SUPPLEMENTARY INFORMATION

2D Multilayered π-Stacked Conjugated Polymers based on a U-turn Pseudo-Geminal [2.2]Paracyclophane Scaffold

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S.1. Experimental Section

**General methods.** All reagents were purchased from commercial sources and used without purification unless stated. THF and dichloromethane were dried using sodium benzophenone ketyl and calcium hydride, respectively, prior to distillation under argon. NMR analysis was performed on a Bruker DSX 300 instrument. Chemical shifts are reported relative to internal tetramethylsilane. Infrared spectra were obtained on a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corp. Ultraviolet-visible analysis was performed on a Shimadzu UV-2401PC spectrometer; and fluorescence spectra were obtained on a Shimadzu RF-5301PC spectrofluorometer. Mass spectra were determined on a VG-70SE instrument.

4,15-Diethyl[2.2]paracyclophane \((8)^{1}\), 4,15-dienyl[2.2]paracyclophane \((9)^{2}\), 4,15-dibromo[2.2]paracyclophane \((\text{pgCP-Br})_{2}^{3}\), 4,15-diiodo[2.2]paracyclophane \((\text{pgCP-I})_{2}^{3}\) and 4,8-dioctylbenzo[1,2-\(b\):4,5-\(b\)]dithiophene \((20)^{4}\) were prepared according to literature procedures. Synthetic procedures and characterization data are provided below for these, and for 2,6-diiodo-4,8-dioctylbenzo[1,2-\(b\):4,5-\(b\)]dithiophene, \(21\).
S.2. Synthetic Schemes

A. Synthesis of pg[2.2]paracyclophane monomers

1. Synthesis of pg[2.2]paracyclophane monomers

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B. Synthesis of 2,6-diiodo-4,8-dioctylbenzo[1,2-b:4,5-b']dithiophene

4,15-Diethynyl[2.2]paracyclophane, 8. The title compound was synthesized by treatment of 4,15-diformyl[2.2]paracyclophane (1.32 g, 5.00 mol) with Bestman reagent (2.5 g, 13 mmol) according to Hopf’s procedure. Recrystallization from hexane afforded 8 as a colorless crystalline solid (420 mg, 33%). m.p. 145-146 °C (Lit. 145 °C). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.67 (d, $J$ = 1.8 Hz, 2 H, Ar–H), 6.47 (d, $J$ = 7.8 Hz, 2 H, Ar–H), 6.41 (dd, $J$ = 7.8, 1.8 Hz, 2 H, Ar–H), 3.77–3.82 (m, 2 H, CH$_2$), 3.04 (s, 2 H, ≡C–H), 2.91–2.99 (m, 6 H, CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 142.4, 139.2, 136.2, 133.9, 133.5, 122.6 (Ar), 83.4, 81.2 (C≡C), 34.8, 33.4 (CH$_2$). IR (ATR): 3301, 3013, 2947, 1588, 1495 cm$^{-1}$. MS (EI): $m/z$ (%) 256.0 (M$^+$, 54), 127.9 (100). HRMS calculated for C$_{20}$H$_{16}$, 256.1248; found 256.1252, $\Delta$ = 1.5 ppm.

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**4,15-Diethenyl[2.2]paracyclophane, 9.** The title compound was prepared by treatment of 4,15-diformyl[2.2]paracyclophane (900 mg, 3.00 mol) with the ylid prepared by the reaction of methyl triphenylphosphonium bromide (3.6 g, 10 mmol) with n-BuLi (4.3 mL of a 1.6 M solution in hexane, 6.8 mmol) according to the method described in reference 2. Recrystallization of the crude product from hexane afforded 9 as a colorless crystalline solid (400 mg, 45%). m.p. 163-164°C (Lit. 2 165 °C). $^1$H NMR (300 MHz, CDCl$_3$) δ 6.82 (dd, $J$ = 17.6, 11.4 Hz, 2 H, vinylic), 6.59 (d, $J$ = 1.2 Hz, 2 H, Ar–H), 6.49 (d, $J$ = 7.9 Hz, 2 H, Ar–H), 6.45 (dd, $J$ = 7.9, 1.8 Hz, 2 H, Ar–H), 5.36 (dd, $J$ = 17.3, 1.4 Hz, 2 H, vinylic), 5.08 (dd, $J$ = 10.8, 1.4 Hz, 2 H, vinylic), 3.48–3.60 (m, 2 H, CH$_2$), 2.90–3.10 (m, 6 H, CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.4, 138.1, 137.3, 135.5, 134.6, 132.4, 129.8, 114.7 (sp$^2$ C), 83.4, 81.2 (C≡C), 35.1, 32.5 (CH$_2$). IR (ATR): 3080, 3000, 2921, 2853, 1629, 1461, 905, 714 cm$^{-1}$. MS (EI): m/z (%) 260.1 (M+, 54), 129.1 (100). HRMS calculated for C$_{20}$H$_{20}$, 260.1565; found 260.1575, Δ = 3.8 ppm.

**4,15-Dibromo[2.2]paracyclophane, 13.** The title compound was prepared by treatment of 4,15-azo[2.2]paracyclophane (500 mg, 2.00 mol) and bromine (343 mg, 4.00 mol) according to literature method$^3$ and isolated as a colorless crystalline solid (510 mg, 65%). m.p. 175-176°C (Lit.$^3$ 180 °C). $^1$H NMR (300 MHz, CDCl$_3$) δ 6.78 (d, $J$ = 1.4 Hz, 2 H, Ar–H), 6.53 (m, 4 H, Ar–H), 3.64–3.80 (m, 2 H, CH$_2$), 2.90–3.15 (m, 6 H, CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.9, 138.5, 135.7, 135.1, 132.3, 125.1 (Ar), 34.7, 34.6 (CH$_2$). IR (ATR): 3068, 3018, 2938, 1896, 1584, 1462, 1031, 867 cm$^{-1}$. MS (EI): m/z (%) 363.9 (M$^+$, 20), 182.0 (100). HRMS calculated for C$_{16}$H$_{14}$Br$_2$, 363.9462; found 363.9467, Δ = 1.4 ppm.

**4,15-Diiodo[2.2]paracyclophane, 14.** The title compound was prepared by treatment of 4,15-azo[2.2]paracyclophane (500 mg, 2.00 mol) with iodine monochloride (382 mg, 2.00 mol) according to the literature method$^3$ and was isolated as a colorless crystalline solid (310 mg, 65%).
32%). m.p. 237-238°C (Lit.4 239 °C). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.06 (d, $J = 1.5$ Hz, 2 H, Ar–H), 6.51 (m, 4 H, Ar–H), 3.51–3.75 (m, 2 H, CH$_2$), 2.88–3.22 (m, 6 H, CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 142.4, 141.8, 140.7, 133.8, 133.3, 99.8 (Ar), 38.9, 34.6 (CH$_2$). IR (AT–IR, neat): 3024, 2955, 1579, 1462, 1026, 866 cm$^{-1}$. MS (EI): $m/z$ (%) 459.9 (M$^+$, 70), 230.0 (100). HRMS calculated for C$_{16}$H$_{14}$I$_2$, 459.9185; found 459.9187, Δ = 0.4 ppm.

2,6-Diiodo-4,8-dioctylbenzo[1,2-b:4,5-b]dithiophene, 21. A solution of $n$-butyllithium (1.9 mL, 1.6 M in hexane, 3.0 mmol) was added dropwise to a solution of 4,8-dioctylbenzo[1,2-b:4,5-b]dithiophene$^4$ (400 mg, 1.00 mmol) in dry THF (20 mL) at -20 °C. The reaction mixture was stirred at room temperature for 2 h, and iodine (900 mg, 4.00 mmol) was added. The mixture was stirred for 12 h, washed with saturated aq. sodium sulfite (50 mL) and water (50 mL), and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by recrystallization from MeOH to give 2,6-diiodo-4,8-dioctylbenzo[1,2-b:4,5-b]dithiophene as yellow powder (640 mg, 99%). m.p. 146-147 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.61 (s, 2 H, Ar–H), 3.0 (t, $J = 7.6$ Hz, 4 H, Ar–CH$_2$), 1.74 (p, $J = 6.0$ Hz, 4 H, C=CH$_2$), 1.20-1.50 (m, 20 H, CH$_2$), 0.88 (t, $J = 6.1$ Hz, 6 H, CH$_3$). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 141.7, 136.6, 131.8, 126.7, 78.3 (Ar), 33.4, 31.9, 29.8, 29.6, 29.4, 29.2, 22.7 (CH$_2$), 14.1 (CH$_3$). IR (ATR): 3010, 2940, 2900, 1446, 1385, 1260, 861, 749, 671 cm$^{-1}$. MS (EI): $m/z$ (%) 666.1 (M$^+$, 100), 566.9 (35). HRMS calculated for C$_{26}$H$_{36}$S$_2$I$_2$, 666.0348; found 666.0350, Δ = 0.3 ppm.
Figure 1A. $^1$H NMR spectrum of 4,15-diethynyl[2.2]paracyclophane, 8 (300 MHz, CDCl$_3$, 23 $^\circ$C).

Figure 1B. $^{13}$C NMR spectrum of 4,15-diethynyl[2.2]paracyclophane, 8 (75 MHz, CDCl$_3$, 23 $^\circ$C).
Figure 2A. $^1$H NMR spectrum of 4,15-dietheny1[2.2]paracyclophane, 9 (300 MHz, CDCl$_3$, 23 °C).

Figure 2B. $^{13}$C NMR spectrum of 4,15-dietheny1[2.2]paracyclophane, 9 (75 MHz, CDCl$_3$, 23 °C).
**Figure 3A.** $^1$H NMR spectrum of 4,15-dibromo[2.2]paracyclophane, \textit{pgCP-Br}_2 (300 MHz, CDCl$_3$, 23 °C).

**Figure 3B.** $^{13}$C NMR spectrum of 4,15-dibromo[2.2]paracyclophane, \textit{pgCP-Br}_2 (75 MHz, CDCl$_3$, 23 °C).
Figure 4B. $^1$H NMR spectrum of 4,15-diiodo[2.2]paracyclophane, \textit{pgCP-Br$_2$} (300 MHz, CDCl$_3$, 23 °C).

Figure 4A. $^{13}$C NMR spectrum of 4,15-diiodo[2.2]paracyclophane, \textit{pgCP-I$_2$} (300 MHz, CDCl$_3$, 23 °C).
Figure 5A. $^1$H NMR spectrum of 2,6-diiodo-4,8-dioctylbenzo[1,2-$b$:4,5-$b'$]dithiophene (300 MHz, CDCl$_3$, 23 °C).

Figure 5B. $^{13}$C NMR spectrum of 2,6-diiodo-4,8-dioctylbenzo[1,2-$b$:4,5-$b'$]dithiophene (75 MHz, CDCl$_3$, 23 °C).
Figure 6A. $^1$H NMR spectrum of Me$_4$PE$_3$ (300 MHz, CDCl$_3$, 23 °C).

Figure 6B. $^{13}$C NMR spectrum of Me$_4$PE$_3$ (75 MHz, CDCl$_3$, 23 °C).
Figure 7A. $^1$H NMR spectrum of Me$_4$PV$_3$ (300 MHz, CDCl$_3$, 23 °C).

Figure 7B. $^{13}$C NMR spectrum of Me$_4$PV$_3$ (75 MHz, CDCl$_3$, 23 °C).
Figure 8A. $^1$H NMR spectrum of E-BDT-Xy$_2$ (300 MHz, CDCl$_3$, 23 °C).

Figure 8B. $^{13}$C NMR spectrum of E-BDT-Xy$_2$ (75 MHz, CDCl$_3$, 23 °C).
Figure 9. IR spectrum of 4,15-diethynyl[2.2]paracyclophane, 8.
Figure 10. IR spectrum of \textit{pg}-poly(PE$_3$).
Figure 11. IR spectrum of \textit{pg}-poly(CP-E-BDT).
Figure 12. IR spectrum of 4,15-diethenyl[2.2]paracyclophane, 9.
Figure 13. IR spectrum of $pg$-poly(PV$_3$).
References


