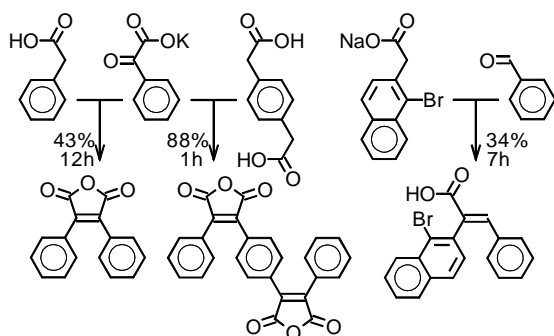


Dipyreno- and diperyleno-anthracenes from glyoxylic Perkin reactions

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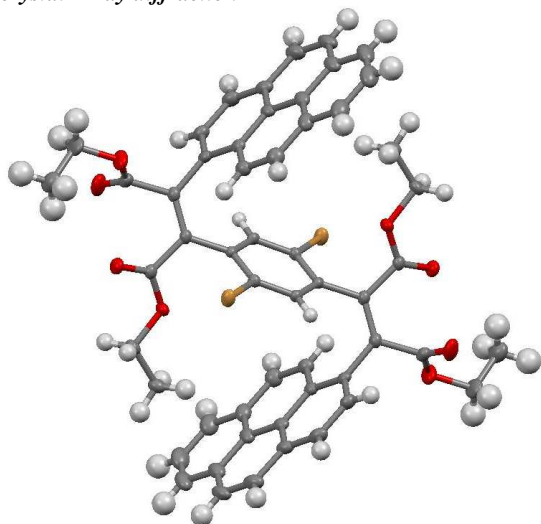
SUPPLEMENTARY INFORMATION

Published Perkin reactions mentioned

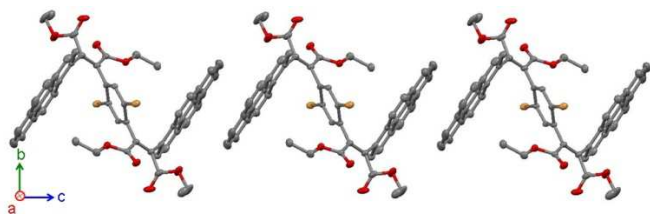


Archetypal Perkin reactions involving either phenylglyoxylic acid or 1-bromo-2-naphthylacetic acid, with reported yields and reaction times in refluxing Ac_2O ^{9, 17, 18}.

Single crystal X-ray diffraction



Structure of tetraethyl 2,5-dibromo-1,4-phenylenebis((1-pyrenyl)maleate) **9a** in the crystal at 120 K. Thermal ellipsoids for non-hydrogen atoms are depicted at 50 % probability level (H white, C grey, O red, Br brown).



Packing of **9a** molecules along the *c* axis. Thermal ellipsoids for non-hydrogen atoms are depicted at 50 % probability level (C grey, O red, Br brown). Hydrogen atoms are omitted for clarity.

The crystallographic data were collected with a Bruker APEX II diffractometer, equipped with a graphite monochromator centred on the path of $\text{MoK}\alpha$ radiation. A single crystal of **9a**, made by slow diffusion of methanol into a DCM solution, was coated with Paratone N-oil and mounted on a fiber loop, followed by data collection at 120 K. The program SAINT was used to integrate the data, which was thereafter corrected using SADABS²⁸. The structure was solved using SHELXS-97 and refined by a full-matrix least-squares method on F^2

using SHELXL-97²⁹. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions using suitable riding models. The CIF file has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 941140.

$\text{C}_{54}\text{H}_{40}\text{Br}_2\text{O}_8$, monoclinic, $P2_1/c$ (no. 14), $a = 8.9924(5)$, $b = 17.9529(10)$, $c = 15.1993(8)$ Å, $\beta = 116.317(3)^\circ$, $V = 2199.4(2)$ Å³, $Z = 2$, $T = 120$ K, 117994 reflections measured, 6445 unique ($R_{\text{int}} = 0.0570$), $\text{GoF} = 1.035$, $R_1 = 0.0362$, wR_2 (all reflections) = 0.0914.

Syntheses

2,5-Dibromophenylene-1,4-diacetic acid **4**

With ice bath cooling, conc. sulfuric acid (800g) is cautiously added to water (400g) in a 2L flask. Once the mixture has cooled back down to room temperature, phenylene-1,4-diacetic acid **3** (126.2g, 194.2 g/mol, 650mmol) is added with stirring, followed by N-bromo-succinimide (231.4g, 178.0 g/mol, 1.30mol), and the resulting suspension is stirred at room temperature for 16h. The suspension is added with stirring to an ice/water mixture (2L), the raw product is filtered off with a large glass filter, washed on the filter with water, oven-dried and recrystallised twice from THF to yield 66.1g of product. The majority of the also formed 2,3-dibromophenylene-1,4-diacetic acid (poorly soluble in boiling ethyl acetate, not isolated pure) is eliminated from the evaporation residue of the THF mother liquors by crystallisation from ethyl acetate. A further crop of 43.7g of the major 2,5-dibromo isomer (poorly soluble in acetone) is then obtained from the evaporation residue of the ethyl acetate mother liquors by boiling in acetone followed by hot filtration. Combined yield: 99.8g (284mmol, 352.0 g/mol, 44%) of colourless crystals.

¹H-NMR (d_6 -DMSO, 400MHz): $\delta = 12.59$ (broad s, 2H), 7.67 (s, 2H), 3.72 (s, 4H) ppm.

¹³C-NMR (d_6 -DMSO, 100MHz): $\delta = 171.1$, 135.9, 135.2, 123.5, 40.3 ppm.

FD-HRMS (*m/z*): M^+ Calcd for $\text{C}_{10}\text{H}_4\text{Br}_2\text{O}_4$ 349.8789; found 349.8799.

Mp.: 257-267°C (accompanied by sublimation)

Ethyl pyrenyl-1-glyoxylate **5**

A solution of pyrene **1** (101.2g, 202.3g/mol, 0.50mol) and ethyl chloroglyoxylate (75.0g, 136.5g/mol, 0.55mol) in DCM (500mL) is cautiously poured at 0°C into a well stirred slurry of zirconium tetrachloride (140g, 233.0g/mol, 0.60mol) in DCM (500mL) in a 2L flask. More DCM (1L) is added and the blue mixture is stirred at room temperature for 16h, and then poured into a stirred mixture of ice and 5% aqueous hydrochloric acid (1L). The phases are separated, the organic phase is dried with sodium sulphate, the solvent is evaporated and the product is purified by precipitation from ethyl acetate solution (300mL) with absolute ethanol (900mL). Yield: 132.2g (437mmol, 302.3 g/mol, 87%) of yellow crystals.

¹H-NMR (CDCl_3 , 400MHz): $\delta = 9.31$ (d, 10Hz, 1H), 8.31 (d, 8Hz, 1H), 8.29-8.23 (m, 3H), 8.18 (d, 9Hz, 1H), 8.13 (d, 8Hz, 1H), 8.06 (t, 8Hz, 1H), 8.02 (d, 9Hz, 1H), 4.56 (q, 7Hz, 2H), 1.49 (t, 7Hz, 3H) ppm.

¹³C-NMR (CDCl_3 , 100MHz): $\delta = 189.4$, 165.3, 135.9, 131.9, 131.3, 131.2, 131.0, 130.6, 130.5, 127.5, 127.24, 127.19, 126.9, 125.0, 124.6, 124.4, 124.1, 124.0, 62.6, 14.4 ppm.

FD-HRMS (*m/z*): M^+ Calcd for $\text{C}_{20}\text{H}_{14}\text{O}_3$ 302.0943; found 302.0940.

Mp.: 83-84°C

Pyrenyl-1-glyoxylic acid 6

Ethyl pyrenyl-1-glyoxylate **5** (30.2g, 302.3g/mol, 100mmol) is dissolved with stirring at reflux in ethanol (300mL). A solution of sodium bicarbonate (30g, 84.0g/mol, 357mmol) in water (300mL) is added, whereupon the ester precipitates partially, and the mixture is refluxed for 3h, whereby the reaction mixture becomes a homogeneous solution. The solution is poured onto a mixture of ice and 5% aqueous hydrochloric acid, and the formed precipitate is filtered off and washed with water. The crude product is dissolved in hot THF, THF-insoluble salts are filtered off and discarded, and the THF is evaporated. The so-obtained acid is used without further purification. Yield: 27.5g (100mmol, 274.3 g/mol, 100%).

¹H-NMR (d₆-DMSO, 400MHz): δ = 9.24 (d, 9Hz, 1H), 8.50-8.39 (m, 6H), 8.27 (d, 9Hz, 1H), 8.19 (t, 8Hz, 1H) ppm.

¹³C-NMR (d₆-DMSO, 100MHz): δ = 191.4, 166.8, 135.2, 131.2, 131.1, 130.53, 130.46, 129.7, 127.6, 127.2, 124.5, 124.0, 123.8, 123.5, 123.0 ppm.

FD-HRMS (m/z): M⁺ Calcd for C₁₈H₁₀O₃ 274.0630; found 274.0638.

Ethyl perylenyl-3-glyoxylate 7

Zirconium tetrachloride (70g, 233.0g/mol, 0.30mol) is added at 0°C to a well stirred suspension of perylene **2** (25.2g, 252.3g/mol, 100mmol) in ethyl chloroglyoxylate (20.0g, 136.5g/mol, 147mmol) and DCM (700mL) in a 1L flask. More DCM (300mL) is added and the green mixture is stirred at room temperature for 16h, and then poured into a stirred mixture of ice and 5% aqueous hydrochloric acid (500mL). The phases are separated, the organic phase is dried with sodium sulphate, the solvent is evaporated and the product is purified by column chromatography in chloroform on silica and recrystallisation from ethyl acetate (2L, dissolves only slowly at reflux). Yield: 28.0g (352.4g/mol, 79mmol, 79%) of red crystals.

¹H-NMR (CDCl₃, 400MHz): δ = 8.91 (d, 9Hz, 1H), 8.09-8.03 (m, 3H), 7.94 (d, 8Hz, 1H), 7.78 (d, 8Hz, 1H), 7.71 (d, 8Hz, 1H), 7.64 (d, 8Hz, 1H), 7.53 (t, 8Hz, 1H), 7.42 (t, 8Hz, 1H), 7.41 (t, 8Hz, 1H), 4.52 (q, 7Hz, 2H), 1.48 (t, 7Hz, 3H) ppm.

¹³C-NMR (CDCl₃, 100MHz): δ = 188.3, 165.2, 138.3, 135.0, 134.3, 132.8, 131.3, 130.5, 130.4, 129.55, 129.50, 129.1, 128.6, 128.0, 127.0, 126.7, 126.3, 125.5, 123.1, 121.7, 121.2, 118.5, 62.5, 14.4 ppm.

FD-HRMS (m/z): M⁺ Calcd for C₂₄H₁₆O₃ 352.1099; found 352.1103.

Mp.: 179-182°C

Perylenyl-3-glyoxylic acid 8

To a stirred refluxing suspension of ethyl perylenyl-3-glyoxylate **7** (9.0g, 352.4g/mol, 26mmol) in ethanol (200mL), a solution of sodium bicarbonate (15g, 84.0g/mol, 179mmol) in water (200mL) is added, and the heterogeneous mixture is refluxed for 20h. The mixture is poured onto a mixture of ice and 5% aqueous hydrochloric acid, and the red precipitate is filtered off and washed with water. The crude product is dissolved in hot THF, THF-insoluble salts are filtered off and discarded, and the THF is evaporated. The so-obtained acid is used without further purification. Yield: 7.9g (24mmol, 326.3 g/mol, 95%).

¹H-NMR (d₆-DMSO, 400MHz): δ = 8.91 (d, 8Hz, 1H), 8.54-8.45 (m, 4H), 8.01 (d, 8Hz, 1H), 7.97 (d, 8Hz, 1H), 7.90 (d, 8Hz, 1H), 7.77 (t, 8Hz, 1H), 7.64 (t, 8Hz, 1H), 7.62 (t, 8Hz, 1H) ppm.

¹³C-NMR (d₆-DMSO, 100MHz): δ = 190.5, 166.7, 137.4, 135.0, 133.9, 132.0, 131.0, 130.5, 129.7, 128.9, 128.4, 127.3, 127.2, 127.1, 125.8, 124.7, 123.8, 122.4, 121.7, 119.6 ppm.

FD-HRMS (m/z): M⁺ Calcd for C₂₂H₁₂O₃ 324.0786; found 324.0796.

Tetrabutyl 2,5-dibromo-1,4-phenylenebis((1-pyrenyl)maleate) 9

2,5-Dibromophenylene-1,4-diacetic acid **4** (1.17g, 352.0g/mol, 3.33mmol), pyrenyl-1-glyoxylic acid **6** (2.19g, 274.3g/mol, 8mmol), triethylamine (2.0g, 101.2g/mol, 20mmol) and acetic anhydride (2.8g, 102.1g/mol, 27mmol) are stirred at reflux in dioxane (20mL) under

exclusion of moisture for 3h. Then a solution of DBU (5.0g, 152.2mmol, 33mmol), 1-bromobutane (9.0g, 137.0g/mol, 66mmol) and butanol (7.4g, 74.1g/mol, 100mmol) in dioxane (30mL) is added and stirring at reflux is continued under exclusion of moisture for 16h. The reaction mixture is poured into methanol (1L), whereupon the product crystallises on standing over night. The yellow precipitate is filtered off and purified by column chromatography in chloroform on silica and recrystallisation from butanol. Yield: 2.68g (1088.9g/mol, 2.46mmol, 74%).

¹H-NMR (CDCl₃, 400MHz): δ = 9.20-7.25 (m, 18H), 7.25-6.50 (m, 2H), 4.75-2.90 (m, 8H), 1.51 (quint, 7Hz, 4H), 1.16 (sext, 7Hz, 4H) 0.73 (t, 7Hz, 6H), 2.10-0.10 (m, 14H) ppm.

FD-HRMS (m/z): M⁺ Calcd for C₆₂H₅₆Br₂O₈ 1086.2342; found 1086.2357.

Mp.: 199-205°C

Tetraethyl 2,5-dibromo-1,4-phenylenebis((1-pyrenyl)maleate) 9a

2,5-Dibromophenylene-1,4-diacetic acid **4** (1.76g, 352.0g/mol, 5mmol), pyrenyl-1-glyoxylic acid **6** (3.29g, 274.3g/mol, 12mmol), triethylamine (5.05g, 101.2g/mol, 50mmol) and acetic anhydride (10.2g, 102.1g/mol, 100mmol) are stirred at reflux in THF under exclusion of moisture for 3h. Water (20mL) is added at reflux through the reflux condenser, the mixture is poured into water (½L), the precipitate is filtered off and dried by thrice adding acetone and then evaporating the solvent under vacuum (c.10mbar, water bath at 60°C) on a rotary evaporator. The resulting crude condensation product is stirred at reflux with DBU (9.1g, 152.2mmol, 60mmol), 1-iodoethane (15.6g, 156.0g/mol, 100mmol) and ethanol (25mL) in THF (50mL) under exclusion of moisture for 16h. The product precipitates during the reaction. The reaction mixture is poured into methanol (1L), and left to stand overnight. The yellow precipitate is filtered off and purified by column chromatography in chloroform on silica. Yield: 3.73g (976.7g/mol, 3.81mmol, 76%).

¹H-NMR (CDCl₃, 400MHz): δ = 9.25-7.25 (m, 18H), 7.25-6.40 (m, 2H), 4.50-4.05 (m, 4H), 5.00-2.75 (m, 4H), 1.16 (t, 7Hz, 6H), 1.70-0.50 (m, 6H) ppm.

FD-HRMS (m/z): M⁺ Calcd for C₅₄H₄₀Br₂O₈ 974.1090; found 974.1048.

Mp.: 271-273 °C

Tetraoctyl 2,5-dibromo-1,4-phenylenebis((3-perylenyl)maleate) 10

2,5-Dibromophenylene-1,4-diacetic acid **4** (1.17g, 352.0g/mol, 3.33mmol), perylenyl-3-glyoxylic acid **8** (2.60g, 324.3g/mol, 8mmol), triethylamine (2.0g, 101.2g/mol, 20mmol) and acetic anhydride (2.8g, 102.1g/mol, 27mmol) are stirred at reflux in dioxane (20mL) under exclusion of moisture for 3h. Then a solution of DBU (5.0g, 152.2mmol, 33mmol), 1-bromooctane (13.0g, 193.1g/mol, 67mmol) and octanol (13.0g, 130.2g/mol, 100mmol) in dioxane (30mL) is added and stirring at reflux is continued under exclusion of moisture for 16h. The product precipitates during the reaction. The reaction mixture is poured into methanol (1L) to complete the precipitation. The orange precipitate is filtered off and purified by column chromatography in chloroform on silica and recrystallisation from butanol. Yield: 3.43g (1413.5g/mol, 2.43mmol, 73%).

¹H-NMR (CDCl₃, 400MHz): δ = 8.35-8.04 (m, 6H), 8.04-7.74 (m, 4H), 7.74-7.61 (m, 4H), 7.61-7.25 (m, 6H), 7.25-6.90 (m, 4H), 4.14 (t, 6Hz, 4H), 4.30-3.45 (m, 4H), 1.58-1.43 (m, 4H), 1.75-0.35 (m, 44H), 0.87 (t, 6Hz, 6H), 0.74 (t, 7Hz, 6H) ppm.

FD-HRMS (m/z): M⁺ Calcd for C₈₆H₉₂Br₂O₈ 1410.5159; found 1410.5160.

Mp.: 145-148°C

Tetrabutyl dipyreno[2,1-a:2',1'-h]anthracene-8,9,19,20-tetracarboxylate 11

Tetrabutyl 2,5-dibromo-1,4-phenylenebis((1-pyrenyl)maleate) **9** (1.09g, 1088.9g/mol, 1mmol), palladium diacetate (0.09g,

225.5g/mol, 0.4mmol), tricyclohexylphosphine (0.20g, 280.4g/mol, 0.7mmol) and potassium carbonate (1.38g, 138.2g/mol, 10mmol) are stirred at reflux in dry dimethylacetamide (20mL) under argon for 20h. After cooling to room temperature, the mixture is purified by column chromatography on silica in chloroform. The solvent is evaporated and the orange-yellow product is purified by recrystallisation from butanol. Yield: 0.74g (927.1g/mol, 0.80mmol, 80%).

¹H-NMR (CDCl₃, 400MHz): δ = 9.43 (s, 2H), 9.15 (s, 2H), 8.58 (d, 9Hz, 2H), 8.22 (d, 9Hz, 2H), 8.19 (d, 9Hz, 2H), 8.09 (d, 9Hz, 2H), 8.09 (d, 8Hz, 2H), 8.00 (d, 8Hz, 2H), 7.68 (t, 8Hz, 2H), 4.83 (t, 7Hz, 4H), 4.57 (t, 7Hz, 4H), 2.05 (quint, 7Hz, 4H), 1.75 (quint, 7Hz, 4H), 1.69 (sext, 7Hz, 4H), 1.37 (sext, 7Hz, 4H), 1.09 (t, 7Hz, 6H), 0.91 (t, 7Hz, 6H) ppm.

¹³C-NMR (CDCl₃, 100MHz): δ = 171.0, 168.7, 131.34, 131.27, 131.1, 130.6, 129.9, 129.5, 129.3, 128.8, 128.0, 127.9, 127.7, 126.5, 126.2, 126.0, 125.9, 125.0, 124.5, 124.2, 121.5, 121.3, 119.4, 66.64, 66.57, 31.2, 30.5, 19.7, 19.4, 14.1, 13.9 ppm.

FD-HRMS (m/z): M⁺ Calcd for C₆₂H₅₄O₈ 926.3819; found 926.3784.
Mp.: 321-323°C

Tetraoctyl diperyleno[3,2-a:3',2'-h]anthracene-12,13,25,26-tetracarboxylate 12

Tetraoctyl 2,5-dibromo-1,4-phenylenebis((3-perylenyl)maleate) **10** (1.41g, 1413.5g/mol, 1mmol), palladium diacetate (0.09g, 225.5g/mol, 0.4mmol), tricyclohexylphosphine (0.20g, 280.4g/mol, 0.7mmol) and potassium carbonate (1.38g, 138.2g/mol, 10mmol) are stirred at reflux in dry dimethylacetamide (20mL) under argon for 20h. After cooling to room temperature, the mixture is purified by column chromatography on silica in hot chloroform. The solvent is evaporated and the red product is purified by precipitation with acetone (200mL) from a solution in chloroform (200mL). Yield: 1.02g (1251.6g/mol, 0.895mmol, 81%).

¹H-NMR (CDCl₃, 400MHz): δ = 9.41 (s, 2H), 9.14 (s, 2H), 8.38 (d, 8Hz, 2H), 8.34 (d, 8Hz, 2H), 8.22 (d, 8Hz, 2H), 8.07 (d, 8Hz, 2H), 7.66 (t, 8Hz, 2H), 7.63 (d, 8Hz, 2H), 7.59 (t, 8Hz, 2H), 7.51 (d, 8Hz, 2H), 7.42 (t, 8Hz, 2H), 4.72 (t, 7Hz, 4H), 4.38 (t, 7Hz, 4H), 1.96 (quint, 7Hz, 4H), 1.66 (quint, 7Hz, 4H), 1.53 (quint, 7Hz, 4H), 1.32 (quint, 7Hz, 4H), 1.26-1.05 (m, 32H), 0.78 (t, 7Hz, 6H), 0.71 (t, 7Hz, 6H) ppm.

¹³C-NMR (CDCl₃, 100MHz): δ = 170.5, 168.4, 134.5, 132.2, 131.44, 131.40, 131.2, 130.8, 130.7, 130.5, 129.33, 129.29, 120.1, 128.4, 128.3, 127.0, 126.91, 126.86, 126.7, 126.4, 124.4, 121.7, 121.6, 121.2, 114.9, 66.9, 66.8, 32.0, 31.9, 29.9, 29.6, 29.5, 29.4, 29.1, 28.5, 26.8, 26.2, 22.8, 22.7, 14.23, 14.16 ppm.

FD-HRMS (m/z): M⁺ Calcd for C₈₆H₉₀O₈ 1250.6636; found 1250.6650.

Mp.: c.365°C (decomp.)

N,N'-di-(1-undecyldodecyl) dipyreno[2,1-a:2',1'-h]anthracene-8,9:19,20-tetracarboxydiimide 13

Tetraoctyl dipyreno[2,1-a:2',1'-h]anthracene-8,9,19,20-tetracarboxylate **11** (0.30g, 927.1g/mol, 0.32mmol), 12-aminotricosane (0.33g, 339.6g/mol, 0.97mmol)²⁴ and imidazole (10g) are stirred at reflux in *o*-dichlorobenzene (15g) under argon for 16h. After cooling to room temperature, the solidified mixture is dissolved in hot chloroform, the solution is washed with 5% aqueous hydrochloric acid, the aqueous phase is discarded, the chloroform solution is filtered through a short plug of silica, and the solvent is thoroughly evaporated under vacuum (c. 10mbar, boiling water bath). The purple product is purified by threefold precipitation from chloroform solution by addition of acetone. Yield: 0.395g (1309.9g/mol, 0.30mmol, 93%).

¹H-NMR (CDCl₃, 400MHz): δ = 10.57 (s, 2H), 9.50 (d, 9Hz, 2H), 9.23 (s, 2H), 8.26 (d, 9Hz, 2H), 8.17 (d, 9Hz, 2H), 8.15 (d, 9Hz, 2H), 8.00 (d, 8Hz, 2H), 7.98 (d, 8Hz, 2H), 7.65 (t, 8Hz, 2H), 4.56 (tt, 10Hz, 5Hz, 2H), 2.44 (m, 4H), 2.05 (m, 4H), 1.63-1.44 (m, 16H), 1.43-1.15 (m, 56H), 0.76 (t, 7Hz, 12H) ppm.

FD-HRMS (m/z): M⁺ Calcd for C₉₂H₁₁₂N₂O₄ 1308.8622; found 1308.8637.

Mp.: 325-328°C

N,N'-di-(1-undecyldodecyl) diperyleno[3,2-a:3',2'-h]anthracene-12,13:25,26-tetracarboxydiimide 14

Tetraoctyl diperyleno[3,2-a:3',2'-h]anthracene-12,13,25,26-tetracarboxylate **12** (0.40g, 1027.2g/mol, 0.32mmol), 12-aminotricosane (0.33g, 339.6g/mol, 0.97mmol)²⁴ and imidazole (10g) are stirred at reflux in *o*-dichlorobenzene (15g) under argon for 16h. After cooling to room temperature, the solidified mixture is partially dissolved in hot chloroform, and the insoluble product is filtered off. The green diimide is purified by recrystallisation from boiling 1,2-dichlorobenzene and washing with hot chloroform and hot acetone on a glass frit. Yield: 0.366g (1410.0g/mol, 0.26mmol, 89%).

¹H-NMR (Cl₂CDCDCl₂, 130°C, 400MHz): δ = 10.98 (s, 2H), 9.71 (s, 2H), 9.44 (d, 8Hz, 2H), 8.77 (d, 8Hz, 2H), 8.52 (d, 8Hz, 2H), 8.36 (d, 8Hz, 2H), 7.95 (d, 8Hz, 2H), 7.88 (t, 8Hz, 2H), 7.84 (t, 8Hz, 2H), 7.83 (d, 8Hz, 2H), 7.62 (t, 8Hz, 2H), 4.55 (m, 2H), 2.37 (m, 4H), 2.03 (m, 4H), 1.63-1.22 (m, 72H), 0.88 (t, 6Hz, 12H) ppm.

FD-HRMS (m/z): M⁺ Calcd for C₁₀₀H₁₁₆N₂O₄ 1408.8935; found 1408.8967.

Mp.: >375°C

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