1. General methods

All solvents and reagents were purchased from commercial sources and used as received without further purification, unless otherwise stated. Solvents for spectroscopic studies were of spectroscopic grade and used as received. $^1$H NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer and calibrated against the residual solvent peak. For the separation of the macrocycles, preparative recycling GPC LC-9105, Japan Analytical Industry Co., Ltd. (JAI) with JAIGEL 2H+2.5H columns was used. UV-vis spectra were measured on a Perkin-Elmer Lambda 950 spectrometer. AFM investigations were performed under ambient conditions using a MultiMode™ Nanoscope IV system (Veeco Metrology, Santa Barbara, CA), operating in tapping mode in air. Silicon cantilevers (Olympus, Japan) with a resonance frequency of ~ 300 kHz and spring constant of ~ 42 N/m were used. Samples were prepared by spin-coating of the respective solution at 4000 rpm onto highly ordered pyrolytic graphite (HOPG).
2. Experimental procedures, analytical and spectroscopic data

Perylene bisimide 2:

A mixture of perylene tetracarboxylic acid bisanhydride 1 (0.50 g, 0.51 mmol), the latter compound was prepared according to literature procedure,\(^1\) 3-iodoaniline (2.45 g, 11.2 mmol) and 2.5 g imidazole was stirred at 120 °C for 30 min under an argon gas atmosphere. After being cooled to room temperature, the reaction mixture was dissolved in 200 mL distilled CH\(_2\)Cl\(_2\), extracted with dilute HCl (2 x 200 mL) and H\(_2\)O (2 x 200 mL) and dried over MgSO\(_4\). The desiccant was filtered off and the solvent was removed at a rotary evaporator. Then the crude product was slowly precipitated from CH\(_2\)Cl\(_2\) solution by addition of methanol to give perylene bisimide 2 as a dark red powder (0.70 g, 0.50 mmol, 99%). \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta\) 8.16 (s, 4H; 2-H, 5-H, 8-H, 11-H), 7.82–7.80 (m, 2H; 3d-H), 7.65–7.64 (m, 2H; 3b-H), 7.28–7.25 (m, 12H; 3e-H, 3f-H, 1c-H, 1e-H), 6.84–6.82 (m, 8H; 1b-H, 1f-H), 1.29 (s, 36H; C(CH\(_3\))\(_3\)). \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta\) 163.7 (C=O), 156.5 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 148.0 (1d-C), 138.2 (3b-C, 3d-C), 137.2 (3a-C), 133.7 (Per-C), 131.2 (3e-C), 128.9 (3f-C), 127.2 (1c-C, 1e-C), 123.0 (Per-C), 121.6 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.4 (Per-C), 119.7 (1b-C, 1f-C), 94.0 (3c-C), 34.9 (C(CH\(_3\))\(_3\)), 31.8 (C(CH\(_3\))\(_3\)). HRMS (ESI, CHCl\(_3\)/acetonitrile 1:1, pos. mode): \(m/z\) 1387.2826 [M+H]\(^+\) (calcd for C\(_{76}\)H\(_{65}\)I\(_2\)N\(_2\)O\(_8\) 1387.2830).
Perylene bisimide 3:

A mixture of compound 2 (0.70 g, 0.50 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 50 µmol) and copper iodide (10 mg, 50 µmol) was dissolved in 30 mL of a degassed and distilled THF/H$_2$NPr$_2$ mixture (1:1) under an argon gas atmosphere. The reaction mixture was heated to 50 °C and triisopropylsilylacetylene (0.9 mL, 0.74 g, 4.0 mmol) was added. After stirring for one hour at this temperature, the solvent was removed at a rotary evaporator. The crude product was purified by silica gel column chromatography (CH$_2$Cl$_2$/n-Hexane = 50:50 as eluent) and then slowly precipitated from CH$_2$Cl$_2$ solution by addition of methanol to give perylene bisimide 3 as a dark red powder (0.74 g, 0.49 mmol, 99%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): δ 8.19 (s, 4H; 2-H, 5-H, 8-H, 11-H), 7.58–7.55 (m, 2H; 3d-H), 7.48–7.44 (m, 2H; 3e-H), 7.38–7.37 (m, 2H; 3b-H), 7.29–7.23 (m, 10H; 3f-H, 1c-H, 1e-H), 6.88–6.84 (m, 8H; 1b-H, 1f-H), 1.29 (s, 36H; C(CH$_3$)$_3$), 1.12 (s, 42H; SiCH(CH$_3$)$_2$). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 298 K): δ 163.8 (C=O), 156.5 (1-C, 6-C, 7-C, 12-C), 153.7 (1a-C), 148.0 (1d-C), 136.2 (3a-C), 133.7 (Per-C), 132.7 (3b-C), 132.6 (3d-C), 129.7 (3e-C), 129.5 (3f-C), 127.2 (1c-C, 1e-C), 125.3 (3c-C), 123.2 (Per-C), 121.5 (Per-C), 120.9 (2-C, 5-C, 8-C, 11-C), 120.4 (Per-C), 119.7 (1b-C, 1f-C), 106.3 (3c’-C), 92.6 (3c’’-C), 34.8 (C(CH$_3$)$_3$), 31.8 (C(CH$_3$)$_3$), 19.0 (SiCH(CH$_3$)$_2$), 11.9 (SiCH). HRMS (ESI, CHCl$_3$/acetonitrile 1:1, pos. mode): m/z 1496.7590 [M+H]$^+$ (calcd for C$_{98}$H$_{107}$N$_2$O$_8$Si$_2$ 1496.7600).
Perylene bisimide building block 4:

Perylene bisimide 3 (0.36 g, 0.24 mmol) was dissolved in 30 mL distilled THF and 3 mL of an nBu₄NF solution (1 M in THF) was added. The reaction was stopped after two minutes by pouring the mixture into 200 mL of a dilute HCl/CH₂Cl₂ mixture (1:1), was then extracted with dilute HCl (2 x 100 mL) and H₂O (2 x 100 mL) and dried over MgSO₄. The crude product was purified by silica gel column chromatography (CH₂Cl₂ as an eluent) and afterwards slowly precipitated from CH₂Cl₂ solution by addition of methanol to give perylene bisimide 4 as a dark red powder (0.26 g, 0.22 mmol, 90%). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 8.19 (s, 4H; 2-H, 5-H, 8-H, 11-H), 7.59–7.65 (m, 2H; 3d-H), 7.50–7.56 (m, 2H; 3e-H), 7.40–7.39 (m, 2H; 3b-H), 7.30–7.18 (m, 8H; 1b-H, 1f-H), 3.18 (s, 2H; 3c′′-H), 1.29 (s, 36H; C(CH₃)₃).

¹³C NMR (100 MHz, CD₂Cl₂, 298 K): 163.7 (C=O), 156.5 (1-C, 6-C, 7-C, 12-C), 153.7 (1a-C), 148.0 (1d-C), 136.2 (3a-C), 133.7 (Per-C), 133.0 (3b-C), 132.8 (3d-C), 130.0 (3f-C), 129.9 (3e-C), 127.2 (1c-C, 1e-C), 123.9 (3c-C), 123.1 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.4 (Per-C), 119.7 (1b-C, 1f-C), 82.9 (3c′-C), 78.8 (3c′′-C), 34.9 (C(CH₃)₃), 31.8 (C(CH₃)₃). HRMS (ESI, CHCl₃/acetonitrile 1:1, pos. mode): m/z 1183.4892 [M+H]⁺ (calcd for C₈₀H₆₇N₂O₈ 1183.4897). UV-vis (CH₂Cl₂): λₘₐₓ (ε) 582 nm (49200 M⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): λₘₐₓ = 611 nm (λₑₓ = 550 nm), Φₕ = 0.95.

[Diagram of Perylene bisimide 4]
Macroyclic trimer 5:

PBI building block 4 (200 mg, 0.169 mmol), Pd(PPh₃)₂Cl₂ (50 mg, 71 µmol) and copper iodide (20 mg, 0.11 mmol) were dissolved in 1 L mixture of distilled CH₂Cl₂ and HNPr₂ (9:1 vol%) at ambient atmosphere and stored in the freezer at -30 °C for three days. The solvent was removed at a rotary evaporator and the reaction mixture was filtered through a silica gel pad with CH₂Cl₂ to remove residual reagents and polymeric side products, and 92 mg (46 %) of a product mixture was obtained. The product mixture was further purified by recycling GPC (JAIGEL 2H+2.5H columns; CHCl₃, 3.5 mL/min) and the trimer 5 (36 mg, 10.2 µmol, 18%) could be isolated after six cycles in pure form. ¹H NMR (600 MHz, CD₂Cl₂, 298 K): δ 8.16 (s, 12H; 2-H, 5-H, 8-H, 11-H), 7.62–7.60 (m, 6H; 3d-H), 7.52–7.49 (m, 6H; 3e-H), 7.41–7.40 (m, 6H; 3b-H), 7.33–7.31 (m, 6H; 3f-H), 7.26–7.24 (m, 24H; 1c-H, 1e-H), 6.83–6.81 (m, 24H; 1b-H, 1f-H), 1.27 (s, 108H; C(CH₃)₃). ¹³C NMR (150 MHz, CD₂Cl₂, 298 K): δ 163.6 (C=O), 156.4 (1-C, 6-C, 7-C, 12-C), 153.6 (1a-C), 147.9 (1d-C), 136.3 (3a-C), 133.6 (Per-C), 133.5 (3b-C), 132.9 (3d-C), 130.6 (3f-C), 130.0 (3e-C), 127.2 (1c-C, 1e-C), 123.2 (3c-C), 123.0 (Per-C), 121.5 (Per-C), 120.8 (2-C, 5-C, 8-C, 11-C), 120.3 (Per-C) 119.6 (1b-C, 1f-C), 81.1 (3c’-C), 75.0 (3c”-C), 34.8 (C(CH₃)₃), 31.7 (C(CH₃)₃). HRMS (ESI, CHCl₃/acetonitrile 1:1, pos. mode): m/z 1772.7022 [M+2H]²⁺ (calcd for C₂₄₀H₁₉₄N₆O₂₄ 1772.7106). UV-vis (CH₂Cl₂): λ_max (ε) 582 nm (139500 M⁻¹ cm⁻¹); fluorescence (CH₂Cl₂): λ_max = 614 nm (ϕ_Fl = 0.91).
3. $^1$H and $^{13}$C NMR spectra

Fig. S1 $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of perylene bisimide 2; inset: an expanded aromatic region.
Fig. S2 $^{13}$C NMR spectrum (100 MHz, CD$_2$Cl$_2$, 298 K) of perylene bisimide 2; inset: an expanded low field region.
Fig. S3 $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of perylene bisimide 3; inset: an expanded aromatic region.
Fig. S4 $^{13}$C NMR spectrum (100 MHz, CD$_2$Cl$_2$, 298 K) of perylene bisimide 3; inset: an expanded low field region.
**Fig. S5** $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of perylene bisimide building block 4; inset: an expanded aromatic region.
Fig. S6 $^{13}$C NMR spectrum (100 MHz, CD$_2$Cl$_2$, 298 K) of perylene bisimide building block 4; inset: an expanded low field region.
**Fig. S7** $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of trimer 5; inset: an expanded aromatic region.
Fig. S8 $^{13}$C NMR spectrum (150 MHz, CD$_2$Cl$_2$, 298 K) of trimer 5; inset: an expanded low field region.
Fig. S9 \((1^H,1^H)\)-COSY NMR spectrum of trimer 5.

Fig. S10 \((1^H,1^C)\)-HSQC NMR spectrum of trimer 5.
Fig. S11 ($^1$H,$^{13}$C)-HMBC NMR spectrum of trimer 5.
4. High resolution mass spectrum

Fig. S12 High resolution mass spectrum (ESI) of macrocycle 5.
5. UV-vis and fluorescence spectra

![Image of UV-vis and fluorescence spectra]

**Fig. S13** UV-vis absorption spectra of monomer 4 (black solid line) and cyclic trimer 5 (red solid line) and the corresponding fluorescence spectra (dashed lines; \( \lambda_{\text{ex}} = 550 \) nm); all measurements were performed at room temperature in CH\(_2\)Cl\(_2\) at a concentration of 7.50 x 10\(^{-6}\) M.

6. Cyclic voltammetry

![Image of cyclic voltammograms]

**Fig. S14** Cyclic voltammograms of monomer 4 (left) and cyclic trimer 5 (right) in CH\(_2\)Cl\(_2\) (vs. Fc/Fc\(^+\)). Scan rate 100 mV s\(^{-1}\); working electrode: Pt disc, \( \varnothing \) 1 mm; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: TBAHFP (0.1 M); concentration ca. 2 x 10\(^{-4}\) M\(^{-1}\).
Tab. S1 Redox properties of the compounds 4 and 5 in CH$_2$Cl$_2$ (vs. Fc/Fc$^+$).$^a$

<table>
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<th>compound</th>
<th>$E_{1/2}^{\text{red}}$/V (PBI/PBI$^{2-}$)</th>
<th>$E_{1/2}^{\text{red}}$/V (PBI/PBI$^-$)</th>
<th>$E_{1/2}^{\text{ox}}$/V (PBI/PBI$^+$)</th>
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</thead>
<tbody>
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<td>4</td>
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<td>+0.87</td>
</tr>
<tr>
<td>5</td>
<td>-1.28</td>
<td>-1.15</td>
<td>+0.87</td>
</tr>
</tbody>
</table>

$^a$Scan rate 100 mV s$^{-1}$; working electrode: Pt disc, $\varnothing$ 1 mm; auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; electrolyte: TBAHFP (0.1 M); concentration ca. 2 x 10$^{-4}$ mol L$^{-1}$.

7. References