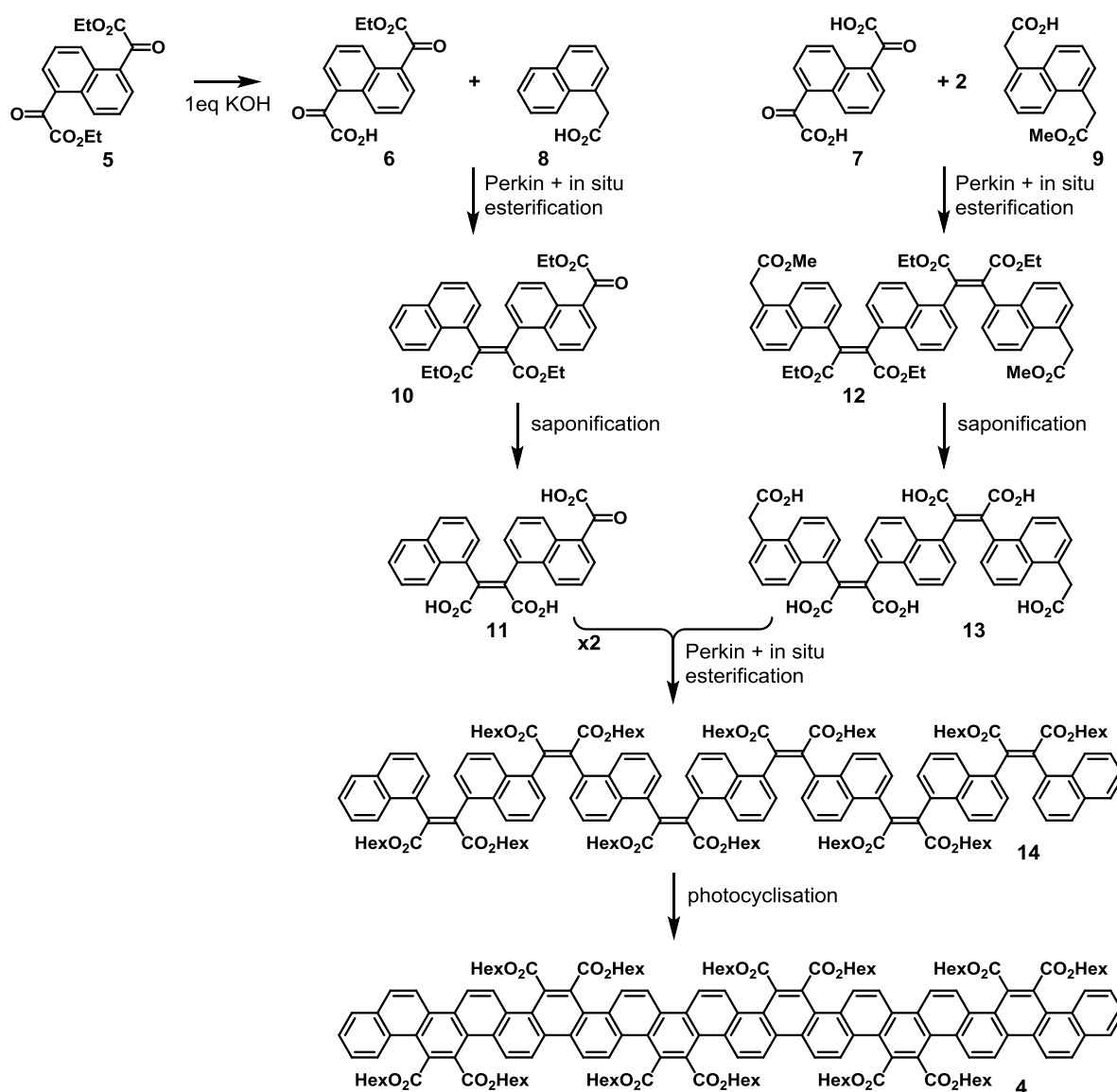


Supporting Information

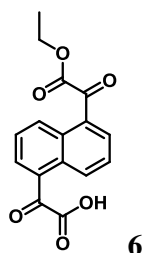
Synthesis of a [20]phenacene dodeca-ester by controlled condensation of seven naphthalene-based building blocks

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Experimental section

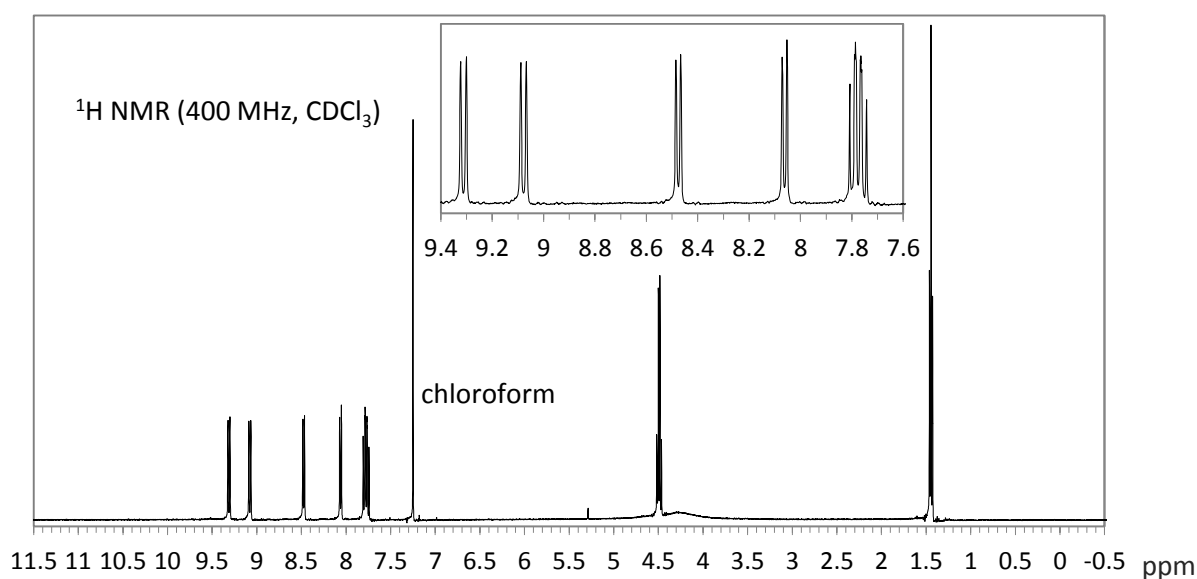


Diethyl naphthylene-1,5-diglyoxylate¹ **5** (5.00 g, 328.32 g/mol, 15.2 mmol) was dissolved in THF (300 mL). Then KOH (853 mg, 56.11 g/mol, 15.2 mmol) was dissolved in 50 mL of EtOH, by sonication, and added to the first solution with stirring. The mixture was heated with stirring at reflux for 75 min. After cooling to room temperature, the solvent mixture was evaporated and the solid obtained was triturated in DCM. Insoluble material was filtered off. The liquid filtrate was dried over sodium sulfate and the solvent was evaporated to recover the unreacted diester **5** (1.40 g) as pale yellow solid.

The solid obtained by filtration was then triturated in 2M aqueous HCl in order to reach pH=0-1, then DCM was added and the mixture was triturated and the remaining solid was filtered off. The liquid phase was kept and the remaining solid was treated four more times as described. The liquid phases (aqueous and organic) were separated and the aqueous phase was extracted with DCM. The organic phases were united and dried over sodium sulfate and the solvent was evaporated to obtain the pure monoester **6**. Yield: 2.21 g (300.27 g/mol, 7.4 mmol, 49%), off-white solid.

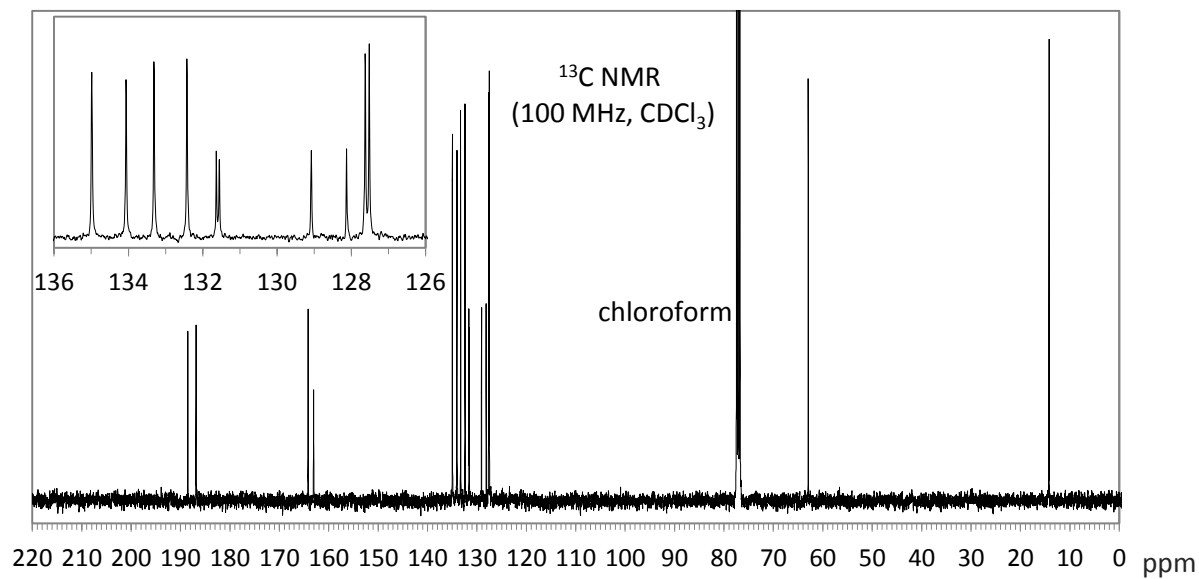
The remaining DCM-insoluble white solid (0.82 g) was a mixture of naphthylene-1,5-diglyoxylic acid **7** and mono-ester **6**.

¹H NMR (400 MHz, CDCl₃): δ = 9.32 (d, 8Hz, 1H), 9.09 (d, 8Hz, 1H), 8.49 (d, 8Hz, 1H), 8.07 (d, 8Hz, 1H), 7.80 (t, 8Hz, 1H), 7.77 (t, 8Hz, 1H), 4.51 (q, 7Hz, 2H), 4.27 (broad s, 1H), 1.45 (t, 7Hz, 3H) ppm.



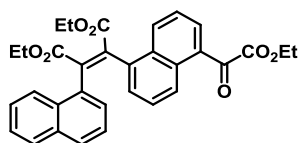
¹ T. S. Moreira, M. Ferreira, A. Dall'armellina, R. Cristiano, H. Gallardo, E. A. Hillard, H. Bock and F. Durola, *Eur. J. Org. Chem.*, 2017, 4548.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 188.6, 186.9, 164.2, 163.1, 135.0, 134.1, 133.4, 132.5, 131.7, 131.6, 129.1, 128.2, 127.7, 127.6, 63.0, 14.3$ ppm.



FD-HRMS: m/z calcd for $\text{C}_{16}\text{H}_{12}\text{O}_6$ $[\text{M}]^+$: 300.06339, found 300.06400.

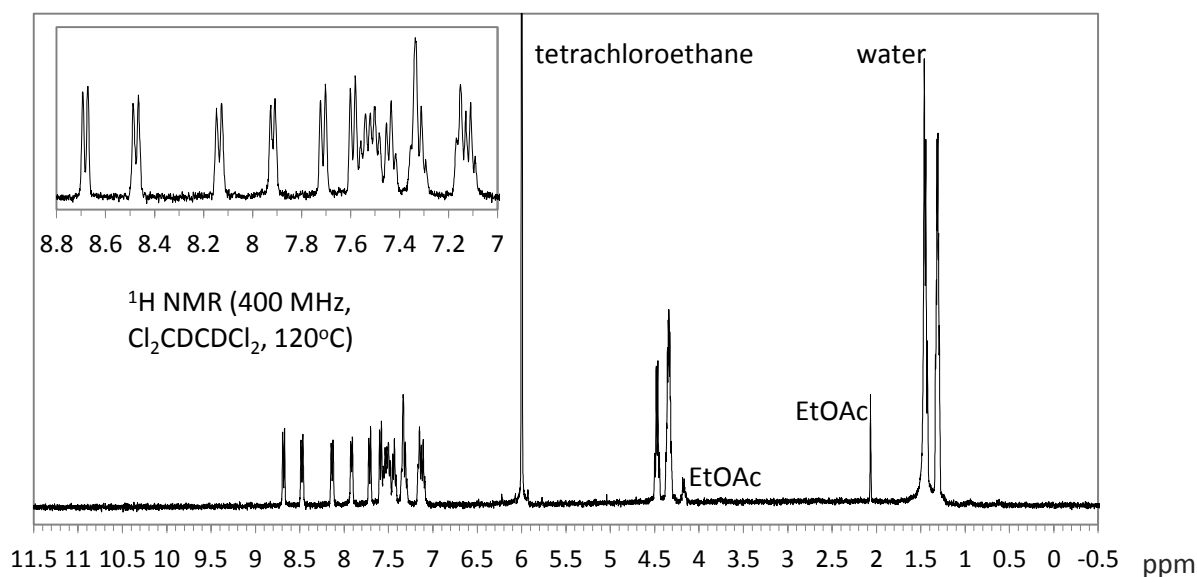
Mp: 128-132°C



10

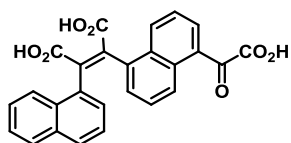
A solution of 1-naphthylacetic acid **8** (670 mg, 186.21 g/mol, 3.6 mmol), ester-acid **6** (1.00 g, 300.27 g/mol, 3.3 mmol), triethylamine (1.4 mL, 101.19 g/mol, 0.726 g/mL, 10 mmol), and acetic anhydride (1.6 mL, 102.09 g/mol, 1.08 g/mL, 17.2 mmol) in dry THF (30 mL) was heated at reflux with stirring under argon overnight. The mixture was cooled to room temperature and a solution of bromoethane (2.4 mL, 108.97 g/mol, 1.47 g/mL, 33 mmol), DBU (2.5 mL, 152.24 g/mol, 1.02 g/mL, 16.8 mmol) and ethanol (2.9 mL, 46.07 g/mol, 0.789 g/mL, 49.7 mmol) in THF (20 mL) was added. The mixture was then heated to reflux for 24 hours. After cooling to room temperature, excess 1M aqueous hydrochloric acid was poured into the mixture. After extraction with DCM, the combined organic phases were dried over sodium sulfate and the solvent was evaporated. The crude product was purified by column chromatography on silica with DCM:petroleum ether 7:3 followed by petroleum ether:ethyl acetate 8:2 and then increasing the amount of ethyl acetate until all product **10** was eluted. Yield: 1.05 g (524.57 g/mol, 2.0 mmol, 61%), pale yellow oil.

^1H NMR (400 MHz, Cl_2CDCl_2 , 120°C): δ = 8.68 (d, 8Hz, 1H), 8.48 (d, 8Hz, 1H), 8.14 (d, 8Hz, 1H), 7.92 (d, 8Hz, 1H), 7.71 (d, 8Hz, 1H), 7.59 (d, 8Hz, 1H), 7.54 (t, 8Hz, 1H), 7.50 (t, 8Hz, 1H), 7.43 (t, 8Hz, 1H), 7.35 (d, 8Hz, 1H), 7.31 (t, 8Hz, 1H), 7.16 (d, 8Hz, 1H), 7.11 (t, 8Hz, 1H), 4.47 (q, 7Hz, 2H), 4.35 (q, 7Hz, 2H), 4.34 (q, 7Hz, 2H), 1.44 (t, 7Hz, 3H), 1.32 (t, 7Hz, 3H), 1.31 (t, 7Hz, 3H) ppm.



Strong signal broadening due to slow rotations and aggregation did not allow the recording of a meaningful ^{13}C NMR spectrum of this and all following compounds.

FD-HRMS: m/z calcd for $\text{C}_{32}\text{H}_{28}\text{O}_7$ $[\text{M}]^+$: 524.18350, found 524.18400.



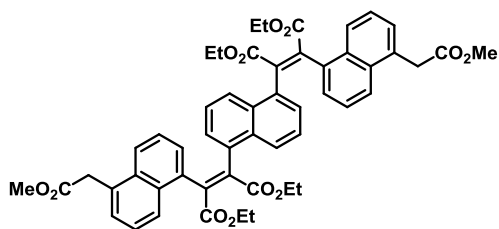
11

To a stirred suspension of the triester **10** (1.046 g, 524.57 g/mol, 2.0 mmol) in ethanol (150 mL) was added a solution of sodium hydrogen carbonate (5.04 g, 84.01 g/mol, 60 mmol) in water (150 mL). The mixture was heated at reflux with stirring for 36 h. After cooling to room temperature, the solution was slowly poured with stirring into 1M aqueous hydrochloric acid (150 mL). The mixture was extracted three times with ethyl acetate and the combined organic phases were dried over sodium sulfate and concentrated. The resulting orange solid was dissolved in THF and filtered to remove inorganic salts and the solution was concentrated. The solid was used without further purification. Yield 881 mg (440.41 g/mol, 2.0 mmol, quantitative).

^1H NMR (400 MHz, CD_3SOCD_3 , 120°C): δ = 8.78 (d, 8Hz, 1H), 8.34 (d, 8Hz, 1H), 7.97-7.95 (m, 2H), 7.91 (d, 8Hz, 1H), 7.83 (d, 8Hz, 1H), 7.69-7.60 (m, 2H), 7.55 (d, 8Hz, 1H), 7.46-7.41 (m, 3H), 7.33 (t, 8Hz, 1H) ppm.

FD-HRMS: m/z calcd for $\text{C}_{26}\text{H}_{14}\text{O}_6$ $[\text{M}]^+$: 422.07904, found 422.08025.

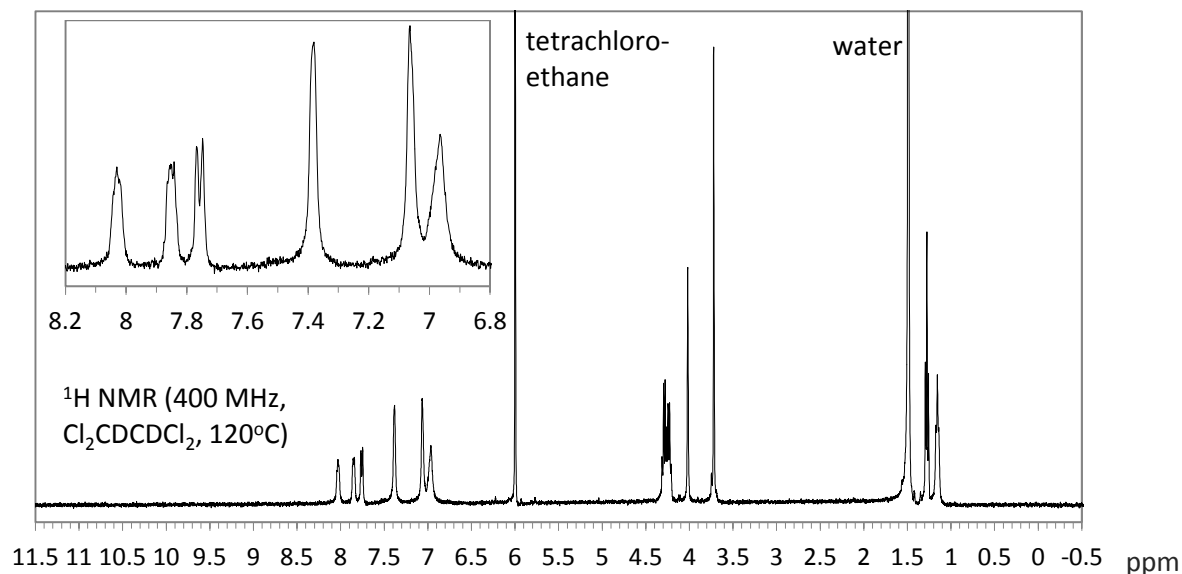
Mp: glassy solid ; 80-90°C



12

A solution of monoprotected naphthylene-1,5-diacetic acid² **9** (1.40 g, 258.27 g/mol, 5.4 mmol), naphthylene-1,5-diglyoxylic acid¹ **7** (626 mg, 272.21 g/mol, 2.3 mmol), triethylamine (1.9 mL, 101.19 g/mol, 0.726 g/mL, 13.8 mmol), and acetic anhydride (2 mL, 102.09 g/mol, 1.08 g/mL, 20.7 mmol) in dry THF (70 mL) was heated at reflux with stirring under argon overnight. The mixture was cooled to room temperature and a solution of bromoethane (3.4 mL, 108.97 g/mol, 1.47 g/mL, 46 mmol), DBU (3.4 mL, 152.24 g/mol, 1.02 g/mL, 23 mmol) and ethanol (4.0 mL, 46.07 g/mol, 0.789 g/mL, 69 mmol) in THF (30 mL) was added. The mixture was then heated to reflux for 24 hours. After cooling to room temperature, excess 1M aqueous hydrochloric acid was poured into the mixture. After extraction with DCM, the combined organic phases were dried over sodium sulfate and the solvent was evaporated. The crude product was purified by recrystallization in ethanol. Yield: 1.93 g (864.94 g/mol, 2.2 mmol, 96%) of gray solid.

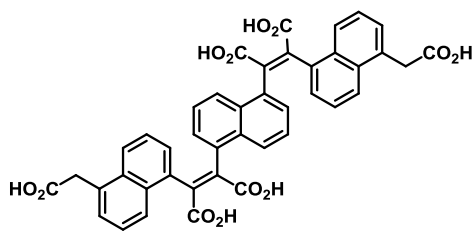
¹H NMR (400 MHz, Cl₂CDCDCl₂, 120°C): δ = 8.03 (broad, 2H), 7.83 (broad, 2H), 7.76 (d, 8Hz, 2H), 7.38 (broad, 4H), 7.06 (broad, 4H), 6.97 (broad, 4H), 4.28 (q, 7Hz, 4H), 4.23 (q, 7Hz, 4H), 4.02 (s, 4H), 3.72 (s, 6H), 1.28 (t, 7Hz, 6H), 1.16 (t, 7Hz, 6H) ppm.



ESI-HRMS: *m/z* calcd for C₅₂H₄₈O₁₂Na [MNa]⁺: 887.3037, found 887.3025.

Mp: 190-193°C

² G. Nault, A. Robert, P. Dechambenoit, H. Bock and F. Durola, *Eur. J. Org. Chem.*, 2018, 619.

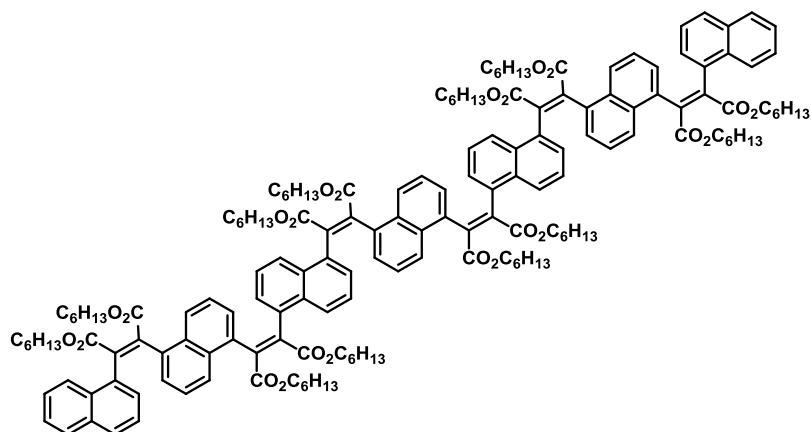


13

To a suspension of the hexa-ester **12** (1.817 g, 864.94 g/mol, 2.1 mmol) in ethanol (200mL), a solution of sodium hydroxide (15.28 g, 40.00 g/mol, 382 mmol) in water (375 mL) was added. The mixture was heated with stirring at reflux for 36h. After cooling to room temperature, excess 2M aqueous hydrochloric acid was added. The mixture was extracted three times with ethyl acetate and the combined organic phases were dried over sodium sulphate and concentrated. The crude product was dissolved in acetone, the acetone-insoluble salts were filtered off and discarded, and the acetone was evaporated. The solid obtained was used without further purification. Yield: 1.34 g (724.67 g/mol, 1.8 mmol, 86%), orange solid.

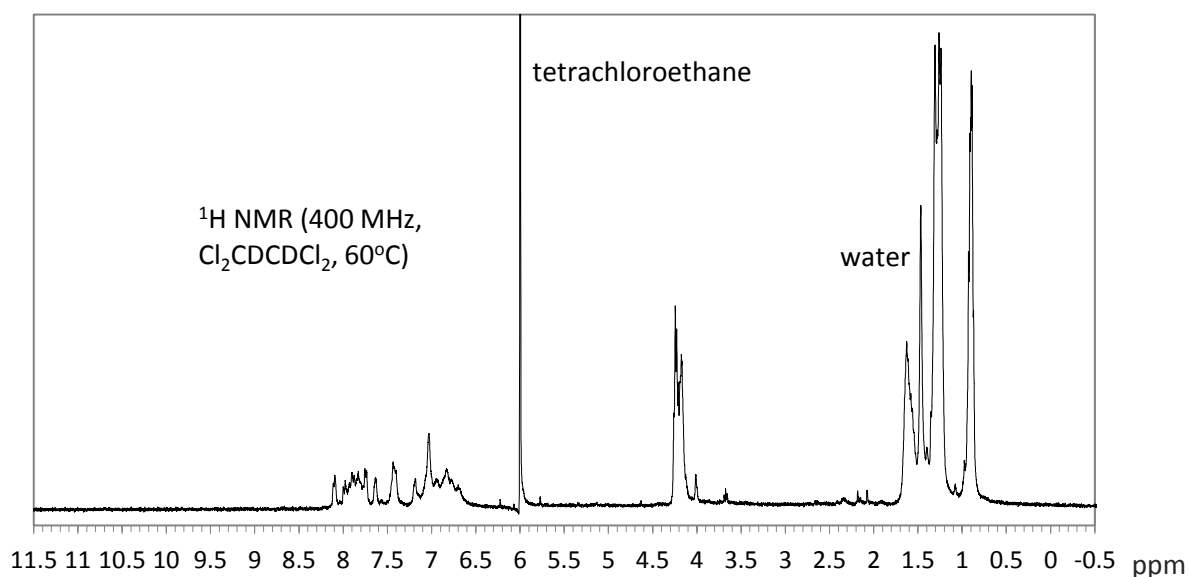
^1H NMR (400 MHz, CD_3SOCD_3 , 120°C): δ = 8.05-8.02 (m, 4H), 7.83 (d, 9Hz, 2H), 7.43 (m, 6H), 7.38 (d, 8Hz, 2H), 7.28 (t, 8Hz, 2H), 7.18 (t, 8Hz, 2H), 3.98 (s, 4H) ppm.

Mp: Solid that softens between 140 and 180°C

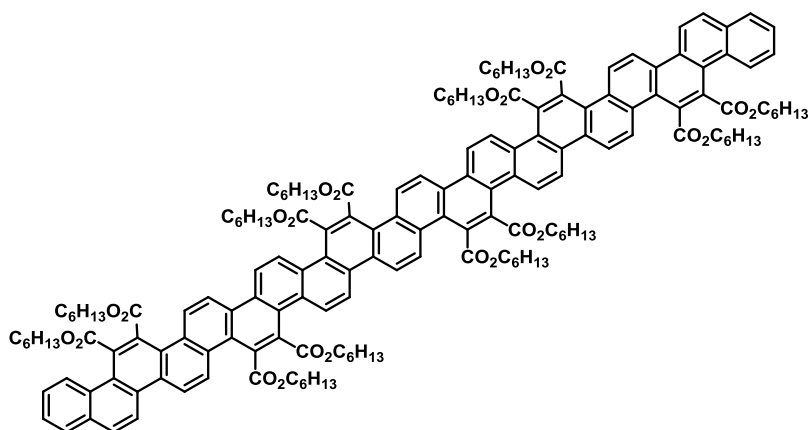


A solution of triacid **11** (344 mg, 440.41 g/mol, 0.78 mmol), hexaacid **13** (250 mg, 724.67 g/mol, 0.34 mmol), triethylamine (0.8 mL, 101.19 g/mol, 0.726 g/mL, 5.7 mmol), and acetic anhydride (0.8 mL, 102.09 g/mol, 1.08 g/mL, 8.5 mmol) in dry THF (50 mL) was heated at reflux with stirring under argon overnight. The mixture was cooled to room temperature and a solution of 1-bromohexane (2.9 mL, 165.07 g/mol, 1.176 g/mL, 20.4 mmol), DBU (1.5 mL, 152.24 g/mol, 1.02 g/mL, 10.2 mmol) and hexan-1-ol (3.8 mL, 102.17 g/mol, 0.82 g/mL, 30.6 mmol) in THF (20 mL) was added. The mixture was then heated to reflux for 24 hours. After cooling to room temperature, excess 1M aqueous hydrochloric acid was poured into the mixture. After extraction with DCM, the combined organic phases were dried over sodium sulfate and the solvent was evaporated. The crude product was purified by column chromatography on silica with DCM:ethanol 99:1. Yield: 0.47 g (2579.40 g/mol, 0.18 mmol, 53%), pale yellow oil.

^1H NMR (400 MHz, $\text{Cl}_2\text{CDCDCl}_2$, 60°C): δ = 8.10 (broad, 2H), 8.00-7.73 (m, 12H), 7.63 (broad, 2H), 7.47-7.40 (m, 4H), 7.20 (broad, 2H), 7.10-6.66 (m, 22H), 4.26-4.13 (m, 24H), 1.65-1.54 (m, 20H), 1.35-1.24 (m, 76H), 0.93-0.87 (m, 36H) ppm.

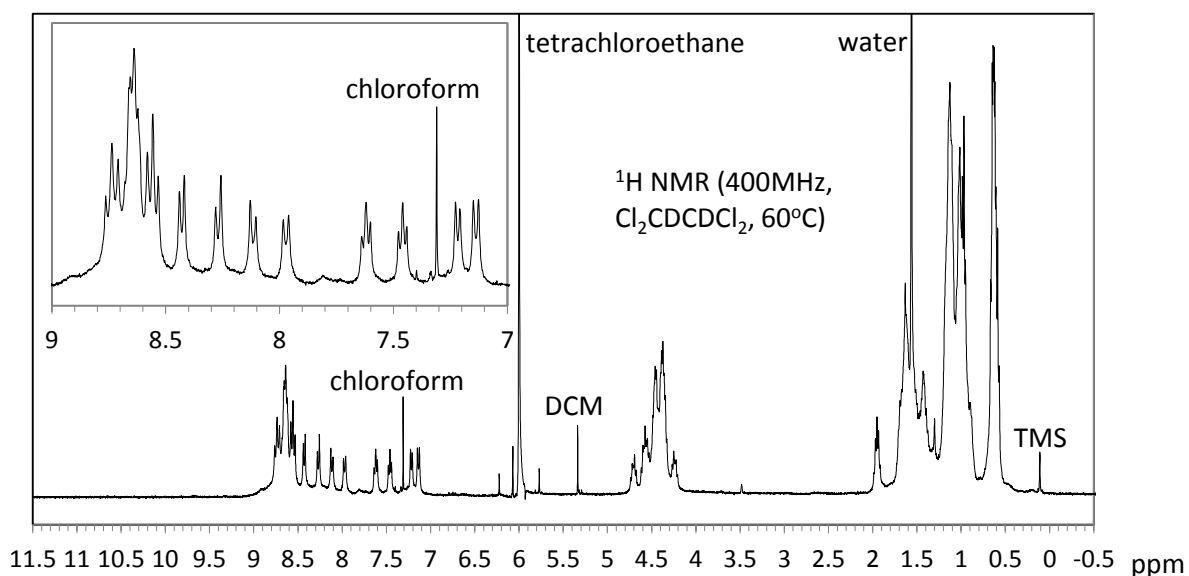


FD-HRMS: m/z calcd for $\text{C}_{166}\text{H}_{200}\text{O}_{24}$ $[\text{M}]^+$: 2577.44295, found 2577.44359.



A solution of hexakis-maleate **14** (240 mg, 2579.40 g/mol, 0.09 mmol) and iodine (200 mg) in ethyl acetate (1 L) was stirred for 10 days at room temperature under air in a Peschl photoreactor with irradiation from a medium-pressure 150 W mercury immersion lamp inside a borosilicate immersion tube in which cooling water circulated. The solvent was evaporated, a 0.4 M aqueous solution of sodium thiosulphate (100mL) was added and the product was extracted with DCM (2×100mL). The organic phases were concentrated and the crude product was purified by repeated column chromatography on silica in DCM:acetone 98.5:1.5 followed by DCM:acetone 97:3. Yield: 31 mg (2567.31 g/mol, 12 μ mol, 13%), yellow solid

^1H NMR (400 MHz, $\text{Cl}_2\text{CDCDCl}_2$, 60°C): δ = 8.77-8.52 (m, 16H), 8.43 (d, 8Hz, 2H), 8.27 (d, 9Hz, 2H), 8.11 (d, 9Hz, 2H), 7.97 (d, 9Hz, 2H), 7.62 (t, 8Hz, 2H), 7.46 (t, 8Hz, 2H), 7.22 (d, 8Hz, 2H), 7.13 (d, 9Hz, 2H), 4.74-4.67 (m, 2H), 4.62-4.52 (m, 4H), 4.51-4.33 (m, 16H), 4.27-4.21 (m, 2H), 1.95 (quint, 7Hz, 4H), 1.75-0.55 (m, 128H) ppm.



FD-HRMS: m/z calcd for $\text{C}_{166}\text{H}_{188}\text{O}_{24}$ $[\text{M}]^+$: 2565.34905, found 2565.34953.

Mp: 250-257°C