7 Experimental Section (Experimenteller Teil)

7.1 General

Reagents and compounds **12**, **15**, **25**, **34**, **40**, 9-BBN, **59**, **60**, **72**, **99, 115**, **118**, and **127** were purchased from Fluka, Aldrich, or Acros and were used without further purification. All solvents were purchased from Fluka, Aldrich, or Acros and were purified and dried by standard methods. Compounds **9**,[59] **11**,[60] **13**,[60] **14**,[60] **17**,[101] **18**,[63] **32**,[67] **53**,[102] **63**,[76] **64**,[76] **74**,[77] **81,**[78] **95**,[82] **101**,[83] and **102**[84] were prepared according to literature procedures. ^{1}H-NMR spectra: Bruker AM270 spectrometer (270 MHz) or Bruker AC500 spectrometer (500 MHz) ($CHCl_3$ at δ = 7.24 or DMSO at δ = 2.49 as internal standard). ^{13}C NMR spectra: Bruker AM 270 spectrometer (67.9 MHz) or Bruker AC 500 spectrometer (126 MHz) ($CDCl_3$ at δ = 77.0 as internal standard). MS: Varian MAT 711 spectrometer. Melting points: Büchi 510 (open capillaries, uncorrected values). Column chromatography: Merck silica gel 60, 0.040 - 0.063 mm (230 - 400 mesh). Analytical TLC: aluminum sheets, silica gel Si 60 F_{254} (Merck), detection: UV absorption. Elemental analyses: Perkin-Elmer EA 240.
Spectrometric grade methylcyclohexane and acetonitrile were used as solvents for the spectroscopic measurements. UV absorption spectra were measured on an ATI UNICAM UV series UV-02113 spectrometer; fluorescence spectra were recorded on an AMINCO-Bowman series 2 spectrofluorimeter. They were corrected for instrumental sensivity.

All compounds were fully characterized by high field ^{1}H- and ^{13}C NMR spectroscopy, correct data from combustion analysis or high resolution mass spectrometry. Combustion analyses were not performed for carboxylic acids **43**, **52**, **93**, **94** and for amine trifluoro acetates **44**, **45**, **106** and **107** because water could not be removed completely from them. Combustion analyses were not performed for **54** and **124** because they were used without any working up procedure.
For many compounds the number of aromatic carbon signals in the ^{13}C NMR spectra is too low because several signals, especially in the pyrene range, coincide.

7.2 General procedures

Suzuki-cross coupling type 1 (SCC 1)

The bromo or iodo compound (1 eq) and the boronic acid or ester (1 eq) were dissolved in toluene. An aqueous solution of Na_2CO_3 (c = 1 mol/l) was added. The mixture was degassed and flushed with N_2 three times and $Pd(PPh_3)_4$ was added under N_2. Then the mixture was degassed and flushed with N_2 three times again. The system was refluxed for 2 days, the phases were separated, and the aqueous layer was washed with toluene two times. The combined organic layers were dried ($MgSO_4$) and toluene removed.

Suzuki-cross coupling type 2 (SCC 2)

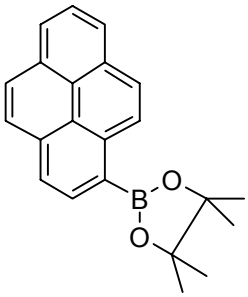
The allyl-compound and 9-BBN were dissolved in dry THF or toluene and the solutions were stirred for 12 h. H_2O (3 drops) was added. If THF was used, it was removed now and the residue dissolved in toluene. To the solution the bromo or iodo compound and an aqueous solution of KOH (c = 1 mol/l) were added. The mixture was degassed three times and flushed with N_2 repeatedly. $Pd(PPh_3)_4$ was added under N_2, the mixture was degassed and flushed with N_2 three times again and then refluxed for 2 d. After cooling to room temperature the layers were separated. The aqueous layer was washed twice with toluene and the combined organic layers were dried ($MgSO_4$) and solvent removed.

Amide coupling (HOBt/EDC method)

To a solution of the acid (1.0 eq) in anhyd. CH_2Cl_2 HOBT (1.1 eq) was added and the solution was stirred for 15 min. DIPEA (2.1 eq) and the amine (1.0 eq) were added and solution stirred for 15 min. EDC (1.1 eq) was added and the mixture was stirred for further 15 h at 25 °C, then washed with an aqueous solution of $NaHCO_3$ (c = 1 mol/l), citric acid (c = 1 mol/l) brine and H_2O. The organic layer was dried ($MgSO_4$) and the CH_2Cl_2 was removed by distillation.

7.3 Synthesis of compounds from chapter 4.3

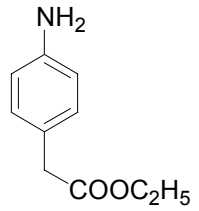
4,4,5,5-Tetramethyl-2-pyrene-1-yl-[1,3,2]dioxaborolane (10)



Pyrene bromide **11** (50g, 0.178 mol) was suspended in dry diethyl ether (1 l) and the mixture was cooled down to –78 °C. A solution of BuLi (250 ml, c = 1.6 M, 0.400 mol) was added dropwhise. The mixture was allowed to come to room temperature in 6 h, then was cooled down to –78°C again and $B(O_iPr)_3$ (101.88 g, 125 ml, 0.542 mol) was added. The mixture came to room temperature while 10 h. Then water (500 ml) was added. The layers were separated and the aqueous layer was washed three times with diethyl ether (3 x 300 ml). The combined organic layers were dried ($MgSO_4$). Filtration over silica gel with first hexane and later with methanol gave the pyrene boronic acid **9** (32.74 g, 0.01 mol, 56%) as a brown oil. Without further purification the pyrene boronic acid **9** and pinakol (21 g, 0.178 mol) were dissolved in acetone (250 ml) and refluxed for 1 h. After removing of the acetone, the crude product was purified with silica gel. Chromatographic separation with hexane: acetic acid ethyl ester 3:1 gave the pyrene pinacol **10** (33.9 g, 58 %) as a yellow solid.

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 1.51 (s, 12H), 8.0-8.27 (m, 7H, H_{pyrene}), 7.62 (d, 1H, H_{pyrene}), 9.12 (d, 1H, H_{pyrene}).
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 25.0, 83.8, 124.0, 124.3, 124.5, 124.8, 125.1, 125.3, 125.6, 127.4, 127.7, 128.0, 128.4, 130.7, 131.0, 133.4, 133.8, 136.4.
MS (EI 80 eV 100°C): m/z (%): 328 (100) [M^+], 228 (28.58) [M^+-$C_6H_{12}O$]
$C_{22}H_{21}BO_2$ (328.22): calcd C 80.51 H 6.45 found C 79.89 H 6.69

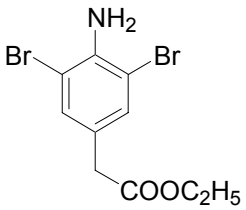
(4-Amino-phenyl)-acetic acid ethyl ester (17)



Phenyl acetic acid **15** (50.0 g, 0.331 mol) was suspended in a mixture of 150 ml ethanol and 150 ml toluene. Conc. sulfuric acid (72.8 ml, 0.728 mol) was added within 15 min. The dark brown solution was refluxed at 140 °C for 5 h with a water separator. After cooling at 0 °C a solution of Na_2CO_3 (750 ml, 1 M) was added. The layers were separated, the aqueous layer was washed three times with toluene (300 ml), and the combined organic layers were dried ($MgSO_4$). Recrystallization in a mixture of hexane: acetic acid ethyl ester 10:1 gave the ester **17** (46.0 g, 0.257 mol, 78%) as pale yellow crystals.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.22 (t, 3H, J = 9 Hz, CH_3), 3.46 (s, 2H, $CH_{2\ benzylic}$), 3.83 (s, 2H, NH_2), 4.10 (q, 2H, J = 9 Hz, CH_2), 6.57 (d, 2H, J = 9 Hz, $H_{aromatic}$), 7.02 (d, 2H, J = 9 Hz, $H_{aromatic}$).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 13.8, 40.1, 60.3, 114.9, 123.4, 129.6, 145.1, 171.9.
MS (EI, 80 eV, 50 °C): m/z (%): 179 (52.09) [M^+], 106 (100) [M^+-$C_3H_5O_2$].
$C_{10}H_{13}NO_2$ (179.22): calcd C 67.02, H 7.31, N 7.82, found C 67.01, H 7.34, N 7.93.

(4-Amino-3,5-dibromo-phenyl)-acetic acid ethyl ester (19)

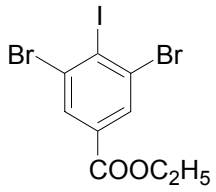


Phenyl acetic ester **17** (23.0 g, 0.128 mol) was dissolved in conc. acetic acid (300 ml) and cooled to 0 °C. A solution of Br_2 (45.1 g, 14.4 ml, 0.282 mol) in acetic acid (50 ml) was added at 0 °C within 1 h. The product started to precipitate immediately. The mixture was stirred for 12 h at room temperature. After cooling to 0 °C the mixture was poured on ice (1 kg). Filtration under vacuum and washing two times with water gave the brominated product **19** (37.0 g, 87%) as a light brown solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.24 (t, 3H, J = 9 Hz, CH_3), 3.41 (s, 2H, $CH_{2\ benzylic)}$, 4.12 (q, 2H, J = 9.3 Hz, CH_2), 7.27 (s, 2H, $H_{aromatic}$).

^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.0, 39.4, 60.9, 108.4, 125.1, 132.3, 140.9, 171.0.
MS (EI, 80 eV, 30 - 40 °C): m/z (%): 335 (22.4) [M^+], 262 (47.7) [M^+-$C_3H_5O_2$], 183 (7.4) [M^+-$C_3H_5O_2Br$], 104 (15.0) [M^+-$C_3H_5O_2Br_2$].
$C_{10}H_{11}NO_2$ (337.01): calcd C 35.64, H 3.29, N 4.16, found C 35.58, H 3.17, N 4.05.

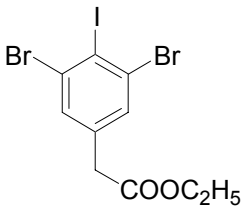
3,5-Dibromo-4-iodo benzoic acid ethyl ester (20)



Ice (100 g), 25% HCl (72 ml, 0.490 mol) and **18** (26 g, 0.081 mol) were mixed and stirred for 30 min. Then an aqueous solution of $NaNO_2$ (7.45 g in 75 ml H_2O) was dropped in within 15 min. The mixture was then stirred for 4 h. The mixture was filtrated and the filtrate was dropped into an aqueous solution of KI (136 g, 0.820 mol, 150 ml H_2O) under vigorous stirring. The mixture was stirred for 12 h at room temperature. Then CH_2Cl_2 (200 ml) and an aqueous solution of sodium disulphite (200 ml, c = 1 mol/l) were added. The organic phase was separated and the aqueous one extracted with CH_2Cl_2 (100 ml). The combined organic layers were extracted with a solution of $NaHCO_3$ (200 ml, c = 1 mol/l) and the CH_2Cl_2 phase was dried ($MgSO_4$). Solvent was removed, recrystallization with ethanol gave iodoester **20** (15.3 g, 0.035 mol, 44%) as a pale orange solid.

^1H NMR (270 MHz, $CDCl_3$): δ = 1.38 (t, J = 9.3 Hz, 3H, CH_3-CH_2), 4.36 (q, J = 9.3 Hz, 2H, CH_3-CH_2), 8.14 (s, 2H, $H_{aromatic}$).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.20, 61.91, 115.48, 131.40, 132.55, 163.81.
MS (EI, 80 eV, 120 °C): m/z (%) = 431.8 (50.3) [M^+], 402.7 (34.2) [M-C_2H_5], 386.7 (50.9) [M-OC_2H_5], 358.7 (12.9) [M-$C_3H_5O_2$], 352.8 (11.8) [M-Br], 231.8 (15.8) [M-$C_3H_5O_2$-I], 180.9 (6.3) [M-C_2H_5O-Br-I], 152.9 (28.9) [M-$C_3H_5O_2$-Br-I].
$C_9H_7Br_2IO_2$ (431.78) calcd C 24.92, H 1.63, found C 25.07, H 1.62.

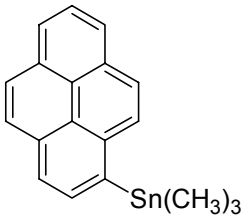
(3,5-Dibromo-4-iodo-phenyl) acetic acid ethyl ester (21)



Amino phenyl ester **19** (14.0 g, 41.5 mmol) was dissolved in conc. acetic acid (220 ml) and added at 0 °C to conc. sulfuric acid (40 ml). This solution was added slowly at 0 °C to a mixture of $NaNO_2$ (7.5 g, 109.0 mmol) conc. sulfuric acid (50 ml) and conc. acetic acid (100 ml). After stirring for 1 h at 0 °C the mixture was added at room temperature to a solution of KI (38.0 g, 228.0 mmol), I_2 (31.0 g, 244.0 mmol), urea (5.0 g, 83.0 mmol), water (500 ml), and $CHCl_3$ (140 ml). The solution was stirred at room temperature for 1 h, then sodium disulphite (46.0 g, 0.242 mol) was added. The layers were separated, the aqueous layer was washed twice with $CHCl_3$ (400 ml), and the combined organic layers were washed with a solution of Na_2CO_3 (250 ml, c = 1 mol/l). The organic phase was dried ($MgSO_4$). Chromatographic filtration through silica gel with hexane:acetic acid ethyl ester 3:1 gave iodophenyl ester **21** (10.0 g, 22.0 mmol, 54 %) as a yellow solid. R_f = 0.47.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.24 (t, 3H, J = 9 Hz, CH_3), 3.48 (s, 2H, $CH_{2\ benzylic}$), 4.14 (q, 2H, J = 9 Hz, CH_2), 7.47 (s, 2H, $H_{aromatic}$).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.0, 38.3, 60.6, 108.1, 130.3, 132.5, 138.1, 170.1.
MS (EI, 80 eV, 140 °C): m/z (%): 446 (44) [M^+], 373 (73.2) [M^+-$C_3H_5O_2$], 246 (24.2) [M^+-$C_3H_5O_2I$], 88 (42.0) [M^+-$C_3H_5O_2Br_2I$].
$C_{10}H_9Br_2IO_2$ (447.89): calcd C 26.82, H 2.03, found C 26.65, H 2.09.

Trimethyl-pyrene-1-yl-stannane (24)

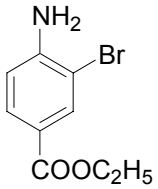


Pyrene bromide **11** (20.0 g, 0.071 mol), was dissolved in dry diethyl ether (300 ml) and the mixture was cooled down to –78 °C. A solution of BuLi (57.8 ml, 1.6 M) was added dropwise. The mixture was allowed to come to room temperature in 5 h, then

cooled down to –78 °C again and $Sn(CH_3)_3Cl$ **25** (19.8 g, 0.100 mol) dissolved in dry diethyl ether (200 ml) was dropped in. The mixture came to room temperature during 12 h, and then an aqueous solution of KF (100 ml, 1M) was added. The layers were separated and the aqueous one was washed with diethyl ether (300 ml). The combined organic layers were dried ($MgSO_4$). The solvent was removed. Recrystallization with ethanol gave the product **24** (14.2 g, 0.039 mol, 55 %) as a pale brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.68 (s, 9H, CH_3), 8.00 – 8.36 (m, 9H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = -8.05, 124.15, 124.85, 125.69, 127.33, 127.44, 127.51, 129.40, 130.82, 131.25, 131.52, 133.62, 136.88, 140.32. (3 signals missing).
MS (EI, 140 °C, 80 eV): m/z (%) = 366 (42.4) [M^+], 351 (100) [M^+-CH_3], 321 (68.6) [M^+-C_3H_9].
EA $C_{19}H_{18}Sn$ (365.04) calcd C 62.52 H 4.97, found C 62.16 H 4.89.

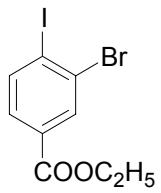
4-Amino-3-bromo-benzoic acid ethyl ester (28)



Benzoic acid ethyl ester **16** (14.1 g, 86.0 mmol) was dissolved in CH_2Cl_2 (200 ml) and cooled to 0 °C. A solution of Br_2 (16.5 g, 5.3 ml, 103.0 mmol) in CH_2Cl_2 (100 ml) was added dropwise in 2 h at 0 °C. The mixture was stirred for 12 h at room temperature. The organic layer was washed first with an aqueous sodium disulphite solution (100 ml, c = 1 mol/l) and two times with water (200 ml). The organic layer was dried ($MgSO_4$) and the CH_2Cl_2 was evaporated. Chromatographic separation with hexane:acetic acid ethyl ester 10:1 gave the product **28** (11.5 g, 47.0 mol, 55%) as a colorless solid. R_f = 0.18.

^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.34 (t, 3H, CH_3), 4.29 (q, 2H, CH_2), 4.57 (s, 2H, NH_2), 6.69 (d, 1H, $H_{aromatic}$), 7.75 (d, 1H, $H_{aromatic}$), 8.07 (s, 1H, $H_{aromatic}$).
^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 14.16, 60.48, 107.56, 114.04, 120.57, 130.39, 134.18, 148.17, 165.47.
MS (EI, 80 eV, 85 °C) m/z = 243 (91.9) [M^+], 215 (23.8) [M^+-C_2H_4], 198 (100) [M^+-C_2H_5O], 164 (7.4) [M^+-Br].
$C_9H_{10}BrNO_2$ (244.09) calcd C 44.29, H 4.13, N 5.74, found C 44.18, H 4.01, N 5.63.

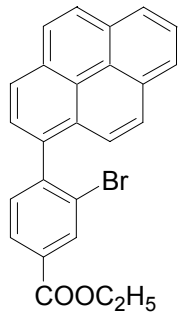
3-Bromo-4-iodo-benzoic acid ethyl ester (30)



Amino bromo ester **28** (10.2 g, 41.8 mmol) was suspended in HCl (40 ml, 25%) and ice (50 g). Then $NaNO_2$ (3.2 g, 46.0 mol) dissolved in water (15 ml) was added dropwise. The mixture was stirred for 3 h at room temperature and then filtrated. The orange filtrate was dropped under vigorous stirring at 0 °C into a solution of KI (35.1 g, 0.209 mol) in water (100 ml). The product started to precipitate immediately. The mixture was stirred 12 h at room temperature. CH_2Cl_2 (250 ml) and sodium disulphite (38.0 g, 0.200 mol) were added. The layers were separated and the organic one was dried ($MgSO_4$). The CH_2Cl_2 was removed, the crude product was a brown oil. Chromatographic separation with first hexane and later hexane:acetic acid ethyl ester 20:1 gave the product **30** (9.3 g, 26.2 mmol, 63%) as a colorless solid. R_f (Hex:EE 3:1) = 0.56.

^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.36 (t, 3H, CH_3), 4.34 (q, 2H, CH_2), 7.57 (d, 1H, $H_{aromatic}$), 7.91 (d, 1H, $H_{aromatic}$), 8.21 (s, 1H, $H_{aromatic}$).
^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 14.13, 61.35, 107.34, 128.65, 129.77, 131.61, 133.00, 140.10, 164.47.
MS (EI, 80 eV, 60 °C) m/z = 354 (83.7) [M^+], 326 (52.9) [M^+ - C_2H_4], 275 (13.6) [M^+ - Br], 199 (2.7) [M^+ - C_2H_4I].
$C_9H_8BrIO_2$ (354.97) calcd C 30.45, H 2.27, found C 30.24, H 2.14.

3-Bromo-4-pyren-1-yl-benzoic acid ethyl ester (31)

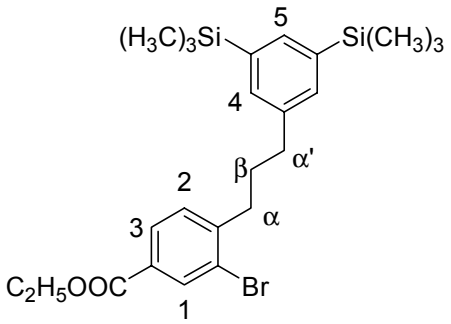


For preparation see general procedure for SCC 1:

Br-I-ester **30** (2.00 g, 5.65 mmol), pinacol ester **10** (1.86 g, 5.65 mmol), toluene (30 ml), Na_2CO_3 (20 ml, c = 1 mol/l), tetrakis(triphenylphosphine)palladium(0) (65.0 mg, 5.65 x 10^{-2} mmol), 4 d.
The residue was recrystallized in hexane. At room temperature the product **31** (0.84 g, 1.95 mmol 34.5%) precipitates as a light brown solid.

^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.46 (t, 3H, CH_3), 4.46 (q, 2H, CH_2), 7.55 (d, 1H, $H_{aromatic}$), 7.65 (d, 1H, H_{pyrene}), 7.86 (d, 1H, $H_{aromatic}$), 7.93-8.34 (m, 8H, H_{pyrene}), 8.50 (s, 1H, $H_{aromatic}$).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 14.33, 61.47, 124.34, 124.53, 124.60, 124.67, 125.25, 125.43, 126.13, 126.87, 127.29, 127.84, 127.90, 128.20, 128.41, 130.75, 131.09, 131.21, 131.38, 132.30, 133.84, 135.32, 146.27, 165.23.
MS (EI, 80 eV, 190 °C) m/z = 428 (98.5) [M^+], 400 (7.7) [M^+ - C_2H_4], 321 (2.0) [M^+ - C_2H_4Br], 226 (2.2) [M^+ - $C_{16}H_{10}$].
$C_{25}H_{17}BrO_2$ (429.31) calcd C 69.94, H 3.99, found C 69.61, H 3.82.
HRMS ($^{12}C_{25}{}^1H_{17}{}^{16}O_2{}^{79}Br$) [$M^+$]: calcd 428.04119, found 428.04434.

4-[3-(3,5-Bis-trimethylsilanyl-phenyl)-propyl]-3-bromo-benzoic acid ethyl ester (33)



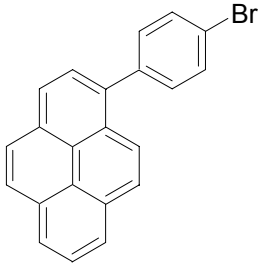
For preparation see general procedure for SCC 2

Allyl-di-TMS **32** (3.00 g, 11.40 mmol), 9-BBN (1.67 g, 13.70 mmol), dry THF (50 ml), 12h, aqueous solution of KOH (20 ml, 1M), toluene (30 ml), bromo-iodo-ester **30** (4.04 g, 11.40 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), 4 d. Chromatographic separation with silica gel and hexane: ethyl acetate 10:1 gave the product **33** (2.44 g, 4.96 mmol, 44 %) as a colorless oil. R_f = 0.09

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.35 (s, 18H, CH_3-Si), 1.44 (t, 3H, CH_3), 2.07 (quin, 2H, β), 2.80 (t, 2H, α), 2.91 (m, 2H, α'), 4.43 (q, 2H, CH_2), 7.34 (d, 1H, 2), 7.42 (s, 2H, 4), 7.59 (s, 1H, 5), 7.97 (d, 1H, 3), 8.28 (s, 1H, 1).

^{13}C NMR (126 MHz, $CDCl_3$): δ = -1.05, 14.26, 31.06, 35.71, 35.98, 61.08, 124.30, 128.39, 130.00, 133.60, 133.80, 133.95, 135.77, 139.67, 139.81, 146.71, 165.17.
MS (EI, 20 – 40 °C, 80 eV): m/z (%) = 490 (40.7) [M^+], 475 (94.9) [M^+-CH_3], 461 (26.3) [M^+-C_2H_5], 397 (25.0) [M^+-CH_2Br], 73 (30.2) [$Si(CH_3)_3^+$].
HRMS $^{12}C_{24}{}^{1}H_{35}{}^{16}O_2{}^{28}Si_2{}^{79}Br_1$ calcd 490.13590, found 490.13842.
EA $C_{24}H_{35}BrO_2Si_2$ (491.61) calcd C 58.64 H 7.18, found C 58.18 H 6.8.

1-(4-Bromo-phenyl)-pyrene (35)

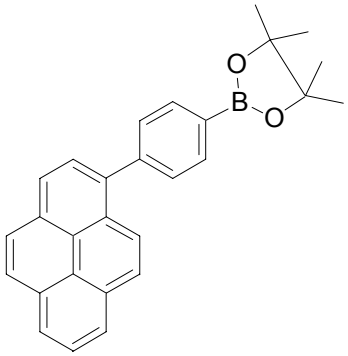


For preparation see general procedure for SCC 1:

Pyrene pinacol **10** (20.00 g, 61.0 mmol), bromoiodobenzene **34** (19.00 g, 67.0 mmol), toluene (150 ml), aqueous solution of Na_2CO_3 (150 ml, c = 1 mol/l), tetrakis(triphenylphosphine)palladium(0) (1.41 g, 1.22 mmol), 2 d, recrystallization in hexane gave **35** (19.8 g, 55.4 mmol, 91 %) as a pale brown solid.

^1H NMR (270 MHz, $CDCl_3$): δ = 7.48 (d, 2H, $H_{aromatic}$), 7.69 (d, 2H, $H_{aromatic}$), 7.87 (d, 1H, H_{pyrene}), 7.96 - 8.24 (m, 8H, H_{pyrene}).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 121.50, 124.57, 124.69, 124.89, 125.19, 125.62, 125.99, 127.21, 127.25, 127.52, 127.66, 128.26, 130.55, 130.72, 130.80, 131.36, 131.46, 132.08, 136.12, 140.02.
MS (EI, 80 eV, 130 °C): m/z (%): 356 (99.6) [M^+], 277 (30.5) [M^+-Br].
$C_{22}H_{13}Br$ (357.25) calcd C 73.97, H 3.67, found C 74.04, H 3.88.

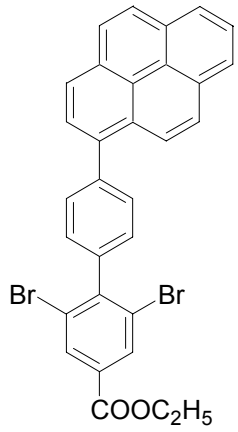
4,4,5,5-Tetramethyl-2(4-pyren-1-yl)-phenyl-1-yl-1,3,2-dioxaborolane (37)



Pyrene phenyl bromide **35** (24.1 g, 67.0 mmol) was suspended in 450 ml abs. THF and the solution was cooled down to –78 °C. A solution of n-BuLi (125.6 ml, 0.202 mol, c = 1.6 M) was added dropwise. The mixture was allowed to come to room temperature in 6 h, then cooled down to –78 °C again, and triisopropyl boric acid ester (44.4 g, 54.5 ml, 0.236 mol) was added. The mixture came to room temperature during 10 h. Then water (250 ml) was added. The layers were separated and the aqueous layer was washed three times with diethyl ether (900 ml). The combined organic layers were dried ($MgSO_4$). Filtration over silica gel with first hexane:acetic acid ethyl ester 3:1 and later with methanol:CH_2Cl_2 5:3 gave the pyrene phenyl boronic acid **36** (17.4 g, 54.0 mmol, 80%) as a brown oil. Without further purification the pyrene phenyl boronic acid and pinacol (7.0 g, 59.0 mmol) were dissolved in acetone (320 ml) and refluxed for 1 h. The acetone was removed through distillation. Chromatographic separation with hexane:acetic acid ethyl ester 3:1 gave the pyrene pinacol **37** (17.0 g, 42.1 mmol, 62 %) as a yellow solid. R_f = 0.47.

^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.41 (s, 12H, Pinacol), 7.68 (d, 2H, $H_{aromatic}$), 7.93 - 8.31 (m, 11 H, $H_{aromatic + pyrene}$).
^{13}C NMR (67.9 MHz, $CDCl_3$) δ = 24.87, 83.80, 124.53, 124.73, 124.86, 125.01, 125.06, 125.54, 125.86, 127.26, 127.33, 127.43, 128.32, 129.97, 130.59, 130.86, 131.35, 134.81, 137.46, 144.12, 154.68, 155.47.
MS (EI, 80 eV, 160 °C) m/z = 404 (100) [M^+], 304 (18.4) [$M^+ - C_6H_{12}O$].
$C_{28}H_{25}BO_2$ (404.31) calcd C 83.18, H 6.23, found C 82.89, H 6.33.

2,6-Dibromo-4'-pyren-1-yl-biphenyl-4-carboxylic acid ethyl ester (38)

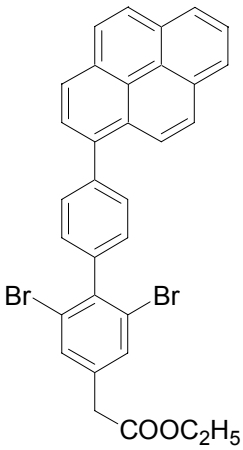


For preparation see general procedure for SCC 1:

Pinacol ester **37** (0.50 g, 1.24 mmol), iodide **20** (0.54 g, 1.24 mmol), m-xylene (20 ml), aqueous solution of Na_2CO_3 (10 ml, c = 1 mol/l), tetrakis(triphenylphosphine)palladium(0) (32.0 mg, 2.80 x 10^{-2} mmol), reflux for 4 d, chromatographic separation R_f (Hex:EE 10:1) = 0.13 gave product **38** (0.38 g, 0.66 mmol, 53 %) as a colorless solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.43 (t, J = 9.3 Hz, 3H, CH_3-CH_2), 4.43 (q, J = 9.3 Hz, 2H, CH_3-CH_2), 7.39 (d, J = 9.3 Hz, 2H, $H_{aromatic}$), 7.72 (d, J = 9.3 Hz, 2H, $H_{aromatic}$), 7.97 – 8.29 (m, 9H, H_{pyrene}), 8.34 (s, 2H, $H_{aromatic}$).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.27, 61.79, 124.63, 124.88, 125.09, 125.15, 125.99, 127.37, 127.49, 127.60, 128.45, 128.80, 130.47, 130.71, 130.93, 131.44, 132.14, 132.81, 137.01, 139.31, 141.27, 163.93.
$C_{31}H_{20}Br_2O_2$ (581.98) calcd C 63.72, H 3.45, found C 63.65, H 3.48.
MS (EI, 80 eV, 30-60 °C): m/z (%) = 582 (50.5), [M^+], 554 (7.3), [M - CO].

(2,6-Dibromo-4'-pyren-1-yl-biphenyl-4-yl) acetic acid ethyl ester (39)

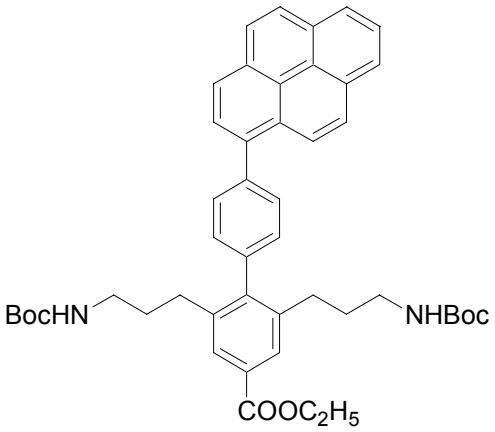


For preparation see general procedure for SCC 1:

Iodophenyl ester **21** (5.54 g, 12.40 mol), pyrene phenyl pinacol **37** (5.00 g, 12.40 mmol), xylene (50 ml), aqueous solution of Na_2CO_3 (25 ml, 1 M), tetrakis(triphenylphosphine)palladium(0) (286.0 mg, 0.25 mmol), 3 d. Chromatographic separation through silica gel with hexane:acetic acid ethyl ester 20:1 gave product **39** (3.23 g, 5.40 mmol, 44%) as a colorless solid. R_f (Hex:EE 3:1) = 0.38.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.34 (t, 3H, J = 9 Hz, CH_3), 3.57 (s, 2H, $CH_{2\ benzylic}$), 4.26 (q, 2H, J = 9 Hz, CH_2), 7.46 (d, 2H, J = 9 Hz, $H_{aromatic}$), 7.65 (s, 2H, $H_{aromatic}$), 7.76 (d, 2H, J = 9 Hz, $H_{aromatic}$), 7.93 - 8.37 (m, 9H, H_{pyrene}).
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.16, 39.93, 61.32, 124.43, 124.60, 124.80, 124.87, 125.06, 125.16, 125.93, 127.34 127.38, 127.49, 127.62, 128.14, 129.01, 130.32, 130.55, 130.86, 131.36, 132.70, 136.23, 137.13, 139.60, 140.74, 141.44, 170.45.
MS (EI, 80 eV, 280 °C): m/z (%) = 596 (51.0) [M^+], 523 (7.2) [$M^+ - C_3H_5O_2$], 365 (11.5) [$M^+ - C_3H_5O_2Br_2$], 276 (4.2) [$C_{22}H12$].
$C_{32}H_{22}Br_2O_2$ (598.33) calcd C 64.24, H 3.71, found C 64.06, H 3.87.

2,6-Bis-(3-tert-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-carboxylic acid ethyl ester (41)

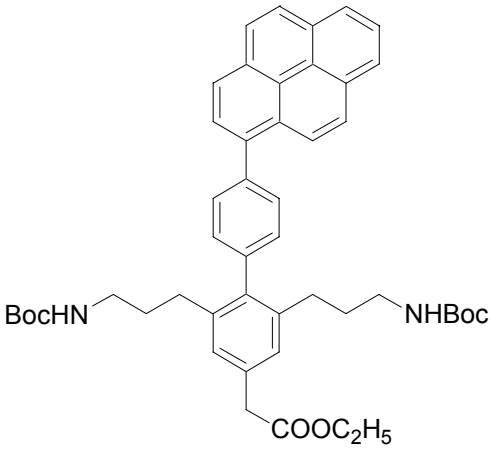


For preparation see general procedure for SCC 2:

Allylamine **40** (0.70 g, 4.11 mmol), 9-BBN (0.63 g, 5.15 mmol), di-bromoester **38** (0.15 g, 0.26 mmol), toluene (10 ml), KOH (10 ml, c = 1 mol/l), $Pd(PPh_3)_4$ (25 mg, 0.02 mmol), reflux for 5 d, chromatographic separation through silica gel with hexane:acetic acid ethyl Ester 7:1 gave product **41** (85.0 mg, 0.12 mmol, 45 %). R_f = 0.08.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.43 (s, 18H, $C(CH_3)_3$), 1.48 (t, 3H, J = 9.3 Hz, CH_3), 1.76 (tt, 4H, J = 9.3 Hz, CH_2), 2.62 (t, 4H, J = 9.3 Hz, $H_{benzylic}$), 3.13 (m, 4H, CH_2-NH-), 4.51 (q, 4H, J = 9.3 Hz, $CH_{2\ ester}$ + NH), 7.40 (d, 2H, J = 9.3 Hz, $H_{aromatic}$), 7.79 (d, 2H, J = 9.3 Hz, $H_{aromatic}$), 7.94 (s, 2H, $H_{aromatic}$), 8.05 – 8.40 (m, 9H, H_{pyrene}).
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.36, 28.60, 30.96, 31.30, 40.15, 60.96, 79.00, 124.59, 124.78, 124.84, 124.88, 125.00, 125.11, 125.97, 127.06, 127.34, 127.43, 127.71, 128.24, 128.34, 129.01, 129.59, 130.52, 130.59, 130.86, 131.36, 136.95, 137.94, 140.16, 140.41, 145.48, 155.83, 166.63.
MS (+FAB, CH_2Cl_2/DMSO/MNBA): m/z (%) = 740 (50.8), [M^+], 566 (11.6), [M^+ – $C_8H_{14}O_4$], 465 (12.7), [M^+ – $C_{13}H_{23}O_6$], 539 (11.3), [M^+ - pyrene], 538 (14.2), [M^+ – $C_{10}H_{18}O_4$].
$C_{47}H_{52}N_2O_6$ (740.86) calcd C 76.19, H 7.07, N 3.78, found C 75.65, H 7.14, N 3.44.
HRMS ($^{12}C_{47}{}^1H_{52}{}^{14}N_2{}^{16}O_6$) [$M^+$] 740.382538 found 740.38452.

[2,6-Bis-(3-tert-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl] acetic acid ethyl ester (42)

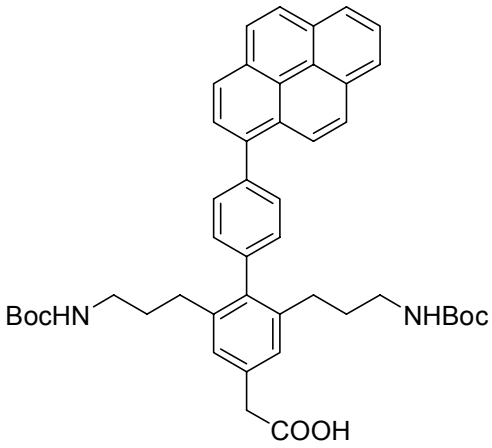


For preparation see general procedure for SCC 2:

Ally amine **40** (4.2 g, 26.70 mmol), 9-BBN (4.1 g, 33.40 mmol), dry THF (20 ml); xylene (25 ml), dibromo ester **39** (1.0 g, 1.70 mmol), KOH (25 ml, c = 1 mol/l), tetrakis(triphenylphosphine)palladium(0) (81.0 mg, 0.07 mmol), 2 d.
Chromatographic separation through silica gel with first hexane:acetic acid ethyl ester 7:1 and later changed to 3:1 gave the product **42** (0.98 g, 1.30 mmol, 76 %) as a yellow fluorescent oil. Freeze drying in benzene gave product **42** as a colorless solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.31 (t, 3H, J = 9 Hz, CH_3), 1.39 (s, 18H, $CH_{3\ Boc}$), 1.69 (tt, 4H, J = 9 Hz, CH_2), 2.50 (t, 4H J = 9 Hz, $CH_{2\ benzylic}$), 3.04 (m, 4H, CH_2N), 3.65 (s, 2H, $CH_{2\ benzylic}$), 4.22 (q, 2H, J = 9 Hz, $CH_{2\ ester}$), 4.48 (s, 2H, NH), 7.10 (s, 2H, $H_{aromatic}$), 7.33 (d, 2H, J = 9 Hz, $H_{aromatic}$), 7.69 (d, 2H, J = 9 Hz, $H_{aromatic}$), 7.93 - 8.34 (m, 9H, H_{pyrene}).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.07, 28.20, 30.86, 31.22, 40.11, 40.93, 60.72, 78.77, 124.46, 124.68, 124.78, 124.95, 125.82, 127.22, 127.51, 127.60, 128.25, 129.48, 130.27, 130.41, 130.77, 131.25, 133.12, 137.07, 138.45, 139.44, 139.62, 140.06, 155.77, 171.59.
MS (EI, 80 eV, 230 °C): m/z (%): 754 (100) [M^+], 680 (62.3) [$M^+ - C_4H_{10}O$], 624 (34.4) [$M^+ - C_6H_{12}NO_2$], 553 (6.0) [$M^+ - C_{16}H_9$].
$C_{48}H_{54}N_2O_6$ (754.96) calcd C 76.36, H 7.21, N 3.71, found C 75.85, H 7.08, N 3.57.
HRMS ($^{12}C_{48}{}^{1}H_{54}{}^{16}O_6{}^{14}N_2$) [$M^+$] calcd. 754.398188, found 754.39508.

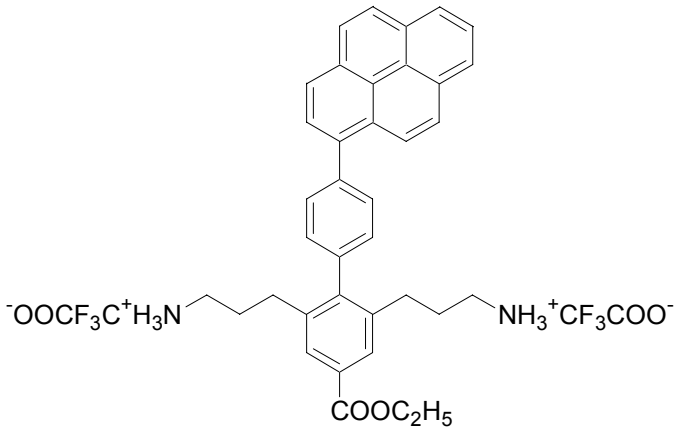
[2,6-Bis-(3-tert-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-acetic acid (43)



The G1 ester **42** (0.70 g, 0.93 mmol) was suspended in methanol (15 ml). KOH (0.156 g, 0.93 mmol) and 5 drops of water were added. To give a clear solution the mixture was refluxed for 2 h. The solvent was removed by distillation and the residue was dissolved in CH_2Cl_2 (25 ml) and water (25 ml). Acetic acid (0.10 g, 1.67 mmol) was added. The phases were separated and the aqueous one was extracted with CH_2Cl_2 two times (50 ml). The combined organic phases were dried ($MgSO_4$) and the CH_2Cl_2 was removed. Chromatographic separation through silica gel with first CH_2Cl_2 and later CH_2Cl_2:methanol 5:1 gave the product **43** as a colorless solid (0.594 g, 0.817 mmol, 88%). R_f (CH_2Cl_2:methanol 5:1) = 0.58.

^{1}H NMR (270 MHz, CD_3OD): δ = 1.24 (s, 18H, H_{Boc}), 1.57 (tt, 4H, CH_2), 2.34 (t, 4H, $CH_{2\ benzylic}$), 2.87 (t, 4H, CH_2-NH), 3.57 (s, 2H, $CH_{2\ benzylic}$), 7.03 (s, 2H, $H_{aromatic}$), 7.17 (d, 2H, $H_{aromatic}$), 7.45 (d, 2H, $H_{aromatic}$), 7.79 - 8.17 (m, 9H, H_{pyrene}).
^{13}C NMR (62.9 MHz, $CDCl_3/CD_3OD$): δ = 27.35, 30.40, 30.62, 37.47, 42.80, 78.29, 123.90, 124.07, 124.16, 124.28, 124.30, 125.27, 126.63, 126.90, 126.95, 127.18, 127.73, 129.12, 129.70, 130.03, 130.33, 130.86, 135.09, 136.58, 138.42, 138.45, 139.13, 139.29, 156.31, 157.55.
MS (EI, 80 eV, 230 °C) m/z = 681 (0.3) [M^+ – COOH], 44 (95.6) [CO_2^+].
MS (+FAB, MNBA/CH_2Cl_2) m/z = 727 (0.26) [M + H]$^+$.

2,6-Bis-(3-amino-propyl)-4'-pyren-1-yl-biphenyl-4-carboxylic acid ethyl ester bis trifluoroacetate (44)



The procedure was analogous to the one described for compound **45** preparation.

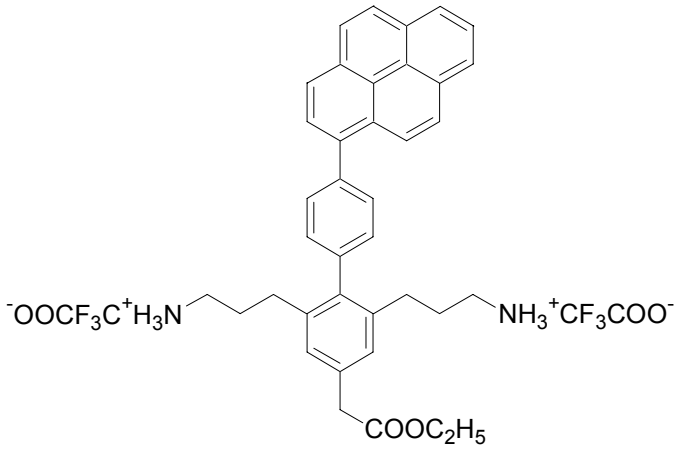
41 (85.0 mg, 0.115 mmol), $CHCl_3$ (5 ml), CF_3COOH (1 ml), 1 h, yielded in **44** (78.6 mg, 0.100 mmol, 89 %).

^1H NMR (270 MHz, CD_3OD): δ = 1.41 (t, 3H, CH_3), 1.88 (tt, 4H, CH_2), 2.62 (t, 4H, $H_{benzylic}$), 2.85 (t, 4H, CH_2), 4.43 (q, 2 H, H_{ester}), 7.37 (d, 2H, $H_{aromatic}$), 7.74 (d, 2H, $H_{aromatic}$), 7.97 – 8.34 (m, 11H, $H_{Pyrene + aromatic}$).

^{13}C NMR (62.9 MHz, CD_3OD) δ = 14.65, 30.02, 31.65, 40.48, 62.36, 114.79, 125.74, 125.93, 126.09, 126.22, 126.51, 127.38, 128.47, 128.73, 128.83, 129.14, 129.59, 130.46, 130.82, 131.35, 132.05, 132.32, 132.95, 138.12, 139.03, 141.18, 142.08, 147.24, 167.92.

MS (+FAB, DMSO/MNBA) m/z (%) = 541 (100) [M^+-CF_3COOH/CF_3COO^-].

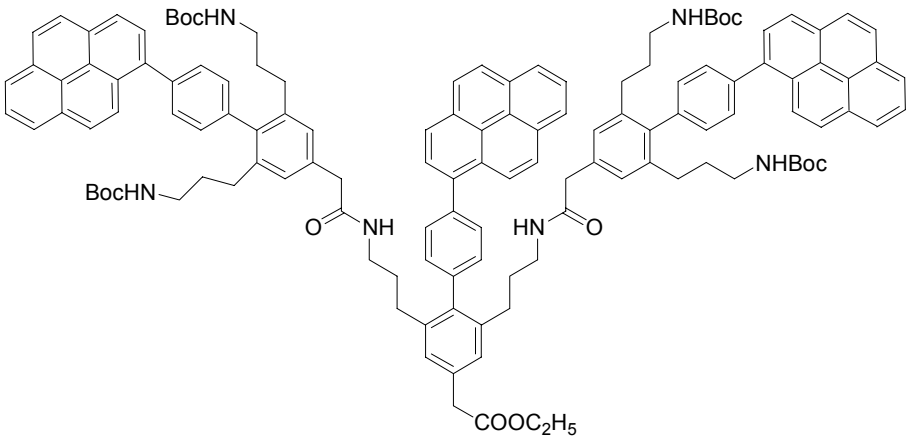
[2,6-Bis-(3-amino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-acetic acid ethyl ester bis trifluoroacetate (45)



Di-boc protected ester **42** (0.111 g, 0.147 mmol) was dissolved in chloroform (7 ml), trifluoroacetic acid was added (1 ml), and the color turned from pale yellow to orange. The solution was stirred for 1 h at room temperature. The solvents were removed through distillation. Freeze drying of the residue gave the product **45** (101 mg, 0.129 mmol, 88 %) as a brown solid.

^{1}H MNR (270 MHz, CD_3OD) δ = 1.24 (t, 3H, CH_3), 1.82 (tt, 4H, CH_2), 2.53 (t, 4H, $CH_{2\ benzylic}$), 2.81 (t, 4H, CH_2NH), 3.67 (s, 2H, $CH_{2\ benzylic}$), 4.17 (q, 2H, CH_2CH_3), 7.15 (s, 2H, $CH_{2\ aromatic}$), 7.34 (d, 2H, $CH_{2\ aromatic}$), 7.67 (d, 2H, $CH_{2\ aromatic}$), 7.86-8.29 (m, 9H, H_{pyrene}).
^{13}C NMR (62.9 MHz, CD_3OD) δ = 14.54, 29.99, 31.57, 40.43, 41.64, 62.05, 125.84, 125.94, 126.09, 126.32, 127.21, 128.38, 128.53, 128.67, 129.26, 129.48, 130.93, 131.76, 132.06, 132.22, 132.80, 135.36, 138.25, 139.62, 140.49, 141.00, 141.44, 173.62 ppm.
MS (+FAB) m/z = 555 (100) [M^+ - CF_3CO_2H/CF_3COO^-], 510 (9.3) [M^+ - $CF_3CO_2H/CF_3COO^{-}C_2H_5O$].

[2,6-Bis-[(3-{2[2,6-bis-(3-tert-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]ethanoylamino}-propyl)4'-pyren-1-yl-biphenyl-4-yl]-acetic acid ethyl ester (50)

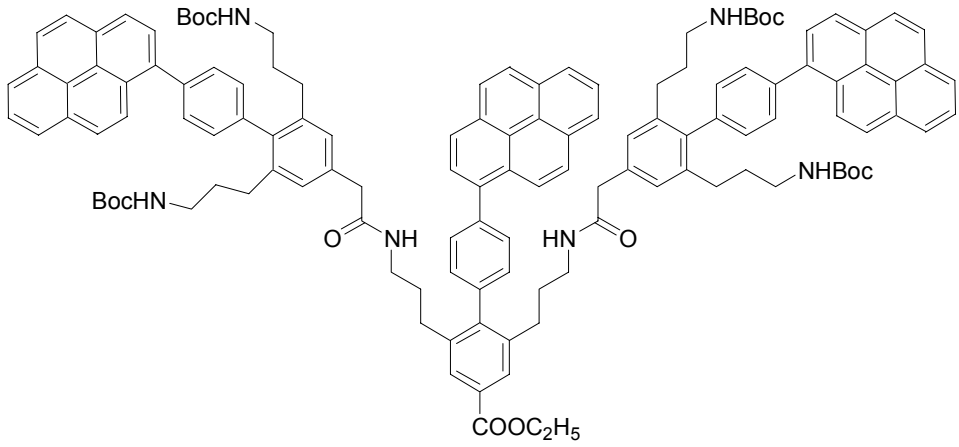


For preparation see general procedure for amide coupling

G1 acid **43** (125.0 mg, 0.172 mmol), dry methylene chloride (20 ml), 1-hydroxybenzotriazole (HOBT) (29.0 mg, 0.189 mmol), diisopropyl ethylamine (DIPEA) (47.2 µl, 35.0 mg, 0.271 mmol), amine **45** (64.1 mg, 0.082 mmol), N'-(3-dimethylaminopropyl)-N-ethyl-carbodiimide hydrochloride (EDC) (36.3 mg, 0.189 mmol), 15 h at 25 °C.
Chromatographic separation with silica gel and hexane:acetic acid ethyl ester 1:2 and freeze drying gave the product **50** (122.0 mg, 0.062 mmol, 75 %) as a colorless solid. R_f = 0.23.

^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.17 - 1.43 (m, 39H, H_{boc} + $CH_{3\ ester}$), 1.55 (tt, 8H, CH_2), 1.74 (tt, 4H, CH_2), 2.38 (t, 8H, $CH_{2\ benzylic}$), 2.48 (t, 4H, $CH_{2\ benzylic}$), 2.94 (m, 8H, CH_2N), 3.21 (m, 4H, CH_2N), 3.45 (s, 4H, $CH_{2\ benzylic}$), 3.65 (s, 2H, $CH_{2\ benzylic}$), 4.21 (q, 2H, $CH_{2\ ester}$), 4.34 (m, 4H, NH), 5.77 (m, 2H, NH), 6.94 (s, 4H, $H_{aromatic}$), 7.10 (s, 2H, $H_{aromatic}$), 7.24 (d, 4H, $H_{aromatic}$), 7.38 (d, 2H, $H_{aromatic}$), 7.60 (d, 4H, $H_{aromatic}$), 7.72 (d, 2H, $H_{aromatic}$), 7.93-8.38 (m, 27H, H_{pyrene}).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 13.97, 28.07, 30.49, 30.70, 30.80, 30.90, 39.25, 39.70, 40.72, 43.26, 60.67, 78.52, 124.31, 124.47, 124.57, 124.65, 124.77, 125.65, 127.04, 127.33, 127.41, 128.01, 129.25, 129.46, 130.07, 130.20, 130.28, 130.55, 131.03, 132.98, 134.14, 136.68, 136.81, 138.15, 138.43, 139.22, 139.36, 139.91, 155.66, 170.83, 171.63.
MS (+FAB) m/z = 1973 (7.1) [M^++H].
$C_{130}H_{134}N_6O_{12}$ (1972.52) calcd C 79.16, H 6.85, N 4.26, found C 79.24, H 7.06, N 3.91.

2,6-Bis(3-{2[2,6-bis-(3-tert-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]ethanoylamino}-propyl)4'-pyren-1-yl-biphenyl-4-carboxylic acid ethyl ester (51)

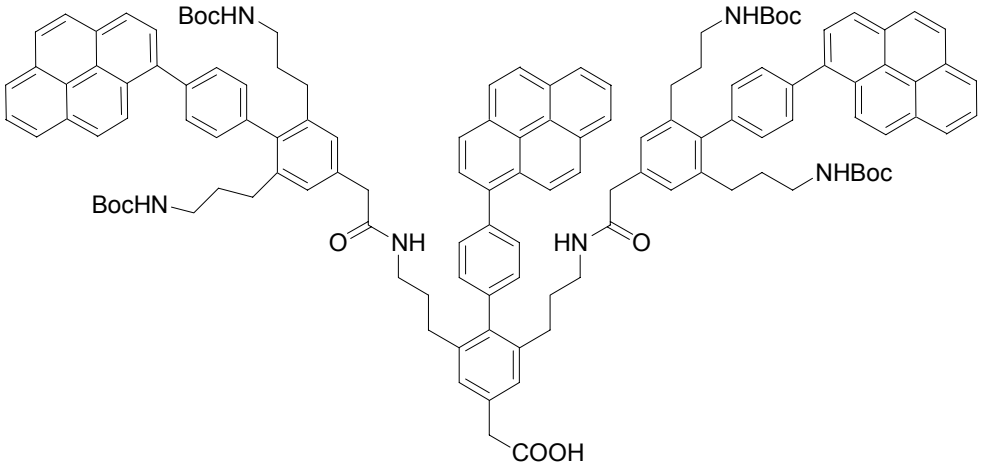


For preparation see general procedure for amide coupling:

Acid **43** (0.12 g, 0.165 mmol), dry CH_2Cl_2 (20 ml), HOBT (34 mg, 0.25 mmol), 15 min, amine **44** (60.5 mg, 0.08 mmol), DIPEA (50 µl, 0.26 mmol), 30 min, EDC (36 mg, 0.182 mmol), 15 h stirring, chromatographic separation with silica gel and hexane:acetic acid ethyl ester 1:2 yielded in **51** (84 mg, 0.043 mmol, 54 %) R_f = 0.31.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.15-1.38 (m, 36 H, $H_{boc + ester}$), 1.45 (t, 3H, CH_3), 1.55 (tt, 8H, CH_2), 1.75 (tt, 8H, CH_2), 2.39 (t, 4H, CH_2), 2.53 (tt, 4H, CH_2), 2.96 (m, 8H, CH_2), 3.21 (t, 4H, CH_2), 3.42 (s, 4H, $H_{benzylic}$), 4.39–4.49(m, 6H, NH + CH_2), 5.75–5.90 (s, 2H, NH), 6.97 (s, 4H, $H_{aromatic}$), 7.24 (d, 4H, $H_{aromatic}$), 7.35 (d, 2H, $H_{aromatic}$), 7.60 (d, 4H, $H_{aromatic}$), 7.75 (d, 2H, $H_{aromatic}$), 7.84 (s, 2H, $H_{aromatic}$), 7.90–8.34 (m, 27H, H_{pyrene}).
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.43, 28.29, 30.71, 31.04, 31.11, 39.44, 39.89, 43.69, 61.07, 78.95, 124.59, 124.81, 124.90, 124.97, 125.09, 125.24, 125.97, 126.07, 127.37, 127.61, 127.72, 127.87, 128.34, 129.16, 129.52, 129.63, 130.39, 130.54, 130.61, 130.69, 130.88, 131.38, 134.17, 136.77, 137.15, 138.08, 138.34, 139.70, 139.75, 140.16, 140.33, 140.46, 145.52, 155.85, 166.70, 171.05.
MS (+FAB, 2KV, MNBA/CH_2Cl_2/DMSO): m/z (%) = 1957 (0.48) [M^+], 1958 (0.8) [$M+H^+$], 1981.0 (0.3) [$M+Na^+$].
$C_{129}H_{132}N_6O_{12}$ (1956.99) calcd C 79.11, H 6.79, N 4.29, found C 78.14, H 6.50, N 4.26.

[2,6-Bis-(3-{2[2,6-bis-(3-tert-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]ethanoylamino}-propyl)4'-pyren-1-yl-biphenyl-4-yl-]acetic acid (52)

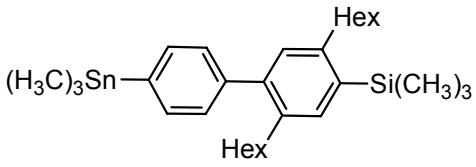


The G2 ester **50** (0.29 g, 0.148 mmol) was dissolved in THF (5 ml) and MeOH (20 ml). KOH (0.57 g, 0.01 mol) and 10 drops of water were added. The mixture was refluxed for 5 h. The solvent was removed through distillation and the residue was dissolved in CH_2Cl_2 (10 ml) and water (25 ml). Acetic acid (1.20 g, 0.02 mol) was added. The phases were separated and the aqueous one was extracted with CH_2Cl_2 (50 ml) two times. The combined organic layers were dried ($MgSO_4$) and the CH_2Cl_2 was removed. Freeze drying with benzene gave the product **52** (0.27 g, 0.141 mmol, 95 %) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.32 (s, 36H, H_{boc}), 1.5-1.67 (m, 8H, CH_2), 1.67-1.81 (m, 4H, CH_2), 2.28-2.68 (m, 12H, CH_2), 2.68-3.10 (m, 8H, CH_2N), 3.10-3.31 (m, 4H, CH_2N), 3.46 (s, 4H, $CH_{2\ benzylic}$), 3.71 (s, 2H, $CH_{2\ benzylic}$), 4.28-4.50 (s, 4H, NH), 5.76 (s, 2H, NH), 6.88-7.15 (m, 6H, $H_{aromatic}$), 7.25-7.40 (m, 4H, $H_{aromatic}$), 7.53-7.80 (m, 8H, $H_{aromatic}$), 7.80-8.34 (m, 27H, H_{pyrene}).
^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 28.33, 30.74, 31.08, 39.59, 39.91, 43.70, 79.05, 124.64, 124.85, 124.93, 125.13, 126.03, 127.41, 127.75, 128.08, 128.37, 129.56, 129.74, 130.44, 130.57, 130.91, 131.42, 134.37, 137.17, 138.39, 139.76, 140.32, 155.88, 156.0, 171.07.
MS (+FAB, 2KV, MNBA/$CHCl_3$) m/z (%) = 1945 (100) [M^++H].

7.4 Synthesis of compounds from chapter 4.4

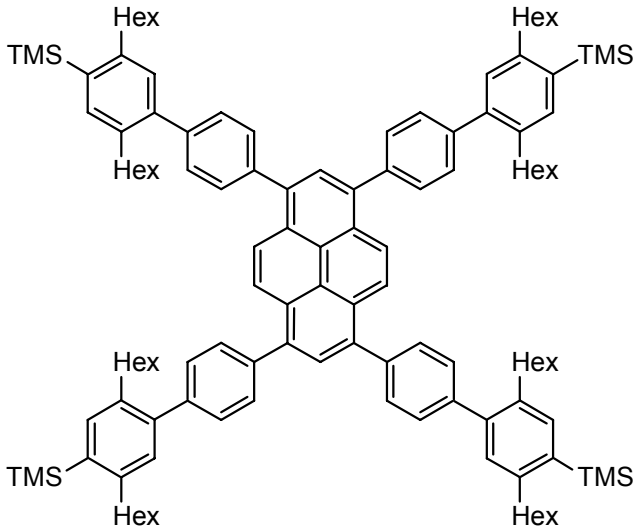
(2,5 Dihexyl-4'-trimethyl stannanyl-biphenyl-4-yl-)trimethyl-silane (54)



Sodium powder (6g, 151 mmol) was suspended in abs. DMF. At 0 °C a solution of trimethylstannanyl chloride (10.00 g, 50.2 mmol) in abs. DMF (20 ml) was added dropwise in 15 min. The reaction mixture was stirred for 12 h at room temperature and the color turned from grey to green. The mixture was filtrated under N_2. To the filtrate a solution of Br-biphenyl **53** (9.37g, 19.8 mmol) dissolved in abs. DMF (30 ml) was dropped within 30 min at 0 °C. NaBr started to precipitate immediately; the color changed from green to colorless. The mixture was stirred for 12 h at room temperature.
An aqueous solution of KF (20 ml, c = 2 mol/l) was added to the reaction mixture. After filtration of the precipitate, the organic layer was separated and dried ($MgSO_4$). The DMF was removed by distillation. The product **54** is a colorless oil (9.20 g, 16.5 mmol, 83.3 %).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.36 (s, 9H, CH_3-Sn), 0.43 (s, 9H, CH_3-Si), 0.93 (t, J = 9.3 Hz, 3H, CH_3), 1.00 (t, J = 9.3 Hz, 3H, CH_3), 1.09-1.83 (m, 16H, CH_2), 2.62 (t, J = 9.3 Hz, 2H, $CH_{2\ benzylic}$), 2.91 (t, J = 9.3 Hz, 2H, $CH_{2\ benzylic}$), 7.12 (s, 1H, $H_{aromatic}$), 7.38 (d, J = 9.3 Hz, 2H, $H_{aromatic}$), 7.45 (s, 1H, $H_{aromatic}$), 7.60 (d, J = 9.3 Hz, 2H, $H_{aromatic}$).
MS (EI, 80 eV, 60 °C): m/z (%) = 473 (22.7) [M^+ -C_6H_{13}], 400 (34.1) [M^+ -C_6H_{13}-$Si(CH_3)_3$], 393 (20.3) [M^+ -$Sn(CH_3)_3$], 388 (9.4) [M^+ –$C_{12}H_{26}$], 320 (9.8) [M^+ -$Sn(CH_3)_3$-$Si(CH_3)_3$], 235 (13.5) [M^+ -$Sn(CH_3)_3$-TMS-Hex], 73 (100) [TMS^+].

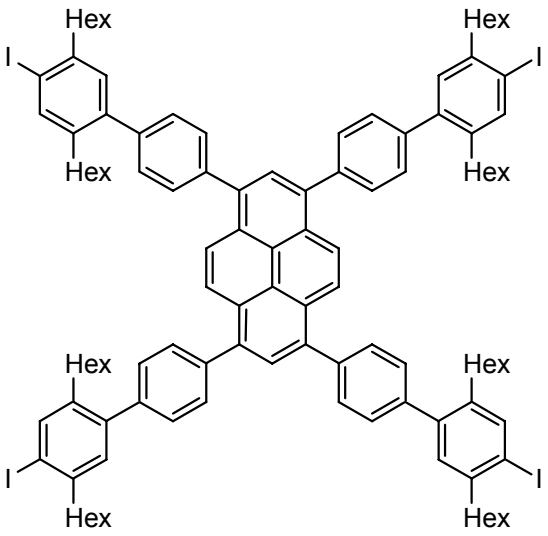
1,3,6,8-Tetrakis-(2',5'-dihexyl-4'-trimethylsilanyl-biphenyl-4-yl)-pyrene (55)



Tetrabromopyrene **13** (1.60 g, 3.08 mmol) and stannanylbiphenyl **54** (8.60 g, 15.4 mmol) were dissolved in toluene (100 ml). The mixture was degassed and flushed with N_2 three times. Then tetrakis(triphenylphosphine)palladium(0) (0.28 g, 0.242 mmol) was added under N_2 and the mixture was degassed and flushed with N_2 three times again. The mixture was refluxed for 2 d, the color changed from yellow to blue. Then an aqueous solution of KF (20 ml, c = 2 mol/l) was added, the precipitate was removed, and the layers were separated. The aqueous layer was washed with toluene (20 ml). The combined organic layers were dried ($MgSO_4$) and the toluene removed. Recrystallization with diethyl ether gave the product **55** (2.10 g, 1.18 mmol, 38 %) as a yellow solid.
Melting point: 207-209 °C

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.55 (s, 36H, CH_3-Si), 1.00 (t, J = 9.3 Hz, 12H, CH_3), 1.10 (t, J = 9.3 Hz, 12H, CH_3), 1.21-1.97 (m, 64H, CH_2), 2.86 (t, J = 9.3 Hz, 8H, CH_2 $_{aromatic}$), 2.93 (t, J = 9.3 Hz, 8H, CH_2 $_{aromatic}$), 7.36 (s, 4H, $H_{aromatic}$), 7.59 (s, 4H, $H_{aromatic}$), 7.69 (d, J = 8.3 Hz, 8H, $H_{aromatic}$), 7.90 (d, J = 8.3 Hz, 8H, $H_{aromatic}$), 8.33 (s, 2H, H_{pyrene}), 8.52 (s, 4H, H_{pyrene}).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.64 (s, CH_3-Si), 14.16 (s, CH_3-CH_2), 22.62, 22.66, 29.33, 29.76, 31.62, 31.87, 32.15, 32.62, 32.86, 36.07, 125.48, 126.19, 128.29, 129.25, 130.32, 130.73, 135.79, 136.37, 136.68, 137.42, 139.48, 141.52, 142.21, 146.07.
MS (EI, 80 eV, 250-300 °C): m/z (%) = 1771 (67.1) [M^+], 1698 (6.7) [M^+- $Si(CH_3)_3$], 73 (19.7) [$Si(CH_3)_3^+$].
$C_{124}H_{170}Si_4$ (1773.05) calcd C 84.00 H 9.66, found C 83.83 H 9.61.

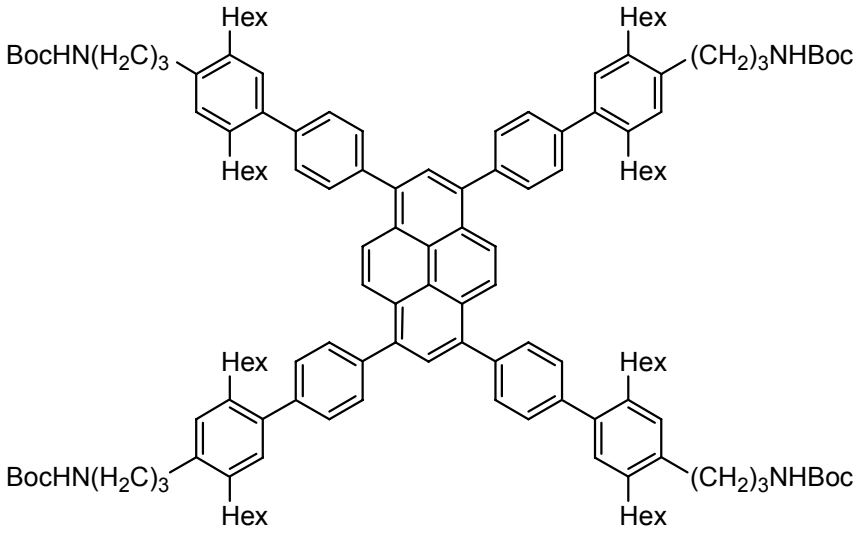
1,3,6,8-Tetrakis-(2',5'-dihexyl-4'iodo-biphenyl-4-yl-)pyrene) (56)



Core **55** (1.00 g, 0.56 mmol) was dissolved in abs. CH_2Cl_2 (40 ml). To the yellow solution ICl (0.55g, 3.38 mmol) in abs. CH_2Cl_2 (20 ml) was dropped in within 1h at –78 °C. The color changed from yellow to dark blue. The mixture was stirred for 1h at –78 °C. Then the mixture was poured into an aqueous solution of sodium disulphite (100 ml, c = 1 mol/l) under vigorous stirring. The layers were separated, the aqueous one was washed two times with CH_2Cl_2 (60 ml). The combined organic layers were dried ($MgSO_4$), the CH_2Cl_2 was removed. The yellow product **56** (1.07 g, 0.54 mmol, 96 %) was recrystallized in diethyl ether.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.79 (t, J = 9 Hz, 12H, CH_3), 0.90 (t, J = 9 Hz, 12H, CH_3), 1.07-1.76 (m, 64H, CH_2), 2.59 (t, J = 9 Hz, 8H, $CH_{2\ benzylic}$), 2.71 (t, J = 9 Hz, 8H, $CH_{2\ benzylic}$), 7.14 (s, 4H, $H_{aromatic}$), 7.48 (d, J = 9 Hz, 8H, $H_{aromatic}$), 7.72 (d, J = 9 Hz, 8H, $H_{aromatic}$), 7.76 (s, 4H, $H_{aromatic}$), 8.12 (s, 2H, H_{pyrene}), 8.31 (s, 4H, H_{pyrene}).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.10, 22.53, 22.62, 29.13, 30.37, 31.27, 31.51, 31.67, 32.28, 40.39, 99.60, 125.42, 128.23, 129.10, 130.40, 130.73, 137.04, 139.68, 139.92, 140.04, 140.25, 141.59, 142.68.
MS (EI, 80 eV, 380 °C): m/z (%) = 1987 (85.5) [M^+], 1860 (22.5) [M^+-I), 1733 (3.7) [M^+-2I].
$C_{112}H_{134}I_4$ (1987.89) calcd C 67.67 H 6.79, found C 67.50 H 6.62.
Melting point: 151 °C

1,3,6,8 Tetrakis-[4'(3-tert-butoxycarbonylamino-propyl)-2',5'-dihexyl-biphenyl-4-yl)-pyrene (57)

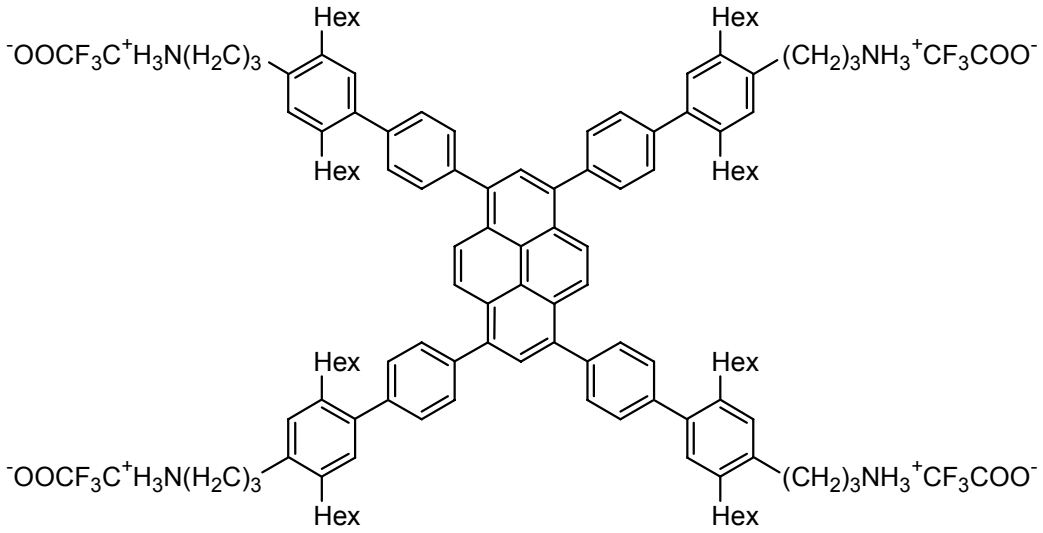


For preparation see general procedure for SCC 2:

Allylamine **40** (2.64 g, 16.8 mmol), 9-BBN (2.46 g, 20.16 mmol), abs. THF (20 ml), 100 ml toluene and 50 ml aqueous KOH (c = 1 mol/l), Tetraiodocore **56** (3.36 g, 1.69 mmol), tetrakistriphenylphoshinepalladium(0) (155 mg, 0.134 mmol), refluxed for 2 days. Chromatographic separation with silica gel, hexane:acetic acid ethyl ester 3:1 gave the product **57** (2.64 g, 1.25 mmol, 74 %) as yellow solid. R_f = 0.11.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.77 (t, 12H, CH_3), 0.86 (t, 12H, CH_3), 1.10-1.72 (m, 100H, $CH_{3\ boc}$ + CH_2), 1.96 (m, 8H, CH_2), 2.63 (m, 24H, $CH_{2\ benzylic}$), 3.24 (s, 8H, CH_2), 4.61 (s, 4H, NH), 7.10 (s, 4H, $H_{aromatic}$), 7.12 (s, 4H, $H_{aromatic}$), 7.50 (d, 8H, $H_{aromatic}$), 7.74 (d, 8H, $H_{aromatic}$), 8.15 (s, 2H, H_{pyrene}), 8.31 (s, 4 H, H_{pyrene}).
^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.99, 22.50, 26.71, 27.53, 28.29, 29.12, 29.41, 29.56, 29.86, 31.15, 31.45, 31.64, 32.19, 32.62, 40.48, 41.69, 78.76, 125.29, 126.03, 128.08, 129.21, 129.57, 129.90, 130.11, 130.79, 137.05, 137.58, 137.66, 138.26, 139.05, 141.07, 155.86.
MS (+FAB, CH_2Cl_2/MNBA) m/z (%) = 2113 (100) [M^++H], 2057 (32.0) [M^+-C_4H_8], 2038 (17.0) [M^+-$C_4H_{10}O$], 1957 (3.3) [M^+-$C_8H_{14}O_2N$].
$C_{144}H_{198}N_4O_8$ (2113.17) calcd C 81.85 H 9.44 N 2.65, found C 81.69 H 9.46 N 2.55.

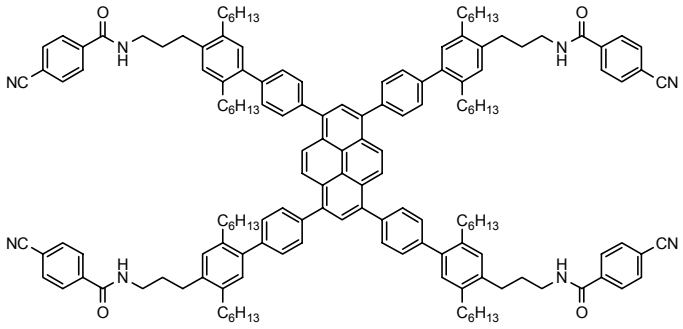
1,3,6,8-Tetrakis-(4'[3-aminopropyl]-2',5'-dihexyl-biphenyl-4-yl)-pyrene tetra trifluoroacetate (58)



Boc protected core **57** (2.0 g, 0.946 mmol) was dissolved in $CHCl_3$ (50 ml). Trifluoracetic acid was added (6 ml) and the solution was stirred for 3 h at room temperature. Solvents were removed and crude product **58** (1.7 g, 0.918 mmol, 97 %) was freeze dried with dioxane.

^{1}H NMR (270 MHz, DMSO): δ = 0.69 (m, 12H, CH_3), 0.82 (m, 12H, CH_3), 0.89-1.62 (m, 64H, CH_2), 1.82 (m, 8H, CH_2), 2.45 (m, 24H, CH_2), 2.86 (m, 8H, CH_2), 7.00 (s, 4H, $H_{aromatic}$), 7.09 (s, 4H, $H_{aromatic}$), 7.36 (d, 4H, $H_{aromatic}$), 7.58 (d, 8H, $H_{aromatic}$), 7.84 (m, 12H, NH_3^+), 8.00 (s, 2H, H_{pyrene}), 8.15 (s, 4H, H_{pyrene}).
^{13}C NMR (125.8 MHz, DMSO) δ = 13.45, 13.52, 14.02, 21.68, 21.82, 28.03, 28.31, 28.51, 29.75, 30.42, 30.61, 30.96, 31.27, 31.94, 38.74, 118.23, 124.51, 125.34, 127.32, 128.66, 129.51, 130.08, 136.48, 136.90, 137.23, 137.52, 138.12, 138.47, 140.49, 158.54, 158.78.
MS (+FAB, DMSO/MNBA) (%) m/z = 1713 (100) [M^++H-$C_8F_{12}O_8H_4$].
$C_{132}H_{170}F_{12}N_4O_8$ (2168.72) calcd C 73.11 H 7.90 N 2.58, found C 72.96 H 7.85 N 2.41.

1,3,6,8-Tetrakis-{4'-[3-(4-cyano-benzoylamino)-propyl]-2',5'-dihexyl-biphenyl-4-yl}-pyrene (61)

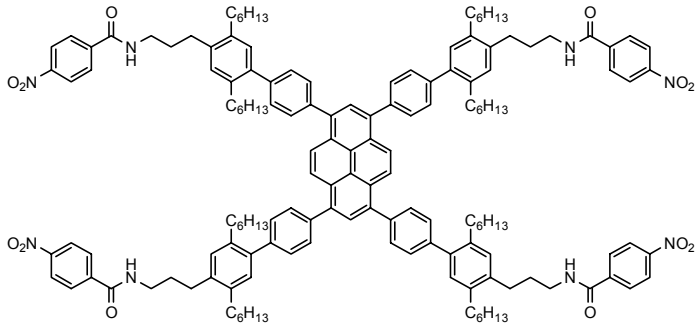


For preparation see general procedure for amide coupling.

Cyano-benzoic acid **59** (149 mg, 1.01 mmol), HOBT (169 mg, 1.10 mmol), dry CH_2Cl_2 (25 ml), tetra amine core **58** (500 mg, 0.23 mmol), DIPEA (300 mg, 2.30 mmol), EDC (212 mg, 1.10 mmol), 1 d. Chromatographic separation with silica gel and CH_2Cl_2:2 % MeOH gave the product **61** (250 mg, 0.112 mmol, 49 %) as a yellow solid. R_f = 0.52.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.87 (t, 12H, CH_3), 0.89 (t, 12H, CH_3), 0.91 – 1.70 (m, 64H, CH_2), 2.06 (quin, 8H, CH_2), 2.50 – 3.00 (m, 24H, CH_2), 3.64 (m, 8H, CH_2), 6.71 (t, 4H, NH), 7.18 (s, 4H, $H_{aromatic}$), 7.20 (s, 4H, $H_{aromatic}$), 7.53 (d, 8H, $H_{aromatic}$), 7.68 – 7.90 (m, 24H, $H_{aromatic}$), 8.23 (s, 2H, H_{pyrene}), 8.41 (s, 4H, H_{pyrene}).
^{13}C NMR (68 MHz, $CDCl_3$): δ = 13.97, 22.41, 22.48, 28.29, 29.12, 29.40, 29.97, 30.63, 31.14, 31.43, 31.45, 31.60, 32.24, 32.63, 40.38, 114.68, 117.88 (CN), 125.30, 126.01, 127.51, 128.09, 129.17, 129.57, 129.90, 130.21, 131.00, 132.18, 136.97, 137.76, 137.87, 137.92, 138.48, 139.25, 139.31, 140.82, 165.51.
MS (EI, 350 °C, 80 eV): m/z (%) = 2228 (0.7) [M^+], 2055 (4.7) [M^+-$C_{10}H_9N_2O$].
EA $C_{156}H_{178}N_8O_4$ (2229.17) calcd C 84.05 H 8.05 N 5.03, found C 83.94 H 8.07 N 4.78.
Melting point: 177 – 182 °

1,3,6,8-Tetrakis-{2',5'-dihexyl-4'-[3-(4-nitro-benzoylamino)-propyl]-biphenyl-4-yl}-pyrene (62)

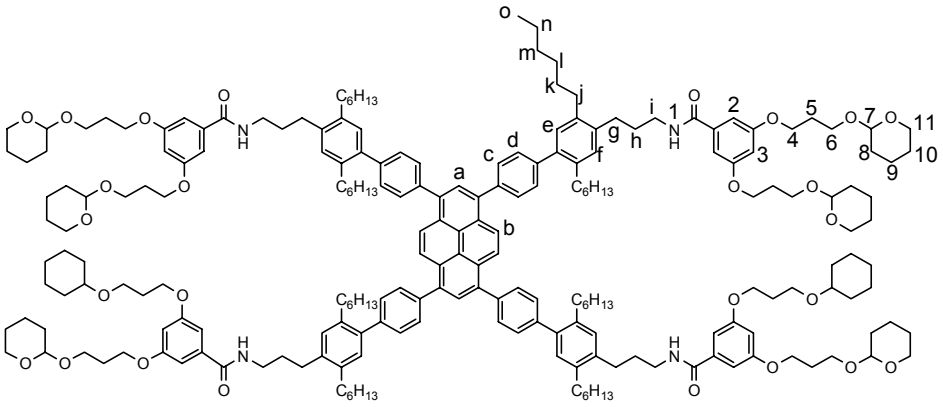


For preparation see general procedure for amide coupling.

Nitro-benzoic acid **60** (169 mg, 1.10 mmol), HOBT (169 mg, 1.10 mmol), dry CH_2Cl_2 (25 ml), tetra amine core **58** (500 mg, 0.23 mmol), DIPEA (300 mg, 2.30 mmol), EDC (212 mg, 1.10 mmol), 2 d. Chromatographic separation with silica gel and CH_2Cl_2:2 % MeOH and freeze drying with benzene gave the product **62** (200 mg, 0.087 mmol, 38 %) as a yellow solid. R_f = 0.58.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, 12H, CH_3), 0.86 (t, 12H, CH_3), 0.11 – 1.72 (m, 64H, CH_2), 2.05 (quin, 8H, CH_2), 2.54 – 2.72 (m, 16H, CH_2), 2.80 (m, 8H, CH_2), 3.64 (m, 8H, CH_2), 6.18 (t, 4H, NH), 7.03 (s, 4H, $H_{aromatic}$), 7.05 (s, 4H, $H_{aromatic}$), 7.47 (d, 8H, $H_{aromatic}$), 7.76 (d, 8H, $H_{aromatic}$), 7.81 (d, 8H, $H_{aromatic}$), 8.17 (s, 2H, H_{pyrene}), 8.24 (d, 8H, $H_{aromatic}$), 8.35 (s, 4H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.00, 22.47, 22.54, 29.18, 29.47, 30.14, 30.64, 31.21, 31.50, 31.67, 32.31, 32.70, 40.56, 123.66, 125.38, 126.09, 127.95, 128.19, 129.23, 129.65, 130.00, 130.30, 131.13, 137.05, 137.88, 137.97, 138.01, 139.39, 139.48, 140.18, 140.86, 149.42, 165.26. (2 signals missing)
MS (+FAB, $CHCl_3$/MNBA): m/z (%) = 2309 (100) [M^++H].
EA $C_{152}H_{178}N_8O_{12}$ (2309.13) calcd C 79.06 H 7.77 N 4.85, found C 78.99 H 7.63 N 4.62.

1,3,6,8-Tetrakis-[4'-(3-{3,5-bis-[3-(tetrahydro-pyran-2-yloxy)-propoxy]-benzoylamino}-propyl)-2',5'-dihexyl-biphenyl-4-yl]-pyrene (65)



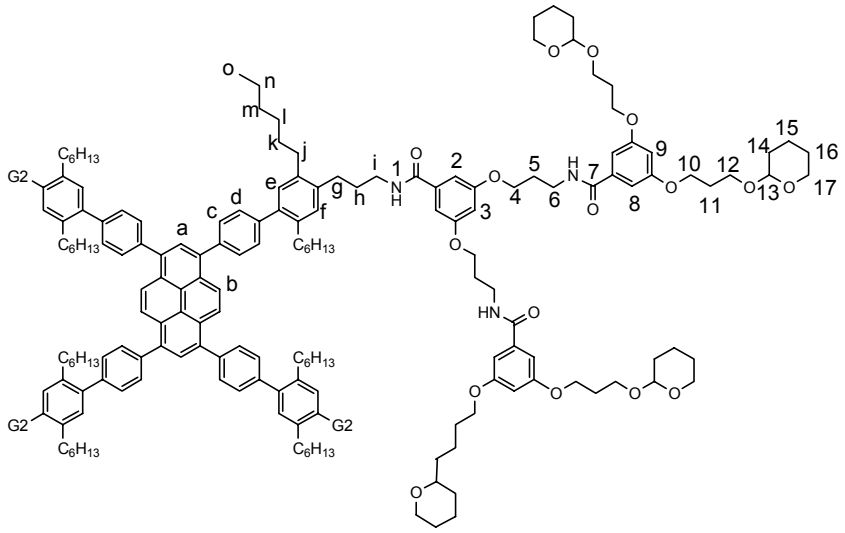
For preparation see general procedure for amide coupling.

G1-acid **63** (85.1 mg, 0.194 mmol), HOBT (27.4 mg, 0.203 mmol), dry CH_2Cl_2 (20 ml), DIPEA (50.1 mg, 0.387 mmol), tetra-amine-core **58** (92.0 mg, 0.042 mmol), EDC (38.9 mg, 0.203 mmol), 14 h. Chromatographic separation with silica gel and first MeOH, then MeOH:CH_2Cl_2 5:3 gave dendrimer **65** (96.0 mg, 0.028 mmol, 67 %) as a yellow solid. R_f (MeOH: CH_2Cl_2 5:3) = 0.42

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.83 (t, 12H, o), 0.88 (t, 12H, o‘), 1.03 – 1.87 (m, 112 H, k, k‘, l, l‘, m, m‘, n, n‘, 8, 9, 10), 1.87 – 2.17 (m, 24H, h, 5), 2.63 (m, 16H, j, j‘), 2.75 (m, 8H, g), 3.41 – 3.69 (m, 24H, i, 6, 11), 3.75 – 4.00 (m, 16H, 6‘, 11‘), 4.10 (t, 16H, 4), 4.58 (t, 8H, 7), 6.26 (t, 4H, 1), 6.58 (s, 4H, 3), 6.87 (s, 4H, e/f), 6.89 (s, 4H, e/f), 7.14 (s, 8H, 2), 7.48 (d, 8H, d), 7.74 (d, 8H, c), 8.15 (s, 2H, a), 8.34 (s, 4H, b).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.99, 19.51, 22.53, 25.39, 29.19, 29.46, 29.63, 29.96, 30.63, 31.06, 31.20, 31.51, 31.69, 32.02, 32.10, 32.33, 32.73, 33.14, 40.17, 43.04, 62.24, 63.85, 65.30, 98.92, 104.37, 105.47, 126.13, 127.67, 128.21, 128.54, 129.31, 129.97, 130.17, 130.34, 130.96, 136.89, 137.22, 137.79, 138.14, 139.30, 141.19, 160.27 (Ar-O), 167.33 (C=O).
MALDI-FOF MS m/z = 3395.8 [M+H$^+$
EA $C_{216}H_{294}N_4O_{28}$ (3394.45) calcd C 76.42 H 8.73 N 1.65, found C 75.94 H 8.55 N 1.21.

1,3,6,8-Tetrakis-(4'-{3-[3,5-bis-(3-{3,5-bis-[3-(tetrahydro-pyran-2-yloxy)-propoxy]-benzoylamino}-propoxy)-benzoylamino]-propyl}-2',5'-dihexyl-biphenyl-4-yl)-pyrene (66)

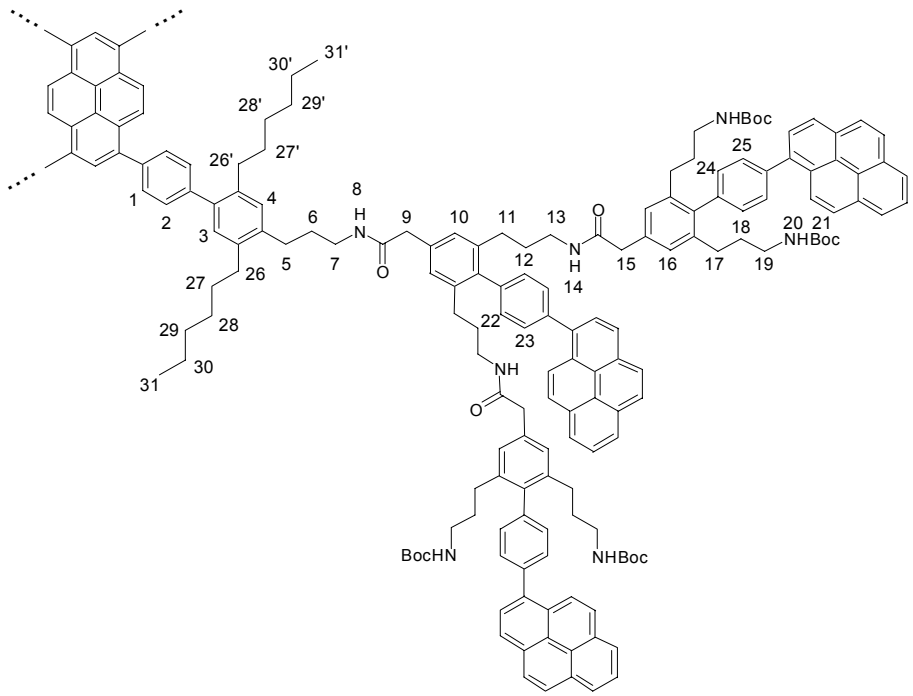


For preparation see general procedure for amide coupling.

G2-acid **64** (307 mg, 0.276 mmol), HOBT (40 mg, 0.295 mmol), dry CH_2Cl_2 (20 ml), DIPEA (74 mg, 0.572 mmol), tetra-amine-core **58** (100 mg, 0.046 mmol), EDC (76 mg, 0.295 mmol), 2 d. Chromatographic separation with silica gel and first MeOH, then MeOH:CH_2Cl_2 5:3 gave dendrimer **67** (120 mg, 0.020 mmol, 43 %) as a yellow solid. R_f (MeOH: CH_2Cl_2 5:3) = 0.41

^{1}H NMR (500MHz, $CDCl_3$): δ = 0.74 (t, 12H, o), 0.80 (t, 12H, o‘), 1.00 – 1.80 (m, 160 H, k, k‘, l, l‘, m, m‘, n, n‘, 14, 15, 16), 1.84 – 2.08 (m, 56H, h, 5, 11), 2.56 (m, 16H, j, j‘), 2.70 (m, 8H, g), 3.30 – 3.55 (m, 56H, i, 6, 12‘, 17‘), 3.55 – 3.87 (m, 32H, 12, 17), 3.98 (m, 48H, 4, 10), 4.49 (m, 16H, 13), 6.45 (s, 4H, 3), 6.49 (s, 8H, 9), 6.60 (s, 4H, 1), 6.75 (s, 8H, 7), 6.83 (s, 24H, 2, 8), 7.03 (s, 4H, e/f), 7.05 (s, 4H, e/f), 7.40 (d, 8H, d), 7.65 (d, 8H, c), 8.08 (s, 2H, a), 8.26 (s, 4H, b).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.02, 19.50, 22.47, 22.53, 25.33, 28.93, 29.19, 29.47, 29.51, 29.84, 30.58, 31.09, 31.17, 31.48, 31.51, 31.68, 32.29, 32.69, 37.57, 40.23, 62.27, 63.81, 65.17, 66.26, 98.91, 104.37, 105.45, 105.67, 128.12, 129.26, 129.60, 129.91, 130.17, 130.85, 136.57, 136.97, 137.06, 137.76, 138.19, 139.14, 141.11, 159.78 (G1:Ar-O), 160.14 (G2:Ar-O), 167.17 (G1:C=O), 167.46 (G2:C=O). (6 signals missing)
MALDI-FOF MS m/z = 6102.52 $[M+Na]^+$
EA $C_{360}H_{494}N_{12}O_{68}$ (6077.27) calcd C 71.14 H 8.19 N 2.77, found C 70.18 H 7.86 N 2.50.

1,3,6,8-Tetrakis-(4'[3-{2-[2,6-bis-(3-{2-[2,6-bis-(3-tert-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-ethanoylamino}-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-ethanoylamino}propyl]-2',5'-dihexyl-biphenyl-4-yl)-pyrene (67)



For preparation see general procedure for amide coupling:

G2-acid **52** (0.17 g, 0.087 mmol), HOBT (14.6 mg, 0.095 mmol), deprotected core **58** (43 mg, 0.020 mmol), DIPEA (21.6 mg, 29 µl, 0.167 mmol) and EDC (18.3 mg, 0.095 mmol) and dry CH_2Cl_2 (20 ml) were used. Chromatographic separation through silica gel with CH_2Cl_2:5 % MeOH gave the product **67** (0.15 g, 0.016 mmol, 81 %) as a yellow oil R_f = 0.65. The product was recrystallized with acetone.

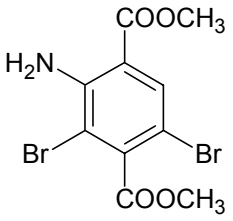
^{1}H NMR (270 MHz, $CDCl_3$) δ = 0.72-0.98 (m, 24 H, H31, 31´), 1.07-2.00 (m, 264 H, H6, 12, 18, 27-30, 27´-30´, 21), 2.41 (m, 32 H, H17), 2.50 (m, 16 H, H11), 2.55-2.79 (m, 24 H, H5, 26, 26´), 2.84-3.10 (m, 32 H, H19), 3.14-3.31 (24 H H7, 13), 3.48 (s, 16 H, H15), 3.62 (s, 8 H, H8), 4.41 (s, 16 H, H20), 5.89 (s, 8 H, H14), 6.45 (s, 4 H, H8), 7.00 (s, 16 H, H16), 7.05-7.21 (m, 16 H, H3, 4, 10), 7.24 (d, 16 H, H24), 7.36 (d, 8H, H22), 7.46 (d, 8H, H2), 7.62 (d, 16 H, H25), 7.65-7.82 (16 H, H1, 23), 7.93-8.43 (m, 114 H, H_{pyrene}).

^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 14.08, 15.06, 22.48, 22.57, 28.28, 29.22, 29.49, 29.82, 30.69, 30.86, 31.03, 31.16, 31.48, 31.57, 31.70, 32.25, 32.70, 39.13, 39.43, 39.87, 43.63, 61.71, 66.45, 71.42, 78.93, 124.55, 124.77, 124.85, 124.94, 125.04, 125.16, 125.92, 126.0, 127.32, 127.45, 127.58, 127.68, 128.07, 128.29, 129.24, 129.49, 129.69, 129.93, 130.19, 130.37, 130.49, 130.58, 130.83, 131.33, 134.24,

134.48, 136.95, 137.07, 137.73, 137.77, 138.31, 138.61, 139.15, 139.65, 139.71, 140.15, 140.27, 141.02, 155.87, 171.07, 171.24.
MS (+FAB, MNBA/CH_2Cl_2/DMSO) m/z (%) = 9441 (100) [M^+ + Na].
$C_{636}H_{678}N_{28}O_{44}$ (9418.51) calcd C 81.11 H 7.26 N 4.16, found C 80.79 H 7.32 N 3.96.

7.5 Synthesis of compounds from chapter 4.5

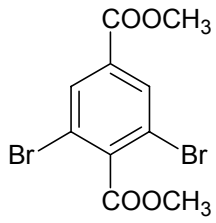
2-Amino-3,5-dibromo-terephthalic acid dimethyl ester (73)



Amino-terephthalic acid dimethyl ester **72** (51.0 g, 0.244 mol) was dissolved in CH_2Cl_2 (200 ml) and refluxed. Then Br_2 (23.0 g, 0.147 mol) dissolved in CH_2Cl_2 (20 ml) was added dropwise. The mixture was refluxed for 12 h, then allowed to cool to room temperature; water and aqueous KOH were added for neutralization. The phases were separated and the aqueous one was extracted with CH_2Cl_2 (200 ml). The combined organic phases were washed with an aqueous disulphite solution (c = 1mol/l, 250 ml). The CH_2Cl_2 phase was separated and dried ($MgSO_4$), recrystallization in hexane:ethyl acetate 3:1 gave product **73** (84.8 g, 0.232 mol, 95 %) as pale orange crystals.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.82 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 6.46 (s, 2H, NH_2), 7.93 (s, 1H, $H_{aromatic}$).
^{13}C NMR (62.9 MHz, $CHCl_3$): δ = 52.10, 52.82, 102.38, 107.37, 112.24, 133.59, 141.40, 146.49, 165.84, 166.02.
MS (EI, 80 eV, 120 °C): m/z (%) = 365 (57.8) [M^+], 333 (38.72) [M^+-CH_3OH], 222 (6.3) [M^+-$C_2H_8BrO_2$], 144 (4.3) [M^+-$C_2H_8Br_2O_2$].
$C_{10}H_9NO_4Br_2$ (366.99) calcd C 32.73 H 2.47 N 3.82, found C 32.82 H 2.55 N 4.02.

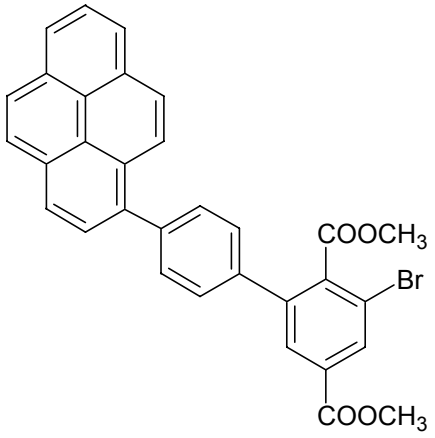
2,6-Dibromo-terephthalic acid dimethyl ester (74)



6-Amino-2,5-dibromo-terephthalicacid dimethyl ester **73** (36.0 g, 0.098 mol) was dissolved in methanol (600 ml) and conc. sulphuric acid (40 ml) was dropped in. After heating to 50 °C, sodium nitrite (16.8 g, 0.244 mol) was added. The reaction mixture was heated up to the boiling point, which started a very strong gas development at 70 °C. After 2 h the flask was cooled to 0 °C and ice water (500 ml) was added for the total precipitation of the product, which was suctioned off. Chromatographic separation with silica gel and hexane:ethyl acetate 10:1 gave the product **74** (28.6 g, 0.081 mol, 83 %) as colorless solid. R_f = 0.37 (hexane:ethyl acetate 3:1).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.83 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 8.07 (s, 2H, $H_{aromatic}$).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 52.71, 53.02, 119.57, 132.18, 132.54, 132.98, 140.91, 163.54, 165.64.
MS (EI, 80 eV, 30-60 °C) m/z (%) = 350 (17.7) [M^+], 271 (1.0) [M^+-Br], 319 (48.5) [M^+-CH_3O], 291 (2.5) [M^+-$C_2H_3O_2$], 276 (4.7) [M^+-$C_3H_6O_2$], 197 (2.5) [M^+-$C_3H_6O_2Br$].
$C_{10}H_8Br_2O_4$ (351.98) calcd C 34.12 H 2.29, found C 33.92 H 2.13.

3-Bromo-4'-pyren-1-yl-biphenyl-2,5-dicarboxylic acid dimethyl ester (75)

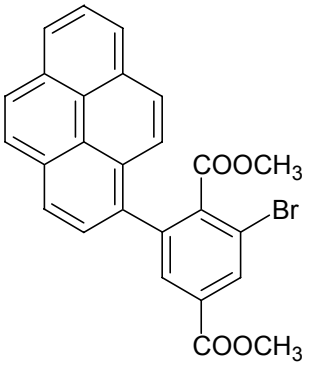


For preparation see general procedure for SCC 1:

4,4,5,5-Tetramethyl-2-pyren-1-yl-1,3,2-dioxaborolane **37** (1.66 g, 4.10 mmol), 2,5 dibromo terephthalic acid dimethylester **74** (1.50 g, 4.10 mmol), toluene (20 ml), Na_2CO_3 (20 ml, c = 1 mol/l), tetrakis(triphenylphosphine)palladium(0) (85 mg, 7.4 x 10^{-2} mmol) 2 d. Chromatographic separation through silica gel with hexane:ethyl acetate 10:1 gave the product **75** (1.35 g, 2.46 mmol, 58 %) as a yellow solid. R_f (hexane:ethyl acetate 3:1) = 0.28.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.86 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 7.55 (d, 2H, $H_{aromatic}$), 7.67 (d, 2H, $H_{aromatic}$), 7.84-8.34 (m, 11H, $H_{pyrene+aromatic}$).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 52.42, 52.56, 111.61, 111.65, 119.44, 119.75, 124.49, 124.55, 124.62, 124.71, 125.04, 125.84, 127.13, 127.28, 127.35, 127.50, 128.08, 129.63, 130.52, 130.63, 131.17, 131.96, 132.12, 136.34, 137.06, 138.64, 141.15, 141.34.
MS (EI, 80 eV, 220 °C): m/z (%) = 548 (96.9) [M^+], 517 (4.4) [M^+-CH_3O], 469 (1.0) [M^+-Br], 348 (13.8) [M^+-$C_{16}H_8$], 202 (5.6) [$C_{16}H_{10}^+$].
HRMS ($^{12}C_{32}{}^1H_{21}{}^{79}Br^{16}O_4$) [$M^+$]: calcd 548.06232 found 548.06683.
$C_{32}H_{21}BrO_4$ (549.42) calcd C 69.96 H 3.85, found C 70.47 H 4.28.

2-Bromo-6-pyren-1-yl-terephthalic acid dimethyl ester (77)



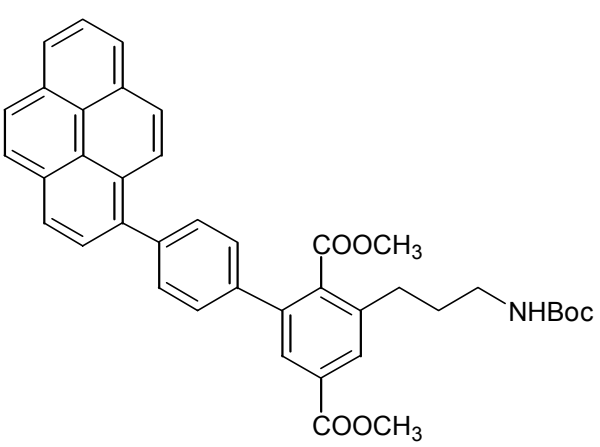
For preparation see general procedure for SCC 1:

Pyrene pinacol **10** (2.50 g, 5.68 mmol), ester **74** (3.00 g, 8.52 mmol), toluene (100 ml), Na_2CO_3 (100 ml, c = 1 mol/l), $Pd(PPh_3)_4$ (0.19 g, 0.154 mmol), 3d;
Chromatographic separation with hexanes-EtOAc, 10:1 gave the product **77** (2.00 g, 4.23 mmol, 74.4 %). R_f = 0.32

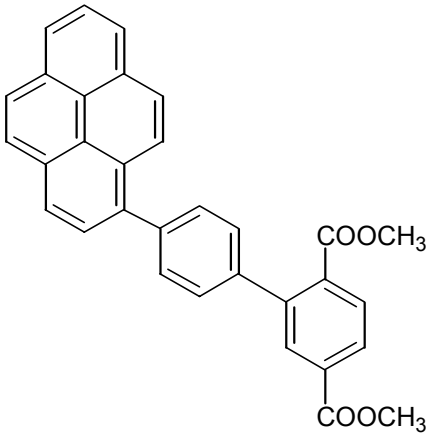
^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.32 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 7.80 (d, 1H, $H_{aromatic}$), 7.90 (d, 1H, $H_{aromatic}$), 7.95-8.27 (m, 8H, $H_{aromatic}$), 8.43 (s, 1H, $H_{aromatic}$).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 52.23, 52.57, 119.67, 124.11, 124.42, 124.54, 125.33, 125.48, 126.15, 127.03, 127.19, 127.96, 127.98, 128.90, 130.73, 131.21, 131.26, 131.37, 131.82, 132.68, 140.56, 141.02, 164.97, 166.91.
MS (EI, 170 °C, 80 eV) m/z (%) = 472 (96.9) [M^+], 439 (2.7) [M^+-CH_3O/H_2], 393 (1.8) [M^+-Br], 275 (24.1) [M^+-$C_4H_6BrO_4$].
$C_{26}H_{17}BrO_4$ (473.32) calcd C 65.98 H 3.62, found C 66.16 H 3.77.

3-(3-tert-Butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-2,5,-dicarboxylic acid dimethyl ester (78) and 4'-Pyren-1-yl-biphenyl-2,5-dicarboxylic acid dimethyl ester (76)



78



76

For preparation see general procedure for SCC 2:

Protected ally amine **40** (0.97 g, 6.19 mmol), dry toluene (25 ml), 9-BBN (1.15 g, 9.40 mmol), 12 h, aqueous solution of KOH (20 ml, c = 1 mol/l), bromo-aryl **75** (0.85g, 1.55 mmol), tetrakis(triphenylphosphine)palladium(0) (22 mg, 1.9 x 10^{-5}mmol), 36 h. Chromatographic separation through silica gel with hexane:ethyl acetate 3:1 gave product **78** (0.47 g, 0.75 mmol, 48 %) as a yellow solid and the proton substituted product **76** (94.0 mg, 0.20 mmol, 13 %) as a colorless solid. R_f (hexane:ethylacetate 3:1) for **76** = 0.24 and for **78** = 0.08.

For **78**:

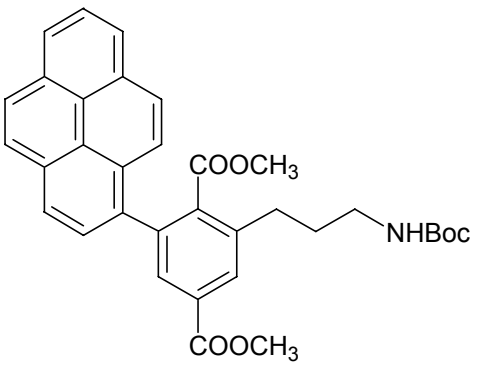
^1H NMR (270 MHz, $CDCl_3$) δ = 1.45 (s, 9H, $CH_{3\ boc}$), 1.93 (m, 2H, CH_2), 2.77 (t, 2H, $CH_{2\ benzylic}$), 3.19 (m, 2H, CH_2-N), 3.74 (s, 3H, CH_3), 3.96 (s, 3H, CH_3), 4.82 (s, 1H, NH), 7.57 (d, 2H, $H_{aromatic}$), 7.69 (d, 2H, $H_{aromatic}$), 7.91-8.29 (m, 11H, $H_{pyrene+aromatic}$).

^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 28.23, 30.58, 31.31, 39.82, 52.08, 52.16, 78.80, 124.44, 124.54, 124.66, 124.96, 125.78, 127.10, 127.26, 127.39, 128.01, 128.11, 128.54, 129.08, 130.40, 130.44, 130.60, 130.92, 131.13, 136.58, 136.71, 138.50, 139.68, 140.01, 140.45, 155.82, 166.06, 169.56.
MS (EI, 80 eV, 200 °C) m/z (%): 627 (18.0) [M^+], 571 (11.2) [M^+-C_4H_8], 554 (47.9) [M^+-C_4H_9O], 523 (3.9) [M^+-$C_5H_{12}O_2$], 496 (2.7) [M^+-$C_6H_{13}NO_2$].
HRMS ($^{12}C_{40}{}^{1}H_{37}{}^{14}N{}^{16}O_6$) [$M^+$] calcd 627.26208, found 627.26422.
$C_{40}H_{37}NO_6$ (627.73) calcd C 76.54 H 5.94 N 2.23, found C 76.18 H 5.73 N 1.95.

For **76**:

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.77 (s, 3H, CH_3), 3.96 (s, 3H, CH_3), 7.53 (d, 2H, $H_{aromatic}$), 7.69 (d, 2H, $H_{aromatic}$), 7.93 (d, 1H, $H_{aromatic}$), 7.96-8.31 (m, 10H, $H_{pyrene+aromatic}$).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 52.25, 52.40, 124.63, 124.84, 125.0, 125.13, 126.0, 127.37, 127.46, 127.55, 127.83, 128.20, 128.35, 128.50, 128.69, 129.87, 130.42, 130.69, 130.95, 131.48, 131.83, 132.55, 134.89, 137.11, 139.18, 140.58, 140.93, 142.15, 166.14, 168.55.
MS (EI, 80 eV, 130 °C): m/z (%) = 470 (100) [M^+], 439 (1.8) [M^+-CH_3O], 350 (6.9) [M^+-$C_4H_8O_4$], 220 (9.2) [M^+-$C_{17}H_{14}O_2$].
HRMS ($^{12}C_{32}{}^{1}H_{22}{}^{16}O_4$) [$M^+$] calcd 470.15181, found 470.15664.

2-(3-tert-Butoxycarbonylamino-propyl)-6-pyren-1-yl-terephthalic acid dimethyl ester (79)



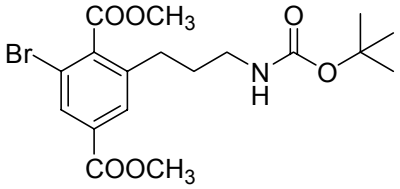
For preparation see general procedure for SCC 2:

Allylamine **40** (1.29 g, 8.23 mmol), dry toluene (25 ml), 9-BBN (1.51 g, 12.30 mmol), KOH (30 ml, c = 1 mol/l), **77** (1.00 g, 2.06 mmol), $Pd(PPh_3)_4$ (47 mg, 41.2 mmol), 3 d.

Chromatographic separation with silica gel and hexane:acetic acid ethyl ester 10:1 yielded in **79** (0.91 g, 1.65 mmol, 80 %). $R_{f\ (Hexane:ethylacetate\ 3:1)}$ = 0.28.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 9H, $CH_{3\ boc}$), 1.95 (tt, 2 H, CH_2-β), 2.80 (m, 2 H, $CH_{2\ benzylic}$), 3.15 (s, 3 H, CH_3), 3.23 (m, 2 H, CH_2-N), 3.90 (s, 3 H, CH_3), 4.80 (s, 1H, NH), 7.80 (d, 1H, $H_{aromatic}$), 7.85 (s, 1H, NH), 7.94-8.23 (m, 9H, $H_{aromatic}$).
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.44, 28.07, 28.28, 30.80, 31.41, 36.08, 39.96, 51.74, 52.26, 78.90, 124.04, 124.40, 124.45, 124.90, 125.04, 125.19, 125.97, 127.0, 127.19, 127.59, 128.16, 129.76, 129.46, 130.07, 130.66, 130.68, 130.85, 131.14, 134.29, 138.47, 139.47, 139.76, 155.87, 166.24, 169.01.
MS (EI, 210 °C, 80 eV): m/z (%) = 551 (64.6) [M^+], 495 (16.6) [M-$C_4H_8^+$], 477 (100) [M^+-$C_4H_{10}O$], 451 (26.7) [M^+-$C_5H_8O_2$], 389 (15.9) [M^+-$C_7H_{14}O_4$].
$C_{34}H_{33}NO_6$ (551.64) calcd C 74.03 H 6.03 N 2.54, found C 74.01 H 6.16 N 2.32.

2-Bromo-6-(3-tert-butoxycarbonylamino-propyl)-terephthalic acid dimethyl ester (80)

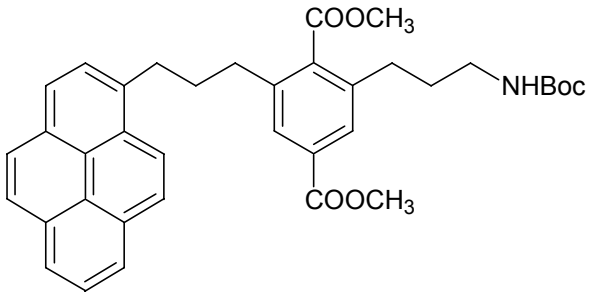


For preparation see general procedure for SCC 2.

Boc protected allyl **40** (0.23 g, 1.44 mmol), 9-BBN (0.40 g, 3.27 mmol), dry THF (15 ml), 12h, di-bromo-di-ester **74** (2.02 g, 5.74 mmol), toluene (100 ml), aqueous solution of Na_2CO_3 (20 ml, 1M), $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), 1d. Chromatographic separation with silica gel and hexane:ethyl acetate 3:1 gave the product **80** (0.18 g, 0.42 mmol, 29 %) as a colorless oil. R_f = 0.20.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 (s, 9H, CH_3), 1.75 (quin 2H, β), 2.59 (t, 2H, α), 3.08 (m, 2H, γ), 3.86 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 4.66 (s, 1H, NH), 7.80 (s, 1H, $H_{aromatic}$), 8.04 (s, 1H, $H_{aromatic}$).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.32, 30.95, 31.24, 39.85, 52.48, 52.68, 79.12, 119.29, 129.02, 129.95, 131.19, 132.24, 141.01, 155.87, 165.04, 167.73.
MS (EI, 100 °C, 80 eV): m/z (%) = 429 (0.1) [M^+], 373 (2.4) [M^+-C_4H_8], 328 (6.0) [M^+-$C_5H_9O_2$], 271 (6.5) [M^+-$C_8H_{16}NO_2$].
HRMS $^{12}C_{18}{}^{1}H_{24}{}^{14}N_1{}^{16}O_6{}^{79}Br_1$ calcd 429.07870, found 429.07653.

2-(3-tert-Butoxycarbonylamino-propyl)-6-(3-pyren-1-yl-propyl)-terephthalic acid dimethyl ester (82)

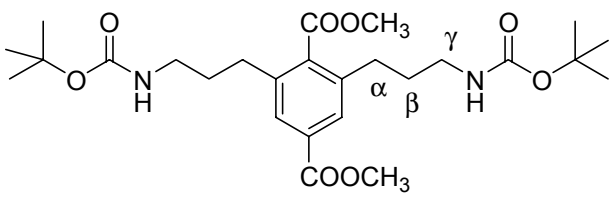


For preparation see general procedure for SCC 2:

Allyl-pyrene **81** (1.40 g, 5.77 mmol), allylamine **40** (0.90 g, 5.74 mmol), 9-BBN (1.76 g, 14.4 mmol), toluene (40 ml), 12 h, aqueous solution of Na_2CO_3 (40ml), dibromo ester 20 (2.02 g, 5.74 mmol), reflux for 5 d.
Chromatographic separation with silica gel and hexane:acetic acid ethyl ester 3:1 gave product **82** (0.21 g, 0.36 mmol, 6%) as a pale yellow oil. R_f = 0.11

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.41 (s, 9H, $CH_{3\ boc}$), 1.77 (tt, 2H, CH_2), 2.15 (tt, 2H, CH_2), 2.56 (m, 2H, CH_2), 2.75 (m, 2H, CH_2), 3.09 (m, 2H, CH_2), 3.60 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 4.71 (s, 1H, NH), 7.62-8.38 (m, 11H, $H_{aromatic}$).
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 28.33, 30.70, 31.34, 32.86, 33.18, 33.60, 39.88, 51.94, 52.21, 79.04, 123.19, 124.66, 124.70, 124.83, 124.97, 125.75, 126.57, 126.96, 127.22, 127.41, 127.91, 128.06, 128.50, 129.77, 130.62, 130.76, 130.86, 131.29, 135.92, 137.54, 138.98, 139.49, 155.87, 166.47, 169.77.
MS (EI, 80 eV, 220 °C) m/z (%) = 593 (3.6) [M^+], 537 (11.2) [M^+-C_4H_8], 519 (20.5) [M^+-$C_4H_{10}O$], 492 (5.4) [M^+-$C_5H_9O_2$], 460 (2.8) [M^+-$C_6H_{13}O_3$], 215 (100) [M^+-$C_{20}H_{28}NO_6$].
HRMS ($^{12}C_{37}{}^1H_{39}{}^{14}N^{16}O_6$) [$M^+$] calcd 593.27774, found 593.27368.

2,6-Bis-(3-tert-butoxycarbonylamino-propyl)-terephthalic acid dimethyl ester (83)

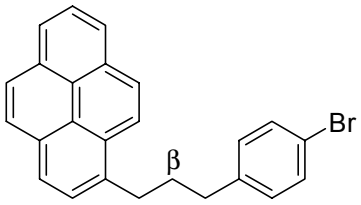


For preparation see general procedure for SCC 2.

Boc protected allyl **40** (1.72 g, 11.0 mmol), 9-BBN (2.00 g, 16.0 mmol), dry toluene (20 ml), 12h, di-bromo-di-ester **74** (1.28 g, 3.6 mmol), $Pd(PPh_3)_4$ (0.05g, 4.3 x 10^{-2} mmol), 1 d. chromatographic separation with silica gel and hexane:ethyl acetate 3:1 gave the product **83** (1.32 g, 2.6 mmol, 72 %) as a yellow oil. R_f = 0.06.

^{1}H NMR (270 MHz, $CDCl_3$):δ = 1.38 (s, 18H, CH_3), 1.57 (quin 4H, β), 1.55 (t, 4H, α), 3.07 (m, 4H, γ), 3.84 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 4.69 (s, 2H, NH), 7.69 (s, 2H, $H_{aromatic}$).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.22, 30.64, 31.27, 39.81, 52.12, 52.19, 78.89, 127.85, 130.86, 137.47, 138.93, 155.84, 166.29, 169.78.
MS (EI, 60 – 100 °C, 80 eV): m/z (%) = 508 (0.2) [M^+], 452 (0.8) [M^+-C_4H_8], 407 (2.9) [M^+-$C_5H_9O_2$], 278 (60.1) [M^+-$C_{11}H_{20}O_4N$].
HRMS $^{12}C_{26}{}^{1}H_{40}{}^{14}N_2{}^{16}O_8$ calcd 508.27847, found 508.27633.
EA $C_{26}H_{40}N_2O_8$ (508.61) calcd C 61.40 H 7.93 N 5.51, found C 60.87 H 7.73 N 4.93.

1-[3-(4-Bromo-phenyl)-propyl]-pyrene (86)

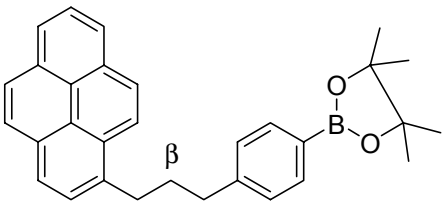


For preparation see general procedure for SCC 2.

Allyl pyrene **81** (4.28 g, 17.7 mmol), 9-BBN (3.00 g, 24.6 mmol), dry THF (10 ml), 12 h, Bromo-iodo benzene **34** (5.00 g, 17.7 mmol), xylene (35 ml), aqueous solution of KOH (25 ml, 1M), $Pd(PPh_3)_4$ (0.41 g, 0.35 mmol), 4 d. Chromatographic separation with silica gel and hexane gave the product **86** (1.20 g, 3.01 mmol, 17 %) as a colorless solid. R_f (hexane:ethyl acetate 20:1) = 0.29.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.16 (quin, 2H, β), 2.72 (t, 2H, CH_2), 3.32 (t, 2H, CH_2), 7.06 (d, 2H, $H_{aromatic}$), 7.44 (d, 2H, $H_{aromatic}$), 7.82 (d, 1H, H_{pyrene}), 7.90 – 8.32 (m, 8H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 32.76, 32.94, 35.08, 119.50, 123.16, 124.65, 124.71, 124.82, 124.93, 125.01, 125.75, 126.55, 127.08, 127.17, 127.42, 128.52, 129.76, 130.15, 130.80, 131.31, 136.18, 140.97. (1 signal missing).
MS (EI, 180 °C, 80 eV): m/z (%) = 399 (6.8) [M^+], 320 (5.1) [M^+-Br], 215 (100) [pyrene+CH_2^+], 202 (7.2) [pyrene$^+$].
EA $C_{25}H_{19}Br$ (399.33) calcd C 75.19 H 4.80, found C 75.24 H 4.89.

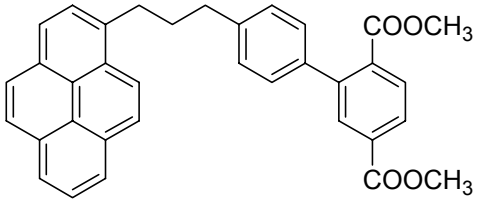
4,4,5,5-Tetramethyl-2-[4-(3-pyrene1-yl-propyl)-phenyl]-[1,3,2]-dioxaborolane (88)



Pyrene bromide **86** (670 mg, 1.67 mmol), was dissolved in dry THF (15 ml) and the yellow solution was cooled down to –78 °C. A solution of BuLi (2.1 ml, 1.6 M) was added dropwise. The mixture was allowed to come to room temperature in 4 h, then cooled down to –78 °C again and $B(O_ipr)_3$ (0.96 ml, 4.17 mmol) was added. The mixture came to room temperature during 12 h, and then water (20 ml) was added. The layers were separated and the aqueous one was washed three times with diethyl ether (60 ml). The combined organic layers were dried ($MgSO_4$). Filtration over silica gel with first hexane:ethyl acetate 3:1 and later with acetone gave the boronic acid **87**. Without further purification pinacol (212 mg, 1.79 mmol) was added to the solution and it was refluxed for 2 h. After removing the acetone, the crude product was purified with silica gel. Chromatographic separation with hexane: ethyl acetate 3:1 gave the product **88** (286 mg, 0.64 mmol, 38 %) as a colorless solid. $R_{f\ (hexane:ethyl\ acetate\ 10:1)}$ = 0.35.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44 (s, 12H, CH_3), 2.25 (quin, 2H, β), 2.87 (t, 2H, CH_2), 3.38 (t, 2H, CH_2), 7.35 (d, 2H, $H_{aromatic}$), 7.86 (d, 1H, H_{pyrene}), 7.93 (d, 2H, $H_{aromatic}$), 7.99 – 8.27 (m, 8H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.80, 32.86, 32.92, 35.95, 83.57, 123.24, 124.57, 124.68, 124.71, 124.93, 124.98, 125.66, 126.46, 127.09, 127.41, 127.95, 128.52, 129.70, 130.81, 131.32, 134.93, 136.43, 145.52. (2 signals missing).
MS (EI, 80 – 90 °C, 80 eV): m/z (%) = 446 (48.3) [M^+], 215 (100) [pyrene+CH_2^+].
HRMS $^{12}C_{31}{}^1H_{31}{}^{11}B_1{}^{16}O_2$ calcd 446.24171, found 446.24533.
EA $C_{31}H_{31}BO_2$ (446.39) calcd C 83.41 H 7.00, found C 83.43 H 7.08.

4'-(3-Pyrene-1-yl-propyl)-biphenyl-2,5-dicarboxylic acid dimethyl ester (89)

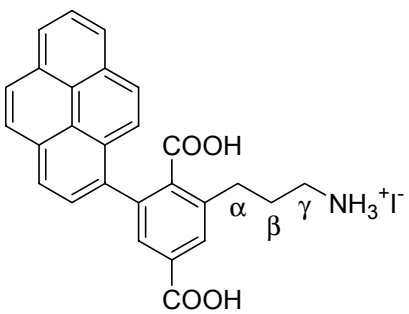


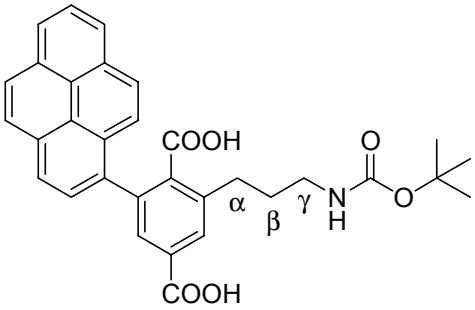
For preparation see general procedure for SCC 1

Di-bromide **74** (497 mg, 1.410 mmol), pyrene-propyl-pinacol **88** (611 mg, 1.370 mmol), toluene (30 ml), aqueous solution of Na_2CO_3 (20 ml, 1M), $Pd(PPh_3)_4$ (24 mg, 0.021 mmol), 2d, chromatographic separation with silica gel and hexane:ethyl acetate 3:1 gave a colorless oil, freeze drying with benzene gave the product **89** as a colorless solid (40 mg, 0.078 mmol, 6 %). R_f = 0.23

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.24 (quin, 2H, CH_2), 2.85 (t, 2H, CH_2), 3.40 (m, 2H, CH_2), 3.65 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 7.28 (s, 4H, $H_{aromatic}$), 7.36 (s, 1H, $H_{aromatic}$), 7.83 (d, 1H, $H_{aromatic}$), 7.88 (d, 1H, $H_{aromatic}$), 7.95 – 8.28 (m, 9H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 32.99, 33.16, 35.51, 52.18, 52.37, 123.31, 124.66, 124.77, 124.83, 124.99, 125.08, 125.77, 126.57, 127.21, 127.48, 127.89, 128.27, 128.30, 128.39, 128.61, 129.64, 129.80, 130.87, 131.40, 131.70, 132.32, 134.90, 136.51, 137.73, 141.65, 142.27, 166.20, 168.74.
MS (EI, 150 – 200 °C, 80 eV): m/z (%) = 512 (56.1) [M^+], 481 (1.6) [M^+-CH_3O], 215 (100) [pyrene+CH_2^+].
HRMS ($^{12}C_{35}{}^1H_{28}{}^{16}O_4$) calcd: 512.19876, found: 512.19574.

2-(3-Ammonio-propyl)-6-pyrene-1-yl-terephthalic acid iodide (93) and 2-(3-tert-Butoxycarbonylamino-propyl)-6-pyrene-1-yl-terephthalic acid (94)





Probe-di-ester **79** (250 mg, 0.453 mmol), dry NaI (570 mg, 3.800 mmol) and TMSCl (320 µl, 2.540 mmol), were dissolved in dry acetonitrile (2 ml) and were heated at 80 °C for 6 d. Water (5 ml) was added and di acid ammonia salt **93** precipitated. An aqueous solution of NaOH was added until pH = 12. Then Boc_2O (500 mg, 2.29 mmol) was added. The solution was stirred at room temperature for 2 d. Acetic acid was dropped in until the product **94** (200 mg, 0.382 mmol, 84 %) precipitated as a yellow solid, which was sucked off and washed with water.

Di-Acid ammonia salt **93**:

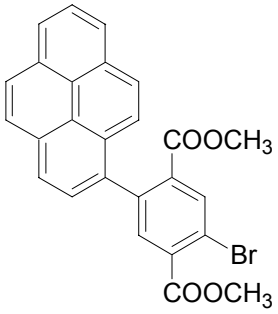
^{1}H NMR (500 MHz, DMSO): δ = 2.00 (m, 2H, β), 2.59 – 2.74 (m, 2H, α), 2.83 (m, 2H, γ), 7.68 (s, 1H, $H_{aromatic}$), 7.80 (d, 1H, H_{pyrene}), 7.90 (s, 1H, $H_{aromatic}$), 7.98 (d, 1H, H_{pyrene}), 8.00 – 8.32 (m, 7H, H_{pyrene}).
^{13}C NMR (126 MHz, DMSO): δ = 28.06, 28.86, 37.31, 123.90, 123.92, 124.16, 124.84, 125.10, 125.65, 126.22, 126.99, 127.18, 127.35, 127.83, 128.37, 128.99, 129.73, 130.00, 130.42, 130.84, 135.69, 136.11, 136.71, 167.54, 171.40. (2 signals missing).
MS (+FAB, DMSO/glycerole): m/z (%) = 446 (1.7) [M^+-I-H+Na], 424 (4.0) [M^+-I].

Di acid-boc-protected-amine **94**:

^{1}H NMR (270 MHz, MeOH): δ = 1.43 (s, 9H, CH_3), 1.94 (m, 2H, β), 2.86 (m, 2H, α), 3.15 (m, 2H, γ), 6.93 (m, 1H, NH), 7.72 (d, 1H, H_{pyrene}), 7.82 (s, 1H, $H_{aromatic}$), 7.94 (d, 1H, H_{pyrene}), 8.00 – 8.30 (m, 8H, $H_{pyrene + aromatic}$).
MS (-FAB, MNBA/CH_2Cl_2): m/z (%) = 522 (66.0) [M^--H], 404 (11.7) [$M^{-}C_5H_{13}NO_2$].

7.6 Synthesis of compounds from chapter 4.6

2-Bromo-5-pyrene-1-yl-terephthalic acid dimethyl ester (96)

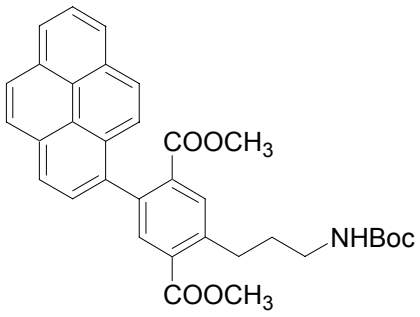


For preparation see general procedure for SCC 1:

Pyrene pinacol **10** (5.0 g, 15.23 mmol), ester **95** (6.0 g, 17.05 mmol), toluene (150 ml), Na_2CO_3 (150 ml, c = 1 mol/l), $Pd(PPh_3)_4$ (0.37 g, 0.32 mmol), 6d;
Chromatographic separation with silica gel and hexane: ethyl acetate 10:1 R_f ($_{Hex:EE\ 3:1}$) = 0.31 yielded in **96**: (3.6 g, 7.50 mmol, 49.3 %) as a light yellow solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.34 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 7.80 (d, 1H, H_{pyrene}), 7.83 (d, 1H, H_{pyrene}), 7.90 (s, 1H, $H_{aromatic}$). 7.94-8.30 (m, 7H, H_{pyrene}), 8.38 (s, 1H, $H_{aromatic}$).
^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 52.11, 52.57, 120.46, 123.99, 124.16, 124.28, 124.44, 124.99, 125.24, 125.90, 126.35, 127.19, 127.50, 127.84, 128.40, 130.55, 130.81, 131.13, 134.22, 134.51, 134.72, 134.94, 135.59, 140.64, 165.58.
MS (EI, 180 °C, 80 eV): m/z (%) = 472 (97.6) [$M^{+\cdot}$], 441 (3.3) [$M^{+\cdot}$ –CH_3O], 463 (8.3) [$M^{+\cdot}$ –CH_3OBr], 275 (54.5) [$M^{+\cdot}$ –$C_4H_6BrO_4$].
EA $C_{26}H_{17}BrO_4$ (473.32 g/mol) calcd. C 65.98 H 3.62 found C 65.76 H 3.46.

2-(3-tert-Butoxycarbonylamino-propyl)-5-pyrene-1-yl-terephthalic acid dimethyl ester (97)

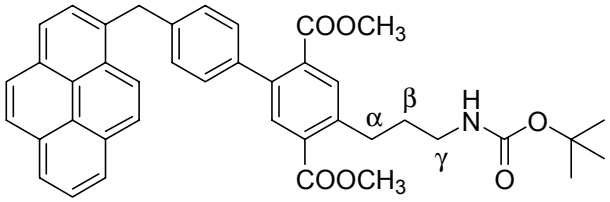


For preparation see general procedure for SCC 2:

Allylamine **40** (4.03 g, 25.64 mmol), dry toluene (100 ml), 9-BBN (7.76 g, 63.50 mmol), KOH (100 ml, c = 1 mol/l), **96** (4.0 g, 8.45 mmol), $Pd(PPh_3)_4$ (0.19 g, 0.16 mmol), 4 d.
Chromatographic separation with silica gel and hexane:acetic acid ethyl ester 10:1 $R_{f\ (Hexane:ethylacetate\ 3:1)}$ = 0.28, yielded in **97** (3.48 g, 6.31 mmol, 75 %). Freeze drying in benzene gave **97** as a pale yellow solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.47 (s, 9H, $CH_{3\ boc}$), 1.94 (m, 2 H, CH_2-β), 3.13 (m, 2 H, $CH_{2\ benzylic}$), 3.26 (m, 2 H, CH_2-N) 3.30 (s, 3 H, CH_3), 3.86 (s, 3 H, CH_3), 4.86 (s, 1H, NH), 7.71 (d, 1H, H_{pyrene}), 7.83 (d, 1H, H_{pyrene}), 7.90-8.28 (m, 9H, $H_{aromatic+pyrene}$).
^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 28.41, 31.20, 31.77, 40.33, 52.00, 52.23, 79.03, 124.26, 124.46, 124.56, 124.71, 124.95, 125.17, 125.94, 126.76, 127.40, 127.64, 128.72, 130.70, 130.80, 131.35, 131.96, 132.52, 134.50, 135.62, 139.27, 142.92, 152.07, 167.08, 167.21.
MS (EI, 120-150 °C, 80 eV): m/z (%) = 551 (20.2) [$M^{+\cdot}$], 494 (26.4) [$M-C_4H_9^{+\cdot}$], 476 (100) [$M^{+\cdot}-C_4H_{10}O$].
EA $C_{34}H_{33}NO_6$ (551.64) calcd C 74.03 H 6.03 N 2.54, found C 74.01 H 6.11 N 2.45.

4-(3-tert-Butoxycarbonylamino-propyl)-4'-pyrene-1-ylmethyl-biphenyl-2,5-dicarboxylic acid dimethyl ester (98)

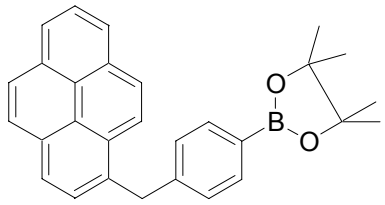


For preparation see general procedure for SCC 2:

Allylamine **40** (0.56 g, 3.55 mmol), dry toluene (25 ml), 9-BBN (0.65 g, 5.32 mmol), KOH (30 ml, c = 1 mol/l), diester **105** (1.0 g, 1.78 mmol), $Pd(PPh_3)_4$ (0.04 g, 0.04 mmol), 3 d.
Chromatographic separation with silica gel and hexane:acetic acid ethyl ester 3:1 $R_{f(Hexane:ethylacetate\ 3:1)}$ = 0.11. yielded in **98** (0.71 g, 1.11 mmol, 62 %) as a pale yellow solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.43 (s, 9H, $CH_{3\ boc}$), 1.78 (m, 2 H, β), 2.95 (m, 2 H, α), 3.15 (m, 2H, γ), 3.61 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 4.67 (s, 2H, CH_2), 4.85 (s, 1H, NH), 7.18 (m, 4H, $H_{aromatic}$), 7.62 (s, 1H, $H_{aromatic}$), 7.77 – 8.12 (m, 9H, $H_{pyrene\ +\ aromatic}$), 8.15 (d, 1H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.30, 30.92, 31.53, 38.85, 40.10, 52.04, 52.08, 78.84, 123.53, 124.65, 124.73, 124.90, 124.96, 125.73, 126.74, 127.31, 128.08, 128.27, 128.36, 128.96, 130.06, 130.62, 131.15, 131.41, 132.01, 132.83, 133.55, 134.07, 137.63, 139.56, 140.41, 142.27, 155.91, 166.91, 168.30. (2 signals missing)
MS (EI, 210 °C, 80 eV): m/z = 641 (7.3) [$M^{+\cdot}$], 585 (5.7) [M^+-C_4H_8], 568 (100) [M^+-C_4H_9O], 215 (25.6) [pyrene-CH_2^+].
EA $C_{41}H_{39}NO_6$ (641.75) calcd: C 76.73 H 6.13 N 2.18, found: C 76.67 H 6.24 N 1.95.

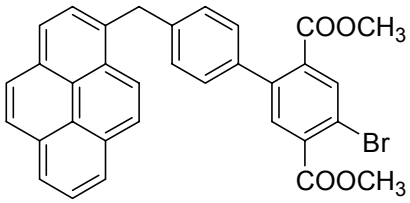
4,4,5,5-Tetramethyl-2-(4-pyrene-1-ylmethyl-phenyl)-[1,3,2]dioxaborolane (104)



Pyrene-methylene-phenyl bromide **102** (1.0 g, 2.69 mmol) was suspended in 100 ml abs. diethylether and the colorless suspension was cooled down to –78 °C. A solution of n-BuLi (4.53 ml, 7.20 mmol, c = 1.6 M) was added dropwise. The mixture was allowed to come to 0 °C in 5 h, the color changed to red, then cooled down to –78 °C again, and triisopropyl boric acid ester (2.0 ml, 1.63 g, 8.67 mmol) was added. The mixture came to room temperature during 10 h. Then water (150 ml) was added. The layers were separated and the aqueous layer was washed three times with diethyl ether (200 ml). The combined organic layers were dried ($MgSO_4$). Filtration over silica gel with first hexane:acetic acid ethyl ester 3:1 and later with acetone gave the pyrene phenyl boronic acid **103** as a brown oil. Without further purification the pyrene-methylene-phenyl boronic acid and pinacol (1.78 g, 15.06 mmol) were dissolved in acetone (320 ml) and refluxed for 1 h. The acetone was removed through distillation. Chromatographic separation with hexane:acetic acid ethyl ester 10:1 gave the pyrene pinacol **104** (0.74 g, 1.77, mmol, 66 %) as a colorless solid. R_f = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 12 H, CH_3), 4.75 (s, 2 H CH_2), 7.28 (d, 2 H, $H_{aromatic}$), 7.80 (d, 2 H, $H_{aromatic}$), 7.87 (d, 1 H, H_{pyrene}), 7.95-8.09 (m, 4 H, H_{pyrene}), 8.10-8.28 (m, 4 H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.77, 39.48, 83.61, 123.61, 124.75, 124.80, 124.84, 124.95, 125.04, 125.80, 126.81, 127.41, 127.45, 128.14, 128.18, 128.61, 130.13, 130.74, 131.25, 134.06, 135.01, 144.50.
MS (EI, 160 °C, 80 eV): m/z = 418 (100) [$M^{+\cdot}$], 360 (1.0) [M^+ -C_3H_6O], 318 (17.8) [M^+-$C_6H_{12}O$], 291 (8.6) [M^+- $C_6H_{12}BO_2$], 215 (34.3) [M^+- $C_{12}H_{16}BO_2$], 202 (26.4) [pyrene$^+$].
HRMS $^{12}C_{29}{}^{1}H_{27}{}^{11}B_1{}^{16}O_2$ calcd 418.21041 found 418.21432.

4-Bromo-4'-pyrene-1-ylmethyl-biphenyl-2,5-dicarboxylic acid dimethyl ester (105)

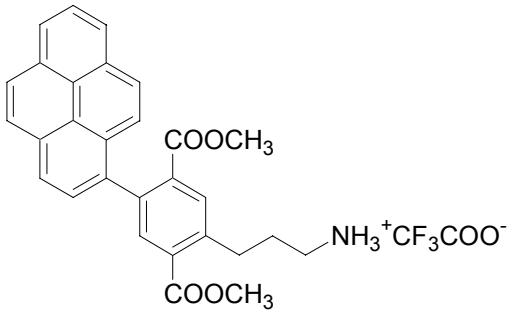


For preparation see general procedure for SCC 1:

Pinacol **104** (0.30 g, 0.717 mmol), diester **95** (0.38 g, 1.080 mmol), toluene (25 ml), Na_2CO_3 (25 ml, c = 1 mol/l), $Pd(PPh_3)_4$ (16.6 mg, 0.014 mmol), 3d;
Chromatographic separation with silica gel and hexane: ethyl acetate 10:1 R_f ($_{Hex:EE\ 3:1}$) = 0.28 yielded in **105**: (0.18 g, 0.323 mmol, 45 %) as a colorless solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.64 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 4.75 (s, 2H, CH_2), 7.17 (d, 2H, $H_{aromatic}$), 7.26 (d, 2H, $H_{aromatic}$), 7.75 (s, 1H, $H_{aromatic}$), 7.90 (d, 1H, H_{pyrene}), 7.94 – 8.32 (m, 9H, $H_{pyrene + aromatic}$).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 38.88, 52.21, 52.49, 119.83, 123.49, 124.49, 124.77, 125.06, 125.77, 126.82, 127.33, 127.39, 128.06, 128.21, 128.50, 129.02, 130.18, 130.69, 131.25, 133.20, 133.96, 134.15, 135.15, 136.76, 140.99, 141.07, 165.60, 166.75. (3 signals missing)
MS (EI, 300 °C, 80 eV): m/z = 562 (95.8) [$M^{+\cdot}$], 531 (4.1) [M^+-CH_3O], 444 (4.7) [M^+-$C_4H_6O_4$], 365 (6.6) [M^+-$C_4H_6O_4Br$], 215 (37.7) [pyrene-CH_2^+].
EA $C_{33}H_{23}BrO_4$ (563.44) calcd C 70.35 H 4.11, found C 70.26 H 4.14.

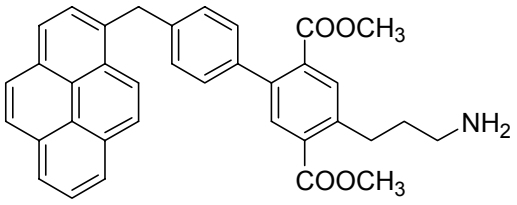
2-(3-Amino-propyl)-5-pyrene-1-yl-terephthalic acid dimethyl ester Trifluoroacetate (106)



Boc protected diester **97** (1.0 g, 1.81 mmol) was dissolved in chloroform (25 ml), trifluoracetic acid was added (2 ml). The solution was stirred for 3 h at room temperature. The solvents were removed through distillation. Freeze drying of the residue gave the product **106** (0.92 g, 1.63 mmol, 90 %) as a brown solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.34 (m 2 H, CH_2), 3.09-3.38 (m, 7 H, CH_2-N, CH_2 $_{benzylic,}$ CH_3), 3.83 (s, 3 H, CH_3), 7.69 (d, 1 H, H_{pyrene}), 7.81 (d, 1 H, H_{pyrene}), 7.84-8.26 (m, 9 H, H_{pyrene}, $H_{aromatic}$).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.18, 30.39, 39.44, 52.04, 52.50, 124.21, 124.33, 124.38, 124.55, 124.92, 125.11, 125.86, 126.61, 127.30, 127.35, 127.67, 128.57, 130.62, 130.65, 131.20, 131.74, 132.64, 134.69, 134.70, 135.29, 139.71, 141.56, 167.07, 167.10
MS (EI, 220 °C, 80 eV): m/z = 452 (100) [$M^{+\cdot}$ +H].

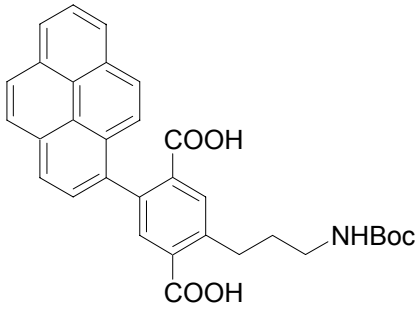
4-(3-Amino-propyl)-4'-pyrene-1-ylmethyl-biphenyl-2,5-dicarboxylic acid dimethyl ester (107)



Boc protected ester **98** (0.29 g, 0.452 mmol) was dissolved in chloroform (5 ml), trifluoroacetic acid was added (2 ml), and the color turned from pale yellow to orange. The solution was stirred for 1 h at room temperature. an aqueous solution of KOH was added until pH = 9. The $CHCl_3$ phase was separated and the aqueous one was etracted two times with $CHCl_3$ (20 ml). The combines organic phases were dried ($MgSO_4$) and the solvent removed. Freeze drying of the residue in dioxane gave the product **107** (0.23 g, 0.0.425 mmol, 94 %) as a brown solid.

^{1}H MNR (500 MHz, DMSO) δ = 1.89 (m, 2H, CH_2), 2.87 (m, 2H, CH_2), 2.98 (m, 2H, CH_2), 3.60 (s, 3H,CH_3), 3.83 (s, 3H, CH_3), 4.73 (s, 2H, CH_2), 7.19 (d, 2H, $H_{aromatic}$), 7.29 (d, 2H, $H_{aromatic}$), 7.70 (s, 1H, $H_{aromatic}$), 7.75 (s, 1H, $H_{aromatic}$), 7.86 – 8.30 (m, 8H, H_{pyrene}), 8.34 (d, 1H, H_{pyrene}).
^{13}C NMR (126 Mhz, DMSO): δ = 28.89, 29.84, 38.01, 38.67, 52.20, 52.41, 123.84, 124.11, 124.45, 125.00, 125.08, 125.17, 126.24, 126.83, 127.47, 128.21, 128.42, 128.52, 128.60, 129.75, 130.40, 130.92, 131.63, 131.83, 132.10, 133.78, 134.88, 136.87, 138.87, 140.90, 141.09, 166.55, 167.87. (1 signal missing).
MS (+FAB, MNBA, CH_2Cl_2): m7z (%) = 542 (81.7) [M^++H], 215 (100) [pyrene+CH_2^+].

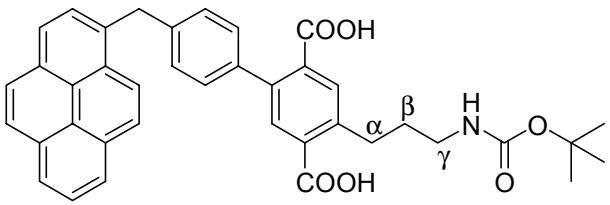
2-(3-tert-Butoxycarbonylamino-propyl)-5-pyrene-1-yl-terephthalic acid (108)



The ester **97** (0.2 g, 0.36 mmol) was suspended in methanol (15 ml). KOH (15 ml, 3 M) and THF (15 ml) were added. The mixture was refluxed for 1 d. The solvents were removed by distillation and the residue was dissolved in water (20 ml). Acetic acid was added until at pH = 4 the product **108** precipitated as a pale yellow solid, which was washed with water. The solid was dissolved in acetone (40 ml), dried ($MgSO_4$) and the acetone removed. The reaction gave product **108** (0.15 g, 0.29 mmol, 80%) as a yellow solid.

^{1}H NMR (500 MHz, DMSO): δ = 1.38 (s, 9 H, CH_3), 1.82, (m, 2 H, CH_2); 2.88-3.21 (m, 4 H, CH_2), 6.90 (s, 1 H, NH), 7.71 (d, 1 H, H_{pyrene})7.75 (s, 1H, $H_{aromatic}$), 7.81-8.40 (m, 9 H, $H_{pyrene + aromatic}$).
^{13}C NMR (126 MHz, DMSO): δ = 28.34, 30.58, 31.51, 40.01, 77.48, 123.82, 124.05, 124.47, 124.83, 124.95, 125.26, 126.30, 127.22, 127.42, 128.24, 129.98, 130.42, 130.93, 131.72, 133.23, 135.41, 136.88, 137.54, 141.47, 155.73, 168.52, 169.50.
MS (-FAB, CH_2Cl_2, DMSO, MNBA): m/z (%) = 522 (100) [M^- -H]
HRMS $^{12}C_{27}{}^{1}H_{18}{}^{14}N_1{}^{16}O_3$ [M^+ -$C_5H_9O_2$/H_2O] calcd 404.12867 found 404.12756.

4-(3-tert-Butoxycarbonylamino-propyl)-4'-pyren-1-ylmethyl-biphenyl-2,5-dicarboxylic acid (109)

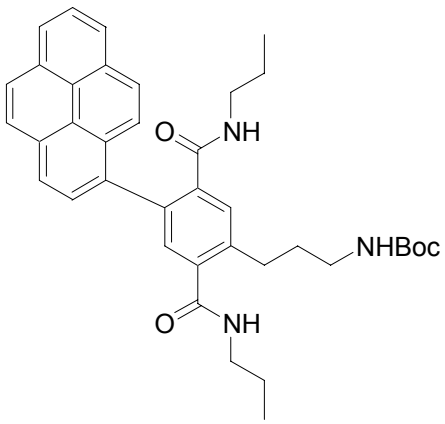


The G1 ester **98** (0.44 g, 0.686 mmol) was dissolved in THF (15 ml), methanol (15 ml) and an aqueous solution of KOH (15 ml, c = 2.5 mol/l) were added. The mixture was refluxed for 2 d. The solvents were removed by distillation and the residue was dissolved in H_2O (40 ml). Acetic acid was added until pH = 4. The product started to

precipitate immediately. The solid was sucked off, washed with water (40 ml) and was dissolved in acetone and dried ($MgSO_4$). Removing the acetone gave the di-acid **109** as a pale yellow solid (0.28 g, 0.460 mmol, 67

^{1}H NMR (500 MHz, DMSO): δ = 1.38 (s, 9H, H_{Boc}), 1.70 (m, 2H, β), 2.84 – 3.09 (m, 4H, α, γ), 4.73 (s, 2H, CH_2), 6.81 (s, 1H, NH), 7.15 – 7.38 (m, 4H, $H_{aromatic}$), 7.57 (s, 1H, $H_{aromatic}$), 7.68 (s, 1H, $H_{aromatic}$), 7.95 - 8.31 (m, 8H, H_{pyrene}), 8.40 (d, 1H, H_{pyrene}).
^{13}C NMR (126 MHz, DMSO): δ = 28.29, 30.36, 31.42, 37.92, 38.37, 77.45, 123.85, 124.09, 124.39, 124.96, 125.09, 125.14, 126.23, 126.80, 127.46, 127.51, 128.36, 128.41, 128.50, 129.68, 130.39, 130.90, 131.03, 131.80, 134.95, 137.69, 140.33, 141.41, 155.65, 168.60, 169.58. (4 signals missing)
MS (-FAB, MNBA, CH_2Cl_2, 3 KV): m/z (%) = 612 (84.1) [M$^-$H].
HRMS $^{12}C_{35}{}^1H_{27}{}^{14}N_1{}^{16}O_5$ (M-C_4H_8O) calcd: 541.18892, found: 541.18756.

N1, N4-Dipropyl-2-(3-tert-butoxycarbonylamino-propyl)-5-pyrene-1-yl-terephthalamide (110)



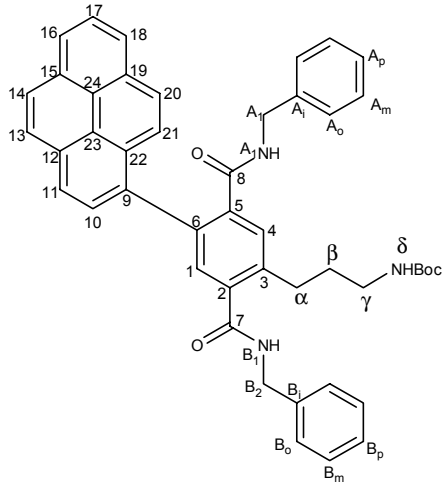
For preparation see general procedure for amide coupling.

Di acid **108** (200.0 mg, 0.382 mmol), HOBT (128.2 mg, 0.840 mmol), dry CH_2Cl_2 (10 ml), propylamine (200.0 mg, 0.800 mmol), DIPEA (210.7 mg, 1.630 mmol), EDC (161.1 mg, 0.840 mmol), 15 h, chromatographic separation with silica gel and Hex:EE 1:3 R_f = 0.15 gave a colorless solid (109.4 mg, 0.181 mmol, 47 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = -0.03 (t, 3 H, CH_3), 0.45 (m, 2 H, CH_2), 0.87 (t, 3 H, CH_3), 1.42 (s, 9 H, CH_3-Boc), 1.54 (m, 2 H, CH_2), 1.90 (m, 2 H, CH_2), 2.65 (m, 2 H, CH_2), 2.87 (m, 2 H, CH_2), 3.16 (m, 2 H, CH_2), 3.31 (m, 2 H, CH_2), 5.17 (s, 1H, NH), 5.29 (s, 1H, NH), 6.40 (s, 1H, NH), 7.42 (s, 1 H, $H_{aromatic}$); 7.73-7.89 (m, 3H, $H_{aromatic + pyrene}$), 7.92-8.25 (m, 7 H, H_{pyrene}).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 10.36, 11.35, 21.54, 22.66, 28.34, 29.12, 29.58, 29.85, 31.14, 39.67, 41.04, 41.57, 78.80, 124.21, 124.38, 124.60, 125.29, 125.47, 126.22, 127.06, 127.11, 127.88, 128.37, 128.89, 130.11, 130.67, 130.80, 131.06, 131.18, 134.14, 135.83, 137.58, 138.32, 139.62, 156.10, 167.50, 169.29.
MS (+FAB, DMSO, CH_2Cl_2, MNBA, 3 KV): m/z (%) = 606 (19.9)[$M^{+\cdot}$ +H], 550 (2.9) [$M^{+\cdot}$ –C_4H_8], 507 (54.5) [$M^{+\cdot}$ –C_7H_{15}].
EA $C_{38}H_{43}N_3O_4$ (605.77) calcd C 75.34 H 7.15 N 6.94 found C 75.06 H 7.23 N 6.92.

N1, N4- Dibenzyl-2-(3- tert- butoxycarbonylamino- propyl)- 5- pyrene- 1- yl- terephthalamide (111)



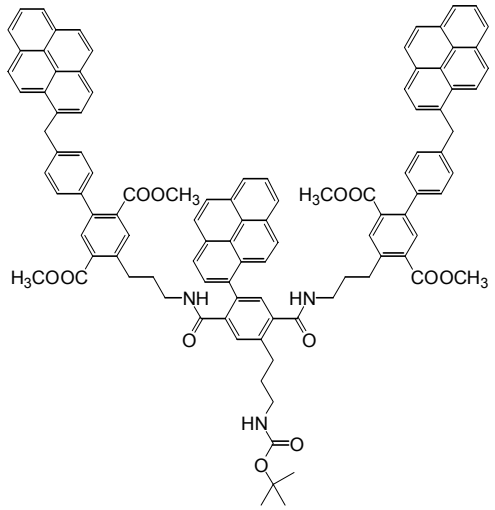
For preparation see general procedure for amide coupling.

Di acid **108** (50.0 mg, 0.096 mmol), HOBT (32.2 mg, 0.210 mmol), dry CH_2Cl_2 (10 ml), benzyl amine (20.5 mg, 20.9 µl, 0.191 mmol), DIPEA (73.2 µl, 0.420 mmol), EDC (40.3 mg, 0.210 mmol), 1d, chromatographic separation with silica gel and CH_2Cl_2:MeOH 2% R_f = 0.19 gave **111** as a colorless solid (38.0 mg, 0.054 mmol, 56 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 9 H, CH_3-Boc), 1.81 (m, 2 H, H_β), 2.81 (m, 2 H, H_α), 3.06, m, 2 H, H_γ), 3.71 (d, 1 H, A_2), 3.85 (d, 1 H, A'$_2$), 4.45 (s, 2 H, B_2), 4.95 (s, 1 H, H_δ), 5.28, (s, 1 H, A_1), 5.89 (d, 1H, A_o), 6.19 (t, 2 H, A_m), 6.36 (s, 1 H, B_1), 6.46 (m, 2 H, A_p), 7.03-7.25 (m, 5 H, B_p, B_m, B_o), 7.32 (s, 1 H, H_1), 7.60 (d, 1 H, H_{21}), 7.68 (m, 1 H, H_{10}), 7.77 (s, 1H, H_4), 7.82 (m, 1 H, H_{20}), 7.86-8.07 (m, 5 H, $H_{12, 13, 14, 17, 18}$), 8.12 (d, 1 H, H_{16}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.41 (CH_3-Boc), 29.98 (α), 31.30 (β), 39.78 (γ), 43.79 (A_2), 43.98 (B_2), 78.94 (C-Boc), 124.00 (21), 124.48 (23), 124.56 (24), 124.71 (11), 125.42 (18), 125.53 (16), 126.29 (17), 126.56 (A_p), 126.70 (A_o), 126.88 (10), 127.19 (13), 127.53 (A_m), 127.61 (B_p), 127.94 (B_o+14), 128.60 (20), 128.72 (B_m),

128.93 (22), 130.05 (1), 130.72 (19), 131.14 (4 + 12), 131.30 (15), 133.78 (9), 136.01 (6), 136.14 (A_i), 137.39 (5), 137.70 (B_i), 137.97 (2), 140.07 (3), 156.12 (C=O Boc), 167.18 (8), 169.00 (7).
MS (EI, 250-300 °C, 80 eV): m/z (%) = 701 (0.6) [$M^{+\cdot}$], 627 (0.9) [$M^{+\cdot}$ –$C_4H_{10}O$], 571 (0.2) [$M^{+\cdot}$ –$C_6H_{12}O_2N$], 494 (0.2) [$M^{+\cdot}$ –$C_{12}H_{17}NO_2$].
HRMS $^{12}C_{46}{}^{1}H_{43}{}^{14}N_3{}^{16}O_4$ calcd 701.32536 found 701.32733.

N1, N4- Bis- (3- [-4'- pyrene- 1- ylmethyl- biphenyl- 4-yl- 2,5- bis- methoxycarbonyl]propyl)-2-(3-tert-butoxycarbonylamino-propyl)-5-pyrene-1-yl- terephthalamide (112)



For preparation see general procedure for amide coupling.

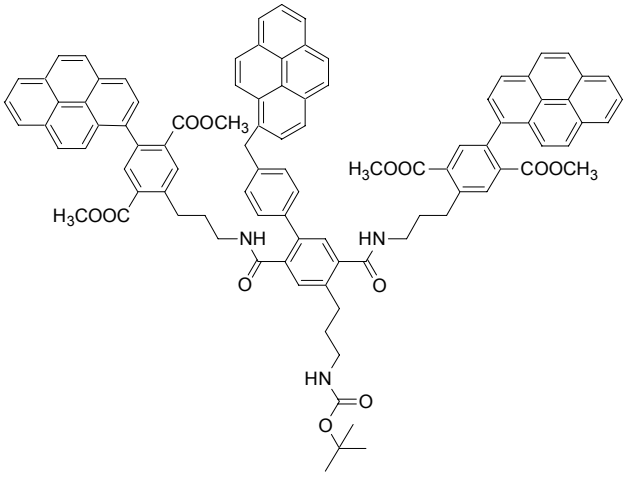
Di acid **108** (92.1 mg, 0.176 mmol), HOBT (59.7 mg, 0.370 mmol), dry CH_2Cl_2 (5 ml), dummy-amine **107** (200.0 mg, 0.370 mmol), DIPEA (98.2 mg, 0.76 mmol), EDC (74.8 mg, 0.390 mmol), 15 h, chromatographic separation with silica gel and Hex:EE 1:2 R_f (CH_2Cl_2:2 % MeOH) = 0.15 gave **112** as a yellow oil (78.0 mg, 0.050 mmol, 28 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.60 – 0.90(m, 2H, CH_2), 1.45 (s, 9H, $CH_{3\ Boc}$), 1.75 – 1.96 (m, 4H, CH_2), 2.01 (m, 2H, CH_2), 2.72 – 2.95 (m, 2 H, CH_2), 3.00 (m, 4 H, CH_2), 3.20 (s, 3 H, CH_3), 3.23 (m, 2 H, CH_2), 3.47 (m, 2 H, CH_2), 3.60 (s, 3 H, CH_3), 3.64 (s, 3 H, CH_3), 3.65 (s, 3H, CH_3), 4.70 (s, 2H, CH_2), 7.78 (s, 2H, CH_2), 5.22 (s, 1H, NH-Boc), 5.65 (s, 1H, NH), 6.88 (s, 1H, NH), 7.00 (s, 1H, $H_{aromatic}$), 7.10 (d, 2H, $H_{aromatic}$), 7.18 (d, 4H, $H_{aromatic}$), 7.25 (d, 2H, $H_{aromatic}$), 7.60 (s, 1H, $H_{aromatic}$), 7.64 (s, 1H, $H_{aromatic}$), 7.67 (s, 1H, $H_{aromatic}$), 7.70 (s, 1H, $H_{aromatic}$), 7.82 – 8.22 (m, 27 H, $H_{pyrene\ +\ aromatic}$), 8.25 (d, 1H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.40, 29.77, 29.85, 29.98, 30.85, 30.96, 31.36, 38.82, 38.95, 38.99, 39.25, 39.77, 51.76, 51.98, 52.08, 52.13, 78.82, 123.63, 123.68,

124.24, 124.47, 124.54, 124.75, 124.81, 124.85, 125.01, 125.03, 125.06, 125.11, 125.37, 125.86, 126.10, 126.86, 127.29, 127.40, 127.42, 127.45, 127.74, 128.18, 128.25, 128.30, 128.41, 128.45, 128.84, 129.06, 129.10, 130.17, 130.20, 130.36, 130.59, 130.72, 130.74, 130.92, 130.97, 130.99, 131.26, 131.28, 131.34, 132.10, 132.66, 132.94, 133.31, 133.81, 134.13, 134.19, 134.40, 135.88, 137.55, 137.72, 137.91, 138.29, 139.22, 139.72, 140.29, 140.50, 140.52, 141.70, 142.30, 156.14, 166.36, 166.81, 168.02, 168.22, 168.26, 169.35. (13 signals missing)

MS(+FAB, DMSO/MNBA, 2KV): m/z = 1570 (18.02) [M^+], 1470 (100) [M^+-$C_5H_8O_2$]. EA $C_{104}H_{87}N_3O_{12}$ (1570.82) calcd. C 79.52 H 5.58 N2.68, found C 78.53 H 5..34 N 2.36.

4-(3-tert-Butoxycarbonylamino-propyl)-4'-pyrene-1-ylmethyl-biphenyl-2,5-dicarboxylic acid bis-{[3-(2,5-bis-methoxycarbonyl-4-pyrene-1-yl)-propyl]-amide} (113)



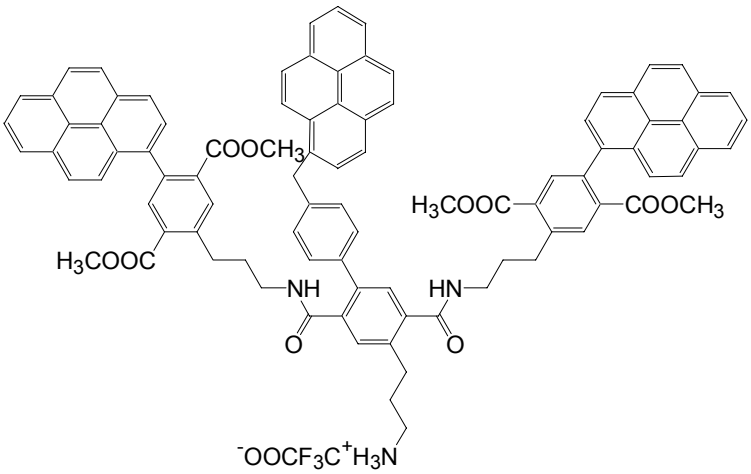
For preparation see general procedure for amide reaction.

Dummy-di-acid **109** (114.0 mg, 0.186 mmol), HOBT (62.6 mg, 0.409 mmol), dry CH_2Cl_2 (15 ml), Amine **106** (176.1 mg, 0.390 mmol) DIPEA (100.8 mg, 0.780 mmol), EDC (74.8 mg, 0.390 mmol), 14 h, chromatographic separation with silica gel and hexane:ethyl acetate 1:2 gave the product **113** (130.0 mg, 0.088 mmol, 47 %) as a pale yellow oil, freeze drying with benzene gave a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (s, 9H, CH_3), 1.73 (m, 2H, CH_2), 1.96 (m, 2H, CH_2), 2.07 (m, 2H, CH_2), 2.61 (m, 2H, CH_2), 2.95 (m, 2H, CH_2), 3.20 (m, 4H, CH_2), 3.24 – 3.38 (m, 8H, CH_3, CH_3, CH_2), 3.43 (s, 3H, CH_3), 3.58 (m, 2H, CH_2), 3.78 (s, 3H, CH_3), 4.67 (s, 2H, CH_2), 5.28 (s, 1H, NH), 6.09 (s, 1H, NH), 6.94 (s, 1H, NH),

7.28 (d, 2H, $H_{aromatic}$), 7.42 (d, 2H, $H_{aromatic}$), 7.54 (s, 1H, $H_{aromatic}$), 7.62 (s, 1H, $H_{aromatic}$), 7.68 – 8.28 (m, 31H, $H_{aromatic + pyrene}$).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.36, 29.76, 30.41, 30.49, 31.05, 31.17, 31.25, 38.81, 39.09, 39.39, 39.66, 52.05, 52.30, 78.74, 123.33, 124.26, 124.37, 124.42, 124.57, 124.62, 124.65, 124.75, 124.96, 125.18, 125.23, 125.75, 125.92, 125.97, 126.69, 126.81, 127.27, 127.36, 127.38, 127.45, 127.68, 127.97, 128.60, 128.65, 128.74, 128.86, 130.09, 130.37, 130.51, 130.66, 130.68, 130.73, 131.09, 131.26, 131.30, 131.37, 131.75, 132.38, 132.62, 133.92, 134.41, 134.50, 134.60, 134.64, 135.45, 136.88, 137.16, 137.23, 137.80, 139.21, 139.35, 139.48, 140.93, 142.70, 143.01, 156.08, 166.81, 166.90, 167.08, 167.14, 169.47, 169.15. (17 signals missing)
MS (+FAB, CH_2Cl_2/MNBA, 2KV): m/z (%) = 1480 (36.4) [M^+], 1379 (73.6) [M^+-$C_5H_9O_2$].
EA $C_{97}H_{81}N_3O_{12}$ (1480.69) calcd C 78.68 H 5.51 N 2.84 found C 77.92 H 5.51 N 2.76.

4-(3-amino-propyl)-4'-pyrene-1-ylmethyl-biphenyl-2,5-dicarboxylic acid bis-{[3-(2,5-bis-methoxycarbonyl-4-pyrene-1-yl)-propyl]-amide} trifluoroacetate (114)



Boc protected G2-dendron **113** (367 mg, 0.248 mmol) was dissolved in chloroform (10 ml), trifluoroacetic acid was added (3 ml). The solution was stirred for 2.5 h at room temperature. The solvents were removed through distillation. Freeze drying of the residue gave the product **114** (426 mg, 0.248 mmol, 100 %) as a brown solid. The product contained some trifluoroacetic acid. The yield was calculated with three molecules of trifluoroacetic acid for every dendron.

^1H NMR (270 MHz, $CDCl_3$): δ = 1.64 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 2.26 (s, 2H, NH_2), 2.58 (m, 2H, CH_2), 2.78 (m, 2H, CH_2), 2.96 (m, 2H, CH_2), 3.16 (m, 2H, CH_2), 3.21 – 3.38 (m, 8H, CH_3, CH_3, CH_2), 3.50 (s, 3H, CH_3), 3.56 (m,

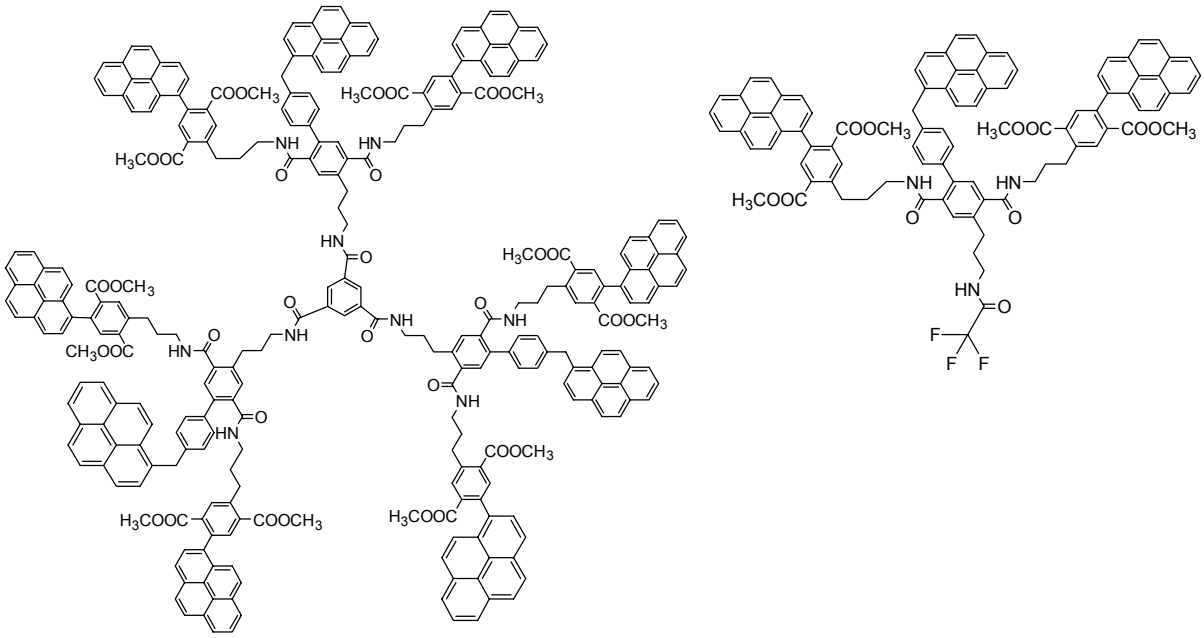
2H, CH_2), 3.75 (s, 3H, CH_3), 4.66 (s, 2H, CH_2), 6.04 (t, 1H, NH), 7.26 (d, 2H, $H_{aromatic}$), 7.41 (d, 2H, $H_{aromatic}$), 7.52 – 7.73 (m, 4H, $H_{aromatic}$ + NH), 7.73 – 8.28 (m, 30H, $H_{aromatic + pyrene}$).

^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 27.36, 27.79, 29.86, 30.07, 30.29, 31.01, 38.93, 39.95, 40.33, 52.20, 52.50, 64.47, 115.00 (q, J = 284 Hz, CF_3), 123.28, 124.21, 124.32, 124.43, 124.60, 124.71, 124.75, 124.89, 125.15, 125.43, 125.51, 125.91, 126.16, 126.18, 126.81, 127.00, 127.36, 127.42, 127.64, 127.71, 127.99, 128.74, 128.79, 128.89, 128.93, 129.20, 129.75, 130.34, 130.63, 130.81, 130.87, 130.97, 131.00, 131.24, 131.33, 131.43, 131.47, 131.87, 132.42, 132.70, 133.82, 134.68, 134.89, 134.96, 135.04, 135.09, 135.90, 136.12, 136.96, 137.69, 138.65, 139.62, 139.77, 142.11, 142.31, 142.81, 159.82 (q, J = 41 Hz, C=O), 167.51, 167.60, 168.31, 168.39, 171.12, 171.63. (16 signals missing)

MS (+FAB, CH_2Cl_2/DMSO/MNBA, 2KV): m/z (%) = 1381 (100) $[M+H]^{+\cdot}$

EA $C_{98}H_{76}N_3O_{16}F_9$ (1722.64) [M+3xCF_3COOH] calcd C 68.33 H 4.45 N 2.44 found C 68.15 H 4.46 N 2.33.

Benzene-1,3,5-(3-{2,5-bis-[3-(2,5-bis-methoxycarbonyl-4-pyrene-1-yl-phenyl)propylcarbamoyl]-4'-pyrene-1-ylmethyl-biphenyl-4-yl}-propylcarbamoyl) (116) and 4-[3-(2,2,2-Trifluoro-acetylamino)-propyl]-4'-pyrene-1-ylmethyl-biphenyl-2,5-dicarboxylic acid bis-{[3-(2,5-bis-methoxycarbonyl)-4-pyrene-1-yl)-propyl]-amide} (117)



For preparation see general procedure for amide coupling.

Acid-core **115** (9.3 mg, 0.044 mmol), HOBt (19.8 mg, 0.147 mmol), dry CH_2Cl_2 (5 ml), DIPEA, (69 µl, 0.400 mmol), G2-amine **114** (420.0 mg, 0.229 mmol), EDC (28.1 mg, 0.147 mmol), 12 h, chromatographic separation with CH_2Cl_2:MeOH 5:1 gave the by-product **117** (44.0 mg, 0.030 mmol, 13 %) and the G2 Dendrimer **116** (101.0 mg, 0.024 mmol, 53 %) as yellow oils. Freeze drying with benzene gave pale yellow solids. For X: R_f = 0.31, for X R_f = 0.15.

For Trifluoroamide **117**:

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.71 (m, 2H, CH_2), 2.06 (m, 4H, CH_2), 2.65 (m, 2H, CH_2), 2.90 (m, 2H, CH_2), 3.17 (m, 2H, CH_2), 3.27 (m, 2H, CH_2), 3.30 (s, 6H, CH_3), 3.37 (m, 2H, CH_2), 3.40 (s, 3H, CH_3), 3.57 (m, 2H, CH_2), 3.77 (s, 3H, CH_3), 4.67 (s, 2H, CH_2), 5.85 (t, 1H, J = 5.4 Hz, NH), 6.89 (t, 1H, J = 5.4 Hz, NH), 7.28 (d, 2H, J = 8.2 Hz, $H_{aromatic}$), 7.38 (d, 2H, J = 8.2 Hz, $H_{aromatic}$), 7.51 (s, 1H, $H_{aromatic}$), 7.63 (s, 1H, $H_{aromatic}$),7.64-8.24 (m, 31H, $H_{pyrene + aromatic}$), 8.65 (t, 1H, J = 5.4 Hz, NH).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 29.21, 29.67, 30.04, 30.56, 31.03, 31.18, 38.46, 38.91, 39.30, 39.60, 52.07, 52.25, 116.66 (q, J = 288 Hz),123.38, 124.31, 124.49, 124.54, 124.73, 124.78, 124.85, 125.06, 125.08, 125.27, 125.33, 125.87, 126.01, 126.07, 126.79, 126.95, 127.35, 127.45, 127.50, 127.57, 127.75, 128.05, 128.78, 128.93, 129.02, 130.27, 130.61, 130.64, 130.83, 131.25, 131.40, 131.44, 131.85, 132.41, 132.63, 133.93, 134.53, 134.71, 134.94, 135.51, 137.11, 137.34, 137.45, 137.75, 139.36, 139.42, 139.53, 139.36, 139.42, 139.53, 141.30, 142.72, 142.94, 158.22 (q, J = 36 Hz) 166.92, 167.07, 167.15, 167.25, 168.92, 170.01. (19 signals missing)
MS (+FAB, 2KV, MNBA/DMSO): m/z (%) = 1477 (23.5) [M^++H].
MALDI-TOF MS: m/z = 1476.64 [M^+].
EA $C_{94}H_{72}F_3N_3O_{11}$ (1476.59) calcd C 76.46 H 4.91 N 2.85; found C 76.15 H 4.73 N 2.64

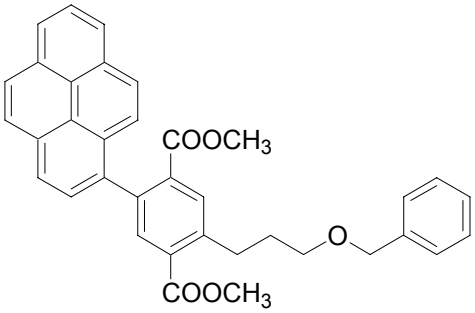
For dendrimer **116**:

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.68 (m, 6H, CH_2), 1.97 (m, 6H, CH_2), 2.04 (m, 6H, CH_2), 2.71 (m, 6H, CH_2) ,2.95 (m, 6H, CH_2),3.03-3.34 (m, 30H, CH_3, CH_2), 3.40 (s, 9H, CH_3), 3.46 (m, 6H, CH_2), 3.54 (m, 6H, CH_2), 3.73 (s, 9H, CH_3), 4.59 (s, 6H, CH_2), 6.10 (s, 3H, NH), 6.92 (s, 3H, NH), 7.05-7.50 (m, 15H, NH + $H_{aromatic}$), 7.50-8.34 (m, 99H, $H_{pyrene+aromatic}$), 8.42 (s, 3H, H_{core}).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.04, 30.13, 30.54, 30.74, 31.20, 31.33, 38.84, 39.31, 39.41, 39.66, 52.01, 52.24, 123.42, 124.28, 124.51, 124.69, 124.74, 124.81, 125.00, 125.22, 125.80, 125.96, 126.81, 127.35, 127.43, 127.69, 128.02, 128.52,

128.73, 128.83, 128.95, 130.15, 130.47, 130.63, 130.75, 130.80, 130.83, 131.20, 131.40, 131.96, 132.36, 132.63, 134.10, 134.44, 134.60, 134.79, 135.17, 135.57, 136.96, 137.15, 137.38, 137.44, 139.23, 139.32, 139.60, 140.84, 142.79, 143.17, 166.14, 166.95, 167.15, 167.25, 169.23, 169.85. (29 signals missing)
$C_{285}H_{219}N_9O_{33}$ (4297.83) MALDI-TOF MS m/z = 4299.01 [M^++H]

7.7 Synthesis of compounds from chapter 4.7

2-(3-Benzyloxy-propyl)-5-pyrene-1-yl-terephthalic acid dimethyl ester (119)



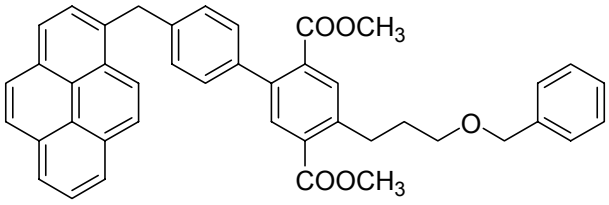
For preparation see general procedure for SCC 2.

Protected allyl **118** (1.44 g, 9.72 mmol), 9-BBN (1.49 g, 12.10 mmol), dry toluene (20 ml), 12 h, bromo – compound **96** (2.3 g, 4.86 mmol), toluene (100 ml), aqueous solution of KOH (50 ml, 1M), $Pd(PPh_3)_4$ (0.14 g, 0.120 mmol), 3 d at 50 °C. Chromatographic separation with silica gel and hexane:ethyl acetate gave product **119** (2.19 g, 4.04 mmol, 83 %) as a yellow oil. (If necessary it could be recrystallized in MeOH, a yellow solid precipitated).

^{1}H NMR (270 MHz, $CDCl_3$):δ = 2.17 (m, 2H, CH_2-β), 3.30 (m, 2H, CH_2-α), 3.38 (s, 3H, CH_3), 3.68 (t, 2H, CH_2-γ), 3.89 (s, 3H, CH_3), 4.63 (s, 2H, CH_2), 7.29 – 7.56 (m, 5H, $H_{aromatic}$), 7.81 (d, 1H, H_{pyrene}), 7.92 (d, 1H, H_{pyrene}), 7.96 – 8.36 (m, 9H, $H_{pyrene\ +\ aromatic}$).
^{13}C NMR (68 MHz, $CDCl_3$): δ = 30.68 (β), 31.32 (α), 51.89 (CH_3), 52.09 (CH_3), 69.70 (γ), 72.85 (CH_2), 124.24, 124.49, 124.60, 124.72, 124.91, 125.13, 125.90, 126.79, 127.38, 127.39, 127.59, 128.29, 128.75, 130.67, 130.81, 131.34, 132.28, 132.61, 134.34, 135.72, 138.57, 139.14, 143.07, 167.15, 167.24. (3 signals missing)
MS (EI, 230 °C, 80 eV): m/z (%) = 542 (100) [M^+], 421 (11.0) [M^+-C_8H_9O], 361 (9.6) [M^+-$C_{10}H_{13}O_3$], 201 (5.0) [pyrene$^+$-H].
HRMS $^{12}C_{36}{}^{1}H_{30}{}^{16}O_5$ calcd 542.20932 found 542.20758.

EA $C_{36}H_{30}O_5$ (542.62) caldc C 79.68 H 5.57, found C 79.37 H 5.44.

4-(3-Benzyloxy-propyl)-4'-pyrene-1-ylmethyl-biphenyl-2,5-dicarboxylic acid dimethyl ester (120)

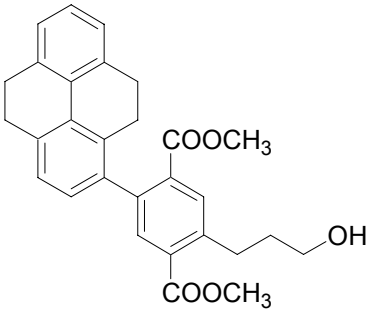


For preparation see general procedure for SCC 2.

Allyl **118** (0.12 g, 0.816 mmol), 9-BBN (0.13 g, 1.020 mmol), dry toluene (20 ml), 12 h, bromo-di-ester **105** (0.23 g, 0.408 mmol), aqueous solution of KOH (15 ml, 1 M), 3 d at 50 °C. Chromatographic separation with silica gel and hexane:ethyl acetate 10:1 gave the product **120** (0.04 g, 0.070 mmol, 17 %) as a yellow oil. R_f (hexane:ethyl acetate 3:1) = 0.08. Educt **105** could be regained (132 mg, 58 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.98 (m, 2H, CH_2), 3.10 (m, 2H, CH_2), 3.54 (t, 2H, CH_2), 3.63 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 4.53 (s, 2H, CH_2), 4.77 (s, 2H, CH_2), 7.18 – 7.33 (m, 4H, $H_{aromatic}$), 7.70 (s, 1H, $H_{aromatic}$), 7.85 (s, 1H, $H_{aromatic}$), 7.90 (d, 1H, H_{pyrene}), 7.95 – 8.23 (m, 7H, H_{pyrene}), 8.27 (d, 1H, H_{pyrene}).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 30.51, 31.25, 39.01, 52.07, 52.09, 69,65, 72.82, 123.69, 124.85, 125.02, 125.15, 125.86, 126.87, 127.45, 127.60, 128.23, 128.30, 128.42, 128.45, 129.15, 130.23, 130.80, 131.33, 131.87, 132.20, 132.82, 133.48, 134.26, 137.87, 138.55, 139.58, 140.46, 142.50, 167.16, 168.45. (4 signals missing)
MS (EI, 100 °C, 80 eV): m/z (%) = 632 (100) [M^+], 215 (56.6) [pyrene+CH_2^+], 91 (42.4) [$C_7H_7^+$].
HRMS $^{12}C_{43}{}^{1}H_{36}{}^{16}O_5$ calcd C 632.25628, found 632.25836.

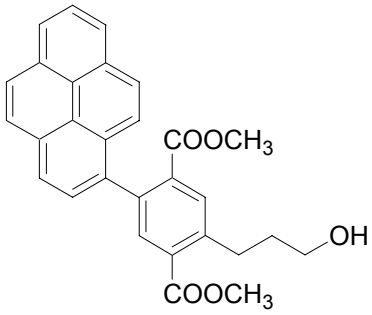
2-(3-Hydroxy-propyl)-5-(4,5,9,10-tetrahydro-pyrene-1-yl)-terephthalic acid dimethyl ester (121)



Benzyl protected probe **119** (1.74 g, 3.21 mmol) was emulgated in MeOH (70 ml) and Pd catalyst (0.46 g, 10%) was added. The mixture was handled in a hydrogenation apparatus at 40 °C and 3 bar H_2 for 2 d. The solution was filtrated over celite and the residue was washed with $CHCl_3$ (200 ml). The organic phases were combined and the solvents removed. Chromatographic separation with silica gel and hexane:ethyl acetate 3:1 gave the product **121** as a colorless oil (0.97 g, 2.13 mmol, 66 %). R_f (hexane:ethyl acetate 1:1) = 0.21.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.00 (m, 2H, β), 2.58 (m, 2H, 19), 2.77 (m, 2H, 18), 2.94 (m, 4H, 11,12), 3.15 (m, 2H, α), 3.65 (s, 3H, 26), 3.71 (m, 2H, γ), 3.90 (s, 3H, 25), 6.99 (d, 1H, 8), 7.06 (d, 1H, 14), 7.08 – 7.20 (m, 3H, 9,15,16), 7.83 (s, 1H, 1), 7.87 (s, 1H, 4).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.58 (19), 28.02 (18), 28.27 + 28.38 (11 + 12), 29.57 (α), 34.25 (β), 52.12 (26), 52.27 (25), 61.57 (γ), 125.21 (9), 125.68 (16), 125.84 (14), 127.05 (15), 127.58 (8), 130.33 (22), 130.68 (21), 131.90 (2), 132.18 (4), 132.94 (20), 133.30 (1), 133.73 (5), 134.80 (10), 135.26 (17), 135.59 (13), 137.11 (7), 139.71 (6), 142.56 (3), 167.27 (24), 167.47 (23).
MS (EI, 170 °C, 80 eV): m/z (%) = 456 (100) [M^+], 407 (19.5) [M^+-CH_5O_2], 365 (18.8) [M^+-$C_3H_7O_3$], 205 (6.9) [tetrahydropyrene$^+$].
EA $C_{29}H_{28}O_5$ (456.53) calcd C 76.30 H 6.18, found C 76.17 H 6.14

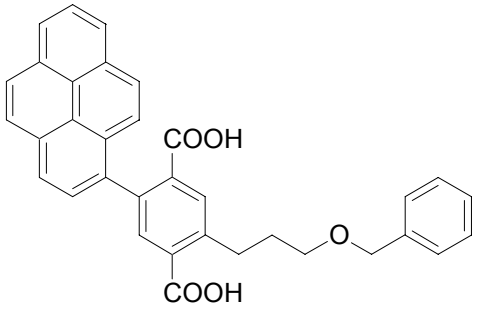
2-(3-Hydroxy-propyl)-5-pyrene-1-yl-terephthalic acid dimethyl ester (122)



Probe-benzylether **119** (384 mg, 0.708 mmol) was suspended in dry MeOH (15 ml), 1,4 cyclohexadien (1.34 ml, 14.2 mmol) and Pd/C catalyst (144 mg, 10% Pd/C) were added. The mixture was refluxed for 2 d. The solution was filtrated with celite, and the filtrate-residue was washed with $CHCl_3$ (100 ml). The organic solvents were combined and evaporated. The crude-product of **122** was dried and gave a yellow oil (307 mg, 0.678 mmol, 96 %).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.08 (m, 2H, β), 2.66 (s, 1H, OH), 3.23 (m, 2H, α), 3.34 (s, 3H, CH_3), 3.75 (t, 2H, γ), 3.86 (s, 3H, CH_3), 7.75 (d, 1H, H_{pyrene}), 7.86 (d, 1H, H_{pyrene}), 7.92 – 8.30 (m, 9H, $H_{pyrene + aromatic}$).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.72 (β), 34.35 (α), 51.98 (CH_3), 52.32 (CH_3), 61.67 (γ), 124.25, 124.47, 124.53, 124.69, 124.94, 125.17, 125.92, 126.76, 127.38, 127.64, 128.23, 128.73, 130.69, 130.79, 131.33, 132.13, 132.62, 134.35, 134.58, 135.58, 139.14, 143.16, 167.45, 167.29.
MS (+FAB, MNBA/CH_2Cl_2, 3 KV): m/z (%) = 453 (90.0) [M^++H], 422 (25.4) [(M^++H)-CH_3O], 276 (13.8) [(M^++H)-$C_7H_{13}O_5$].
HRMS $^{12}C_{29}{}^1H_{24}{}^{16}O_5$ calcd 452.16237, found 452.16687.

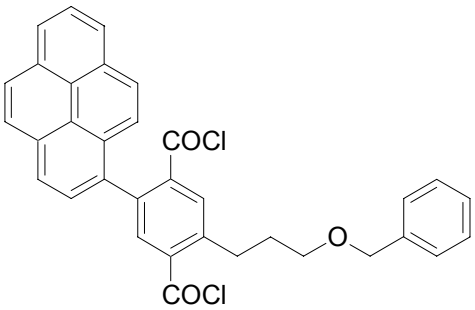
2-(3-Benzyloxy-propyl)-5-pyrene-1-yl-terephthalic acid (123)



Di ester **119** (0.53 g, 0.975 mmol), was dissolved in a mixture of THF (20 ml), MeOH (20 ml) and KOH (20 ml, 1M). Solid KOH (1.78 g, 31.786 mmol) was added and the mixture was refluxed for 36 h. The solvents were removed and water (40 ml) was added to give a clear solution. An aqueous solution of HCl (25 %) was dropped in until the di-acid precipitated. The product was sucked off immediately and was washed with water. It was dissolved in acetone and dried. Evaporation of the acetone gave the product **123** as a yellow solid (0.48 g, 0.933 mmol, 96 %).

^{1}H NMR (250 MHz, DMSO): δ = 2.00 (m, 2H, β), 3.16 (m, 2H, α), 3.54 (m, 2H, γ), 4.48 (s, 2H, CH_2), 7.12 – 7.54 (m, 5H, $H_{aromatic}$), 7.74 (d, 1H, H_{pyrene}), 7.80 – 8.50 (m, 10H, $H_{pyrene + aromatic}$).
^{13}C NMR (63 MHz, DMSO): δ = 30.03, 31.02, 69.25, 71.84, 123.81, 124.01, 124.48, 124.63, 124.99, 125.29, 126.28, 127.32, 127.49, 128.23, 130.09, 130.39, 130.90, 132.01, 133.44, 133.94, 135.30, 136.41, 137.84, 138.69, 141.94, 168.07, 168.59. (5 signals missing)
MS (EI, 200 °C, 80 eV): m/z (%) = 514 (100) [M^+], 422 (4.1) [M^+-C_7H_8], 406 (14.0) [M^+-C_7H_8O], 289 (11.2) [M^+-$C_{11}H_{13}O_5$].
HRMS $^{12}C_{34}{}^{1}H_{26}{}^{16}O_5$ calcd 514.17802 found 514.17572.

2-(3-Benzyloxy-propyl)-5-pyrene-1-yl-terephthaloyl dichloride (124)

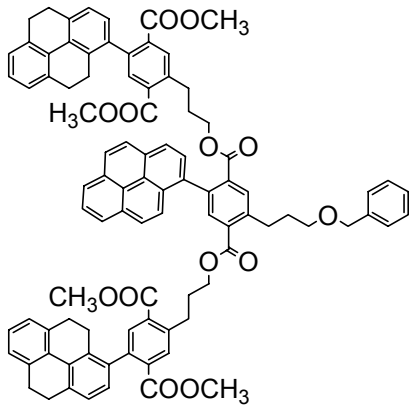


Di-acid **123** (205 mg, 0.398 mmol), was suspended in dry CH_2Cl_2 (10 ml), $SOCl_2$ (3 ml) was added. The mixture was refluxed and became a clear orange solution after 10 min. The solution was refluxed for 1.5 h, then the solvents were removed by distillation and the residue was dried. The product **124** was an orange amorph oil (219 mg, 0.397 mmol, 99.8 %).

^{1}H NMR (270 MHz, CD_2Cl_2): δ = 2.08 (m, 2H, β), 3.19 (m, 2H, α), 3.64 (t, 2H, γ), 4.56 (s, 2H, CH_2), 7.19 – 7.54 (m, 5H, $H_{aromatic}$), 7.75 (d, 1H, H_{pyrene}), 7.90 (d, 1H, H_{pyrene}), 7.98 – 8.43 (m, 9H, $H_{pyrene + aromatic}$).
^{13}C NMR (68 MHz, CD_2Cl_2): δ = 31.05, 31.28, 69.64, 73.26, 124.19, 124.86, 124.96, 125.81, 126.12, 126.73, 127.47, 127.65, 127.88, 127.99, 128.46, 128.69, 128.83,

129.23, 131.12, 131.72, 131.86, 133.22, 133.98, 136.75, 137.04, 139.08, 139.49, 139.60, 144.19, 167.46, 167.63. (1 signal missing)
MS (+FAB, CH_2Cl_2/MNBA, 3 KV): m/z (%) = 552 (0.3) [M^++H].

2-(3-Benzyloxy-propyl)-5-pyrene-1-yl-terephthalic acid bis-{3-[2,5-bis-methoxycarbonyl-4-(4,5,9,10-tetrahydro-pyrene-1-yl)-phenyl]-propyl} ester (125)

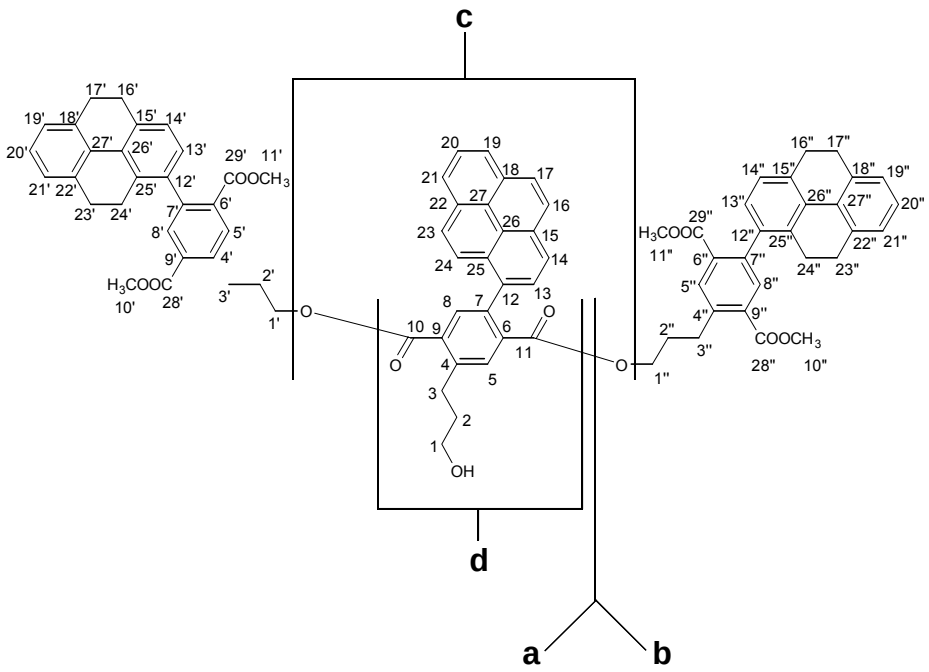


Di acid chloride **124** (194.7 mg, 0.353 mmol) was dissolved in dry THF (10 ml), the orange solution was cooled to –5 °C, then DMAP (16.0 mg, 0.131 mmol), dry NEt_3 (214.0 mg, 2.120 mmol) and the alcohol **121** (580 mg, 1.27 mmol) were added. The color changed to yellow and a solid precipitated. The mixture was stirred for 6 h, then was diluted with CH_2Cl_2 (20 ml). Water (30 ml) was added and the organic phase was separated and dried ($MgSO_4$). Chromatographic separation with hexane:ethyl acetate 3:1 gave the G2 dendron **125** (164.0 mg, 0.118 mmol, 33 %) as a colorless oil. R_f = 0.22.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 – 1.22 (m, 4H, CH_2), 1.94 – 2.17 (m, 6H, CH_2), 2.39 (m, 4H, CH_2), 2.58 (m, 2H, CH_2), 2.65 (m, 2H, CH_2), 2.70 – 2.86 (m, 8H, CH_2), 3.00 (m, 2H, CH_2), 3.20 (m, 2H, CH_2), 3.40 (s, 3H, CH_3), 3.43 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), 3.57 (s, 3H, CH_3), 3.66 – 3.70 (m, 2H, CH_2), 4.31 (t, 2H, CH_2), 4.47 (s, 2H, CH_2), 6.78 (d, 1H, $H_{aromatic}$), 6.82 – 7.04 (m, 9H, $H_{aromatic}$), 7.08 – 7.33 (m, 6H, $H_{aromatic}$), 7.57 (d, 1H, H_{pyrene}), 7.61 – 8.17 (m, 13H, $H_{pyrene + aromatic}$).
^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.68, 25.53, 27.97, 28.03, 28.24, 28.37, 28.97, 29.60, 30.24, 30.51, 30.72, 31.38, 51.67, 51.81, 51.84, 52.01, 64.68, 64.91, 69.72, 72.81, 124.28, 124.42, 124.52, 124.64, 124.84, 125.06, 125.18, 125.21, 125.65, 125.66, 125.81, 126.87, 127.02, 127.11, 127.27, 127.38, 127.52, 127.56, 127.70, 128.24, 128.92, 130.28, 130.64, 130.68, 131.16, 131.27, 131.31, 131.43, 131.70, 131.99, 132.52, 132.55, 132.77, 132.86, 133.18, 133.30, 133.47, 133.59, 134.22, 134.69, 134.72, 135.21, 135.52, 135.56, 136.04, 137.05, 137.15, 138.52, 138.85,

139.50, 139.56, 139.95, 141.46, 141.77, 143.12, 166.50, 166.53, 166.64, 166.78, 166.98, 167.18. (9 signals missing)
MS (+FAB, CH_2Cl_2/MNBA, 2 KV): m/z (%) = 1393 (100) [M^++H].
HRMS $^{12}C_{91}{}^{13}C_1{}^1H_{78}{}^{16}O_{13}$ calcd 1391.54760**,** found 1391.54340.
EA $C_{92}H_{78}O_{13}$ (1391.60) calcd C 79.40 H 5.65, found C 78.79 H 5.58.

2-(3-Hydroxy-propyl)-5-pyrene-1-yl-terephthalic acid bis-{3-[2,5-bis-methoxycarbonyl-4-(4,5,9,10-tetrahydro-pyrene-1-yl)-phenyl]-propyl} ester (126)



Procedure was analogous to the one described for G1-Alkohol.

Benzyl protected G2 dendron **125** (144.0 mg, 0.104 mmol), dry MeOH (10 ml), 1,4 cyclohexadiene (2 ml), Pd 10%/C (109 mg), 5 d, chromatographic separation with silica gel and hexane:ethyl acetate 1:1 gave the G2 alkohol **126** (89.0 mg, 0.068 mmol, 66 %) as a colorless oil, freeze drying in benzene gave a colorless solid. R_f = 0.19

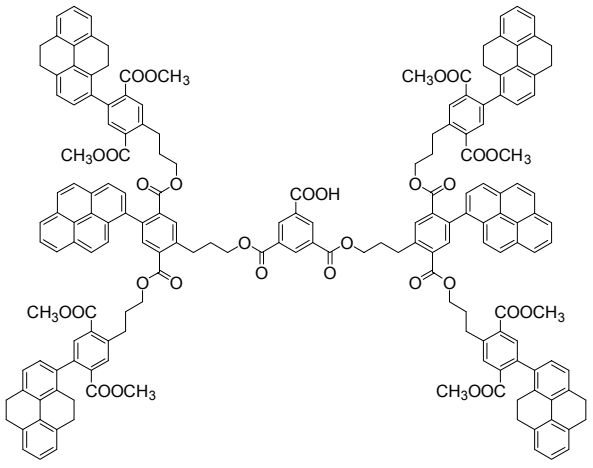
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03-1.30 (m, 2H, 2''), 2.06-2.27 (m, 7H, 2, 2', 3'', OH), 2.46 (m, 4H, 24', 24''), 2.69 (m, 2H, 23''), 2.75 (m, 2H, 23'), 2.83-2.98 (m, 8H, 16', 16'', 17', 17''), 3.02-3.20 (m, 2H, 3'), 3.20-3.25 (m, 2H, 3), 3.49-3.58 (m, 6H, 10', 11'), 3.63 (m, 3H, 11''), 3.70 (m, 3H, 10''), 3.74-3.91 (m, 4H, 1, 1''), 4.43 (t, 2H, 1'), 6.89 (m, 1H, 13'), 6.93-6.99 (m, 1H, 13''), 7.00-7.16 (m, 12H, 14', 14'', 19, 19', 19'', 20, 20', 20'', 21, 21', 21'', 24), 7.21 (m, 1H, 5''), 7.66 (m, 1H, 8''), 7.70-7.84 (m, 3H, 5', 8', 17), 7.90-8.03 (m, 3H, 13, 16, 23), 8.05-8.15 (m, 2H, 5, 8), 8.21 (m, 1H, 14).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.61 (24', 24''), 28.06 (23'), 28.12 (23''), 28.35 (16', 16''), 28.47 (17', 17''), 29.09 (2''), 29.77 (3, 3''); 30.28 (2'); 30.58 (3'), 34.51 (2), 51.95 (10', 10''), 52.15 (11', 11''), 61.74 (1), 64.80 (1''), 65.24 (1'), 124.38 (14), 124.53 (22), 124.64 (18), 124.68 (17), 124.97 (24), 125.19 (20), 125.25 (14', 14''); 125.75 (21', 21''), 124.93 (20', 20''); 126.93 (13), 127.12 (19', 19''); 127.22 (16), 127.34 (19), 127.61 (13', 13''),127.82 (23), 129.01 (26), 130.39 (26', 26''), 130.75 (27', 27''), 130.79 (15), 131.29 (25), 131.42 (5''), 131.77 (9', 9''), 132.06 (5'), 132.60 (9), 132.89 (5), 132.96 (25', 25''), 133.30 (8''), 133.42 (6''), 133.57 (8'), 133.70 (6'), 134.29 (8), 134.87 (15', 15''), 134.94 (6), 135.34 (22', 22''), 135.67 (18', 18''); 135.99 (12), 137.12 (12'), 137.29 (12''), 139.02 (7), 139.60 (7''), 140.04 (7'), 141.55 (4''), 141.81 (4'), 143.13 (4), 166.70 (28''), 166.83 (28'), 167.22 (11, 29', 29''), 167.27 (10). (22 signals missing, carbon 21 and 27 not found).
MS (+FAB, MNBA/CH_2Cl_2): m/z (%) = 1301 (5.69) [M^+].

High resolution mass spectroscopy for structurally specific fragments **a**, **b**, **c**, **d**:
a: [M^+-$C_{29}H_{28}O_5$] = $C_{56}H_{44}O_8$ calcd 844.30362 found 844.30847
b: [M^+-$C_{56}H_{44}O_8$] = $C_{29}H_{28}O_5$ calcd 456.19368 found 456.19632
c: [M^+-$C_{58}H_{52}O_8$] = $C_{27}H_{20}O_5$ calcd 424.13108 found 424.13455
d: [M^+-$C_{58}H_{53}O_{10}$] = $C_{27}H_{19}O_3$ calcd 391.13342 found 391.13546

M = $C_{85}H_{72}O_{13}$ (1301.47)

Benzene-1,3,5-tricarboxylic acid bis-[3-(2,5-bis-{3-[2,5-bis-methoxycarbonyl-4-(4,5,9,10-tetrahydro-pyrene-1-yl)-phenyl]-propoxycarbonyl}-4-pyrene-1-yl-phenyl)-propyl] ester (128)



G2-alkohol **126** (71.0 mg, 0.055 mmol), DMAP (1.8 mg, 0.015 mmol) and NEt_3 (8.5 µl, 6.2 mg, 0.062 mmol) were dissolved in dry CH_2Cl_2 (3 ml). Benzenetricarbonyl

chloride **127** (4 mg, 0.015 mmol) dissolved in dry CH_2Cl_2 (2 ml) was dropped in. The yellow solution was stirred for 12 h, diluted with CH_2Cl_2 (20 ml) and extracted with water (10 ml). The organic phase was dried and the solvent removed. Chromatographic separation with silica gel and CH_2Cl_2:MeOH 2% gave the di-substituted core **128** (24.0 mg, 0.009 mmol, 58 %) R_f =0.05
G2 alcohol **126** (39 mg, 0.030 mmol) could be reisolated R_f = 0.17.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00-1.28 (m, 4H, 2''), 2.04 (m, 4H, 2'), 2.11 (m, 4H, 2), 2.28 (m, 4H, 24''), 2.42 (m, 8H, 3'', 24'), 2.63 (m, 4H, 23''), 2.68 (m, 4H, 23'), 2.75-2.91 (m, 16H, 16', 16'', 17', 17''), 2.91-3.18 (m, 4H, 3'), 3.18-3.40 (m, 4H, 3), 3.45 (s, 6H, CH_3), 3.50-3.59 (4xs, 12H, CH_3), 3.61 (s, 3H, CH_3), 3.64 (s, 3H, CH_3), 3.76 (4H, 1''), 4.38 (t, 4H, 1'), 4.53 (m, 4H, 1), 6.78-7.12 (m, 18H, $H_{aromatic}$), 7.15 (s, 2H, 5''), 7.53-8.24 (m, 30H, $H_{aromatic}$), 8.94 8s, (s, 2H, H_{core}), 8.97 (s, 1H, H_{core}).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.04, 28.30, 28.39, 28.63, 28.73, 29.35, 29.94, 30.65, 30.79, 31.19. 52.26, 52.40, 65.12, 65.35, 65.72, 124.62, 124.80, 124.90, 124.97, 125.23, 125.40, 125.50, 126.01, 126.17, 126.74, 127.20, 127.37, 127.48, 127.64, 127.89, 128.08, 129.26, 130.66, 131.06, 131.56, 131.62, 131.65, 131.78, 131.90, 132.35, 132.51, 132.68, 133.06, 133.22, 133.54, 133.71, 133.83, 134.04, 134.79, 135.12, 135.23, 135.45, 135.61, 135.86, 135.94, 136.29, 137.36, 137.48, 139.57, 139.84, 139.90, 140.27, 141.82, 142.27, 142.92, 165.30, 166.34, 166.76, 167.02, 167.28, 167.38, 167.61. (19 signals missing).
$C_{179}H_{146}O_{30}$ (2774.99) MALDI-ZOF MS: m/z = 2776 $[M+H]^+$.

7.8 Absorptions- und Emissionswellenlängen der Verbindungen in Methylcyclohexan und Acetonitril

Verbindung	$\lambda_{max.}$ **Absorption** (nm)		$\lambda_{max.}$ **Fluoreszenz** (nm)	
	Methylcyclohexan	*Acetonitril*	*Methylcyclohexan*	*Acetonitril*
41	342	344	384	381
42	344	344	399	384
55	-	-	432	445
61	393	393	435	435
62	393	393	436	436
67	362	363	453	447
78	344	344	396	B / A 402/585
79	343	342	437	546
82	344	342	377	377
89	342	344	377	377
97	344	344	425	534
98	344	344	378	378
110	344	345	401	381
111	346	344	385	430
112	344	343	378	378
113	346	344	430	521
116	-	363	-	500
119	344	344	427	531
120	344	344	378	378
121	282	283	382	485
125	344	344	427	520
128	344	344	432	509