Synthesis of novel dendritic molecules based on pyrroloanthracene units

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Dedicated to Professor Georges Hoornaert on his 65th birthday

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Abstract

Novel pyrroloanthracenes were efficiently synthesized starting from Diels-Alder adducts of anthracene. Some of these orthogonally bridged, rigid and bulky compounds were used as building blocks for the construction of monodisperse dendritic macromolecules. Molecular masses over 4 kDa could be obtained. Further propagation was problematic because of the particular stability of the 4-(1-pyrrolyl)benzyl cation causing the instability or difficulty of formation of the analogous benzyl ether linkage in the proposed dendritic structures.

Keywords: Dendrimers, pyrroloanthracenes, Mitsunobu reaction

Introduction

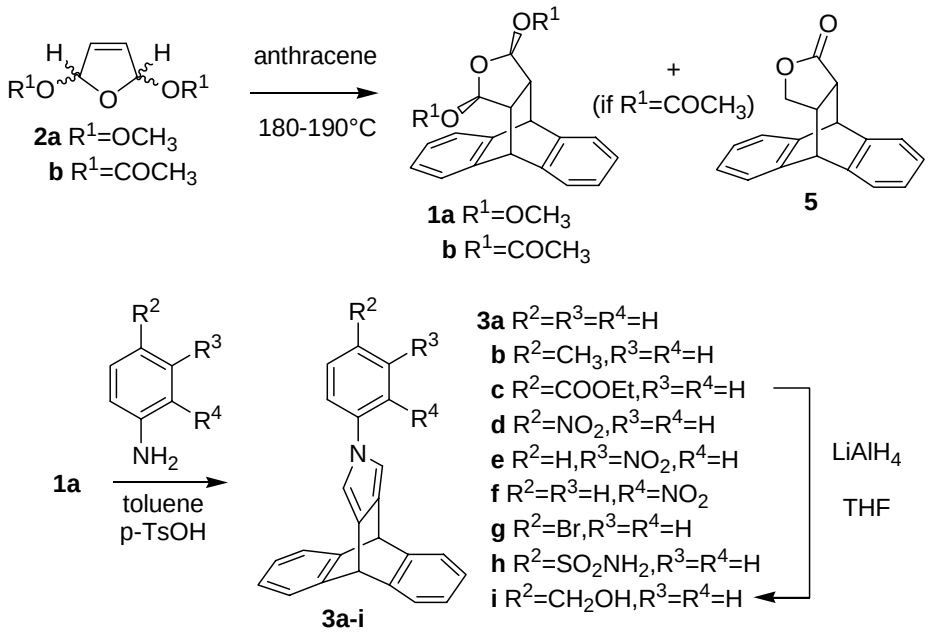
During the last decade, dendrimers have attracted a lot of attention because of their unique molecular architecture.[1] Numerous applications have been foreseen for these molecules e.g. as complexing agents for small molecules and indeed this concept has been experimentally proved.[2] One possible strategy to increase the loading capacity of dendrimers is to incorporate bulky units in order to create large cavities in the macromolecule. The use of highly rigid building blocks will avoid collapse of the dendrimer in poor solvents. It has been demonstrated that Diels-Alder adducts of anthracene, which are highly rigid, orthogonally bridged structures, possess interesting properties to construct supramolecular entities with excellent complexing behaviour. Hydrocarbon dendrimers with triptycene monomeric units have been shown to form crystalline complexes with acetone.[3] Cyclophanes consisting of Diels-Alder adducts of anthracene were found to display strong affinity towards certain tetraalkylammonium salts.[4] Simple Diels-Alder adducts of anthracene were found to form clathrates with several solvents with a stoichiometry depending upon the nature of the solvent and the structure of the host.[5] Fluorescent polymers in which similar entities had been incorporated were shown to be useful for the construction of sensors for dinitrotoluene which allows their use in detectors for land mines as this compound is a volatile impurity in trinitrotoluene.[6] It was proved that the cavities introduced in the polymer films by the presence of the bulky anthracene adducts were essential to allow the analyte to

penetrate in the structure and hence to induce a detectable change of the fluorescence properties of the polymers. Our group has been interested in the chemistry of anthracene for several years and we have shown that N-phenylmaleimidoanthracenes also have remarkable inclusion properties.[7]

Results and Discussion

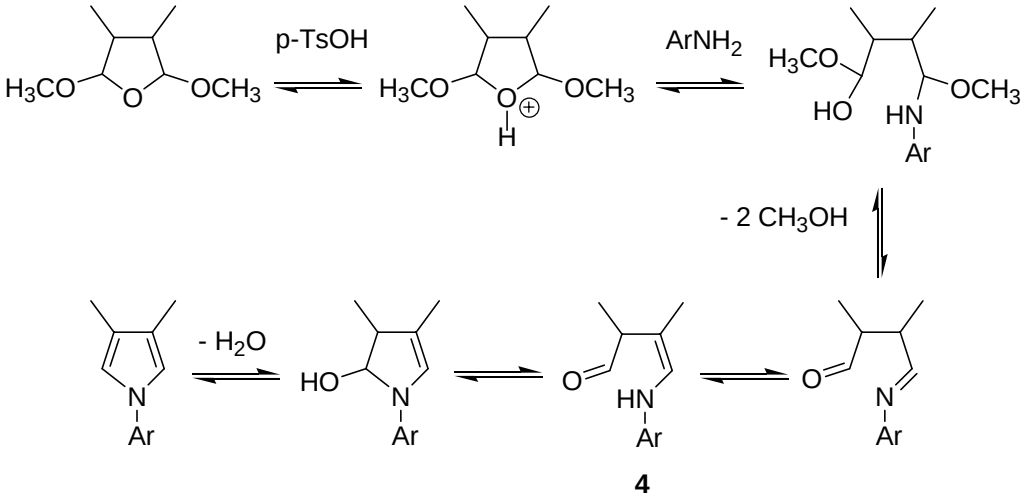
Taking into account the described interesting properties of orthogonally bridged Diels-Alder adducts of anthracene, we wished to explore the possibility to construct dendrimers based on these species as the AB_2 monomer. We chose to functionalize such adducts with ester (as protected A functionality) and phenol groups (as B functionality) allowing a deprotection strategy by reduction of the ester to alcohol and activation for coupling by well established strategies such as the Mitsunobu reaction or halogenation and subsequent Williamson ether synthesis.

In a first approach, we started from the Diels-Alder adduct **1a** of anthracene and 2,5-dimethoxy-2,5-dihydrofuran (**2a**) (Scheme 1). Although the commercial *cis-trans* mixture of the latter was used, only the *cis* adduct was isolated. Addition of 10 mol% of potassium carbonate was found to increase the yield significantly, most probably by avoiding the acid catalyzed decomposition of the dihydrofuran. The obtained adduct **1a** could readily be condensed in the presence of a catalytic amount of p-TsOH with anilines bearing an electron withdrawing or neutral substituent yielding the pyrroloanthracenes **3a-h** listed in scheme 1. However, the reaction was found to fail when strongly electron donating substituents are present on the aniline. This can be explained assuming the mechanism presented in scheme 2. Electron donating substituents will destabilize the supposed enamine intermediate **4** and hence disfavor the cyclization to the pyrrole. Our observation that aliphatic amines, in spite of their higher nucleophilicity, fail to react as well is consistent with this reasoning as is the observation that the yields are significantly higher when strong electron withdrawing substituents are present on the aniline.



Scheme 1

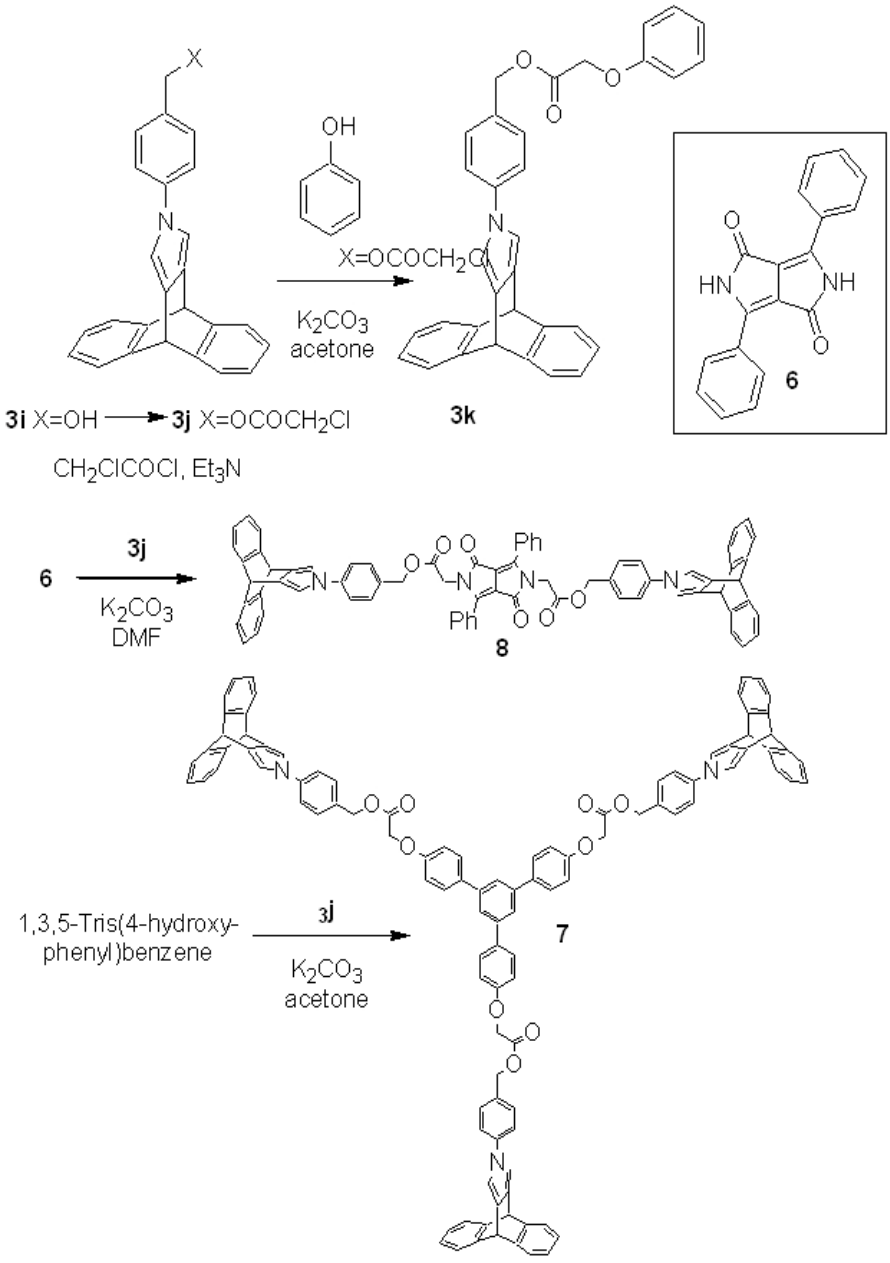
In order to extend the scope of this reaction towards anilines bearing electron donating substituents, we prepared the Diels-Alder adduct **1b** of anthracene and 2,5-bisacetoxy-2,5-dihydrofuran (**2b**). The latter compound was prepared via a literature procedure.[8] Also in this case, addition of KOAc as a base dramatically improved the yield of the adduct although a rearrangement to lactone **5** could not be completely avoided as still 10% of this compound was formed. However, adduct **1b** was found not to react with aromatic amines and hence this approach turned out to be useless.



Scheme 2

The ethyl ester **3c** could readily be reduced with $LiAlH_4$ yielding the benzyl alcohol **3i** which we intended for use as peripheral unit for our dendritic branches. In order to allow easy coupling under Williamson conditions we tried to convert the alcohol function of **3i** into a leaving group. However, numerous experiments towards this goal failed: neither the chloride (by treatment of

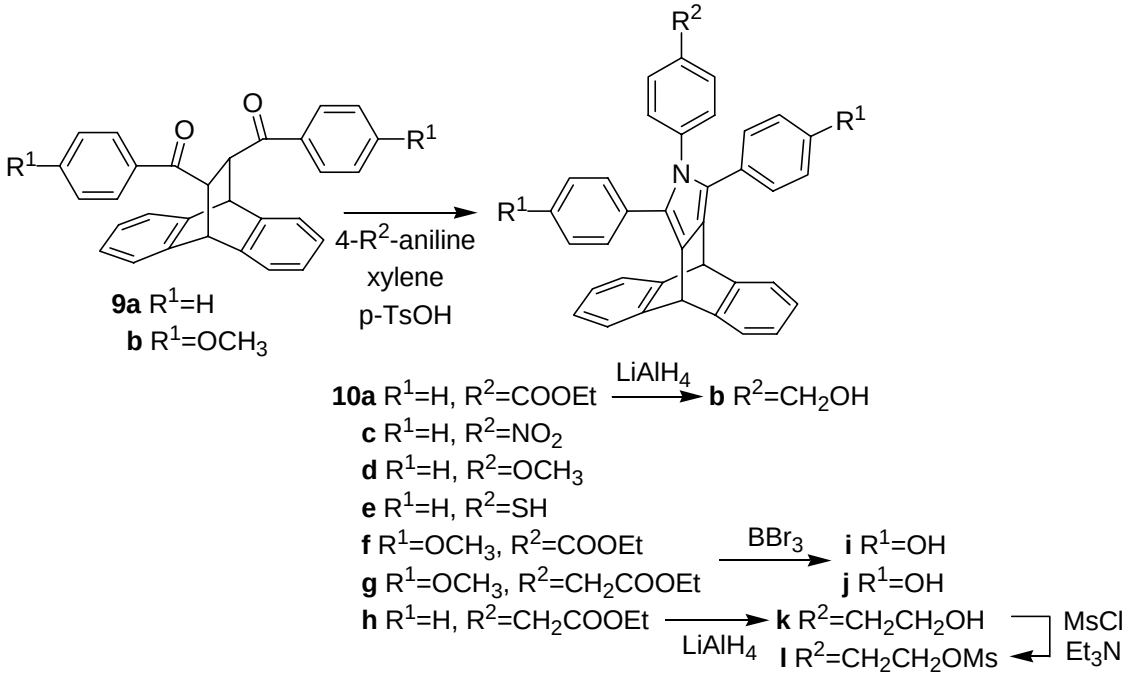
the alcohol with $SOCl_2$) nor the bromide (by treatment with CBr_4/PPh_3), nor the trifluoroacetate (by treatment with trifluoroacetic anhydride/Et_3N), nor the trichloroacetate (by treatment with trichloroacetyl chloride/Et_3N) could be detected by TLC or mass spectrometry. We found the dichloroacetate stable enough to be detected by TLC but after work up of the reaction mixture, this compound had decomposed as well. Finally, the monochloroacetate **3j** could be obtained, characterized and substituted in a test experiment with phenolate (Scheme 3). As could be expected, this substitution did not proceed on the benzyl position but on the chloromethyl residue yielding phenoxyacetate **3k**. On the same principle, chloroacetate **3j** could be coupled with 1,3,5-tris(4-hydroxyphenyl)benzene and with 3,6-diphenyl-2,5-diketopyrrolopyrrole **6**[9] affording the respective dendritic molecules **7** and **8** of generation 0.



Scheme 3

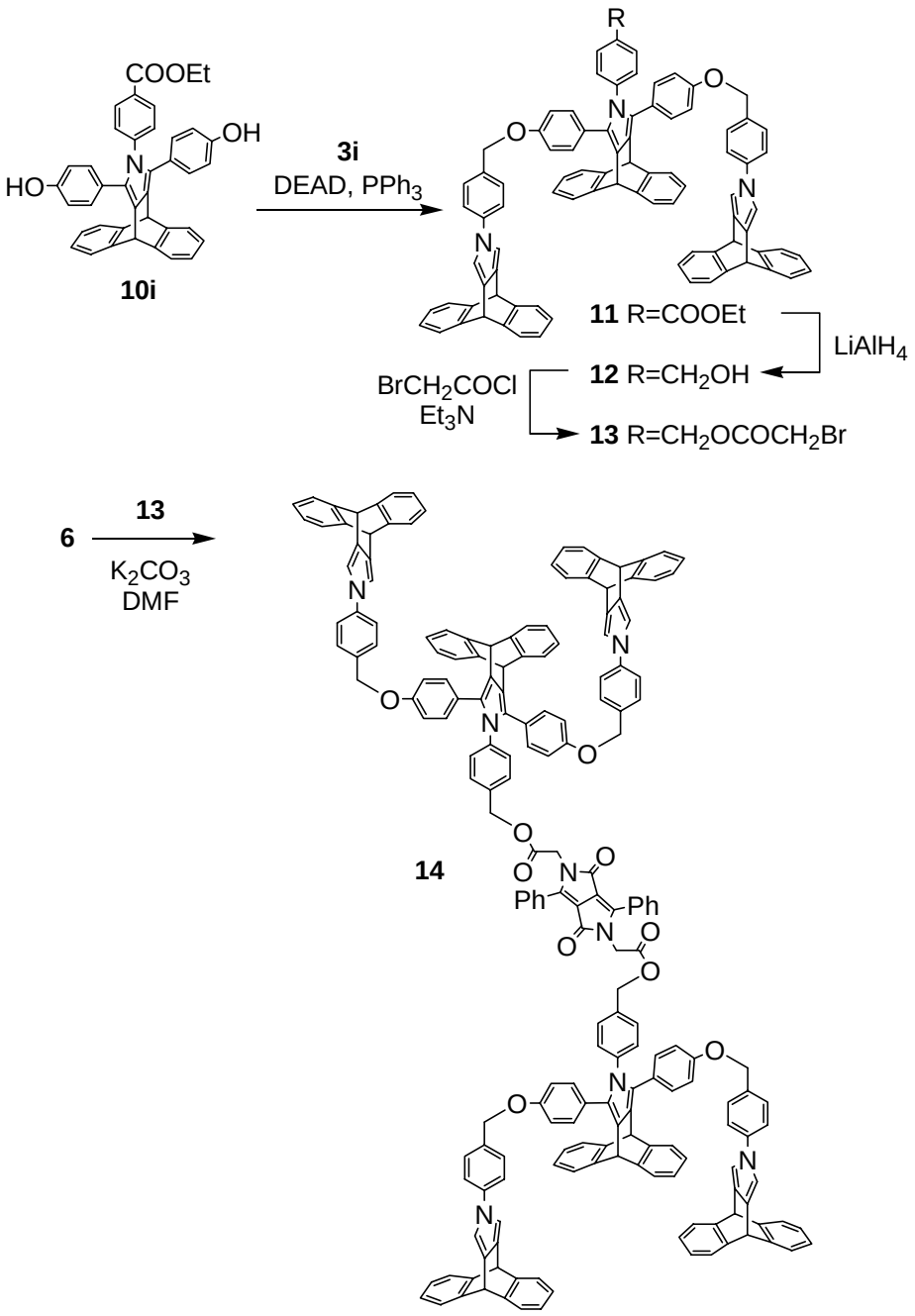
In order to overcome the instability problems preventing the conversion of the alcohol function of **3i** into a leaving group, we prepared analogous pyrroloanthracenes starting from the Diels-Alder adduct **9a** of anthracene and trans 1,2-dibenzoylethylene (Scheme 4).[10] Although we found that this compound required more drastic conditions to be transformed into the corresponding N-phenylpyrroloanthracenes **10a**,**c-e** (refluxing xylene instead of toluene), this adduct also afforded the desired compounds when reacted with anilines bearing electron donating substituents. After reduction of the ester **10a** to the benzyl alcohol **10b**, we encountered the same problem to convert the alcohol function into a leaving group.

For the construction of a functional AB_2 monomer we prepared the Diels-Alder adduct **9b** of 1,2-bis(4-methoxybenzoyl)ethylene and anthracene. This compound could readily be transformed into the bishydroxybenzyl alcohol **10i** by cyclization with ethyl 4-aminobenzoate followed by demethylation of **10f** with BBr_3. The latter reaction resulted to some extent in hydrolysis of the ethyl ester. However, by working at –20°C this side reaction could be reduced to acceptable proportions.

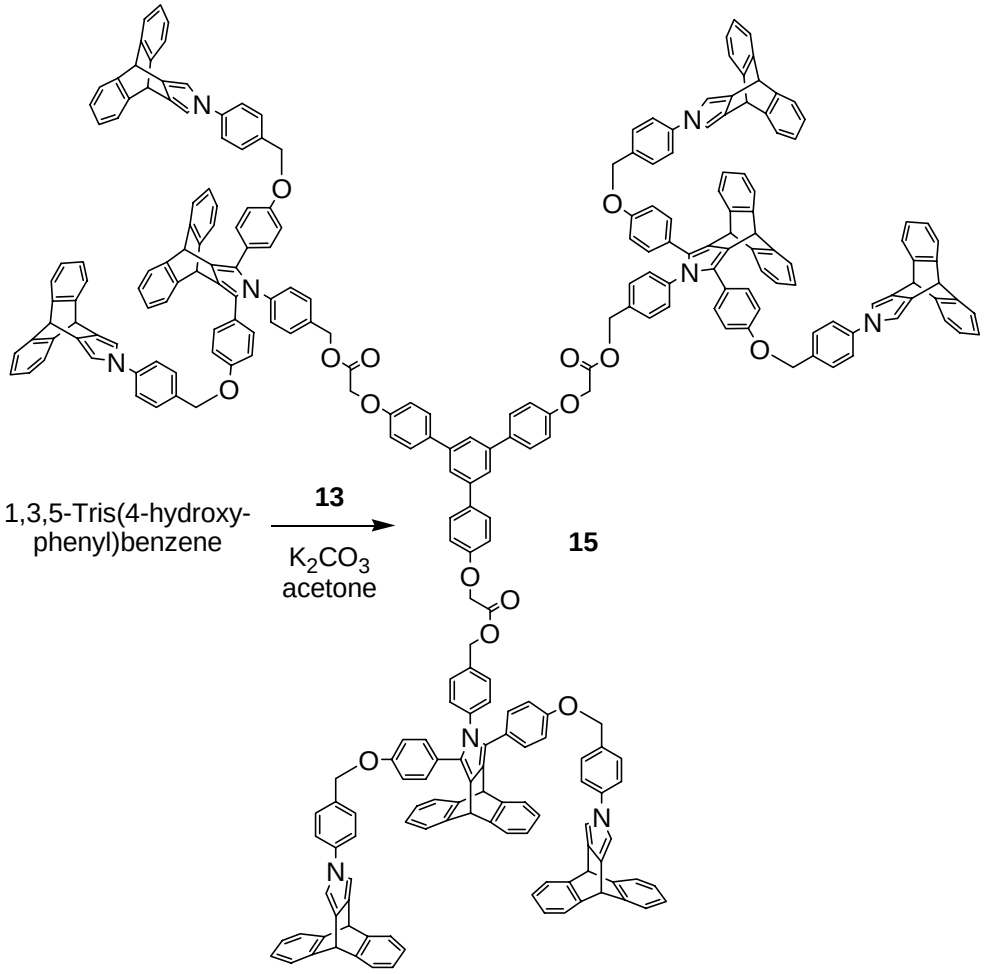


Scheme 4

To avoid Williamson ether synthesis and hence the necessity of transforming the benzylic alcohol **3i** into a leaving group, we coupled AB_2 monomer **10i** with the peripheral unit **3i** under Mitsunobu conditions (Scheme 5). The obtained G1-ester **11** was reduced to the G1-alcohol **12** with $LiAlH_4$ and converted into the bromoacetate **13**. The latter compound allowed smooth coupling with the same core reagents as cited higher yielding the G1-dendrimers **14** and **15** (Scheme 6) which could be characterized by NMR spectroscopy. ES mass spectrometry allowed to confirm the molecular mass of 2762 and 4064 Da respectively. These macromolecules were found to degrade to a large extent when kept in solution in chloroform for a few weeks. Careful analysis of the degradation products showed that the benzyl acetate groups were hydrolyzed. This is consistent with the observed instability of the 4-(pyrrol-1-yl)benzyl moiety.

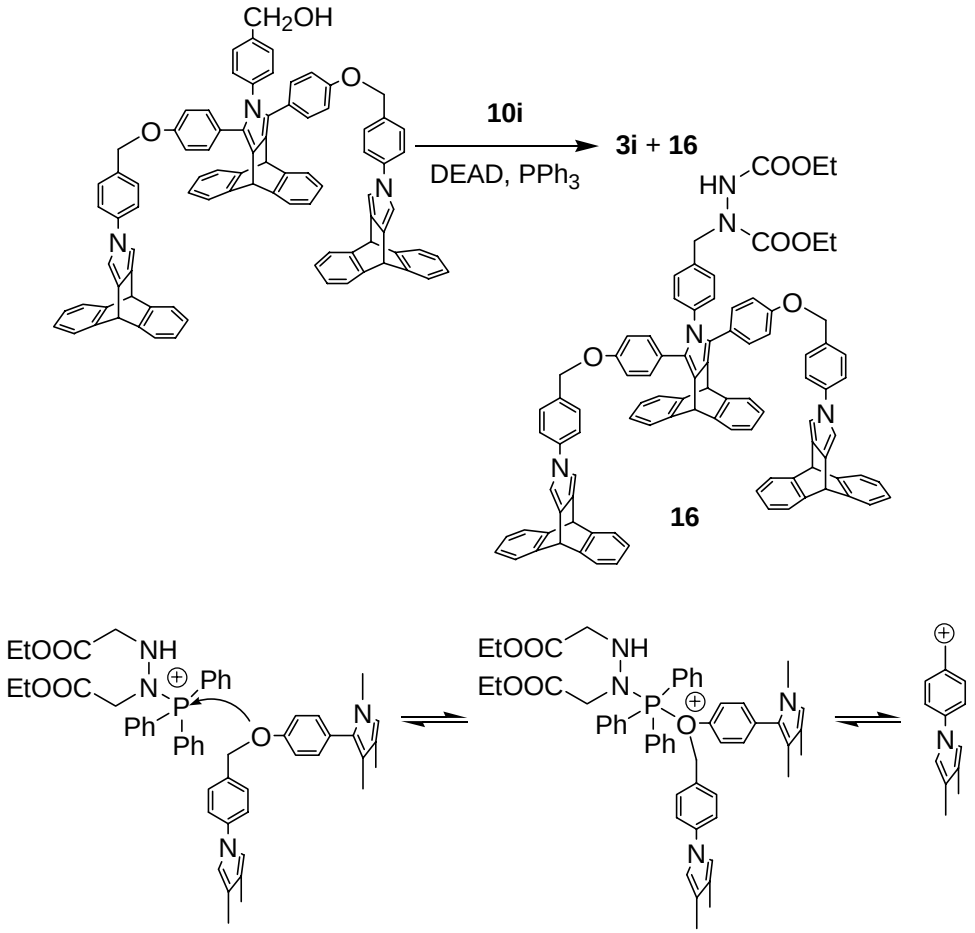

COOEt
OH
HO
N
10i
3i
DEAD, PPh3
R
O
N
11 R=COOEt
LiAlH4
12 R=CH2OH
BrCH2COCl
Et3N
13 R=CH2OCOCH2Br
6
13
K2CO3
DMF
14
Ph
Ph

Scheme 5



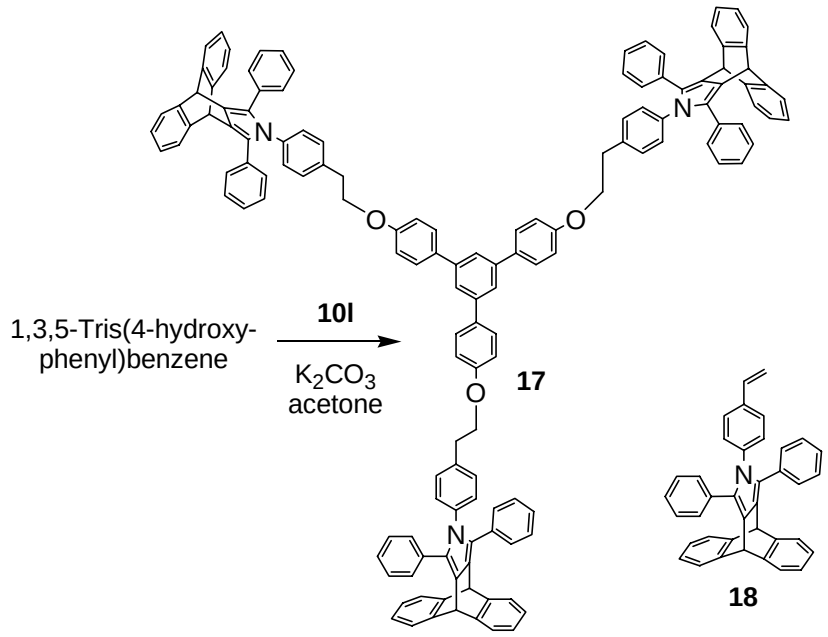
Scheme 6

Moreover, we found that even Mitsunobu coupling between G1-alcohol **12** and AB_2 monomer **10i** failed. Two possible side reactions were experimentally confirmed. The first one yields the hydrazine derivative **16**. It is well known that products of this type can be formed upon treatment of benzyl and allyl alcohols with DEAD and PPh_3 in the absence of a good nucleophile.[11] It is evident, however, that there is no reason why our AB_2 monomer **10i** would show a lack of reactivity. Therefore, we think the extreme activation of benzyl alcohol **12** is likely to facilitate the formation of **16** to a notable extent. A second side reaction results in cleavage of already formed benzyl ether linkages, which is detected by the presence of alcohol **3i** in the reaction mixture. Most probably, the benzyl ether bonds are cleaved under the influence of the intermediate formed from DEAD and PPh_3 (Scheme 7). Again, this is a reaction for which excellent stabilization of the intermediate benzyl carbocation is a necessity. The fluorescence of the DPP core of dendrimer **14** was found to be almost totally quenched. This is in sharp contrast with the analogous G0-dendrimer **8** which was highly fluorescent. Most probably, backfolding of the highly electron rich 2,5-bis(4-benzyloxyphenyl)pyrrole units to the core region results in quenching of the fluorescence by electron transfer.



Scheme 7

Facing these problems mentioned above, we turned our attention towards the analogous AB_2 monomer **10j** and peripheral unit **10k** in which an extra methylene group is present (Scheme 4). The synthesis of these compounds was straightforward following the same strategy as described above. In this case, the removal of the methyl groups with BBr_3 was found to be cleaner as almost no hydrolysis of the ester occurred. Conversion of alcohol **10k** into mesylate **10l** was unproblematic. A test experiment in which mesylate **10l** was coupled with 1,3,5-tris(4-hydroxyphenyl)benzene under Williamson conditions showed that, although G0-dendrimer **17** could be obtained in reasonable yield, elimination giving rise to the alkene **18** would be a problem for further propagation towards higher generations (Scheme 8).

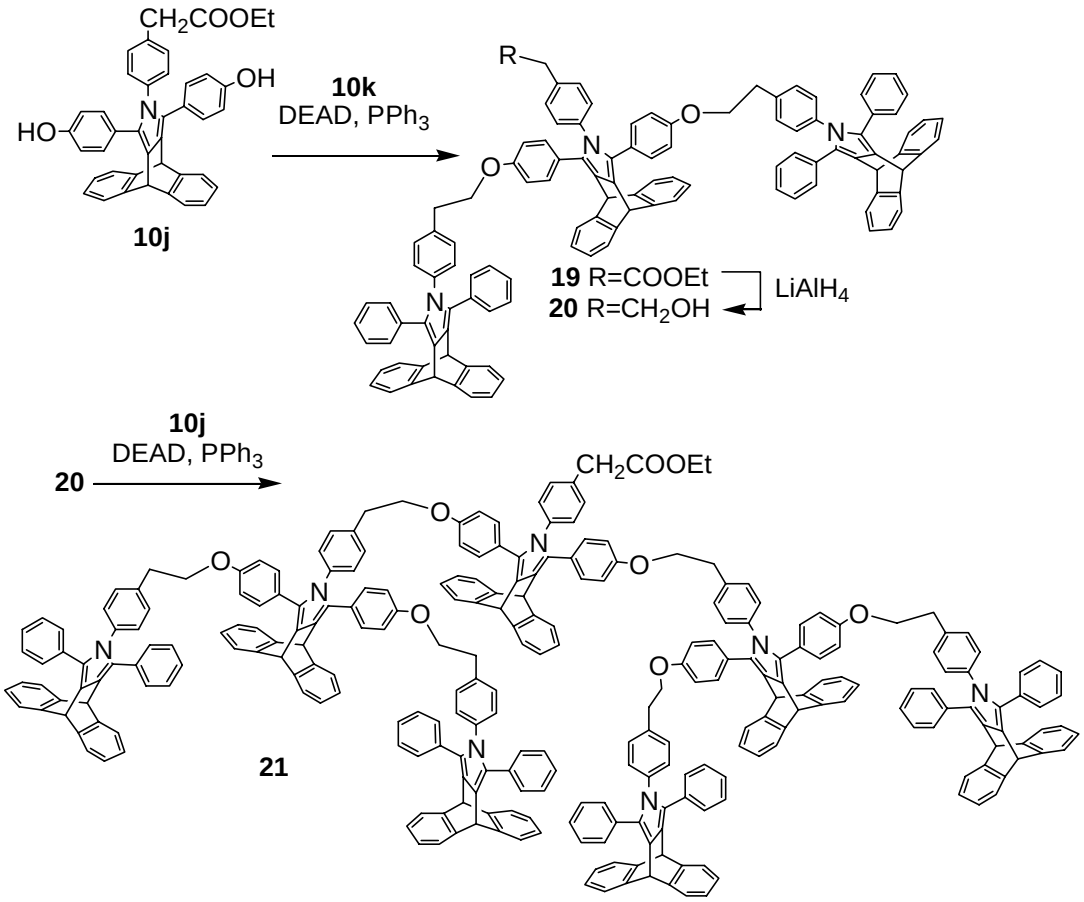


Scheme 8

Therefore, we coupled the alcohol **10k** with our new AB_2 monomer **10j** under Mitsunobu conditions which afforded G1-dendron **19** in reasonable yield (Scheme 9). This dendron could be fully characterized by NMR spectroscopy and MS mass spectrometry (m/z = 1586) and could be reduced cleanly with $LiAlH_4$ affording G1-alcohol **20**. However, coupling of the latter alcohol **20** with AB_2 monomer **10j** under Mitsunobu conditions failed, as only traces of the desired G2-ester **21** could be detected by mass spectrometry.

Conclusions

We have prepared a number of new variably substituted pyrroloanthracenes by condensation of anilines with Diels-Alder adducts of anthracene. These compounds could be transformed into dendritic, monodisperse macromolecules of molecular masses exceeding 4000 g/mol. Severe problems occurred, however, upon trying to obtain higher generations, mainly caused by the very strong stabilization of the 4-(1-pyrrolyl)benzyl cation. More sophisticated coupling strategies will be necessary to overcome these problems.



Scheme 9

Experimental Section

Synthesis of adduct 1a. A suspension of anthracene (14 g; 0.078 mol), the commerical *cis-trans* mixture of 2,5-dimethoxy-2,5-dihydrofuran **(2a)** (10 g; 0.078 mol) and K_2CO_3 (1.1 g; 7.8 mmol; 10 mol%) was heated for 15 h at 185°C. The mixture was cooled down and the residue was crystallized from methanol yielding the adduct **1a** as a white solid (22 g; 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.05 (3 x m, 8H), 4.63 (s, 2H), 4.38 (t, J = 1.4 Hz, 2H), 3.30 (s, 6H), 2.85 (t, J = 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.4, 126.3, 126.0, 124.7, 123.7, 109.6, 55.2, 52.0, 46.5. MS (EI): 308 (M^+).

Synthesis of adduct 1b. 2,5-Diacetoxy-2,5-dihydrofuran **(2b)** (5.0 g; 27 mmol), anthracene (5.9 g; 33 mmol) and KOAc (0.5 g) were heated together at 180 °C for 15 h under argon atmosphere. The mixture was cooled down and dissolved in dichloromethane. Adduct **1b** was obtained after column chromatography. (SiO_2, CH_2Cl_2 followed by 9:1 CH_2Cl_2-diethyl ether) as an oil (7.6 g; 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m,4H), 7.16-7.14 (m, 2H), 7.11-7.09 (m, 2H), 5.85 (s, 2H), 4.52 (s, 2H), 2.91 (s, 2H),2.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 142.4, 139.4, 126.8, 126.2, 125.0, 123.8, 102.9, 51.9, 45.74, 21.2; MS (EI): 364 (M^+). Lactone **5** was isolated as a white solid (0.71 g; 10%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 4H), 7.17-7.12 (m, 4H), 4.69 (d, J = 3.6 Hz, 1H), 4.30 (t J = 9.2 Hz, 1H), 4.25 (d, J = 3.2 Hz, 1H), 3.77 (d, J

= 4.1 Hz, 1H), 3.74 (d, J = 4.1 Hz, 1H), 3.16 (d, J = 3.6 Hz), 3.13 (d, J = 3.6 Hz, 1H), 3.05-2.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 142.3, 141.6, 139.9, 138.7, 127.0, 126.8, 126.4, 126.4, 125.5, 125.1, 124.1, 123.8, 69.9, 47.5, 47.2, 45.7, 40.3; MS (EI): 262 (M^+).

General procedure for the synthesis of pyrroloanthracenes 3a-h. Diels-Alder adduct (0.50 g; 1.6 mmol), the appropriate amine (2.1 mmol) and p-TsOH (15 mg) were dissolved in toluene (40 ml). The solution was refluxed under argon atmosphere during 12 h. After cooling to room temperature, the solvent was evaporated and the residue purified by column chromatography (SiO_2, 2:1 CH_2Cl_2-hexane).

***N*-phenylpyrroloanthracene (3a).** Obtained as an oil (65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.26 (dt, 2H), 7.17 (dt, 2H), 7.07 (tt, 1H), 6.97 1H), 6.79 (m, 4H), 6.85 (s, 2H), 5.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 141.1, 132.8, 129.3, 125.0, 124.6, 123.4, 119.9, 111.1, 47.2; MS (EI): 319 (M^+).

***N*-(4-methylphenyl)pyrroloanthracene (3b).** Obtained as an oil (58 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.35 (m, 4H), 7.09 (s, 4H), 6.79 (m, 4H), 6.84 (s, 2H), 5.32 (s, 2H), 2.29 (s, 3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 138.8, 134.2, 132.5, 129.8, 125.0, 123.3, 119.9, 111.2, 47.2, 20.7; MS (EI): 333 (M^+).

***N*-(4-ethoxycarbonylphenyl)pyrroloanthracene (3c).** Obtained as an amorphous solid after column chromatography (SiO_2, CH_2Cl_2) (86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 2H), 7.30-7.38 (m, 4H), 7.22 (d, 2H), 6.96-7.02 (m, 4H), 6.92 (s, 2H), 5.32 (s, 2H), 4.33 (q, 2H), 1.35 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 146.1, 144.0, 133.8, 131.1, 126.1, 125.2, 123.4, 118.4, 110.7, 60.8, 47.0, 14.3; MS (EI): 391 (M^+).

***N*-(4-nitrophenyl)pyrroloanthracene (3d).** Obtained as a yellow amorphous solid (85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, 2H), 7.32-7.40 (m, 4H), 7.27 (d, 2H), 6.99-7.17 (m, 4H), 6.97 (s, 2H), 5.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 145.7, 143.8, 134.8, 125.5, 125.4, 123.5, 118.3, 110.7, 46.9; MS (EI): 364 (M^+).

***N*-(3-nitrophenyl)pyrroloanthracene (3e).** Obtained as a yellow amorphous solid (76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, J_m = 2.5 Hz, 1H), 7.93 (dt, J_o = 10.5 Hz, J_m = 2.5 Hz, 1H), 7.52 (dt, J_o = 10.5 Hz, J_m = 2.5 Hz, 1H), 7.46 (t, J_o 10.5 Hz, 1H), 7.34-7.39 (m, 4H), 6.98-7.05 (m, 4H), 6.94 (s, 2H), 5.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 146.0, 141.9, 134.3, 130.3, 125.3, 124.7, 123.5, 118.9, 114.0, 110.8, 46.9; MS (EI): 364 (M^+).

***N*-(2-nitrophenyl)pyrroloanthracene (3f).** Obtained as a yellow amorphous solid (65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J_o = 10.5 Hz, J_m = 2.5 Hz, 1H), 7.52 (td, J_o = 10.5 Hz, J_m = 2.5 Hz, 1H), 7.28-7.37 (m, 6H), 6.96-7.05 (m, 4H), 6.57 (s, 2H), 5.29 s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 144.6, 134.3, 133.6, 132.9, 127.3, 126.2, 125.1, 124.8, 123.5, 112.8, 47.0; MS (EI): 364 (M^+).

***N*-(4-bromophenyl)pyrroloanthracene (3g).** Obtained as a white amorphous solid (46%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 2H), 7.03 (d, 2H), 6.94-7.00 (m, 4H), 6.79 (s, 2H), 5.30 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.1, 133.3, 125.1, 123.4, 121.2 (2C), 117.4, 110.9, 47.1; MS (EI): 399-397 (M^+).

***N*-(4-sulfamidophenyl)pyrroloanthracene (3h).** Obtained as a white amorphous solid (62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 2H), 7.62 (d, 2H), 7.35-7.42 (m, 4H), 7.31 (s, 2H), 7.29 (s, 2H, NH_2), 6.94-7.03 (m, 4H), 5.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 142.7, 139.3, 133.3, 127.3, 124.9, 123.4, 118.3, 110.9, 45.8; MS (EI): 398 (M^+).

G0-OH 3i. Ethyl ester **3c** (4.7 g; 12 mmol) was dissolved in dry THF (50 ml). This solution was added in a dropwise manner to a suspension of $LiAlH_4$ (0.5 g; 14 mmol) in dry THF (10 ml) in an ice bath. After complete addition the solution was refluxed for 1 h. After cooling to room temperature, an aqueous solution of NaOH (1M) was added dropwise (approx. 20 ml). The precipitate was filtered and washed with THF. The solution was washed with $MgSO_4$ and evaporated. After column chromatography SiO_2 3:1 CH_2Cl_2-Et_2O), the alcohol **3i** was obtained as a foam (3.6 g; 86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.38 (m, 4H), 7.26 (d, 2H), 7.17 (d, 2H), 6.95-7.02 (m, 4H), 6.86 (s, 2H), 5.32 (s, 2H), 4.56 (s, 2H), 1.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 140.5, 137.0,132.8, 128.1, 125.1, 123.3, 119.8, 111.0, 64.7, 47.1; MS (EI): 349 (M^+).

Chloroacetate 3j. The alcohol **3i** (1.2 g; 3.5 mmol) and Et_3N (0.70 g; 6.9 mmol) were dissolved in CH_2Cl_2 (20 ml) and the solution was cooled to -10°C. Chloroacetyl chloride (0.78 g; 6.9 mmol) was added and the mixture was stirred for 30 min at room temperature. The reaction mixture was quenched with water and the organic layer was separated, dried over $MgSO_4$ and evaporated. Chloroacetate **3j** was obtained after column chromatography (SiO_2, CH_2Cl_2) as a colorless oil (1.2 g; 81%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.36-7.34 (m, 4H), 7.31 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.01-6.95 (m, 4H), 6.88 (s, 2H), 5.33 (s, 2H), 5.13 (s, 2H), 4.07 (s, 2H); MS (EI) 425 (M^+).

G0-dendrimer 7. Chloroacetate **3j** (0.52 g; 1.2 mmol), 1,3,5-tris(4-hydroxyphenyl)benzene (0.11 g; 0.31 mmol) and K_2CO_3 (17 mg; 1.2 mmol) were suspended in acetone and the suspension was refluxed during 48 hours under argon atmosphere. After evaporation of the reaction mixture and column chromatography (SiO_2, CH_2Cl_2) G0-dendrimer **7** was obtained as glassy solid (0.32 g; 68%: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.63 (s, 3H), 7.58 (d, J = 8.2 Hz, 6H), 7.35-7.30 (m,12 H), 7.28 (d, J = 8.2 Hz, 6H), 7.16 (d, J = 8.2 Hz, 6H), 7.01-6.93 (m, 18H), 6.83 (s, 6H), 5.31 (s, 6H), 5.19 (s, 6H), 4.69 (s, 6H) MS (ES) m/z: 1523 (MH^+).

G0-dendrimer 8. DPP **6** (0.17 g; 0.59 mmol), chloroacetate **3j** (0.75 g, 1.8 mmol) and K_2CO_3 (0.25 g; 1.8 mmol) were suspended in DMF (20 ml) and the mixture was heated at 80°C during 48 hours. After cooling to room temperature, evaporation of the solvent and column chromatography (SiO_2, CH_2Cl_2) G0-dendrimer **8** was obtained as a yellow fluorescing oil (0.47 g; 73%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.68-7.63 (m, 4H), 7.43-7.32 (m, 10H), 7.23-7.18 (m, 8H), 7.01-6.97 (m, 8H), 6.87 (s, 4H), 5.33 (s, 4H), 5.11 (s, 2H), 4.51 (s, 4H); MS (ES) m/z: 1067 (MH^+).

General procedure for the preparation of triphenylpyrroloanthracenes 10a,c-e. Diels-Alder adduct **9a** (1.0 g; 2.4 mmol), the appropriate amine (0.44 g; 2.7 mmol) and p-TsOH (15 mg) were dissolved in m-xylene (40 ml) and refluxed under argon atmosphere during 48 h under azeotropic removal of water. After cooling to room temperature the residue was crystallized from methanol (20 ml).

***N*-(4-ethoxycarbonylphenyl)diphenylpyrroloanthracene (10a)** was obtained as a white solid (1.1 g; 83%): Mp > 300°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.38-7.32 (m, 4H), 7.25-7.20 (m, 6H), 7.06-6.95 (m, 6H), 6.79 (d, J = 8.0 Hz, 2H), 5.39 (s, 2H), 4.28 (q, J = 6.7 Hz, 2H), 1.33 (t, J = 6.7 Hz, 3H); MS (EI) 543 (M^+).

***N*-(4-nitrophenyl)diphenylpyrroloanthracene (10c)** was obtained as a yellow solid (78%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.41-7.36 (m, 4H), 7.29-7.24 (m, 6H), 7.05-6.99 (m, 6H), 6.84 (d, J = 8.8 Hz, 2H), 5.39 (s, 2H); MS (EI) 516 (M^+).

***N*-(4-methoxyphenyl)diphenylpyrroloanthracene (10d)** was obtained as a white solid (73%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.41-7.36 (m, 4H), 7.29-7.24 (m, 6H), 7.05-6.99 (m, 6H), 6.71 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 5.39 (s, 2H), 3.67 (s, 3H); MS (EI) 501 (M^+).

***N*-(4-sulfanylphenyl)diphenylpyrroloanthracene (10e)** was obtained as a white solid (78%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.41-7.36 (m, 4H), 7.29-7.24 (m, 6H), 7.04-6.97 (m, 10H), 6.62 (d, J = 8.4 Hz, 2H), 5.39 (s, 2H), 3.37 (s, 1H); MS (EI) 503 (M^+).

Benzyl alcohol 10b. The ester **10a** (1.0 g; 1.7 mmol) was dissolved in dry THF (5 ml) and was added in a dropwise manner to a suspension of $LiAlH_4$ (0.13 g; 3.3 mmol) in THF (5 ml). After complete addition, the solution was refluxed for 30 min. After cooling down to room temperature, a solution of NaOH (1M) was added (approx. 3ml) and the suspension was filtered and the precipitate washed with THF. The organic layer was dried over $MgSO_4$ and evaporated. The alcohol **10b** was obtained after column chromatography (SiO_2, CH_2Cl_2) as a foam (0.85 g; 89%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39-7.33 (m, 4H), 7.24-7.18 (m, 6H), 7.06-6.98 (m, 8H), 6.78 (d, J = 8.5 Hz, 2H, 5.39 (s, 2H), 4.57 (d, br, 2H); MS (EI) 501 (M^+).

11,12-Bis(4-methoxyphenylcarbonyl)-9,10-ethanoanthracene (9b). Bis-1,2-(4-methoxybenzoyl)ethylene (10 g; 34 mmol) and anthracene (6.0 g; 34 mmol) were heated together at 80°C during 1 h. The reaction mixture was cooled down to 50°C and ethanol (120 ml) was added. After vigorous stirring, the precipitate was filtered off, washed with methanol (3 x 20 ml) and dried in vacuum which yielded **9b** as a white solid (14 g; 87%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 4H), 7.38 (d, J = 7 Hz, 2H), 7.17 (td, J = 7 Hz, J = 2 Hz, 2H), 7.08 (td, J = 7 Hz, J = 2 Hz, 2H), 7.01 (d, J = 7 Hz, 2H), 6.92 (d, J = 8.5 Hz, 4H), 4.60 (s, 2H), 4.49 (s, 2H), 3.88 (s, 6H); MS (EI) m/z: 474 (M^+).

Ethyl ester 10f. Diels-Alder adduct **9b** (0.50; 1.1 mmol), ethyl 4-aminobenzoate (0.26 g; 1.6 mmol) and p-TsOH (0.1 g) were dissolved in m-xylene (40 ml) and the mixture was heated at reflux temperature in a Dean-Stark tube during 24 h. After cooling to room temperature and evaporation of the solvent, methanol (20 ml) was added. After filtration and washing with methanol (3 x 5 ml), pyrroloanthracene **10f** was obtained as a white solid (0.57 g; 84%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.76 (d, J = 8.5 Hz, 2H), 7.39-7.33 (m, 4H), 7.03-6.98 (m, 4H), 6.92 (d, J = 8 Hz, 4H), 6.79-6.73 (2 x d, 6H), 5.37 (s, 2H), 4.29 (q, J = 7 Hz, 2H), 3.81 (s, 6H), 1.33 (t, J = 7 Hz, 3H); MS (EI) m/z: 603 (M^+).

Diphenol 10i. Dimethoxy derivative **10f** (0.20; 0.33 mmol) was dissolved in dichloromethane (20 ml) and the solution was placed under argon and cooled to -78°C. Via a septum, BBr_3 (0.33 g; 1.3 mmol) was added and the mixture was kept at -18°C during 15 h. Water (5 ml) and ethyl acetate (20 ml) were added and the water layer was extracted once more with ethyl acetate (20 ml). The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. Diphenol **10i** was obtained as a light brown powder (0.14 g; 75 %) after column chromatography (SiO_2, 9:1 CH_2Cl_2-ethyl acetate): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 7.35-7.32 (m, 4H), 7.01-6.99 (m, 4H), 6.87 (d, J = 8.6 Hz, 4H), 6.78 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 5.31 (s, 2H), 4.55 (s, br, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.22, 154.44, 146.86, 143.23, 131.19, 130.29, 129.94, 129.66, 128.90, 128.06, 125.88, 125.09, 124.87, 123.47, 115.23, 61.05, 47.18, 14.24; MS (EI) m/z: 575 (M^+).

G1-ester 11. Diphenol **10i** (0.56 g; 0.97 mmol), alcohol **3i** (0.75 g; 2.1 mmol) and PPh_3 (0.77 g; 2.9 mmol) were dissolved in dry THF (10 ml). DEAD (0.51 g; 2.9 mmol) was added and the mixture was stirred at room temperature during 5 h under argon atmosphere. The solvent was

evaporated and G1-ester **11** was obtained after column chromatography (SiO_2, 2:1 CH_2Cl_2-petroleumether) as an amorphous solid (0.56 g; 47%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.5 Hz, 4H), 7.35-7.33 (m, 12H), 7.25-7.23 (d, J = 8.5 Hz, 4H), 7.00-6.98 (m, 12H), 6.90(d, J = 8.5 Hz, 4H), 6.90 (s, 4H), 6.84 (d, J = 8.5 Hz, 4H), 6.77 (d, J = 8.5 Hz, 2H), 5.33 (s, 6H), 4.97 (s, 4H), 4.27 (q, J = 7 Hz, 2H), 1.29 (t, J = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.49, 146.74, 146.59, 133.07, 133.03, 130.92, 129.65, 128.87, 128.83, 125.10, 125.05, 124.86, 123.47, 123.39, 119.96, 114.48, 111.08, 69.57, 47.21, 47.02, 14.23; MS (ES) m/z: 1255.6 (MNH_4^+), 1238.6 (MH^+).

G1-alcohol 12. G1-ester **11** (0.50 g; 0.40 mmol) was dissolved in dry THF (5 ml) and added dropwise to a suspension of $LiAlH_4$ (32 mg; 84 mmol) in dry THF (5 ml). After complete addition the suspension was refluxed for 10 min. After cooling to room temperature a solution of NaOH (1M; app. 5 ml) was added dropwise and the solution was filtered and the precipitate washed with THF (2 x 5 ml). After column chromatography (SiO_2, CH_2Cl_2) the alcohol **12** was obtained as an amorphous solid (0.44 g; 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.5 Hz, 4H), 7.35-7.31 (m 12H), 7.22 (d, J = 8.5 Hz, 4H), 7.01 (d, J = 8.5 Hz, 2H), 6.99-6.96 (m, 12H), 6.91 (d, J = 8.5 Hz, 4H), 6.88 (s, 4H), 6.81 (d, J = 8.5 Hz, 4H), 6.72 (d, J = 8.5 Hz, 2H), 5.34 (s, 2H), 5.33 (s, 4H), 4.96 (s, 4H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.23, 146.96, 146.57, 140.89, 138.74, 138.27, 133.12, 133.02, 130.85, 129.58, 129.16, 128.84, 127.40, 126.68, 125.93, 125.28, 125.10, 124.93, 123.38, 119.90, 114.37, 111.05, 69.52, 64.62, 47.19.

G1-bromoacetate 13. G1-alcohol **12** (3.6 g; 3.0 mmol) and Et_3N (0.76 g; 7.5 mmol) were dissolved in CH_2Cl_2 (10 ml) and the solution was placed under argon and cooled to 0°C. Via a septum, bromoacetyl bromide was added (1.4 g; 7.0 mmol) and the mixture was stirred at room temperature during 30 min. The solvent was evaporated and after column chromatography (SiO_2, CH_2Cl_2), the bromide **13** was obtained as an amorphous solid (3.3 g; 83%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.50-7.46 (m, 16H), 7.17 (AA'BB', 8H), 6.99 (d, J = 8.5 Hz, 2H), 6.98-6.95 (m, 12H), 6.92 (d, J = 8.5 Hz, 4H), 6.85 (s, 4H), 6.82 (d, J = 8.5 Hz, 4H), 6.72 (d, J = 8.5 Hz, 2H), 5.36 (s, 2H), 5.31 (s, 4H), 4.99 (s, 2H), 4.89 (s, 4H), 3.67 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 157.27, 146.81, 146.50, 140.79, 139.08, 132.96, 132.88, 130.80, 129.72, 129.21, 128.97, 128.75, 128.16, 127.94, 125.84, 125.04, 124.92, 123.33, 119.80, 114.36, 110.98, 69.42, 67.00, 47.12, 25.55.

G1-dendrimer 14. G1-bromoacetate **13** (0.18 g; 0.14 mmol), DPP **6** (18 mg; 0.064 mmol), K_2CO_3 (36 mg; 0.25 mmol) were suspended in DMF (15 ml) and heated under argon atmosphere during 48 h. The reaction mixture was evaporated and after column chromatography (SiO_2, CH_2Cl_2) G1-dendrimer **14** was obtained a yellow glassy solid (0.13 g; 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.1 Hz, J = 1.2 Hz, 4H), 7.35-7.28 (m, 38H), 7.19 (d, J = 8.5 Hz, 8H), 7.00-6.96 (m, 24H), 6.89 (2 x d, J = 8.6 Hz, 12H), 6.86 (s, 8H), 6.80 (d, J = 8H), 6.69 (d, J = 4H), 5.34 (s, 4H), 5.13 (s, 8H), 4.96 (s, 4H), 4.90 (s, 8H), 4.14 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.18, 162.08, 157.34, 146.91, 146.57, 140.88, 139.03, 133.08, 133.01, 131.55, 130.84, 129.75, 128.90, 128.54, 127.83, 127.31, 125.89, 125.09, 124.98, 123.38, 119.87, 114.38, 111.04, 109.62, 69.49, 47.190, 47.189, 43.48; MS (ES) 2761.9 (MH^+).

G1-dendrimer 15. This dendrimer was obtained analogously to but with use of 1,3,5-tris(4-hydroxyphenyl)benzene in refluxing acetone. This procedure afforded **15** in 65% yield as a white glassy solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.51 (s, 3H), 7.47 (d, J = 8.5 Hz, 6H), 7.34-7.28 (m, 48H), 7.16 (d, J = 8.5 Hz, 12H), 7.04 (d, J = 8.5 Hz, 6H), 7.00-6.93 (m, 54H), 6.91 (d, J = 8.5

Hz, 12H), 6.83 (s, 12H), 6.82 (d, J = 8.5 Hz, 12H), 6.77 (d, J = 8.5 Hz, 6H), 5.34 (s, 6H), 5.29 (s, 12H), 5.11 (s, 6H), 4.89 (s, 12H, 4.56 (s, 6H); MS (ES) m/z 2032 $(MH_2)^{2+}$.

Ethyl ester 10h. Diels-Alder adduct **9b** (5.5 g; 13 mmol) and ethyl 4-aminophenyl acetate (2.84 g; 16 mmol) and p-TsOH (0.5 g) were dissolved in m-xylene (40 ml) and the mixture was heated at reflux temperature in a Dean-Start apparatus during 24 h under argon atmosphere. After cooling to room temperature and evaporation of the solvent, methanol (20 ml) was added. After filtration and washing with methanol (3 x 5 ml), pyrroloanthracene **10h** was obtained as a white solid (4.65 g; 63%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39-7.36 (m, 4H), 7.24-7.20 (m, 6H), 7.03-7.00 (m, 10H), 6.73 (d, J = 8 Hz, 2H), 5.41 (s, 2H), 4.12 (q, J = 7 Hz, 2H), 3.48 (s, 2H), 1.28 (t, J = 7 Hz, 3H); MS (EI) m/z 557 (M^+).

Alcohol 10k. The ester **10h** (4.6 g; 8.3 mmol) was dissolved in dry THF (25 ml) and added in a dropwise manner to a suspension of $LiAlH_4$ (0.61 g; 16 mmol) in dry THF (5 ml). After complete addition, the mixture was refluxed for 1h. After analogous work-up as before and column chromatography (SiO_2, 20:1 CH_2Cl_2-ethyl acetate), alcohol **10k** was obtained as a foaming thick oil (4.0 g; 93 %): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38-7.32 (m, 4H), 7.23-7.19 (m, 6H), 7.02-6.98 (m, 8H), 6.91 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 8.5 Hz, 2H), 5.40 (s, 2H), 3.71 (t, J = 7 Hz, 2H), 2.73 (t, J = 7 Hz, 2H); MS (EI) m/z: 515 (M^+).

Mesylate 10l. The alcohol **10k** (0.50 g; 0.97 mmol), Et_3N (0.60 g; 6.0 mmol) and DMAP (0.050 g) were dissolved in CH_2Cl_2 (20 ml) and the solution was cooled to 0°C under argon atmosphere. Mesyl chloride (0.55g; 4.9 mmol) was added and the mixture was stirred at room temperature during 30 min. After evaporation of the solvent and column chromatography (SiO_2; CH_2Cl_2) the mesylate **10l** was obtained as a yellowish oil (0.53 g; 93%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.38-7.32 (m, 4H), 7.23-7.19 (m, 6H), 7.02-6.98 (m, 8H), 6.91 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 5.41 (s, 2H), 4.27 (t, J = 7 Hz, 2H), 2.87 (t, J = 7 Hz, 2H), 2.63 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 146.76, 137.85, 134.63, 132.15, 130.35, 129.59, 129.35, 128.86, 127.92, 126.68, 126.23, 124,95, 123.42, 69.88, 47.05, 37.08, 34.86; MS (CI) m/z: 594 (MH^+).

G0-dendrimer 17. The mesylate **10l** (0.35 g; 0.69 mmol), 1,3,5-tris(4-hydroxyphenyl)benzene (74 mg; 0.21 mmol), K_2CO_3 (0.14 g; 1.0 mmol) and 18-crown-6 (25 mg) were dissolved in acetone (15 ml) and refluxed under argon atmosphere during 48 h. After evaporation and column chromatography (SiO_2, 2:1 CH_2Cl_2-petroleum ether) dendrimer **17** was obtained as a white solid (0.14 g; 35%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.62 (s, 3H), 7.57 (d, J = 8.5 Hz, 6H), 7.42-7.34 (m, 12H), 7.23-7.17 (m, 18H), 7.06-6.98 (m, 24H), 6.92 (d, J = 8.5 Hz, 6H), 6.73 (d, J = 8.5 Hz, 6H), 5.42 (s, 6H), 4.13 (t, J = 7 Hz, 6H), 3.03 (t, J = 7 Hz, 6H).

Ethyl ester 10g. Diels-Alder adduct **9b** (0.50 g; 1.1 mmol), ethyl 4-aminophenyl acetate (0.25 g; 1.4 mmol) and p-TsOH (50 mg) were dissolved in m-xylene (20 ml) and the solution was refluxed during 48 h under argon atmosphere under azeotropic removal of water in a Dean-Start tube. After cooling down and evaporation, methanol (10 ml) was added. Compound **10g** was obtained after filtration and washing with methanol (2 x 5 ml) (0.58 g; 85%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.37-7.33 (m, 4H), 7.00-6.97 (m, 6H), 6.93 (d, J = 8.5 Hz, 4H), 6.76 (d, J = 8.5 Hz, 4H), 6.73 (d, J = 8.5 Hz, 2H), 5.38 (s, 2H), 4.09 (q, J = 7 Hz, 2H), 3.76 (s, 6H), 3.48 (s, 2H), 1.18 (t, J = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.19, 158.00, 146.98, 137.87, 130.78, 129.40, 129.14, 129.08, 125.90, 124.90, 123.36, 113.40, 60.69, 55.06, 47.13, 40.87, 14.06; MS (EI) m/z: 617 (M^+).

Diphenol 10j. Dimethoxy derivative **10g** (0.36 g; 0.58 mmol) was dissolved in dichloromethane (20 ml) and the solution was cooled to -78°C under argon atmosphere. Via a septum, BBr_3 (1.46 ml (1M); 1.5 mmol) was added and the mixture was stirred at –20°C during 15 h. Water (5 ml) and ethyl acetate (20 ml) were added and the mixture was extracted once more with ethyl acetate (10 ml). The diphenol **10j** was obtained as a light brown powder (0.27 g; 75 %) after column chromatography (SiO_2, 9:1 CH_2Cl_2-ethyl acetate): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.35-7.32 (m, 4H), 6.98-6.92 (m, 6H), 6.86 (d, J = 8.5 Hz, 4H), 6.70-6.65 (m, 6H), 5.91 (s, 2H), 5.34 (s, 2H), 4.12 (q, J = 7 Hz, 2H), 3.48 (s, 2H), 1.26 (t, J = 7 Hz, 3H); MS (ES) m/z 589 (M^+).

G1-ester 19. The alcohol **10k** (1.0 g; 1.9 mmol), AB_2 monomer **10j** (0.52 g; 0.88 mmol) and PPh_3 (0.69 g; 2.6 mmol) were dissolved in dry THF (10 ml). To this solution, DEAD (0.46 g; 2.6 mmol) was added and the mixture was stirred during 3 h under argon atmosphere. After evaporation and column chromatography (SiO_2, 2:1 CH_2Cl_2-petroleum ether), G1-ester **19** was obtained as a white solid (1.0 g; 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 8H), 7.34-7.32 (m, 4H), 7.22-7.18 (m, 8H), 7.03-6.99 (m, 20H), 6.89 (d, J = 8.5 Hz, 4H), 6.74-6.70 (m, 10H), 5.41 (s, 4H), 5.32 (s, 2H), 4.08-4.03 (m, 6H), 3.44 (s, 2H), 2.97 (t, J = 7 Hz, 4H), 1.13 (t, J = 7 Hz, 3H); ^{13}H NMR (100 MHz, $CDCl_3$) δ 171.19, 157.24, 147.01, 146.95, 137.90, 137.32, 136.57, 132.35, 132.23, 130.79, 130.29, 129.68, 129.48, 129.11, 128.87, 127.92, 126.66, 126.16, 125.93, 124.99, 124.93, 123.48, 123.40, 114.13, 68.35, 60.71, 47.22, 40.86, 35.26, 14.08; MS (ES) m/z: 1586 (MH^+).

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