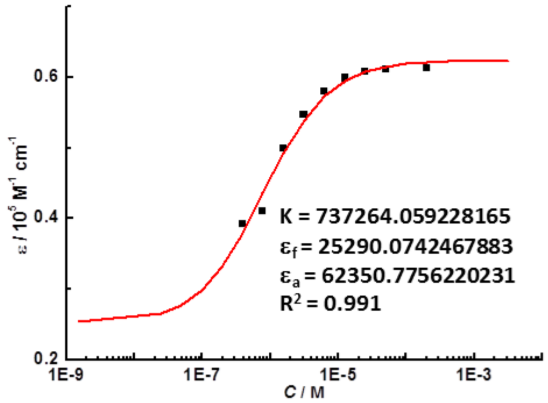
$$K = \exp((T\Delta S - \Delta H)/RT) \qquad \text{(S2)}$$

Where T is the absolute temperature, ΔS is the entropy change, ΔH is the enthalpy change, and R is the ideal gas constant of 8.314 J K^{-1} mol^{-1}.



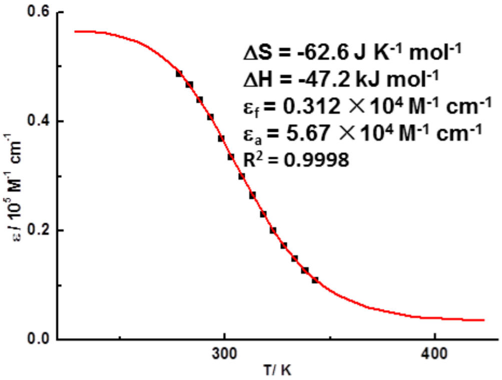
C / M	ε / M^{-1} cm^{-1}
2.0E-04	52085
1.0E-04	50120
5.0E-05	47750
2.5E-05	46336
1.3E-05	42789
6.3E-06	36906
3.1E-06	31878
1.6E-06	24577
7.8E-07	17286
3.9E-07	12311

Figure S10. Non-linear fitting of extinction coefficients of **PEP** at 600 nm as a function of concentration in CH.



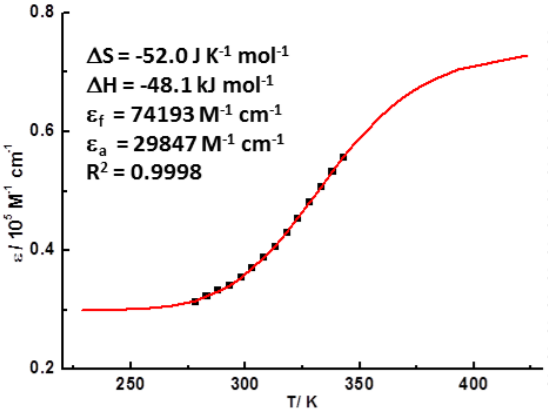
C / M	ε / M^{-1} cm^{-1}
2.0E-04	61325
5.0E-05	61128
2.5E-05	60764
1.3E-05	59878
6.3E-06	58059
3.1E-06	54642
1.6E-06	49955
7.8E-07	40986
3.9E-07	39258

Figure S11. Non-linear fitting of extinction coefficients of **PBP** at 507 nm as a function of concentration in CH.



T / K	ε / M^{-1} cm^{-1}
278.15	48639.64
283.15	46786.49
288.15	43938.74
293.15	40770.27
298.15	36863.06
303.15	33415.32
308.15	29927.93
313.15	26444.14
318.15	23027.03
323.15	19964.86
328.15	17222.52
333.15	14791.89
338.15	12704.5
343.15	10968.47

Figure S12. Non-linear fitting of extinction coefficients of **PEP** at 600 nm as a function of temperature in CH.



T/K	ε/M^{-1} cm^{-1}
278.15	31310
283.15	32360
288.15	33270
293.15	34010
298.15	35380
303.15	37000
308.15	38740
313.15	40640
318.15	43040
323.15	45410
328.15	48120
333.15	50720
338.15	53210
343.15	55640

Figure S13. Non-linear fitting of extinction coefficients of **PBP** at 537 nm as a function of temperature in CH.

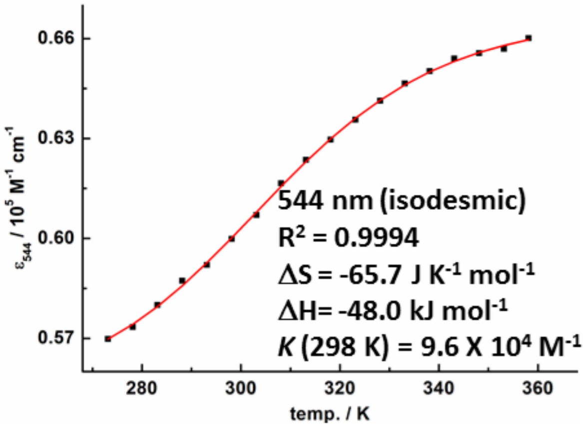


Figure S14. Non-linear fitting of extinction coefficients of **PBPBP** at 544 nm as a function of temperature in toluene.

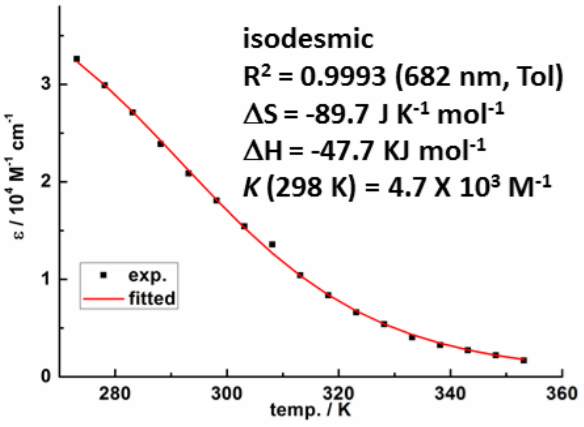


Figure S15. Non-linear fitting of extinction coefficients of **PEPEP** at 682 nm as a function of temperature in toluene.

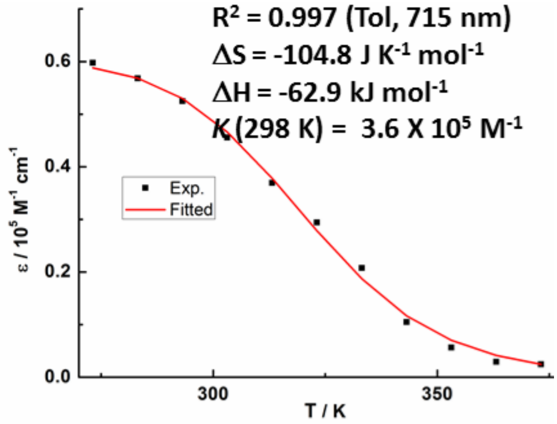


Figure S16. Non-linear fitting of extinction coefficients of **PE(PE)$_2$P** at 715 nm as a function of temperature in toluene.

IV. DFT calculations and molecular mechanics optimization

The geometry was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional[S4] with a basis set limited to 6-31g**. TD-DFT calculations were performed at optimized geometries using the same theory level. Quantum-chemical calculation was performed with the Gaussian03[S5] package and the orbital pictures were prepared using Gaussview.[S6] All *N*-hexylheptyl substituents were replaced with methyl groups in the DFT calculations. The dimer geometry with *N*-hexylheptyl substituents was optimized with Hyperchem 8.0 using MM+ force and AM1 Basis.[S7]

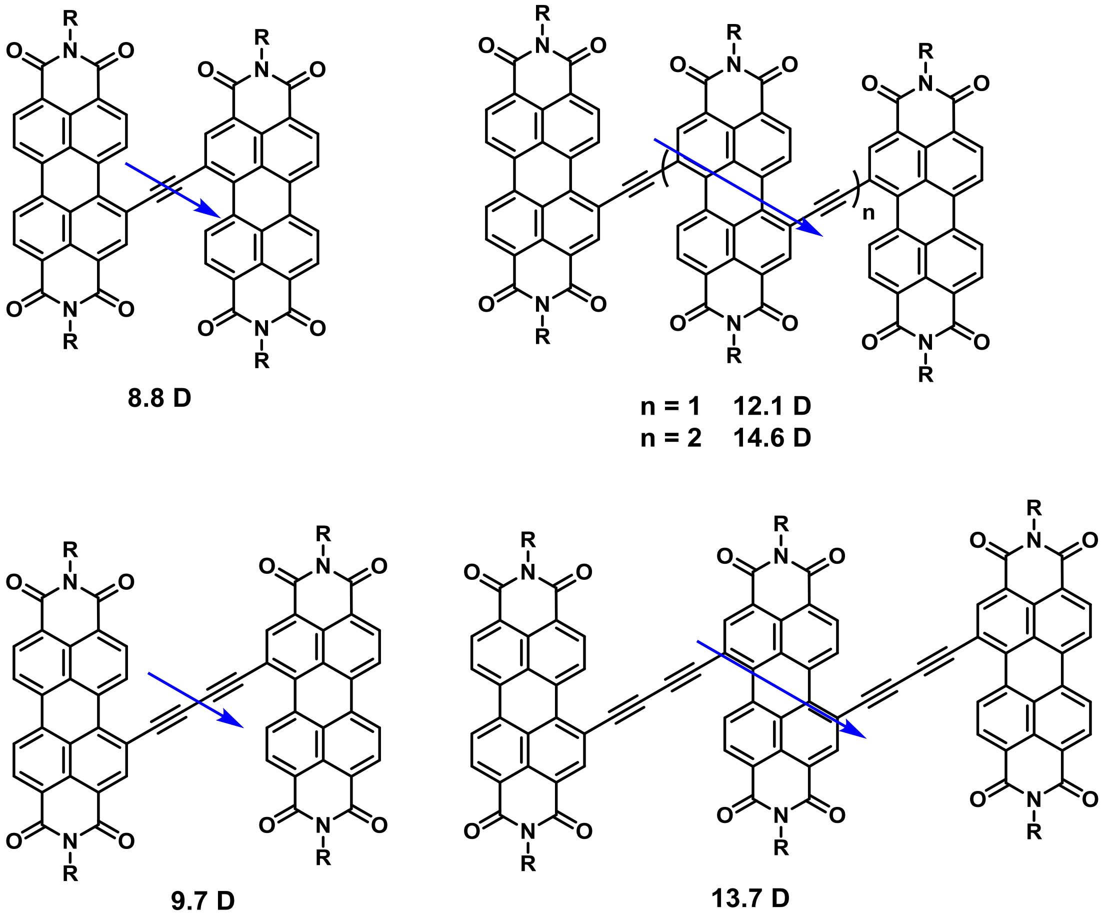


Figure S17. DFT calculated S_0-S_1 transition dipole moments of **PDI** and oligomers (arrows indicate the direction of transition dipoles)

Table S1. TD-DFT calculated S_0-S_1 electron transition of PDI-oligomers

compd	λ/nm（transition dipole/Debye）	assignments
PDI	508 (8.5)	H → L (100%)
PEP	637 (8.8)	H → L (97%)
PEPEP	714 (12.1)	H → L (100%)
PE(PE)$_2$P	756 (14.6)	H → L (100%)
PBP	641 (9.7)	H → L (100%)
PBPBP	718 (13.7)	H → L (100%)

H: HOMO, L: LUMO.

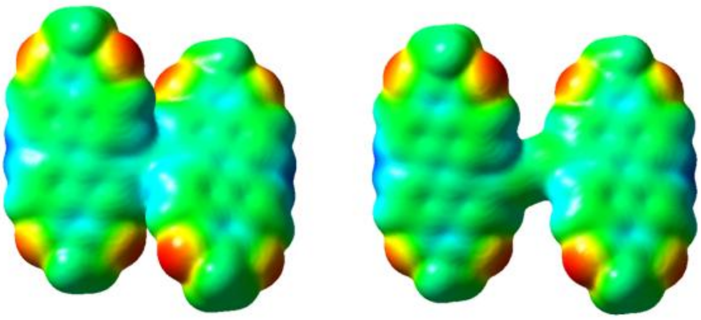


Figure S18. Electrostatic potential plots of **PEP** and **PBP.**

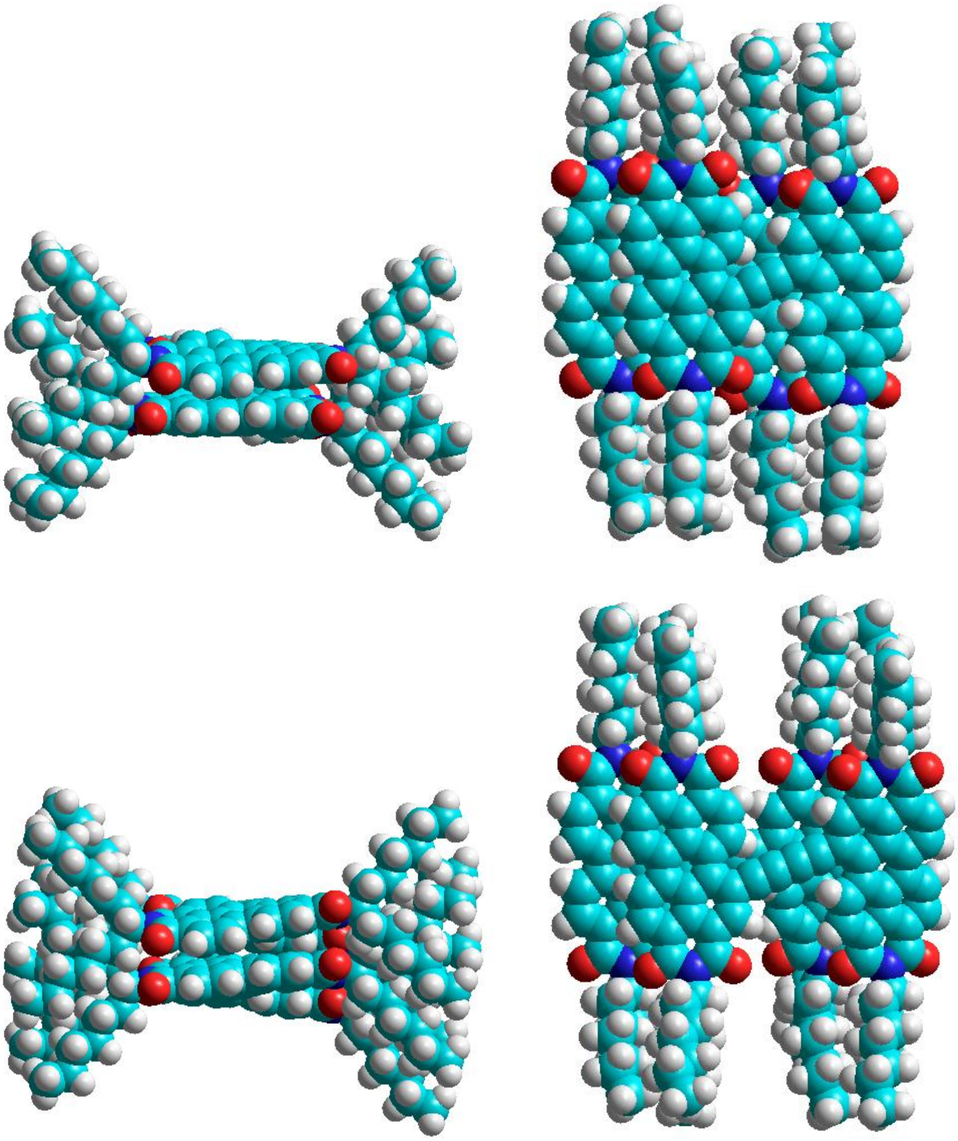


Figure S19. Simulated dimer structures of **PEP** (top) and **PBP** (bottom) from molecular mechanics optimization using HyperChem 8.0 (with MM+ force field), which estimated similar slip angles (~ 47^o) for the two molecules.

The mechanics optimization results could not explain the minor aggregate structure differences between the two dimers but showed that with similar slip angles a larger surface of **PBP** was exposed to the empty region between the two PDI units of adjacent molecule than **PEP**.

V. References

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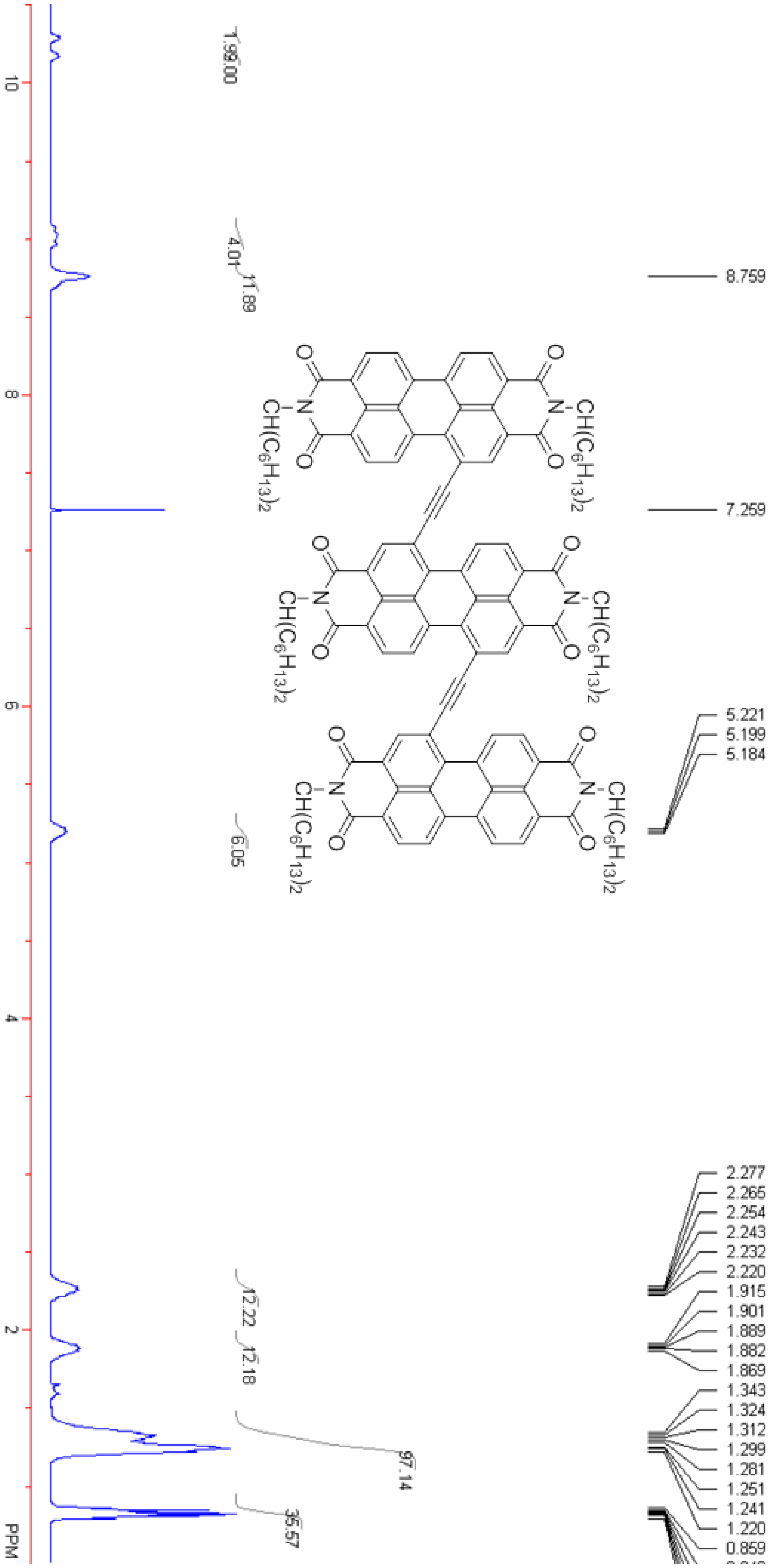
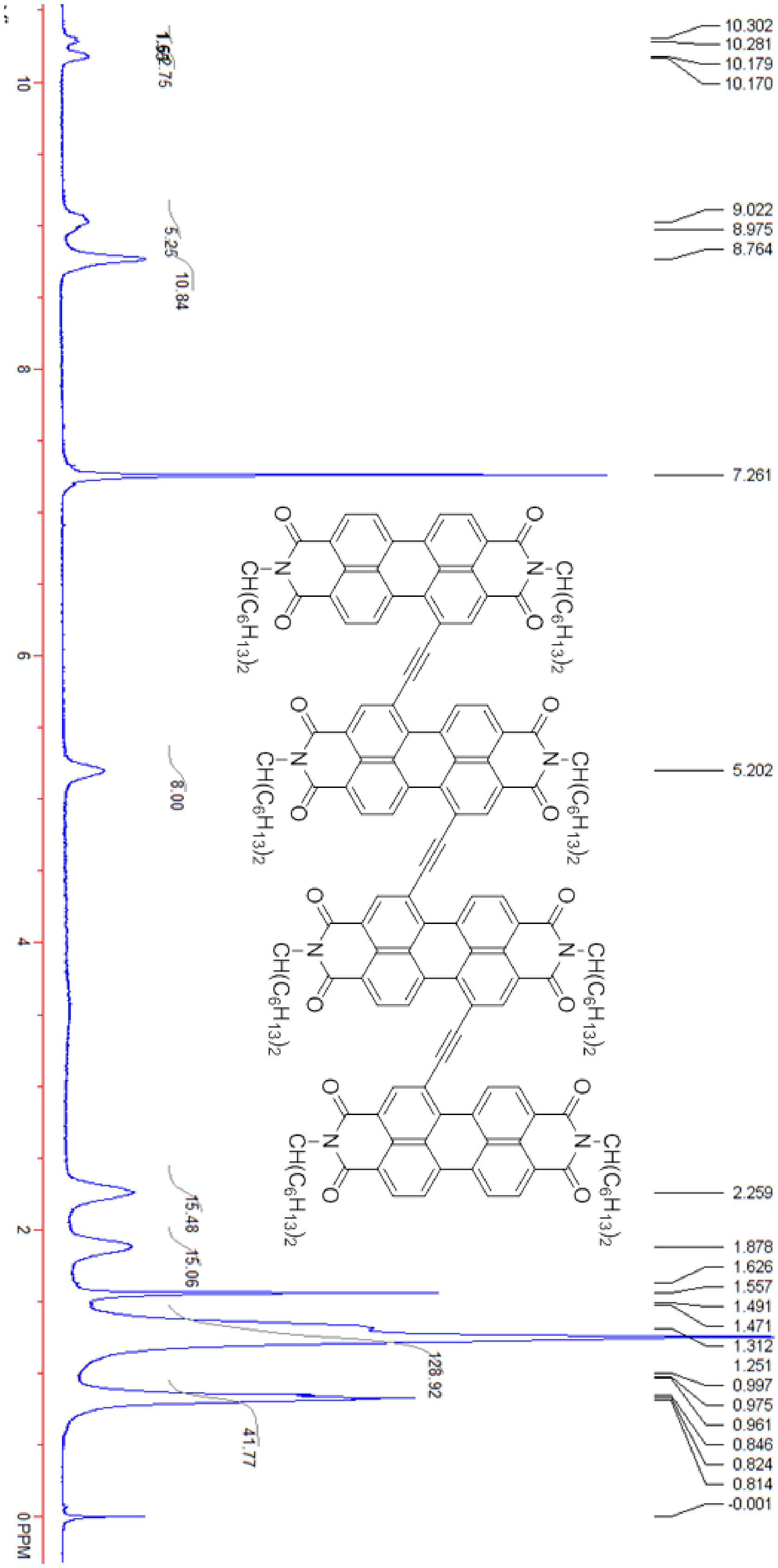
S7. U. Mayerhöffer, F. Würthner, *Angew. Chem. Int. Ed.* **2012**, *51*, 1 – 6.

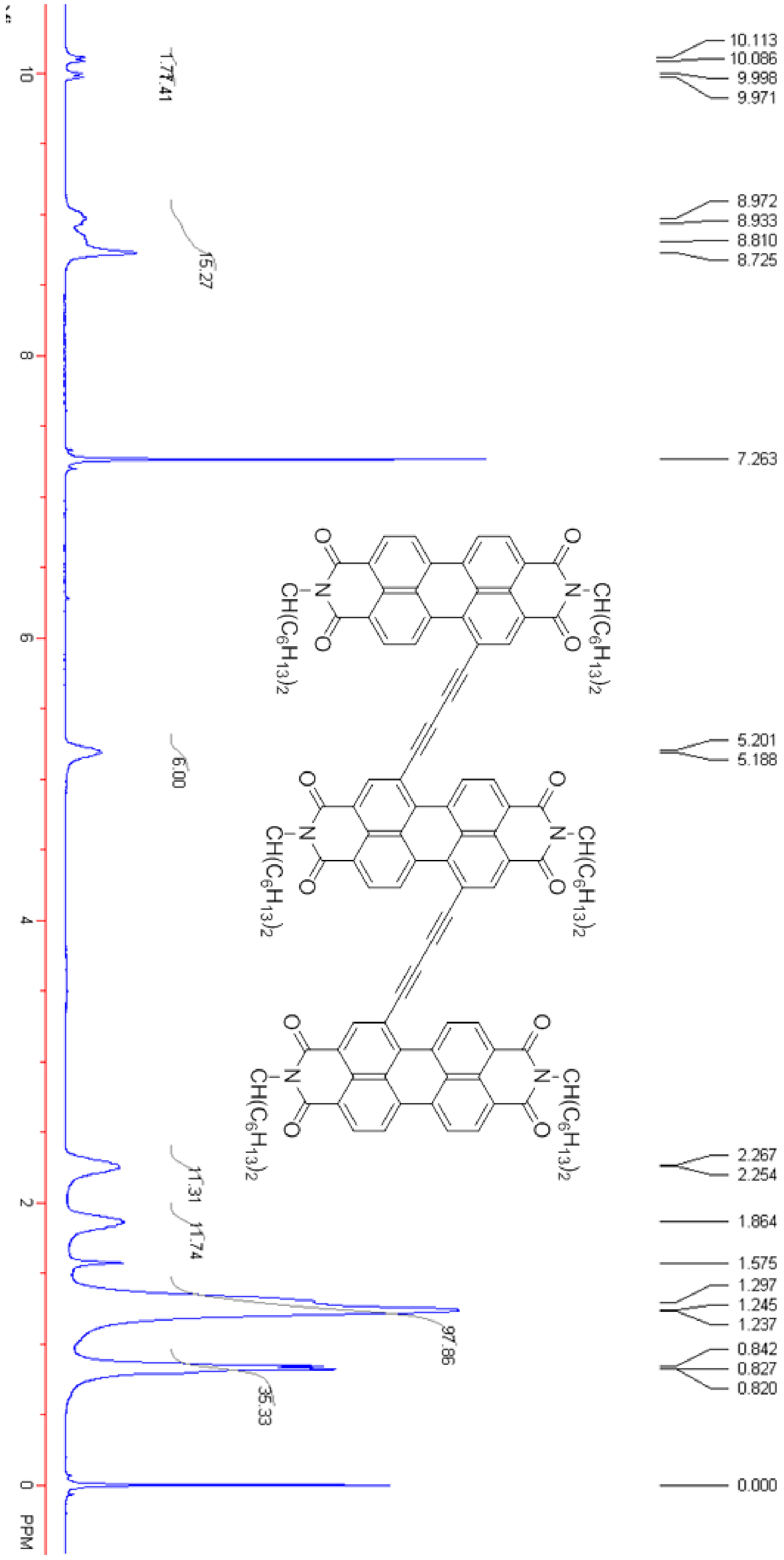
VI. Copies of NMR spectra



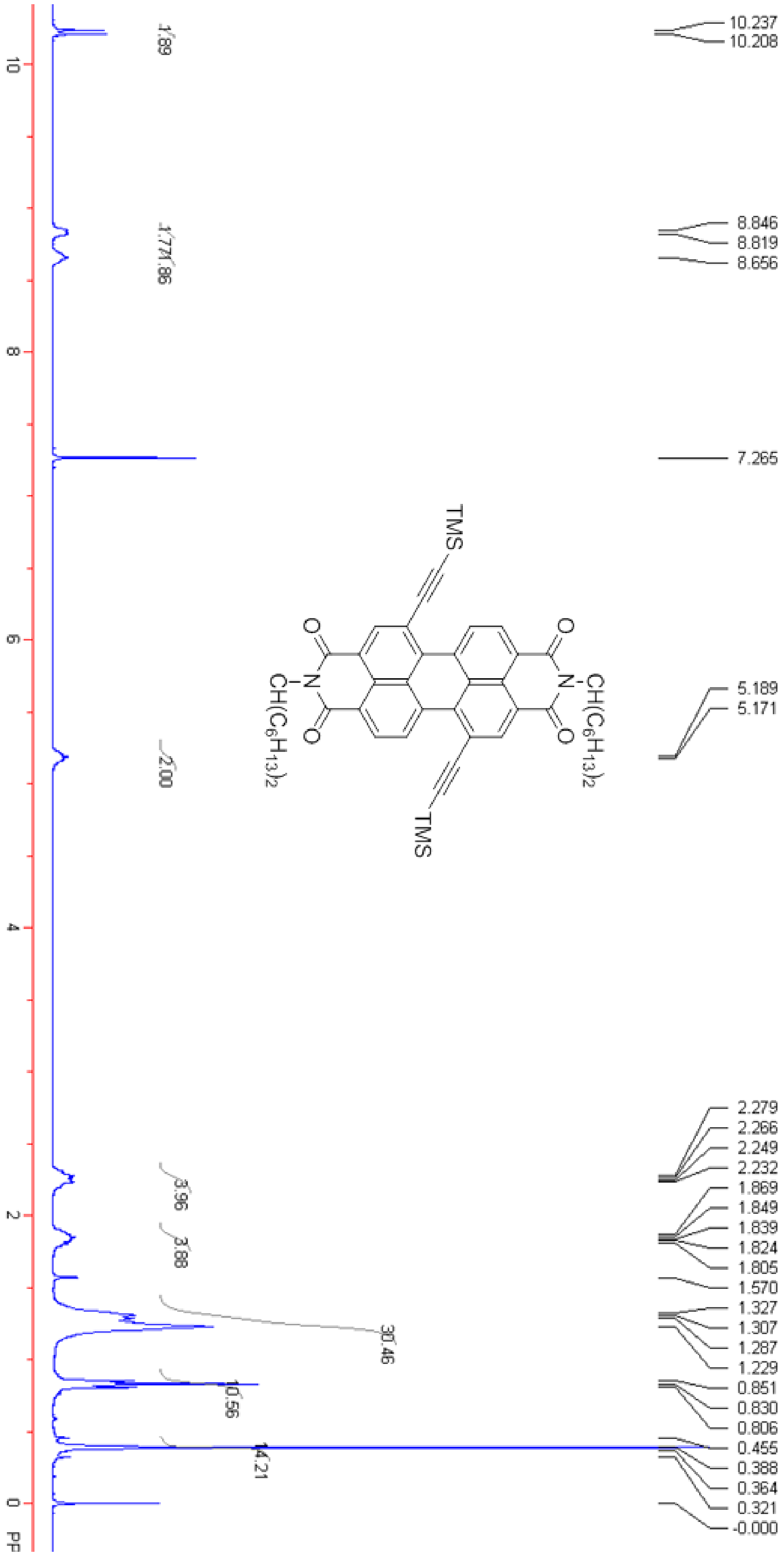
^{1}H NMR spectrum of **PEPEP**



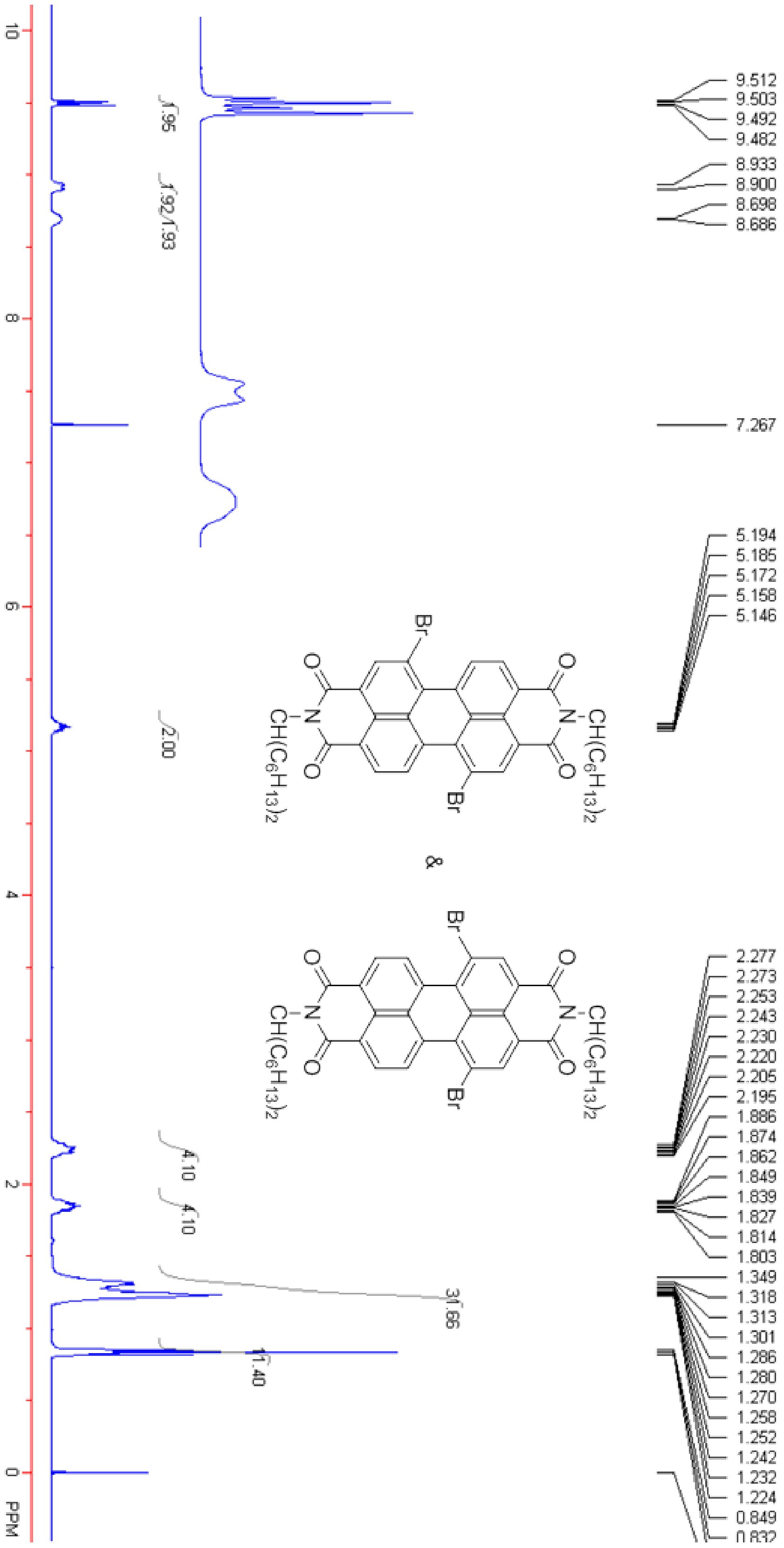
^{1}H NMR spectrum of **PE(PE)$_2$P**



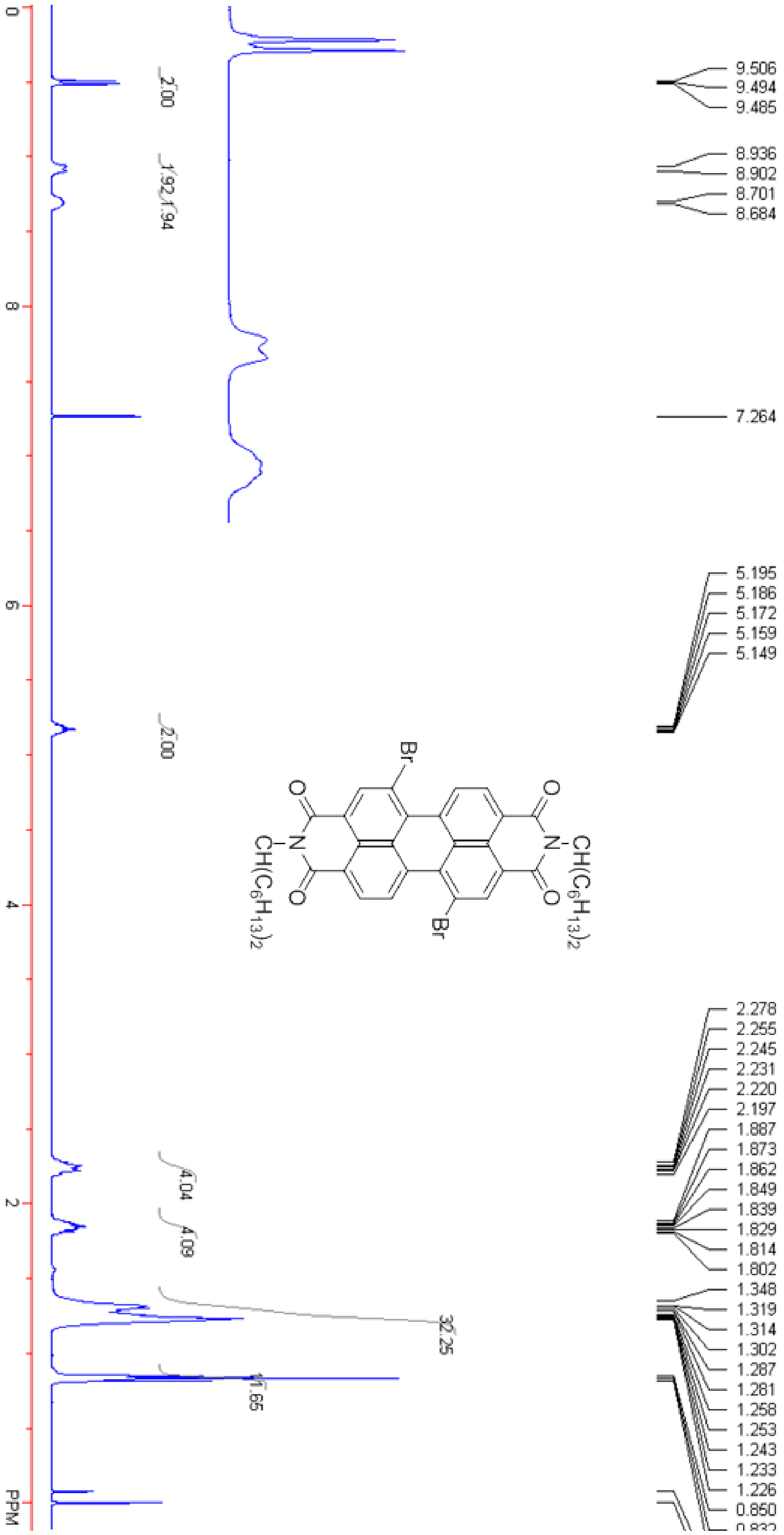
^{1}H NMR spectrum of **PBPBP**



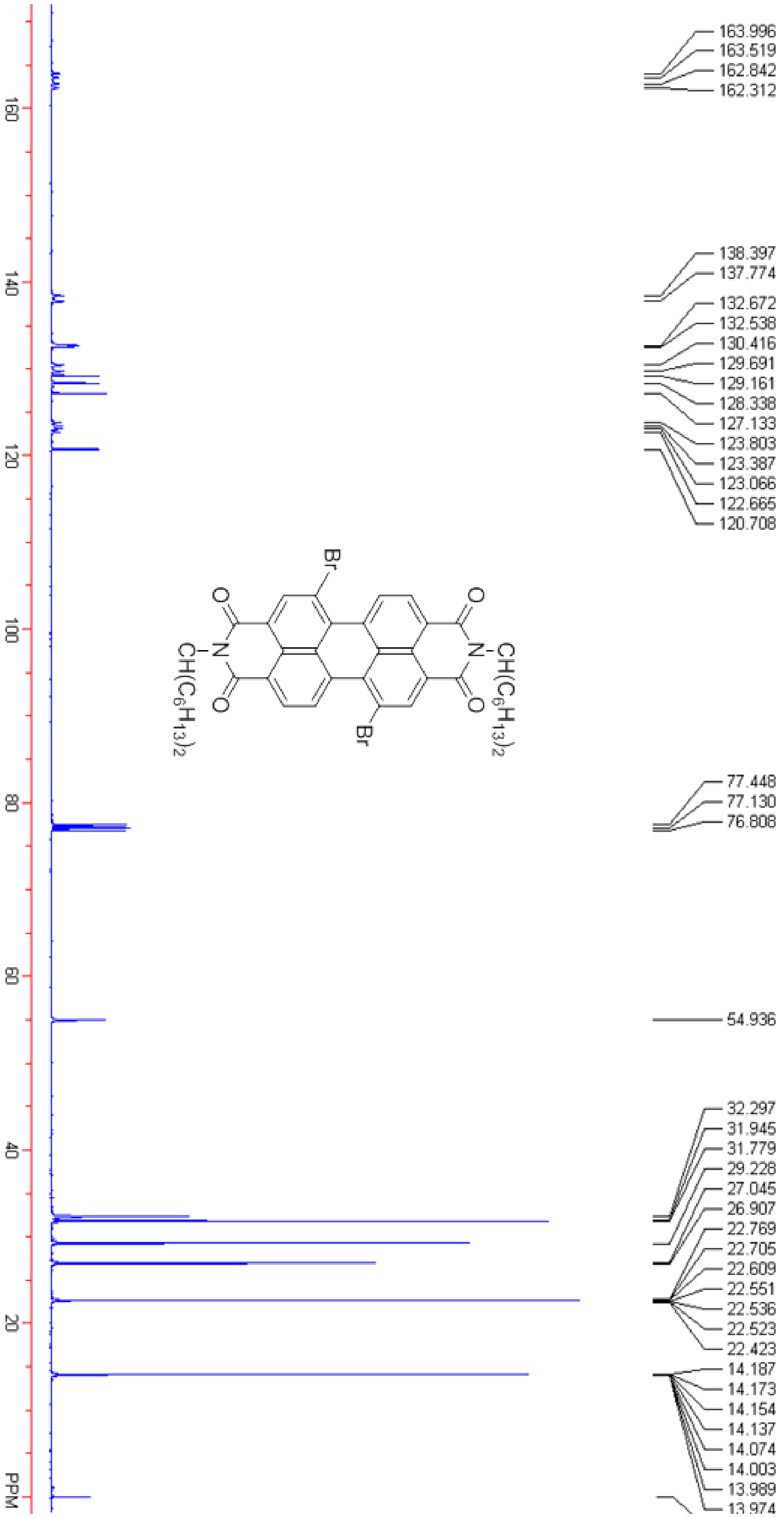
^{1}H NMR spectrum of **1,7-PDI-TMSE$_2$**



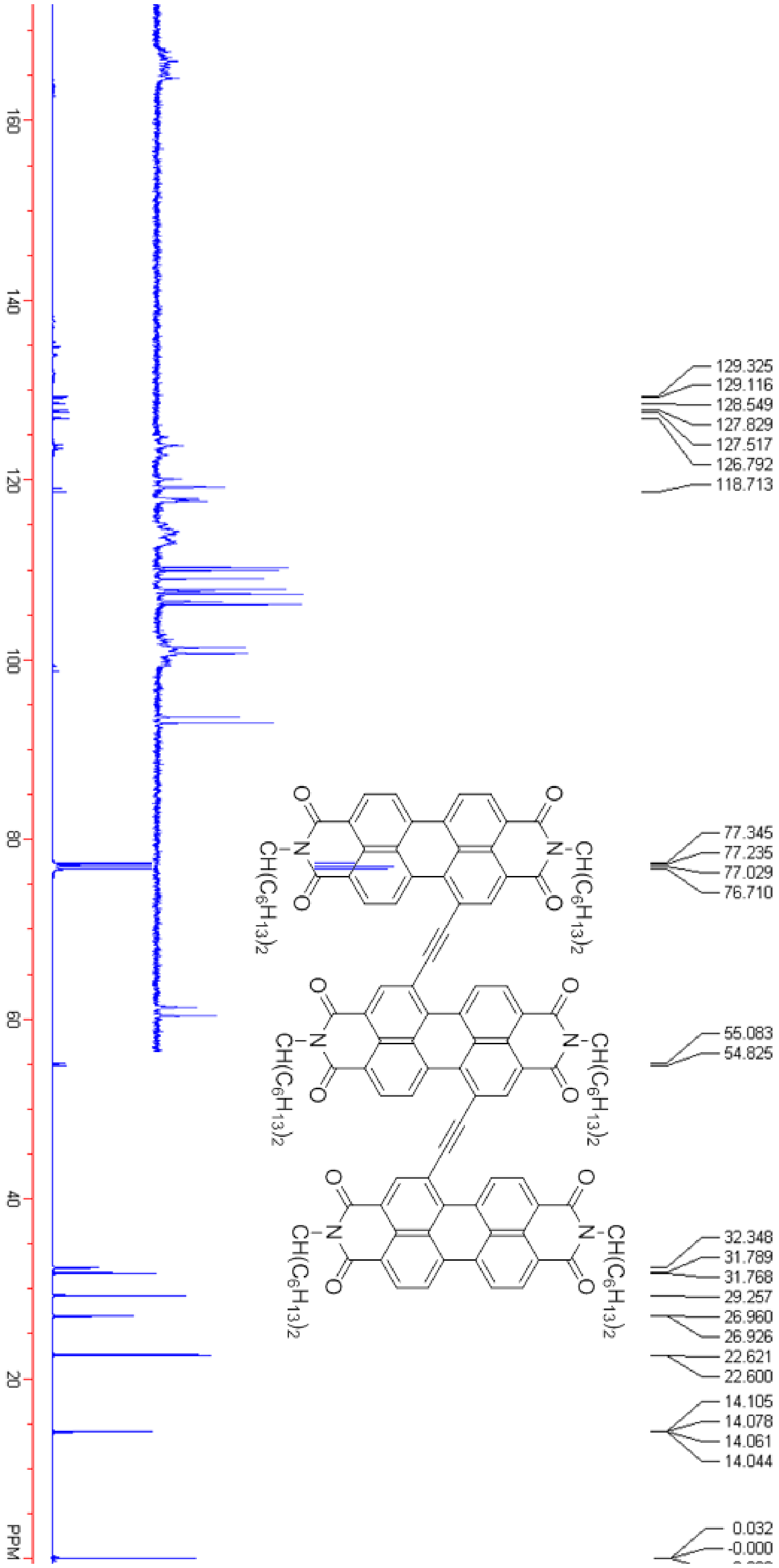
^{1}H NMR spectrum of regio-isomer mixture of **BrPBr**



^{1}H NMR spectrum of regio-isomer pure **BrPBr**



^{13}C NMR spectrum of **BrPBr**



^{13}C NMR spectrum of **PEPEP**