Supporting Information for
Chiral Nano-ribbons Based on
Doubly-linked Oligo-perylene Bisimides

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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 CaH₂. N,N'-di(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic bisimide 1 was prepared according to known procedure.¹
¹H NMR and ¹³C NMR spectra were recorded in deuterated solvents on a Bruker DMX 300 NMR Spectrometer, a Bruker ADVANCE 400 NMR Spectrometer and a Bruker ADVANCE 600 NMR Spectrometer. ¹H 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, and High resolution mass spectra (HRMS) were determined on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (APEX IV).
Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell, fluorescence measurements were carried out with a Hitachi (model F-4500) spectrophotometer in a 1-cm quartz cell. The fluorescence quantum yield was determined by the optically dilute method with N,N'-Di(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic bisimide S1² (Φ_f = 1.00 in CHCl₃) as reference. 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 (TBAPF₆) dissolved in CH₂Cl₂ (HPLC grade) was employed as the supporting electrolyte. CH₂Cl₂ was dried over calcium hydride and degassed prior to measurement. Circular dichroism (CD) measurements were carried out on a Jasco-810 spectropolarimeter in a 1cm path-length cell at room temperature. Spectra were collected with scan speed of 500 nm/min and response time of 0.5 s. Each spectrum was the average of three scans and corrected by chloroform. The isomers of dimer 2 and trimer 3 were separated by HPLC using Chiralcel OD as the column and a mixture of n-hexane and isopropanol as the eluent.
Synthesis of PBI-based dimer 2 and trimer 3
A Schlenk flask was charged with tetrachloroperylene bisimide 1 (1.0 g, 1.18 mmol), copper powder (Aldrich, <100 nm particle size, 99.8%) (720 mg, 11.3 mmol) and 160 ml dry DMSO under argon. The mixture was heated to 110 °C with vigorous stirring for 22 h. The cooled mixture was poured into water and the product was extracted with ethyl acetate. The organic layers were

S1
separated, dried over Na$_2$SO$_4$, and purified by column separation (silica gel, petroleum ether/CH$_2$Cl$_2$ = 4:1). Yield 2 (229 mg, 25.0%) and 3 (89 mg, 10.0%) as red solids, while 20.0% of 1 was recovered unchanged.

**Dimer 2**: $^1$H NMR (acetone-d$_6$, 400 MHz, 298 K): $\delta = 8.74$ (d, 4H, perylene-H), 8.16 (s, 4H, perylene-H), 7.45 (t, 4H, phenyl-H), 7.33 (m, 8H, phenyl-H), 2.76-2.92 (m, 8H, isopropyl-H), 1.13 (d, 12H, isopropyl-H), 1.09 (d, 24H, isopropyl-H), 0.99 (d, 12H, isopropyl-H); $^{13}$C NMR (acetone-d$_6$, 100 MHz, 298 K): $\delta = 164.6, 164.0, 141.9, 141.9, 134.6, 130.9, 127.2, 125.5, 125.3, 124.5, 24.9, 24.8$; MS (MALDI-TOF): cacld for M, 1552.4; found, 1552.7. HRMS cacld for C$_{96}$H$_{77}$Cl$_4$N$_4$O$_8$$^+$$[M+H]^+$, 1553.4490; found, 1553.4499.

**Trimer 5**: $^1$H NMR (CDCl$_3$CDCl$_2$, 300 MHz, 340 K): $\delta = 8.86$ (s, 4H, perylene-H), 8.28 (s, 2H, perylene-H), 8.23 (s, 2H, perylene-H), 8.13 (s, 2H, perylene-H), 8.03 (s, 2H, perylene-H), 7.43 (m, 6H, phenyl-H), 7.28 (m, 12H, phenyl-H), 2.71 (m, 12H, isopropyl-H), 1.20 (m, 48H, isopropyl-H), 0.92 (m, 24H, isopropyl-H); $^{13}$C NMR (CDCl$_3$CDCl$_2$, 150 MHz, 298 K): $\delta = 163.0, 162.8, 162.3, 162.9, 145.7, 145.4, 140.7, 134.6, 133.8, 129.8, 129.6, 129.3, 126.7, 124.0, 123.4, 123.3, 29.6, 29.0, 24.3, 24.1, 24.0; MS (MALDI-TOF): cacld for M, 2258.7; found, 2259.5. HRMS cacld for C$_{144}$H$_{115}$Cl$_4$N$_6$O$_{12}$+$[M+H]^+$, 2259.7322; found, 2259.7333.

**Chiral HPLC chromatograms of dimer 2 and trimer 3:**

**Figure S1.** (a) Resolution of dimer 2 (Chiralcel OD column; Hex/i-PrOH = 95/5; 0.7 mL/min; UV, 519nm). (b) Resolution of trimer 5 (Chiralcel OD column; Hex/i-PrOH = 90/10; 1 mL/min; UV, 519nm)

**Investigation on physical and electronic properties of dimer 2 and trimer 3**

**Table S1.** Photophysical and Electrochemical properties of dimer 2 and trimer 3 compared with perylene bisimides.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$\Phi_{\text{fl}}^a$</th>
<th>$E_{1r}^b$</th>
<th>$E_{2r}^b$</th>
<th>$E_{3r}^b$</th>
<th>$E_{4r}^b$</th>
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<tbody>
<tr>
<td>PBI S1</td>
<td>527</td>
<td>80900</td>
<td>534</td>
<td>1</td>
<td>-0.96</td>
<td>-1.22</td>
<td>-</td>
<td>-</td>
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<tr>
<td>4Cl-PBI 1</td>
<td>522</td>
<td>47300</td>
<td>548</td>
<td>0.85</td>
<td>-0.74</td>
<td>-1.06</td>
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<tr>
<td>dimer 2</td>
<td>528</td>
<td>83000</td>
<td>552</td>
<td>0.66</td>
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<td>-0.83</td>
<td>-0.95</td>
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<tr>
<td>trimer 3</td>
<td>528</td>
<td>93800</td>
<td>562</td>
<td>0.51</td>
<td>-0.67</td>
<td>-0.78</td>
<td>-0.93</td>
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</table>

a. Determined with N,N'-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid bisimide S1 as reference.

b. Measured in 0.1 M solution of Bu$_4$NPF$_6$ in dichloromethane with a scan rate of 100 mV/s (in V vs Fc/Fc$^+$).
Computational details
Quantum chemical calculations were carried out on models of 4Cl-PBI 1, dimer 2, trimer 3, featuring methyl substituents instead of the isopropyl units on the phenyl rings. Atomic structures of 2 and 3 were optimized with density functional theory (DFT) calculations using the B3LYP hybrid functional with the basis set limited to 3-21G* owing to the large dimension of the chromophores. In general, time dependent (TD) DFT erroneously predicts the wrong order of charge transfer states and neutral states. For this reason, to compute vertical excitation energies, absorption and CD spectra of the doubly linked oligo PBIs at their optimized structures we run TD calculations employing the long-range corrected CAM-B3LYP functional and the 3-21G* basis set. This functional has been shown to perform well for charge transfer excitations. Electronic excitation energies and oscillation strengths were computed for the 140 lowest singlet excited electronic states of 2 and 3. The lowest computed excited states are neutral states and dipole allowed transitions are correspondingly computed (see Table S3). Charge transfer states are located above the allowed transitions. In plotting computed electronic absorption and CD spectra a Lorentzian line-width of 0.1 eV was superimposed to each computed intensity to facilitate the comparison with experimental spectra. Because the CAM-B3LYP/3-21G* excitation energies are slightly overestimated compared with the experimental values, to facilitate comparison, the computed CD spectra were red shifted to match the first observed band. All quantum-chemical calculations were performed with the Gaussian03 and Gaussian09 packages. Molecular orbital shapes and energies discussed in the text are those calculated at the optimized geometries. Orbital pictures were prepared with Molekel 4.3 visual software. The computed structures of the two enantiomers of 2 and 3 feature PBI units in their more stable twisted (anti) configuration (see Figure S2, top). In contrast the mesomer of 3 contains a central PBI unit in its high energy syn configuration (see Figure S2, bottom). Quantum chemical calculations on the single 4Cl-PBI 1 depicted in Figure S2 predict the syn structure 11.15 Kcal/mol above the anti. This energy difference is partially reduced in the mesomeric configuration of 3 whose computed energy is only 8.6 Kcal/mol above the enantiomers of 3.

Figure S2: B3LYP/3-21G* computed Anti and Syn structures (hydrogens not shown) and energy difference of 4Cl-PBI 1
Figure S3: frontier molecular orbitals of 2 from CAM-B3LYP/3-21G* calculations.

Figure S4: frontier molecular orbitals of 3 from CAM-B3LYP/3-21G* calculations.
Table S2: MO energies (eV) and HOMO-LUMO gaps (eV) of 4Cl-PBI 1, 2 and 3. From B3LYP/3-21G* calculations at optimized geometries

<table>
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<tr>
<th></th>
<th>HOMO-2</th>
<th>HOMO-1</th>
<th>HOMO</th>
<th>LUMO</th>
<th>LUMO+1</th>
<th>LUMO+2</th>
<th>E(H-L)</th>
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<tr>
<td>4Cl-PBI 1</td>
<td>-6.49</td>
<td>-3.86</td>
<td>---</td>
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<td>3.63</td>
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<td>dimer 2</td>
<td>-6.59</td>
<td>-6.53</td>
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<td>-3.92</td>
<td>---</td>
<td>3.60</td>
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<tr>
<td>trimer 3</td>
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<td>-3.94</td>
<td>-3.93</td>
<td>-3.90</td>
<td>3.57</td>
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</table>

Table S3: Excitation energies E (eV) and oscillator strengths (f) (for the lowest allowed electronic transitions from TDDFT CAM-B3LYP/3-21G* calculations) and computed rotatory strengths (R) (10^-40 erg esu cm/Gauss) at the same level of theory

<table>
<thead>
<tr>
<th></th>
<th>E (f)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 enantiomer</td>
<td>(S0→S1) 2.73 (0.61)</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>(S0→S2) 2.85 (0.73)</td>
<td>-3.06</td>
</tr>
<tr>
<td>3 enantiomer</td>
<td>(S0→S1) 2.67 (0.24)</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td>(S0→S2) 2.79 (1.20)</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>(S0→S3) 2.86 (0.32)</td>
<td>-4.04</td>
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</table>

References


MALDI-TOF MS of dimer 4
$^1$H NMR spectrum of dimer 4
$^{13}$C NMR spectrum of dimer 4
MALDI-TOF MS of trimer 5

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$^1$H NMR spectrum of trimer 5
$^{13}$C NMR spectrum of trimer 5