Synthesis of Pyrene Containing Building Blocks for Dendrimer Synthesis

Claudia Modrakowski, Silvia Camacho Flores, Matthias Beinhoff, A. Dieter Schlüter*

Freie Universität Berlin, Institut für Chemie, Takustr. 3, 14195 Berlin, Germany
Fax +49(30)838 53357; E-mail: adschlue@chemie.fu-berlin.de

Received 26 June 2001; revised 21 August 2001

Abstract: Efficient syntheses of the novel, pyrene containing branched building blocks **10**, **13**, **22**, **25** and of a pyrene based core molecule **16** for the construction of dendrimers are reported. The main tool is a Suzuki cross-coupling. The functional groups for further growth are amines and carboxylic acids, which were used in an orthogonally protected fashion. It was proven that the building blocks could be assembled to a low generation dendrimer **17**.

Key words: arenas, dendrimers, cross-coupling, pyrenes, protecting groups

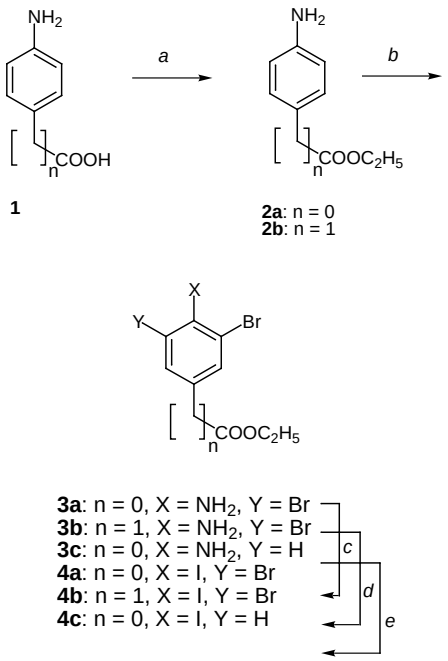
The spherically shape, dendrimers,[1] are unlike practically all other chemical compounds and can potentially be used to generate and investigate a directed charge transfer.[2,3] If the interior of dendrimers is equipped with electron acceptors at defined positions (generations), an electron transfer should be possible from acceptor to acceptor if there is a gradient, which provides the necessary driving force. We are presently pursuing a project to construct dendrimers with a polar gradient and to use them as components to investigate a photochemically induced energy and charge transfer.[4] The polarity gradient should serve as a driving force for either of these transfers and the large distance between the dendrimers' core and surface ought to increase the life-time of an eventual charge separated state. Both an outline of the concept[4] as well as first spectroscopical results[5] have been preliminarily published. We here report in detail the basic synthetic sequences involved. The aim is to construct pyrenes containing branched building blocks like compounds **10** and **13** for dendron and dendrimer synthesis and therefore carry an AB_2 functionality pattern (A: carboxylic acid; B: amine) to allow for application of repetitive growth schemes. The coupling between individual dendritic blocks is based on peptide derived amide bond formation, which has been proven to be very efficient in dendrimer chemistry.[6]

The concept involves the use of fluorescence probes and dummies,[7] whereby the latter should structurally resemble the former as closely as possible. This is why in the following some of the dendrons carry a methylene spacer between pyrene and acceptor-substituted branching unit (potential dummies) and others do not (potential probes). Tests on model compounds have shown that the incorporation of just a methylene spacer is sufficient for that purpose.[5]

Synthesis 2001, No. 14, 26 10 2001. Article Identifier:
1437-210X,E;2001,0,14,2143,2155,ftx,en;T05201SS.pdf.

ISSN 0039-7881

The whole strategy rests upon compounds **4a** and **4b** (Scheme 1), which besides the ester (as the protected A of an AB_2 building block), carry two bromo functionalities and one iodo functionality. It was anticipated that, by utilizing the high iodo selectivity[8] of Suzuki cross-coupling (SCC)[9] that the required functionality could be incorporated into the molecule. If both iodinated and brominated sp^2-hybridized C-atoms are present in the same molecule, the pyrene unit and two N-protected amine-terminated arms (as the B's of an AB_2 building block) could be incorporated at C–I and C–Br, respectively.

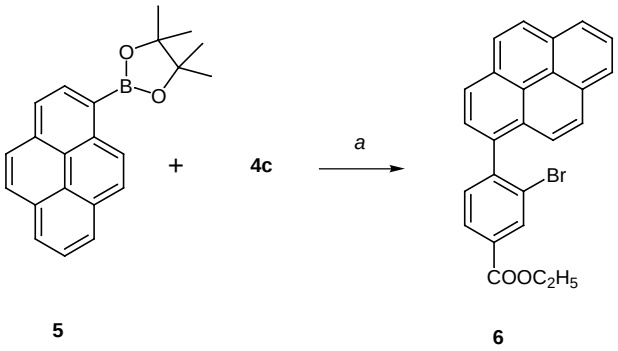


Scheme 1 Reagents and conditions: (a) EtOH, toluene, H_2SO_4, reflux, 5 h, 78% (b) concd HOAc, Br_2, 0 °C, 12 h, 87% (c) i. H_2O, $NaNO_2$, HCl ii. KI, H_2O, 59% (d) i. concd HOAc, H_2SO_4, $NaNO_2$, 0 °C ii. KI, I_2, H_2O, $CHCl_3$, 1 h, 54% (e) analogous to (c), 63% yield.

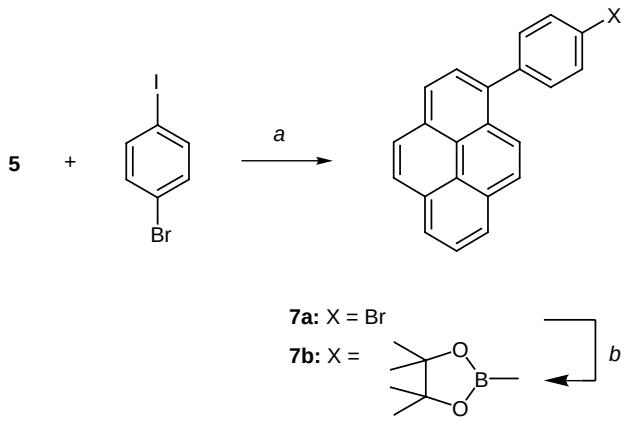
The synthesis of **3a** starting from *p*-aminobenzoic acid has already been published.[10] Compound **3b**[11] is new and was prepared in an analogous way starting from the corresponding amino acid **1**, the only difference being the conditions for the diazotization step. In contrast to **3a**, **3b** cannot be converted into its diazonium salt by treating the respective amine **2b** with an aqueous solution of sodium nitrite and hydrochloric acid. A mixture of concentrated acetic acid, sodium nitrite and sulfuric acid had to be used instead, presumably because of the amine's reduced polarity over that of **2a**. The reaction of the diazonium salt

derived from **3b** proceeded smoothly and furnished **4b** on a 10 g scale as analytically pure material.

For the SCC at the iodo positions of **4a** and **4b** in the initial experiments pyrene pinacole boronic ester **5**[5] was chosen. Despite the application of a broad variety of reaction conditions, the anticipated products **8c** and **8d** (for structures see Scheme 4) could unfortunately not be obtained. Since steric reasons may be responsible for this unsuccessful model compound, **4c** was tested, which carries one bromo atom less in the *ortho* position relative to the iodo-coupling site. The synthesis of the corresponding ester **3c** was carried out at relatively high dilution, low temperature and in a non-polar solvent in order to suppress dibromination as far as possible. Some **3a** formed and was removed by column chromatography. Conversion of the diazonium salt derived from **3c** proceeded smoothly and gave **4c.** To test the above hypothesis of steric hindrance model compound **4c** was used applying the same SCC conditions, which had been unsuccessful for the coupling of **4b** and **5**, **4c** easily underwent the coupling with pyrene boronic ester **5** and gave compound **6** (Scheme 2).

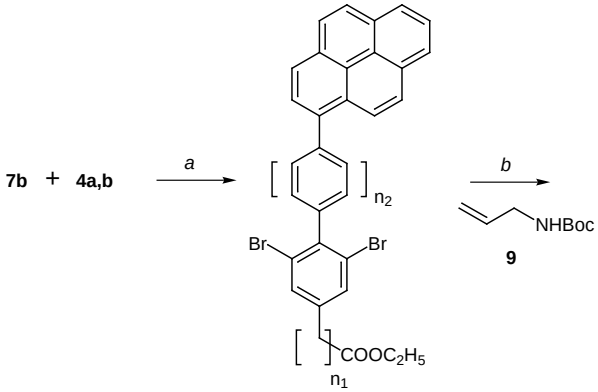


Scheme 2 Reagents and conditions: (a) toluene, Na_2CO_3, $Pd(PPh_3)_4$, 4 d, reflux, 35%.

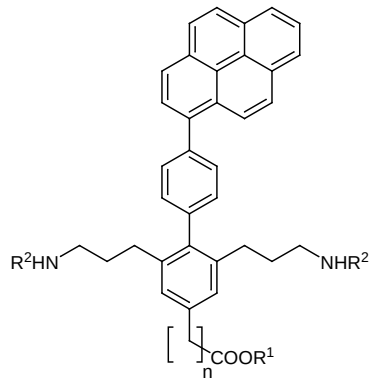


Scheme 3 Reagents and conditions: (a) toluene, Na_2CO_3, $Pd(PPh_3)_4$, 2 d, 91% (b) i. anhyd THF, BuLi, –78 °C ii. $B(O\text{-}iPr)_3$, –78 °C, 62%.

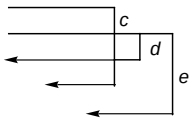
It was therefore decided to replace **5** by **7b** (Scheme 3) in which the pyrene unit is separated from the boronic acid ester coupling site by a phenylene linker, which ought to reduce steric hindrance during the mechanistically complex SCC bond formation step. Compound **7b** was prepared from **5** and 4-bromo iodobenzene followed by standard boronification/pinacolization of the bromo site of the initially formed **7a** (Scheme 3). As was hoped, SCC of **7b** with **4a** and **4b**, did in fact give products **8a** and **8b** (Scheme 4). Although their yields of 53% and 44%, respectively, were lower than in many other SCC applications,[9,12] they still are satisfactory.



8a: $n_1 = 0$, $n_2 = 1$
8b: $n_1 = 1$, $n_2 = 1$
8c: $n_1 = 0$, $n_2 = 0$
8d: $n_1 = 1$, $n_2 = 0$

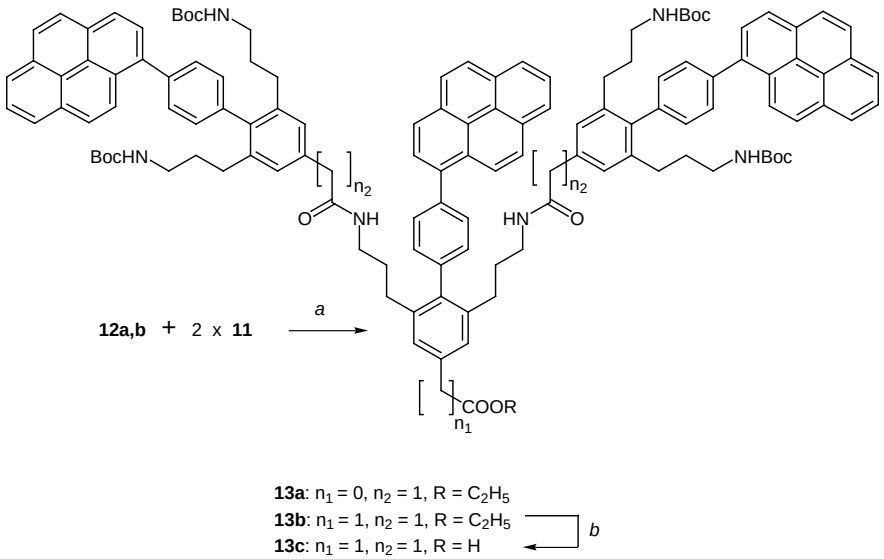


10a: n = 0, $R^1 = C_2H_5$, R^2 = Boc
10b: n = 1, $R^1 = C_2H_5$, R^2 = Boc
11: n = 1, R^1 = H, R^2 = Boc
12a: n = 0, $R^1 = C_2H_5$, $R^2 = NH_3^{\oplus}\,CF_3COO^{\ominus}$
12b: n = 1, $R^1 = C_2H_5$, $R^2 = NH_3^{\oplus}\,CF_3COO^{\ominus}$



Scheme 4 Reagents and conditions: (a) for **8a**: *m*-xylene, Na_2CO_3, $Pd(PPh_3)_4$, 3 d reflux, 53%, analogous for **8b**, 44% yield (b) for **10a:** toluene, KOH, $Pd(PPh_3)_4$, 2 d reflux, 45%, analogous for **10b**, 78% yield (c) $CHCl_3$, CF_3COOH, 1 h, 89% (d) MeOH, KOH, H_2O, 2 h, reflux, 88% (e) analogous to (c), yield 88%.

In the next step, the amine-terminated arms were incorporated by chemistry developed by Suzuki,[13] which had proven to be successful in our lab[14]. Hydroboration of *tert*-butyloxycarbonyl (Boc)-protected allylamine **9** with 9-borabicyclo[3.3.1]nonane (9-BBN) and its in situ reaction with **8a** and **8b** under SCC conditions furnished **10a**



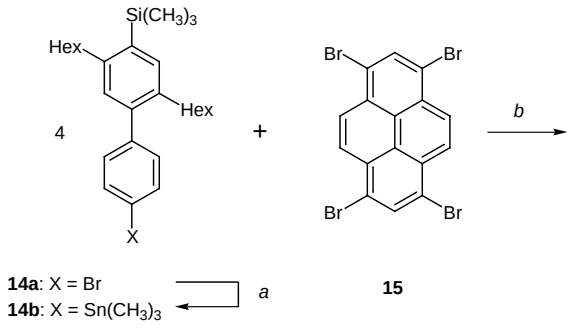
Scheme 5 Reagents and conditions: (a) anhyd CH_2Cl_2, HOBT, DIPEA, EDC, 15 h; 54% yield for **13a**, 75% for **13b** (b) THF, MeOH, KOH, H_2O, 5 h reflux, 95%.

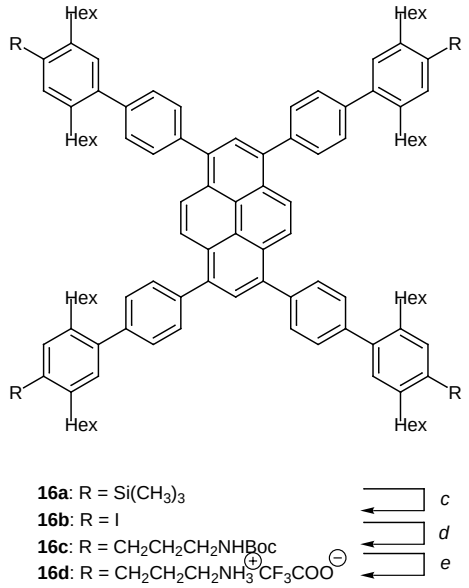
and **10b**, respectively. These compounds may be viewed either as orthogonally protected AB_2 building blocks or first generation (G1) dendrons.

For the anticipated dendrimer construction it was essential to prove that the functional groups of **10** can actually be deprotected independently from one another. The liberated amines and carboxylic acids could then be subjected to known peptide synthesis (derived amidation chemistry), which has already been employed in dendrimer synthesis as well.[6] Saponification of the ethyl ester in **10b** with potassium hydroxide in methanol/water easily gave carboxylic acid **11** and treatment of **10a** and **10b** with trifluoroacetic acid afforded the expected corresponding ammonium trifluoroacetates **12a** and **12b**, respectively in virtually quantitative yield.

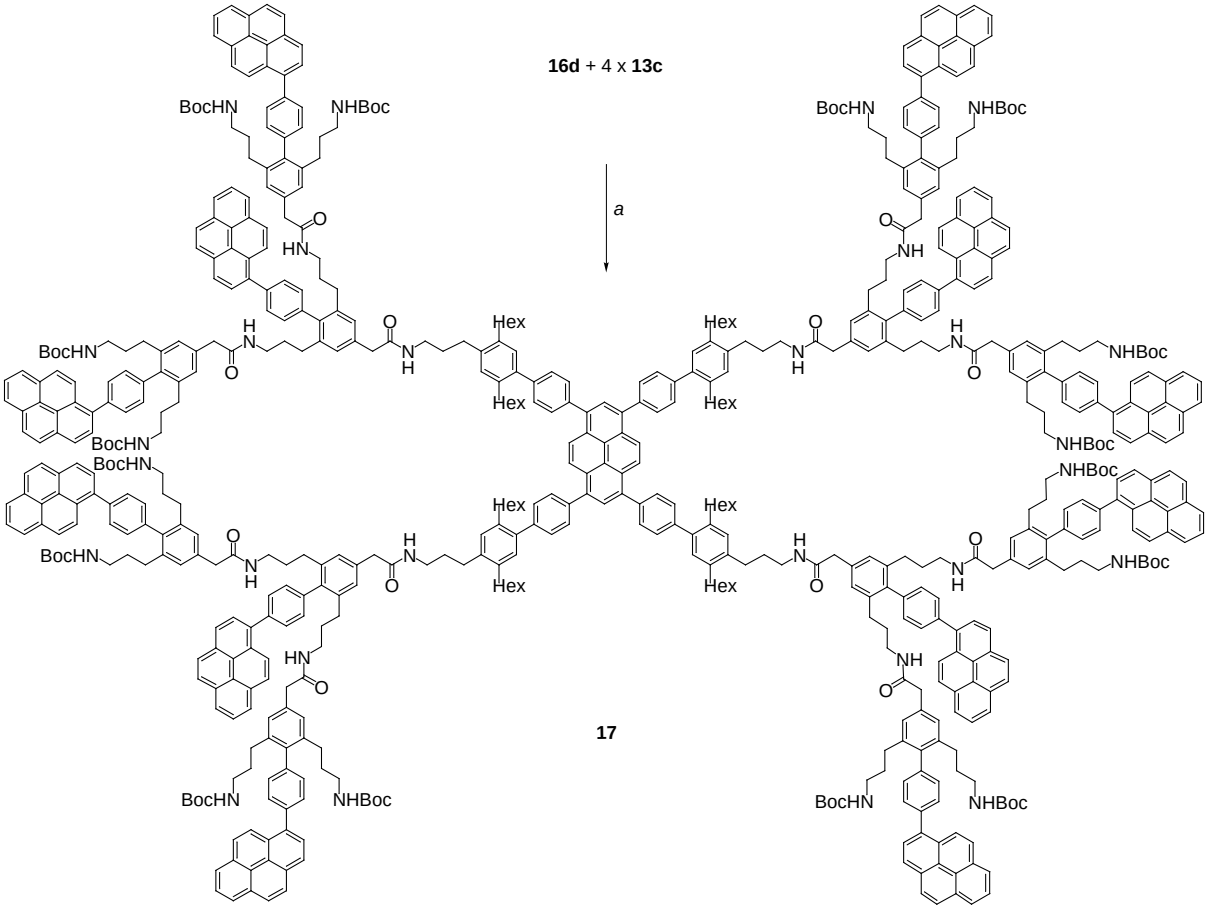
The amide coupling was achieved with 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC)/*N*-hydroxybenzotriazole (HOBt)[15] and gave the G2 dendrons **13a** and **13b** in yields of 54% and 75%, respectively (Scheme 5). Saponification of the carboxylic ester function of **13b** under the above conditions proceeded cleanly and gave **13c**. This dendron, activated at its focal point, was then used for dendrimer synthesis (Scheme 6).

The synthesis of the core unit is depicted in Scheme 6. It started from the biphenyl derivative **14a**, which was available from a project on the modular chemistry of oligophenylenes.[15] Electrophilic stannylation at bromo gave the stannyl derivative **14b**, which was not isolated because its trimethyltin group was cleaved on silica gel and even on neutral or basic alumina. Instead it was directly used in the coupling[17a] with the tetrabromopyrene **15**.[17b] The resulting tetrasilylated and hexyl chain decorated pyrene derivative **16a** was converted in three standard steps to the amine terminated, tetrafunctional core **16d**, which was obtained on a 2 g scale. It should be noted that these steps could only be brought about by the substitution of **16a**





Scheme 6 Reagents and conditions: (a) i. Na, anhyd DMF, 0 °C, $Sn(CH_3)_3Cl$, 12 h, 20 °C; ii. **14a**, 12 h, anhyd DMF, 20 °C, 83% (b) toluene, $Pd(PPh_3)_4$, reflux, 2 d, 38%, (c) anhyd CH_2Cl_2, ICl, –78 °C, 1 h, 96 % (d) i. **9**, 9-BBN, anhyd THF, ii. KOH, **16b**, toluene $Pd(PPh_3)_4$, 2 d, 74% (e) $CHCl_3$, CF_3COOH, 3 h, 97%.

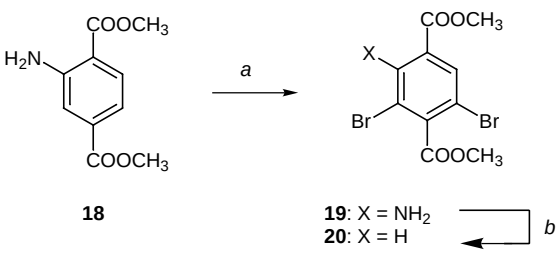


Scheme 7 Reagents and conditions: (a) anhyd CH_2Cl_2, HOBT, EDC, DIPEA, 12 h, 81%.

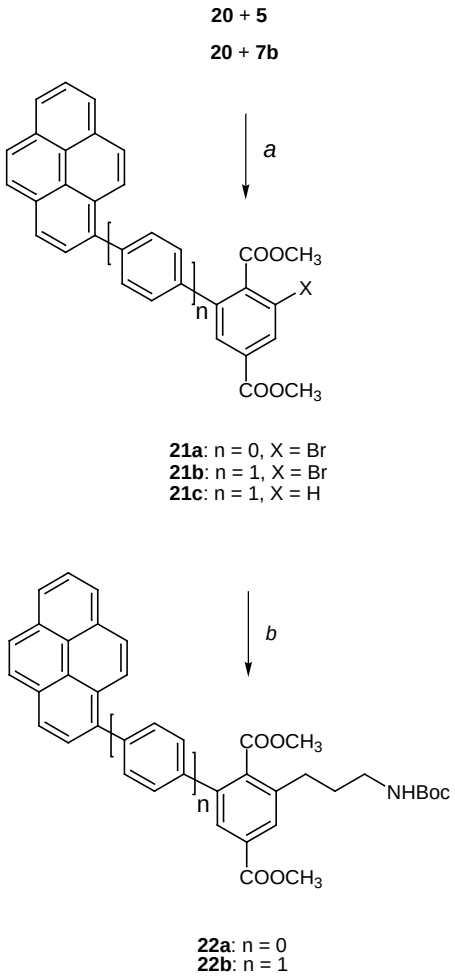
with hexyl chains, which are known to significantly increase the solubility of conformationally rigid molecules mostly for entropic reasons.[18] The solubility of compound **16a** in $CHCl_3$ is 380 mg/mL at room temperature. The iododesilylation step, if done at low temperature, proceeded cleanly and no iodation of the pyrene nucleus was observed. Reaction of **16d** with the G2 dendron **13c** was reconducted using standard amidation chemistry (Scheme 7) whereby **13c** was used in a slight excess of 1.2 equivalents per amine function. G2 dendrimer **17** was obtained on 150 mg scale in pure form in a yield of 81%. Possible by-products from incomplete reactions could be removed using column chromatography. The purity of **17** was tested with GPC, which gave a dispersity of 1.06

In addition to this set of compounds the three G1 building blocks **22a**, **22b** (Scheme 9), and **25** (Scheme 10) were also prepared, which differ by their substitution pattern at the branching unit. Instead of two aminoalkyl groups and one carboxylic ester (AB_2) as for the above compounds they carry one aminoalkyl group and two carboxylic acids (BA_2). Both series differ in their propensity to accept electrons at the branching unit (which is supposed to serve as a relay function for electrons) and complement each other in this sense. Here the key compound is **20**[19] (Scheme 8), which is obtained from the commercially available **18** by bromination and deamination chemistry.

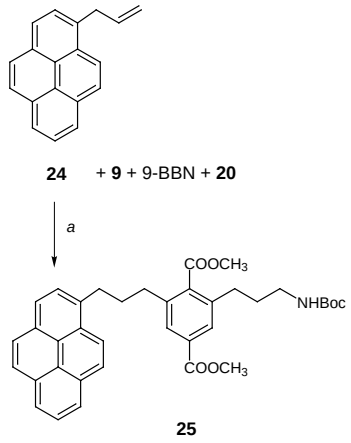
SCC of **20** with **5** and **7b** gave the corresponding products **21a** and **21b** in yields of 58% and 74%, respectively (Scheme 9). The reason for these relatively low yields is due to the fact that the incorporation of two pyrene arms (structure not shown) cannot easily be suppressed even if compound **20** is used in excess. Additionally, the latter coupling was accompanied by some inadvertent debromination. Side product **21c** was isolated in a yield of 13%. The reason for this is not yet understood. The Boc-protected aminopropyl group was introduced to **21a** and **21b** by



Scheme 8 Reagents and conditions: (a) CH_2Cl_2, Br_2, 70 °C, 12 h, 95% (b) MeOH, H_2SO_4, $NaNO_2$, 70 °C, 2 h, 83%.



Scheme 9 Reagents and conditions: (a) toluene, Na_2CO_3, $Pd(PPh_3)_4$, reflux, 2 d (b) for **22a**: i. toluene, 9-BBN, **9**, 12 h, 20 °C ii. toluene, KOH, water, $Pd(PPh_3)_4$, 36 h, reflux, 71% yield, analogous for **22b**, 48% yield.



Scheme 10 Reagents and conditions: (a) i. anhyd toluene, **9**, 24, 9-BBN, 12 h, 20 °C ii. Na_2CO_3, $Pd(PPh_3)_4$, 5 d, reflux, 6%.

the chemistry described in Scheme 4 and gave **22a** and **22b**, respectively.

Finally the BA_2 building block **25** was prepared by allylation of 1-bromopyrene (**23**), in situ 9-BBN addition to the initially formed compound **24** and Boc-protected allylamine **9** and SCC of these 9-BBN adducts with the dibromodiester **20**.

General: Reagents and compounds **1**, **2a**, 4-bromoiodo benzene, 9-BBN and **9** 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 **2b**,[20] **3a**,[9] **3b**,[11] **5**,[5] **14a**,[16] **20**,[19] **23**,[21] and **24**[22] were prepared according to literature procedures. ^{1}H NMR spectra were recorded on a Bruker AM270 spectrometer (270 MHz) or Bruker AC500 spectrometer (500 MHz) and were referenced to $CHCl_3$ at $\delta = 7.24$ or DMSO at $\delta = 2.49$ as internal standard. ^{13}C NMR spectra were recorded on a Bruker AM 270 spectrometer (67.9 MHz) or Bruker AC 500 spectrometer (126 MHz) and were referenced to $CDCl_3$ at $\delta = 77.0$ as internal standard. MS were recorded on a Varian MAT 711 spectrometer. Melting points were measured on a Büchi 510 (open capillaries) and are uncorrected. Column chromatography was preformed using Merck silica gel 60, 0.040–0.063 mm (230–400 mesh). Analytical TLC was preformed on aluminum sheets, silica gel 60 F_{254} (Merck), and detection were carried out by UV absorption. Elemental analyses were recorded on a Perkin-Elmer EA 240.

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 **11** and **13c** and for amine trifluoro acetates **12a** and **12b** because water could not be removed completely from them.

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.

Ethyl (4-amino-3,5-dibromophenyl)acetate (2b)

To a suspension of (4-aminophenyl) acetic acid (**1b**) (50.0 g, 0.331 mol) in a mixture of EtOH (150 mL) and toluene (150 mL) was added concd H_2SO_4 (72.8 mL, 0.728 mol) over 15 min. The dark brown solution was refluxed at 140 °C for 5 h with a Dean–Stark apparatus fitted. After cooling to 0 °C a solution of Na_2CO_3 (750 mL, 1 M) was added. The layers were separated, the aqueous layer was washed with toluene (3×100 mL) and the combined organic layers were dried ($MgSO_4$). Recrystallization from a mixture of hexanes–EtOAc, 10:1 gave the ester **2b** (46.0 g, 0.257 mol, 78%) as pale yellow crystals.

^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 1.22$ (t, 3 H, $J = 9$ Hz, CH_3), 3.46 (s, 2 H, $CH_{2\ \text{benzylic}}$), 3.83 (s, 2 H, NH_2), 4.10 (q, 2 H, $J = 9$ Hz, CH_2), 6.57 (d, 2 H, $J = 9$ Hz, H_{aromatic}), 7.02 (d, 2 H, $J = 9$ Hz, H_{aromatic}).

^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 13.8$, 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) [$M^+ - C_3H_5O_2$].

Anal Calcd for $C_{10}H_{13}NO_2$ (179.22): C, 67.02; H, 7.31; N, 7.82. Found: C, 67.01; H, 7.34; N, 7.93.

Ethyl (4-Amino-3,5-dibromophenyl)acetate (3b)

Phenyl acetic ester **2b** (23.0 g, 0.128 mol) was dissolved in concd HOAc (300 mL) and cooled to 0 °C. A solution of Br_2 (45.1 g, 14.4 mL, 0.282 mol) in HOAc (50 mL) was added at 0 °C over 1 h. The product started to precipitate immediately and the mixture was

stirred for 12 h at r.t. After cooling to 0 °C the mixture was poured onto ice (1 kg). Filtration under vacuum and washing with H_2O (2 × 400 mL) gave the brominated product **3b** (37.0 g, 87%) as a pale brown solid.

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

^{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^+–$C_3H_5O_2Br_2$].

Anal Calcd for $C_{10}H_{11}NO_2$ (337.01): C, 35.64; H, 3.29; N, 4.16. Found: C, 35.58; H, 3.17; N, 4.05.

Ethyl 4-Amino-3-bromobenzoate (3c)

Benzoic acid ethyl ester **2a** (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 drop wise over 2 h at 0 °C. The mixture was stirred for 12 h at r.t. The organic layer was washed first with an aq Na_2SO_3 solution (100 mL, c = 1 mol/L) and then H_2O (2 × 200 mL). The organic layer was dried ($MgSO_4$) and the CH_2Cl_2 was evaporated. Chromatographic separation with hexanes–EtOAc, 10:1 gave the product **3c** (11.5 g, 47.0 mol, 55%) as a colorless solid.

R_f (hexanes:EtOAc, 10:1) = 0.18.

^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.34 (t, 3 H, *J* = 8.3 Hz, CH_3), 4.29 (q, 2 H, *J* = 8.3 Hz, CH_2), 4.57 (s, 2 H, NH_2), 6.69 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.75 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 8.07 (s, 1 H, $H_{aromatic}$).

^{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].

Anal Calcd for $C_9H_{10}BrNO_2$ (244.09): C, 44.29; H, 4.13; N, 5.74. Found: C, 44.18; H, 4.01; N, 5.63.

Ethyl 3,5-Dibromo-4-iodobenzoate (4a)

Ice (100 g), HCl (25%, 72 mL, 0.490 mol) and **3a** (26 g, 0.081 mol) were mixed and stirred for 30 min. An aq solution of $NaNO_2$ (7.45 g in 75 mL H_2O) was added drop wise over 15 min and the mixture stirred for 4 h. The mixture was filtered and the filtrate was added drop wise into an aq solution of KI (136 g, 0.820 mol, 150 mL H_2O) with vigorous stirring. The mixture was stirred for 12 h at r.t. Then CH_2Cl_2 (200 mL) and an aq solution of Na_2SO_3 (200 mL, c = 1 mol/L) were added. The organic phase was separated and the aqueous phase 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 and recrystallization from EtOH gave iodoester **4a** (15.3 g, 0.035 mol, 44%) as a pale orange solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.38 (t, 3 H, *J* = 9.3 Hz, CH_3CH_2), 4.36 (q, 2 H, *J* = 9.3 Hz, CH_3CH_2), 8.14 (s, 2 H, $H_{aromatic}$).

^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.20, 61.91, 115.48, 131.40, 132.55,163.81, (1 signal missing).

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^+–$C_3H_5O_2I$], 180.9 (6.3) [M^+–C_2H_5OBrI].

Anal Calcd for $C_9H_7Br_2IO_2$ (431.78): C, 24.92; H, 1.63. Found: C, 25.07; H, 1.62.

Ethyl (3,5-dibromo-4-iodophenyl)acetate(4b)

Amino phenyl ester **3b** (14.0 g, 41.5 mmol) was dissolved in concd HOAc (220 mL) and added to concd H_2SO_4 (40 mL) at 0 °C. This solution was added slowly at 0 °C to a mixture of $NaNO_2$ (7.5 g, 109.0 mmol), concd H_2SO_4 (50 mL) and concd HOAc (100 mL) at 0 °C. After stirring for 1 h at 0 °C the mixture was warmed to r.t., added 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), H_2O (500 mL) and $CHCl_3$ (140 mL). The solution was stirred at r.t. for 1 h, then Na_2SO_3 (46.0 g, 0.242 mol) was added. The layers were separated, the aqueous layer was washed with $CHCl_3$ (2 × 200 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 hexanes–EtOAc, 3:1 gave iodophenyl ester **4b** (10.0 g, 22.0 mmol, 54%) as a yellow solid.

R_f (hexanes–EtOAc, 3:1) = 0.47.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.24 (t, 3 H, *J* = 9 Hz, CH_3), 3.48 (s, 2 H, $CH_{2\ benzylic}$), 4.14 (q, 2 H, *J* = 9 Hz, CH_2), 7.47 (s, 2 H, $H_{aromatic}$).

^{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^+–$C_3H_5O_2Br_2I$].

Anal Calcd for $C_{10}H_9Br_2IO_2$ (447.89): C, 26.82; H, 2.03. Found: C, 26.65; H, 2.09.

Ethyl 3-bromo-4-iodobenzoate (4c)

$NaNO_2$ (3.2 g, 46.0 mol) dissolved in water (15 mL) was added dropwise to a suspension of amino bromo ester **3c** (10.2 g, 41.8 mmol) in HCl (40 mL, 25%) and ice (50 g). The mixture was stirred for 3 h at r.t. and then filtered. The orange filtrate was dropped under vigorous stirring at 0 °C into a solution of KI (35.1 g, 0.209 mol) in H_2O (100 mL). The product started to precipitate immediately. The mixture was stirred for 12 h at r.t. CH_2Cl_2 (250 mL) and Na_2SO_3 (38.0 g, 0.200 mol) were added. The layers were separated and the organic layer was dried ($MgSO_4$). The CH_2Cl_2 was removed and the crude product, a brown oil was subjected to chromatographic separation with hexanes, 100%→ hexanes–EtOAc, 20:1 to give the product **4c** (9.3 g, 26.2 mmol, 63%) as a colorless solid.

R_f (Hexanes–EtOAc, 3:1) = 0.56.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.36 (t, 3 H, *J* = 8.3 Hz, CH_3), 4.34 (q, 2 H, *J* = 8.3 Hz, CH_2), 7.57 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.91 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 8.21 (s, 1 H, $H_{aromatic}$).

^{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].

Anal Calcd for $C_9H_8BrIO_2$ (354.97): C, 30.45; H, 2.27. Found: C, 30.24; H, 2.14.

Ethyl 3-Bromo-4-pyren-1-ylbenzoate(6)

Ester **4c** (2.00 g, 5.65 mmol) and pinacol ester **5** (1.86 g, 5.65 mmol) were dissolved in toluene (30 mL). An aq solution of Na_2CO_3 (20 mL, c = 1 mol/L) was added. The mixture was degased and flushed with N_2 three times and $Pd(PPh_3)_4$ (65.0 mg, 5.65×10^{-2} mmol) was added under N_2. Then the mixture was degassed and flushed with N_2 three times again. The system was refluxed for 4 d, the phases were separated and the aqueous layer was washed with toluene (20 mL). The combined organic layers were dried ($MgSO_4$) and the toluene removed. The residue was recrystallized from hexanes. At r.t. the product **6** (0.84 g, 1.95 mmol 34.5%) precipitates as a pale brown solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.46 (t, 3 H, *J* = 8.0 Hz, CH_3), 4.46 (q, 2 H, *J* = 8.0 Hz, CH_2), 7.55 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.65 (d, 1 H, *J* = 9.3 Hz, H_{pyrene}), 7.86 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.93–8.34 (m, 8 H, H_{pyrene}), 8.50 (s, 1 H, $H_{aromatic}$).

^{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, 131.21, 131.38, 132.30, 133.84, 135.32, 146.27, 165.23, (2 signals missing).

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^+–$C_{16}H_{10}$].

Anal Calcd for $C_{25}H_{17}BrO_2$ (429.31): C, 69.94; H, 3.99. Found: C, 69.61; H, 3.82.

HRMS (*m/z*): ($C_{25}H_{17}O_2{}^{79}Br$) [M^+] calcd 428.04119, found 428.04434.

1-(4-Bromophenyl)pyrene (7a)

The procedure was analogous to the one described for compound **6**.

Pyrene pinacol **5** (20.00 g, 61.0 mmol), *p*-bromoiodobenzene (19.00 g, 67.0 mmol), toluene (150 mL), aq solution of Na_2CO_3 (150 mL, c = 1 mol/l), $Pd(PPh_3)_4$ (1.41 g, 1.22 mmol), 2 d, recrystallization from hexanes gave **7a** (19.8 g, 55.4 mmol, 91%) as a pale brown solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.48 (d, 2 H, *J* = 8.5 Hz, $H_{aromatic}$), 7.69 (d, 2 H, *J* = 8.5 Hz, $H_{aromatic}$), 7.87 (d, 1 H, *J* = 8.5 Hz, H_{pyrene}), 7.96–8.24 (m, 8 H, 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, (2 signals missing).

MS (EI, 80 eV, 130 °C) *m/z*: 356 (99.6) [M^+], 277 (30.5) [M^+–Br].

Anal Calcd for $C_{22}H_{13}Br$ (357.25): 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 (7b)

A solution of n-BuLi (125.6 mL, 0.202 mol, c = 1.6 M) was added dropwise to a suspension of pyrene phenyl bromide **7a** (24.1 g, 67.0 mmol) in THF (450 mL) at –78 °C. The mixture was allowed to warm to r.t. over 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 was allowed to warm to r.t. over 10 h. H_2O (250 mL) was added, the layers were separated and the aqueous layer was washed with Et_2O (3 × 300 mL). The combined organic layers were dried ($MgSO_4$). Filtration over silica gel with hexanes–EtOAc, 3:1→ MeOH–CH_2Cl_2, 5:3 gave the pyrene phenyl boronic acid (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 by distillation. Chromatographic separation with hexanes–EtOAc, 3:1 gave the pyrene pinacol **7b** (17.0 g, 42.1 mmol, 62%) as a yellow solid.

R_f (hexanes–EtOAc, 3:1) = 0.47.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.41 (s, 12 H, $H_{pinacol}$), 7.68 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 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, (3 signals missing).

MS (EI, 80 eV, 160 °C) *m/z*: 404 (100) [M^+], 304 (18.4) [M^+ – $C_6H_{12}O$].

Anal Calcd for $C_{28}H_{25}BO_2$ (404.31): C, 83.18; H, 6.23. Found: C, 82.89; H, 6.33.

Ethyl (2,6-dibromo-4'-pyren-1-yl-biphenyl)-4-carboxylate (8a)

The procedure is analogous to the one described for compound **6**.

Pinacol ester **7b** (0.50 g, 1.24 mmol), iodide **4a** (0.54 g, 1.24 mmol), *m*-xylene (20 mL), aq solution of Na_2CO_3 (10 mL, c = 1 mol/L), $Pd(PPh_3)_4$ (32.0 mg, 2.80×10^{-2} mmol), reflux for 4 d, chromatographic separation with hexanes–EtOAc, 10:1 gave product **8a** (0.38 g, 0.66 mmol, 53%) as a colorless solid.

R_f (hexanes–EtOAc, 10:1) = 0.13

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.43 (t, 3 H, *J* = 9.3 Hz, CH_3CH_2), 4.43 (q, 2 H, *J* = 9.3 Hz, CH_3CH_2), 7.39 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.72 (d, *J* = 9.3 Hz, 2 H, $H_{aromatic}$), 7.97–8.29 (m, 9 H, H_{pyrene}), 8.34 (s, 2 H, $H_{aromatic}$).

^{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, (5 signals missing).

MS (EI, 80 eV, 30–60 °C) *m/z:* 582 (50.5), [M^+], 554 (7.3), [M^+–CO].

Anal Calcd for $C_{31}H_{20}Br_2O_2$ (581.98): C, 63.72; H, 3.45. Found: C, 63.65; H, 3.48.

Ethyl (2,6-Dibromo-4'-pyren-1-yl-biphenyl-4-yl)acetate (8b)

The procedure was analogous to the one described for compound **6**.

Iodophenyl ester **4b** (5.54 g, 12.40 mol), pyrene phenyl pinacol **7b** (5.00 g, 12.40 mmol), xylene (50 mL), aq solution of Na_2CO_3 (25 mL, 1 M), $Pd(PPh_3)_4$ (286.0 mg, 0.25 mmol), 3 d. Chromatographic separation with hexanes–EtOAc, 20:1 gave product **8b** (3.23 g, 5.40 mmol, 44%) as a colorless solid.

R_f (hexanes–EtOAc, 3:1) = 0.38.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.34 (t, 3 H, *J* = 9 Hz, CH_3), 3.57 (s, 2 H, $CH_{2\ benzylic}$), 4.26 (q, *J* = 9 Hz, 2 H, CH_2), 7.46 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.65 (s, 2 H, $H_{aromatic}$), 7.76 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.93–8.37 (m, 9 H, 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, (1 signal missing).

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) [$C_{22}H_{12}{}^+$].

Anal Calcd for $C_{32}H_{22}Br_2O_2$ (598.33): C, 64.24; H, 3.71. Found: C, 64.06; H, 3.87.

Ethyl 2,6-Bis-(3-*tert*-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-carboxylate (10a)

The procedure was analogous to the one described for preparation of compound **10b**.

9 (0.70 g, 4.11 mmol), 9-BBN (0.63 g, 5.15 mmol), **8a** (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 with hexanes–EtOAc, 7:1 gave product **10a** (85.0 mg, 0.12 mmol, 45%).

R_f (hexanes–EtOAc, 7:1) = 0.08.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.43 (s, 18 H, $C(CH_3)_3$), 1.48 (t, 3 H, *J* = 9.3 Hz, CH_3), 1.76 (quin, 4 H, *J* = 9.3 Hz, CH_2), 2.62 (t, 4 H, *J* = 9.3 Hz, $H_{benzylic}$), 2.93–3.19 (m, 4 H, CH_2NH), 4.29–4.50 (m, 4 H, $CH_{2\ ester}$, NH), 7.40 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.79 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.94 (s, 2 H, $H_{aromatic}$), 8.05–8.40 (m, 9 H, 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, (1 signal missing).

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^+–$C_{10}H_{18}O_4$].

Anal Calcd for $C_{47}H_{52}N_2O_6$ (740.86): C, 76.19; H, 7.07; N, 3.78. Found: C, 75.65; H, 7.14; N, 3.44.

HRMS: [M^+] calcd for $C_{47}H_{52}N_2O_6$, 740.382538; found, 740.38452.

Ethyl [2,6-Bis-(3-*tert*-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl] Acetate (10b)

Protected allylamine **9** (4.2 g, 26.70 mmol) and 9-BBN (4.1 g, 33.40 mmol) were dissolved in anhyd THF (20 mL) and the solution was stirred for 12 h. H_2O (3 drops) were added and the THF removed. The residue was dissolved in xylene (25 mL), dibromo ester **8b** (1.0 g, 1.70 mmol) and KOH (25 mL, c = 1 mol/L) were added. The mixture was degassed three times and flushed with N_2 repeatedly. $Pd(PPh_3)_4$ (81.0 mg, 0.07 mmol) was added, the mixture was degassed and flushed with N_2 three times again and then was refluxed for 2 d. After cooling to r.t. the layers were separated. The aqueous layer was washed with toluene (2 × 25 mL) and the combined organic layers were dried ($MgSO_4$). Chromatographic separation with hexanes–EtOAc, 7:1→3:1 gave the product **10b** (0.98 g, 1.30 mmol, 76%) as a yellow fluorescent oil. Freeze drying in benzene gave product **10b** as a colorless solid.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.31 (t, 3 H, *J* = 9 Hz, CH_3), 1.39 (s, 18 H, $CH_{3\ Boc}$), 1.69 (quintet, 4 H, *J* = 9 Hz, CH_2), 2.50 (t, 4 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 2.91–3.19 (m, 4 H, CH_2N), 3.65 (s, 2 H, $CH_{2\ benzylic}$), 4.22 (q, 2 H, *J* = 9 Hz, $CH_{2\ ester}$), 4.48 (s, 2 H, NH), 7.10 (s, 2 H, $H_{aromatic}$), 7.33 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.69 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.93–8.34 (m, 9 H, 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, (4 signals missing).

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^+–$C_{16}H_9$].

Anal Calcd for $C_{48}H_{54}N_2O_6$ (754.96): C, 76.36; H, 7.21; N, 3.71. Found: C, 75.85; H, 7.08; N, 3.57.

HRMS: [M^+] calcd for ($C_{48}H_{54}O_6N_2$), 754.398188; found, 754.39508.

[2,6-Bis-(3-*tert*-butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-acetic Acid (11)

To a suspension of ester **10b** (0.70 g, 0.93 mmol) in MeOH (15 mL) were added KOH (0.156 g, 0.93 mmol) and H_2O (5 drops) to give a clear solution. The resulting mixture was refluxed for 2 h. The solvent was removed by distillation and the residue was dissolved in CH_2Cl_2 (25 mL), H_2O (25 mL) and HOAc (0.10 g, 1.67 mmol) were added. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic phases were dried ($MgSO_4$) and the CH_2Cl_2 was removed. Chromatographic separation with CH_2Cl_2, 100%→CH_2Cl_2–MeOH, 5:1 gave the product **11** as a colorless solid (0.594 g, 0.817 mmol, 88%).

R_f (CH_2Cl_2–MeOH, 5:1) = 0.58.

^{1}H NMR (270 MHz, CD_3OD): δ = 1.24 (s, 18 H, H_{Boc}), 1.57 (quintet, 4 H, *J* = 8 Hz, CH_2), 2.34 (t, 4 H, *J* = 8 Hz, $CH_{2\ benzylic}$), 2.87 (t, 4 H, *J* = 8 Hz, CH_2NH), 3.57 (s, 2 H, $CH_{2\ benzylic}$), 7.03 (s, 2 H, $H_{aromatic}$), 7.17 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.45 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.79–8.17 (m, 9 H, 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, (3 signals missing).

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].

Ethyl 2,6-Bis-(3-ammonio-propyl)-4'-pyren-1-yl-biphenyl-4-carboxylate Bis-trifluoroacetate (12a)

The procedure was analogous to the one described for compound **12b**.

10a (85.0 mg, 0.115 mmol), $CHCl_3$ (5 mL), CF_3COOH (1 mL), 1 h, gave **12a** (78.6 mg, 0.100 mmol, 89%).

^{1}H NMR (270 MHz, CD_3OD): δ = 1.41 (t, 3 H, *J* = 8.5 Hz, CH_3), 1.88 (quintet, 4 H, *J* = 8.5 Hz, CH_2), 2.62 (t, 4 H, *J* = 8.5 Hz, $H_{benzylic}$), 2.85 (t, 4 H, *J* = 8.5 Hz, CH_2), 4.43 (q, 2 H, *J* = 8.5 Hz, H_{ester}), 7.37 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.74 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.97–8.34 (m, 11 H, $H_{pyrene\ +\ aromatic}$).

^{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, (1 signal missing).

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

Ethyl [2,6-Bis-(3-amino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-acetate Bis-trifluoroacetate (12b)

Di-Boc protected ester **10b** (0.111 g, 0.147 mmol) was dissolved in $CHCl_3$ (7 mL), CF_3COOH (1 mL) was added and the color turned from pale yellow to orange. The solution was stirred for 1 h at r.t. The solvents were removed by distillation. Freeze drying of the residue gave the product **12b** (101 mg, 0.129 mmol, 88%) as a brown solid.

^{1}H MNR (270 MHz, CD_3OD): δ = 1.24 (t, 3 H, *J* = 9 Hz, CH_3), 1.82 (quintet, 4 H, *J* = 9 Hz, CH_2), 2.53 (t, 4 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 2.81 (t, 4 H, *J* = 9 Hz, CH_2NH), 3.67 (s, 2 H, $CH_{2\ benzylic}$), 4.17 (q, 2 H, *J* = 9 Hz, CH_2CH_3), 7.15 (s, 2 H, $CH_{2\ aromatic}$), 7.34 (d, 2 H, *J* = 9 Hz, $CH_{2\ aromatic}$), 7.67 (d, 2 H, *J* = 9 Hz, $CH_{2\ aromatic}$), 7.86–8.29 (m, 9 H, H_{pyrene}).

^{13}C NMR (62.9 MHz, CD_3OD): δ = 14.54, 29.99, 31.57, 40.43, 41.64, 62.05, 125.80, 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, (2 signals missing).

MS (FAB) *m/z*: 555 (100) [M^+–CF_3CO_2H/CF_3COO^-], 510 (9.3) [M^+–CF_3CO_2H/CF_3COO^-, C_2H_5O].

Anal Calcd for $C_{42}H_{40}N_2O_6F_6$ (782.77): C, 64.45; H, 5.15; N, 3.58. Found: C, 62.45; H, 5.10; N, 3.36.

Ethyl 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-carboxylate(13a)

The procedure was analogous to the one described for compound **13b**.

11 (0.12 g, 0.165 mmol), anhyd CH_2Cl_2 (20 mL), HOBT (34 mg, 0.25 mmol), 15 min, **12a** (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 hexanes–HOAc, 1:2 gave **13a** (84 mg, 0.043 mmol, 54%).

R_f (hexanes–HOAc, 1:2) = 0.31.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.15–1.38 (m, 36 H, $H_{Boc\ +\ ester}$), 1.45 (t, 3 H, *J* = 9 Hz, CH_3), 1.55 (quintet, 8 H, *J* = 9 Hz, CH_2), 1.63–1.91 (m, 8 H, CH_2), 2.39 (t, 4 H, *J* = 9 Hz, CH_2), 2.53 (quintet, *J* = 9 Hz, 4 H, CH_2), 2.84–3.07 (m, 8 H, CH_2), 3.21 (t, 4 H, *J* = 9 Hz, CH_2), 3.42 (s, 4H, $H_{benzylic}$), 4.39–4.49(m, 6 H, NH, CH_2), 5.75–5.90 (m, 2 H, NH), 6.97 (s, 4 H, $H_{aromatic}$), 7.24 (d, 4 H, *J* = 9 Hz, $H_{aromatic}$), 7.35 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.60 (d, *J* = 9 Hz, 4 H, $H_{aromatic}$), 7.75 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.84 (s, 2 H, $H_{aromatic}$), 7.90–8.34 (m, 27 H, 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, (16 signals missing).

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].

Anal Calcd for $C_{129}H_{132}N_6O_{12}$ (1956.99): C, 79.11; H, 6.79; N, 4.29. Found: C, 78.14; H, 6.50; N, 4.26.

Ethyl [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]-acetate (13b)

To a solution of the acid **11** (125.0 mg, 0.172 mmol) in anhyd CH_2Cl_2 (20 mL) HOBT (29.0 mg, 0.189 mmol) was added and the solution was stirred for 1 h. DIPEA (47.2 µL, 35.0 mg, 0.271 mmol) and amine **12b** (64.1 mg, 0.082 mmol) were added and solution stirred for 15 min. EDC (36.3 mg, 0.189 mmol) was added and the mixture was stirred for a further 15 h at 25 °C, then washed with an aq solution of $NaHCO_3$ (20 mL, c = 1mol/L), citric acid (20 mL, c = 1 mol/L) and H_2O. The organic layer was dried ($MgSO_4$) and the CH_2Cl_2 was removed by distillation. Chromatographic separation with hexanes–EtOAc, 1:2 and freeze-drying gave the product **13b** (122.0 mg, 0.062 mmol, 75%) as a colorless solid.

R_f (hexanes–EtOAc, 1:2) = 0.23.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.17–1.43 (m, 39 H, H_{boc}, $CH_{3\ ester}$), 1.55 (quintet, 8 H, *J* = 9 Hz, CH_2), 1.74 (quintet, 4 H, *J* = 9 Hz, CH_2), 2.38 (t, 8 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 2.48 (t, 4 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 2.82–3.07 (m, 8 H, CH_2N), 3.14–3.31 (m, 4 H CH_2N), 3.45 (s, 4 H, $CH_{2\ benzylic}$), 3.65 (s, 2 H, $CH_{2\ benzylic}$), 4.21 (q, 2 H, *J* = 9 Hz, $CH_{2\ ester}$), 4.27–4.43 (m, 4 H, NH), 5.77 (s, 2 H, NH), 6.94 (s, 4 H, $H_{aromatic}$), 7.10 (s, 2 H, $H_{aromatic}$), 7.24 (d, 4 H, *J* = 9 Hz, $H_{aromatic}$), 7.38 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.60 (d, 4 H, *J* = 9 Hz, $H_{aromatic}$), 7.72 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.93–8.38 (m, 27 H, 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, (22 signals missing).

MS (FAB) *m/z*: 1973 (7.1) [M^++H].

Anal Calcd for $C_{130}H_{134}N_6O_{12}$ (1972.52): 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-yl-]acetic Acid (13c)

To a solution of ester **13b** (0.29 g, 0.148 mmol) dissolved in THF (5 mL) and MeOH (20 mL) was added KOH (0.57 g, 0.01 mol) and H_2O (10 drops). The resulting mixture was refluxed for 5 h. The solvent was removed by distillation and the residue was dissolved in CH_2Cl_2 (10 mL), H_2O (25 mL) and HOAc (1.20 g, 0.02 mol) were added. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were dried ($MgSO_4$) and the CH_2Cl_2 was removed. Freeze drying with benzene gave the product (0.27 g, 0.141 mmol, 95%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (s, 36 H, H_{Boc}), 1.5–1.67 (m, 8 H, CH_2), 1.67–1.81 (m, 4 H, CH_2), 2.28–2.68 (m, 12 H, CH_2), 2.68–3.10 (m, 8 H, CH_2N), 3.10–3.31 (m, 4 H, CH_2N), 3.46 (s, 4 H, $CH_{2\ benzylic}$), 3.71 (s, 2 H, $CH_{2\ benzylic}$), 4.28–4.50 (s, 4 H, NH), 5.76 (s, 2 H, NH), 6.88–7.15 (m, 6H, $H_{aromatic}$), 7.25–7.40 (m, 4 H, $H_{aromatic}$), 7.53–7.80 (m, 8 H, $H_{aromatic}$), 7.80–8.34 (m, 27 H, 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, (31 signals missing).

MS (FAB, 2KV, MNBA–$CHCl_3$) *m/z*: 1945 (100) [M^++H].

(2,5 Dihexyl-4'-trimethyl stannanyl-biphenyl-4-yl-)trimethylsilane (14b)

To a suspension of sodium powder (6g, 151 mmol) in abs DMF (40 mL) at 0 °C a solution of trimethylstannanyl chloride (10.00 g, 50.2 mmol) in abs DMF (20 mL) was added drop wise over 15 min. The reaction mixture was stirred for 12 h at r.t. and the color turned from grey to green. The mixture was filtered under N_2 and to the filtrate a solution of Br-biphenyl **14a** (9.37g, 19.8 mmol) dissolved in abs DMF (30 mL) was added drop wise over 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 r.t. An aq 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 ($MgSO_4$) and the DMF was removed by distillation to give **14b** as a colorless oil (9.20 g, 16.5 mmol, 83.3%).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.36 (s, 9 H, CH_3Sn), 0.43 (s, 9 H, CH_3Si), 0.93 (t, 3 H, *J* = 9.3 Hz, CH_3), 1.00 (t, 3 H, *J* = 9.3 Hz, CH_3), 1.09–1.83 (m, 16 H, CH_2), 2.62 (t, 3 H, *J* = 9.3 Hz, 2 H, $CH_{2\ benzylic}$), 2.91 (t, 2 H, *J* = 9.3 Hz, $CH_{2\ benzylic}$), 7.12 (s, 1 H, $H_{aromatic}$), 7.38 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.45 (s, 1 H, $H_{aromatic}$), 7.60 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$).

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^+–$Sn(CH_3)_3Si(CH_3)_3$], 235 (13.5) [M^+–$Sn(CH_3)_3$TMSHex], 73 (100) [TMS^+].

1,3,6,8-Tetrakis-(2',5'-dihexyl-4'-trimethylsilanyl-biphenyl-4-yl)-pyrene (16a)

Tetrabromopyrene **15** (1.60 g, 3.08 mmol) and stannanylbiphenyl **14b** (8.60 g, 15.4 mmol) were dissolved in toluene (100 mL). The mixture was degassed and flushed with N_2 three times. $Pd(PPh_3)_4$ (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. An aq 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 from Et_2O gave the product **16a** (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, 36 H, CH_3Si), 1.00 (t, 12 H, *J* = 9.3 Hz, CH_3), 1.10 (t, 12 H, *J* = 9.3 Hz, CH_3), 1.21–1.97 (m, 64 H, CH_2), 2.86 (t, 8 H, *J* = 9.3 Hz, $CH_{2\ aromatic}$), 2.93 (t, 8 H, *J* = 9.3 Hz, $CH_{2\ aromatic}$), 7.36 (s, 4 H, $H_{aromatic}$), 7.59 (s, 4 H, $H_{aromatic}$), 7.69 (d, 8 H, *J* = 8.3 Hz, $H_{aromatic}$), 7.90 (d, 8 H, *J* = 8.3 Hz, $H_{aromatic}$), 8.33 (s, 2 H, H_{pyrene}), 8.52 (s, 4 H, H_{pyrene}).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.64 (s, CH_3Si), 14.16 (s, CH_3CH_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, (2 signals missing).

MS (EI, 80 eV, 250–300 °C) *m/z*: 1771 (67.1) [M^+], 1698 (6.7) [M^+–$Si(CH_3)_3$], 73 (19.7) [$Si(CH_3)_3^+$].

Anal Calcd for $C_{124}H_{170}Si_4$ (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) (16b)

To a solution of **16a** (1.00 g, 0.56 mmol) in abs CH_2Cl_2 (40 mL) at –78 °C was added a yellow solution of ICl (0.55g, 3.38 mmol) in abs CH_2Cl_2 (20 mL) dropwise over 1h at –78 °C. The color changed from yellow to dark blue and the mixture was stirred for 1h at –78 °C. The mixture was poured into an aq solution of Na_2SO_3 (100 mL, c = 1 mol/L) with vigorous stirring. The layers were separated and the aqueous phase was washed with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried ($MgSO_4$), the CH_2Cl_2 was removed and gave the yellow product **16b** (1.07 g, 0.54 mmol, 96%), which was recrystallized from Et_2O.

Melting point: 151 °C

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.79 (t, 12 H, *J* = 9 Hz, CH_3), 0.90 (t, 12 H, *J* = 9 Hz, CH_3), 1.07–1.76 (m, 64 H, CH_2), 2.59 (t, 8 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 2.71 (t, 8 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 7.14 (s, 4 H, $H_{aromatic}$), 7.48 (d, 8 H, *J* = 9 Hz, $H_{aromatic}$), 7.72 (d, 8 H, *J* = 9 Hz, $H_{aromatic}$), 7.76 (s, 4 H, $H_{aromatic}$), 8.12 (s, 2 H, H_{pyrene}), 8.31 (s, 4 H, H_{pyrene}).

^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.10, 22.53, 22.62, 29.13, 30.37, 31.26, 31.51, 31.67, 32.29, 40.39, 99.61, 125.42, 126.10, 128.25, 129.11, 129.64, 130.40, 130.73, 137.04, 139.69, 139.92, 140.04, 140.26, 141.60, 142.68, (2 signals missing).

MS (EI, 80 eV, 380 °C) *m/z*: 1987 (85.5) [M^+], 1860 (22.5) [M^+−I), 1733 (3.7) [M^+−2I].

Anal Calcd for $C_{112}H_{134}I_4$ (1987.89): C, 67.67; H, 6.79. Found: C, 67.50, H, 6.62.

1,3,6,8 Tetrakis-[4'(3-*tert*-butoxycarbonylamino-propyl)-2',5'-dihexyl-biphenyl-4-yl)-pyrene (16c)

Protected allylamine **9** (2.64 g, 16.8 mmol) and 9-BBN (2.46 g, 20.16 mmol) were dissolved in abs THF (20 mL) and stirred r.t. for 12h. H_2O (1 drop) was added and the solvent was removed. The residue was dissolved in toluene (100 mL) and aqueous KOH (50 mL) (c = 1 mol/L). **16b** (3.36 g, 1.69 mmol) was added and the mixture was degassed three times. $Pd(PPh_3)_4$ (155 mg, 0.134 mmol) was added and followed by degassing three more times. The mixture was refluxed for 2 days. After cooling to r.t. the layers were separated, the aqueous layer was extracted with toluene (2 × 50 mL). The combined organic layers were dried ($MgSO_4$) and the solvent removed. Chromatographic separation with hexanes–EtOAc, 3:1 gave the product **16c** (2.64 g, 1.25 mmol, 74%) as yellow solid.

R_f (hexanes–EtOAc, 3:1) = 0.11.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.77 (t, 12 H, *J* = 9 Hz, CH_3), 0.86 (t, 12 H, *J* = 9 Hz, CH_3), 1.10–1.72 (m, 100 H, $CH_{3\ Boc}$,CH_2), 1.96 (quintet, 8 H, *J* = 9 Hz, CH_2), 2.63 (quintet, 24 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 3.14–3.38 (m, 8 H, CH_2), 4.61 (s, 4 H, NH), 7.10 (s, 4 H, $H_{aromatic}$), 7.12 (s, 4 H, $H_{aromatic}$), 7.50 (d, 8 H, *J* = 9 Hz, $H_{aromatic}$), 7.74 (d, 8 H, *J* = 9 Hz, $H_{aromatic}$), 8.15 (s, 2 H, 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, (1 signal missing).

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^+–$C_8H_{14}O_2N$].

Anal Calcd for $C_{144}H_{198}N_4O_8$ (2113.17): 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-ammoniopropyl]-2',5'-dihexyl-biphenyl-4-yl)pyrene Tetra-trifluoroacetate (16d)

To a solution of Boc protected **16c** (2.0 g, 0.946 mmol) dissolved in $CHCl_3$ (50 mL) was added CF_3COOH (6 mL) and the solution was stirred for 3 h at r.t. Solvents were removed and crude product **16d** (1.7 g, 0.918 mmol, 97%) was freeze-dried with dioxane.

^{1}H NMR (270 MHz, DMSO): δ = 0.69 (t, 12 H, *J* = 9 Hz, CH_3), 0.82 (t, 12 H, *J* = 9 Hz, CH_3), 0.89–1.62 (m, 64 H, CH_2), 1.69–1.96 (m, 8 H, CH_2), 2.31–2.70 (m, 24 H, CH_2), 2.81–3.03 (m, 8 H, CH_2), 7.00 (s, 4 H, $H_{aromatic}$), 7.09 (s, 4 H, $H_{aromatic}$), 7.36 (d, 4 H, *J* = 9 Hz, $H_{aromatic}$), 7.58 (d, 8 H, *J* = 9 Hz, $H_{aromatic}$), 7.84 (s, 12 H, NH_3^+), 8.00 (s, 2 H, H_{pyrene}), 8.15 (s, 4 H, 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 (CF_3), 124.51, 125.34, 127.32, 128.66, 129.62, 129.51, 130.08, 136.48, 136.90, 137.23, 137.52, 138.12, 138.47, 140.49, 158.66 (COO^-), (1 signal missing).

MS (FAB, DMSO–MNBA) *m/z*: 1713 (100) [M^++H–$C_8F_{12}O_8H_4$].

Anal Calcd for $C_{132}H_{170}F_{12}N_4O_8$ (2168.72): 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-{2-[2,6-bis-(3-{2-[2,6-bis-(3-*tert*-butoxy-carbonylamino-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-ethano-ylamino}-propyl)-4'-pyren-1-yl-biphenyl-4-yl]-ethanoyl-amino}propyl]-2',5'-dihexyl-biphenyl-4-yl)-pyrene (17)

The procedure was analogous to the one described for **13a,b**.

Acid **13c** (0.17 g, 0.087 mmol), HOBT (14.6 mg, 0.095 mmol), deprotected **16d** (43 mg, 0.020 mmol), DIPEA (21.6 mg, 29 l, 0.167 mmol) and EDC (18.3 mg, 0.095 mmol) and anhyd CH_2Cl_2 (20 mL) were used. Chromatographic separation with CH_2Cl_2–MeOH (5%) gave the product **17** (0.15 g, 0.016 mmol, 81%) as a yellow oil The product was recrystallized with acetone.

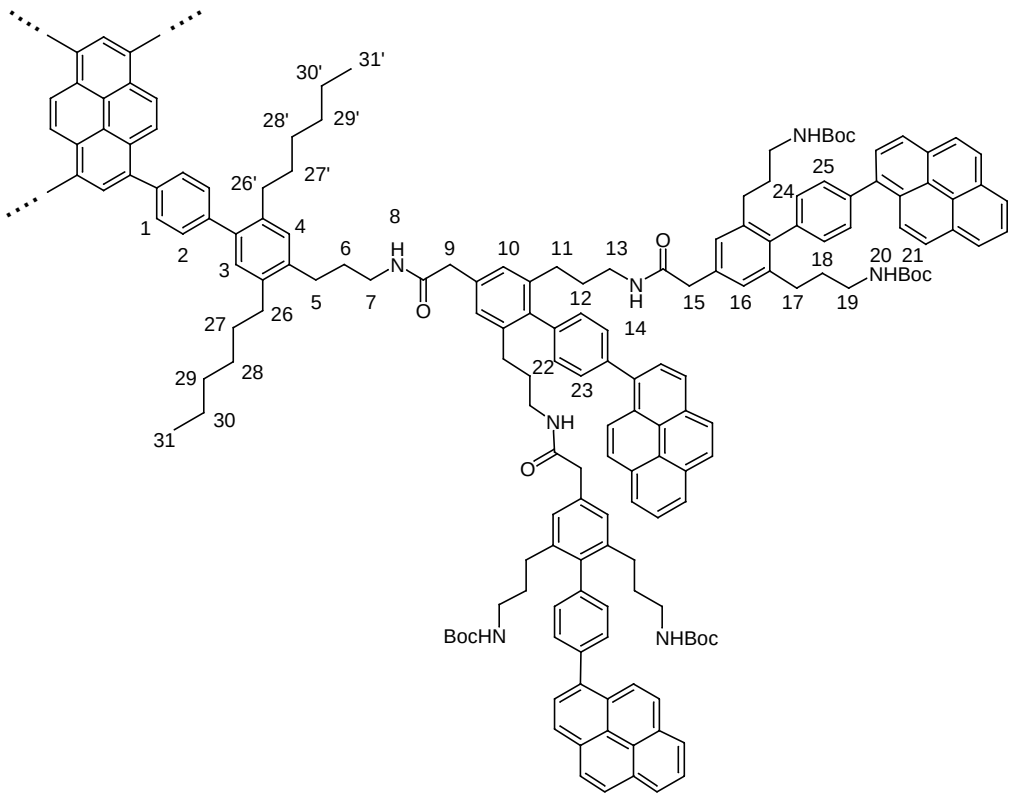
R_f (CH_2Cl_2–MeOH, 5%) = 0.65.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.72–0.98 (m, 24 H, 31, 31´), 1.07–2.00 (m, 264 H, 6, 12, 18, 27–30, 27´–30´, 21), 2.31–2.46 (m, 32 H, 17), 2.46–2.55 (m, 16 H, 11), 2.55–2.79 (m, 24 H, 5, 26, 26& acute;), 2.84–3.10 (m, 32 H, 19), 3.14 - 3.31 (m, 24 H, 7, 13), 3.48 (s, 16 H, 15), 3.62 (s, 8 H, 8), 4.41 (s, 16 H, 20), 5.89 (s, 8 H, 14), 6.45 (s, 4 H, 8), 7.00 (s, 16 H, H16), 7.05– 7.21 (m, 16 H, 3, 4, 10), 7.24 (d, *J* = 9 Hz, 16 H, 24), 7.36 (d, *J* = 9 Hz, 8 H, 22), 7.46 (d, *J* = 9 Hz, 8 H, 2), 7.62 (d, *J* = 9 Hz, 16 H, 25), 7.65–7.82 (m, 16 H, 1, 23), 7.93–8.43 (m, 114 H, H_{pyrene}). (Figure)

^{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, 125.30, 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, 137.00, 137.07, 137.73, 137.77, 138.31, 138.35, 138.61, 139.05, 139.15, 139.60, 139.65, 139.71, 140.15, 140.27, 141.02, 155.87, 171.07, 171.24, (20 signals missing).

MS (FAB, MNBA–CH_2Cl_2–DMSO) *m/z*: 9441 (100) [M^++Na].

Anal Calcd for $C_{636}H_{678}N_{28}O_{44}$ (9418.51): C, 81.11; H, 7.26; N, 4.16. Found: C, 80.79; H, 7.32; N, 3.96.



Figure

2-Amino-3,5-dibromo-terephthalic Acid Dimethyl Ester (19)
To a solution of amino-terephthalic acid dimethyl ester **18** (51.0 g, 0.244 mol) in refluxing CH_2Cl_2 (200 mL) was added a solution of Br_2 (23.0 g, 0.147 mol) in CH_2Cl_2 (20 mL) drop wise. The mixture was refluxed for 12 h, then allowed to cool to r.t.; H_2O and aq KOH were added to neutralize the solution. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (200 mL). The combined organic phases were washed with an aq Na_2SO_3 solution (c = 1mol/L, 250 mL). The CH_2Cl_2 layer was separated and dried ($MgSO_4$), recrystallization in hexanes:EtOAc, 3:1 gave product **19** (84.8 g, 0.232 mol, 95%) as pale orange crystals.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, CH_3), 3.93 (s, 3 H, CH_3), 6.46 (s, 2 H, NH_2), 7.93 (s, 1 H, $H_{aromatic}$).

^{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^+–$C_2H_8Br_2O_2$].

Anal Calcd for $C_{10}H_9NO_4Br_2$ (366.99): 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 (20)
To a solution of 6-amino-2,5-dibromo-terephthalicacid dimethyl ester **19** (36.0 g, 0.098 mol) was dissolved in MeOH (600 mL) was added concd H_2SO_4 (40 mL) drop wise. After heating to 50 °C, $NaNO_2$ (16.8 g, 0.244 mol) was added. The reaction mixture was heated to its boiling point, which at 70 °C resulted in a strong evolution of gas. After 2 h the flask was cooled to 0 °C and ice water (500 mL) was added, this resulted in precipitation of the product, which was removed by vacuum fitration. Chromatographic separation with hexanes−EtOAc, 10:1 gave the product **20** (28.6 g, 0.081 mol, 83%) as colorless solid.

R_f = 0.37 (hexanes−EtOAc, 3:1).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, CH_3), 3.93 (s, 3 H, CH_3), 8.07 (s, 2 H, $H_{aromatic}$).

^{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^+–$C_3H_6O_2Br$].

Anal Calcd for $C_{10}H_8Br_2O_4$ (351.98): C, 34.12; H, 2.29. Found: C, 33.92; H, 2.13.

2-Bromo-6-pyren-1-yl-terephthalic Acid Dimethyl Ester (21a)
The procedure was analogous to the one described for the preparation of compound **21b**. Pyrene pinacol **5** (2.50 g, 5.68 mmol), ester **20** (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), 3 d, chromatographic separation with hexanes–EtOAc, 10:1 gave the product **21a**: (2.00 g, 4.23 mmol, 74.4%).

R_f (hexanes–EtOAc, 3:1) = 0.32.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.32 (s, 3 H, CH_3), 3.91 (s, 3 H, CH_3), 7.80 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.90 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.95–8.27 (m, 8 H, $H_{aromatic}$), 8.43 (s, 1 H, $H_{aromatic}$).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 52.23, 52.57, 119.67, 124.11, 124.42, 124.54, 124.64, 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, 132.72, 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^+–$C_4H_6BrO_4$].

Anal Clacd for $C_{26}H_{17}BrO_4$ (473.32): C, 65.98; H, 3.62. Found: C, 66.16; H, 3.77.

3-Bromo-4'-pyren-1-yl-biphenyl-2,5-dicarboxylic Acid Dimethyl Ester (21b)

4,4,5,5-Tetramethyl-2-pyren-1-yl-1,3,2-dioxaborolane **7b** (1.66 g, 4.10 mmol) and 2,5 di-bromo terephthalic acid dimethylester **20** (1.50 g, 4.10 mmol) were dissolved in toluene (20 mL). The solution was degassed and flushed with N_2 repeatedly. An aq solution of Na_2CO_3 (20 mL, c = 1 mol/L) was added. The mixture was degassed again and $Pd(Ph_3)_4$ (85 mg, 7.4×10^{-2} mmol) was added. The mixture was refluxed for 2 d with vigorous stirring and then allowed to cool to r.t. The layers were separated and the aqueous layer was washed with toluene (2 × 20 mL). The combined organic layers were dried ($MgSO_4$); chromatographic separation with hexanes–EtOAc,10:1 gave the product **21b** (1.35 g, 2.46 mmol, 58%) as a yellow solid.

R_f (hexanes−EtOAc, 3:1) = 0.28.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, CH_3), 3.91 (s, 3 H, CH_3), 7.55 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.67 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.84–8.34 (m, 11 H, $H_{pyrene+aromatic}$).

^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 52.42, 52.56, 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, 164.65, 167.49, (3 signals missing).

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 (*m/z*): [M^+] calcd for ($C_{32}H_{21}{}^{79}BrO_4$), 548.06232; found, 548.06683.

Anal Calcd for $C_{32}H_{21}BrO_4$ (549.42): C, 69.96; H, 3.85. Found: C, 70.47; H, 4.28.

2-(3-*tert*-Butoxycarbonylamino-propyl)-6-pyren-1-yl-terephthalic Acid Dimethyl Ester (22a)

The procedure was analogous to the one described for compound **10b**.

9 (1.29 g, 8.23 mmol), anhyd toluene (25 mL), 9-BBN (1.51 g, 12.30 mmol), KOH (30 mL, c = 1 mol/L), **21a** (1.00 g, 2.06 mmol), $Pd(PPh_3)_4$ (47 mg, 41.2 mmol), 3 d, chromatographic separation with hexanes–EtOAc, 10:1 gave the product **22a** (0.91 g, 1.65 mmol, 80%).

R_f (hexanes−EtOAc, 3:1) = 0.28.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 9 H, $CH_{3\ boc}$), 1.95 (quin, 2 H, *J* = 9.3 Hz, CH_2-β), 2.74–2.88 (m, 2 H, $CH_{2\ benzylic}$), 3.15 (s, 3 H, CH_3), 3.18–3.28 (m, 2 H, CH_2N), 3.90 (s, 3 H, CH_3), 4.80 (s, 1 H, NH), 7.80 (d, *J* = 9.3 Hz, 1 H, $H_{aromatic}$), 7.85 (s, 1 H, NH), 7.94–8.23 (m, 9 H, $H_{aromatic}$).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 28.28, 30.80, 31.41, 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, 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, (1 signal missing).

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^+–$C_7H_{14}O_4$].

Anal Calcd for $C_{34}H_{33}NO_6$ (551.64): C, 74.03; H, 6.03; N, 2.54. Found: C, 74.01; H, 6.16; N, 2.32.

3-(3-tert-Butoxycarbonylamino-propyl)-4'-pyren-1-yl-biphenyl-2,5,-dicarboxylic Acid Dimethyl Ester (22b) and 4'-Pyren-1-yl-biphenyl-2,5-dicarboxylic Acid Dimethyl Ester (21c)

The procedure was analogous to the one described for the preparation of compound **10b**.

Protected allylamine **9** (0.97 g, 6.19 mmol), anhyd toluene (25 mL), 9-BBN (1.15 g, 9.40 mmol), 12 h, aq solution of KOH (20 mL,c = 1 mol/L), bromo-aryl **21b** (0.85g, 1.55 mmol), $Pd(PPh_3)_4$ (22 mg, 1.9×10^{-5}mmol), 36 h, chromatographic separation with hexanes–EtOAc, 3:1 gave the product **22b** (0.47 g, 0.75 mmol, 48%) as a yellow solid and the proton substituted product **21c** (94.0 mg, 0.20 mmol, 13%) as a colorless solid.

22b

R_f (hexanes−EtOAc, 3:1) = 0.08.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, $CH_{3\ boc}$), 1.81–2.03 (m, 2 H, CH_2), 2.77 (t, 2 H, *J* = 9 Hz, $CH_{2\ benzylic}$), 3.09–3.31 (m, 2 H, CH_2N), 3.74 (s, 3 H, CH_3), 3.96 (s, 3 H, CH_3), 4.82 (s, 1 H, NH), 7.57 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.69 (d, 2 H, *J* = 9 Hz, $H_{aromatic}$), 7.91–8.29 (m, 11 H, $H_{pyrene+aromatic}$).

^{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, (3 signals missing).

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 (*m/z*): ($C_{40}H_{37}NO_6$) [M^+] calcd for, 627.26208; found, 627.26422.

Anal Calcd for $C_{40}H_{37}NO_6$ (627.73): C, 76.54; H, 5.94; N, 2.23. Found: C, 76.18; H, 5.73; N, 1.95.

21c

R_f (hexane−EtOAc, 3:1) = 0.24.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 3.77 (s, 3 H, CH_3), 3.96 (s, 3 H, CH_3), 7.53 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.69 (d, 2 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.93 (d, 1 H, *J* = 9.3 Hz, $H_{aromatic}$), 7.96–8.31 (m, 10 H, $H_{pyrene+aromatic}$).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 52.25, 52.40, 124.65, 124.86, 125.02, 125.15, 126.02, 127.39, 127.48, 127.57, 128.21, 128.37, 128.52, 129.89, 130.43, 130.71, 130.97, 131.50, 131.85, 132.57, 134.91, 137.13, 139.20, 140.60, 142.17, 166.14, 168.55, (3 signals missing).

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 (*m/z*): [M^+] Calcd for ($C_{32}H_{22}O_4$), 470.15181; found, 470.15664.

2-(3-tert-Butoxycarbonylamino-propyl)-6-(3-pyren-1-yl-propyl)-terephthalic Acid Dimethyl Ester (25)

The procedure was analogous to the one described for compound **10b**.

Allylpyrene **24** (1.40 g, 5.77 mmol), allyl amine **9** (0.90 g, 5.74 mmol), 9-BBN (1.76 g, 14.4 mmol), toluene (40 mL), 12 h, aq solution of Na_2CO_3 (40mL), dibromo ester **20** (2.02 g, 5.74 mmol), were refluxed for 5 d. Chromatographic separation with hexanes–EtOAc, 3:1 gave the product **25** (0.21 g, 0.36 mmol, 6%) as a pale yellow oil.

R_f (hexanes–EtOAc, 3:1) = 0.11

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, $CH_{3\ boc}$), 1.77 (quintet, 2 H, *J* = 8.3 Hz, CH_2), 2.15 (quintet, 2 H, *J* = 8.3 Hz, CH_2), 2.50–2.68 (m, 2 H, CH_2), 2.68–2.86 (m, 2 H, CH_2), 2.98–3.21 (m, 2 H, CH_2), 3.32 (t, 2 H, *J* = 8.3 Hz, CH_2), 3.60 (s, 3 H, CH_3), 3.88 (s, 3 H, CH_3), 4.71 (s, 1 H, NH), 7.62–8.38 (m, 11 H, $H_{aromatic}$).

^{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 (*m/z*): [M^+] calcd for ($C_{37}H_{39}NO_6$), 593.27774; found, 593.27368.

References

(1) For general information about dendrimers see for example: (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules - Concepts, Syntheses, Perspectives*; VCH: Weinheim, **1996**. (b) Zeng, F.; Zimmerman, S. C. *Chem Rev.* **1997**, *97*, 1681. (c) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem Rev.* **1999**, *99*, 1665. (d) Fischer, M.; Vögtle, F. *Angew. Chem. Int. Ed.* **1999**, *38*, 885. (e) Schlüter, A. D.; Rabe, J. P. *Angew. Chem. Int. Ed.* **2000**, *39*, 864.

(2) For an elegant study on electron transfer in a dendrimer from a porphyrine core through a Fréchet-type shell, see: Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895.

(3) For the related antenna effect in dendrimers and a comprehensive survey of methods with which the interior of dendrimers have been investigated, see: (a) Hecht, S.; Fréchet, J. M. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 74; and references therein. (b) Gust, D.; Moore, T. A. *Adv. Photochem.* **1992**, *16*, 1. (c) Burrell, A. K.; Wasieleski, M. R. *J. Porphyr. Phthalocya.* **2000**, *4*, 401.

(4) Beinhoff, M.; Modrakowski, C.; Weigel, W.; Rettig, W.; Schlüter, A. D. *Mater. Sci. Engin.* **2001**, *84*, 751.

(5) Beinhoff, M.; Weigel, W.; Jurczok, M.; Rettig, W.; Modrakowski, C.; Brüdgam, I.; Hartl, H.; Schlüter, A. D. *Eur. J. Org. Chem.* submitted.

(6) For example, see: (a) Voit, B.; Wolf, D. *Tetrahedron* **1997**, *53*, 15535. (b) Mulders, S. J. E.; Brouwer, A. J.; van der Meer, P. G. J.; Liskamp, R. M. J. *Tetrahedron Lett.* **1997**, *38*, 631. (c) Mulders, S. J. E.; Brouwer, A. J.; Liskamp, R. M. J. *Tetrahedron Lett.* **1997**, *38*, 3085. (d) Neubert, I.; Schlüter, A. D. *Macromolecules* **1998**, *31*, 9372. (e) Yamakawa, Y.; Ueda, M.; Takeuchi, K.; Asai, M. *Macromolecules* **1999**, *32*, 8363. (f) Appelhans, D.; Komber, H.; Voigt, D.; Häussler, L.; Voit, B. *Macromolecules* **2000**, *33*, 9494. (g) Shu, L.; Schäfer, A.; Schlüter, A. D. *Macromolecules* **2000**, *33*, 4321. (h) Shu, L.; Schlüter, A. D. *Macromol. Chem. Phys.* **2000**, *201*, 239. (i) Brouwer, A. J.; Mulders, S. J. E.; Liskamp, R. M. J. *Eur. J. Org. Chem.* **2001**, 1903. (j) Vetter, S.; Koch, S.; Schlüter, A. D. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 1940.

(7) We consider a dummy a non-fluorescent fragment of virtually the same space demand as the fluorescent probe.

(8) Hensel, V.; Schlüter, A. D. *Chem. — Eur. J.* **1999**, *5*, 421; and references cited therein.

(9) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(10) Achira, J. N.; Astik, R. R.; Thaller, K. A. *J. Inst. Chem.* **1975**, *47*, 247.

(11) Ueda, Y.; Hattori, H.; Yamamoto, J.; Hashimoto, K. Brit. UK Pat Appl., CODEN: Baxxon GB 2207 683, A1 19890208, **1989**.

(12) Schlüter, A. D. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 1533.

(13) Miyaura, N.; Ishiyamo, T.; Ishikawa, M.; Suzuki, A. *Tetrahedron Lett.* **1986**, *27*, 6369.

(14) For example, see: Vetter, S.; Zhang, A.; Koch, S.; Schlüter, A. D. *Macromol. Chem. Phys.* submitted.

(15) (a) *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed., Vol. XV; Wünsch, E., Ed.; Thieme: Stuttgart, **1974**, 103ff. (b) *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed., Vol. II; Wünsch, E., Ed.; Thieme: Stuttgart, **1974**, 326ff.

(16) Hensel, V.; Schlüter, A. D. *Lieb. Ann./Recueil* **1997**, 303.

(17) (a) Stille, J. K. *Angew. Chem.* **1986**, *98*, 504. (b) Ogino, K.; Iwashima, S.; Inokuchi, H.; Harada, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 474.

(18) For example, see: Langhals, H.; Demmig, S.; Potrawa, T. *J. Prakt. Chem.* **1991**, *333*, 733.

(19) For a synthesis which was not used here, see: Blight, M. M.; Coppen, J. J. W.; Grove, J. F. *J. Chem. Soc. (C)* **1969**, 552.

(20) Beer, M. S. *J. Med. Chem.* **1993**, *36*, 1529.

(21) Vollmann, H.; Becker, H.; Corell, M.; Streeck, H.; Langbein, G. *Lieb. Ann. Chem.* **1937**, *531*, 1.

(22) Takuwa, A.; Kanaue, T.; Yamashita, K.; Nishigaishi, Y. *J. Chem. Soc., Perkin Trans.(1)* **1998**, 1309.