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Shape persistent hybrid dendrimers from benzene and triazole via 'click chemistry'☆

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ABSTRACT

Fully aromatic rigid dendrimers have been synthesized at room temperature based on two different 'click'-reactions: The dendronization was carried out via the copper catalyzed azide–alkyne Huisgen cycloaddition or Diels–Alder cycloaddition, respectively. The feasible combination of both reactions leads to dendrimer hybrids. Stiff aromatic dendrimers, whose highly nitrogen containing scaffolds are solely based on interconnected benzene and triazole rings, were created.

1. Introduction

Dendrimers represent macromolecules with a monodisperse structure and a defined number of functional groups, which can be build-up by a huge variety of different synthetic methods.[1] Within all these methods easily manageable and exothermic reactions with high yields and selectivity are necessary to achieve full conversion of all reactive groups. So called 'click reactions'[2] enable 'clicking' together different suitably functionalized components. In dendrimer chemistry, click reactions have been used for the functionalization of dendrimer peripheries,[3] for linking together several ready-made dendrons to a single core (convergent synthesis)[4] or for divergent dendrimer growth.[5,6] Triazole-rich flexible dendrimers have been synthesized by a convergent approach using the Huisgen reaction.[7] With regard to dendrimer synthesis, the copper catalyzed Huisgen cycloaddition between azides and alkynes is not the only type of 'click reaction' that has been utilized. More and more procedures are now being developed, which do not require metal catalysis.[8] The Diels–Alder [4+2]-cycloaddition can be used for the modular synthesis of polyphenylene dendrimers (PPD), by reacting alkynes with a tetracylones to form new benzene rings. PPDs constitute a special class of dendrimers due to their shape persistent character, which does not allow for either collapsing or swelling of the scaffold.[9]

Within this work, experiments have been made regarding the applicability of click chemistry for the synthesis of stiff dendrimers at room temperature. The final nitrogen rich macromolecules were built up from benzene and triazole rings forming a polyphenylene-triazole dendrimer.† The requirement of ethynyl functions for both PPD chemistry[10] and azide–alkyne click chemistry[11] invites for a combination of both concepts for dendrimer hybrids (see Fig. 1).

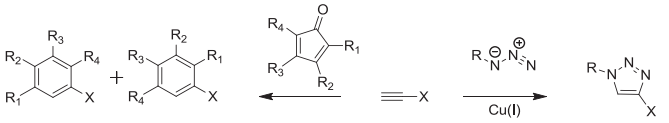

Fig. 1. Schematic illustration of azide–alkyne Huisgen cycloaddition and Diels–Alder cycloaddition.

☆ Parts of this work were taken from the Dissertation Dendronized Ions by Dr. David Türp, Mainz 2012.

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† We use the term 'polyphenylene-triazole dendrimer' somewhat undefined. The presented dendrimers are built from different substituted benzene rings, which are tilted packed and twisted. The name polyphenylene dendrimers in principle does not adequately reflect the different substituent types ranging from phenyl to tetraphenyl substituted benzene. The triazole unit occurs as a twofold substituted entity.

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2. Results/discussion

2.1. Synthesis

A dendritic shell is always built around a single core to obtain a dendrimer. We used 1,3,5-triethynylbenzene (**8**) and tetrakis(4-ethynylphenyl)methane (**14**)[12] to grow dendrimers in a trigonal planar or a tetrahedral geometry, respectively. To enable the synthesis of dendritically branched polyphenylene-triazole scaffolds, an ethynyl functionalized phenyl azide is required that can serve as a branching unit. Phenyl azides can easily be obtained via conversion of the according phenyl amines.[13] ((5-Azido-2-methyl-1,3-phenylene)bis(ethyne-2,1-diyl))bis(triisopro pylsilane) (**3**) was selected as a suitable building block for dendritic growth, which can be synthesized in two steps starting from 3,5-dibromo-4-methylaniline (**1**) as described for comparable compounds (Fig. 2).[6] After functionalization with Triisopropylsilyl (TIPS)-acetylene via Sonogashira coupling, azide **3** was obtained using *tert*-butyl nitrite (*t*-BuONO) and trimethylsilyl azide ($TMSN_3$) as azide source.[13] Although azide **3** could be stored at 3 °C, it was usually prepared freshly for every growth step. Aniline **4** is a very large and bulky aryl amine that somewhat resembles the structure of polyphenylenes (compare Figs. 2 and 3).[14] It was converted to the according azide **5** using the above mentioned method. For the end capping of phenylene-triazole dendrimers, the bulky phenyl azide **5** and the commercially available azidobenzene **6** or tetracyclone **7** have been tested.

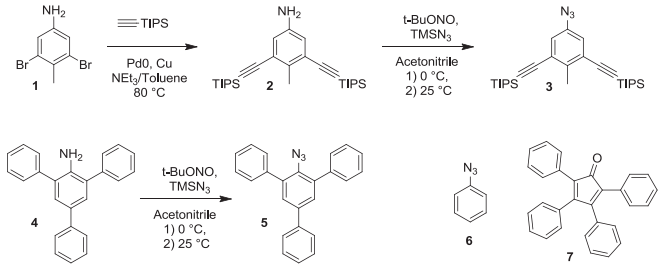

Fig. 2. Synthesis of branching unit **3** for the build-up of dendritic polyphenylene-triazole scaffolds and suitable phenyl azide end capping unit **5**, **6**, and **7**.

The build-up of dendritic scaffolds from benzene rich and hydrophobic building blocks makes the use of non-aqueous reaction media necessary, in contrast to many other 'click reactions'. Instead of mixtures of water and *tert*-butanol, THF was used for dissolving all starting materials, reagents and products. A catalytically active Cu^+ species is required, which is well soluble in the organic reaction medium. To ensure a good solubilization of the Cu^+ in THF, the effective ligand Tris-benzyltriazolylmethyl amine (TBTA) was employed. The ligand was previously synthesized by a click reaction itself.[15] Moreover, to ensure complete conversion of all alkyne moieties, an excess of the azide component (about 2–3 equiv per alkyne function) was generally used. For the growth of the first generation polyphenylene-triazole dendrimer **9** from a trigonal planar core, 1,3,5-triethynylbenzene (**8**) was reacted with the bulky azide **5** (Fig. 3a). To enable the synthesis of a second generation polyphenylene-triazole dendrimer, azide building block **3** was connected to the trigonal planar core **8**, followed by an activation of the resulting species **10** for another growth step via removal of its TIPS-groups with TBAF in THF (see Fig. 3a) towards compound (**11**). Compound **11** was converted to second generation polyphenylene-triazole dendrimer **12** in THF at room temperature using bulky azide **5** for end capping (Fig. 3a). Thermal degradation of 1,2,3-triazole occurs between 218 °C and 338 °C.[16] Thus we were able to disperse the ethynyl functionalized species **11** in *ortho*-xylene and react with tetracyclone **7** at 160 °C to achieve the polyphenylene-triazole dendrimer **13**. We proved that polyphenylene-triazole scaffolds are stable enough to endure the harsh conditions that are required for the growth of PPDs via Diels–Alder-reaction.[17]

The resulting dendrimers were purified first by column chromatography, precipitation in hexane and recycling gel permeation chromatography (GPC). Surprisingly, the solubility of **11** in methylene chloride was relatively low so that this solvent could be used to purify **11** by the extraction of impurities from the non-dissolved raw product. It is noteworthy that ethynyl functionalized species **10** and even more the deprotected species **11** both tend to form aggregates. Aggregate formation was evidenced by the appearance of white, solid precipitate in their solutions even at moderate concentrations (approx. 10 mg/mL) in comparatively good solvents, such as THF.

To reduce the tendency of aggregate formation the geometry needs to be more sphere like to minimize interactions and increase the solubility. Ethynyl functionalized tetraphenylmethane **14** has frequently been utilized as a core for the build-up of polyphenylene dendrimers.[18] Due to its tetrahedral geometry, tetraphenylmethane orients growing dendrons into all three spatial dimensions, and the dendrimer adopts an overall globular shape already at comparatively low generations and low degrees of branching.[10] Copper catalyzed cycloaddition of bulky azide **5** gave the first generation polyphenylene-triazole dendrimer **15** with a tetrahedral core (see Fig. 3b). Dendrimer **15** can be regarded as a related structure to the triazole-phenyl functionalized tetraphenylmethane **20** described in literature (compare Fig. 3b and crystal structure in Fig. 4).[19] In analogy to the synthesis of **12**, second generation dendrimers with a tetrahedral core were obtained upon a tetraphenylmethane core **14** (Fig. 3b) and were purified in the same way as the trigonal planar dendrimers. Despite the tetrahedral geometry of its core, dendrimer **15** still showed a considerable tendency to aggregate. The higher density second generation dendrimer **19** exhibited much better solubility in THF and a reduced tendency to aggregate than dendrimer **15** and **18**, probably due to its more sphere like character.

2.2. Characterization

^1H and ^{13}C NMR signals of all dendrimers could readily be assigned and were used to confirm complete conversion as well as purity. A detailed analysis of the proton NMR spectra is given in Supplementary data. Measurements by means of MALDI-TOF mass spectrometry show the formation of monodisperse macromolecules but also demonstrate that polyphenylene-triazole compounds decompose easily upon laser irradiation. Three additional signals at lower *m*/*z* ratios of 26 *m*/*z* appear due to a release of nitrogen from triazole moieties (see Fig. 4 and Supplementary data). It is however surprising that cleavage of nitrogen only occurs up to three times, although four triazole rings are present in the structure.

2.3. Structure and shape persistence of polyphenylene-triazole dendrimers

The crystal structure of a fourfold functionalized tetraphenylmethane comparable to **20** has been described and can be assigned as a first generation triazole dendrimer,[19] which indicates a strong preference for a coplanar alignment of triazole and neighboring benzene rings due to electronic conjugation and limited flexibility based on the sp^2-character of the aromatic subunits. Thus a relatively flat overall orientation of dendrons could be expected, due to the preference for coplanar alignment. Dendrimer **9** was

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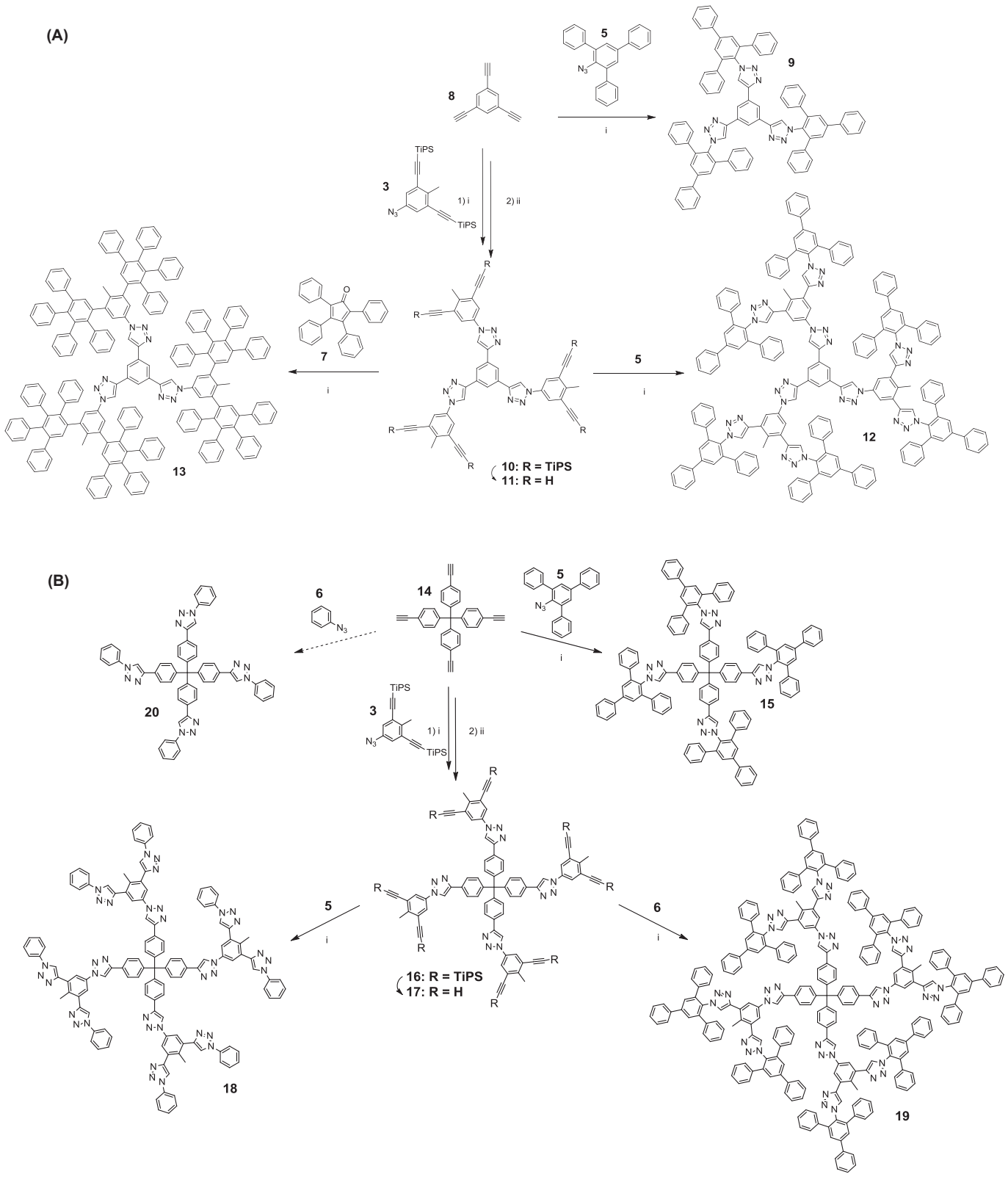

Fig. 3. a: Synthesis of first generation polyphenylene-triazole dendrimer **9** and first generation of ethynyl functionalized polyphenylene-triazole dendrimer **10** and **11**, respectively, with a trigonal planar core via copper catalyzed Huisgen cycloaddition at room temperature. Synthesis of second generation polyphenylene-triazole dendrimer **12** and second generation polyphenylene-triazole hybrid dendrimer **13**. (i) Cu^{+}, TEA, TBTA, THF, 23 °C; (ii) TBAF, THF, 23 °C. b: Synthesis of first generation polyphenylene-triazole dendrimer **15** and first generation of ethynyl functionalized polyphenylene-triazole dendrimer **16** and **17**, respectively, with a tetrahedral core via copper catalyzed Huisgen cycloaddition at room temperature. Structure of tetrakis(4-(1-phenyl-1*H*-1,2,3-triazol-4-yl)phenyl)methane **20**. Synthesis of second generation polyphenylene-triazole dendrimer **18** and **19** acting on **17** by using of different end capping agents **5** or **6**. (i) Cu^{+}, TEA, TBTA, THF, 23 °C; (ii) TBAF, THF, 23 °C.

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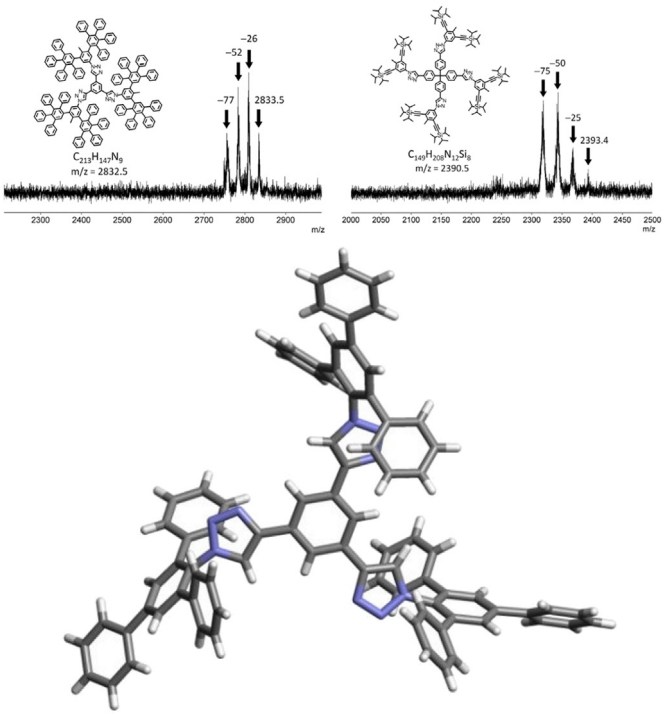

Fig. 4. MALDI-TOF of polyphenylene-triazole compounds **13** (up left) and **16** (up right). Single crystal structure of first generation polyphenylene-triazole dendrimer **9** with a trigonal planar core (mid). For crystallographic data of compound **9** see Supplementary data and the Cambridge Crystallographic Data Centre (CCDC).

crystallized as colorless triclinic prisms (Fig. 4). In contrast to **20** the steric demand of the *ortho*-phenyl rings of each 2,4,6-triphenylbenzene moiety enforces a twisting of benzene rings out of their common plane with neighboring triazole rings, while all triazole rings retain their almost coplanar alignment with the central benzene ring of the core. The alignment is only slightly disturbed due to packing effects in the crystal lattice.

A comparison of the modeled structures of the second generation dendrimers **18** and **19** (see Supplementary data) indicates that the energetically favored coplanar alignment of phenyl and triazole rings is not only disturbed by the large spatial demand of bulky 2,4,6-triphenylbenzene moieties in **19**, but also by the methyl group of each branching phenyl ring in both dendrimers **18** an **19**. Due to the largely increased solubility and reduced aggregation of dendrimers endcapped with bulky azide **5** as compared to small azidobenzene **6**, the larger azide **5** is the preferable end capping unit. The dendritic scaffold resulting from building block **3** is not as rigid as typical PPD scaffolds, but should nevertheless be much stiffer than the dendritic scaffolds based on triazoles via click reactions that have been reported so far due to the conjugation between connected rings.[5a]

3. Conclusion

A new class of dendrimer hybrids has been presented. Utilization of the copper catalyzed azide-alkyne Huisgen- and Diels–Alder cycloaddition has enabled the synthesis of a number of different dendrimers at room temperature, which are entirely constituted from benzene and triazole rings. Thus the introduction of temperature sensitive groups becomes possible. Two distinct cores with different geometries (trigonal planar and tetrahedral) have been used to generate polyphenylene-triazole dendrimers with either preferentially flat or globular overall shapes. Many of the intermediate aryl-triazole species as well as some of the final aryl-triazole dendrimers showed a pronounced tendency to form aggregates. Employment of bulky surface groups and an overall spherical geometry helped to reduce their tendency to aggregate and increased their solubility in THF and DCM. In addition to aryl-triazole dendrimer synthesis, the potential for a combination with polyphenylene dendrimer chemistry was tested. It was found that the thermal stability of the triazole linkage is sufficient to allow for a functionalization of dendritic aryl-triazole scaffolds with rigid polyphenylenes. Due to the comparatively large size of the dendrons and the energetic preference for a coplanar alignment of neighboring triazole and benzene rings, the resulting dendritic scaffolds are fairly stiff and hence retain voids. Moreover, the large number of triazole moieties leads to nitrogen rich scaffolds in which the nitrogen atoms may serve as coordination sites. The combined properties of inherently porous aryl-triazole dendrimers offers the possibility to use such dendrimers as host material for sensing or storage application or might be suitable for ion complexation.

In the future, polyphenylene-triazole dendrimers of higher generations as well as dendrimers with different core geometries or alternative building blocks will be synthesized. The applicability of these nitrogen rich, stiff and porous materials as sensing layers for the detection of specific guest molecules will be tested. More fundamentally, the concept of reacting ethynyl groups at room temperature might be exploited to functionalize polyphenylene dendrimers with temperature sensitive surface moieties.

4. Experimental section

4.1. General information

Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 300, 500 or 700 MHz and 100, 125 or 175 MHz, respectively. The chemical shifts are given in parts per million. The solvent proton signals were used as a reference value. Data are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). Column chromatography was done using 32–63, 60 Å silica gel. All solvents were dried before using. The starting materials was purchased from Sigma Aldrich and used without further purification.

4.2. 4-Methyl-3,5-bis((triisopropylsilyl)ethynyl)aniline (2)

15.00 g (56.61 mmol) 3,5-dibromo-4-methylaniline **1**, 2.97 g (11.32 mmol) PPh_3, 2.16 g (11.32 mmol) CuI, and 3.97 g (5.66 mmol) $Pd(PPh_3)_2Cl_2$ were dissolved in a mixture of 140 mL triethylamine and 150 mL toluene. The mixture was heated to 80 °C under argon. 21.68 g (26.67 mL, 118.89 mmol) TiPS-acetylene was added dropwise (orange suspension turns black) and the mixture was stirred at 80 °C over night. Water was added to the mixture and the organic phase was washed with satd NH_4Cl (aq), 1 N HCl(aq), 10% Na_2CO_3 (aq), and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography using firstly hexane and then a 10:1 mixture of petrol ether and ethyl acetate as eluent to yield 22.71 g (86%) of the pure compound as viscous yellow oil. R_f (PE/EtOAc=10/1)=0.65. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 6.72 (s, 2H, H_c), 4.46 (s, 2H, H_a), 2.47 (s, 3H, H_f), 1.16 (m, 42H, H_i+H_j). ^{13}C NMR (75 MHz, THF-d_8, 298 K) δ 146.95 (C, C_b), 131.34 (C, C_e), 124.76 (C, C_d), 119.66 (C–H, C_c), 107.88 (C, C_g), 93.38 (C, C_h), 19.30 (CH3, C_j), 18.84 (CH3, C_f), 12.45 (C–H, C_i) FDMS (*m*/*z*): calcd for $C_{29}H_{49}NSi_2$: 467.3, found: 467.4.

4.3. ((5-Azido-2-methyl-1,3-phenylene)bis(ethyne-2,1-diyl)) bis(triisopropylsilane) (3)

1.320 g (2.824 mmol) **2** were dissolved in a mixture of acetonitrile and THF (9:1) in an open flask. The mixture was cooled to

0 °C. 0.874 g (8.473 mmol, 1.01 mL) *tert*-butyl nitrite and 0.814 g (7.061 mmol, 0.93 mL) trimethylsilyl azide (release of N_2!) were added dropwise and the solution was allowed to warm to room temperature. Two liquid phases were obtained, which were homogenized by addition of THF. The orange solution was adsorbed on silica and purified by column chromatography using hexane as eluent to yield 1289 g (92%) of the pure product as viscous yellow oil. R_f (hexane)=0.50. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 7.12 (s, 2H, H_b), 2.61 (s, 3H, H_e), 1.17 (m, 42H, H_h+H_i).

4.4. 2′-Azido-5′-phenyl-1,1′:3′,1″-terphenyl (5)

2.000 g (6.223 mmol) 5′-phenyl-[1,1′:3′,1″-terphenyl]-2′-amine **4** were dissolved in a mixture of acetonitrile and THF (5:1) in an open flask. The mixture was cooled to 0 °C. 1.925 g (18.668 mmol, 2.22 mL) *tert*-butyl nitrite and 1.792 g (15.556 mmol, 2.05 mL) trimethylsilyl azide (release of N_2!) were added dropwise and the solution was allowed to warm to room temperature. The solution was adsorbed on silica and purified by column chromatography using a 4:1 mixture of hexane and ethyl acetate as eluent to yield 2.108 g (98%) of the pure product as viscous yellow oil. R_f (hexane/EtOAc=4/1)=0.80. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 7.69 (d, 3JHH=7.2 Hz, 2H, H_b), 7.61 (s, 2H, H_a), 7.58 (d, 3JHH=7.0 Hz, 4H, H_e), 7.49–7.29 (m, 9H, H_c+H_d+H_f+H_g). ^{13}C NMR (75 MHz, THF-d_8, 298 K) δ 140.94 (C), 139.84 (C), 139.71 (C), 138.28 (C), 134.91 (C), 130.46 (C–H, C_f), 129.91 (C–H), 129.78 (C–H), 129.31 (C–H, C_e), 128.65 (C–H), 128.49 (CH, C_d), 127.89 (C–H) FDMS (m/z): calcd for $C_{24}H_{17}N_3$: 347.1, found: 346.7.

4.5. 1-(1-(5′-Phenyl-[1,1′:3′,1″-terphenyl]-2′-yl)-1*H*-1,2,3-triazol-4-yl)-3,5-bis(1-(5′-phenyl-[1,1′:3′,1″-terphenyl]-4′-yl)-1*H*-1,2,3-triazol-4-yl)benzene (9)

10 mg (0.067 mmol) of 1,3,5-triethynylbenzene **8** and 139 mg (0.400 mmol) of azide **5** were dissolved in THF. To the solution were added 10 mg (0.051 mmol) sodium ascorbate, 13 mg (0.025 mmol) TBTA, 0.5 mL triethylamine, and 6 mg (0.025 mmol) $CuSO_4 \cdot 5H_2O$. The solution was stirred at room temperature for 16 h and then purified by column chromatography using firstly a mixture of hexane and ethyl acetate (4:1) and then THF as eluent. After removal of the solvent in vacuum, the crude product was dissolved in methylene chloride, precipitated in hexane, filtered, dried, dissolved in chloroform, and purified by recycling GPC to afford 50 mg (0.042 mmol, 63%) of the compound as a colorless powder. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 8.02 (s, 3H, Ha), 7.95 (s, 3H, H_d), 7.83 (s, 6H, H_g), 7.82 (d, 3JHH=7.4 Hz, 6H, H_j), 7.48 (t, 3JHH=7.4 Hz, 6H, H_k), 7.39 (t, 3JHH=7.3 Hz, 3H, H_l), 7.28–7.14 (n.r., 30H, H_n+H_o+H_p). ^{13}C NMR (75 MHz, THF-d_8, 298 K) δ 147.25 (C, C_c), 144.01 (C), 142.10 (C, C_m), 140.69 (C), 139.22 (C, C_e), 133.61 (C), 132.85 (C), 129.93 (C–H, C_k), 129.57 (C–H, C_g+C_o), 129.10 (C–H, C_l+C_n), 128.59 (C–H, C_p), 128.31 (C–H, C_j), 125.01 (C–H, C_a), 122.35 (C–H, C_d) FDMS (m/z): calcd for $C_{84}H_{57}N_9$: 1191.5, found: no signal due to UV laser induced decomposition. XRD: colorless prisms, triclinic, P-1.

4.6. 1,3,5-Tris(1-(4-methyl-3,5-bis((triisopropylsilyl)ethynyl)phenyl)-1*H*-1,2,3-triazol-4-yl)benzene (10)

50 mg (0.333 mmol) 1,3,5-triethynylbenzene **8** and 0.987 g (1.998 mmol) of AB2 azide **3** were dissolved in THF. To the solution were added 50 mg (0.253 mmol) sodium ascorbate, 67 mg (0.127 mmol) TBTA, 2 mL triethylamine and 32 mg (0.127 mmol) $CuSO_4 \cdot 5H_2O$. The solution was stirred at room temperature for 15 h. After adsorption to silica, the solution was purified by column chromatography using firstly hexane and then mixtures of hexane and ethyl acetate (10:1 to 4:1; consumption of large amounts of solvent) as eluent to yield 490 mg (90%) of the product as a colorless solid. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 9.27 (s, 3H, H_d), 8.63 (s, 3H, H_a), 8.10 (s, 6H, H_f), 2.74 (s, 9H, H_i), 1.21 (s, 126H, H_l+H_m). ^{13}C NMR (75 MHz, THF-d_8, 298 K) δ 148.70 (C, C_c), 143.78 (C), 136.33 (C), 133.38 (C), 126.13 (C, C_g), 124.25 (C–H, C_f), 123.15 (C–H, C_a), 120.10 (C–H, C_d), 105.51 (C, C_j), 97.60 (C, C_k), 19.91 (CH_3, C_i), 19.27 (CH_3, C_m), 12.43 (C–H, C_l) MALDI-TOF (m/z): calcd for $C_{99}H_{147}N_9Si_6$: 1631.0, found: 1633.5.

4.7. 1,3,5-Tris(1-(3,5-diethynyl-4-methylphenyl)-1*H*-1,2,3-triazol-4-yl)benzene (11)

To a solution of 200 mg (0.123 mmol) **10** in THF (50 mL) was added dropwise a solution of tetrabutylammonium fluoride (240 mg, 0.858 mmol) in THF (10 mL). The mixture was stirred for 2 h at room temperature and then filtered over silica. After removal of the solvent under vacuum, the solid remainder was dispersed in methylene chloride, filtered, washed with methylene chloride and dried to afford 66 mg (0.095 mmol, 78%) of the compound as a colorless powder. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 9.22 (s, 3H, H_d), 8.63 (s, 3H, Ha), 8.16 (s, 6H, H_f), 4.06 (s, 6H, H_k), 2.66 (s, 9H, H_i). ^{13}C NMR (176 MHz, THF-d_8, 298 K) δ 148.82 (C), 143.72 (C), 136.38 (C), 133.38 (C), 125.50 (C, Cg), 124.70 (C–H, C_f), 123.28 (C–H, C_a), 119.79 (C–H, Cd), 84.83 (C_j), 81.87 (C_k), 19.08 (CH_3, C_i) MALDI-TOF (m/z): calcd for $C_{45}H_{27}N_9$: 693.2, found: no signal due to UV laser induced decomposition.

4.8. Compound (12)

40 mg (0.058 mmol) of ethynyl functionalized compound 11 and 240 mg (0.692 mmol) of azide **5** were dissolved in THF. To the solution were added 17 mg (0.088 mmol) sodium ascorbate, 23 mg (0.044 mmol) TBTA, 1 mL triethylamine and 11 mg (0.044 mmol) $CuSO_4 \cdot 5H_2O$. The solution was stirred at room temperature for 16 h and then purified by column chromatography using firstly a mixture of hexane and ethyl acetate (4:1) and then THF as eluent. After removal of the solvent in vacuum, the crude product was dissolved in THF, precipitated in hexane, filtered, dried, dissolved in chloroform and purified by recycling GPC to afford 68 mg (0.024 mmol, 42%) of the compound as a colorless powder. ^{1}H NMR (700 MHz, THF-d_8, 298 K) δ 9.11 (s, 3H, H_b), 8.67 (s, 3H, H_a), 8.05 (s, 6H, H_c), 7.88 (s, 12H, H_f), 7.86 (s, 6H, H_e), 7.83 (d, 3JHH=8.1 Hz, 12H, H_g), 7.49 (t, 3JHH=7.7 Hz, 12H, Hh), 7.40 (t, 3JHH=7.3 Hz, 3H, Hi), 7.33–7.28 (n.r., 60H, H_j+H_k+H_l), 1.87 (s, 9H, H_d). ^{13}C NMR (126 MHz, THF-d_8, 298 K) δ 146.33 (C), 144.16 (C), 142.12 (C), 140.68 (C), 139.28 (C), 137.06 (C), 133.58 (C), 129.97 (C–H), 129.71 (C–H), 129.66 (C–H), 129.55 (C–H), 129.25 (C–H), 129.10 (C–H), 128.95 (C–H), 128.79 (C–H), 128.33 (C–H), 18.11(CH_3) MALDI-TOF (m/z): calcd for $C_{189}H_{129}N_{27}Si_6$: 2778.1, found: no signal due to UV laser induced decomposition.

4.9. Compound (13)

22 mg (0.019 mmol) of ethynyl functionalized compound **11** and 89 mg (0.231 mmol) tetraphenylcyclopentadienone 7 were dispersed in *o*-xylene (5 mL) in a microwave tube. The argon bubbled mixture was stirred at 160 °C for 14 h. After cooling to room temperature, the mixture was purified by column chromatography using firstly a 10:1 mixture of hexane and ethyl acetate and then methylene chloride as eluent. After removal of the solvent in vacuo, the product was dissolved in methylene chloride, precipitated in hexane, filtered and dried to afford 44 mg (0.055 mmol, 81%) of the pure compound as a colorless powder. In NMR measurements, two local conformations A and B could be discerned (see paragraph 3.3.3 for details): ^{1}H NMR (700 MHz, THF-d_8, 298 K) δ 8.84–8.81 (≥3s, 3H), 8.56–8.53 (3s, 3H), 8.52–8.41 (≥8s, 3H+3H), 7.72 (≥3s, 6H), 7.57 (≥3s, 6H), 7.46 (≥3s, 6H), 7.16–7.05 (n.r., 30H+30H), 7.11 (≥3s, 6H),

6.98 (s), 6.95–6.77 (n.r.), 6.61 (s), 2.23 (s, 9H), 1.92 (s, 9H). ^{13}C NMR (176 MHz, THF-d_8, 298 K) δ 148.31 (C), 148.18 (C), 144.39 (C), 144.37 (C), 143.23 (C), 142.94 (C), 142.87 (C), 142.75 (C), 141.88 (C), 141.79 (C), 141.48 (C), 141.41 (C), 141.17 (C), 141.13 (C), 141.07 (C), 140.98 (C), 140.93 (C), 140.82 (C), 140.74 (C), 135.15 (C), 135.01 (C), 134.60 (C), 134.52 (C), 133.40 (C), 133.32 (C), 132.68 (C–H), 132.64 (C–H), 132.54 (C–H), 132.49 (C–H), 132.39 (C–H), 131.92 (C–H), 130.98 (C–H), 130.92 (C–H), 128.52 (C–H), 128.49 (C–H), 127.97 (C–H), 127.88 (C–H), 127.77 (C–H), 127.69 (C–H), 127.62 (C–H), 127.58 (C–H), 127.55 (C–H), 127.22 (C–H), 127.18 (C–H), 126.84 (C–H), 126.79 (C–H), 126.57 (C–H), 126.34 (C–H), 126.27 (C–H), 121.69 (C–H), 121.53 (C–H), 19.77 (CH_3), 19.30 (CH_3), MALDI-TOF (m/z): calcd for $C_{213}H_{147}N_9$: 2832.5, found: 2833.5 (+decomposition due to UV laser irradiation: $-N_2$, $-2N_2$, $-3N_2$).

4.10. Tetrakis(4-(1-(5′-phenyl-[1,1′:3′,1″-terphenyl]-2′-yl)-1*H*-1,2,3-triazol-4-yl)phenyl)methane (15)

10 mg (0.024 mmol) ethynyl functionalized tetraphenylmethane core **14** and 67 mg (0.192 mmol) bulky azide **5** were dissolved in THF. To the solution were added 5 mg (0.024 mmol) sodium ascorbate, 6 mg (0.012 mmol) TBTA, 0.5 mL triethylamine and 3 mg (0.012 mmol) $CuSO_4 \cdot 5H_2O$. The solution was stirred at room temperature for 16 h, whereupon a yellow-white suspension was obtained. The suspension was purified by column chromatography using firstly a 4:1 mixture of hexane and ethyl acetate and then methylene chloride as eluent to yield 0.017 g (40%) of the compound as a white solid. ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) δ 7.79 (s, 8H, H_j), 7.75 (d, 3JHH=7.7 Hz, 8H, H_m), 7.51 (t, 3JHH=7.5 Hz, 8H, H_n), 7.49 (s, 4H, H_g), 7.49 (d, 3JHH=8.4 Hz, 8H, H_c), 7.44 (t, 3JHH=7.4 Hz, 4H, Ho), 7.28 (m, 24H, H_q+H_s), 7.24 (d, 3JHH=8.4 Hz, 8H, H_d), 7.23 (m, 16H, H_r). ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K) δ 146.98 (C), 146.87 (C), 143.63 (C), 141.10 (C), 140.00 (C), 138.41 (C), 132.53 (C), 131.52 (C–H, Cd), 129.61 (C–H, C_n), 129.37 (C–H, C_j), 128.98 (C–H, C_r), 128.87 (C–H, Co+C_q), 128.64 (C), 128.37 (C–H, C_s), 127.86 (C–H, C_m), 125.59 (C–H, C_c), 123.74 (C–H, C_g) FDMS (m/z): calcd for $C_{129}H_{88}N_{12}$: 1805.7, found: no signal due to UV laser induced decomposition.

4.11. Tetrakis(4-(1-(4-methyl-3,5-bis((triisopropylsilyl)ethynyl)phenyl)-1*H*-1,2,3-triazol-4-yl)-phenyl)methane (16)

117 mg (0.281 mmol) ethynyl functionalized tetraphenylmethane core **14** and 1.110 g (2.247 mmol) of AB2 azide **3** were dissolved in THF. To the solution were added 56 mg (0.281 mmol) sodium ascorbate, 75 mg (0.140 mmol) TBTA, 3 mL triethylamine and 35 mg (0.140 mmol) $CuSO_4 \cdot 5H_2O$. The solution was stirred at room temperature for 16 h. After adsorption to silica, the solution was purified by column chromatography using firstly hexane and then a mixture of hexane and ethyl acetate (10:1) as eluent to yield 578 mg (88%) of the product as a colorless solid. R_f (hexane/EtOAc=10/1)=0.72. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 8.93 (s, 4H, H_g), 8.00 (s, 8H, H_i), 7.93 (d, 3JHH=8.5 Hz, 8H, H_c), 7.48 (d, 3JHH=8.5 Hz, 8H, H_d), 2.71 (s, 12H, H_l), 1.19 (m, 168H, H_o+H_p). ^{13}C NMR (75 MHz, THF-d_8, 298 K) δ 148.67 (C), 147.53 (C), 143.52 (C), 136.19 (C), 132.35 (C–H, C_d), 129.89 (C), 125.93 (C), 125.90 (C–H, C_c), 124.16 (C–H, C_i), 119.13 (C–H, C_g), 105.36 (C, C_n), 97.47 (C, C_m), 19.75 (CH3, C_l), 19.12 (CH3, C_p), 12.28 (C–H, C_o) MALDI-TOF (m/z): calcd for $C_{149}H_{208}N_{12}Si_8$: 2390.5, found: 2393.4 (and fragments from UV induced decomposition).

4.12. Tetrakis(4-(1-(3,5-diethynyl-4-methylphenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)methane (17)

To a solution of 238 mg (0.102 mmol) **16** in THF (50 mL) was added dropwise a solution of tetrabutylammonium fluoride (273 mg, 0.978 mmol) in THF (10 mL). The mixture was stirred for 2 h at room temperature. After washing three times with a concentrated aqueous solution of sodium chloride, the solution was filtered over silica and the solvent removed under vacuum to afford 44 mg (0.039 mmol, 38%) of the product as a beige-white powder. R_f (hexane/EtOAc=10/1)=0.00. ^{1}H NMR (300 MHz, THF-d_8, 298 K) δ 8.90 (s, 4H, H_g), 8.05 (s, 8H, H_i), 7.93 (d, 3JHH=8.5 Hz, 8H, H_c), 7.47 (d, 3JHH=8.5 Hz, 8H, H_d), 4.03 (s, 8H, H_n), 2.63 (s, 12H, H_l). ^{13}C NMR (75 MHz, THF-d_8, 298 K) δ 148.83 (C), 147.66 (C), 143.59 (C), 136.32 (C), 132.54 (C–H, C_d), 129.99 (C), 125.99 (C), 125.37 (C–H, C_c), 124.55 (C–H, C_i), 118.98 (C–H, C_g), 85.08 (C_n), 81.80 (C_m), 19.10 (C_l) MALDI-TOF (m/z): calcd for $C_{77}H_{48}N_{12}$: 1140.4, found: no signal due to UV laser induced decomposition.

4.13. Tetrakis(4-(1-(4-methyl-3,5-bis(1-phenyl-1*H*-1,2,3-triazol-4-yl)phenyl)-1*H*-1,2,3-triazol-4-yl)phenyl)methane (18)

20 mg (0.018 mmol) of ethynyl functionalized compound **17** and 33 mg (0.280 mmol) of phenyl azide **6** were dissolved in THF. To the solution were added 7 mg (0.035 mmol) sodium ascorbate, 9 mg (0.018 mmol) TBTA, 0.5 mL triethylamine and 9 mg (0.018 mmol) $CuSO_4 \cdot 5H_2O$. The solution was stirred at room temperature for 15 h. The obtained suspension was exposed to ultrasonic sound and filtered. The remaining solid was washed firstly with a mixture of hexane and ethyl acetate (4:1) and then acetonitrile, whereupon the solid was transferred into THF for dissolution. After 2 h, the obtained solution was filtered over cotton fibers and the solvent removed in vacuum to yield 8 mg (0.004 mmol, 23%) of the compound as a white solid. ^{1}H NMR (500 MHz, THF-d_8, 298 K) δ 9.00 (s, 4H, H_c), 8.83 (s, 8H, H_f), 8.37 (s, 8H, H_d), 7.98 (d, 3JHH=7.7 Hz, 16H, H_g), 7.97 (d, 3JHH=8.1 Hz, 8H, H_a), 7.58 (t, 3JHH=7.7 Hz, 16H, H_h), 7.50 (d, 3JHH=8.1 Hz, 8H, H_b), 7.45 (t, 3JHH=7.4 Hz, 8H, H_i), 2.79 (s, 12H, H_e). ^{13}C NMR (126 MHz, THF-d_8, 298 K) δ 149.19 (C), 148.07 (C), 147.72 (C), 142.92 (C), 137.75 (C), 134.44 (C), 132.49 (C–H, C_b), 130.72 (C–H, C_h), 129.41 (C–H, C_i), 126.07 (C–H, C_a), 122.36 (C–H, C_f), 121.20 (C–H, C_d), 121.15 (C–H, C_g), 119.16 (C–H, C_c), 19.03 (C–H, C_e) MALDI-TOF (m/z): calcd for $C_{125}H_{88}N_{36}$: 2093.8, found: no signal due to UV laser induced decomposition.

4.14. Compound (19)

50 mg (0.044 mmol) of ethynyl functionalized compound **17** and 244 mg (0.701 mmol) of azide **5** were dissolved in THF. To the solution were added 17 mg (0.088 mmol) sodium ascorbate, 23 mg (0.044 mmol) TBTA, 1 mL triethylamine and 11 mg (0.044 mmol) $CuSO_4 \cdot 5H_2O$. The solution was stirred at room temperature for 16 h. The yellow solution was purified by column chromatography using firstly a mixture of hexane and ethyl acetate (4:1) and then THF as eluent. After removal of the solvent in vacuum, the crude product was dissolved in methylene chloride, precipitated in hexane, filtered, dried, dissolved in chloroform and purified by recycling GPC to afford 88 mg (0.022 mmol, 51%) of the compound as a colorless powder. ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K) δ 8.30 (s, 4H, H_c), 7.91 (d, 3JHH=8.5 Hz, 8H, H_a), 7.85 (s, 8H, H_d), 7.83 (s, 16H, H_g), 7.76 (d, 3JHH=7.3 Hz, 16H, H_h), 7.53 (d, 3JHH=8.5 Hz, 8H, H_b), 7.52 (t, 3JHH=7.7 Hz, 16H, H_i), 7.46 (s, 8H, H_f), 7.45 (t, 3JHH=7.4 Hz, 8H, H_j), 7.35–7.31 (m, 48H, H_k+H_m), 7.28–7.25 (m, 32H, H_l), 1.71 (s, 12H, H_e). ^{13}C NMR (176 MHz, CD_2Cl_2, 298 K) δ 148.29 (C), 147.22 (C), 145.76 (C), 143.77 (C), 141.08 (C), 139.94 (C), 138.44 (C), 135.34 (C), 135.29 (C), 133.22 (C), 132.45 (C), 132.13 (C–H, C_b), 129.62 (C–H, C_i), 129.33 (C–H, C_g), 129.01 (C–H, C_k), 128.97 (C–H, C_l), 128.90 (C–H, C_j), 128.45 (C–H, C_m), 127.87 (C–H, C_h), 127.13 (C–H, C_f), 125.78 (C–H, C_a), 121.17 (C–H, C_d), 118.47 (C–H, C_c), 18.37 (CH_3, C_e) MALDI-

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TOF (m/z): calcd for $C_{269}H_{184}N_{36}$: 3919.6, found: no signal due to UV laser induced decomposition.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.03.037.

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