Chiral Perylene Bisimide Dyes by Interlocked Arene Substituents in the Bay Area

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1. Experimental Part

1.1. General Methods

Unless otherwise stated, all chemicals, reagents and solvents were purchased from commercial suppliers and used after appropriate purification. The 1,6,7,12-tetrachloroperylene bis(dicarboximides) 1a - e were synthesized according to literature.\(^{[S1]}\) Toluene was of HPLC grade and dried prior to use by an Innovative Technology PureSolv solvent purification system. Dichloromethane was distilled prior to use. Column chromatography was performed with commercial glass columns using silica gel 60 M (particle size 0.04 – 0.063 mm; Merck KGaA) as stationary phase. Normal phase HPLC was performed on a Japan Analytical Industry (JAI) recycling preparative HPLC system LC-9105 equipped with a VP 250/21 NUCLEOSIL 100-7 column of Macherey-Nagel. For the chiral separation of the enantiomers, the same HPLC system was equipped with a Reprosil 100 Chiral-NR 8 µm column from Trentec. NMR spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer and are calibrated to the residual proton signal of the used deuterated solvent. The chemical shifts (δ) are reported in parts per million (ppm). Multiplicities for proton signals are abbreviated as s, bs, d, bd, t, sep, m and bm for singlet, broad singlet, doublet, broad doublet, triplet, septet, multiplet and broad multiplet respectively. MALDI-TOF mass spectra were recorded with a Bruker Daltonics GmbH ultrafileXtreme mass spectrometer using DCBT (2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile) as matrix. High resolution mass spectra were measured by electrospray ionization (ESI) with an ESI microTOF Focus mass spectrometer from Bruker Daltonics GmbH. The melting points were determined using a SMP50 from Stuart. UV/Vis/NIR absorption spectra were recorded on a Jasco V-770 or Jasco V-670 spectrometer. Fluorescence spectra were recorded on a FLS980 fluorescence spectrometer (Edinburgh Instruments) and were corrected against the photomultiplier sensitivity and the lamp intensity. CD spectra were recorded on a Jasco J-810.
spectropolarimeter. CPL spectra were recorded with a customised JASCO CPL-300/J-1500 hybrid spectrometer. Cyclic voltammetry measurements were conducted on an EC epsilon (BASi instruments, UK) potentiostat connected to a three-electrode single-compartment cell. A Pt disc electrode was used as working electrode, a platinum wire as counter electrode and an Ag/AgCl reference electrode. The spectra were referenced using the ferrocenium/ferrocene redox couple as an internal standard. Single crystal X-ray diffraction data were collected at 100 K on a Bruker D8 Quest Kappa diffractometer with a Photon II CPAD detector and multilayered mirror monochromated CuKα radiation. The structures were solved using direct methods, expanded with Fourier techniques and refined with the Shelx software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 2086018 (2c), 2086019 (4a) and 2086020 (6a). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data.request/cif. Theoretical calculations were performed by the Gaussian software using B3LYP/6-31G(d) level of theory for structure optimization and B3LYP/def2-SVP level of theory for TD-DFT simulation of electron transitions.

1.2. General Procedure for the synthesis of the tetraarylated PBI derivatives

The respective 1,6,7,12-tetrachloroperylene bis(dicarboximide) (100 µmol), the arylboronic acid (2.00 mmol, 20 eq.), anhydrous potassium carbonate (145 mg, 1.05 mmol, 10.5 eq.) and tetrakis(triphenylphosphine)palladium (34.7 mg, 30.0 µmol, 0.3 eq.) were added to a Schlenk tube. Toluene (3.2 mL), ethanol (0.6 mL) and water (1.6 mL), which were degassed prior to use, were added and the solution was subjected to three freeze-pump-thaw cycles. After stirring overnight at 80 °C, the mixture was extracted with dichloromethane and washed three times
with water. The organic phases were combined, and the solvent removed under reduced pressure. The crude product was purified by column chromatography and HPLC.

1.2.1. Synthesis of 2a

Solvent column chromatography and HPLC: hexane/dichloromethane = 1/3; Yield: 58.9 mg (73.0 mmol, 73%) of a blue-purple solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 8.24$ (s, 4H), 7.22 (t, 4H), 7.08 (bs, 8H), 6.70 (bs, 8H), 4.18 (t, 4H), 1.74 (m, 4H), 1.47 (m, 4H), 1.00 (t, 6H); $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 163.9, 142.7, 140.9, 133.6, 132.3, 131.7, 129.2, 127.9, 126.4, 122.8, 40.6, 30.7, 20.8, 14.1; MS (MALDI-TOF, pos. mode, DCTB in CHCl$_3$): $m/z$ calculated for C$_{56}$H$_{42}$N$_2$O$_4^+$ [M]$^+$: 806.31, found: 806.30; HRMS (ESI-TOF, pos. mode, MeCN/CHCl$_3$): $m/z$ calculated for C$_{56}$H$_{42}$N$_2$NaO$_4^+$ [M+Na]$^+$: 829.3037, found 829.3040; m.p. >390 °C.

1.2.2. Synthesis of 2b

Solvent column chromatography and HPLC: hexane/dichloromethane = 1/3; Yield: 75.8 mg (74.6 mmol, 75%) of a dark blue-purple solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 8.35$ (s, 4H), 7.53 (t, 2H), 7.38 (d, 4H), 7.26 (m, 4H), 7.15 (bs, 8H), 6.83 (bs, 8H), 2.87 (sep, 4H),
1.22 (d, 12H), 1.15 (d, 12H); $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 166.1, 148.4, 145.3, 142.9, 136.3, 134.6, 134.1, 133.5, 133.0, 131.8, 131.1, 130.0, 129.0, 126.4, 124.5, 31.4, 26.1, 26.05; MS (MALDI-TOF, pos. mode, DCTB in CHCl$_3$): $m/z$ calculated for C$_{78}$H$_{58}$N$_2$O$_4^+$ [M]$^+$: 1014.43, found: 1014.40; HRMS (ESI-TOF, pos. mode, MeCN/CHCl$_3$): $m/z$ calculated for C$_{78}$H$_{58}$N$_2$NaO$_4^+$ [M+Na]$^+$: 1037.4289, found 1037.4310; m.p. >390 °C.

1.2.3. Synthesis of 2c

Solvent column chromatography and HPLC: hexane/dichloromethane = 1/3; Yield: 56.6 mg (65.9 mmol, 66%) of a dark black-purple solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 8.22$ (s, 4H), 7.20 (m, 4H), 7.08 (bs, 8H), 6.70 (bs, 8H), 5.04 (m, 2H), 2.56 (m, 4H), 1.90 (m, 4H), 1.75 (m, 4H), 1.46 (m, 4H), 1.34 (m, 4H); $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 164.3, 142.6, 141.0, 133.5, 132.0, 131.6, 129.0, 127.8, 126.4, 123.3, 32.0, 29.6, 29.5, 27.0, 25.9, 23.0, 14.3; MS (MALDI-TOF, pos. mode, DCTB in CHCl$_3$): $m/z$ calculated for C$_{60}$H$_{46}$N$_2$O$_4^+$ [M]$^+$: 858.35, found: 858.34; HRMS (ESI-TOF, pos. mode, MeCN/CHCl$_3$): $m/z$ calculated for C$_{60}$H$_{46}$N$_2$NaO$_4^+$ [M+Na]$^+$: 881.3350, found 881.3339; m.p. >390 °C.

1.2.4. Synthesis of 2d

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Solvent column chromatography and HPLC: hexane/dichloromethane = 1/3; Yield: 38.1 mg (45.6 mmol, 46%) of a dark purple solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 8.23$ (s, 4H), 7.20 (m, 4H), 7.10 (bs, 8H), 6.72 (bs, 8H), 5.05 (m, 2H), 2.25 (m, 4H), 1.94 (m, 4H), 0.95 (m, 12H); $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 142.8, 141.0, 133.7, 132.1, 131.7, 130.7, 129.0, 127.7, 126.6, 122.8, 57.8, 25.44, 25.40, 11.56, 11.55$; MS (MALDI-TOF, pos. mode, DCTB in CHCl$_3$): $m/z$ calculated for C$_{58}$H$_{46}$N$_2$O$_4$ $^+$ [M]$^+$: 834.35, found: 834.37; HRMS (ESI-TOF, pos. mode, MeCN/CHCl$_3$): $m/z$ calculated for C$_{58}$H$_{46}$N$_2$NaO$_4$ $^+$ [M+Na]$^+$: 857.3350, found 857.3317; m.p. >390 °C.

1.2.5. **Synthesis of 2e**

![](image.png)

Solvent column chromatography and HPLC: dichloromethane/ethylacetate = 99/1; Yield: 36.6 mg (50.6 mmol, 51%) of a dark black-purple solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 8.24$ (s, 4H), 7.19 (bs, 4H), 7.06 (bs, 8H), 6.65 (bs, 8H), 3.63 (s, 6H); $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 142.5, 140.6, 133.4, 132.2, 131.6, 131.0, 129.0, 127.8, 126.4, 123.3, 27.1$; MS (MALDI-TOF, pos. mode, DCTB in CHCl$_3$): $m/z$ calculated for C$_{56}$H$_{42}$N$_2$O$_4$ $^+$ [M]$^+$: 722.22, found: 722.19; HRMS (ESI-TOF, pos. mode, MeCN/CHCl$_3$): $m/z$ calculated for C$_{56}$H$_{43}$N$_2$NaO$_4$ $^+$ [M+Na]$^+$: 745.2098, found 745.2093; m.p. >390 °C.
1.2.6. Synthesis of 3a

Solvent column chromatography and HPLC: hexane/dichloromethane = 1/3; Yield: 65.1 mg (60.3 mmol, 60%) of a purple solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 8.33$ (s, 4H), 7.39 (bs, 8H), 6.88 (bd, 8H), 4.21 (t, 4H), 1.75 (m, 4H), 1.48 (m, 4H), 1.01 (t, 6H); $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 163.4, 144.2, 141.2, 133.8, 131.8, 131.6, 130.1, 129.7, 127.2, 125.8, 123.7, 40.8, 30.7, 20.8, 14.1$; MS (MALDI-TOF, pos. mode, DCTB in CHCl$_3$): m/z calculated for C$_{60}$H$_{38}$N$_2$O$_4^+$ [M]$^+$: 1078.26, found: 1078.30; HRMS (ESI-TOF, pos. mode, MeCN/CHCl$_3$): m/z calculated for C$_{60}$H$_{38}$N$_2$NaO$_4^+$ [M+Na]$^+$: 1101.2532, found 1101.2589; m.p. >390 °C.

1.2.7. Synthesis of 4a

Solvent column chromatography and HPLC: hexane/dichloromethane = 1/3; Yield: 28.3 mg (28.1 mmol, 28%) of a purple solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 8.37 – 6.61$ (bm, 32H), 4.03 (bs, 4H), 1.71 (bs, 4H), 1.45 (m, 4H), 1.00 (t, 6H); $^1$H-NMR (400 MHz, TCE-d$_2$,
390 K): δ = 8.38 (s, 4H), 7.70 (d, 4H), 7.43 (t, 4H), 7.31 (bm, 8H), 6.90 (bm, 8H), 6.63 (d, 4H), 4.23 (t, 4H), 1.80 (m, 4H), 1.50 (m, 4H), 1.02 (t, 6H); 13C-NMR (100 MHz, CD2Cl2, 293 K): δ = 163.9, 142.5, 138.2, 135.0, 134.0, 132.5, 132.2, 131.8, 128.4, 127.9, 127.4, 126.9, 126.5, 123.1, 40.5, 30.6, 20.8, 14.1; MS (MALDI-TOF, pos. mode, DCTB in CHCl3): m/z calculated for C72H50N2O4+ [M]+: 1006.38, found: 1006.36; HRMS (ESI-TOF, pos. mode, MeCN/CHCl3): m/z calculated for C72H50N2NaO4+ [M+Na]+: 1029.3663, found 1029.3660; m.p. >390 °C.

1.2.8. Synthesis of 5a

Solvent column chromatography and HPLC: hexane/dichloromethane 1/3; Yield: 37.8 mg (37.5 mmol, 38%) of a purple solid; 1H-NMR (400 MHz, CD2Cl2, 293 K): δ = 8.42 – 6.14 (m, 32H), 4.12 (m, 4H), 1.71 (m, 4H), 1.44 (m, 4H), 0.97 (m, 6H); 13C-NMR (100 MHz, CD2Cl2, 293 K): δ = 164.0, 163.8, 142.3, 141.9, 141.0, 140.6, 139.9, 139.8, 139.2, 139.0, 138.9, 138.8, 137.2, 136.9, 135.4, 135.1, 135.0, 134.9, 134.8, 134.6, 134.5, 134.0, 133.96, 133.91, 133.8, 133.6, 132.4, 131.9, 131.2, 131.2, 131.1, 131.0, 130.9, 129.9, 129.6, 129.4, 129.2, 128.9, 128.8, 128.5, 128.4, 128.3, 126.8, 126.7, 126.5, 126.4, 126.1, 125.92, 125.88, 125.79, 125.7, 125.5, 125.3, 125.2, 124.4, 124.3, 123.4, 123.3, 123.2, 121.7, 121.6, 121.4, 40.6, 30.6, 20.8, 14.0; MS (MALDI-TOF, pos. mode, DCTB in CHCl3): m/z calculated for C72H50N2O4+ [M]+: 1006.38, found: 1006.38; HRMS (ESI-TOF, pos. mode, MeCN/CHCl3): m/z calculated for C72H50N2NaO4+ [M+Na]+: 1029.3663, found 1029.3648; m.p. >390 °C.
1.2.9. Synthesis of 6a

Solvent column chromatography and HPLC: hexane/dichloromethane 1/3; Yield: 28.1 mg (21.6 mmol, 22%) of a blue solid; $^1$H-NMR (400 MHz, CD$_2$Cl$_2$, 293 K): $\delta$ = 8.55 – 5.93 (m, 40H), 4.15 (m, 4H), 1.75 (m, 4H), 1.45 (m, 4H), 0.99 (m, 6H); $^{13}$C-NMR (100 MHz, CD$_2$Cl$_2$, 293 K): $\delta$ = 164.1, 142.5, 137.0, 136.0, 134.3, 134.23, 134.18, 132.3, 130.7, 130.6, 130.2, 129.0, 128.7, 127.4, 127.0, 126.2, 125.8, 125.6, 125.2, 125.0, 123.6, 122.1, 121.6, 40.7, 30.7, 20.8, 14.1; MS (MALDI-TOF, pos. mode, DCTB in CHCl$_3$): $m/z$ calculated for C$_{96}$H$_{59}$N$_2$O$_4^+$ [M+H]+: 1302.44, found: 1302.53; HRMS (ESI-TOF, pos. mode, MeCN/CHCl$_3$): $m/z$ calculated for C$_{96}$H$_{58}$N$_2$NaO$_4^+$ [M+Na]+: 1325.4289, found 1325.4214; m.p. >390 °C.
2. Structural Analysis

**Table S1** Structural parameters found in the single crystal structures of 2c, 4a and 6a.

| PBI  | Space Group | Core twist[a] [°] | Θ (C1-C12b-C12a-C12)[b] [°] | Θ (C13a-C12a-C12b-C13b)[b] [°] | Θ (C12b-C1-C1'-C2')[b,c] [°] |
|------|-------------|------------------|-----------------------------|-----------------------------|-----------------------------|
| 2c   | P2/c        | 34.3             | 32.7/33.4                   | 33.2/33.6                   | 42.1/42.1/43.1/43.1         |
| 4a   | P–1         | 36.6             | 33.5/33.5                   | 34.1/35.4                   | 39.4/41.2/41.2/43.3         |
| 6a   | P–1         | 29.5             | 29.2/29.9                   | 27.7/29.1                   | 46.6/50.2/54.6/56.9         |

[a] Angle between the two naphthalene subunits of the PBI; [b] Numbering of carbon atoms according to Scheme 1; [c] For 4a the angle was measured between C12-b-C1-C2'-C3'.

**Table S2** Crystallographic data for compounds 2c, 4a and 6a.

|                  | Compound 2c | Compound 4a | Compound 6a |
|------------------|-------------|-------------|-------------|
| CCDC Number      | 2086018     | 2086019     | 2086020     |
| Empirical Formula| C_{60}H_{46}N_{2}O_{4} | C_{72}H_{50}N_{2}O_{4} | C_{96}H_{58}N_{2}O_{4} |
| Formula weight / g mol\(^{-1}\) | 859.04 | 1007.20 | 1303.53 |
| Crystal size / mm | 0.295 x 0.2687 x 0.192 | 0.132 x 0.108 x 0.044 | 0.180 x 0.072 x 0.020 |
| Measurement Temperature | 100(2) K | 100(2) K | 100(2) K |
| Crystal system   | monoclinic  | triclinic   | triclinic   |
| Space group      | C2/c        | P-1         | P-1         |
| Lattice parameters |             |             |             |
| a /Å              | 11.0037(3)  | 13.6566(11) | 15.5878(5)  |
| b /Å              | 22.5842(7)  | 14.4337(12) | 15.6577(5)  |
| c /Å              | 21.5026(6)  | 17.9111(15) | 16.4702(5)  |
| α /°              | 90          | 93.237(4)   | 70.229(2)   |
| β /°              | 101.5000(10)| 105.997(4)  | 68.009(2)   |
| γ /°              | 90          | 94.521(4)   | 61.8400(10) |
| Volume/ Å\(^3\)  | 5236.3(3)   | 3371.7(5)   | 3221.40(19) |
| Z value           | 4           | 2           | 2           |
| Calculated Density / g m⁻³ | 1.337  | 1.103  | 1.344  |
|---------------------------|--------|--------|--------|
| F(000)                    | 2196   | 1172   | 1360   |
| Number of reflections measured | 39057 | 50760  | 63653  |
| Number of unique reflections | 5171  | 13160  | 12693  |
| Theta range for data collection | 3.915 ° to 72.295 ° | 2.575 ° to 72.593 ° | 2.952 ° to 72.267 ° |
| Completeness               | 100%   | 99.6%  | 99.9%  |
| Rint                      | 0.0243 | 0.0321 | 0.0448 |
| Minimum and maximum transmission | 0.5924/0.7536 | 0.6806/0.7536 | 0.5985/0.7536 |
| Goodness of fit indicator | 1.059  | 1.056  | 1.035  |
| Final R₁ indices [I > 2σ(I)] | 0.0418, 0.1114 | 0.0639, 0.1615 | 0.0508, 0.1343 |
| (Robs, wRall)              |        |        |        |
| R indices [all data] (Robs, wRall) | 0.0425, 0.1120 | 0.0718, 0.1670 | 0.0652, 0.1438 |
| Largest diff peak and hole (e·Å⁻³) | 0.410/–0.289 | 0.522/–0.414 | 0.482/–0.432 |

**Figure S1** Aromatic region of ¹H-NMR spectra of 2a, measured in 1,1,2,2-tetrachloroethane-UPLOAD-d at different temperatures in steps of 20 K from 243 K (bottom) to 383 K (top).
Figure S2 Aromatic region of $^1$H-NMR spectra of 4a, measured in 1,1,2,2-tetrachloroethane-$d_2$ at different temperatures in steps of 20 K from 243 K (bottom) to 383 K (top).

Figure S3 Aromatic region of $^1$H-NMR spectra of 5a, measured in 1,1,2,2-tetrachloroethane-$d_2$ at different temperatures in steps of 20 K from 243 K (bottom) to 383 K (top).
**Figure S4** Relative energies in kJ mol$^{-1}$ of the transition states of the a) $M/P$-racemization and b) rotation of one phenyl ring relative to the ground state energies of the $M$-enantiomer of PBI derivative 2e calculated by the Gaussian 09 program using DFT B3LYP/6-31G (d).

**Figure S5** Possible arrangements of the four 2-naphthalene substituents in the bay-region of the $P$-enantiomer of 4a.
Figure S6 Possible arrangements of the four 1-pyrene substituents in the bay-region of the $P$-enantiomer of 6a.
3. Optical and Electrochemical Characterization

![Chemical structures of reference compounds 7 and 8.](image)

**Figure S7** Chemical structures of reference compounds 7 and 8.

![UV/Vis/NIR absorption spectra](image)

**Figure S8** a) UV/Vis/NIR absorption spectra of 2a-2e as well as b) normalized emission spectra measured in DCM ($c_0 \approx 4 \cdot 10^{-6}$ M) at 293 K.
Table S3 Summary of the optical properties of 2a-2e measured in DCM at 293 K.

| PBI   | $\lambda_{\text{abs}}$ [nm] | $\varepsilon_{\text{max}}$ [M$^{-1}$ cm$^{-1}$] | $\lambda_{\text{em}}$ [nm] | $\delta_{\text{Stokes}}$ [cm$^{-1}$] | $\Phi_f$ [b] [%] | $\tau_F$ [c] [ns] |
|-------|-----------------------------|-----------------------------------------------|-----------------------------|-------------------------------------|-----------------|-----------------|
| 2a    | 602 452                     | 22500 17600                                  | 663                         | 1530                                | 43              | 11.9            |
| 2b    | 609 455                     | 23300 14300                                  | 680                         | 1690                                | 46              | 10.9            |
| 2c    | 601 449                     | 21000 14100                                  | 666                         | 1620                                | 49              | 12.0            |
| 2d    | 602 449                     | 24200 14700                                  | 671                         | 1740                                | 55              | 11.7            |
| 2e    | 601 448                     | 20000 14300                                  | 667                         | 1650                                | 41              | 12.3            |
| 7     | 527 491                     | 93000 60800                                  | 534                         | 210                                 | 99              | 3.7             |
| 8     | 576 444                     | 48800 16500                                  | 608                         | 920                                 | 96              | 6.0             |
| Pyrene | 337 322                    | 34400 23400                                  | 372$^{[d,S4]}$              | 700$^{[d,S4]}$                      | 64$^{[d,S4]}$   | 354$^{[d,S4]}$  |

[a] Spectra were measured in dichloromethane ($c_0 \approx 4 \cdot 10^{-6}$ M) at 293 K. [b] Fluorescence quantum yields were determined using the dilution method (OD < 0.05) with Oxazine 1 in ethanol ($\Phi_f = 11\%$) as standard.$^{[S5]}$ [c] Fluorescence lifetimes were determined with EPL picosecond pulsed diode lasers ($\lambda_{\text{ex}} = 560$ nm) for time correlated single photon counting; [d] in hexane.

Figure S9 Calculated HOMO (bottom) and LUMO (top, isovalue = 0.2 a.u.) of PBIs 2 - 6 at B3LYP/6-31g(d) level theory. The imide-substituents have been replaced by methyl groups for simplicity.
Figure S10 Circular dichroism (CD, $c_0 = 1 \cdot 10^{-5} \text{ M}$) spectra of $P$- (black) and $M$- (red) enantiomers of PBIs a) 2b, b) 2c, c) 2d, d) 2e and e) 3a as well as circular polarized luminescence (CPL, $c_0 = 2 \cdot 10^{-6} \text{ M}$) spectra of 3a in DCM at 293 K.
Figure S11 Elugrams of the HPLC separation on a chiral stationary phase of a) the successful separation of the atropoenantiomers of 4a, and the non-successful separations of b) 6a, as well as c) and d) for 5a using mixtures of hexane and DCM as eluent. The collection times of the respective fractions are highlighted. Detection by UV/Vis analysis at 550 nm. According to CD spectral analysis, no separation of atropoenantiomers was achieved for 5a. Thus, 5a was for one run separated in c) two fractions and for another separated in d) five fractions. For each fraction a CD spectrum and a $^1$H-NMR spectrum was measured, but no CD signals were obtained and the $^1$H-NMR spectra all look identical to the spectrum shown in Figure S34. Similar results were obtained for 6a.
Figure S12 Time-dependent CD spectra of the $P$-enantiomer of 2a in 1,1,2,2-tetrachloroethane at a) 383 K, b) 388 K, c) 393 K and d) 398 K.
**Figure S13** Time-dependent CD spectra of the P-enantiomer of 4a in 1,1,2,2-tetrachloroethane at a) 383 K, b) 388 K, c) 393 K and d) 398 K.

**Table S4** Kinetic data for the racemization process of 2a and 4a in 1,1,2,2-tetrachloroethane at four different temperatures obtained by CD spectroscopy.\[^{[86]}\]

|        | 2a           | 4a           |
|--------|--------------|--------------|
|        | T [K]        | k [10^-5 s^-1] | t_{1/2} [min] | ΔG‡ [kJ mol^-1] | T [K] | k [10^-5 s^-1] | t_{1/2} [min] | ΔG‡ [kJ mol^-1] |
| 383    | 19.7         | 59           | 119.6         | 383             | 27.1             | 43           | 118.6         |
| 388    | 33.1         | 35           | 119.8         | 388             | 38.5             | 30           | 119.3         |
| 393    | 43.1         | 27           | 120.2         | 393             | 59.1             | 20           | 119.2         |
| 398    | 87.2         | 13           | 119.5         | 398             | 82.8             | 14           | 119.6         |
**Figure S14** Cyclic voltammograms (solid lines) and square wave voltammograms (dashed lines) of PBIs a) 3a and b) 4a. Measurements were performed using DCM solutions \( (c_0 \approx 2 \cdot 10^{-4} \text{ M}) \) at 293 K, using tetrabutylammonium hexafluorophosphate (TBAHFP, 0.1 M) as electrolyte.

**Figure S15** Cyclic voltammograms (solid lines) and square wave voltammograms (dashed lines) of PBI a) 5a and b) 2b. Measurements were performed using DCM solutions \( (c_0 \approx 2 \cdot 10^{-4} \text{ M}) \) at 293 K, using TBAHFP (0.1 M) as electrolyte.
Figure S16 Cyclic voltammograms (solid lines) and square wave voltammograms (dashed lines) of a) 2c and b) 2d. Measurements were performed using DCM solutions ($c_0 \approx 2 \cdot 10^{-4}$ M) at 293 K, using TBAHFP (0.1 M) as electrolyte.

Figure S17 Cyclic voltammogram (solid lines) and square wave voltammogram (dashed lines) of 2e. Measurements were performed using DCM solutions ($c_0 \approx 2 \cdot 10^{-4}$ M) at 293 K, using TBAHFP (0.1 M) as electrolyte.
Table S5 Summary of the redox properties of 2a - 2e. Half-wave potentials were determined by cyclic or square wave voltammetry measured in DCM (0.1 M TBAHFP) vs. Fc/Fc\(^+\) at 293 K.

| PBI   | \(E_{\text{red1}}\) [V] | \(E_{\text{red2}}\) [V] | \(E_{\text{ox1}}\) [V] | \(E_{\text{ox2}}\) [V] | \(E_{\text{HOMO}}\) [eV] | \(E_{\text{LUMO}}\) [eV] | \(E_{\text{gap}}\) [eV] |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2a    | -1.05           | -1.21           | 0.97            |                | -6.12           | -4.10           | 2.02            |
| 2b    | -1.02           | -1.25           | 1.01            | 1.19           | -6.16           | -4.13           | 2.03            |
| 2c    | -1.12           | -1.31           | 0.96            | 1.28           | -6.11           | -4.03           | 2.08            |
| 2d    | -1.08           | -1.29           | 0.99            | 1.29           | -6.14           | -4.07           | 2.07            |
| 2e    | -1.07           | -1.26           | 0.97            |                | -6.12           | -4.08           | 2.04            |
| 7     | -1.00           | -1.22           | 1.30            |                | -6.45           | -4.15           | 2.30            |
| 8     | -1.10           | -1.29           | 0.90            | 1.21           | -6.05           | -4.05           | 2.00            |
| Pyrene|                |                | 0.63            |                | -5.78           |                |                 |

[a] Calculated according to literature known procedure using the experimentally determined redox potentials \((E_{\text{HOMO}} = -[E_{\text{ox1}} +5.15 \text{ eV}])\) and \((E_{\text{LUMO}} = -[E_{\text{red1}} +5.15 \text{ eV}])\) and the energy level of Fc/Fc\(^+\) with respect to the vacuum level (–5.15 eV). [b] Not observed.
Table S6 Calculated UV/Vis/NIR transitions for compound 2 using TD-DFT (B3LYP/def2-SVP).

| Transition  | % Character | Wavelength / nm | Oscillator strength |
|-------------|-------------|-----------------|---------------------|
| 188 → 189   | 100         | 669.44          | 0.2596              |
| 187 → 189   | 100         | 485.49          | 0.0420              |
| 186 → 189   | 97.3        | 472.05          | 0.2050              |
| 188 → 192   | 2.7         |                 |                     |
| 184 → 189   | 100         | 412.04          | 0.0087              |

Table S7 Calculated UV/Vis/NIR transitions for compound 3 using TD-DFT (B3LYP/def2-SVP).

| Transition  | % Character | Wavelength / nm | Oscillator strength |
|-------------|-------------|-----------------|---------------------|
| 252 → 253   | 100         | 792.38          | 0.1358              |
| 251 → 253   | 100         | 532.93          | 0.0272              |
| 248 → 253   | 26.4        | 471.17          | 0.1506              |
| 250 → 253   | 68.9        |                 |                     |
| 252 → 256   | 4.7         |                 |                     |
| 248 → 253   | 72.6        | 467.75          | 0.0622              |
| 250 → 253   | 25.2        |                 |                     |
| 252 → 256   | 2.2         |                 |                     |
| 239 → 253   | 10.3        | 407.63          | 0.0033              |
| 246 → 253   | 42.3        |                 |                     |
| 252 → 254   | 26.4        |                 |                     |
| 252 → 255   | 21.0        |                 |                     |
| 239 → 253   | 36.8        | 399.83          | 0.0194              |
| 246 → 253   | 15.3        |                 |                     |
| 252 → 254   | 24.7        |                 |                     |
| 252 → 255   | 23.2        |                 |                     |
| 237 → 253   | 4.0         | 397.19          | 0.0154              |
| 238 → 253   | 5.6         |                 |                     |
| 244 → 253   | 8.5         |                 |                     |
| 247 → 253   | 81.9        |                 |                     |
Table S8 Calculated UV/Vis/NIR transitions for compound 4 using TD-DFT (B3LYP/def2-SVP).

| Transition | % Character | Wavelength / nm | Oscillator strength |
|------------|-------------|-----------------|---------------------|
| 240 → 241  | 100         | 760.46          | 0.1012              |
| 239 → 241  | 100         | 624.61          | 0.0573              |
| 238 → 241  | 100         | 623.55          | 0.0431              |
| 236 → 241  | 100         | 510.93          | 0.1211              |
| 235 → 241  | 100         | 466.05          | 0.2160              |
| 234 → 241  | 97.7        | 436.71          | 0.0248              |
| 230 → 241  | 3.0         | 400.05          | 0.0525              |
| 234 → 241  | 2.1         |                 |                     |
| 240 → 243  | 92.6        |                 |                     |
| 240 → 247  | 2.3         |                 |                     |

Table S9 Calculated UV/Vis/NIR transitions for compound 5 using TD-DFT (B3LYP/def2-SVP).

| Transition | % Character | Wavelength / nm | Oscillator strength |
|------------|-------------|-----------------|---------------------|
| 236 → 241  | 3.6         | 693.53          | 0.1344              |
| 240 → 241  | 96.4        |                 |                     |
| 239 → 241  | 100         | 658.56          | 0.0699              |
| 237 → 241  | 100         | 599.36          | 0.0292              |
| 236 → 241  | 96.5        | 499.27          | 0.1542              |
| 240 → 241  | 3.5         |                 |                     |
| 234 → 241  | 100         | 420.41          | 0.0031              |
| 226 → 241  | 2.3         | 402.74          | 0.0088              |
| 233 → 241  | 93.8        |                 |                     |
| 240 → 245  | 3.9         |                 |                     |
| 232 → 241  | 48.2        | 396.86          | 0.0066              |
| 240 → 243  | 51.8        |                 |                     |
Table S10 Calculated UV/Vis/NIR transitions for compound 6 using TD-DFT (B3LYP/def2-SVP).

| Transition | % Character | Wavelength / nm | Oscillator strength |
|------------|-------------|-----------------|---------------------|
| 316 → 317  | 100         | 907.21          | 0.0101              |
| 315 → 317  | 100         | 885.97          | 0.1173              |
| 313 → 317  | 100         | 743.48          | 0.0491              |
| 312 → 317  | 100         | 513.35          | 0.0619              |
| 311 → 317  | 20.4 79.6   | 466.17          | 0.0404              |
| 316 → 318  | 79.4 20.6   | 453.49          | 0.2214              |
4. NMR spectra

Figure S18 $^1$H-NMR spectrum of 2a in CD$_2$Cl$_2$ recorded at 295 K.
Figure S19 $^{13}$C-NMR spectrum of 2a in CD$_2$Cl$_2$ recorded at 295 K.

Figure S20 $^1$H-NMR spectrum of 2b in CD$_2$Cl$_2$ recorded at 295 K.
Figure S21 $^{13}$C-NMR spectrum of 2b in CD$_2$Cl$_2$ recorded at 295 K.

Figure S22 $^1$H-NMR spectrum of 2c in CD$_2$Cl$_2$ recorded at 295 K.
Figure S23 $^{13}$C-NMR spectrum of $2c$ in CD$_2$Cl$_2$ recorded at 295 K.

Figure S24 $^1$H-NMR spectrum of $2d$ in CD$_2$Cl$_2$ recorded at 295 K.
Figure S25 $^{13}$C-NMR spectrum of 2d in CD$_2$Cl$_2$ recorded at 295 K.

Figure S26 $^1$H-NMR spectrum of 2e in CD$_2$Cl$_2$ recorded at 295 K.
Figure S27 $^1$H-NMR spectrum of 2e in C$_2$D$_2$Cl$_4$ recorded at 390 K.

Figure S28 $^{13}$C-NMR spectrum of 2e in CD$_2$Cl$_2$ recorded at 295 K.
Figure S29 $^1$H-NMR spectrum of 3a in CD$_2$Cl$_2$ recorded at 295 K.

Figure S30 $^{13}$C-NMR spectrum of 3a in CD$_2$Cl$_2$ recorded at 295 K.
Figure S31 $^1$H-NMR spectrum of 4a in CD$_2$Cl$_2$ recorded at 295 K.

Figure S32 $^1$H-NMR spectrum of 4a in C$_2$D$_2$Cl$_4$ recorded at 390 K.
Figure S33 $^{13}$C-NMR spectrum of 4a in CD$_2$Cl$_2$ recorded at 295 K.

Figure S34 $^1$H-NMR spectrum of 5a in CD$_2$Cl$_2$ recorded at 295 K.
Figure S35 ¹³C-NMR spectrum of 5a in CD₂Cl₂ recorded at 295 K.

Figure S36 ¹H-NMR spectrum of 6a in CD₂Cl₂ recorded at 295 K.
Figure S37 $^{13}$C-NMR spectrum of 6a in CD$_2$Cl$_2$ recorded at 295 K.
5. Supporting References

[S1] a) F. Würthner, A. Sautter, J. Schilling, *J. Org. Chem.* **2002**, *67*, 3037-3044; b) B. Pagoaga, L. Giraudet, N. Hoffmann, *Eur. J. Org. Chem.* **2014**, 5178-5195; c) S. Mathew, M. R. Johnston, *Chem. Eur. J.* **2009**, *15*, 248-253; d) K. Mahata, P. D. Frischmann, F. Würthner, *J. Am. Chem. Soc.* **2013**, *135*, 15656-15661.

[S2] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112-122.

[S3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ransinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Wallingford, CT, **2016**.

[S4] J. Merz, J. Fink, A. Friedrich, I. Krummenacher, H. H. Al Mamari, S. Lorenzen, M. Hähnel, A. Eichhorn, M. Moos, M. Holzapfel, H. Braunschweig, C. Lambert, A. Steffen, L. Ji, T. B. Marder, *Chem. Eur. J.* **2017**, *23*, 13164-13180.

[S5] R. Sens, K. H. Drexhage, *J. Lumin.* **1981**, *24*, 709-712.

[S6] P. Osswald, F. Würthner, *J. Am. Chem. Soc.* **2007**, *129*, 14319-14326.