Supporting Information for:

N-Alkylated and N,N-Dialkylated 1,6-Diaminoperylene Diimides via Copper Catalyzed Direct Aromatic Amination

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1 Synthesis

1.1 General methods
Commercially available chemicals were used as received, unless otherwise stated. Prior to characterization and further processing, all solids and oils were dried at room temperature under vacuum. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DPX 300, DPX 400 and DRX 500 (300, 400, and 500 MHz for $^1$H and 75.5, 100.6 and 125.8 MHz for $^{13}$C). Chemical shifts are given in parts per million (ppm) referenced to residual $^1$H or $^{13}$C signals in deuterated solvents. Mass spectra were measured on a Finnigan ThermoQuest MAT 95 XL (EI-MS) and a Bruker Daltronics autoflex TOF/TOF (MALDI-MS; matrix material: trans-2-[3-(4-t-Butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), dithranol). Thin layer chromatography was conducted on silica gel coated aluminium plates (Macherey-Nagel, Alugramm SIL G/UV254, 0.25 mm coating with fluorescence indicator). Silica gel 60 M (Macherey-Nagel, 0.04-0.063 mm) was used as the stationary phase for column chromatography. Gel permeation chromatography (GPC) was performed in THF (HPLC grade, stabilized with 2.5 ppm BHT) at room temperature. GPC analyses were run on an Agilent Technologies system at a flow rate of 1 mL/min using an IsoPump G1310 A, a UV detector (G1314B) and PSS columns (Polymer Standards Service, Mainz, Germany; $10^2$, $10^3$, and $10^5$ Å, 5μ, 8 x 300 mm). For purification, a Shimadzu Recycling GPC system, equipped with a LC-20 AD pump, a SPD-20 A UV detector and a set of three preparative columns from PSS ($10^3$ Å, 5μ, 20 x 300 mm) was employed. The system operated at a flow rate of 6 mL/min.
1.2 Synthesis

\( 1 \)

The compound was synthesized according to literature procedure\(^{[1]} \) starting from 1-hexylheptylamine and perylene-3,4,9,10-tetracarboxylic dihydrid.

\( 1' \)\(^{[2]} \)

Perylene-3,4,9,10-tetracarboxylic dihydrid (0.78 g, 2.0 mmol), 2,6-dibromo-4-tert-butyl-aniline (1.84 g, 6 mmol), \( \text{Zn(OAc)}_2 \) (0.11 g, 0.6 mmol) and imidazole (2.72 g, 40 mmol) were heated at 180 °C for 72 h. After cooling to rt, the cold mixture was poured into dichloromethane (200 mL). The organic layer was washed with 1M HCl (50 mL) and water (50 mL) and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/\( \text{CH}_2\text{Cl}_2 \) 1:9) to give \( 1' \) (670 mg, 688 \( \mu \)mol, 35 %) as a red solid.

\(^{1}\text{H NMR (400 MHz, CD}_2\text{Cl}_2, \text{rt}): \delta = 8.82 (d, J = 8.0 \text{ Hz, 4H}), 8.75 (d, J = 8.1 \text{ Hz, 4H}), 7.73 (s, 4H), 1.39 (s, 18H) ppm; MS (MALDI TOF, matrix: DCTB) \text{C}_{44}\text{H}_{30}\text{Br}_4\text{N}_2\text{O}_4 (965.9): m/z(\%) : 965.9 (100) [M]^{+} \)
2b

Pyrrolidine (0.6 mL) was added to 1 (28 mg, 37.2 µmol) and CuCl₂ (5 mg, 37.2 µmol). After stirring overnight at rt, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH₂Cl₂, 1:1) to give 2b (16 mg, 18 µmol, 49 %) as a dark blue solid.

¹H NMR (400 MHz, CD₂Cl₂, rt): δ = 8.67-8.56 (m, 2H), 8.34-8.28 (m, 2H), 7.93 (d, J = 8.09 Hz, 2H), 5.27-5.11 (m, 2H), 3.72 (br, 4H), 2.79 (br, 4H), 2.34-2.18 (m, 4H), 2.01 (br, 8H), 1.89-1.77 (m, 4H), 1.39-1.16 (m, 32H), 0.87-0.80 (m, 12H) ppm; ¹H NMR (400 MHz, CD₂Cl₂, 333 K): δ = 8.65 (d, J = 7.66 Hz, 2H), 8.36 (s, 2H), 8.03 (d, J = 8.09 Hz, 2H), 5.26 (m, 1H), 5.19 (m, 1H), 3.73 (br, 8H), 2.36-2.22 (m, 4H), 2.03 (s, 8H), 1.95-1.82 (m, 4H), 1.44-1.20 (m, 32H), 0.89-0.81 (m, 12H).

¹³C-NMR (100 MHz, CDCl₃): δ = 165.67*, 165.36*, 164.57*, 164.43*, 150.01, 135.58*, 135.49*, 131.05, 130.70, 129.87, 128.45*, 128.42*, 123.43, 123.32, 122.70, 118.42*, 118.13*, 117.63*, 117.38*, 117.32*, 116.97*, 54.63, 54.27, 52.09, 32.50, 31.79, 31.76, 29.32, 29.23, 27.01, 26.89, 25.65, 22.62, 22.58, 14.05 ppm; ¹ MS (MALDI TOF, matrix: DCTB) C₅₈H₇₆N₄O₄ (892.59): m/z (%): 892.6 (100) [M⁺].

2´b

Pyrrolidine (2 mL) was added to 1´ (30 mg, 31 µmol) and CuCl₂ (2 mg, 15 µmol). After 1 h stirring at rt, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH₂Cl₂, 3:1) to give 2´b (28 mg, 25 µmol, 82 %) as a dark blue solid.

¹H NMR (500 MHz, C₂D₂Cl₄): δ = 8.66 (d, J = 8.06 Hz, 2H), 8.30 (s, 2H), 7.72 (d, J = 8.03 Hz, 2H), 7.67 (s, 2H), 7.66 (s, 2H), 3.68 (br, 4H), 2.73 (br, 4H), 2.20 (br, 4H), 1.91 (br, 4H), 1.31 (s, 9H), 1.30 (s, 9H) ppm; ¹³C-NMR (125 MHz, C₂D₂Cl₂): δ = 163.32, 162.95, 155.80, 155.51, 150.30, 136.68, 132.85, 132.11, 131.70, 131.21, 130.14, 129.57, 128.88, 124.13, 123.97, 123.49, 122.74, 118.09, 117.28, 116.96, 52.82, 35.41, 35.38, 35.38, 22.62, 22.58, 14.05 ppm; ¹ MS (MALDI TOF, matrix: DCTB) C₅₈H₇₆N₄O₄ (892.59): m/z (%): 892.6 (100) [M⁺].
Pyrrolidine (1 mL) was added to 1′′ (10 mg, 13 µmol) and CuCl₂ (2 mg, 15 µmol). After 3 h stirring at rt, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH₂Cl₂) to give 2′′b (8 mg, 9 µmol, 68 %) as a dark blue solid.

1H NMR (500 MHz, CDCl₃): δ = 8.74 (d, J = 8.05 Hz, 2H), 8.41 (d, J = 1.09 Hz, 2H), 7.92 (dd, J = 8.05, 2.00 Hz, 2H), 7.62-7.59 (m, 2H), 7.49-7.45 (m, 2H), 7.02 (t, J = 1.93 Hz, 1H), 7.00 (t, J = 1.92 Hz, 1H), 3.77 (br, 4H), 2.85 (br, 4H), 2.21-1.90 (m, 8H), 1.38-1.31 (m, 36H) ppm, 13C-NMR (125 MHz, CDCl₃): δ = 165.36, 165.16, 150.06*, 150.05*, 150.02*, 149.99*, 149.94*, 149.92*, 143.87*, 143.84*, 136.03*, 136.02*, 133.59*, 133.56*, 132.95*, 132.93*, 131.45, 130.66, 128.87*, 128.86*, 128.73*, 128.72*, 128.66, 127.78, 127.67, 126.18, 126.01, 123.34, 123.24, 118.10, 117.93, 117.38, 117.37, 117.14, 52.20, 35.58, 35.58, 35.56, 34.23, 31.85, 31.83, 31.82, 31.26, 31.22, 25.72 ppm, 2 MS (MALDI TOF, matrix: DCTB) C₆₀H₆₄N₄O₄ (904.49): m/z(%): 904.6 (100) [M]+.
Scheme 2: Synthesis of 1-piperidin-PDIs and 1,6-dipiperidin-PDIs 3a, 3b, 3’b, 3’’ a and 3’’b.

3a/3b

Piperidine (2 mL) was added to 1 (100 mg, 132 µmol) and CuCl₂ (3 mg, 22 µmol). After stirring overnight at 60 °C, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH₂Cl₂, 1:1) to give 3b (35 mg, 38 µmol, 28 %) as a dark blue solid and 3a (67 mg, 80 µmol, 60 %) as a green solid.

3b

1H NMR (400 MHz, CDCl₃, 333 K): δ = 9.73 (d, J = 8.29 Hz, 2H), 8.59 (d, J = 8.13 Hz, 2H), 8.42 (s, 2H), 5.25-5.13 (m, 2H), 3.43-3.35 (m, 4H), 2.95-2.87 (m, 4H), 2.31-2.21 (m, 4H), 1.94-1.74 (m, 14H), 1.40-1.21 (m, 34H), 0.87-0.82 (m, 12H) ppm, 13C-NMR (100 MHz, CDCl₃): δ = 164.81 (br), 163.78 (br), 152.76, 135.85, 134.71, 133.91, 131.77, 131.37, 131.02, 130.61, 130.59, 130.57, 129.33, 128.98, 128.27, 127.01, 125.92, 125.25,
125.19, 125.18, 124.64, 123.58, 123.35, 123.33, 123.31, 123.07, 122.62, 122.34, 122.31, 122.29, 121.84, 121.45, 121.07, 54.70, 54.68, 54.52, 52.96, 32.40, 31.75, 29.25, 29.21, 26.95, 26.93, 25.84, 23.73, 22.58, 14.03 ppm; MS (MALDI TOF, matrix: DCTB) C_{60}H_{80}N_{4}O_{4} (920.62): m/z\%: 920.7[M]+.

3a

$^1$H NMR (400 MHz, CDCl$_3$, 333 K): δ = 9.84 (d, $J$ = 8.33 Hz, 1H), 8.66-8.58 (m, 3H), 8.54-8.49 (m, 3H), 5.24-5.14 (m, 2H), 5.31-3.45 (m, 2H), 3.50-3.29 (m, 2H), 2.31-2.21 (m, 4H), 1.98-1.81 (m, 8H), 1.42-1.20 (m, 34H), 0.89-0.81 (m, 12H) ppm

$^1$H NMR (400 MHz, CDCl$_3$, 273 K): δ = 9.79 (d, $J$ = 8.32 Hz, 1H), 8.66-8.51 (m, 3H), 8.54-8.51 (m, 3H), 5.24-5.12 (m, 2H), 3.49-3.41 (m, 2H), 2.98-2.89 (m, 2H), 2.31-2.18 (m, 4H), 1.97-1.77 (m, 8H), 1.40-1.15 (m, 34H), 0.87-0.76 (m, 12H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): δ = 165.05 (br), 163.93 (br), 153.31, 153.83, 135.80, 131.69, 131.17, 130.38, 128.97, 127.99, 123.85, 123.19, 123.16, 122.89, 122.21, 121.04, 54.68, 54.38, 53.12, 32.46, 31.76, 29.27, 29.21, 26.98, 26.89, 25.86, 23.81, 22.60, 22.57, 14.03 ppm; MS (MALDI TOF, matrix: DCTB) C$_{55}$H$_{71}$N$_{3}$O$_{4}$ (837.54): m/z\%: 837.6 (100) [M]+.

3b

Piperidine (2 mL) was added to 1* (20 mg, 21 µmol) and CuCl$_2$ (2 mg, 15 µmol). After stirring over night at rt, the mixture was poured into dichloromethane (20 mL) and H$_2$O (20 mL). The organic layer was separated, washed with aq H$_2$SO$_4$ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO$_4$ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH$_2$Cl$_2$, 3:1) to give 3*b (21 mg, 18 µmol, 89 %) as a dark blue solid.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ = 9.77 (d, $J$ = 8.30 Hz, 2H), 8.68 (d, $J$ = 8.31 Hz, 2H), 7.78 (d, $J$ = 2.36 Hz, 4H), 3.49-3.41 (m, 4H), 3.01-2.92 (m, 4H), 1.93-1.73 (m, 12H), 1.44-1.38 (m, 12H) ppm, $^{13}$C-NMR (100 MHz, CDCl$_3$): δ = 162.37, 162.21, 155.25, 154.97, 153.48, 136.75, 132.15, 132.11, 131.67, 131.44, 129.87, 129.84, 129.68, 128.39, 123.76, 123.70, 123.57, 123.41, 123.04, 122.98, 121.24, 119.82, 53.12, 35.17, 35.12,

3 Not all signals are visible, doubled signals
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31.08, 31.07, 25.81, 23.75 ppm, MS (MALDI TOF, matrix: DCTB) C_{54}H_{48}Br_4N_4O_4 (1136.04): m/z(%): 1135.8 (100) [M]^+.

3''a/3''b

Pyrrolidine (1 mL) was added to 1'' (40 mg, 52 µmol) and CuCl_2 (3 mg, 22 µmol). After 14 h stirring at 80 °C, the mixture was poured into dichloromethane (20 mL) and H_2O (20 mL). The organic layer was separated, washed with aq H_2SO_4 (20 mL), water (20 mL) and brine (20 mL), dried over MgSO_4 and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (cyclohexane/CH_2Cl_2, 2:3 to 1:3) to give 3''b (3 mg, 4 µmol, 7 %) as a dark blue solid and 3''a (25 mg, 29 µmol, 56 %) as a dark green solid.

3''b

^1H NMR (500 MHz, CDCl_3): δ = 9.79 (d, J = 8.28 Hz, 2H), 8.67 (d, J = 8.26 Hz, 2H), 8.46 (s, 2H), 7.62-7.59 (m, 2H), 7.49-7.45 (m, 2H), 7.02-7.01 (m, 1H), 6.99-6.98 (m, 1H); 3.49-3.37 (m, 4H), 2.99-2.87 (m, 4H), 1.94-1.74 (m, 12H), 1.35-1.31 (m, 36H) ppm, ^13C-NMR (125 MHz, CDCl_3): δ = 164.78, 164.67*, 164.66*, 153.43, 150.07*, 150.05*, 149.98*, 149.95*, 143.89*, 143.88*, 143.81, 136.39*, 136.37*, 133.21*, 133.18*, 132.73*, 132.71*, 132.08, 131.14, 129.35*, 129.34*, 128.77*, 128.75*, 128.71*, 128.69*, 128.30, 127.74, 127.57, 126.24*, 126.13*, 123.87*, 123.86*, 123.58*, 123.57*, 123.46*, 123.43*, 122.86*, 122.85*, 121.16, 120.59*, 120.59*, 53.22, 53.19, 53.08, 53.05, 35.57, 35.56, 35.55, 34.24, 34.23, 31.83, 31.82, 31.80, 31.25, 31.22, 29.69, 26.90, 25.86, 25.84, 23.77, ppm;^5 MS (MALDI TOF, matrix: DCTB) C_{62}H_{68}N_4O_4 (932.52): m/z(%): 932.5 (100) [M]^+.

3''a

^1H NMR (400 MHz, CD_2Cl_2): δ = 9.94 (dd, J = 6.45 Hz, J =8.29 Hz, 1H), 8.77-8.71 (m, 2H), 8.68 (d, J = 1.98 Hz, 1H), 8.66-8.59 (m, 3H), 7.64-7.58 (m, 2H), 7.51-7.45 (m, 2H), 3.64-3.47 (m, 2H), 3.11-2.93 (m, 2H), 2.00-1.78 (m, 6H), 1.39-1.29 (m, 36H) ppm, ^13C-NMR (100 MHz, CDCl_3): δ = 164.77, 164.69, 164.49, 164.42, 152.94*, 152.92*, 150.10*, 150.07*, 150.06*, 150.04*, 143.79*, 143.77*, 136.50,* 136.47*, 135.38*, 5 * : doubled signals

5 * : doubled signals
135.34*, 134.49*, 134.47*, 132.86*, 132.85*, 132.63*, 132.62*, 131.85, 131.43, 129.73, 129.69, 129.44*, 129.42*, 129.00, 128.75, 127.71*, 127.70*, 127.63*, 127.62*, 127.45*, 127.43*, 126.28, 126.23, 125.95, 125.52, 125.48, 124.68, 123.97, 123.90*, 123.88*, 123.19*, 123.16*, 122.96*, 122.93*, 122.83*, 122.81*, 121.72, 121.58*, 121.56*, 53.22, 53.07, 52.92, 52.75, 35.53, 34.23, 31.76, 31.21, 29.67, 26.89, 25.86, 25.80, 23.68 ppm. MS (MALDI TOF, matrix: DCTB) C₅₇H₅₉N₃O₄ (849.45): m/z(%): 849.5(100) [M]+.  

Scheme 3: Synthesis of 1-amino-PDIs 4a-6a.

4a
Hexylamine (4 mL) was added to 1 (200 mg, 265 µmol) and CuCl₂ (36 mg, 268 µmol). After stirring 24 h at 90 °C, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel.

6*: doubled signals
(cyclohexane/CH₂Cl₂, 3:2) and by recGPC to give 5a (14 mg, 15 µmol, 4 %) as a turquoise solid.

1H NMR (400 MHz, CD₂Cl₂): δ = 8.88 (d, J = 8.24 Hz, 1H), 8.70-8.55 (m, 2H), 8.55-8.38 (m, 3H), 5.24-5.12 (m, 2H), 3.52 (t, J = 7.13 Hz, 1H), 2.31-2.18 (m, 4H), 1.91-1.79 (m, 6 H), 1.58-1.49 (m, 2H), 1.44-1.15 (m, 37H), 0.97-0.91 (m, 3H), 0.86-0.77 (m, 12H).

MS (MALDI TOF, matrix: DCTB) C₅₅H₇₂N₄O₄ (853.58): m/z(%):853.6 (100) [M]+.

5a
1-Methylpiperazine (2 mL) was added to 1 (28 mg, 37 µmol) and CuCl₂ (5 mg, 37 µmol). After stirring 24 h at 110 °C, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (EtOAc/CH₂Cl₂, 2:1) to give 6a (8 mg, 9.4 µmol, 25 %) as a dark grey blue solid.

1H NMR (400 MHz, CD₂Cl₂, rt): δ = 9.94 (d, J = 8.28 Hz, 1H), 8.67-8.45 (m, 6H), 5.23 -5.11 (m, 2H), 3.49-3.42 (m, 2H), 3.17-3.08 (m, 2H), 2.89-2.81 (m, 2H), 2.60-2.51 (m, 2H), 2.40 (s, 3H), 2.30-2.17 (m, 4H), 1.89-1.79 (m, 4H), 1.38-1.16 (m, 32H), 0.86-0.80 (m, 12H) ppm. MS (MALDI TOF, matrix: DCTB) C₅₅H₇₂N₄O₄ (852.56): m/z(%):(100) [M]+.

6a
Morpholine (2 mL) was added to 1 (30 mg, 40 µmol) and CuCl₂ (5 mg, 37 µmol). After stirring 24 h at 110 °C, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH₂Cl₂/cyclohexane, 3:1) and recGPC to give 7a (6 mg, 7.1 µmol, 18 %) as a dark grey blue solid.

1H NMR (400 MHz, CDCl₃, rt): δ = 10.12-10.02 (m, 1H), 8.74-8.51 (m, 6H), 5.25-5.12 (m, 2H), 4.09-3.93 (m, 4H), 3.46-3.36 (m, 2H), 3.23-3.12 (m, 2H), 2.33-2.16 (m, 4H),
The compound was synthesized according to literature procedure [H. Langhals, S. Kinzel, *J. Org. Chem.*, **2010**, 75, 7781-7784.] starting from 1,4,5,8-naphthalenetetracarboxylic dianhydride and 1-hexylheptylamine.

2,6-Diisopropylaniline (1.72 g, 1.12 mL, 9.69 mmol) was added to a mixture of 1,4,5,8-Naphthalenetetracarboxylic dianhydride (1.00 g, 3.73 mmol) in DMF (30 mL). After stirring 4 h at 130 °C, the solution was poured into dichloromethane (20 mL) and H2O (20 mL). The organic layer was separated, washed with water (50 mL), 1M HCl (50 mL), water (50 mL) and brine (50 mL), dried over MgSO4 and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH2Cl2/cyclohexane, 2:1) to give 7′ (188 mg, 320 µmol, 9 %) as a white solid.

1H NMR (400 MHz, CDCl3, rt): δ = 8.89 (s, 4H), 7.53 (t, J = 7.77 Hz, 2H), 7.37 (d, J = 7.78 Hz, 4H), 2.71 ( sept., J = 6.81 Hz, 4H), 1.17 (d, J = 6.86 Hz, 24H) ppm, 13C-NMR (100 MHz, CDCl3): δ = 162.90, 145.51, 131.56, 129.99, 129.96, 127.65, 126.89, 124.21, 29.30, 23.94, ppm
Pyrrolidine (2 mL) was added to 7 (100 mg, 159 µmol) and CuCl₂ (10 mg, 74 µmol). After stirring 24 h at rt, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH₂Cl₂/cyclohexane, 1:1) to give 8b (15 mg, 20 µmol, 12 %) and 8a (25 mg, 36 µmol, 22 %) as red solids.

8b:

1H NMR (400 MHz, CDCl₃, 333 K): δ = 8.00 (s, 2H), 5.17-5.08 (m, 2H), 3.56-3.51 (m, 8H), 2.39-2.30 (m, 2H), 2.25-2.15 (m, 2H), 2.08-2.03 (m, 8H), 1.86-1.73 (m, 4H), 1.38-1.17 (m, 32H), 0.87-0.80 (m, 12H) ppm, 1H NMR (400 MHz, CDCl₃, rt): δ = 7.99 (d, J = 11.91 Hz, 2H), 5.18-5.06 (m, 2H), 3.55-3.48 (m, 8H), 2.41-2.29 (m, 2H), 2.25-2.14 (m, 2H), 2.08-2.01 (m, 8H), 1.84-1.68 (m, 4H), 1.39-1.12 (m, 32H), 0.85-0.79 (m, 12H) ppm, 13C NMR (100 MHz, CDCl₃): 165.50*, 164.38*, 164.08*, 163.29*, 150.45*, 150.12*, 132.95, 132.24, 125.42, 124.68, 116.06, 115.30, 112.01, 106.23, 105.45, 54.99, 54.73, 52.53, 33.18, 32.42, 31.86, 31.73, 29.27, 29.18, 27.12, 26.93, 26.82, 25.92, 22.57, 14.05, 14.03 ppm; 7 MS (MALDI TOF, matrix: DCTB) C₄₈H₇₂N₄O₄ (768.56): m/z(%): 768.5 (100) [M]+.

8a:

1H NMR (400 MHz, CDCl₃, 333 K): δ =8.62 (d, J = 7.77 Hz, 1H), 8.40 (s, 1H), 8.35 (d, J = 7.78 Hz, 1H), 5.22-5.09 (m, 2H), 3.61-3.52 (m, 4H), 2.33-2.17 (m, 4H), 2.14-2.07 (m, 4H), 1.89-1.78 (m, 4H), 1.39-1.16 (m, 32H), 0.88-0.80 (m, 12H) ppm, 1H NMR (400 MHz, CDCl₃, rt): δ = 8.62 (s, 1H), 8.44-8.29 (m, 2H), 5.23-5.07 (m, 2H), 3.55 (br, 4H), 2.39-2.14 (m, 4H), 2.13-2.05 (m, 4H), 1.88-1.71 (m, 4H), 1.38-1.11 (m, 32H), 0.86-0.76 (m, 12H) ppm, 13C NMR (100 MHz, CDCl₃): 164.81*, 164.62*, 163.78*, 163.66*, 163.42*, 163.15*, 162.36*, 150.01, 149.65, 130.86, 130.05, 126.18, 125.99, 125.52, 125.50* ppm;

7*: doubled signals
125.29, 124.93, 124.19, 123.78, 123.03, 120.06, 55.00*, 54.81*, 54.63*, 54.61*, 52.87, 32.85, 32.33*, 32.21*, 31.77, 31.70, 29.14, 26.88, 26.82, 25.81, 22.55, 22.53, 14.03, 14.01 ppm; MS (MALDI TOF, matrix: DCTB) C_{44}H_{65}N_{3}O_{4} (699.50): m/z (‰): 699.5 (100) [M]^+.

8′a/8′b

Pyrrolidine (4 mL) was added to 7′ (50 mg, 85 µmol) and CuCl₂ (10 mg, 74 µmol). After stirring 24 h at rt, the mixture was poured into dichloromethane (20 mL) and H₂O (20 mL). The organic layer was separated, washed with aq H₂SO₄ (20 mL), water (20 mL) and brine (20 mL), dried over MgSO₄ and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH₂Cl₂/cyclohexane, 6:1) to give 8′b (22 mg, 30 µmol, 36 %) and 8′a (11 mg, 17 µmol, 20 %) as red solids.

8′b

1H NMR (400 MHz, CDCl₃, rt): δ = 8.10 (s, 2H), 7.49 (t, J = 7.76 Hz, 1H), 7.48 (t, J = 7.73 Hz, 1H), 7.34 (d, J = 7.81 Hz, 2H), 7.33 (d, J = 7.64 Hz, 2H), 3.55 (broad, 8H), 2.87 (sept, J = 6.80 Hz, 2H), 2.74 (sept, J = 6.83 Hz, 2H), 2.01 (broad, 8H), 1.18 (d, J = 6.81 Hz, 12H), 1.17 (d, J = 6.84 Hz, 12H) ppm, 13C-NMR (100 MHz, CDCl₃): δ = 164.13, 162.26, 151.01, 146.25, 145.59, 133.99, 131.85, 130.67, 129.55, 129.28, 125.31, 124.02, 123.97, 116.19, 112.42, 105.39, 52.88, 29.15, 29.12, 26.89, 25.75, 24.20, 23.96 ppm. MS (MALDI TOF, matrix: DCTB) C_{46}H_{52}N_{4}O_{4} (724.40): m/z (‰): 724.4 (100) [M]^+.

8′a:

1H NMR (400 MHz, CDCl₃, rt): δ = 8.76 (d, J = 7.76 Hz, 1H), 8.52 (s, 1H), 8.48 (d, J = 7.77 Hz, 1H), 7.51 (t, J = 7.76 Hz, 1H), 7.50 (t, J = 7.74 Hz, 1H), 7.35 (d, J = 7.77 Hz, 2H), 7.35 (d, J = 7.72 Hz, 2H), 3.59 (braod, 4H), 2.81-2.67 (m, 4H), 2.07 (broad, 4H), 1.20-1.15 (m, 24H) ppm, 13C-NMR (100 MHz, CDCl₃): δ = 163.68, 163.65, 163.30, 161.56, 150.31, 145.71, 145.56, 131.27, 131.18, 131.04, 130.32, 129.76, 129.53, 126.03, 125.98, 125.02, 124.88, 124.22, 124.11, 124.05, 120.86, 103.41, 53.17, 29.69, 29.23, 8*: doubled signals
29.18, 26.91, 25.73, 24.20, 23.98, 23.96, 23.73 ppm. MS (MALDI TOF, matrix: DCTB) C\textsubscript{42}H\textsubscript{45}N\textsubscript{3}O\textsubscript{4} (655.34): m/z(%): 655.4 (100) [M]+.

9\textsubscript{a}
Piperidine (4 mL) was added to 7 (202 mg, 0.32 mmol) and CuCl\textsubscript{2} (32 mg, 0.24 mmol). After stirring 24 h at 90 °C, the mixture was poured into dichloromethane (20 mL) and H\textsubscript{2}O (20 mL). The organic layer was separated, washed with aq H\textsubscript{2}SO\textsubscript{4} (20 mL), water (20 mL) and brine (20 mL), dried over MgSO\textsubscript{4} and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH\textsubscript{2}Cl\textsubscript{2}/cyclohexane, 1:1) to give 9\textsubscript{a} (13 mg, 18 µmol, 6 %) as a red solid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, rt): δ = 8.79-8.29 (m, 3H), 5.25-5.07 (m, 2H), 3.57-3.45 (m, 4H), 2.34-2.11 (m, 4H), 1.89-1.73 (m, 10H), 1.39-1.09 (m, 32H), 0.95-0.75 (12H) ppm. MS (MALDI TOF, matrix: DCTB) C\textsubscript{45}H\textsubscript{67}N\textsubscript{3}O\textsubscript{4} (713.51): m/z(%): 713.5 (100) [M]+.

9\textsuperscript{´a}
Piperidine (4 mL) was added to 7\textsuperscript{´} (50 mg, 85 µmol) and CuCl\textsubscript{2} (10 mg, 74 µmol). After stirring 24 h at 60 °C, the mixture was poured into dichloromethane (20 mL) and H\textsubscript{2}O (20 mL). The organic layer was separated, washed with aq H\textsubscript{2}SO\textsubscript{4} (20 mL), water (20 mL) and brine (20 mL), dried over MgSO\textsubscript{4} and concentrated under vacuum. Product purification was performed by column chromatography on silica gel (CH\textsubscript{2}Cl\textsubscript{2}/cyclohexane, 6:1) to give 9\textsuperscript{´a} (11 mg, 16 µmol, 19 %) as a red solid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, rt): δ = 8.73 (d, J = 7.8 Hz, 1H), 8.57 (s, 1H), 8.50 (d, J = 7.7 Hz, 1H), 7.53-7.46 (m, 2H), 7.36 (d, J = 5.8 Hz, 2H), 7.34 (d, J = 5.8 Hz, 2H), 3.57-3.52 (m, 4H), 2.78-2.65 (m, 4H), 1.85-1.70 (m, 6H), 1.20-1.14 (m, 24H) ppm, \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): δ = 163.54, 163.37, 163.27, 161.75, 154.27, 145.54, 145.51, 131.70, 131.21, 131.11, 130.28, 129.77, 129.49, 127.33, 126.33, 126.01, 125.88, 125.29, 124.10, 124.05, 121.70, 106.37, 53.51, 29.69, 29.24, 26.91, 26.29, 24.15, 23.99, 23.95, 23.76, 23.63 ppm. MS (MALDI TOF, matrix: DCTB) C\textsubscript{43}H\textsubscript{47}N\textsubscript{3}O\textsubscript{4} (669.36): m/z(%): 669.4 (100) [M]+.
2 UV/Vis

**Figure 1:** Normalized absorption spectra of 1 (red line), 3a (green line) and 3b (blue line).

In Figure 1 the absorption spectra of the unsubstituted (1), the mono (3a) and the diamino (3b) substituted PDIs are compared. While 1 has its longest wavelength absorption maximum at 526 nm, the maximum is shifted for the monosubstituted PDI 3a to 602 nm and disubstituted PDI 3b to 653 nm, respectively. The data are well in accordance with those of similar reference products.[3-6]

**Figure 2:** Normalized absorption spectra of 4a, 5a and 6a.
Figure 3: Normalized absorption spectra of 2b and 3b.

![Normalized absorption spectra of 2b and 3b.](image)

Figure 4: Normalized absorption spectra of 7’ (red line), 8’a (green line) and 8’b (blue line).

![Normalized absorption spectra of 7’, 8’a and 8’b.](image)

In Figure 4 the absorption spectra of the unsubstituted (7’), the mono (8’a) and the diamino (8’b) substituted NDIs are compared. While 7’ has its longest wavelength absorption maximum at 381 nm, the maximum of monosubstituted NDI 8’a is shifted to 527 nm and similar to disubstituted NDI 8’b (536 nm).
3 NMR Data

2b

500 MHz in CDCl₃, 60 °C

Figure 5: ¹H-NMR 2b.

2'b

500 MHz in C₂D₂Cl₄, rt

Figure 6: ¹H-NMR 2'b.
Figure 7: $^1$H-NMR $2''b$.  

Figure 8: $^1$H-NMR 3a.
Figure 9: $^1$H-NMR 3b.

$^1$H-NMR 3b.

Figure 10: $^1$H-NMR 3’b.

$^1$H-NMR 3’b.
Figure 11: $^1$H-NMR 3''a.

400 MHz in CDCl$_3$, rt

Figure 12: $^1$H-NMR 3''b.

400 MHz in CDCl$_3$, rt
Figure 13: $^1$H-NMR 4a.

Figure 14: $^1$H-NMR 5a.
**Figure 15**: $^1$H-NMR 6a.

**Figure 16**: $^1$H-NMR 7'.

$^1$H-NMR spectra of 6a and 7' in CDCl$_3$, rt.
Figure 17: $^1$H-NMR 8a.

Figure 18: $^1$H-NMR 8b.
Figure 19: 'H-NMR 8’a.

8’a 400 MHz in CDCl₃, rt

Figure 20: 'H-NMR 8’b.

8’b 400 MHz in CDCl₃, rt
Figure 21: $^1$H-NMR 9a.

Figure 22: $^1$H-NMR 9'a.
3.1 Additional NMR spectra

3.1.1 NMR NOE-spectra of 2´b

![NOE spectra](image)

Figure 23: a) 1H-NMR spectra of 2´b (aromatic part); b-e) respective NOE spectra.

The $^1$H-NMR spectra (Figure 23, a) of 2´b is in accordance with a molecule of high symmetry. By using NOE spectroscopy we were able to relate the two doublets at 8.66 ppm and 7.72 ppm to the hydrogen atoms 7, 8, 11 and 12 because they interact with each other exclusively (Figure 23, b and d). The singlet at 8.30 ppm shows no interaction at all since the hydrogen atoms 2 and 5 are rather isolated from the other protons (Figure 23, c). The two singlet signals at 7.67 and 7.66 ppm are assigned to the hydrogens located at the dibromo-tert-butyl phenyl substituents; they interact with the t-butyl groups. The data are well in accordance with those of similar reference products.$^{[3,6]}$

3.1.2 Comparison of 2b and PDIs synthesized according to literature

We synthesized 1,7-diamino PDI and 1,6-diamino PDI according to literature$^{[7]}$ in a two-step syntheses (Scheme 5). Mono and di substituted PDI were separated after
bromination. After amination it was possible to separate 1,6-diamino PDI and 1,7-diamino PDI.

Scheme 5: Synthesis of Lit 1,6 and Lit 1,7 according to literature[7].

In Figure 24 1-H-NMR spectra (aromatic parts) at room temperature of 2b, Lit 1,6 and Lit 1,7 are shown. The shifts of Lit 1,6 and 2b are the same and they show an obvious difference to the spectra of Lit 1,7.
3.1.3 Temperature dependence in 1H-NMR spectra

The NMR spectra of molecules with a swallow tail at the imid (R=`) show at room temperature (298 K) a doubled signal set in the aromatic region. In Figure 25 the 1H-NMR spectra for 2b at rt (top) and 60 °C (bottom) are displayed. At rt the signals at 8.67 ppm and 8.34 ppm are doubled. At 60 °C they were converted to a doublet at 8.64 ppm and a singlet at 8.36 ppm, as expected.

We investigated the concentration dependence (Figure 26) and solvent dependence (Figure 27) of the splitting. There is no concentration effect. Because of this we suppose that the molecules form two rotamers and no π-π stacking. The rotation of the swallow tail is hindered at room temperature. These results are in accordance with literature.\[4\]
Figure 25: $^1$H-NMR of 2b at room temperature (298 K, top) and 60 °C (333 K, bottom).

Figure 26: $^1$H-NMR of 2b, different concentrations.
3.1.4 Additional $^1$H-NMR spectra at different temperatures

Figure 27: $^1$H-NMR of 2b in toluene (top) and CDCl$_3$ at room temperature.

Figure 28: $^1$H-NMR of 3a at room temperature (298 K, top) and 60 °C (333 K, bottom).
Figure 29: \(^1\)H-NMR of \(3b\) at room temperature (298 K, top) and 60 °C (333 K, bottom).

Figure 30: \(^1\)H-NMR of \(8a\) at room temperature (298 K, top) and 60 °C (333 K, bottom).
Figure 31: $^1$H-NMR of 8b at room temperature (298 K, top) and 60 °C (333 K, bottom).
4 Mass spectra

**Figure 32:** MS (Maldi-pos, DCTB) of 2b.

**Figure 33:** MS (Maldi-pos, DCTB) of 2'\ b.
Figure 34: MS (Maldi-pos, DCTB) of 2’b.

Figure 35: MS (Maldi-pos, DCTB) of 3a.
Figure 36: MS (Maldi-pos, DCTB) of 3b.

Figure 37: MS (Maldi-pos, DCTB) of 3’b.
Figure 38: MS (Maldi-pos, DCTB) of 3’a.

Figure 39: MS (Maldi-pos, DCTB) of 3’b.
Figure 40: MS (Maldi-pos, DCTB) of 4a.

Figure 41: MS (Maldi-pos, DCTB) of 5a.
Figure 42: MS (Maldi-pos, DCTB) of 6a.

Figure 43: MS (Maldi-pos, DCTB) of 8a.
Figure 44: MS (Maldi-pos, DCTB) of 8b.

Figure 45: MS (Maldi-pos, DCTB) of 8’a.
Figure 46: MS (Maldi-pos, DCTB) of 8′b.

Figure 47: MS (Maldi-pos, DCTB) of 9a.
Figure 48: MS (Maldi-pos, DCTB) of 9’a.