Electronic Supplementary Information (ESI) for

Structure-property relationships for 1,7-diphenoxy-perylene bisimides in solution and in the solid state

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1. Materials and Methods

Ortho-cresol, 2,6-dimethylphenol, 2,6-diisopropylphenol, potassium carbonate (≥ 99%) and N-methyl-2-pyrrolidone (NMP, 99.5%) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. NMP was fractionally distilled prior to use and potassium carbonate was dried under vacuo at 100 °C for 24 h. N,N’-Dicyclohexyl-1,7-dibromopyrene-3,4:9,10-tetracarboxylic acid bisimide (2), reference compound N,N’-dicyclohexyl-3,4:9,10-tetracarboxylic acid bisimide (4a), N,N’-dicyclohexyl-1,7-diphenylpyrene-3,4:9,10-tetracarboxylic acid bisimide (4b), and N,N’-dicyclohexyl-1,7-diphenylphenoxypylene-3,4:9,10-tetracarboxylic acid bisimide (4f) were prepared according to literature procedures. Flash column chromatography was performed using silica gel (Si60, mesh size 40-63 μm) from Merck. NMR spectra were recorded with a Bruker Avance 400 MHz instrument. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. 1H coupling constants J are given in Hertz (Hz). MALDI-TOF mass spectra were recorded on an Autoflex II from Bruker Daltonics spectrometer. ESI-TOF mass spectra were recorded on a Bruker Daltonics micrOTOF focus instrument.

All the solvents used for the spectroscopic measurements were of spectroscopic grade (Uvasol®) and were used without further purification. The UV/Vis spectra were recorded on a Perkin Elmer PE 950 spectrometer equipped with a PTP-1 Peltier element for temperature control and corrected against the reference solution. The fluorescence spectra were recorded with a PTI QM-4/2003 instrument. All fluorescence measurements were performed under ambient conditions and corrected against photomultiplier and lamp intensity. The fluorescence quantum yields were determined as the average value for three different excitation wavelengths using N,N’-di(2,6-di-isopropylphenyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide as reference (Φf = 1.00 in dichloromethaneS2) by applying high dilution conditions (A < 0.05). Solid state absorption spectra of PBIs 4a and 4b were determined by applying the Kubelka-Munk theory to reflectance spectra of trituration of PBIs in BaSO4 measured with a Lambda 950 UV/Vis/NIR spectrometer of Perkin Elmer equipped with an integrating sphere. Absolute fluorescence quantum yields were...
determined on a Hamamatsu Absolute PL Quantum Yield Measurement System CC9920-02. The system is made up of an excitation source that uses a 150 W CW Xenon light source, a monochromator (250-700 nm, FWHM 10 nm), an integrating sphere, and a multi-channel spectrometer capable of simultaneously measuring multiple wavelengths between 300 and 950 nm and counting the number of absorbed and emitted photons.

2. Synthesis of PBIs

Procedure: To a degassed solution of PBI 2 (0.35 g, 0.49 mmol) and potassium carbonate (200 mg, 2.30 mmol) in dry NMP (20 mL) under argon, excess amounts of ortho-cresol 3c, 2,6-dimeylylphenol 3d, or 2,6-diisopropylphenol 3e (1.20 mmol) were added and the mixture was stirred at 120 °C for 3 h. After being cooled to room temperature, the reaction mixture was slowly dropped into 250 mL of 1N HCl under stirring. The solid material was separated by filtration and then washed successively with water (3 × 30 mL) and methanol (3 × 30 mL). The crude product was purified by column chromatography on silica gel using CH₂Cl₂ as an eluent and afforded red solid PBIs 4c, 4d and 4e in 87%, 74% and 88% yield, respectively.

PBI 4c: M.p.: 399 °C; ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ = 9.66 (d, J = 8.0 Hz, 2H), 8.54 (d, J = 8.0 Hz, 2H), 8.08 (s, 2H), 7.43 (dd, J = 1.0 Hz, 2H), 7.3-7.2 (m, 4H), 7.02 (dd, J = 1.0 Hz, 2H), 5.0-4.9 (m, 2H), 2.5-2.4 (m, 4H), 2.36 (s, 6H), 1.9-1.8 (m, 4H), 1.7-1.6 (m, 6H), 1.4-1.3 (m, 4H), 1.3-1.2 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 163.8, 163.4, 155.7, 152.7, 133.4, 132.3, 130.0, 129.9, 129.3, 128.8, 128.0, 125.7, 124.7, 124.3,
122.6, 122.5, 121.7, 120.3, 54.0, 29.1, 26.5, 25.4, 16.2. ESI-TOF-MS, calculated for C_{50}H_{42}N_{2}O_{6}: 766.3043; found: m/z = 766.3112.

**PBI 4d**: M.p.: 232 °C; ^1^H NMR (400 MHz, CD_{2}Cl_{2}, ppm): δ = 9.78 (d, J = 8.0 Hz, 2H), 8.51 (d, J = 8.0 Hz, 2H), 7.81 (s, 2H), 7.22-7.16 (m, 6H), 4.91-4.83 (m, 2H), 2.34-2.34 (m, 4H), 2.12 (s, 12H), 1.80-1.77 (m, 4H), 1.63-1.60 (m, 6H), 1.39-1.29 (m, 6H). ^13^C NMR (100 MHz, CDCl_{3}, ppm): δ = 164.1, 163.7, 155.9, 150.9, 134.0, 131.5, 130.1, 129.7, 129.6, 126.7, 124.9, 124.8, 122.9, 121.4, 118.5, 54.0, 29.4, 26.9, 25.9, 16.5. ESI-TOF-MS, calculated for C_{52}H_{46}N_{2}O_{6}: 794.3356; found: m/z = 794.3428.

**PBI 4e**: M.p.: 198 °C; ^1^H NMR (400 MHz, CD_{2}Cl_{2}, ppm): δ = 9.87 (d, J = 8.0 Hz, 2H), 8.57 (d, J = 8.0 Hz, 2H), 7.94 (s, 2H), 7.43-7.38 (m, 6H), 4.97-4.90 (m, 2H), 3.07-2.99 (m, 4H), 2.52-2.42 (m, 4H), 1.87-1.84 (m, 4H), 1.71-1.68 (m, 6H), 1.43-1.39 (m, 6H), 1.23 (d, J = 8.0 Hz, 12H), 1.11 (d, J = 8.0 Hz, 12H). ^13^C NMR (100 MHz, CD_{2}Cl_{2}, ppm): δ = 164.1, 163.6, 157.1, 147.7, 141.9, 134.2, 129.9, 129.7, 129.2, 127.5, 125.6, 124.8, 124.6, 122.9, 121.0, 118.9, 54.1, 29.4, 27.9, 26.9, 25.9, 24.9, 22.7. ESI-TOF-MS, calculated for C_{60}H_{62}N_{2}O_{6}: 906.4608; found: m/z = 906.4598.
3. **Single Crystal X-ray Analysis**

Single crystals suitable for X-ray diffraction were obtained by dissolving the PBIs 4d and 4e in a mixture of CH₂Cl₂/EtOH = 90:10, followed by slow evaporation of the solvents (for single crystal data of PBI 4f, see ref. S1c and CCDC 901365). Crystal data were collected on a Bruker X8APEX-II_KAPPA diffractometer with a CCD area detector and multi-layer mirror monochromated MoKα radiation. The structure was solved using direct methods (SHELXS), expanded using Fourier techniques and refined with SHELXL.³ Hydrogen atoms were included in structure factors calculations at idealized positions and refined using a riding model.

*Crystal data for PBI 4d*: C₅₂H₄₆N₂O₆ · 0.5 CH₂Cl₂; \( M_r = 837.37 \), 0.2x0.2x0.1 mm³, monoclinic space group C2/c, \( a = 22.8894(13) \) Å, \( b = 12.5211(6) \) Å, \( c = 15.4873(7) \) Å, \( \beta = 90.723(3)° \), \( V = 4438.3(4) \) Å³, \( Z = 4 \), \( T = 100(2) \) K. The unit cell contains 4 PBI molecules positioned on a crystallographic centre of symmetry, therefore \( Z = 4 \), and furthermore 4 isolated regions (voids) with additional electron density, positioned each about a crystallographic 2-fold axis. This additional density could only partly be modelled as discrete atomic sites (\( \text{GooF}(F²) = 1.128 \), \( R_1 = 0.073 \), \( wR² = 0.229 \) for \( I > 2\sigma(I) \) and was attributed to disordered solvent of \( ½ \) CH₂Cl₂ per void. This formula C₅₂H₄₆N₂O₆ · 0.5 CH₂Cl₂ leads to the derived constants \( \rho_{\text{calc}} = 1.253 \text{ g·cm}^{-3} \), \( \mu = 0.139 \text{ mm}^{-1} \), \( F(000) = 1764 \).

At this stage further additional electron density could still be found in difference fourier maps. So the “squeeze” procedure with PLATON⁴ was applied to calculate the contribution to the diffraction from this region, which found 4 voids in the cell, each with a volume of 127 Å³, each occupied by 31 electrons. Compared to 42 electrons per molecule of CH₂Cl₂ this finding leads to a different sum formula of the investigated compound namely C₅₂H₄₆N₂O₆·0.74 (CH₂Cl₂), which means there are 0.74 disordered solvent molecules per void.
Final refinements where calculated from filtered intensity data with masked out regions of the disordered electron density: $GooF(F^2) = 1.066$, $R_1 = 0.0585$, $wR^2 = 0.1722$ for $I>2\sigma(I)$, $R_1 = 0.0692$, $wR^2 = 0.1808$ for all data, 4537 independent reflections [$2 \theta \leq 52.84^\circ$] and 294 parameters.

**Crystal data for PBI 4e:** $C_{60}H_{62}N_2O_6$; $M_r = 907.12$, red block, $0.28\times0.17\times0.10$ mm$^3$, orthorhombic space group $Pna2_1$, $a = 22.956(2)$ Å, $b = 9.4115(19)$ Å, $c = 22.7754(8)$ Å, $V = 4920.7(11)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.224$ g·cm$^{-3}$, $\mu = 0.078$ mm$^{-1}$, $F(000) = 1936$, $T = 100(2)$ K, $GooF(F^2) = 1.065$, $R_1 = 0.0537$, $wR^2 = 0.1315$ for $I > 2\sigma(I)$, $R_1 = 0.0661$, $wR^2 = 0.1382$ for all data, 10041 independent reflections [$2 \theta \leq 52.74^\circ$] and 725 parameters. The fairly large number of restraints had to be applied to model disordered $i$-propyl groups and a disordered N-hexyl group with physically sensible parameters.

A second phase of PBI 4e could be observed for some crystals which included CH$_2$Cl$_2$ from the same solvent mixture of CH$_2$Cl$_2$/EtOH = 90:10. Crystal data were collected on a 3 circle Rigaku CCD diffractometer at room temperature with a sealed molybdenum tube and graphite monochromator.

**Crystal data for PBI 4e:** $(C_{60}H_{62}N_2O_6 \cdot 0.89$ (CH$_2$Cl$_2$)) ; $M_r = 992.04$, red block, $0.36\times0.32\times0.26$ mm$^3$, monoclinic space group $P2_1/n$, $a = 13.495(3)$ Å, $b = 14.896(3)$ Å, $c = 26.835(5)$ Å, $V = 5326.8(19)$ Å$^3$, $\beta=99.08(2)$, $Z = 4$, $\rho_{calc} = 1.237$ g·cm$^{-3}$, $\mu = 0.175$ mm$^{-1}$, $F(000) = 2104$, $T = 293(2)$ K, $GooF(F^2) = 1.326$, $R_1 = 0.1354$, $wR^2 = 0.2393$ for $I>2\sigma(I)$, $R_1 = 0.1537$, $wR^2 = 0.2485$ for all data, 7622 independent reflections [$2 \theta \leq 46.5^\circ$] and 688 parameters, 128 restraints. The fairly large number of restraints had to be applied to model disordered $i$-propyl groups, a disordered $N$-cyclohexyl group and a partially occupied solvent molecule with physically sensible parameters.
**Fig. S1** Molecular structure in front view (a) and in side view (b), and molecular packing (c) of PBI 4e in the solvent-free single crystal.

**Fig. S2** Molecular structure in front view (a) and in side view (b) of PBI 4f (from ref. S1c).

Crystallographic data for the three new crystal structures (one for 4d, two for 4e) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 952111-952113. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
4. Absorption and Fluorescence Spectra in Solution and in the Solid State

**Fig. S3** UV/Vis absorption and emission spectra (both at a concentration of 7.0 \times 10^{-6} M) of PBI 4a in dichloromethane at room temperature.

**Fig. S4** UV/Vis absorption and emission spectra (both at a concentration of 2.0 \times 10^{-5} M) of PBI 4b in dichloromethane at room temperature.
**Fig. S5** UV/Vis absorption and emission spectra (both at a concentration of $1.9 \times 10^{-5}$ M) of PBI 4c in dichloromethane at room temperature.

**Fig. S6** UV/Vis absorption and emission spectra (both at a concentration of $4.0 \times 10^{-6}$ M) of PBI 4d in dichloromethane at room temperature.
Fig. S7 UV/Vis absorption and emission spectra (both at a concentration of \(4.0 \times 10^{-6}\) M) of PBI 4e in dichloromethane at room temperature.

Fig. S8 UV/Vis absorption and emission spectra (both at a concentration of \(4.0 \times 10^{-6}\) M) of PBI 4f in dichloromethane at room temperature.
Fig. S9 Solid state absorption and emission spectra of PBI 4b at room temperature.

Fig. S10 Solid state absorption and emission spectra of PBI 4c at room temperature.
**Fig. S11** Solid state absorption and emission spectra of PBI 4d at room temperature.

**Fig. S12** Solid state absorption and emission spectra of solvent-free crystal of PBI 4e at room temperature. In green the fluorescence spectrum of 4e from crystals where one molecule of PBI crystallizes per 0.898 molecules of CH₂Cl₂ is shown.
5. Theoretical Calculation Details

5.1 Calculation of the potential energy curves (PECs)

The potential energy curves were calculated on the assumption of $C_2$ symmetry. The assumption of $C_2$ symmetric molecular structures were tested by geometry optimizations without any symmetry constraint starting from the minima of the PECs. For the three studied compounds the minima structures determined without symmetry deviate at most by 0.02° from the $C_2$ symmetric structure for the studied dihedral angle. The energetic differences between both structures are in the order of $10^{-3}$ kJ mol$^{-1}$, which is below the accuracy of the employed DFT method. In order to validate the DFT results, we computed the PECs for 4a and 4g using the more accurate RI-SCS-MP2/cc-pVTZ level of theory (Table 3).$^{55}$

Table S1. Characterization of the θ(C12a-C13a-C13b-C12b) bending potentials for PBI 4a and 4g using SCS-CC2/cc-pVTZ.

<table>
<thead>
<tr>
<th>PBI</th>
<th>θ(C12a-C13a-C13b-C12b) (°)</th>
<th>Energy required for planarization (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SCS-MP2</td>
</tr>
<tr>
<td>4a</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>4g</td>
<td>7.3</td>
<td>3.6</td>
</tr>
</tbody>
</table>

5.2 Molecular dynamics (MD) simulations

MD simulations were performed to get a more detailed look into the rotational degree of freedom and the dependencies between θ(C12b-C1-O-C14) and θ(C1-O-C14-C15). Simulations were performed for PBIs 4b, 4c and 4d, respectively. All simulations contained 100.000 timesteps of 1 femtosecond each, from which the first 20.000 steps were
used to equilibrate the system. The simulations were performed at 300 K using a Nose-Hoover thermostat. All calculations were carried out with the in-house CAST program. Recent investigations showed that common force fields are too inaccurate, whereas DFT computations are far too expensive. For this reason the simulations were based on the PM6-DH2 method by employing an interface between CAST and the MOPAC program.

5.3 Restricted geometry optimizations

An indirect influence of the packing can occur if the planarity of inner $\pi$-conjugated PBI core is induced by the orientations of the outer lying substituents which themselves are determined by packing effects. Since DFT calculations of whole crystals, including periodic boundary conditions, are far too expensive or even not possible, we performed restricted geometry optimizations to somewhat include the influence of the orientations of the outer lying substituents. The orientation of the substituents themselves is determined by packing effects. The starting geometries were based on the X-ray structures of the crystals taken from experiments. For structure 4e the data obtained by co-crystallization with CH$_2$Cl$_2$ was taken.

For the restricted geometry optimizations the positions of all non-hydrogen atoms (oxygen and carbon) of the bay substituents were fixed. The hydrogen atoms of the substituents were allowed to relax, since hydrogen atoms are strictly connected to the heavier centers, and the X-ray data provide no clear data about the positions. Furthermore, no restrictions were applied to the rest of the system. All calculations were performed using BLYP-D3(BJ).
**Fig. S13** Illustrative example for the restricted geometry optimizations of molecule 4d. The red atoms were fixed in space during the optimization, while the green atoms were allowed to relax. Starting point for each *optimization* was the respective crystal structure.
6. $^1$H and $^{13}$C NMR Spectra of PBIs

Fig. S14 $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) of PBI 4c.

Fig. S15 $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) of PBI 4c.
Fig. S16 $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) of PBI 4d.

Fig. S17 $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) of PBI 4d.
Fig. S18 $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K) of PBI 4e.

Fig. S19 $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 298 K) of PBI 4e.
7. References


