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Sourfold Diels-Alder Reaction of Tetraethynylsilane

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Abstract: A series of ethynylated silanes, including tetraethynylsilane, was treated with tetraphenylcyclopentadienone at 300 °C under microwave irradiation to give the aromatized Diels–Alder adducts as sterically encumbered mini-dendrimers with up to 20 benzene rings. The sterically most congested adducts display red-shifted emission through intramolecular π - π interactions in the excited state.

Tetraethynylsilane (11) is now an easily produced and surprisingly stable, non-explosive material, accessible on gram scale.^[1a] It should be a powerful core for dendrimers or other spherical assemblies. Functional molecules with fourfold tetrahedral reactivity are known, but often not easily prepared, in contrast to 11.^[1b-f] The tetrayne 11 has been functionalized using organometallic fragments to give its dicobalt hexacarbonyl and similar complexes.^[2a] In addition a number of its derivatives have been studied in detail^[2b,c] while the parent compound 11 has been neglected so far—probably due to the explosive side products from the original syntheses.^[2d,e]

However, when we tried to perform more mainstream coupling reactions with **11**, such as Sonogashira or Hay reactions, the core collapsed. Attempts to metalate **11** using Lappert's reagent (Me₂NSnMe₃) or *n*BuLi followed by reaction with classic electrophiles, such as methyl iodide or tributylchlorostannane, also destroyed the scaffold. While nucleophilic exchange reactions of diethynylsilanes were observed in the past,^[3] the situation significantly worsens for **11**. Partially desilylated derivatives, even though now easily obtained, did not fare better in attempts for functionalization.

At that point we surmised that both electrophilic metal centers, but also bases induced catastrophic core failure. Consequently, thermal reactions such as Diels–Alder cycloadditions might work for **11**. To test our hypothesis, we prepared the thermally equally stable, but less sensitive silanes **8–10** with an increasing number of free alkyne units, employing reaction conditions successful for the preparation of **11** (Scheme 1). Separation by chromatographic columns is only necessary after deprotection and only for **8** and **9**, while **10** is sublimed

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Scheme 1. Preparation of the phenylethynyl silanes 8–10 and their reaction with tetraphenylcyclopentadienone 12.

for purification, similar to **11**, the synthesis of which is described elsewhere,^[1a] the alkynes are colorless and crystalline solids. While all of these are literature known, they have rarely been investigated or used as substrates for further functionalization. The ethynylated silanes were isolated and characterized. Compound **14** was claimed (1968) to form by boiling **9** in xylene with **12**^[4]—in our hands we did not observe formation of any product under these conditions.

We treated **8–10** with tetraphenylcyclopentadienone^[5a] to successfully isolate unsymmetrical, truncated Müllen-type^[5] mini-dendrimers **13–15**. While **13** and **14** formed in reasonable yields, the already sterically overcrowded mini-dendrimer **15** formed in only 5% yield. While the cycloaddition and decarbonylative aromatization of tetraphenylcyclopentadienone **12** is known, usually less drastic conditions are required.^[5] However, the cycloadditions work only at extreme temperature with microwave irradiation (300 °C) in sealed tubes and were carried out in diphenyl ether for that very reason (b.p. 258 °C).

The first approach to prepare **16a** is depicted in Scheme 2. We initially hoped to carry out the cycloaddition of **7**, as **11**



Scheme 2. Thermal reaction of tetraethynylsilane derivative 7 (prepared according to reference [1a]) with four equivalents tetraphenylcyclopentadienone 12 under ambient atmosphere results in cleavage of the central Si–C bonds and formation of 17.

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cannot be used—it is too volatile at these extreme temperatures. We anticipated that the TMS-groups would be cleaved eventually, but neither **16a** nor **16c** could be isolated. Reaction with sub-stoichiometric amounts of **12** (e.g., 1–3 equiv) did not show conversion to the expected products. Instead, the central Si–C bonds are cleaved. Compound **7** acts as a substitute for TMS-acetylene, and **17** is the only isolated product.

Using sealed tubes **11** reacted with **12** (Scheme 3) for 2 h under microwave irradiation ($300^{\circ}C$). The main product is the



Scheme 3. Reaction of tetraethynylsilane **11** (prepared according to reference [1a]) with tetraphenylcyclopentadienone **12**.

alkyne 16b (27%) and 16a (4%). The final cycloaddition is most demanding from a steric point of view. A longer reaction time does not increase but rather lowers the yield. Thermal decomposition is an issue especially for this last addition, as it apparently requires a high activation energy. Separation of 16a and 16b is difficult and could only be achieved using a dichloromethane (CH₂Cl₂) in petroleum ether (PE) gradient for chromatography, followed by a second purification column. The crude yield of 16a is 14%, but this fraction shows impurities in the alkane region. Repeated precipitation gave pure 16a at cost of the yield. Alkyne 16b itself is quite interesting as a bulky alkyne substituent and could be used to tune the film-forming properties of various organic electronic materials that are prone to crystallization, which is unfavorable in organic solar cells or for matrix materials.^[6] In further experiments, we could increase the raw yield (column) of 16a to 34%, while 16b was only formed as a trace product. Experiments to increase the yield of 16b by reacting 11 with only three equivalents of 12 failed-the yield remained almost constant compared to our initial synthesis. Compound 16a is crowded according to DFT calculations (see Figure 1), probably more than other oligophenyl compounds known so far. Figure 1 shows the crowding at the silicon center testified to by the elongated central Si-C_{Ar} bond that stretches from 1.90 to 1.93 Å. This makes 16a fundamentally interesting as a core for dendrimers, if a more sophisticated tetracyclone derivative is used.

Figure 2 shows the aromatic regions of the ¹H NMR spectra of oligophenyl compounds **13–16a**. The single proton at the tetraphenylbenzene ring shows as a singlet between 7.4 and 7.8 ppm for each compound. This single hydrogen atom is diagnostic for the increasing steric demand of the compounds, while the phenyl rings are successively substituted with tetraphenylbenzene groups. One notes a significant upfield shift when going from **13** to **16a**: 7.70 (**13**), 7.65 (**14**), 7.52 (**15**),



Figure 1. Molecular structure of tetrakis(1,2,3,4-tetraphenylphenyl)silane (**16***a*) according to DFT (B3LYP 6-31G*//B3LYP 6-31G*) geometry optimization. Left: Van der Waals model, right: stick model. The central Si–C bond length is 1.93 Å. In tetraphenylsilane the analogous bond is calculated to be 1.90 Å (DFT, B3LYP 6-31G*//B3LYP 6-31G*).



Figure 2. Aromatic region of the oligophenyl dendrimers (600 MHz, CD_2Cl_2). Spectra are normalized on the number of protons of the respective compound.

7.44 ppm (16a), well explained by the hydrogen atom being increasingly magnetically shielded when surrounded by bulky tetraphenylbenzene groups. This goes hand in hand with the broadening of the signal from 13-16a-another observation that is to be expected for increasing steric crowding. From Figure 1, we can see that the geometry optimized structure shows that the single hydrogen atom rests deep within the oligophenylene core. The broadening of this signal also suggests that the rotation slows down, at least in 16a. To test this hypothesis, we performed variable-temperature ¹H NMR spectra. In dichloromethane, when going from ambient temperature to -78 °C one can see broadening and split of the signals due to further restriction of rotation. If one heats the solutions of 16a in [D₂]tetrachloroethane, up to 100 °C, a significant sharpening of the signals is observed. Interestingly, the two NMR spectra taken at ambient temperature, one in dichloromethane and the other in tetrachloroethane, are surprisingly different, with the latter showing broadened signals (Figure 3). We assume that this is due the size of the solvent and its interaction with 16a. Overall, 16a must experience severe and solvent-dependent restricted rotation around its many phenyl-phenyl bonds.

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Figure 3. Temperature dependent ¹H NMR spectroscopy (500 MHz) of the aromatic reagion of compound 16a.

The absorption spectra of all of the cycloadducts are broad and featureless (see Supporting Information). The emission of **13** and **15** resemble that of *o*-terphenyl and *p*-terphenyl, the innate chromophores of the structures (Figure 4); the bands of **16a** and particularly **14** are broadened and spread well into the visible (blue). This is unexpected when looking at the molecular structure. Particularly the emission of **14** looks different



Figure 4. Normalized emission spectra of oligophenyl compounds **13–16a**. For comparison, the spectra of biphenyl and *o/p*-terphenyl are included. Excitation wavelength 275 nm (for the absorption spectra see Supporting Information).



Figure 5. Left: calculated DFT ground state structure of **14** (B3LYP 6-31G*). Well visible (circle) is the overlap of a phenyl ring positioned on the Si center with the phenyl group of a tetraphenylbenzene unit. Right: **14** dissolved in 1,3-dichlorobenzene and irradiated with 365 nm light. Top: room temperature, bottom: 170 °C.

from that of the other oligomers-quantum chemical calculations give a hint why this could be (Figure 5). A phenyl group attached to the Si center lies almost parallel to a second phenyl ring, part of a tetraphenylbenzene dendrimer arm with the ring planes showing distances of 3.3-3.8 Å between them according to ground state quantum chemical calculations. In the excited state, we presume that an exciton which is localized on the interacting tetraphenylbenzene ring is also stabilized by the nearby phenyl ring, therefore leading to something akin to an intramolecular heteroexcimer, stabilizing the excited state of 14 significantly, and leading to the observed, broadened, red-shifted emission feature. Following this hypothesis, the fluorescence intensity should decrease upon heating due to the thermal activation of the constricted rotations-thus destabilizing the exited state. This feature that can indeed be observed when heating a solution of 14 in 1,3-dichlorobenzene from ambient temperature to 170°C. Following image analysis (see Supporting Information), the fluorescence decreased to approximately half of its initial value (Figure 5).

In the solid state (Figure 6) compound **13** is non fluorescent, but the sterically more congested derivatives **14**, **15**, and **16a** display a moderately intense, blue fluorescence. The fluorescence is similar to that observed for **14–16a** in solution. We assume that in the solid state the conformation of the phenyl rings is frozen and that—in the excited state—there are signifi-



Figure 6. Appearance of 13–16 a. Top row: normal light. Bottom row: Fluorescence color of the materials while irradiated with 365 nm UV light.

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cant enforced π - π interactions which stabilize the excited state and lead to the observed blue emission. The phenyl groups will also suppress intermolecular interactions, which otherwise would deactivate the excited state through several different decay pathways. The exact mechanism, however, is difficult to unravel at the moment.

In conclusion, multiply ethynylated silanes react with tetraphenylcyclopentadienone to give stable and isolable yet sterically encumbered mini-dendrimers such as **16a** or **14**. Thermal reactions are the only way to functionalize compounds such as **11**; other reactions failed in our hands. This is the first time that tetraethynylsilane (**11**) was fully functionalized. Apparently, even drastic conditions can be applied to force **11** and related derivatives into reactions. The steric overcrowding leads to unusual red-shifted emission spectra in **16a** and **14**; in the excited state, the substituents separated by the silicon center must interact to a significant extent. In the future we aim to build up more complex mini-dendrimers using **11** with substituted and functional tetraarylcyclopentadienones. Simplicity of synthesis and, therefore, accessibility make **11** a promising core for the construction of further materials.

Experimental Section

All reagents and solvents were obtained from ABCR, Sigma-Aldrich, VWR or Grüssing GmbH and were used without further purification. Preparation of air- and moisture-sensitive materials was carried out in flame-dried flasks under an atmosphere of nitrogen by using Schlenk techniques. Thin-layer chromatograms were obtained using polygram-TLC-plates (40×80 mm, SIL G/UV254, 0.2 mm layer thickness, Macherey-Nagel). For reactions carried out in a microwave, an Anton Paar Microwave Synthesis Reactor Monowave 300 was used. For column chromatography the Isolera Prime flash system with self-packed columns (SiO₂, grain size 0.04-0.063 mm, Macherey-Nagel) was used. Melting points were determined with a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK) and reported uncorrected. ¹H and ¹³C spectra were recorded on Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz), Bruker Avance 500 (500 MHz), or Bruker Avance 600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts million (ppm) relative to traces of CHCl₃ per or [D₂]dichloromethane in the deuterated solvent. Coupling constants (J) are reported in Hz. All NMR spectra were integrated and processed by using TopSpin 3.0 (Bruker). MS spectra were recorded on a Vacuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometers. Infrared (IR) spectra are reported in wavenumbers (cm⁻¹) and were recorded on a Jasco FT/IR-4100 spectrometer. Semi-empirical calculations were carried out using Spartan 10, Version 1.1.0. 7 and 11 were prepared according to literature.^[1]

For Figure 5 a solution of **14** (2.7 mg) in 1,3-dichlorobenzene (2 mL) was prepared and irradiated with 365 nm UV light. Photographs were acquired with a Canon EOS 7D fitted with a Canon Macro Lens EF-S 60 mm, both images were acquired with a shutter speed of 0.25 s, aperture F2.8 and ISO100 (color space sRGB).

Synthesis and characterization

General procedure (GP1) for the synthesis of 4–6: A solution of trimethylsilyl acetylene (1.10 equiv per chlorine) in dry diethyl ether (50 mL) was cooled to -78 °C. *n*-Butyllithium (2.5 μ in

hexane; 1.05 equiv) was slowly added and the solution warmed up to 0 °C. After being stirred for 1 h, the respective phenylchlorosilane (1 equiv) was added to the solution followed by the reaction turning opaque. The mixture was slowly allowed to warm to ambient temperture, while being stirred overnight. Deionized water (50 mL) was added, the mixture stirred for an additional 5 min. The now clear organic layer was separated from the aqueous layer, which was extracted with diethyl ether (3×100 mL). The combined organic layers were dried over anhydrous magnesium sulfate, the solvent removed under reduced pressure. The product was crystallized from hot hexane.

(*Trimethylsilyl*)*ethynyltriphenylsilane* (4): Prepared according to GP1. *n*-Butyllithium (1.42 mL, 3.56 mmol, 1.05 equiv 2.5 м hexane solution) was added to trimethylsilyl acetylene in diethyl ether (531 μL, 3.37 mmol, 1.10 equiv). A solution of chlorotriphenylsilane (1.00 g, 3.39 mmol, 1.00 equiv) in dry diethyl ether (10 mL) was added to the acetylide solution. After crystallization, **4** was obtained (colorless crystals, 1.18 g, 4.00 mmol, 98%). *R*_f (petroleum ether/ethyl acetate 2:1)=0.79; m.p. 67 °C; ¹H NMR (300.51 MHz, CDCl₃, 25 °C): δ =7.70–7.63 (m, 6H), 7.51–7.35 (m, 10H), 0.27 ppm (s, 9H); ¹³C NMR (75.76 MHz, CDCl₃, 25 °C): δ =135.56, 133.48, 129.86, 127.92, -0.16 ppm; IR (neat): $\tilde{\nu}$ =3067 (w), 3049 (w), 2961 (w), 2898 (w), 2103 (w), 1428 (m), 1248 (m), 1112 (s), 839 (s), 768 (s), 761 (s), 739 (s), 707 (s), 694 (s), 677 (m), 502 cm⁻¹ (s). Spectral data in agreement to reported literature.^[7,8]

Bis((trimethylsilyl)ethynyl)diphenylsilane (**5**): Prepared according to GP1. *n*-Butyllithium (3.24 mL, 8.10 mmol, 2.10 equiv, 2.5 м hexane solution) was added to trimethylsilyl acetylene in diethyl ether (1.18 mL, 8.29 mmol, 2.20 equiv). Dichlorodiphenylsilane (831 μL, 3.95 mmol, 1.00 equiv) was added to the acetylide solution. After crystallization, **5** was obtained (colorless crystals, 1.30 g, 5.14 mmol, 87%). *R*_f (petroleum ether/ethyl acetate 2:1)=0.81; m.p. 64°C, ¹H NMR (300.51 MHz, CDCl₃, 25°C): δ =7.78-7.72 (m, 4H), 7.45-7.35 (m, 6H), 0.24 ppm (s, 9H); IR (neat): $\tilde{\nu}$ =3067 (w), 3049 (w), 2961 (w), 2899 (w), 2109 (w), 1429 (m), 1249 (m), 1110 (m), 840 (m), 759 (m), 740 (m), 694 (s), 501 (m), 495 (m), 489 (m), 484 cm⁻¹ (m). Spectral data in agreement to reported literature.^[9,10]

Tris((*trimethylsily*))*ethyny*)*pheny*/*silane* (**6**): Prepared according to GP1. *n*-Butyllithium in hexane (5.96 mL, 14.9 mmol, 3.15 equiv, 2.50 м hexane solution) was added to trimethylsilyl acetylenein diethyl ether (2.22 mL, 15.6 mmol, 3.30 equiv). Chlorotriphenylsilane (755 μL, 4.73 mmol, 1.00 equiv) was added to the acetylide solution. After crystallization, **6** was obtained (colorless crystals, 1.78 g, 4.49 mmol, 95%). *R*_f (petroleum ether/ethyl acetate 2:1)=0.83; m.p. 114°C; ¹H NMR (500.13 MHz, CDCl₃, 25°C): δ =7.85–7.78 (m, 2H), 7.50–7.39 (m, 3H), 0.22 ppm (s, 27 H); ¹³C NMR (125.77 MHz, CDCl₃): δ =134.48, 131.55, 130.44, 128.00, 117.85, 105.05, -0.45 ppm; MS (El⁺): *m/z* calcd for C₄₈H₃₆Si: 396.1581 [*M*]⁺; found: 396.1569, correct isotope distribution; IR (neat): $\tilde{\nu}$ =3072 (w), 3056 (w), 2962 (w), 2898 (w), 2115 (w), 1428 (w), 1251 (m), 1112 (m), 836 (m), 780 (m), 757 (s), 740 (m), 694 (s), 497 (s), 494 cm⁻¹ (s). Spectral data in agreement to reported literature.^[9]

Ethynyltriphenylsilane (8): Compound **4** (684 mg, 1.92 mmol) was dissolved in methanol/THF (1:1, 100 mL). Potassium carbonate (663 mg, 4.80 mmol, 2.50 equiv) was added and the solution stirred for 15 min before water (100 mL) was added. The aqueous phase was extracted with dichloromethane (5×100 mL); the combined organic layers were dried over anhydrous magnesium sulfate the solvent evaporated. Crude **8** was purified by column chromatography (SiO₂, petroleum ether/ethyl acetate), *R*_f (petroleum ether/ethyl acetate 3:1)=0.69, to yield a colorless solid (343 mg, 1.21 mmol, 63%). ¹H NMR (400.33 MHz, CDCl₃, 25 °C): δ =7.68–7.63 (m, 6H), 7.49–7.38 (m, 9H), 2.50 ppm (s, 1H); ¹³C NMR (100.64 MHz, CDCl₃,

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25 °C) δ = 135.17, 134.99, 130.12, 127.93 ppm; IR (neat): $\tilde{\nu}$ = 3287, 3266, 3074, 3056, 2039, 1430, 1113, 690, 668, 650, 573 cm⁻¹. Spectral data in agreement to reported literature.^[10]

Diethynyldiphenylsilane (9): Compound 5 (500 mg, 1.33 mmol) was dissolved in dry dichloromethane (5 mL) in a flame dried Schlenk flask under nitrogen atmosphere. The solution was cooled to $0\,^\circ\text{C}$ and triflic acid (234 $\mu\text{L},$ 2.65 mmol, 2.00 equiv) was added slowly through a syringe. The brownish solution was allowed to warm up to ambient and stirred under light protection for 16 h. After addition of deionized water (100 mL) and extraction with pentane (3×100 mL), the combined organic layers were dried over anhydrous magnesium sulfate. Solvent removal reduced pressure is followed by Kugelrohr distillation. A heat gradient from 190 $^\circ\text{C}$ to -78°C at 1.1 mbar was applied. A slightly reddish liquid condensed as the room temperature fraction, which was purified by column chromatography (SiO₂, petroleum ether/ethyl acetate) yielding 9 (colorless solid, 163 mg, 705 µmol, 53%). R_f (petroleum ether/ethyl acetate 2:1) = 0.63; ¹H NMR (300.51 MHz, CDCl₃, 25 $^{\circ}$ C): $\delta =$ 7.89–7.80 (m, 4H), 7.55–7.40 (m, 6H), 2.79 ppm (s, 2H); IR (neat): $\tilde{v} = 3281$ (m), 3072 (w), 3036 (w), 2049 (s), 1255 (m), 1080 (s), 1060 (s), 842 (s), 714 (s), 680 (s), 615 (s), 610 cm⁻¹ (s); Spectral data in agreement to reported literature.[3,6,9]

Triethynylphenylsilane (10): Compound 6 (500 mg, 1.26 mmol) was dissolved in dry dichloromethane (5 mL) in a flame-dried Schlenk flask under nitrogen atmosphere. The solution was cooled to 0 $^\circ\text{C}$ and triflic acid (334 μL 3.78 mmol, 3.00 equiv) was slowly added through a syringe. The now brownish solution brought to ambient and stirred under light protection for 16 h. Deionized water (100 mL) was added and the mixture intensively shaken in an extraction funnel, upon which the organic phase lost its brown color but remained slightly beige. The aqueous phase was extracted with pentane (3×100 mL) and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give an off-white crystalline solid, purified by Kugelrohr distillation applying a heat gradient from 85 °C to -78 °C at 7.4×10^{-1} mbar. Compound **10** condensed at the ambient fraction (colorless needles, 143 mg, 793 µmol, 59%). ¹H NMR (300.51 MHz, CDCl₃, 25 °C): δ = 7.87–7.80 (m, 2 H), 7.56-7.42 (m, 3H), 2.70 ppm (s, 3H); ¹³C NMR (75.57 MHz, CDCl₃, 25 °C): $\delta = 134.30$, 131.19, 128.35, 96.75, 81.82 ppm; MS (El⁺): m/zcalcd for C₁₂H₈Si: 180.0395 [M]⁺; found: 396.1581, correct isotope distribution. Spectral data in agreement to reported literature.^[2e,9]

General procedure (GP2) for the cycloaddition of 12 with ethynylphenylsilanes 8–10 and 11: Compounds 8–10 or 11 and 1.00 equiv 12 per alkyne unit were dissolved in diphenyl ether under nitrogen atmosphere. While being stirred for 1 h (8–10) or 2 h (11) in a microwave, the reaction mixture turned from magenta to brown. After cooling to ambient, the solvent was removed using a Kugelrohr apparatus. The crude product was purified by column chromatography (SiO₂, petroleum ether/dichloromethane) and, for further purification, precipitated several times from dichloromethane by addition of methanol.

1,2,3,4-(*Tetraphenylphenyl*)*triphenylsilane* (**13**): Prepared according to GP2. Compounds **8** (150 mg, 527 µmol) and **12** (203 mg, 527 µmol, 1.00 equiv) were reacted in diphenyl ether (5 mL). Column chromatography yielded a yellowish solid (R_f (petroleum ether/dichloromethane 5:1)=0.46), further purified by repeated precipitation (3×) by dissolving the material in dichloromethane (2 mL) and adding methanol (10 mL) to give a colorless, blue fluorescent (irradiated with 365 nm) solid (181 mg, 279 µmol, 53%). M.p. 189°C, ¹H NMR (600.25 MHz, CD₂Cl₂, 25°C): δ =7.70 (s, 1H), 7.51–7.48 (m, 6H), 7.35–7.31 (m, 3H), 7.27–7–25 (m, 6H), 7.11–7.06 (m, 3H), 7.06–7.02 (m, 2H), 6.94–6.91 (m, 3H), 6.90–6.86 (m, 2H),

6.80–6.75 (m, 3H), 6.71–6.40 (m, 2H), 6.68–6.64 (m, 1H), 6.56–6.53 (m, 2H), 6.49–6.44 ppm (m, 2H); ¹³C NMR (150.95 MHz, CD₂Cl₂, 25 °C): δ = 149.22 (Cq), 152.58 (Cq), 142.48 (Cq), 142.06 (Cq), 141.54 (Cq), 141.00 (Cq), 140.81 (Cq), 139.79 (CH), 139.77 (Cq), 136.69 (CH), 135.85 (CH), 133.12 (CH), 131.91 (CH), 131.87 (CH), 131.51 (CH), 130.43 (CH), 129.48 (CH), 128.07 (CH), 128.02 (CH), 127.34 (CH), 126.82 (CH), 126.58 ppm (CH); HR-MS (DART⁺): *m/z* calcd for C₄₈H₃₆Si: 640.2586 [*M*]⁺; found: 658.2925 [*M*+NH₄]⁺; found: 658.2934, correct isotope distribution; *m/z* calcd for C₄₈H₄₀NSi: 658.2925 [*M*+NH₄]⁺; found: 658.2934, correct isotope distribution; *m/z* calcd for C₄₈H₄₀NSi: 658.2925 [*M*+NH₄]⁺; found: 658.2934, correct isotope distribution; *m/z* calcd for C₄₈H₄₀NSi: 658.2925 [*M*+NH₄]⁺; found: 658.2934, correct isotope distribution; *IR* (neat): $\ddot{\nu}$ = 3058 (w), 3020 (w), 1428 (m), 1111 (m), 740 (m), 694 (s), 502 cm⁻¹ (s).

Bis(1,2,3,4-tetraphenylphenyl)diphenylsilane (14): Prepared according to GP2. Compounds 9 (95.0 mg, 409 µmol, 1.00 equiv) and 12 (314 mg, 818 µmol, 2.00 equiv) were reacted in diphenyl ether (7 mL). Column chromatography yielded a yellowish solid ($R_{\rm f}$ (petroleum ether/dichloromethane 5:1)=0.52), which was then purified by repeated precipitation (3×) by dissolving the material in dichloromethane (2 mL) and adding methanol (10 mL) to give a colorless, blue fluorescent (irradiated with 365 nm) solid (107 mg, 114 μmol, 28%). m.p. 205 °C ¹H NMR (600.25 MHz, CD₂Cl₂, 25 °C): δ = 7.65 (s, 2 H), 7.36–7.33 (m, 4 H), 7.27–7.23 (m, 2 H), 7.20–7.16 (m, 4H), 7.15-7.09 (m, 6H), 7.07-7.04 (m, 4H), 6.95-6.92 (ml, 6H), 6.88-6.84 (m, 4H), 6.82-6.76 (m, 8H), 6.73-6.69 (m, 8H), 6.66-6.62 ppm (m, 4 H); ^{13}C NMR (150.95 MHz, CD_2Cl_2, 25 °C): $\delta\,{=}\,147.73$ (Cq), 142.63 (Cq), 142.35 (Cq), 142.01 (Cq), 141.54 (Cq), 141.24 (Cq), 140.92 (Cq), 139.39 (Cq), 139.33 (CH), 137.12 (CH), 136.63 (Cq), 134.16 (Cq), 131.98 (CH), 131.92 (CH), 131.85 (CH), 130.56 (CH), 128.98 (CH), 127.93 (CH), 127.64 (CH), 127.32 (CH), 126.83 (CH), 126.59 (CH), 126.50 (CH), 126.05 (CH), 125.47 ppm (CH); HR-MS (DART⁺):m/z calcd for C₇₂H₅₂Si: 944.3838 [M]⁺; found: 944.3894, correct isotope distribution; m/z calcd for C₇₂H₅₆NSi: 962.4177 [M+ $[NH_4]^+$; found: 962.4208, correct isotope distribution; IR (neat): $\tilde{\nu} =$ 3052 (w), 3022 (w), 1600 (w), 1491 (w), 1441 (m), 1428 (m), 1098 (m), 1071 (m), 1019 (m), 795 (m), 760 (m), 693 (s), 635 (m), 514 (m), 500 (s), 489 (m), 485 cm⁻¹ (m).

Tris(1,2,3,4-tetraphenylphenyl)phenylsilane (15): Prepared according to GP2. Compounds 10 (100 mg, 555 $\mu mol,$ 1.00 equiv) and 12(640 mg, 1.66 mmol, 3.00 equiv) were reacted in diphenyl ether (15 mL). Column chromatography yielded a yellowish solid (R_f (petroleum ether/dichloromethane 5:1)=0.68) which was then purified by repeated precipitation (3×) by dissolving the material in dichloromethane (2 mL) and adding methanol (10 mL) to give a colorless, blue fluorescent (irradiated with 365 nm) solid (35.9 mg, 27.8 μmol, 5%). M.p. 274°C; ¹H NMR (600.25 MHz, CD₂Cl₂, 25°C): $\delta =$ 7.52 (s, 3 H), 7.22–7.18 (m, 1 H), 7.12–7.09 (m, 9 H), 7.09–7.06 (m, 2H), 7.04-7.01 (m, 2H), 6.95-6.92 (m, 6H), 6.92-6.89 (m, 9H), 6.82-6.78 (m, 6H), 6.78-6.73 (m, 9H), 6.69-6.66 (m, 6H), 6.66-6.63 (m, 9H), 6.60-6.56 ppm (m, 6H); ¹³C NMR (150.95 MHz, CD₂Cl₂, 25 °C): $\delta =$ 142.65 (Cq), 142.41 (Cq), 141.99 (Cq), 141.48 (Cq), 141.06 (Cq), 140.97 (Cq), 139.66 (CH), 138.71 (Cq), 137.77 (CH), 136.72 (Cq), 134.91 (Cq), 132.16 (CH), 132.02 (CH), 131.89 (CH), 130.78 (CH), 128.78 (CH), 127.85 (CH), 127.32 (CH), 127.24 (CH), 126.73 (CH), 126.64 (CH), 126.35 (CH), 125.96 (CH), 125.34 ppm (CH); HR-MS (DART⁺): *m/z* calcd for C₉₆H₆₈Si: 1249.5124 [*M*]⁺; found: 1249.5115, correct isotope distribution; m/z calcd for C₉₆H₇₂NSi: 1267.5426 $[M + NH_4]^+$; found: 1267.5412, correct isotope distribution; m/zcalcd for C₉₆H₇₂NOSi: 1283.5411 [*M*+NH₄+O]⁺; found: 1283.5401; IR (neat): $\tilde{v} = 3052$ (w), 3017 (w), 1598 (w), 1491 (w), 1441 (w), 1426 (w), 1364 (w), 1072 (w), 1017 (w), 759 (m), 693 (s), 506 cm⁻¹ (m).

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Tetrakis(1,2,3,4-tetraphenylphenyl)silane (16a) and ethynyltris(1,2,3,4tetraphenylphenyl)silane (16b): Prepared according to GP2.Compounds 11 (8.25 mg, 64.3 µmol, 1.00 equiv) and 12 (99.0 mg, 257 µmol, 4.00 equiv) were dissolved in diphenyl ether (5 mL). Column chromatography yielded two yellowish solids (R_f (petroleum ether/dichloromethane 1:1) = 0.64 (16b), 0.71 (16a)). Each fraction was subjected to chromatography again (same eluent). Crude 16a was obtained as off-white solid (28 mg, 18.3 µmol, 14%). To obtain pure material, 16a was repeatedly precipitated (3×) by dissolving in dichloromethane (2 mL) and adding methanol (10 mL) to a give a colorless, blue fluorescent (irradiated with 365 nm) 16a: (4.00 mg, 2.58 μmol, 4%). Alkyne **16b**: (26.0 mg, 17.4 μmol, 26%). Optimized conditions for 16a: Compounds 11 (51 mg, 398 µmol, 1.00 equiv) and 12 (612 mg, 1.59 mmol, 4.00 equiv) were dissolved in diphenyl ether (2 mL) and heated in a sealed tube to 300 °C for 2 h in a reaction microwave Crude 16a was obtained as off-white solid (213 mg, 137 µmol, 34%). Traces of 16b were removed by a single column (eluent as above). Purification by repeated precipitation from dichloromethane with methanol yielded 16a (107 mg, 97 μmol). *R*_f=0.71; m.p. 175 °C; ¹H NMR (600.25 MHz, CD₂Cl₂, 25 °C): δ = 7.44 (s, 4 H), 7.20–7.10 (m, 12 H), 6.95–6.87 (m, 21 H), 6.86–6.82 (m, 8H), 6.74-6.68 (m, 12H), 6.65-6.57 (m, 19H), 6.51-6.46 ppm (m, 8H); ¹³C NMR (150.95 MHz, CD₂Cl₂, 25 °C): $\delta = 146.73$ (Cq), 142.84 (Cq), 142.54 (Cq), 141.62 (Cq), 141.30 (Cq), 141.22 (Cq), 141.00 (Cq), 138.59 (Cq), 132.62 (CH), 131.99 (CH), 131.92 (CH), 130.82 (CH), 127.82 (CH), 127.22 (CH), 126.64 (CH), 126.32 (CH), 126.15 (CH), 125.93 (CH), 125.20 ppm (CH); HR-MS (DART⁺): *m/z* calcd for C₁₂₀H₈₄Si: 1553.6376 [M]⁺; found:1553.6375, correct isotope distribution; m/z calcd for C₁₂₀H₈₈NSi: 1571.6714 [*M*]⁺; found: 1571.6636, correct isotope distribution; m/z calcd for C₁₂₀H₈₈NOSi: 1587.6663 [*M*+NH₄+O]⁺; found: 1587.6625, correct isotope distribution; m/z calcd for $C_{120}H_{88}NO_2Si$: 1603.6612 $[M + NH_4 + 2O]^+$; found: 1603.6584, correct isotope distribution; m/z calcd for C₁₁₄H₈₄NSi: 1495.6401 [*M*+NH₄-Ph]⁺; found: 1495.6407, correct isotope distribution; IR (neat): $\tilde{\nu} = 3052$ (w), 3022 (w), 1071 (m), 695 cm⁻¹ (s).

Data for ethinyltris(1,2,3,4-tetraphenylphenyl)silane (**16b**): $R_{\rm f}$ =0.64. m.p. 180 °C (decomp); ¹H NMR (600.25 MHz, CD₂Cl₂, 25 °C): δ =7.50 (s, 3 H), 7.20–7.10 (m, 10 H), 7.04–6.96 (m, 6 H), 6.95–6.87 (m, 16 H), 6.85–6.73 (m, 23), 6.73–6.67 (m, 6 H), 2.08 ppm (s, 1 H); ¹³C NMR (150.95 MHz, CD₂Cl₂, 25 °C): δ =147.35 (Cq), 142.622 (Cq), 141.88 (Cq), 141.66 (Cq), 141.60 (Cq), 141.16 (Cq), 140.89 (Cq), 139.28 (Cq), 139.17 (CH), 133.40 (Cq), 132.15 (CH), 131.98 (CH), 131.81 (CH), 130.58 (CH), 127.90 (CH), 127.27 (CH), 126.83 (CH), 126.74 (CH), 126.68 (CH), 126.50 (CH), 126.04 (CH), 125.51 (CH), 97.83 (CH), 86.73 ppm (Cq); HR-MS (DART⁺): *m/z* calcd for C₉₂H₆₄Si: 1196.4777 [*M*]⁺, found: 1196.4755, correct isotope distribution; *m/z* calcd for C₉₂H₆₈NSi: 1214.5116 [*M*+NH₄]⁺; found: 1214.5067, correct isotope distribution; m/z calcd for C₉₂H₆₈NOSi: 1231.5099 [M+NH₄+O]⁺; found: 1231.5092, correct isotope distribution; IR (neat): $\tilde{\nu}$ =3281 (w), 3053 (w), 3023 (w), 2036 (w), 694 cm⁻¹ (s).

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Keywords: dendrimer · Diels-Alder reaction · ethynyl · oligophenyl · silane

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COMMUNICATION

Thermal enforcement: Naked tetraethynylsilane reacts with tetracyclone at 300 °C under microwave addition to give the sterically hindered fourfold cycloaddition product (see figure).



Diels-Alder Reaction

F. L. Geyer, A. Rode, U. H. F. Bunz*



Fourfold Diels-Alder Reaction of Tetraethynylsilane