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Dendritic and Hyperbranched Polyphenylenes via a simple Diels-Alder Route

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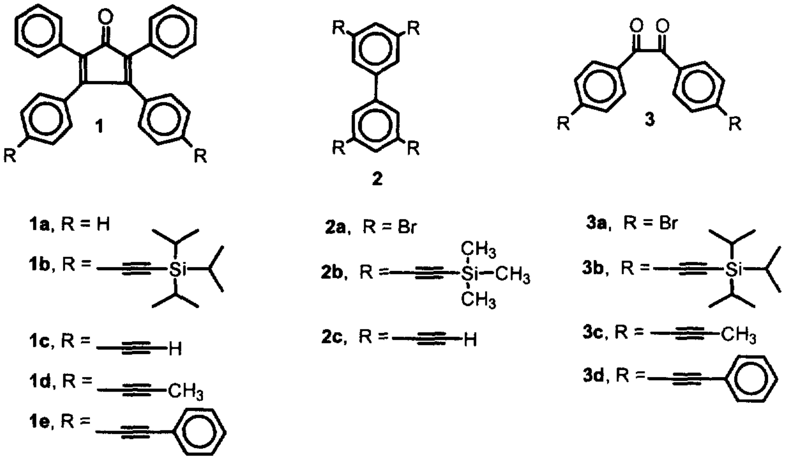
Abstract: A Diels-Alder route to dendritic and hyperbranched polyphenylenes, based on hexa(penta)phenylbenzene units, is described. Using ethynyl-, propynyl- and phenylethynyl-substituted tetraphenylcyclopentadienones **1c-e**, hyperbranched polymers with molecular weights M_w as high as 107,000 g mol^{-1} are obtained. The new dendritic polyphenylene **5c** is synthesized starting from 3,3',5,5'-tetraethynylbiphenyl (**2c**) via a repetitive Diels-Alder-deprotection sequence, employing tetraphenylcyclopentadienones **1a** and **1b**. © 1997 Elsevier Science Ltd.

1. INTRODUCTION

The Diels-Alder reaction [1,2,3] has proved to be of outstanding value in modern organic synthesis. In addition to its major role in the total synthesis of natural products [4,5], the [2+4]cycloaddition has also achieved considerable impact on the synthesis of polymers. Initiated by the pioneering work of Stille et. al. [6], which has been revised recently [7], Diels-Alder polymersations are today an active field of research, due to the increasing interest in practical applications of the obtained materials. [8,9,10] In particular linear and hyperbranched polyphenylenes have been synthesized. For this purpose, [2+4]cycloadditions have a significant importance alongside aryl-aryl coupling methods. [11,12] Polyphenylene polymers are attractive due to their promising properties, such as thermal stability and film-forming capabilities.

We recently introduced 3,4-bis(4-triisopropylsilylethynyl-phenyl)-2,5-diphenylcyclopenta-2,4-dienone (**1b**) as a building block for the synthesis of a new type of nanosized hydrocarbon dendrimers such as **4a**, **5a** and **7** (Scheme 1, Scheme 2). [13,14] The key-step of our dendrimer synthesis was the [2+4]cycloaddition of **1b** to a core, such as 3,3',5,5'-tetraethynylbiphenyl (**2c**)

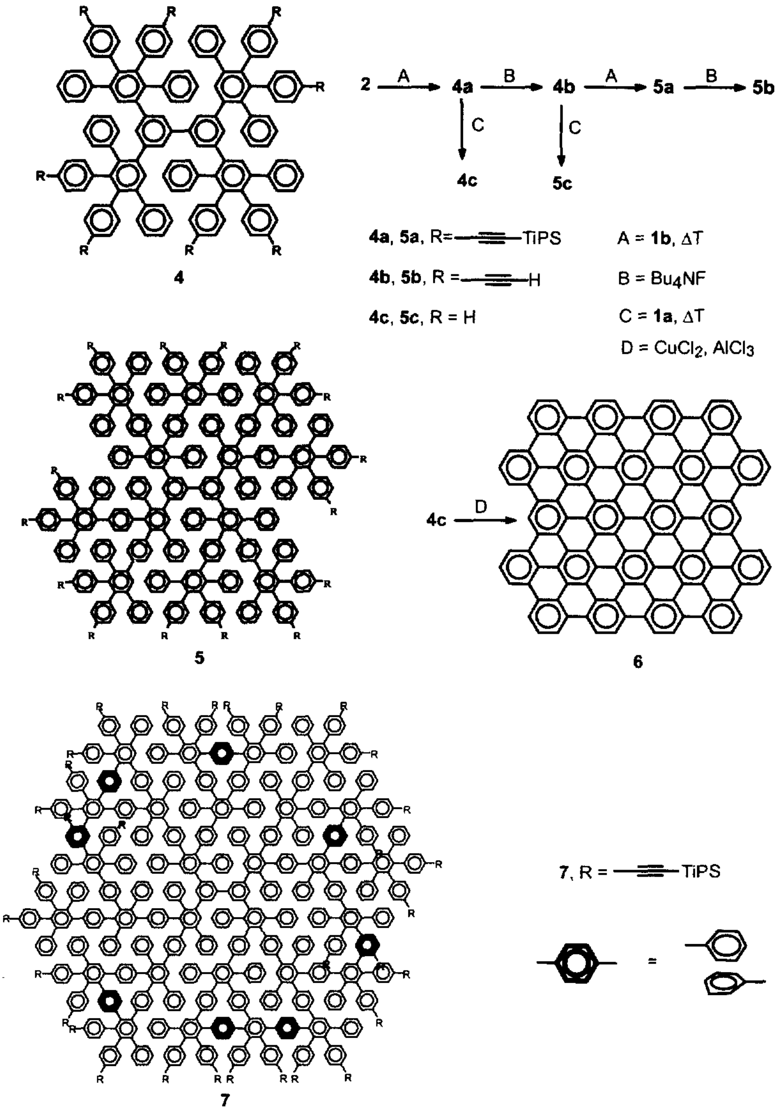
(Scheme 1). After cleavage of the triisopropylsilyl groups, the obtained oligoethynyl was ready for further Diels-Alder reactions. By this repetitive cycloaddition-deprotection sequence, the construction of dendrimer generations G_1 (**4a**), G_2 (**5a**) and G_3 (**7**) has been accomplished. As discussed below in detail, most noteworthy about this synthetic concept is that, for the first time, a polyphenylene dendrimer based upon pentaphenylbenzene units has been prepared.



Scheme 1: Tetraphenylcyclopentadienones, tetraethynylbiphenyl and benzils

Thereby, a very dense packing of 22, 62 and 142 benzene rings, in generations G_1, G_2 and G_3, respectively, could be created. As a consequence of the dense packing, the conformational mobility of the higher generations G_2 and G_3 was predicted to be limited. Indeed, molecular dynamic simulations of G_2 revealed that selected inner distances of the molecule varied only in the range of 5 -10 % during the simulations, thus indicating that the overall shape of the molecule did not significantly change throughout the simulation time. [14]

As part of our work directed towards monodisperse and polydisperse non-linear polyphenylenes with extremely dense packing of benzene rings, we describe here a new route to hyperbranched polyphenylenes **8a-c** and the synthesis of the new dendritic polyphenylene **5c** [15].



Scheme 2: Concept for dendrimer synthesis which provides an entry to monodisperse polyphenylenes and to extremely large PAHs. Overlapping phenyl rings in the 2 D projection of 7 are darkened.

The high packing density of benzene rings distinguishes our polyphenylenes from those previously obtained by common aryl-aryl coupling methods [16]. While synthetic routes using Grignard reagents or Kumada's procedure, for example, suffer from low yields and sideproducts [17], the method according to Suzuki provided an access to hyperbranched [12c,12d] and dendritic polyphenylenes [17]. However, the palladium catalyzed coupling of arylboronic acids with aryl halides led only to materials based upon 1,3,5-linked triphenylbenzene units. Therefore, these materials possess less densely packed benzene ring architectures than the polyphenylenes presented here.

The compact packing of benzene rings is of considerable synthetic interest, since it enables intramolecular dehydrogenation reactions leading to polycyclic aromatic hydrocarbons (PAHs).

We have shown oligophenylenes, such as **4c**, to be precursors of extremely large PAHs, such as **6**, which are obtained by cyclodehydrogenation under Kovacic conditions (Scheme 2). [18,19] Here, we give experimental details for the synthesis of oligophenylene **4c** and its cyclodehydrogenation to PAH **6**.

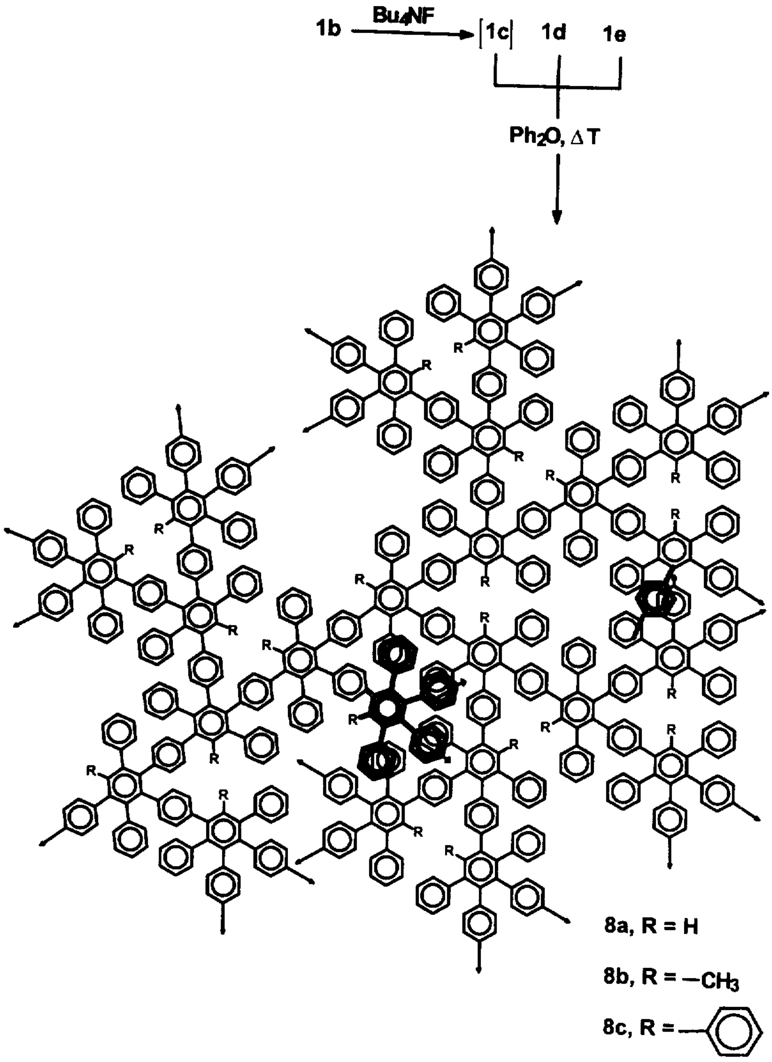
2. RESULTS AND DISCUSSION

2.1. Hyperbranched Polyphenylenes

Our approach rests on the fact that [2+4]cycloaddition of tetraphenylcyclopentadienone (**1a**) with di(mono)phenylacetylene leads to hexa(penta)phenylbenzene. [20] Having this principle in mind, we choose the tetraphenylcyclopentadienones **1c**-**1e** as starting compounds for the synthesis of hyperbranched polyphenylenes. The cyclopentadienones applied contain a diene function and two dienophile functions and can thus be considered as AB_2-building blocks. Accordingly, repetitive intermolecular Diels-Alder reactions of **1c**, **1d** or **1e** lead to extensively branched polyphenylenes **8a**, **8b** and **8c** under extrusion of carbon monoxide (Scheme 3). The created hyperbranched architectures are based upon hexa(penta)phenyl-substituted benzene units. The three phenyl substituents in the 1-, 2- and 4-position of this hexa(penta)phenylbenzene units are linked via their para-positions with the next hexa(penta)phenylbenzene units. As a result of the 1:2 stoichiometry of diene and dienophile in monomers **1c**-**1e**, the resulting polymers **8a**, **8b** and **8c** represent a poly(ethynyl)-, a poly(methylethynyl)- and a poly(phenylethynyl)-substituted polyphenylene, respectively.

Polymerization of the A_2B-monomer **1c** is achieved by heating a mixture of one equivalent **1b** with two equivalents of tetrabutylammonium fluoride (Bu_4NF) in diphenylether at 180 °C, thereby creating in situ the dienophiles for the following Diels-Alder reactions. Within 12 hours the reaction mixture changes its color from deep purple to redbrown, indicating that all monomer has disappeared. The monomers **1d** and **1e** are polymerized analogously by heating these cyclopentadienones in diphenylether to reflux. In the case of **1d**, the reaction is either stopped after the aforementioned change of color has taken place or when a noticeable amount of polymer has formed, according to TLC. Polymers **8a-c** are recovered by precipitation from toluene with ethanol. Characterization of the polymers is accomplished by size-exclusion chromatography (SEC) analysis, ^1H and ^{13}C NMR spectroscopy. Additionally, we use matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry. Due to the inherent physical principles of this method, it gives very accurate information about the low molecular weight fraction of the polymer distribution (see Table 1). [21]

The SEC analysis of polymers **8a-c** reflects a strong dependence of the obtained molecular weights upon the employed monomer. Consideration of entries [1], [2] and [5] of Table 1, in which lower monomer concentrations are used, reveals that the most reactive dienophile **1c** yields the highest molecular weight (polymer **8a**) after the shortest reaction time. The less reactive monomer **1e** (polymer **8c**) requires a reaction time 28 times longer than monomer **1c** (entries [1] and [5]). Despite the very long reaction time of entry [5], the molecular weight of polymer **8c** is much lower than that of polymer **8a** or **8b**. A comparison of entry [4] and [5] shows that the highest molecular weights are obtained if the reaction is not terminated until the monomer has reacted completely. When using the less reactive monomer **1e**, the resulting polymer weights increase dramatically with monomer concentration (entries [4] and [6]). Also the concentration of the more reactive monomer **1d** has a notable effect on the molecular weight of



*Scheme 3: Hyperbranched polymers: The nature of the endgroups (not shown in the scheme) is discussed in the text. Overlapping phenyl rings in the 2 D projection of **8a-c** are darkened.*

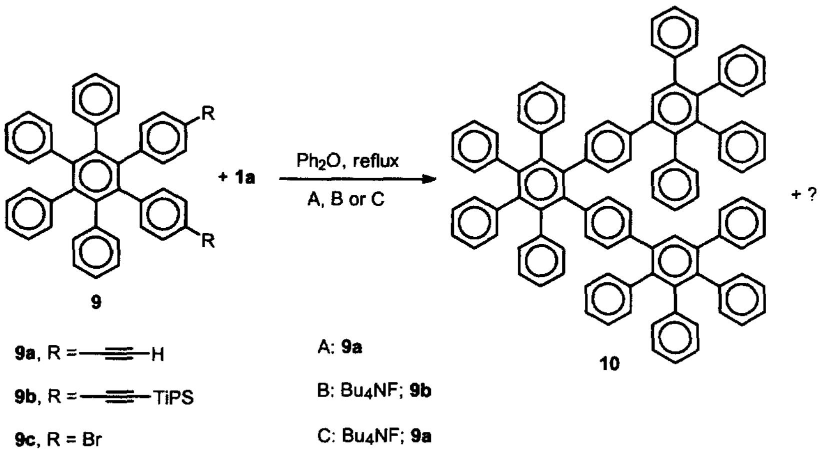
polymer **8b** (entries [2] and [3]). Characterization of polymethylethynyl **8b** and polyphenylethynyl **8c** is possible by ^{13}C NMR spectroscopy, IR spectroscopy and MALDI-TOF mass spectrometry. Due to the 1:2 stoichiometry of diene and dienophile, the characteristic resonances of the carbonyl carbon of the cyclopentadienone monomers, at about δ = 200 ppm in the ^{13}C NMR spectrum, disappear in these polymers. The resonances of the cyclopentadienones are replaced by a more complex aromatic region, caused by the increasing number of benzene rings. In accordance with the NMR data, the very intense absorption bands of the C=O vibration in the IR, in the range of 1700 to 1720 cm^{-1}, disappear or are extremely weak in all cases. The ^{13}C NMR spectra of polymers **8b** and **8c** show characteristic acetylene resonances at δ = 86.2 ppm, 80.1 ppm and δ = 90.5 ppm, 90.1 ppm. The 1:3 ratio of aliphatic and aromatic H atoms in monomer **1d** is not changed upon its polymerization to polymer **8b**. In agreement with this fact, the relative intensities of aliphatic and aromatic protons in the ^{1}H NMR spectrum of polymer **8b** exhibit a ratio of 1:3. The MALDI-TOF spectra of polymers **8b** and **8c** contain peaks which are in good agreement with the calculated *m/z* ratio of the polymers.

[entry] / monomer / polymer	monomer concentration [mol l^{-1}]	reaction time [h]	M_w[a] [g mol^{-1}]	M_n[a] [g mol^{-1}]	M_w / M_n	MALDI-TOF (highest detected species)
[1] / **1c**[b] / **8a**	0.0537 [c]	12	17046	2487	6.85	[d]
[2] / **1d** / **8b**	0.0542	12	11920	5245	2.27	18mer
[3] / **1d** / **8b**	0.434	12	95994	19585	4.90	18mer
[4] / **1e** / **8c**	0.0684	45	3048	1832	1.66	12mer
[5] / **1e** / **8c**	0.0684	336	5668	2632	2.15	15mer
[6] / **1e** / **8c**	0.342	45	107455	25089	4.28	15mer

[a] M_w, M_n determined with polystyrene as standard; [b] in-situ generated from **1b**; [c] assuming a quantitative deprotection of **1b** to **1c**; [d] nothing detectable

*Table 1: Results from SEC and MALDI-TOF-MS analysis for polymers **8a-c***

Characterization of the endgroups of polymer **8a** turns out to be more difficult. ^{1}H NMR spectroscopy fails to detect the characteristic signal for free acetylenic protons. The MALDI-TOF mass spectrum of **8a** shows no signal. Therefore, we chose the diethynyl-substituted oligophenyls **9a** and **9b** to confirm that it is possible to deprotect a TiPS-substituted oligoethynyl compound in-situ under Diels-Alder reaction conditions, by treatment with tetrabutylammonium fluoride (Bu_4NF). The Diels-Alder reaction of the diethynyl **9a** with tetraphenylcyclopentadienone (**1a**) in refluxing diphenylether affords the oligophenylene **10** (approach A in Scheme 4). **10** is also obtained in the presence of Bu_4NF by [2+4]cycloaddition of diene **1a** with **9a** or with the TiPS-protected acetylene **9b** (approaches B and C). **10** is fully characterized by ^{1}H, ^{13}C NMR and mass spectrometry.



Scheme 4: Model reactions investigating the in-situ deprotection of TiPS-substituted acetylenes for [2+4]cycloaddition

Thermogravimetric analysis (TGA) reflects the high thermal stability of polymers **8c** and **8d** in air. The thermal stability does not depend on the degree of polymerization. The thermogram of **8d** shows only one step at 593 °C connected with a weight loss of 24 %. It should be emphasized that polymers **8c** and **8d** are readily soluble in toluene and benzene. Allowing for the fact that M_w's of 95,000 (**8b**) or 107,000 (**8c**) correspond to polyphenylenes consisting of 220 (**8b**) or 190 (**8c**) benzene rings, this processability is surprising and qualifies the polymers for use in coating systems.

2.1. Monodisperse Polyphenylenes and PAHs.

As noted in the introduction, oligophenylenes may be employed in the synthesis of PAHs. For this purpose, a sufficiently dense packing of benzene rings is required, which is planarizeable in two dimensions without spatial overlap of the benzene rings. Polyphenylenes **4c** and **5c** fulfill this requirement. Accordingly, **4c** can be cyclodehydrogenated under Kovacic conditions ($AlCl_3$ / $CuCl_2$ / $C_2H_2Cl_4$) [18] to yield PAH **6** in 83 % yield. Due to its insolubility in common organic solvents, **6** is characterized by the loss of 56 protons using LD-TOF.

The synthesis of polyphenylene **5c** is accomplished in a straightforward manner, based on our synthetic concept for the production of dendrimers. Fourfold [2+4]cycloaddition of cyclopentadienone **1b** with 3,3',5,5'-tetraethynylbiphenyl (**2c**) leads to dendrimer generation G_1 (compound **4a**). **4a** is converted into the octaethynyl compound **4b** by treatment with Bu_4NF. Finally, **5c** is synthesized by eightfold Diels-Alder reaction of tetracyclone (**1a**) with the oligoethynyl **4b**. From molecular models, the diameter of **5c** is estimated to be about 3.8 nm.

Concerning the Diels-Alder reaction of tetraethynylbiphenyl **2c** with tetraphenylcyclopentadienones, such as **1a** or **1b**, it is essential to achieve quantitative formation of the desired fourfold Diels-Alder product. Heating of a solution of five equivalents of cyclopentadienone **1a** (or **1b**) and tetraethynylbiphenyl **2c** in diphenylether to 180 - 200 °C for one hour, results in a mixture of two-, three- and fourfold cycloaddition products. In contrast, a pure formation of oligophenylene **4a** (or **4c**) is obtained by slowly adding **2c** in α-methylnaphthalene to a hot solution of five equivalents **1b** (or **1a**) in diphenylether. For the synthesis of **5c** via Diels-Alder reaction, a longer reaction time (12 hours) is essential, in order to ensure quantitative transformation.

Characterization of the colorless polyphenylene **5c** is accomplished by matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry as well as ^1H and ^{13}C NMR spectroscopy.

Our current studies concern the cyclodehydrogenation of polyphenylene **5c**. Polyphenylenes corresponding to higher dendrimer generations than G_2 cannot be fused in the described manner, because a two-dimensional arrangement of their benzene rings is not possible without overlap of benzene rings. [22]

4. SUMMARY AND CONCLUSION

We present a simple synthetic process, leading to dendritic and hyperbranched polyphenylenes, which uses tetraphenylcyclopentadienones as readily available starting compounds. Both, the monodisperse and the polydisperse polyphenylenes are based upon hexa(penta)phenylbenzene units. Hyperbranched polymers are prepared by a one-step synthetic process, using the ethynyl-substituted tetraphenylcyclopentadienones **1c**, **1d**, and **1e**. Their polymer analogous Diels-Alder reaction provides access to structures consisting of covalently linked pentaphenyl- (**8a**, R= H), methylpentaphenyl- (**8b**, R =-CH_3), or hexaphenylbenzene units (**8c**, R = phenyl), respectively. Monodisperse polyphenylenes are obtained by [2+4]cycloaddition reactions of tetraethynylbiphenyl **2c** with cyclopentadienones **1a** and **1b**. Our synthetic concept allows the synthesis of large polyphenylenes, with an extremely dense packing of benzene rings. Until now, it has not been possible to obtain such large and densely packed polyphenylenes by common aryl-aryl coupling methods. Moreover, in contrast to aryl-aryl coupling methods, no catalyst is required. The dense packing of benzene rings also provides an entry to large PAHs by cyclodehydrogenation of polyphenylenes, such as **4c**.

The polymers show good thermal stability and are soluble in organic solvents such as toluene. Therefore, they can be processed without difficulty and are attractive candidates for advanced coating systems. With respect to the latter point, it should be mentioned that we are working on the polymerization of AB- and AB_2-monomers, such as **1c-e**, in films.

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5. EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini 200 NMR spectrometer or at 500 MHz on a Bruker DRX 500 spectrometer. ^{13}C NMR spectra were recorded on the same instruments at 50 MHz or 125 MHz, respectively. Chemical shifts are given in parts per million (ppm), using the solvent signal as reference.[23] Mass spectral analyses were carried out on ZAB2-SE-FPD (VG Analytical) and Bruker Reflex-TOF. MALDI-TOF-mass spectra were measured using 1,8,9-trihydroxyanthracene as matrix. FT-IR spectra were recorded on a Nicolet FT-IR 320. UV-Vis spectra were obtained using a Perkin Elmer Lambda 15 spectrometer. Thermogravimetrical measurements were carried out on Mettler TG50 in air. The heating rate was 10 K/minute. SEC analyses were accomplished on a Waters SEC, equipped with a PPS gel column using polystyrene standards. Detection was achieved with a Soma-UV/Vis or with a diffraction index detector.

Tetracyclone **1a** was commercially available. The tetraphenylcyclopentadienones **1b**-**1e** were synthesized by methods analogous to those already published in the literature starting from commercially available 4,4′-dibromobenzil (**3a**). After Sonogashira[24] coupling of **3a** with triisopropylsilylacetylene, propyne or phenylacetylene, the obtained benzil derivatives **3b-e** were condensed with 1,3-diphenylacetone in the presence of KOH in EtOH to give the tetraphenylcyclopentadienones **1b**-**1e**.[25, 26]

*General procedure for benzils **3b**, **3d** and oligophenylene **9b**:*

Bis(triphenylphosphine)-palladium(II)chloride (0.05 eq.), copper(I)iodide (0.1 eq.) and triphenylphosphine (0.1 eq.) were added to a degassed mixture (30 ml / g of the dibromide) of triethylamine / toluene (2:1), **3a** or 1,2-di(4-bromophenyl)-3,4,5,6-tetraphenylbenzene (**9c**)[25b] (1 eq.) under argon. After the solution had been heated with stirring at 60 °C for 10 minutes, the terminal acetylene compound (2.1 eq.) was added and the solution was stirred at 90 °C for 4 (in case of **3b** and **3d**) or 15 hours (in case of **9c**). After the usual work-up, the crude product was purified by column chromatography on silica gel, eluting with petroleum ether / dichloromethane (2:1 or 3:1).

3b: Yield: 86 %; FD-MS: *m/z* = 570.2, calculated for $C_{36}H_{50}Si_2O_2$ 570.3; ^{1}H-NMR δ (200 MHz, CD_2Cl_2, 303 K): 7.98-7.93 (d, $^3J = 8.4$ Hz, 4 H), 7.66-7.62 (d, $^3J = 8.4$ Hz, 4 H), 1.19-1.07 (br, 42

H); ^{13}C-NMR δ (50 MHz, CD_2Cl_2, 303 K): 193.8, 133.1, 132.9, 130.9, 130.4, 106.6, 97.3, 19.2, 12.1; IR (KBr) υ = 2158 cm^{-1} (-C≡C-), 1673 cm^{-1} (C=O), 843 cm^{-1} (1,4-substitution); UV-Vis ($CHCl_3$, λ[nm] (ε)): 285 (53500), 313 (57000); yellow oil which crystallised upon standing at 5 °C.

3d: Yield: 81%; FD-MS: *m/z* = 409.9, calculated for $C_{30}H_{18}O_2$ 410.4; ^{1}H-NMR δ (200 MHz, CD_2Cl_2, 303 K): 8.02-7.96 (d, ^{3}J = 8.2 Hz, 4 H), 7.71-7.66 (d, ^{3}J = 8.2 Hz, 4 H), 7.61-7.56 (br, 4 H), 7.42-7.39 (br, 6 H); ^{13}C-NMR δ (50 MHz, CD_2Cl_2, 303 K): 194.5, 135.7, 135,5, 132.7, 132.5, 130.5, 129.8, 129.3, 123.1, 94.7, 89.1; IR (KBr) υ = 2212 cm^{-1} (-C≡C-), 1679 cm^{-1} (C=O), 835 cm^{-1} (1,4-substitution); UV-Vis ($CHCl_3$, λ[nm] (ε)): 239 (18500), 340 (32200); above 225 °C decomposition.

9b: Yield: 85%; FD-MS: *m/z* = 894.5, calculated for $C_{64}H_{70}Si_2$ 895.4; ^{1}H-NMR δ (200 MHz, CD_2Cl_2, 303 K): 6.75-7.10 (br, 28 H), 0.873-1.28 (br, 42 H); ^{13}C-NMR δ (50 MHz, CD_2Cl_2, 303 K): 141.9, 141.7, 141.5, 141.3, 141.1, 140.1, 132.1, 132.0, 131.1, 127.4, 127.3, 126.2, 126.0, 121.2, 107.7, 91.1, 19.1, 12.1; mp. 252 °C.

3c: A flask equipped with a -78 °C cold condenser and a balloon was charged with a degassed mixture, of triethylamine (80 ml) and toluene (40 ml), **3a** (4.40 g, 0.0119 mol), bis(triphenylphosphine)-palladium(II)chloride (839 mg, 1.19 mmol), copper(I)iodide (455 mg, 2.39 mmol) and triphenylphosphine (627 mg, 2.39 mmol) under argon. After stirring the solution for 30 minutes at 25 °C, propyne (1.05 g, 0.0262 mol) was added over four hours, avoiding the formation of bubbles. Then propyne (10.5 g, 0.262 mol) was bubbled through the solution for 5 hours. The propyne was allowed to reflux at room temperature overnight. After the usual work-up, the crude product was purified by column chromatography, eluting with petroleum ether / dichloromethane (2:1).

3c: Yield: 76 %; FD-MS: *m/z* = 285.9, calculated for $C_{20}H_{14}O_2$ 286.3; ^{1}H-NMR δ (200 MHz, CD_2Cl_2, 303 K): 7.89-7,85(d, ^{3}J = 8.0 Hz, 4 H), 7.52-7.48 (d, ^{3}J = 8.0 Hz, 4 H), 2.08 (s, 6 H); ^{13}C-NMR δ (50 MHz, CD_2Cl_2, 303 K): 193.9, 132.3, 131.9, 131.5, 130.0, 91.9, 79.3, 4.6; IR (KBr) υ = 2212 cm^{-1} (-C≡C-), 1660 cm^{-1} (C=O), 837 cm^{-1} (1,4-substitution); UV-Vis ($CHCl_3$, λ[nm] (ε)): 308 (42100) broad; mp. 222 °C.

*General procedure for cyclopentadienones **1b**, **1d** and **1e**:*

A suspension of the benzil (1 eq.) and 1,3-diphenylacetone (0.95 eq.) in ethanol (2.2 ml / g of benzil) was heated to gentle reflux, to give a yellow solution. Then a solution of KOH (0.56 eq.) in ethanol (7,6 ml / g of KOH) was added and the resulting deep purple solution was refluxed for additional 12 minutes. The reaction mixture was cooled to 5 °C for 6-12 hours. During this time, the cyclopentadienone precipitated as a red-purple solid, which was filtered, washed with cold ethanol and dried in vacuo.

1b: Yield: 21 %; FD-MS: *m/z* = 744.9, calculated for $C_{51}H_{60}Si_2O$ 744.4; ^{1}H NMR δ (200 MHz, CD_2Cl_2, 303 K): 7.33-7.21 (m, 14 H), 6.90-6.86 (d, ^3J = 8.4 Hz, 4 H), 1.19-1.07 (2s, 42 H); ^{13}C NMR δ (50 MHz, CD_2Cl_2, 303 K): 200.0, 153.7, 133.3, 132.2, 130.6, 130.3, 129.7, 129.0, 128.6, 128.5, 128.1, 124.2, 107.2, 19.1, 11.8; IR (KBr) υ = 2154 cm^{-1} (-C≡C-), 1712 cm^{-1} (C=O), 831cm^{-1} (1,4-substituted benzene); UV-Vis (CH_2Cl_2, λ[nm] (ε)): 260 (40600), 304 (20700), 360 (10500), 505 (600); mp. 101 °C (decomposition).

1d: Yield: 71 %; FD-MS: *m/z* = 459.9, calculated for $C_{35}H_{24}O$ 460.5; ^{1}H NMR δ (200 MHz, CD_2Cl_2, 303 K): 7.24-7.17 (br, 14 H), 6.87-6.84 (br, 4 H), 2.03 (s, 6 H); ^{13}C NMR δ (50 MHz, CD_2Cl_2, 303 K): 200.2, 154.5, 133.0, 131.8, 131.5, 130.8, 130.0, 128.7, 128.3, 126.4, 125.1, 88.3, 79.9, 4.76; IR (KBr) υ = 2213 cm^{-1} (-C≡C-), 1708 cm^{-1} (C=O), 847 cm^{-1} (1,4-substituted benzene); UV-Vis (CH_2Cl_2, λ[nm] (ε)): 248 (24400), 299 (6000), 363 (8600); 513 (310); mp. 262 °C (decomposition).

1e: Yield: 69 %; FD-MS: *m/z* = 583.9, calculated for $C_{45}H_{28}O$ 584.7; ^{1}H NMR δ (200 MHz, $CDCl_3$, 303 K): 7.55-7.46 (br, 4 H), 7.38-7.20 (br, 20 H), 6.97-6.90 (br, 4 H); ^{13}C NMR δ (50 MHz, $CDCl_3$, 303 K): 200.1, 153.2, 132.8, 131.6, 131.2, 130.4, 130.1, 129.4, 128.4, 128.3, 128.1, 127.7, 125.7, 123.5, 122.9, 90.9, 89.0; IR (KBr) υ = 2212 cm^{-1} (-C≡C-), 1706 cm^{-1} (C=O), 845 cm^{-1} (1,4-substituted benzene); UV-Vis (CH_2Cl_2, λ[nm] (ε)): 269 (34300), 307 (35400), 371 (15400), 506 (200); mp. 263 °C (decomposition).

*Polymerization of **1b-e***

The procedures are described in the text. For a typical polymerization, 200 mg of the monomer was dissolved in 1 ml degassed diphenylether.

The ^1H NMR and ^{13}C NMR spectra of polymers **8b** and **8c** showed broad peaks. The spectra for a given polymer did not significantly depend on the reaction conditions.

8b: ^1H NMR δ (500 MHz, CD_2Cl_2, 303 K): 7.25-6.28 (br, relative intensity 3), 2.14-1.23 (br, relative intensity 1); ^{13}C NMR δ (125 MHz, CD_2Cl_2, 303 K): 142.0-139.0 (br), 132.1-126.3 (br), 121.5 (br), 86.2 (br), 80.1 (br), 20.8-19.8 (br), 4.84-4.65 (br).

MALDI-TOF-MS in the presence of silver: calculated (dimer-19mer): *m/z* = 1000, 1433, 1866, 2298, 2731, 3163, 3596, 4028, 4461, 4893, 5326, 5759, 6191, 6624, 7056, 7489, 7921, 8356.

entry [3], found: *m/z* = 1434, 1867, 2300, 2733, 3166, 3600, 4030, 4465, 4900, 5335, 5770, 6195, 6627, 7061, 7489, 7926, 8357.

entry [4], found: *m/z* = 1003, 1434, 1867, 2300, 2733, 3166, 3599, 4031, 4467, 4897, 5329, 5762.

8c: ^1H NMR δ (500 MHz, benzene, 303 K): 7.52-6.48 (br); ^{13}C NMR δ (125 MHz, benzene, 303 K): 141.8-140.4 (br), 138.3-136.7 (br), 133.6-123.9 (br), 121.3-120.6 (br), 90.5-90.1 (br); IR (KBr) υ = 3080, 3055, 3029 (C-H in benzene), 2261 cm^{-1} (-C≡C-), 1600, 1584, 1513 (C=C in benzene), 839 cm^{-1} (1,4-substitution).

MALDI-TOF-MS in the presence of silver: calculated (dimer-16mer): *m/z* = 1249, 1805, 2362, 2919, 3476, 4032, 4589, 5146, 5702, 6259, 6816, 7372, 7929, 8486, 9043.

entry [5], found: *m/z* = 1251, 1807, 2364, 2920, 3477, 4033, 4589, 5146, 5701, 6257, 6815.

entry [6], found: *m/z* = 1250, 1806, 2363, 2919, 3475, 4032, 4588, 5144, 5700, 6256, 6813, 7370, 7927, 8479.

entry [7], found: *m/z* = 1806, 2363, 2920, 3476, 4033, 4589, 5146, 5703, 6260, 6815, 7370, 7950, 8490.

9a: Bu_4NF (1.569 g, 6.000 mmol) in THF (20 ml) was added to a solution of **9b** (2.686 g, 3.000 mmol) in THF (50 ml) and stirred at 25 °C for 2 hours. The reaction mixture was diluted with CH_2Cl_2 (200 ml) and H_2O (100 ml). The organic layer was washed with H_2O, dried over $MgSO_4$ and concentrated on a rotary evaporator. The crude product was purified by column chromatography (silica gel, petrolether / CH_2Cl_2 (4:1)) to afford **9a** as a white solid in quantitative yield.

FD-MS: *m/z* = 582.4, calculated for $C_{46}H_{30}$ 582.7; ^1H-NMR δ (500 MHz, CD_2Cl_2, 303 K): 7.02-7.01(br, 4 H), 6.90-6.83 (br, 24 H), 3.75 (s, 2 H); ^{13}C-NMR δ (125 MHz, CD_2Cl_2, 303 K): 142.4, 141.7, 141.3, 141.1, 141.0, 139.9, 132.1, 132.0, 131.3, 127.5, 127.3, 126.2, 126.1, 119.7, 84.3, 77.5; mp. 294 °C.

*Model reaction: Diels-Alder reaction of **9a**,**9b** with **1a**.*

A) A degassed solution of **9a** (50.0 mg, 0.08580 mmol) and **1a** (67.3 mg, 0.2754 mmol) in diphenylether (2 ml) was heated to reflux for 12 hours. The cold reaction mixture was diluted with CH_2Cl_2 (1 ml) and added dropwise to ethanol (50 ml). The crude product of **10** was filtered and recrystallized from n-heptane. Yield: 98,9 mg (0,07633 mmol, 89 %).

B) **9b** (50.0 mg, 0.05583 mmol) and **1a** (47.22 mg, 0.1228 mmol) were reacted as described for approach A) in the presence of Bu_4NF (43.8 mg, 0.1675 mmol).

C) **9a** (50.0 mg, 0.08580 mmol), **1a** (67.3 mg, 0.2754 mmol) and Bu_4NF (67.3 mg, 0.2754 mmol) were reacted as described for approach A).

10: FD-MS: *m/z* = 1296.9, calculated for $C_{102}H_{70}$ 1295.7; ^{1}H-NMR δ (500 MHz, CD_2Cl_2, 303 K): 7.38 (s, 2 H), 7.14 (br, 10 H), 6.94-6.70 (br, 50 H), 6.69-6.65 (br, 4 H), 6.55-6.51(br, 4H); ^{13}C-NMR δ (125 MHz, CD_2Cl_2, 303 K): 142.27, 142.07, 141.21, 141.09, 141.07, 141.01, 140.79, 140.70, 140.68, 140.61, 140.40, 140.28, 139.55, 139.44, 138.91, 138.67, 131.88, 131.77, 131.43, 131.25, 130.27, 128.64, 127.86, 127.18, 127.12, 126.89, 126.83, 126.55, 125.86, 125.59, 125.48; mp. > 300 °C.

*3,3',5,5'-Substituted biphenyls **2b** and **2c***

2b: A degassed suspension of 3,3',5,5'-tetrabromobiphenyl [27] (20.2 g, 0.0429 mol), $Pd(Ph_3)_2Cl_2$(5.84 g 8,33 mmol), CuI (3.063 g, 0.0161 mol), $P(Ph_3)$ (4.338 g, 0.0165 mol), Et_3N (475 ml) and toluene (285 ml) was stirred at 60 °C for 15 minutes under argon. Trimethylsilylacetylene (45.9 ml, 0.437 mol) was added with a syringe, the flask was sealed and the suspension was stirred for 5 hours at 80 °C. After the usual work up, column chromatography (silica gel, petroleum ether / dichloromethane (4:1)) afforded **2b** (12 g, 22.3 mmol, 61 %).

FD-MS: *m/z* = 539.5, calculated for $C_{32}H_{42}Si_4$ 539.03; ^{1}H NMR δ (200 MHz, CD_2Cl_2, 303 K):): 7.62 (br, 4 H), 7.54 (br, 2 H), 0.25 (s, 36 H); ^{13}C-NMR δ (50 MHz, CD_2Cl_2, 303 K): 140.5, 135.0, 131.0, 124.9, 104.3, 96.2, 0.286; mp. 170 °C.

2c: A solution of Bu_4NF (10.91g, 0.0418 mol) in THF (100 ml) was added to **2b** (12.00 g, 0.0224 mol) in THF (150 ml). After stirring at 25 °C for two hours, the reaction mixture was diluted with CH_2Cl_2 (500 ml) and H_2O (400 ml). The organic layer was washed with H_2O, dried over $MgSO_4$

and concentrated on a rotary evaporator. The crude product was purified by column chromatography (silica gel, petroleum ether / toluene (3:1)) to afford **2c** as a white amorphous solid (3.82 g, 15.28 mmol, 96 %).

FD-MS: *m/z* = 250.4, calculated for $C_{20}H_{10}$ 250,1; ^{1}H-MNR δ (200 MHz, CD_2Cl_2, 303 K): 7.69-7.63 (br, 6 H), 3.20 (s, 4 H); ^{13}C-NMR δ (50 MHz, CD_2Cl_2, 303 K): 140.6, 135.6, 131.7, 124.1, 82.9, 79.1; mp. 189 °C (decomposition).

*Polyphenylenes **4c** and **5c***

4c: To a degassed solution of cyclopentadienone **1a** (553.3 mg, 1.439 mmol) in diphenylether (4 ml), tetraethynylbiphenyl **2c** (50.0 mg, 0.200 mmol) in α-methylnaphthalene (2 ml) was added over 30 minutes at 200 - 250 °C under a stream of argon. After stirring for 1 hour at this temperature, the mixture was allowed to cool. The cold reaction mixture was diluted with CH_2Cl_2 (1 ml) and added dropwise to EtOH (200 ml). After stirring for 2 hours at 25 °C, a crude, light red product was filtered and washed with cold acetone to give white **4c** (308.1 mg, 0.1838 mmol, 91 %).

FD-MS: *m/z* = 1676.6, calculated for $C_{132}H_{90}$ 1676.2; ^{1}H-NMR δ (500 MHz, $C_2D_2Cl_4$, 373 K): 7.19-7.02 (br, 25 H), 6.90-6.65 (br, 65 H); mp. > 300 °C.

5c: To a degassed solution of **1a** (475.8 mg, 1.070 mmol) in a mixture of diphenylether / α-methylnaphthalene (2 ml / 2 ml), oligoethynyl **4b** (50.0 mg, 0.02676 mmol) in α-methylnaphthalene (3 ml), was added over 10 hours at 180 - 200 °C, under a stream of argon. After stirring for an additional 5 hours at this temperature, the mixture was allowed to cool. The cold reaction mixture was diluted with methanol (40 ml) and stirred for 2 hours at 25 °C. A light red, crude product **5c**, was filtered and purified by reprecipitation from acetone / CH_2Cl_2 (2:1) with ethanol (Yield: 109.1 mg, 0.02311 mmol, 86%).

MALDI-TOF-MS in the presence of silver: *m/z* = 4827, calculated for $C_{372}H_{250}$, Ag^+ 4827; ^{1}H-NMR δ (500 MHz, $C_2D_2Cl_4$, 373 K): 6.79 (br, 6H), 6.73 (br, 6 H), 6.49-6.39 (br, 91 H), 6.31-5.79 (br, 247 H); ^{13}C-NMR δ (125 MHz, $C_2D_2Cl_4$, 373 K): 142.31, 142.08, 141.39, 140.83, 140,70, 140.49, 139.48, 139.41, 138.99, 138.66, 138.32, 132.73, 132.01, 131.86, 131.55, 131.27, 130,40, 130.23, 128.86, 128.57, 127.69, 127.18, 126.97, 126.67, 126.32, 125.90, 125,63, 125.35; mp. > 300 °C.

*PAH **6***

Cupric chloride (144.2 mg, 1.0728 mmol) and sublimed aluminium chloride (143.0 mg, 1.0728 mmol) were added to a degassed solution of **4c** (25.0 mg, 0.01491 mmol) in 1,1,2,2-tetrachlorethane (50ml) under argon. The solution was stirred at 100 °C for 9 hours and allowed to cool over night. After cooling and addition of methanol (20 ml), the reaction mixture was filtered and the residue washed extensively with acetone, conc. HCl / H_2O = 1:1, H_2O and CS_2. The crude product was further purified by continuous extraction with CS_2 for one week to give a black solid (20.1 mg, 0.01240 mmol, 83%).

LD-TOF-MS: *m/z* = 1619.3, calculated for $C_{132}H_{34}$ 1619.7; mp. > 300 °C.

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