Supplementary Material (ESI) for PCCP

Supplementary Information

Photophysics of aminophenylsubstituted Pyrrolopyrrole Cyanines

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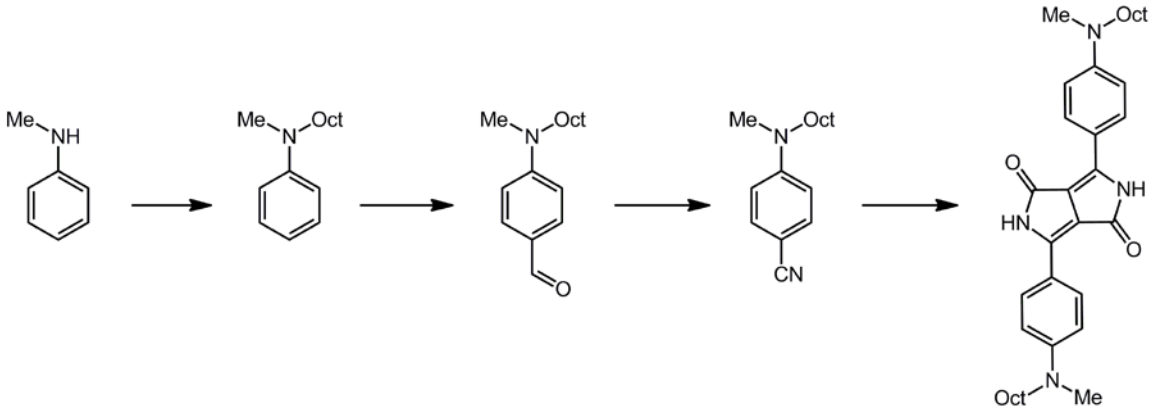
S1: Synthesis and characterization of aminophenylsubstituted DPPs **1a**, **1b** and **1c**

S2: Absorption spectra of protonation experiments for compounds **4a′**, **4b′** and **5a″**

S1: Synthesis and characterization of aminophenylsubstituted DPPs **1a**, **1b** and **1c**

3,6-bis(4-(methyl(octyl)amino)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1a)



1a* **1a**** **1a*** **1a**

N-methyl-*N*-octylaniline (1a***)

150.0 g (1.40 mol) freshly distilled *N*-methyl-aniline and 69.6 g (0.50 mol) K_2CO_3 were stirred for 20 minutes in 35 mL DMSO. 271.7 g (1.41 mol) *n*-octylbromide was added and the solution was heated for 20 h at 80 °C. The solids were filtered off. The filtrate was diluted in dichloromethane and washed with water. The solution was dried over $MgSO_4$ and the solvent was removed in vacuum. The residue was distilled at 1 mbar using a 10 cm mirrored Vigreux column. At 152 °C **1a*** ** was obtained as a slightly yellow liquid in 40 % yield (123.0 g, 0.56 mol).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (m, 2 H, PhH), 6.68 (m, 3 H, PhH), 3.30 (t, ^{3}J = 7.6 Hz, 2 H, NCH_2), 2.91 (s, 3 H, NCH_3), 1.57 (m, 2 H, NCH_2CH_2), 1.31 (m, 10 H, $N(CH_2)_2(CH_2)_5$), 0.90 (t, ^{3}J = 6.8 Hz, 3 H, $N(CH_2)_7CH_3$)

4-(methyl(octyl)amino)benzaldehyde (1a**)[1]

123.0 g (0.56 mol) **1a*** ** were dissolved in 216 mL DMF and cooled to -5 °C. 93.7 g (0.61 mol) $POCl_3$ were added in small portions so that the temperature did not exceed +10 °C. The solution was then heated at 100 °C for 3 h. The excess $POCl_3$ was removed with saturated $NaHCO_3$ solution. The solution was extracted with dichloromethane. The organic layer was washed with water, dried over $MgSO_4$ and the solvent was removed in vacuum. The crude product was purified on a filtration column (CH_2Cl_2). **1a**** was obtained as an almost colourless liquid in 65 % yield (90.0 g, 0.36 mol).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.72 (s, 1 H, CHO), 7.72 (m, 2 H, AA′), 6.68 (m, 2 H, XX′), 3.40 (t, ^{3}J = 7.6 Hz, 2 H, NCH_2), 3.04 (s, 3 H, NCH_3), 1.61 (m, 2 H, NCH_2CH_2), 1.29 (m, 10 H, $N(CH_2)_2(CH_2)_5$), 0.88 (t, ^{3}J = 6.8 Hz, 3 H, $N(CH_2)_7CH_3$)

4-(methyl(octyl)amino)benzonitrile (1a*)[2]

26.6 g (0.38 mol) hydroxylammonium chloride were dissolved in 90 mL water and 185 mL pyridine. 90.0 g (0.36 mol) **1a**** were added and the mixture was stirred for 75 min at room temperature. 18.2 g (0.07 mol) $CuSO_4 \cdot 5\ H_2O$ were added and the mixture stirred for 5 minutes. Then a solution of 102 mL NEt_3 in 173 mL CH_2Cl_2 was slowly added and the mixture was stirred for 15 minutes. Then 89.3 g (0.43 mol) dicyclohexylcarbodiimide (DCC), dissolved in 540 mL dichloromethane, were added dropwise and the mixture was stirred overnight at room temperature. Then 63 mL formic acid were added. The solid was filtered off and washed with dichloromethane. The organic phase was washed twice with 1 M HCl and then twice with water, dried over $MgSO_4$ and the solvent was removed in vacuum. Column chromatography (CH_2Cl_2) afforded **1a*** as a yellow oil in 83 % yield (74 g, 0.30 mol).

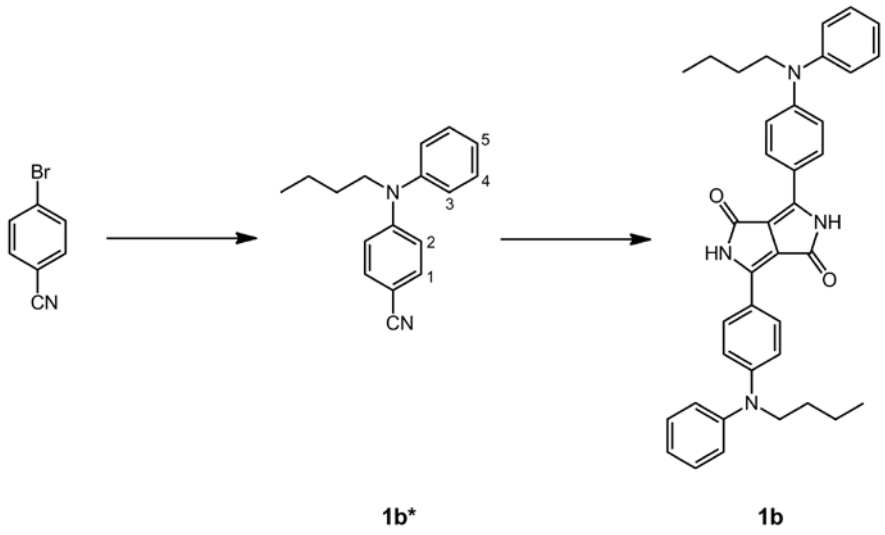
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (m, 2 H, AA′), 6.61 (m, 2 H, XX′), 3.34 (t, ^{3}J = 7.6 Hz, 2 H, NCH_2), 2.99 (s, 3 H, NCH_3), 1.57 (m, 2 H, NCH_2CH_2), 1.28 (m, 10 H, $N(CH_2)_2(CH_2)_5$), 0.88 (t, ^{3}J = 6.8 Hz, 3 H, $N(CH_2)_7CH_3$)

3,6-bis(4-(methyl(octyl)amino)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1a)[3, 4]

Under nitrogen atmosphere 621 mg (27.01 mmol) Na were dissolved in 6.1 mL *tert*-amylalcohol at reflux with a spatula tip of water-free $FeCl_3$. After complete dissolving of Na the solution was cooled to ca. 90 °C and 2.0 g (8.18 mmol) **1a*** were added and the mixture was heated to reflux again. 942 mg (4.09 mmol) di-*tert*-butyl succinate, dissolved in 2 mL *tert*-amylalcohol, were added dropwise over a period of 17 h. The reaction mixture was cooled to room temperature and methanol was added. 1 mL formic acid was added slowly. The precipitated solid was filtered and washed with methanol. The solid was digested in refluxing methanol for 20 min and filtered. This procedure was repeated until the filtrate went colorless. **1a** was obtained as a violet solid in 18 % yield (420 mg, 0.74 mmol).

^{1}H NMR (400 MHz, DMSO-d_6, 100 °C): δ = 10.80 (s, 2 H, NH), 8.31 (m, 2 H, AA′), 6.78 (m, 2 H, XX′), 3.42 (t, ^{3}J = 6.8 Hz, 2 H, NCH_2), 3.01 (s, 3 H, NCH_3), 1.53 (m, 2 H, NCH_2CH_2), 1.27 (m, 10 H, $N(CH_2)_2(CH_2)_5$), 0.86 (t, ^{3}J = 6.8 Hz, 3 H, $N(CH_2)_7CH_3$)

3,6-bis(4-(butyl(phenyl)amino)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1b)



1b* **1b**

4-(*n*-butyl(phenyl)amino)benzonitrile (1b*)[5]

Under nitrogen atmosphere 30.0 g (0.16 mol) 4-brombenzonitrile, 23.8 g (0.25 mol) sodium *tert*-butoxide and 26.4 mL (0.16 mol) *N*-*n*-butylaniline were dissolved in 300 mL absolute toluene and the mixture was degassed three times (freeze-pump-thaw). 0.95 g (1.65 mmol, 1 mol %) $Pd(dba)_2$ and 0.27 g (1.32 mmol, 0.8 mol %) tri-*tert*-butylphosphine were added and the mixture was stirred at room temperature overnight. The solids were filtered off and the solvent was removed in vacuum. Column chromatography (petroleum ether/ethyl acetate, 50:1) afforded **1b*** as a colourless oil in 65 % yield (26.8 g, 0.11 mol).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (m, 2 H; H-4), 7.38 (m, 2 H; H-1), 7.28 (m, 1 H; H-5), 7.18 (m, 2 H; H-3), 6.64 (m, 2 H; H-2), 3.68 (m, 2 H; NCH_2), 1.65 (m, 2 H; NCH_2CH_2), 1.36 (m, 2 H; $N(CH_2)_2CH_2$), 0.93 (t, ^{3}J = 7.35 Hz, 3 H; $N(CH_2)_3CH_3$)
ESI-MS (acetone): calcd. for $C_{17}H_{19}N_2$ $[M + H]^+$ 251.2; found 251.2
Elemental analysis: $C_{17}H_{18}N_2$ (250.34): calcd. C 81.56, H 7.25, N 11.19; found C 80.53 H 7.15 N 11.77

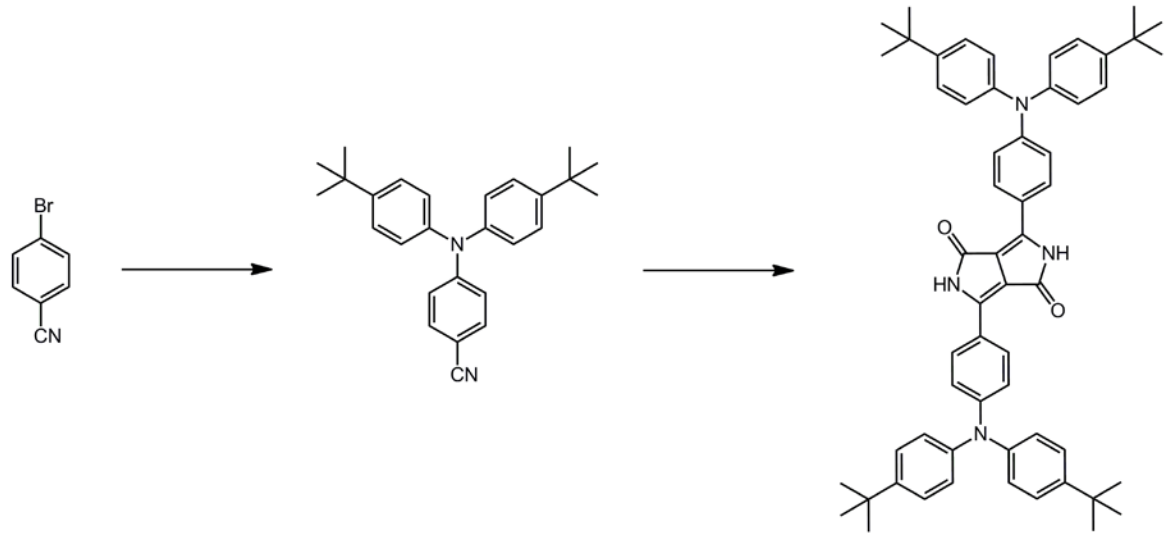
3,6-bis(4-(*n*-butyl(phenyl)amino)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1b)

Under nitrogen atmosphere 8.1 g (0.35 mmol) Na were dissolved in 80 mL *tert*-amylalcohol at reflux with a spatula tip of water-free $FeCl_3$. After complete dissolving of Na the solution was cooled to ca. 90 °C and 26.8 g (0.11 mmol) **1b*** were added and the mixture was heated to reflux again. 8.9 mL (53.5 mmol) diethyl succinate were added dropwise over a period of 3 h. The reaction mixture was cooled to room temperature and methanol was added. 13.3 mL formic acid was added slowly. The

precipitated solid was filtered and washed with methanol. The solid was digested in refluxing methanol for 20 min and filtered. This procedure was repeated until the filtrate went colorless. **1b** was obtained as a violet solid in 5 % yield (3.2 g, 5.5 mmol).

ESI-MS (acetone): calcd. for $C_{38}H_{39}N_4O_2$ $[M + H]^+$ 583.3; found 583.1

3,6-bis(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1c)



1c* **1c**

4-(bis(4-(tert-butyl)phenyl)amino)benzonitrile (1c*)[5]

Under nitrogen atmosphere 13.3 g (73.2 mmol) 4-brombenzonitrile, 10.2 g (106.6 mmol) sodium *tert*-butoxide and 20.0 g (71.1 mmol) bis(4-*tert*-butylphenyl)amine were dissolved in 100 mL absolute toluene and the mixture was degassed three times (freeze-pump-thaw). 409 mg (711 µmol, 1 mol %) $Pd(dba)_2$ and 115 mg (569 µmol, 0.8 mol %) tri-*tert*-butylphosphine were added and the mixture was stirred at room temperature for 2 h. The solids were filtered off and the solvent was removed in vacuum. Column chromatography (petroleum ether/CH_2Cl_2, 3:1) afforded **1c*** as a white solid in 45 % yield (12.5 g, 33 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (m, 2 H, *ortho*-CNH), 7.34 (m, 4 H, *ortho*-*t*-BuH), 7.07 (m, 2 H, *meta*-CNH), 6.91 (m, 4 H, *meta*-*t*-BuH), 1.32 (s, 18 H, *t*-BuH)
ESI-MS (acetone): calcd. for $C_{27}H_{31}N_2$ $[M + H]^+$ 383.3; found 383.2

3,6-bis(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1c)

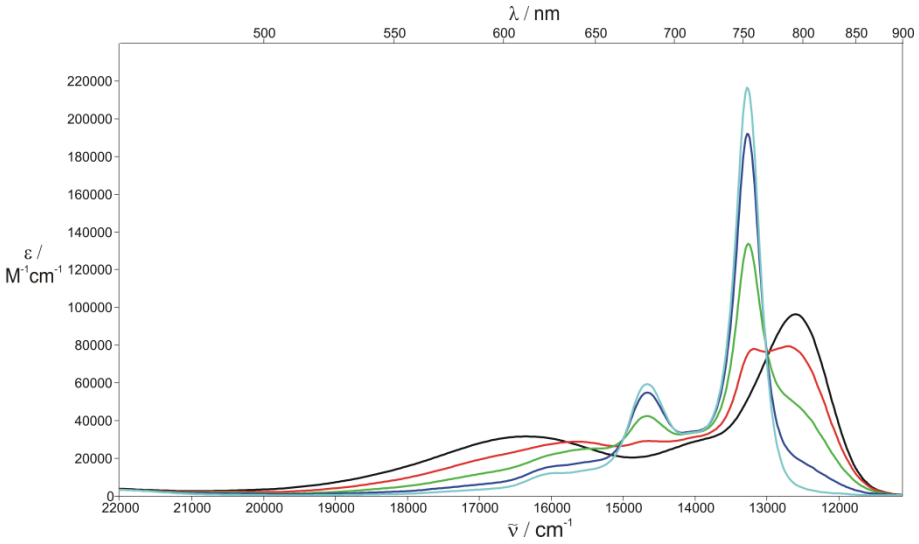
Under nitrogen atmosphere 794 mg (35 mmol) Na were dissolved in 7.8 mL *tert*-amylalcohol at reflux with a spatula tip of water-free $FeCl_3$. After complete dissolving of Na the solution was cooled to ca. 90 °C and 4.0 g (10 mmol) **1c*** were added and the mixture was heated to reflux again. 1.20 g (5 mmol) di-*tert*-butyl succinate, dissolved in 2 mL *tert*-amylalcohol, were added dropwise over a period of 17 h. The reaction mixture was cooled to room temperature and methanol was added. 1.3 mL formic acid was added slowly. The precipitated solid was filtered and washed with methanol. The solid was digested in refluxing methanol for 20 min and filtered. This procedure was repeated until the filtrate went colorless. **1a** was obtained as a violet solid in 58 % yield (2.6 g, 4.8 mmol).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): δ = 7.92 (b, 4 H, AA′), 7.62 (s, 2 H, NH), 7.31 (b, 8 H, NPhH), 7.07 (b, 8 H, NPhH), 6.95 (b, 4 H, XX′), 1.31 (s, 36 H, *t*-BuH)

S2: Absorption spectra of protonation experiments for compounds **4a′**, **4b′** and **5a″**

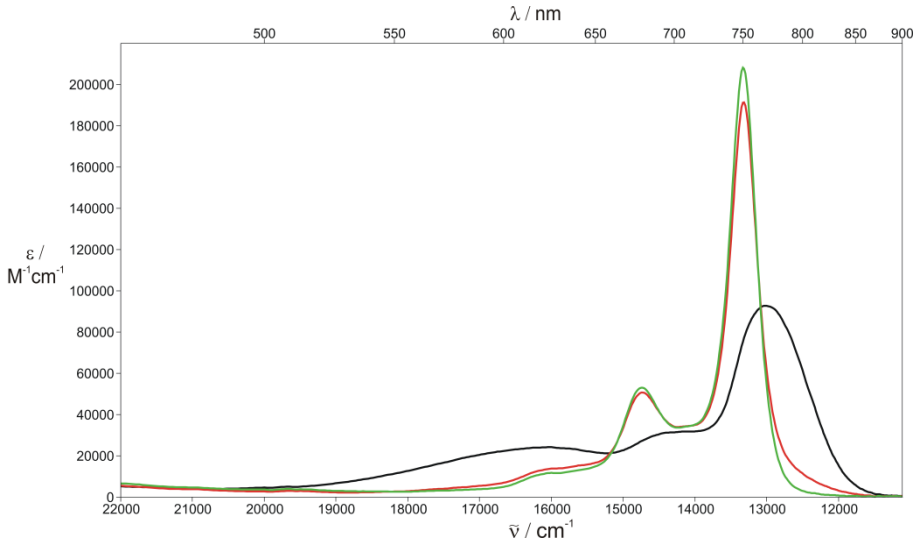
The protonation experiments were conducted as follows: in a 1 cm quartz cuvette (3 mL) a diluted solution of the dye was prepared (concentrations between $4 \cdot 10^{-6}$ M and $6 \cdot 10^{-6}$ M). An absorption spectrum was recorded. Then ~ 0.03 mL of a solution of trifluoroacetic acid in dichloromethane (~ 10 % vol. TFA; ~ 3000 eq) or concentrated sulfuric acid (96 %, ~ 30000 eq) was added and an absorption spectrum again recorded. The procedure was repeated until the absorption spectrum did not change anymore.

*Compound **4a′**:*



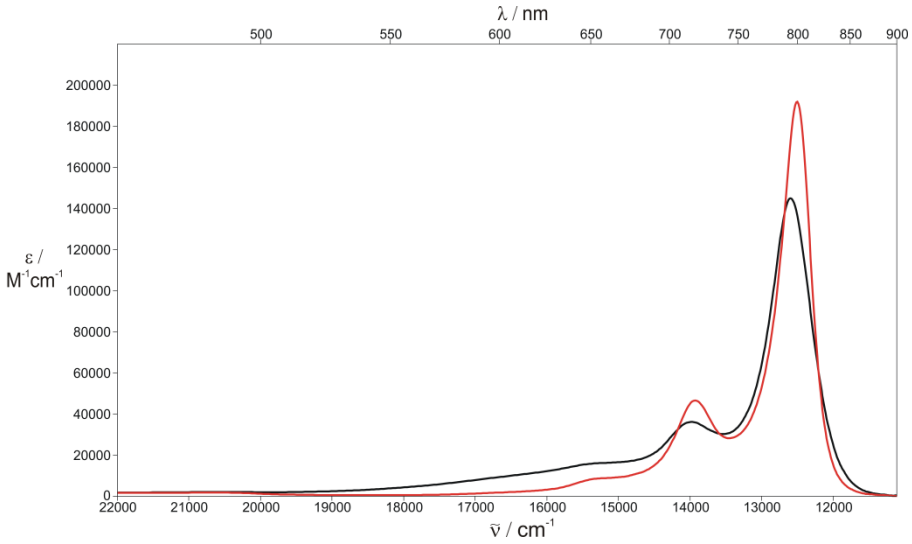
Supp. Fig. 1 Absorption spectra for the protonation of **4a′** in dichloromethane using diluted trifluoroacetic acid; **4a′** unprotonated (black), successive addition of acid to **4a′** (in the order: red, green, dark blue), **4a′** fully protonated (light blue).

*Compound **4b′**:*



Supp. Fig. 2 Absorption spectra for the protonation of **4b′** in *n*-butyronitrile using concentrated sulfuric acid; **4b′** unprotonated (black), addition of acid to **4b′** (red), **4b′** fully protonated (green).

*Compound **5a''**:*



Supp. Fig. 3 Absorption spectra for the protonation of ***5a''*** in dichloromethane using diluted trifluoroacetic acid; ***5a''*** unprotonated (black), ***5a''*** fully protonated (red).

References

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