

Electronic Supplementary Information

Unprecedented non-aromatic, conformationally locked dibenzohexaphyrin analogs carrying multiple meso- exocyclic double bonds

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Experimental

¹H NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer using TMS as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; brs, broad singlet; d, doublet; t, triplet; m, multiplet. ¹³C NMR spectra were proton decoupled and recorded on a 100 MHz NMR spectrometer using TMS as the internal standard. All the other chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise mentioned. Column chromatography was performed over silica gel.

Compound (2)

meso-Compound **1** (0.12 g, 0.22 mmol) was dissolved in CH₂Cl₂ (30 mL), then acetone (2.5 mL, 34.0 mmol) and trifluoroacetic acid (0.08 mL, 1.06 mmol) was added. The mixture was stirred for 3 hr at room temperature (25 °C). Then, the mixture was combined with aqueous NaOH (0.1 N, 50 mL) and extracted with CH₂Cl₂ (50 mL × 3). The organic layer was dried (anhyd. Na₂SO₄) and solvent was removed under reduced pressure. The residual solid was purified by column chromatography on silica gel (CHCl₃/EtOAc = 19/1) to afford pure product. Yield: 0.022 g (16%); ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.07 (bs, 4H), 7.21 (bs, 2H), 7.04 (bs, 6H), 5.60 (bs, 4H), 5.31 (bs, 4H), 4.49 (d, *J* = 12.22 Hz, 4H), 4.25 (d, *J* = 12.22 Hz, 4H), 4.04-3.80 (m, 16H), 1.42 (br s, 12H), 1.01-0.94 (m, 24H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.

61, 167.32, 141.60, 138.61, 130.23, 128.09, 126.23, 104.04, 103.71, 79.54, 61.13, 57.30, 29.24, 14.09, 13.96; MALDI-TOF MS Calcd for C₆₆H₈₀N₄O₁₆, exact mass 1184.56, Found 1185.59.

Compound (4)

Compound **5** (0.11 g, 0.20 mmol) and acetone (2.5 mL, 34.0 mmol) were dissolved in CH₂Cl₂ (33 mL) and then TFA (0.08 mL, 1.06 mmol) was added. The whole mixture was stirred for 3 hr at room temperature. Then Aqueous NaOH (0.1 N, 30 mL) was added to quench the reaction and extracted with CH₂Cl₂ (50 mL × 3). The organic layer was dried (anhydrous Na₂SO₄) and the solvent was removed in vacuo. The residual solid was purified by column chromatography on silica (CHCl₃/EtOAc = 19/1) to afford pure product **4**. Yield: 0.014 g (12%); ¹H NMR (300 MHz, DMSO-d₆) δ 9.99 (br s, 4H), 7.49 (t, J = 7.76 Hz, 2H), 7.03 (d, J = 7.76 Hz, 4H), 5.68 (br s, 4H), 5.37 (br s, 4H), 4.65 (d, J = 11.53 Hz, 4H), 4.47 (d, J = 11.53 Hz, 4H), 4.05-3.85 (m, 16H), 1.43 (br s, 12H), 1.02-0.95 (m, 24H); MALDI-TOF MS Calcd. for C₆₄H₇₈N₆O₁₆ exact mass 1186.55, Found 1187.55.

Compound (8)

Compound **1** (0.017 g, 0.014 mmol) was dissolved in CH₂Cl₂ (2 mL), then added DDQ (0.013 g, 0.057 mmol). The mixture was stirred for 1 hr at room temperature. The mixture was combined with brine (10 mL), then extracted with CH₂Cl₂ (20 mL × 3). The organic layer was dried (anhyd. Na₂SO₄) and solvent was removed under reduced pressure. Column chromatography on silica gel (CHCl₃/EtOAc = 19/1) afforded pure compound **6**. Yield: 0.009 g (58%); ¹H NMR (300 MHz, CDCl₃) δ 11.86 (br s, 4H), 7.35 (d, J = 7.30 Hz, 4H), 7.28-7.23 (m, 6H), 7.08 (br s, 2H), 6.06 (br s, 4H), 5.92 (br s, 4H), 4.26 (q, J = 7.11 Hz, 8H), 3.91-3.89 (m, 8H), 1.79 (s, 12H), 1.28 (t, J = 7.11 Hz, 12H), 1.08 (t, J = 7.11 Hz, 12H) ¹³C NMR (100 MHz, DMSO-d₆) δ 167.08, 166.97, 146.07, 138.08, 129.11, 128.44, 126.62, 115.49, 107.23, 61.44, 60.84, 35.99, 26.15, 14.45, 13.93; MALDI-TOF MS Calcd for C₆₆H₇₂N₄O₁₆ 1176.49, Found 1176.52.

Figure S1. ^1H NMR spectrum of compound **2** in CDCl_3 .

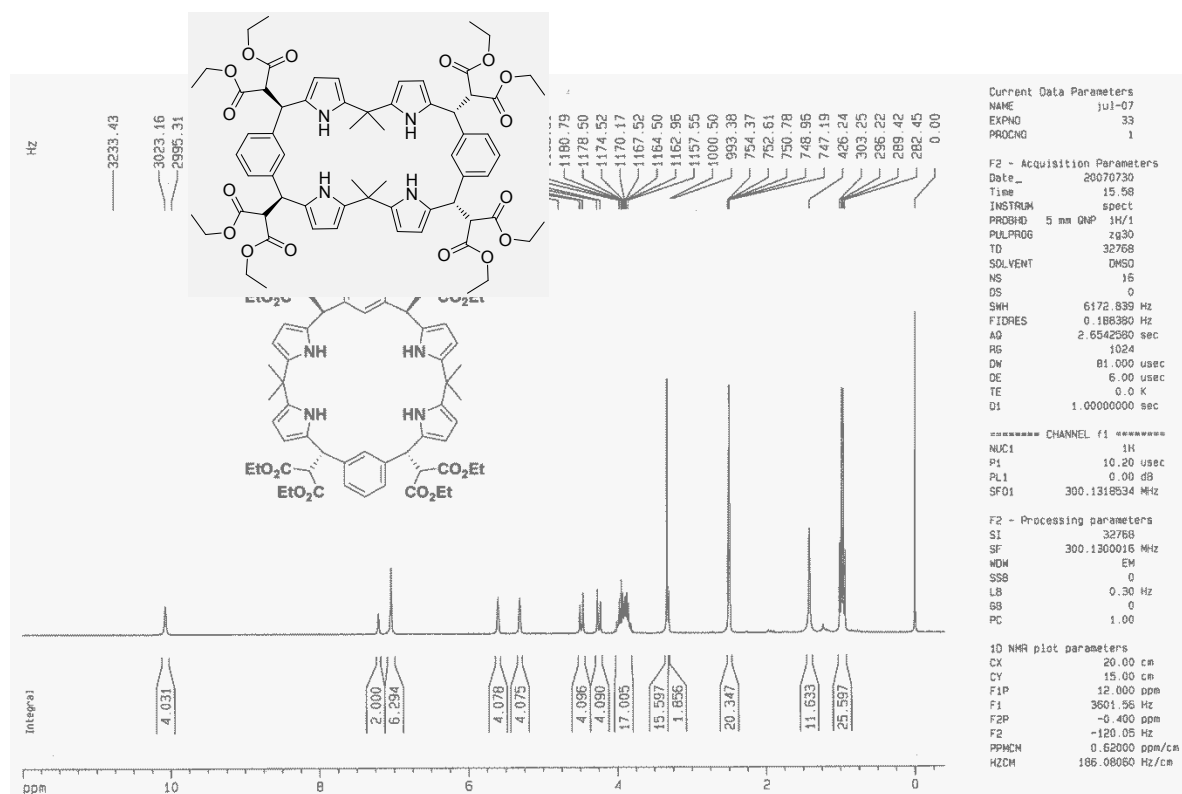


Figure S2. MALDI-TOF mass spectrum of compound **2**.

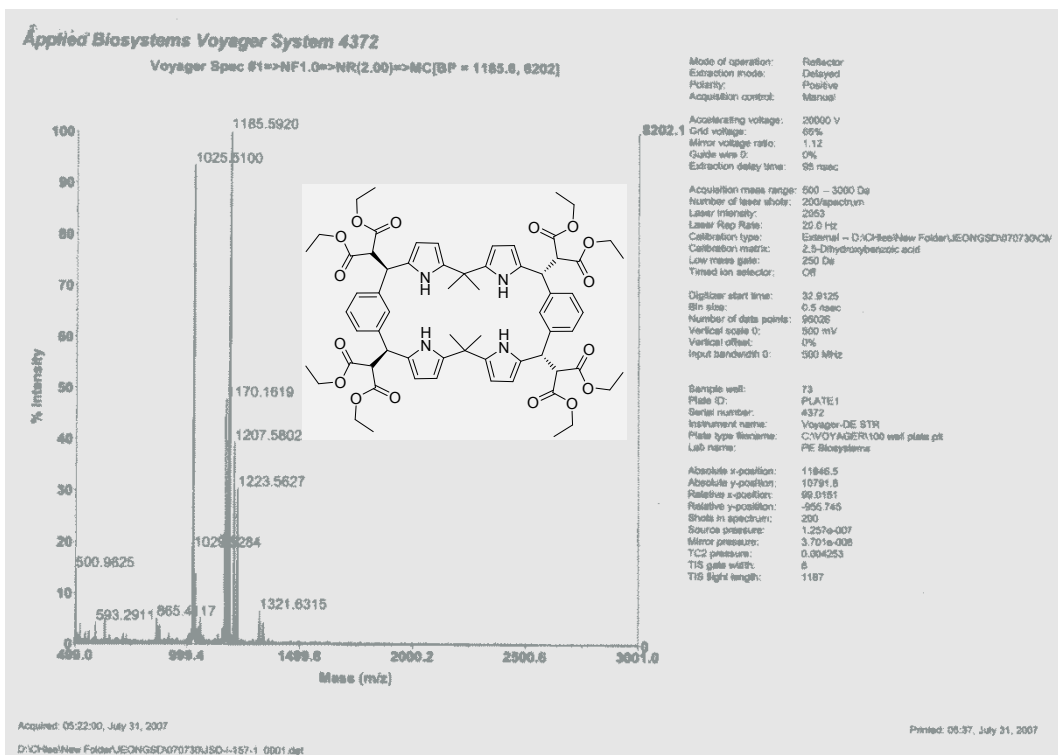


Figure S3. ^{13}C NMR spectrum of compound **2** in CDCl_3 .

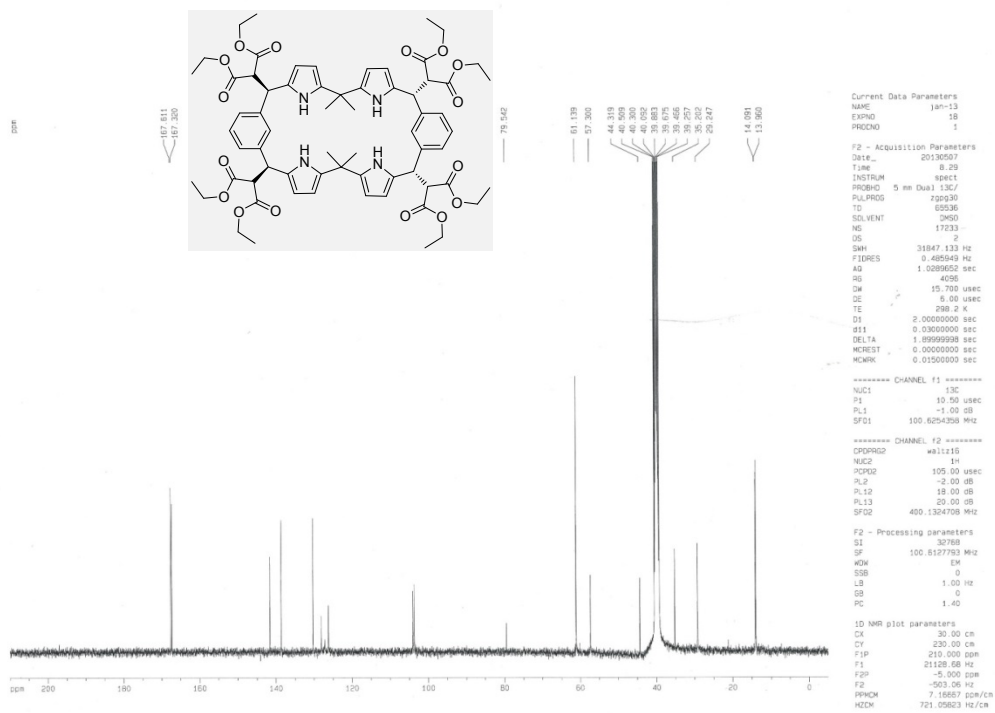


Figure S4. ^1H NMR spectrum of compound 4 in CDCl_3 .

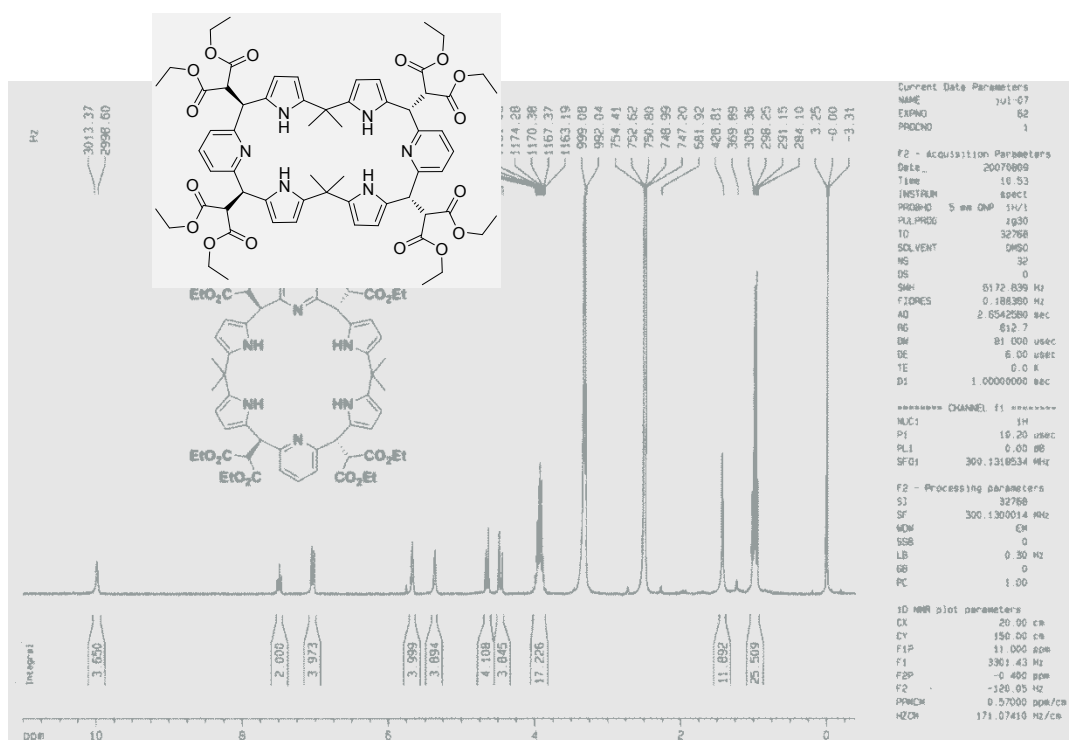


Figure S5. MALDI-TOF mass spectrum of compound 4 in CDCl₃.

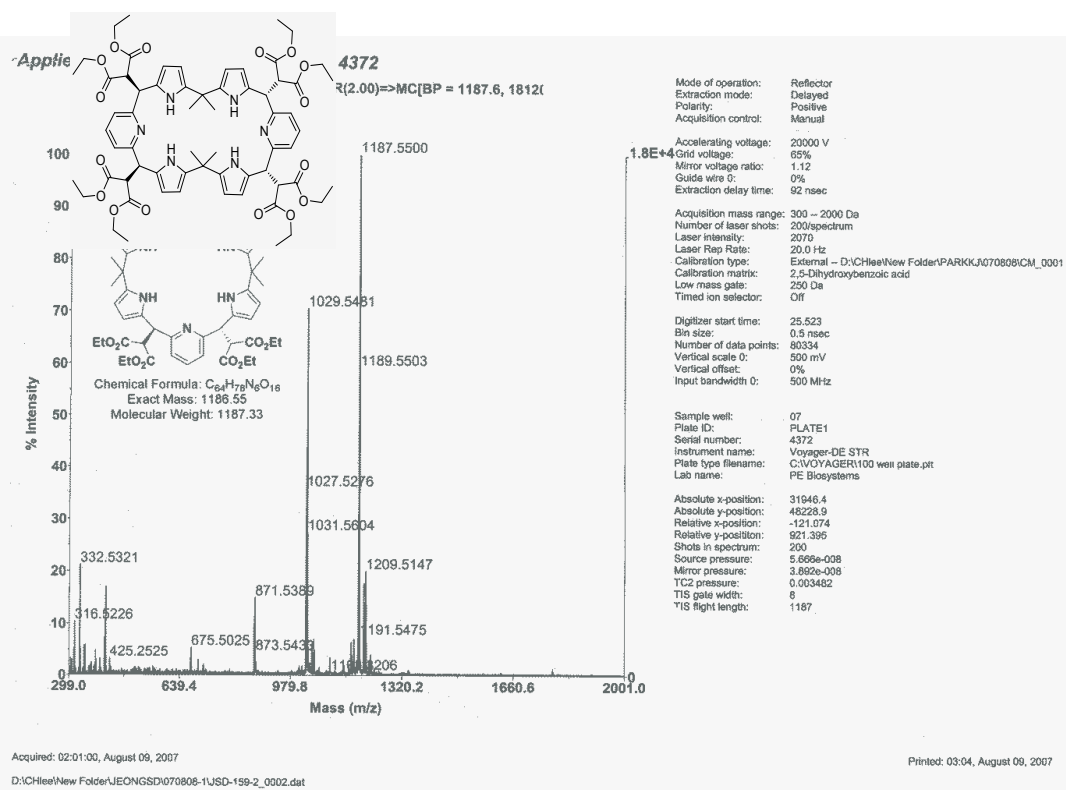


Figure S7. 1H NMR spectrum of compound **8** in $CDCl_3$.

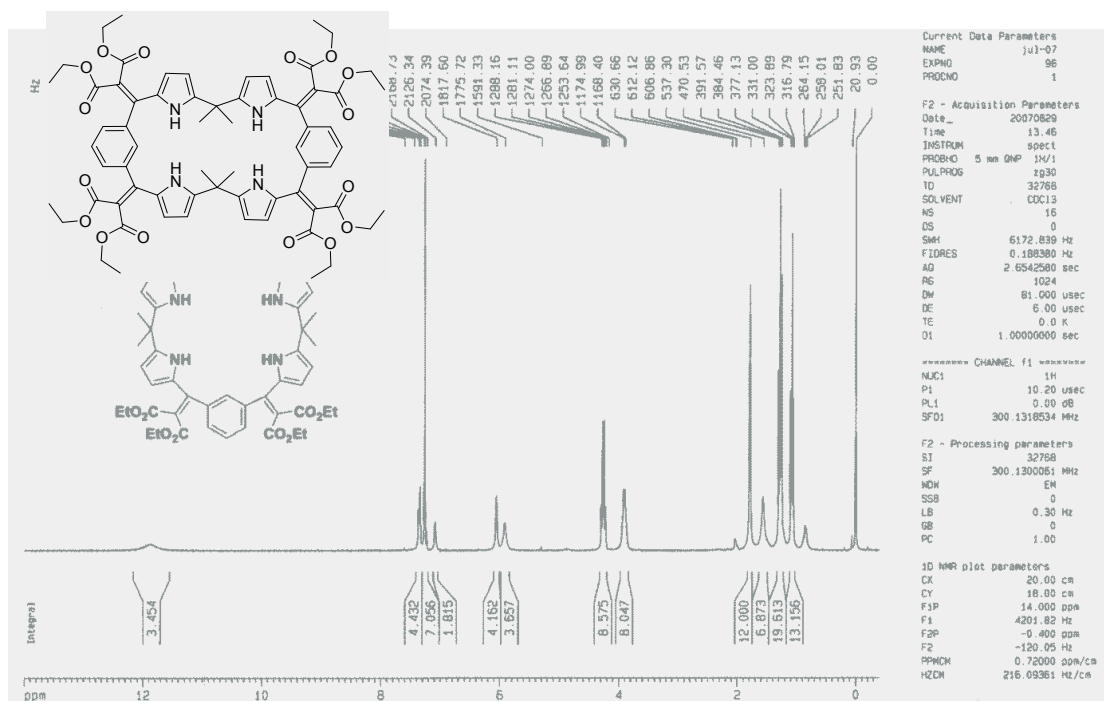


Figure S8. MALDI-TOF mass spectrum of compound 8.

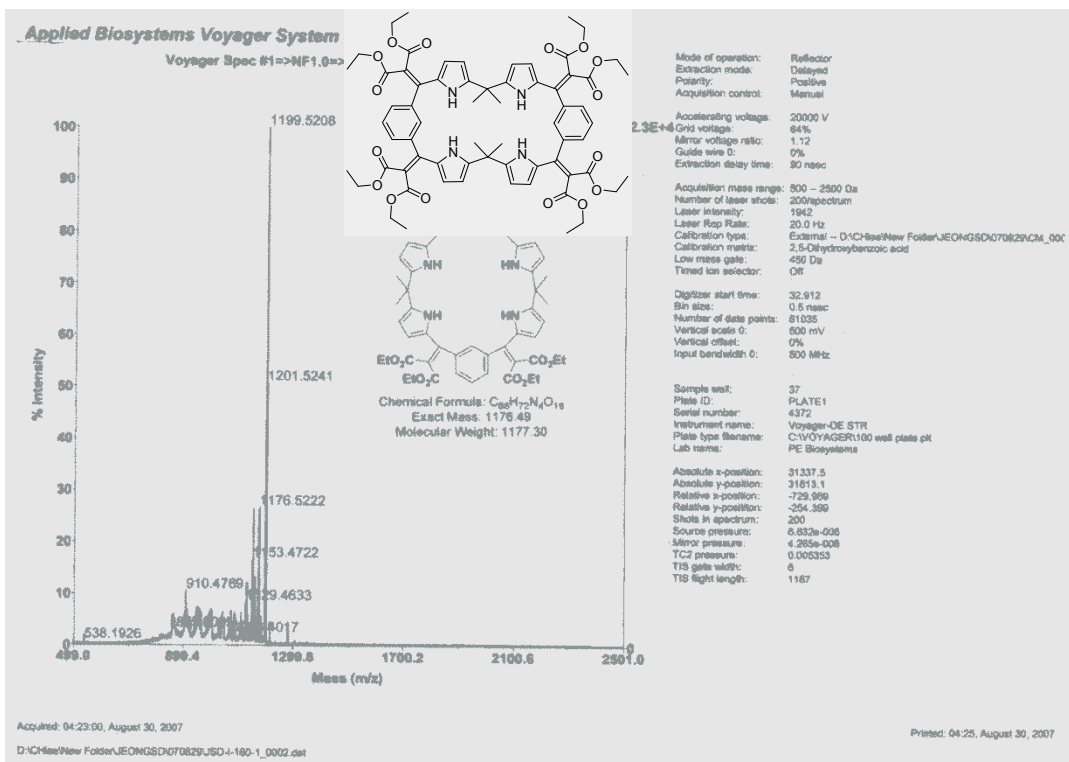
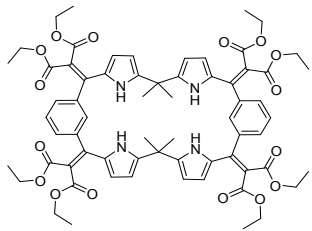
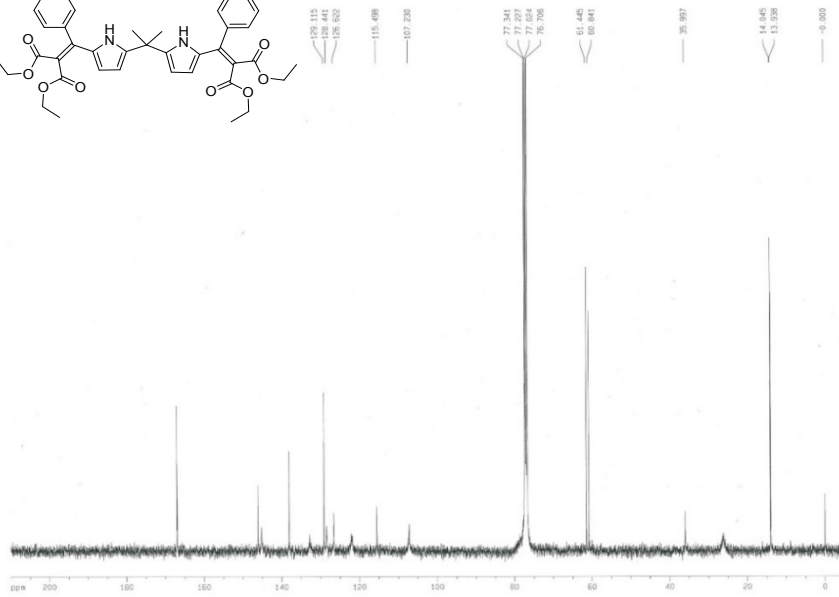


Figure S9. ¹³C NMR spectrum of compound 8 in CDCl₃.



PDW-II-97-1



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PROCNO        1

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F2P           -5.000 ppm
F2            -503.00 Hz
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HZCH         721.05817 Hz/cm

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Figure S10. UV-vis absorption spectra of compound **8** (red line) in CHCl_3 ($[\mathbf{8}] = 1.68 \times 10^{-5} \text{ M}$) and compound **2** (Black line).

