Supplementary Material (ESI) for Chemical Communications

Tetrachloro-Tetra(perylene bisimides) : An Approach towards *N*-type Graphene Nanoribbons

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Materials and Methods

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. DMSO was freshly distilled from CaH_2. N,N'-di(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic bisimide **2** was prepared according to known procedure,[1] and 4Cl-diPBI **3** was prepared according to the literature reported by our group. [2]

^{1}H NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer and a Bruker ADVANCE 600 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer.

Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammograms (CVs) were recorded on a Zahner IM6e electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker. 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) dissolved in CH_2Cl_2 was employed as the supporting electrolyte. CH_2Cl_2 was dried over calcium hydride and degassed prior to measurement. Two isomers of 4Cl-tetra(perylene bisimides) were separated by HPLC, using Cosmosil Buckyprep as the column and toluene as the eluent.

Synthesis and characterization of 4Cl-tetraPBIs 1a and 1b

A mixture of 4Cl-diPBI **3** (1.1 g, 0.71 mmol), nano copper powder (440mg, 6.92 mmol), $Pd(PPh_3)_4$ (220 mg, 0.19 mmol) in 400 ml dry DMSO was heated at 110 under Ar for 10 h. The cooled mixture was poured into water and the product was extracted with ethyl acetate. The organic layers were separated, washed with brine, dried over Na_2SO_4, and purified by column separation (silica gel, petroleum ether/CH_2Cl_2 = 1:1). Yield 88 mg (8.4%) **4Cl-tetraPBIs** as dark-green solids, the obtained **4Cl-tetraPBIs** were separated by HPLC into two fractions using Cosmosil Buckyprep as the column and toluene as the eluent. After separation, **4Cl-tetraPBI 1a** (22 mg) and **1b** (66 mg) were obtained, in yield of 2.1% and 6.3%, respectively. MS (MALDI-TOF): calcd for **4Cl-tetraPBIs** $C_{144}H_{114}N_6O_{12}$, 2963.0 $[M]^-$ (maximum peak), found, **4Cl-tetraPBI 1a** *m/z* = 2963.4 (maximum peak); **4Cl-tetraPBI 1b** *m/z* = 2963.4 (maximum peak).

4Cl-tetraPBI 1a. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 11.30 (s, 1H, perylene-H), 10.83 (d, 2H, perylene-H), 10.71 (s, 1H, perylene-H), 10.66 (s, 1H, perylene-H), 10.37 (s, 1H, perylene-H), 9.42 (s, 2H, perylene-H), 9.13 (s, 2H, perylene-H), 7.46-7.58 (m, 16H, phenyl-H), 7.35 (d, 2H, phenyl-H), 7.22

(d, 2H, phenyl-H), 7.17 (d, 2H, phenyl-H), 7.03 (d, 2H, phenyl-H), 7.02 (m, 2H, phenyl-H), 4.27 (b, 1H, isopropyl-H), 3.66-3.73 (m, 4H, isopropyl-H), 3.21 (m, 1H, isopropyl-H), 3.02 (m, 2H, isopropyl-H), 2.58 (m, 2H, isopropyl-H), 2.33 (m, 4H, isopropyl-H), 2.10 (m, 2H, isopropyl-H), 1.86 (m, 2H, isopropyl-H), 1.70-1.78 (m, 24H, isopropyl-H), 1.30 (m, 24H, isopropyl-H), 1.03-1.11 (m, 24H, isopropyl-H), 0.65-0.87 (m, 18H, isopropyl-H), 0.55 (m, 6H, isopropyl-H). ^{13}C NMR ($CDCl_3$, 150 MHz, 298K): δ =163.7, 163.0, 147.4, 146.4, 145.4, 144.8, 136.4, 130.9, 130.6, 130.4, 129.9, 129.8, 127.3, 127.1, 126.4, 124.8, 124.6, 124.3, 123.8, 121.4, 120.9, 119.2, 31.9, 30.6, 29.9, 29.7, 29.3, 24.9, 24.1, 23.8, 23.5, 22.7.

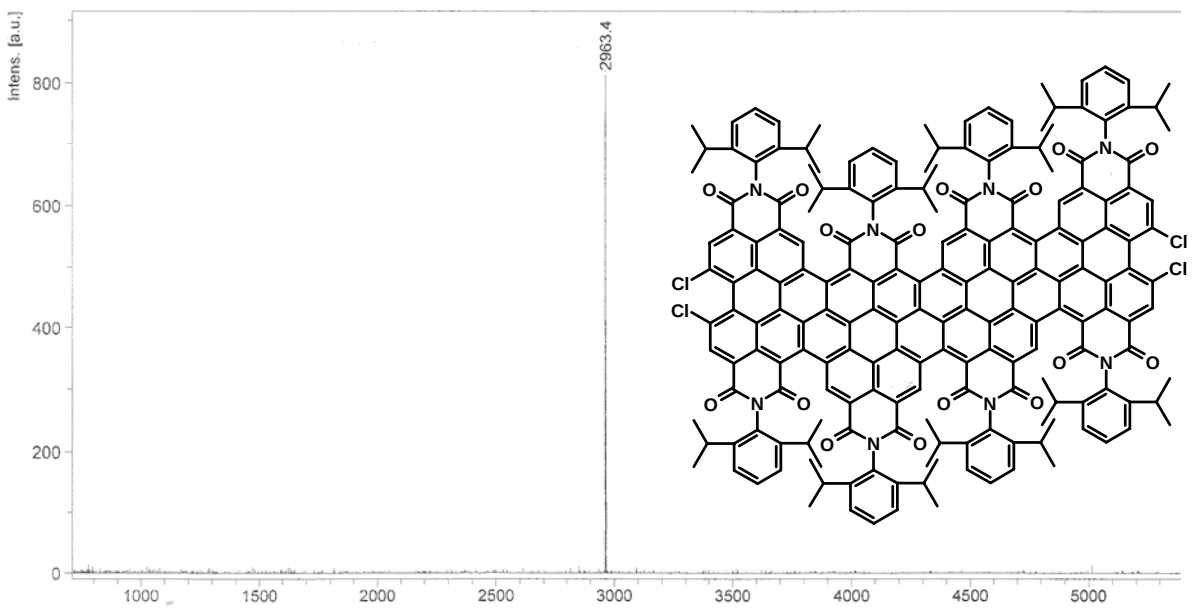
4Cl-tetraPBI 1b. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 11.15 (s, 2H, perylene-H), 10.68 (s, 2H, perylene-H), 10.64 (s, 2H, perylene-H), 9.42 (s, 2H, perylene-H), 9.12 (s, 2H, perylene-H), 7.45-7.59 (m, 18H, phenyl-H), 7.33 (d, 2H, phenyl-H), 7.29 (d, 2H, phenyl-H), 7.08 (d, 2H, phenyl-H), 4.24 (b, 2H, isopropyl-H), 3.64 (m, 2H, isopropyl-H), 3.21 (m, 2H, isopropyl-H), 3.01 (m, 2H, isopropyl-H), 2.58 (m, 2H, isopropyl-H), 2.36 (m, 4H, isopropyl-H), 1.86 (m, 2H, isopropyl-H), 1.78 (m, 12H, isopropyl-H), 1.70 (m, 6H, isopropyl-H), 1.48 (m, 6H, isopropyl-H), 1.34 (m, 30H, isopropyl-H), 1.09 (m, 6H, isopropyl-H), 1.02 (m, 12H, isopropyl-H), 0.85 (m, 18H, isopropyl-H), 0.55 (m, 6H, isopropyl-H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298K): δ = 163.7, 163.4, 163.2, 163.1, 163.0, 147.1, 146.4, 146.2, 145.4, 145.1, 144.4, 136.5, 136.4, 131.5, 130.8, 130.6, 130.4, 130.3, 130.0, 129.8, 129.6, 129.0, 127.9, 127.6, 127.0, 126.4, 124.8, 124.6, 124.4, 124.2, 123.8, 123.0, 121.5, 120.8, 119.6, 119.2, 30.2, 29.7, 29.2, 29.1, 28.9, 25.2, 24.9, 24.5, 24.3, 24.1, 23.8.

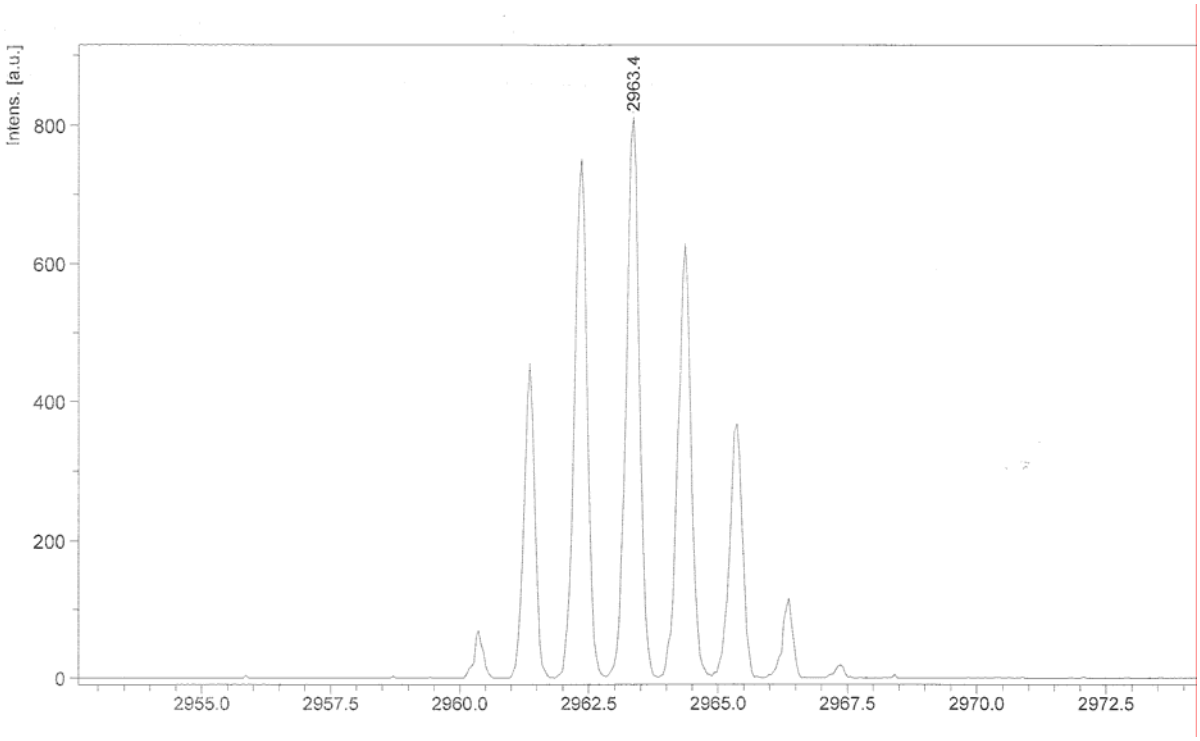
Additional References

S1. (*a*) H. Quante and K. Müllen, *Angew. Chem. Int. Ed.*, 1995, **34**, 1323; (*b*) Würthner, F., Sautter, A. And Schilling, J. *J. Org. Chem.*, 2002, **67**, 3037.

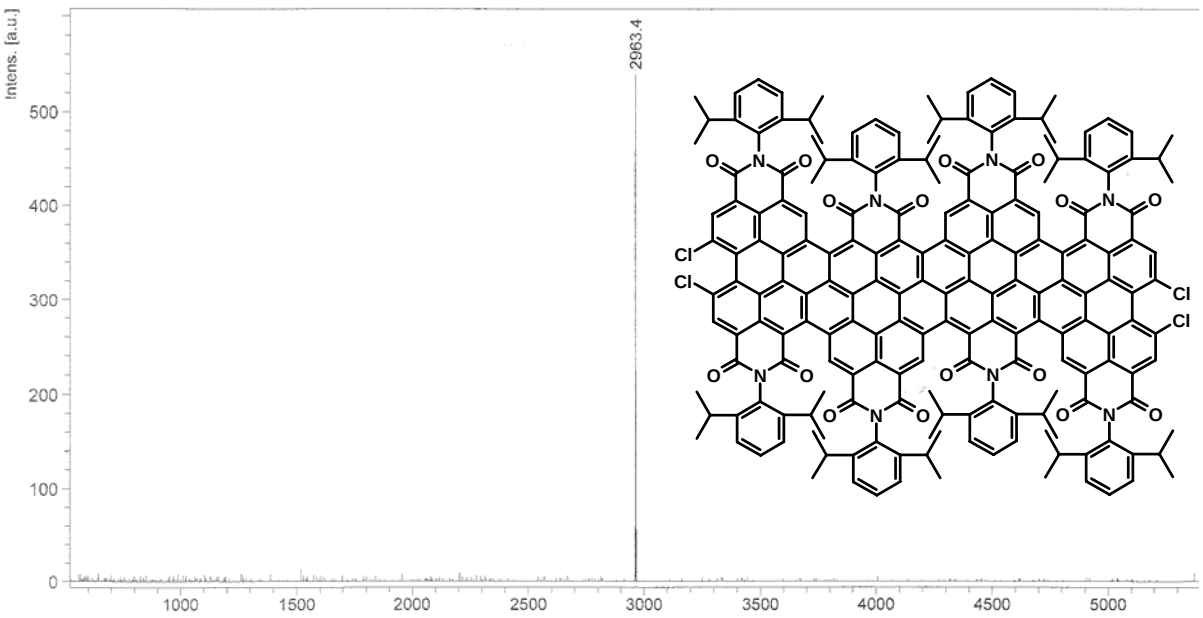
S2. H. Qian, Z. Wang, W. Yue and D. Zhu, *J. Am. Chem. Soc*., 2007, **129**, 10664.

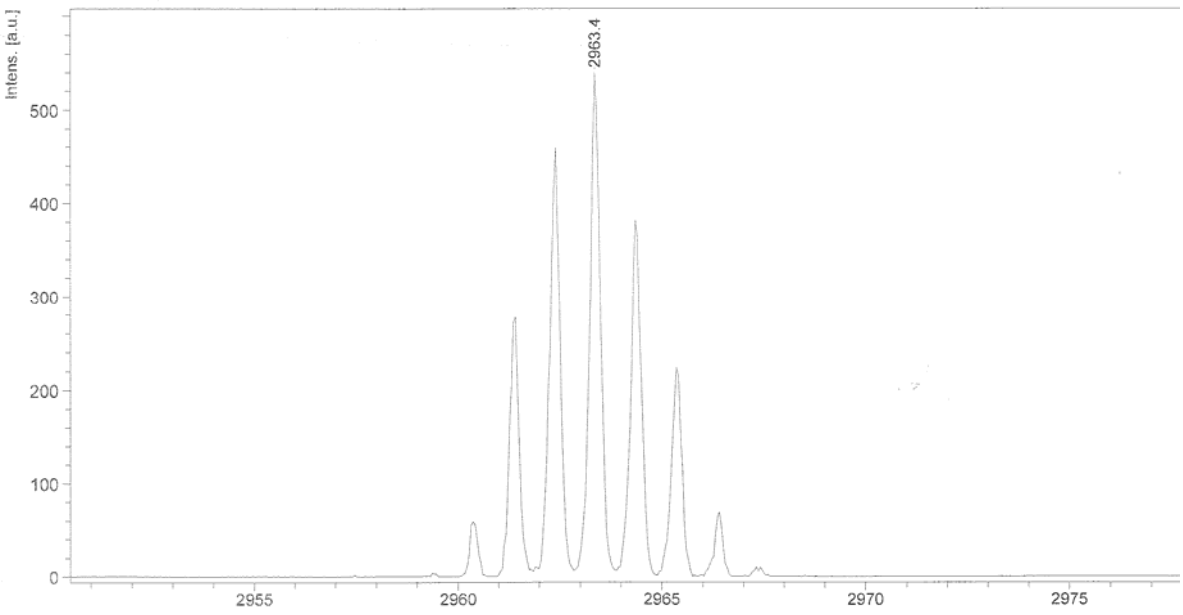
MALDI-TOF MS of 1a



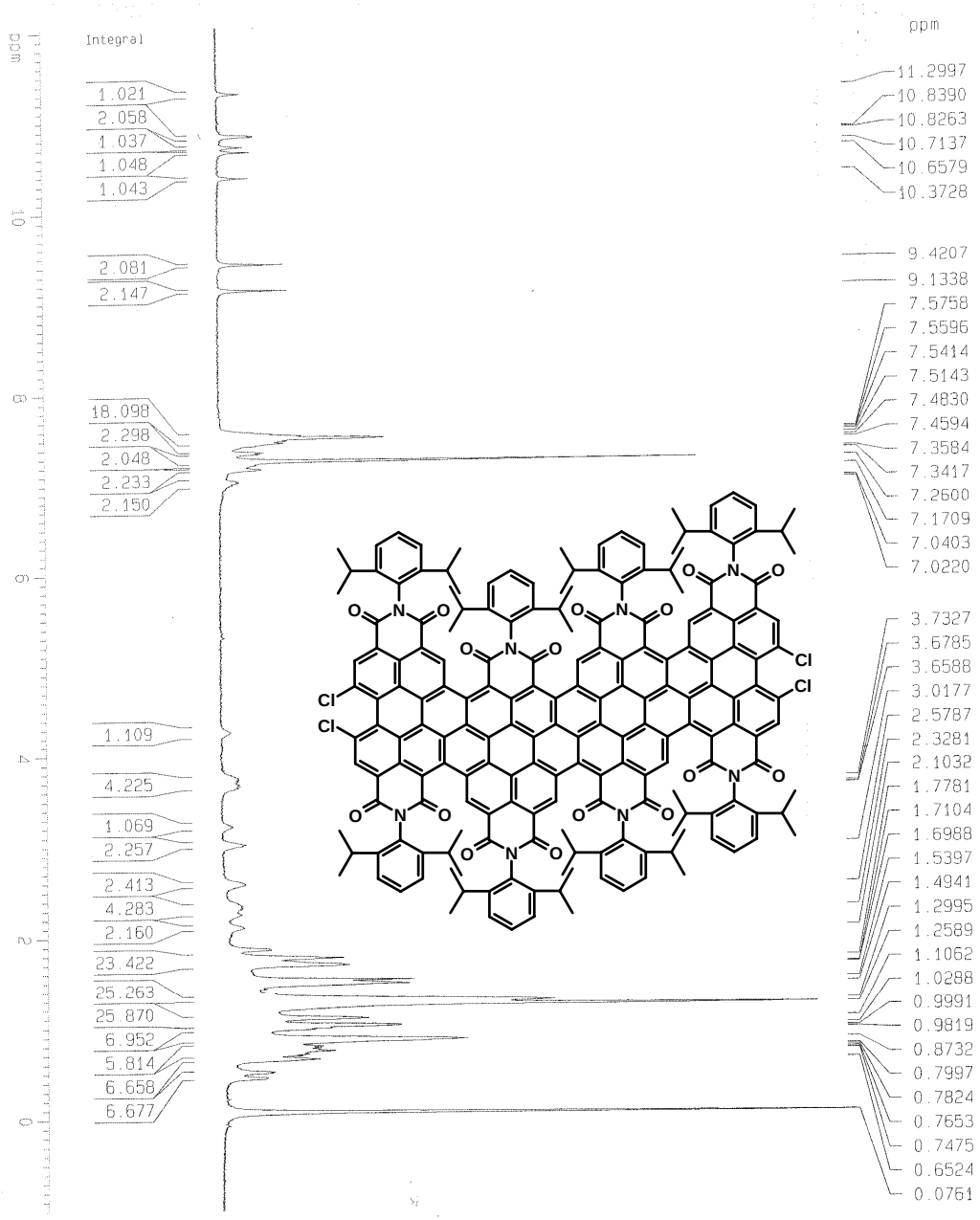


MALDI-TOF MS of 1b





^{1}H NMR spectrum of 1a



^{1}H NMR spectrum of 1b