Supramolecular Dendritic π-Conjugated Systems: Synthesis of Glycinylurea Functionalized π-Conjugated Diphenylanthracene Guests and their Complexation with Dendritic Hosts. Part I

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Glycinylurea functionalized π-conjugated diphenylanthracene guests (DPA guests) that bind to adamantyl urea modified dendritic hosts were synthesized and fully characterized by NMR spectroscopy (^{1}H-NMR, ^{13}C-NMR) and MALDI-TOF-MS. The resulting supramolecular assemblies have been investigated with respect to their binding properties. DPA guests molecules were able to click into urea functionalized N,N-bis[(3-adamantyl ureido) propyl] methyl amine host as a result of acid-base (between COOH of the guest and amines of the host) and hydrogen bonding interactions (between the urea linkages of dendrimer and the guest). The guest molecules were bound as 1:1 inclusion complexes and the association constants for both guests have been calculated. Subsequently, an adamantyl urea modified fifth generation poly(propylene imine) dendrimer was synthesized as a multivalent host which contains 32 N,Nbis[(3-adamantyl ureido) propyl] amine binding sites. Size exclusion chromatography showed that 32 of the DPA guests strongly bind to the fifth generation adamantyl functionalized dendritic host.

Keywords: dendrimers, supramolecular assemblies, host, guest, binding properties, "click-in" concept

Dendrimers are large and complex macromolecules, which are characterized by a combination of a high number of functional groups and a compact molecular structure [1]. From a polymer chemistry point of view, dendrimers are nearly perfect monodisperse macromolecules (unlike linear polymers) with a regular and highly branched three-dimensional architecture. They consist of three major architectural components, namely core, branches and end groups. There are now more than fifty families of dendrimers, each of them with unique properties, since the surface, interior and core can be tailored to different sorts of applications. Chiral dendrimers [2], liquid-crystalline structures [3], dendrimers with catalytic sites [4], dendritic box [5], unimolecular micelles [6], host-guest chemistry [7], light-harvesting antennae for photoinduced energy [8] and molecular electronics [9] are just a few examples of the broad development that has taken place in the dendrimer field.

A characteristic of dendritic macromolecules is the presence of a high density of peripheral chain ends. The existence of a high number of functional moieties at the periphery of the dendrimer can easily modulate the properties of these macromolecules [10]. Physical properties of dendrimers are dependent on the nature of the endgroups, e.g. Tg, solubility, fluorescence. In most cases, the end group modifications are based on covalent bonding. Only few examples are known in which non-covalent interactions are used to modify the dendritic periphery [11,12]. Baars et al. [12] published results on a new strategy for modifying the periphery of the poly(propyleneimine) dendrimer using a supramolecular aproach. The covalently attached adamantyl-urea end groups of the dendrimer were used as a scaffold to reversibly bind glycine-urea building blocks in organic media using multiple interactions: hydrogen bonding and acid-base interactions. They also disclosed evidence for an increase of the rigidity of the dendrimer shell upon clicking.

Another example of non-covalent interactions used to modify the dendritic periphery has been published in Journal of American Society [13]. A detailed study of binding and optical properties of π-conjugated guests to N, N-*bis*[(3-adamantyl ureido) propyl] methylamine, and to a adamantyl urea modified fifth generation poly(propylene imine) dendritic hosts that contain 32 of these binding sites is described. Guests consisting of urea glycine moiety are bound most strongly at the periphery of dendritic hosts. Moreover, the conjugated guests show improved emission upon binding. In the solid state this enhancement is 10 times higher than the guest itself. The remarkable difference in spectroscopic properties between the free guest and the bound guest can be understood in terms of changes in the flexibility of the systems. The non-covalent interactions are highly specific and strong and an increase in the rigidity of the host/guest systems is proposed based on these results.

There has been an impressive progress in understanding that the conformational behavior of the dendrimers can be strongly influenced by the medium around the dendrimer and also by the secondary interactions. A complete control over the arrangement of the individual molecules in the bulk is required for using dendrimers in the area of organic light emitting diodes (LED's). Only few studies of electroactive dendrimers have been reported [14] so far. Dendrimers with π-conjugated oligomers at the periphery have also been synthesized [15]. It was proved [16] that the conjugated dendrimers can improve the device efficiency and lifetime and control the color of material. The durability of LED's devices can be enhanced by prevention of crystallization [17] of the active component as a result of three-dimensional architecture leading to highly amorphous films. This seems to be very important because crystal formation destroys the device [18].

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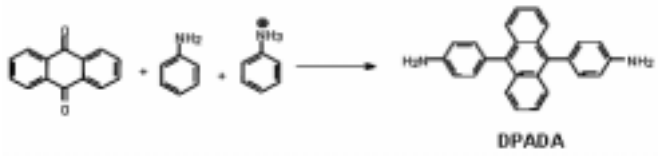
One tool to overcome this problem is branching of π-conjugated systems. It can prevent formation H-aggregates while π - π stacking, important for high mobility, can still be present. A strategy is the use of molecules containing a tetrahedral framework. This framework orients the chromophore (oligoPPVs) so that the possibility of intramolecular stacking is minimized [19]. These tetrahedral arrays do not crystallize and forms a stable amorphous phase. The approach makes use of the advantages of small molecules (well defined) with those of polymers (amorphous morphology). Another route to obtain branched systems is the use of dendritic materials. These materials possess ordered, covalent three-dimensional structures, which permit spatial control of the active components and, thus, the electroluminescent properties of materials.

Here, the design and synthesis of glycinylurea functionalized π-conjugated diphenylanthracene guests that bind to adamantyl urea modified dendritic hosts is reported. Adamantyl dendrimers are known to adopt a persistent globular conformation, similar to the dendritic box, due to the three-dimensional dendritic scaffold, resulting in the formation of the amorphous films.

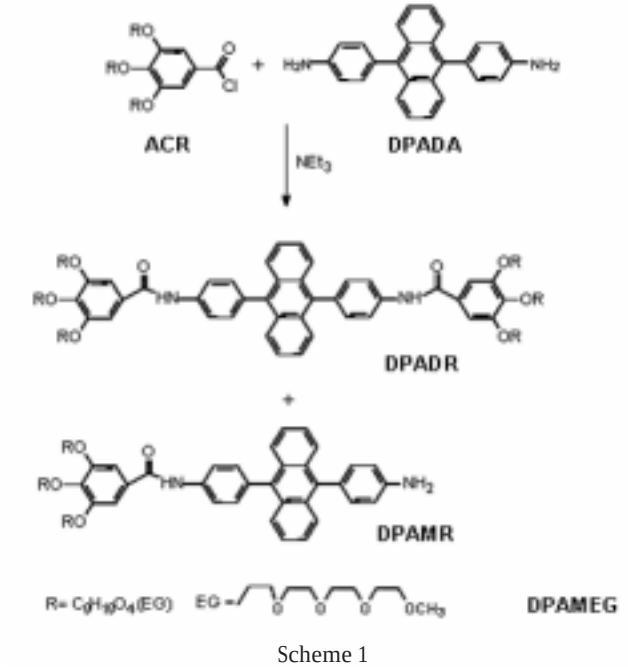
Experimental Part

The diaminated precursor 9,10-*bis*-(4-aminophenyl)-anthracene (DPADA) has already been described in literature, in accordance with the reaction:[20]



Further, by condensing 1 equivalent pure amine **DPADA** with 2 equivalents of acid chloride (**ACR**) using triethylamine as acid acceptor and dry CH_2Cl_2 as solvent, a reaction product that contain unreacted amine, monosubstituted and disubstituted product is obtained. The reactions are presented in scheme 1.

After workup, the reaction product was purified by column chromatography. The three spots that eluted in CH_2Cl_2/MeOH= 9/1 were found to contain the product, as suggested by proton NMR. First fraction was unreacted amine **DPADA**, as revealed from ^{1}H-NMR, MALDI-TOF and GPC. The other two fractions were further separated using bioeads SX1 column in CH_2Cl_2. The two fractions collected



Scheme 1
The reactions that have taken place by condensing of acid chloride (**ACR**) with **DPADA**

from Biobeads were subjected to MALDI-TOF analysis. It showed that one of the fractions is the monocoupled product DPAMEG [9-(4-aminophenyl)-10-{4-[(tris 3,4,5-tri (tetraethylen-oxy) benzamide] phenyl}-anthracene] (m/z = 1083). The other fraction showed the dimer DPADEG [9,10 –di-{4-[(tris 3,4,5-tri (tetraethylen -oxy- benzamide] phenyl} anthracene] (m/z = 1806). The MALDI-TOF of compound **DPAMEG** and **DPADEG** are showed in figures 1 and 2.

All three compounds **DPADA**, **DPAMEG** and **DPADEG** were readily detected by UV-Vis spectroscopy in solution in the spectral range 350-410 nm by three bands characterisic of anthracenic core at 360, 378 and 397 nm (ε_{378} nm **DPADA**=10 340 $M^{-1}cm^{-1}$, ε_{378} nm **DPAMEG**=11 737 $M^{-1}cm^{-1}$, ε_{378} nm **DPADEG**=24 443 $M^{-1}cm^{-1}$). Unfortunately transformation of the monocoupled product (30% yield) in the isocyanate with di-tertbuthyltricarbonate didn't work as it was expected. Compound **DPADDR (dimer of DPAMR)** was formed as well, while surprisingly a lot of **DPAMR (9-(4-aminophenyl)-10-{4-[(tris 3,4,5-tri (R-oxy) benzamide] phenyl}-anthracene**) (R=EG=**tetra-ethylene**) was still unreacted (scheme 2). This method

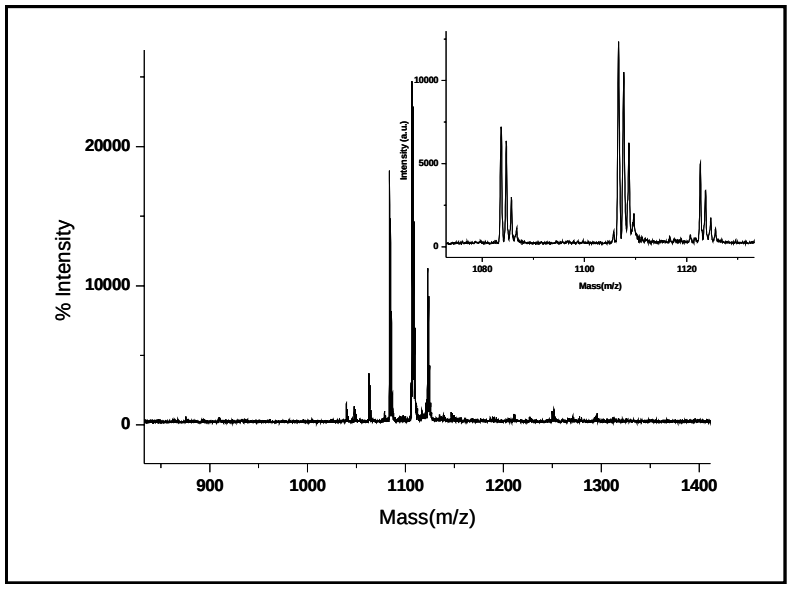


Fig. 1. MALDI-TOF analysis of DPAMEG

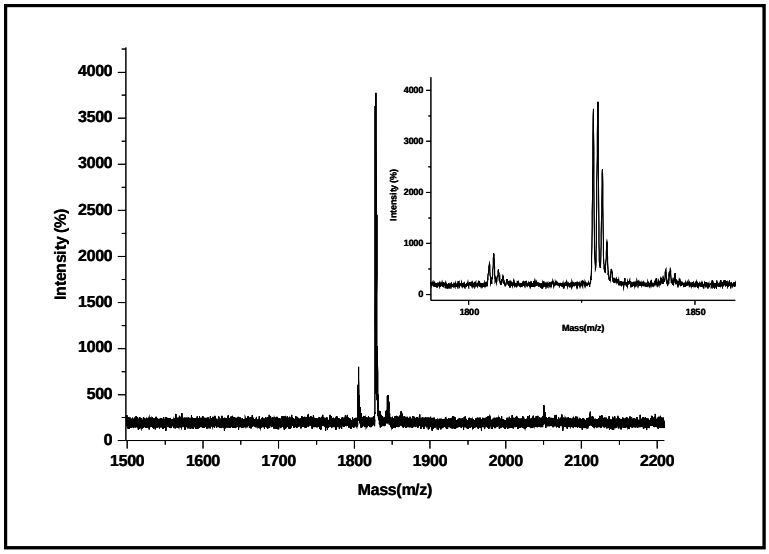
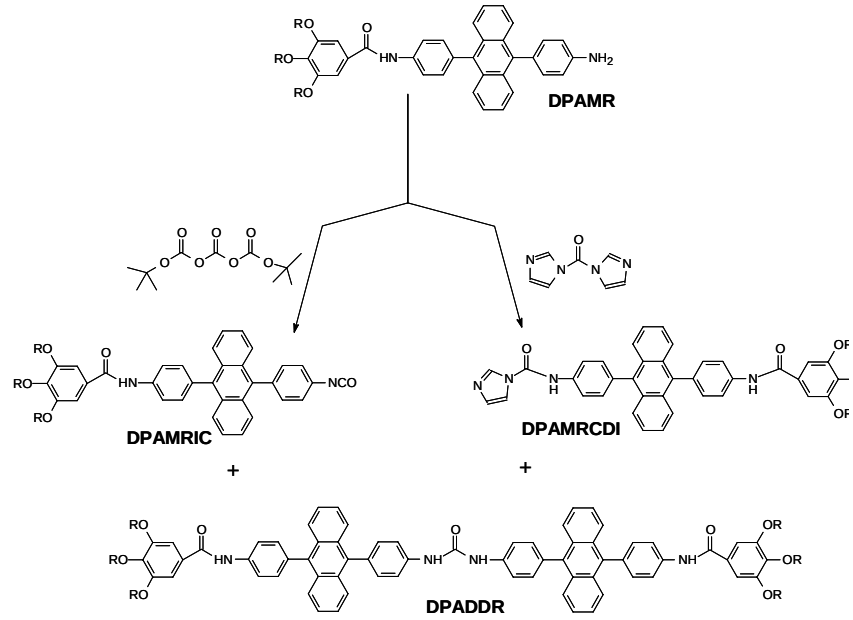


Fig. 2. MALDI-TOF analysis of DPADEG



Scheme 2. Synthetic route for obtaining the isocyanate {DPAMRIC = 9-(4-phenylizocyanate)-10-{4-[(tris 3,4,5-tri(R-oxy) benzamide] phenyl} –anthracene} and activated ester (DPAMRCDI)

where R is described in Scheme 1.

wasabandoned since the desired compounds were obtained in very low yield.

The use of carbodiimidazole to obtain the activated amine was tried as well, but unfortunately, this reaction didn't work as it was expected. Compound **DPAMRCDI (9-(4-phenyl carboimidazole)-10-{4-[(tris 3, 4, 5-tri (R-oxy) benzamide] phenyl}-anthracene)** was formed in only 40%, while surprisingly, a lot of **DPADDR** were observed as revealed from ^{1}H-NMR, ^{13}C-NMR and MALDI-TOF (scheme 2, fig. 3 and 4).

The route that usually works the best was the one in which the phosgene in toluene was used. The reactions for synthesis of functionalised diphenylanthracene-R guests are presented in scheme 3.

Purification of compound **DPAMMR** proceeds with difficulty, probably due to the similar properties of the starting material **DPAMR**, the product **DPAMMR** and the intermediate **DPAMRIC-1.** Unfortunately, due to the existence of the amide linkage we have observed with GPC and MALDI-TOF the presence of another peak very close to the one of the desired compound (**DPAMMR**) (fig. 5), which was attributed to the amidine formation.

It is clear that modification of this amine gives rise to side-products. To avoid this, the use of another component was tried: instead of glycine methylester hydrochloride, the commercially available ethyl isocyanato-acetate was used, which was coupled directly with the amine. The reaction was performed in pyridine and, in this case, no side-products were observed. Hydrolysis was done further with LiOH in THF and the acid functionality was obtained in good yield (90%).

The methods used for characterization of intermediaries and final products

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 300 or 400 MHz spectrometer in deuterated chloroform (or deuterated DMSO at 80°C as in the case of guest molecules) and tetramethylsilane (TMS) was used as internal reference. Abbreviations used are s =singlet, d = doublet, t = triplet, m = multiplet, and b = broad. Preparative size exclusion chromatography was carried out with Biobeads S-X1 Beads (200-400 mesh) with a cutoff of 14 kD, and were obtained from Bio-Rad Laboratories; dichloromethane was used as eluent. Elemental analyses were performed on a Perkin-Elmer, Series II, 2400. Determination of the association constants (*K*a) was carried out under Benesi-Hildebrand conditions at 25°C in $CDCl_3$ [1]. The concentration of the host was kept constant (1 mM), whereas the guests' concentrations were varying in the range 0.1-2 mM. UV-vis spectra and fluorescence spectra were recorded on a Perkin- Elmer Lambda 40 Spectrometer and a Perkin-Elmer luminescence spectrometer LS 50 B instrument. Infrared spectra were recorded on a Perkin-Elmer Spectrum one

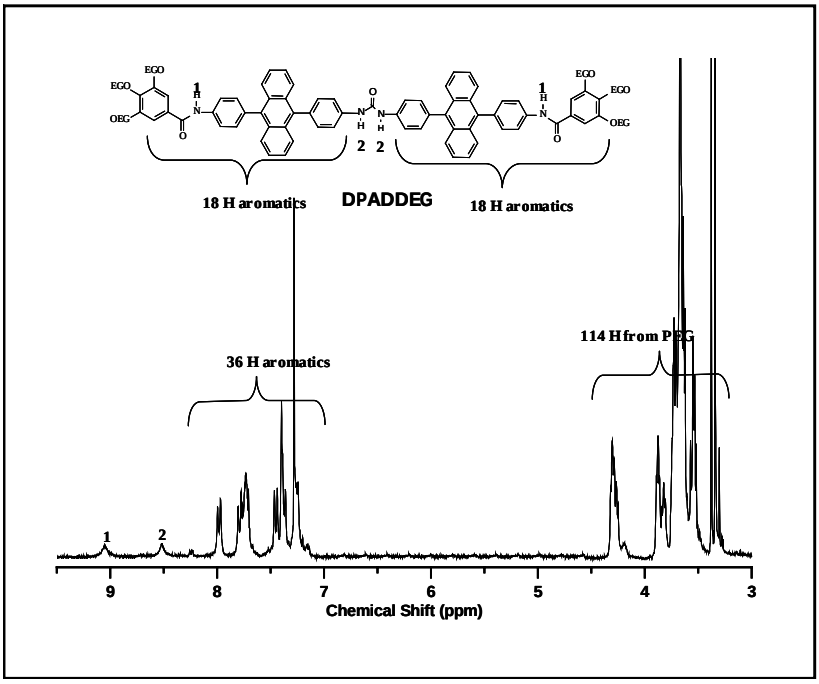


Fig. 3. ^{1}H-NMR spectra of DPADDEG

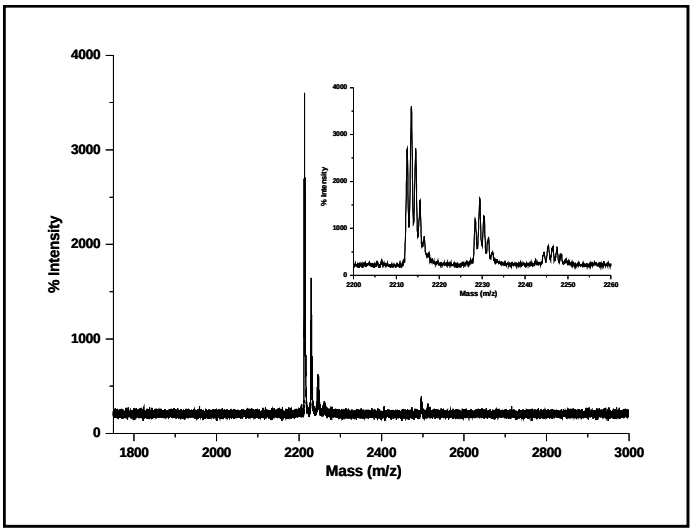


Fig. 4. MALDI-TOF analysis of DPADDEG

with an ATR sampling accessory. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry were measured on a Perspective Biosystems Voyager- DE PRO instrument in reflector mode, using R-cyano-4- hydroxy-cinnamic acid as the matrix. Spin-coated thin films were prepared by spin-coating from THF solutions using a Headway Research Spin-coat apparatus.

General procedures for synthesis and characterization of intermediaries and final products

1. Synthesis and characterization of 9,10-*bis*(4-amino-phenyl)-anthracene (DPADA)

Under an inert atmosphere of argon anthraquinone (5 g, 0.024 mol, 1Eq.), aniline (11.18 g, 0.12 mol, 5 Eq.) and aniline chlorhydrate (7.77 g, 0.06 mol, 2.5 Eq.) were heated together at 200 °C. After 4 h stirring at this temperature, the mixture was cool down to room temperature. 175 mL EtOH was added and then let stir for another 30 min. The formed solid is filtered off and 80 mL of demi-water was added over it. The mixture is refluxed for one hour and let cool down for another 1 hour. Check the *p*H (should be around 2-3). The powder is filtered out of the solution and then washed with demi-water till neutral *p*H. The solid is dried under vacuum at 30°C and was purified by sublimation under vacuum at 250°C, to give a yellow substance. The yield of the reaction was 45 %.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83 (m, 4H, H1 anth), 7.30 (m+d, 8H, H3 ph + H2 anth), 6.95 (d, 4H, H2 ph), 3.70 (s, 4H, NH_2).

^{13}C-NMR (300 MHz, $CDCl_3$): δ 146 (C1 ph), 137 (C9+C10 anth), 132 (C4 ph), 130 (C3 ph), 129 (C1+C4+C5+C8 anth), 127 (C2+C3+C6+C7 anth), 125 (C11+C12+C13+C14 anth), 115 (C2 ph).

IR (ATR) ν 3435, 3357 cm^{-1}.

MALDI-TOF (MW= 360.451) m/z = 360.81

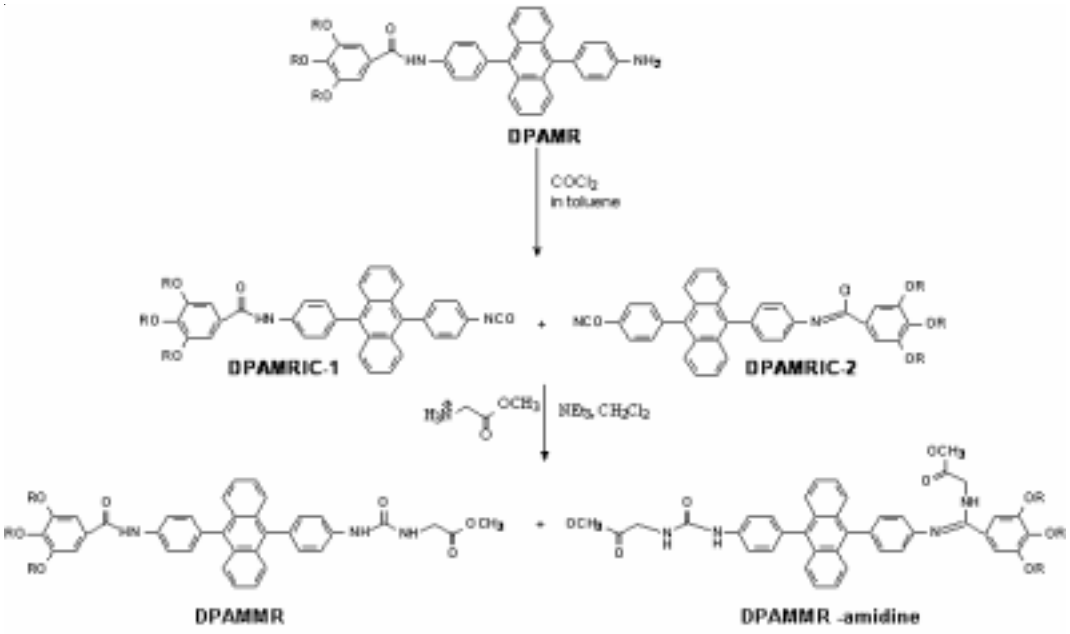
UV-Vis ($CHCl_3$): λ_{max}= 360, 378, 397 nm, $\varepsilon_{378\ nm\ \mathbf{DPADA}}$=10 340 $M^{-1}cm^{-1}$

Anal. Calc. For $C_{26}H_{20}N_2$ (360.451) C, 86.66 %; H, 5.55 %; N, 7.79 %. Found: C, 86.51 %; H, 5.58 %; N, 7.91 %.

2. Synthesis and characterization of 9-(4-aminophenyl)-10-{4-[(tris 3,4,5-tri (R-oxy) benzamide] phenyl} –anthracene, DPAMR [R= EG (tetraethylene)]

DPAMR (R= EG, ALK)

1 Eq of acid chloride **ACR** and triethylamine (NEt_3) were stirred together in dry CH_2Cl_2. 1 Eq. of **DPADA** dissolved in dry CH_2Cl_2 was added to the solution of acid chloride. The mixture was stirred over night at room temperature under argon atmosphere. The monosubstituted **DPAMR**, disubstituted **DPADR** and unreacted **DPADA** were separated with SX1-size exclusion column chromatography



Scheme 3. The reactions for synthesis of diphenylanthracene-R guests
DPAMRIC-1 = 9-(4-phenylizocyanate)-10-{4-[(tris 3,4,5-tri(R-oxy) benzamide] phenyl} –anthracene (izocyanate 1)
DPAMMR = 10-{4-[(tris 3,4,5-tri(R-oxy) benzamide] phenyl}–9-(4-ureido acetic acid methyl ester phenyl)-anthracene , R=EG= tetraethylene
DPAMMR–amidine = 10-{4-[(tris 3,4,5-tri(R-oxy) benzamide] phenyl}–9-(4-ureido acetic acid methyl ester phenyl)-anthracene –amidine
DPAMRIC-2 =9-(4-phenylizocyanate)-10-{4-[(tris 3,4,5-tri(R-oxy)-chlorine-benzimine] phenyl} –anthracene (izocyanate 2)

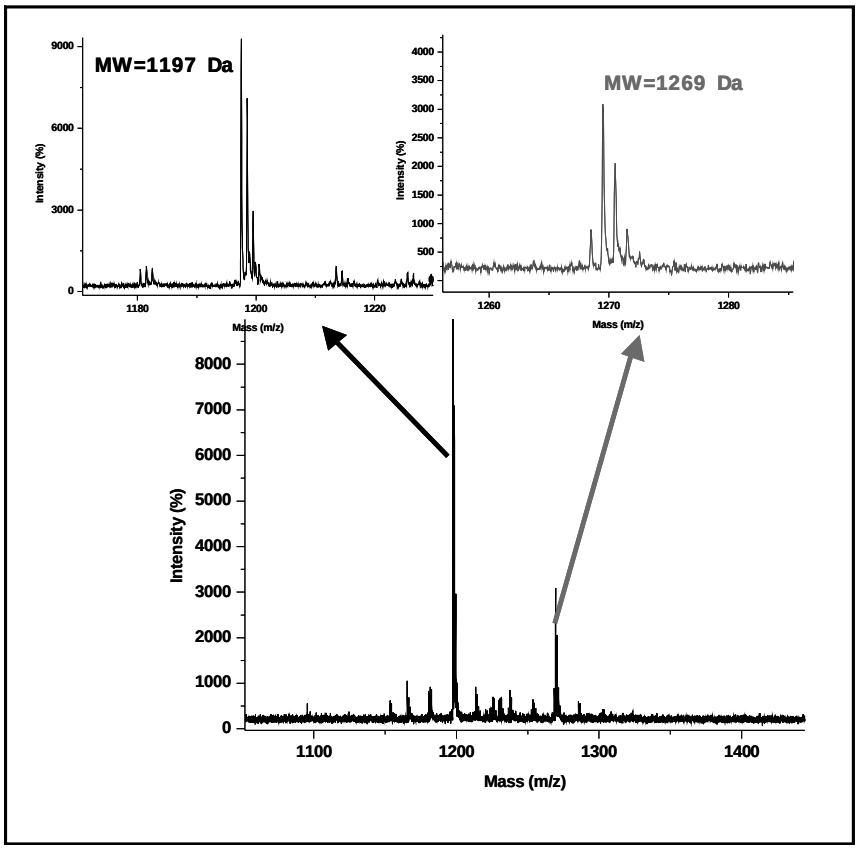


Fig. 5. MALDI-TOF analysis of DPAMMEG (m/z = 1197) and of DPAMMEG-amidine (m/z = 1269)

(CH_2Cl_2), to give 30-40% **DPAMR** (yellowish oily when **R= EG).**

DPAMEG: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H, NH), 7.95 (d, 2H, H2 ph), 7.80 (m, 4H, H1 anth), 7.46 (s, 2H, Ar-*H*), 7.30 (m+d, 8H, H3 ph + H2 anth), 6.95 (d, 2H, H2 ph), 4.30 (t, 2H, OCH_2CH_2O), 4.25 (m, 6H, Ar-$(OCH_2CH_2O)_2$), 3.56-3.90 (m, 21H, OCH_2), 3.42 (s, 6H, $(OCH_3)_2$), 3.39 (s, 3H, (OCH_3)), 2.1 (s, 2H, NH_2).

^{13}C-NMR (300 MHz, $CDCl_3$): δ 60.1 (3C, OCH_3), 69.9/ 70.7/ 71.5-71.9/ 72.9/ 73.5 (24C, OCH_2), 110.4 (2C, Ar-*C*2/*C*4), 115 (2C, *C*2 ph), 120 (4C, *C*11+*C*12+*C*13+*C*14 anth), 125.7 (1C, Ar-*C*1), 127 (4C, *C*2+*C*3+*C*6+*C*7 anth), 129 (4C, *C*1+*C*4+*C*5+*C*8 anth), 130 (2C, *C*3 ph), 132 (2C, *C*4 ph), 134 (2C, *C*3 ph), 137 (2C, *C*9+*C*10 anth),138 (2C, *C*2 ph), 143.7 (1C, Ar-*C*5), 153.2 (2C, Ar-*C*4/*C*6), 150 (1C, *C*1ph), 159 (1C, *C*1 ph), 165 (1C, *C*ONH).

MALDI-TOF (MW= 1083.265) m/z = 1105.46 (M+Na)
UV-Vis ($CHCl_3$): λ_{max} = 359, 377, 397 nm, $\varepsilon_{378\ nm\ \mathbf{DPAMEG}}$ =11 737 $M^{-1}cm^{-1}$

DPADEG: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.1 (s, 2H, NH), 7.95 (d, 4H, H2 ph), 7.70-7.80 (m, 4H, H1 anth), 7.46 (s, 4H, Ar-*H*), 7.30 (m+d, 8H, H3 ph + H2 anth), 4.30 (t, 2H, OCH_2CH_2O), 4.25 (m, 12H, Ar-$(OCH_2CH_2O)_2$), 3.56-3.90 (m, 42H, OCH_2), 3.42 (s, 12H, $(OCH_3)_2$), 3.39 (s, 6H, (OCH_3)).

^{13}C-NMR (300 MHz, $CDCl_3$): δ 165 (2C, *C*ONH), 153.2 (4C, Ar-C4/C6), 146 (2C, C1 ph), 143.7 (2C, Ar-*C*5), 137 (2C, C9+C10 anth), 134 (4C, *C*3 ph), 132 (2C, C4 ph), 130 (4C, C3 ph), 129 (4C, C1+C4+C5+C8 anth), 127 (4C, C2+C3+C6+C7 anth), 125.7 (2C, Ar-*C*1), 121 (4C, C11+C12+C13+C14 anth), 115 (4C, C2 ph), 110.4 (4C, Ar-*C*2), 60.1 (6C, OCH_3), 69.9/ 70.7/ 71.5-71.9/ 72.9/ 73.5 (48C, OCH_2).

MALDI-TOF (MW= 1806.005) m/z = 1828.259 (M+Na)

DPADDEG: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.1 (s, 2H, N*H*COPh), 8.5 (s, 2H, N*H*CON*H*), 7.95 (d, 8H, H2 ph), 7.70-7.80 (m, 8H, H1 anth), 7.46 (s, 4H, Ar-*H*), 7.30 (m+d, 16H, H3 ph + H2 anth), 4.30 (t, 4H, OCH_2CH_2O), 4.25 (m, 8H, Ar-$(OCH_2CH_2O)_2$), 3.56-3.90 (m, 84H, OCH_2), 3.42 (s, 12H, $(OCH_3)_2$), 3.39 (s, 6H, (OCH_3)).

MALDI-TOF (MW= 2192.005) m/z = 2214.15 (M+Na).

3. Synthesis and characterization of 10-{4-[(tris 3,4,5-tri(R-oxy) benzamide] phenyl}–9-(4-ureido acetic acid ethyl ester phenyl)-anthracene, DPAMEEG [R= EG (tetraethylene)]

1Eq. of amine (9-(4-aminophenyl)-10-{4-[(tris 3,4,5-tri (R-oxy) benzamide] phenyl} –anthracene) was dissolved in pyridine. 1 Eq. of ethyl isocyanato-acetate was dissolved in pyridine and injected into the amine under Ar atmosphere. The mixture is refluxed overnight. Then the mixture with pyridine as solvent is co-evaporated several times with toluene. After precipitation in diethylether DPAMEEG was obtained as a very fine precipitate.

DPAMEEG: ^{1}H-NMR (400 MHz, $CDCl_3$): dδ 9.05 (s, 1H, N*H*), 7.80 (m, 4H, H1 anth), 7.46 (s, 2H, Ar-*H*), 7.30 (m+d, 8H, H3 ph + H2 anth), 6.95 (d, 2H, H2 ph), 6.05 (s, 1H, N*H*) 6.7 (t, 1H, N*H*), 4.30 (t, 2H, OCH_2CH_2O), 4.25 (m, 6H, Ar-$(OCH_2CH_2O)_2$), 3.56-3.90 (m, 21H, OCH_2), 3.42 (s, 6H, $(OCH_3)_2$), 3.39 (s, 3H, (OCH_3)), 2.8 (d, 2H, $NHCH_2CO$), 1.3 (t, 3H, $COCH_2CH_3$).

^{13}C-NMR(300MHz,$CDCl_3$):δ 42 (1C, NHCONHC*H*$_2$COOH), 53.9 (1C, OCH_2CH_3), 60.1 (3C, OCH_3), 69.9/ 70.7/ 71.5-71.9/ 72.9/ 73.5 (24C, OCH_2), 110.4 (2C, Ar-*C*2/*C*4), 115 (2C, *C*2 ph), 120 (4C, *C*11+*C*12+*C*13+*C*14 anth), 125.7 (1C, Ar-*C*1), 127 (4C, *C*2+*C*3+*C*6+*C*7 anth), 129 (4C, *C*1+*C*4+*C*5+*C*8 anth), 130 (2C, *C*3 ph), 132 (2C, *C*4 ph), 134 (2C, *C*3 ph), 137 (2C, *C*9+*C*10 anth),138 (2C, *C*2 ph), 143.7 (1C, Ar-*C*5), 153.2 (2C, Ar-*C*4/*C*6), 150 (1C, *C*1ph), 153 (1C, Ar-*C*ONH), 157 (1C, NHCONH), 159 (1C, *C*1 ph), 165 (1C, *C*ONH), 171 (1C, CH_2COOH).

MALDI-TOF (MW= 1211.379) m/z = 1234.35 (M+Na)
UV-Vis ($CHCl_3$): λ_{max} = 359, 377, 397 nm.

4. Synthesis and characterization of obtaining the GUEST: 10-{4-[(tris 3,4,5-tri(R-oxy) benzamide] phenyl}–9-(4-ureido acetic acid phenyl)-anthracene, DPAGEG [R=EG (tetraethylene)]

1 Eq. of ester 10-{4-[(tris 3,4,5-tri(R-oxy) benzamide] phenyl}–9-(4-ureido acetic acid ethyl ester phenyl)-anthracene was dissolved in THF. 1,2-2 Eq. of LiOH x H_2O was dissolved in 1 mL H_2O and then added over the ester. The mixture was stirred about 24 h at room temperature under argon atmosphere. The THF was removed under reduced pressure, after which it was slightly acidified by addition of 1M HCl (approx. 2 mL) (to neutralize the excess of LiOH). At *p*H around 1-2 a precipitate is formed. The precipitate is filtered, is washed with water till neutrality and is dried in vacuo. ^{1}H-NMR is recorded at 80°C, by dissolving the sample in deuterated DMSO. At room temperature the guest is gelating (in deuterated $CDCl_3$ or DMSO).

DPAGEG: ^{1}H-NMR (400 MHz, DMSO, 80°C): δ 9.05 (s, 1H, N*H*), 7.80 (m, 4H, H1 anth), 7.46 (s, 2H, Ar-*H*), 7.30 (m+d, 8H, H3 ph + H2 anth), 6.95 (d, 2H, H2 ph), 6.05 (s, 1H, N*H*) 6.7 (t, 1H, N*H*), 4.30 (t, 2H, OCH_2CH_2O), 4.25 (m, 6H, Ar-$(OCH_2CH_2O)_2$), 3.56-3.90 (m, 21H, OCH_2), 3.42 (s, 6H, $(OCH_3)_2$), 3.39 (s, 3H, (OCH_3)), 2.8 (d, 2H, $NHCH_2CO$).

^{13}C-NMR (300 MHz, DMSO, 80°C): δ 42 (1C, NHCONHC*H*$_2$COOH), 60.1 (3C, OCH_3), 69.9/ 70.7/ 71.5-71.9/ 72.9/ 73.5 (24C, OCH_2), 110.4 (2C, Ar-*C*2/*C*4), 115 (2C, *C*2 ph), 120 (4C, *C*11+*C*12+*C*13+*C*14 anth), 125.7 (1C, Ar-*C*1), 127 (4C, *C*2+*C*3+*C*6+*C*7 anth), 129 (4C, *C*1+*C*4+*C*5+*C*8 anth), 130 (2C, *C*3 ph), 132 (2C, *C*4 ph), 134 (2C, *C*3 ph), 137 (2C, *C*9+*C*10 anth),138 (2C, *C*2 ph), 143.7 (1C, Ar-*C*5), 153.2 (2C, Ar-*C*4/*C*6), 150 (1C, *C*1ph), 153 (1C, Ar-*C*ONH), 157 (1C, NHCONH), 159 (1C, *C*1 ph), 165 (1C, *C*ONH), 171 (1C, CH_2COOH).

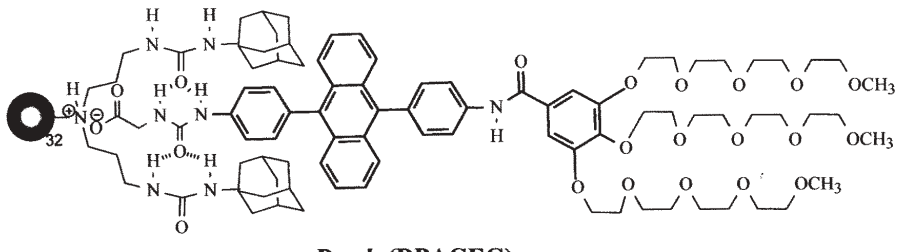
MALDI-TOF (MW= 1183.379) m/z = 1206.35 (M+Na)
UV-Vis ($CHCl_3$): λ_{max}= 359, 377, 397 nm.

Results and Discussion

As descried above, a new type of guest molecule has been synthesized (**DPAGEG)**, which is able to click into urea functionalized dendritic hosts as a result of acid-base and hydrogen bonding interactions. The structure of guest together with the synthesis is shown in scheme 4.

The synthesized guest was fully characterized by NMR spectroscopy (^{1}H-NMR, ^{13}C-NMR) and MALDI-TOF-MS.

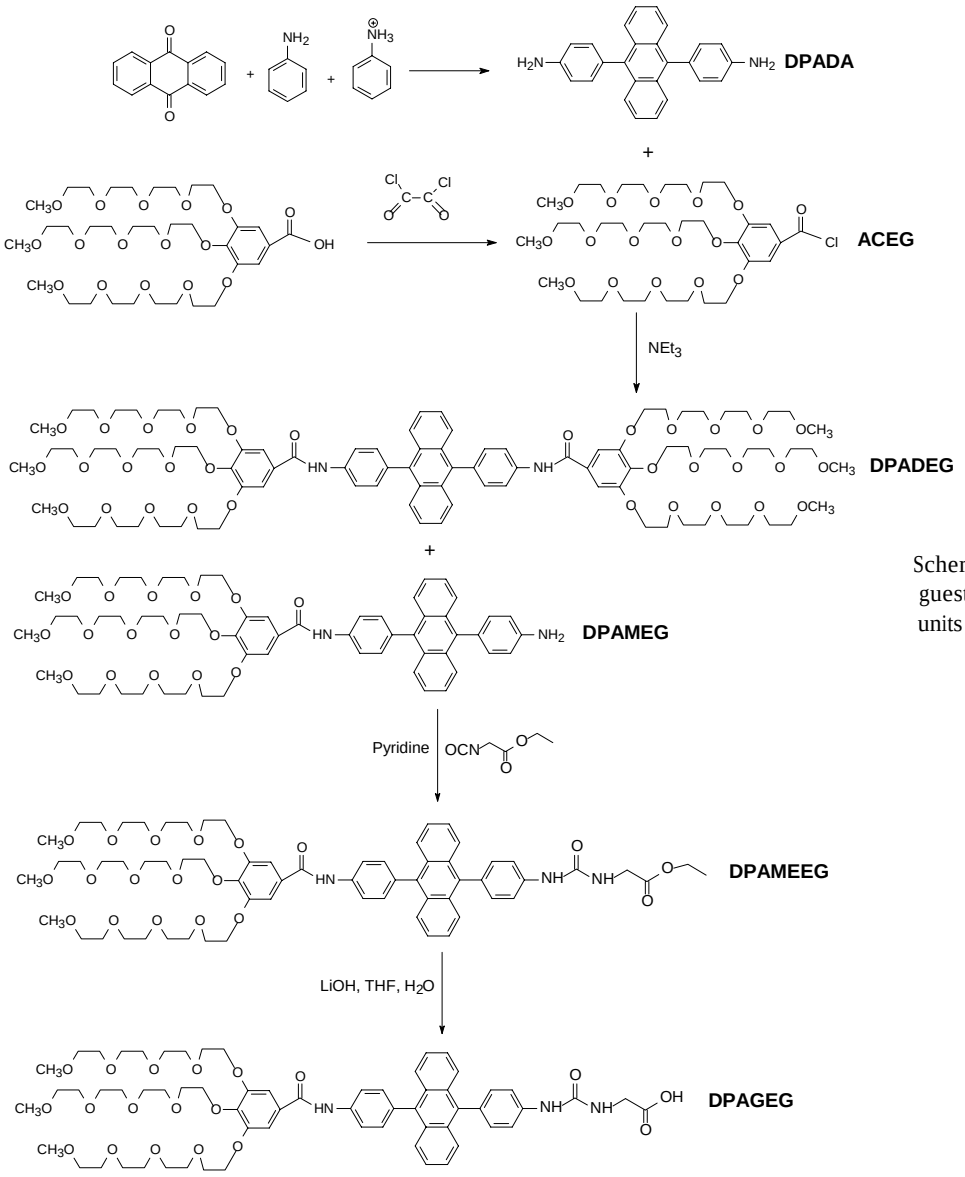
The binding properties of diphenylanthracene guest were first tested with *N*,*N*-bis[(3-adamantylureido) propyl]methylamine (***Pincer***), which is the binding moiety in the fifth generation poly(propyleneimine) dendrimer functionalized with urea adamantyl units at the periphery (***Dendr***, fig. 6).



***Dendr*-(DPAGEG)$_{32}$**

= dendrimeric framework

Fig. 6. The fifth generation poly(propylene imine) dendrimer functionalized with urea adamantyl units at the periphery (*Dendr*) complexed with 32 guests molecules.



Scheme 4. Synthetic route for obtaining the guest functionalised with diphenylanthrac units containing a hydrophilic surrounding Ethylene Glycol (EG)

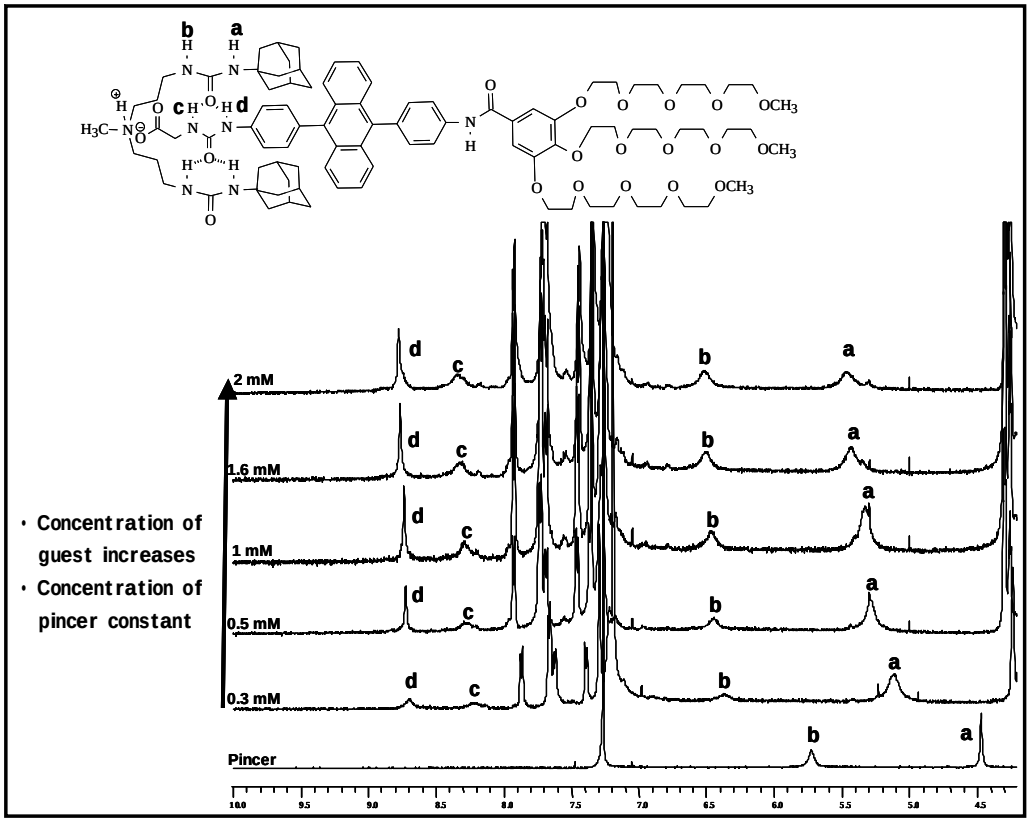


Fig. 7. NMR spectra of DPAGEC and Pincer upon increasing the concentration of the DPAGEC

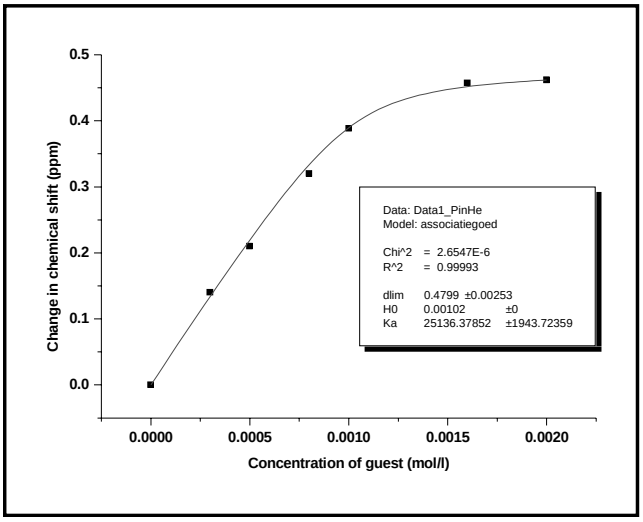


Fig. 8. Changes in chemical shift of DPAGEC and Pincer upon increasing the concentration of the DPAGEC

The urea NH resonances of ***Pincer*** as well as for the guest show a downfield shift, being in full agreement with the previous results already published. The binding constants were determined by following the urea hydrogen resonances of the ***Pincer***. Determination of the association constants (Ka) was carried out at 25°C in CDCl3. The concentration of ***Pincer*** was kept constant (1 mM) while the guest concentration (**DPAGEG**) was varying in the range 0.3-2 mM (fig. 7).

In figure 7 the NMR spectra are nicely illustrated the changes in chemical shift of DPAGEC and Pincer upon increasing the concentration of the DPAGEC. Based on these spectra the association constants have been calculated (fig. 8) by using a non-linear fitting procedure.

The guest molecules were bound as 1:1 inclusion complexes and the association constants for the guest has been calculated and resulted to be in the range of K_a = 2.2- 2.7 x 10^4 $M^{-1.}$

The properties of **DPAGEG** were further investigated with fifth generation adamantyl functionalized propylene dendrimer (***Dendr***)**.** In the NMR spectrum the urea-protons of the dendritic scaffold show a downfield shift, indicating binding at the periphery of the host. In both cases, a maximum of 30 ± 2 guests were bound and this stoichiometry is preserved after repeated preparative size exclusion chromatography.

Conclusions

In conclusion, we have studied the binding properties of glycinylurea functionalized π-conjugated diphenyl-anthracene guests to *N, N-bis*[(3-adamantyl ureido)-propyl]methylamine, and to a adamantyl urea modified fifth generation poly(propylene imine) dendritic hosts that contain 32 of these binding sites.

It is of high interest to analyze further the optical properties of these dendritic supramolecular systems, taking into account the fact that these dendritic macromolecules offer a special opportunity: combine the advantages of small-molecule and those of polymer-emitters.

The rational design of supramolecular systems that use dendrimers and the reversible nature of the binding described above are clearly an emerging area with unlimited possibilities for fundamental new discoveries and practical applications.

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