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Dendritic Encapsulation – "Postsynthetic" Functionalizations of a Single Benzophenone Shielded by Shape-Persistent Polyphenylene Dendrons

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First- and second-generation polyphenylene dendrimers were synthesized starting from benzophenone as core. Variation of the size and the density of the dendrimer shell resulted in different isolation of the cores. To investigate the effect of shielding upon the reactivity of the core, chemical functionalizations as well as the alkali-metal reduction of the encapsulated benzophenone core were performed. The herein presented synthetic concept opens the way to spatially well-defined spherical nanoparticles bearing a single isolated function in the center.

Introduction

Dendrimers represent a class of organic materials that can be obtained in a monodisperse way on the nanometer scale. In the last decade, the introduction of functionalities, either in the core, in the dendritic backbone, or on the surface of dendrimers has been a main focus of research.[1] Beyond a certain molecular weight, a dendrimer core is expected to be shielded from the surrounding medium by a close-packed shell. The degree of branching, the structure and chemical nature of the repeating unit, and the spatial orientation of the dendrons are the main factors, that determine the shielding of a central core.[2] Almost all knowledge about dendritic encapsulation has been derived from the investigation of the effect that the dendrimer shell has on the physical properties of an internal photoactive[3] and/or redox-active probe.[4] In this regard, Gorman et al. demonstrated, that a rigid dendritic backbone blocked the electron transfer from an electrode to an iron–sulfur core more efficiently than a flexible one.[4c,4e] Furthermore, computationally derived models indicated a highly mobile core in the flexible dendrimers and a more immobilized core in the rigid dendrimers. Polyphenylene dendrimers with their stiff and shape-persistent dendrons have shown to be very efficient in the encapsulation of chromophores. The prevented aggregation of a dye, as, for example, perylene, led to improved optical properties of the chromophore, such as an increased fluorescence quantum yield.[5] Recently, we reported the "postsynthetic" functionalization of polyphenylene dendrimers bearing multiple benzophenones in their scaffold.[6] Twyman et al. presented the modification at the focal point of a hyperbranched polymer and observed that the level of incorporation was strongly influenced by the size of the reagent.[7] However, the core of polyphenylene dendrimers has not yet been the subject of such a "postsynthetic" functionalization.

In this paper, we present the synthesis and characterization of polyphenylene dendrimers with a single benzophenone core. Placing the benzophenone in the core was expected to significantly increase the shielding as compared to the benzophenones in the dendrimer scaffold.[6] To investigate the influence of the dendrimer shell upon the reactivity of the benzophenone core, chemical functionalizations of the core were tested by reacting the encapsulated benzophenone with aryl-/alkyl-lithium and Grignard reagents of various sizes. Furthermore, the alkali-metal reduction of the dendrimers was carried out and yielded the corresponding benzophenone radical anions. Their biradical formation was used to further investigate the shielding of the core.

Results and Discussion

Synthesis of the Dendrimers: For the synthesis of polyphenylene dendrimers with a benzophenone core, its corresponding ethynyl-substituted derivative must be available. After monolithiation of 1,3,5-tribromobenzene (**1**), the reaction was quenched with 3,5-dibromobenzaldehyde (**2**) to give the tetrabromo-substituted diphenylmethanol derivative **3** (Scheme 1). The subsequent Swern oxidation[8] generated 3,3′,5,5′-(tetrabromo)benzophenone (**4**), which, after subsequent Hagihara–Sonogashira cross-coupling reaction[9] with (triisopropysilyl)ethyne, yielded the benzophenone derivative **5**, possessing four triisopropylsilyl (TIPS) protected ethynyl groups. Deprotection of the TIPS protecting groups with tetrabutylammonium fluoride (TBAF) furnished the desired core 3,3′,5,5′-(tetraethynyl)benzophe-

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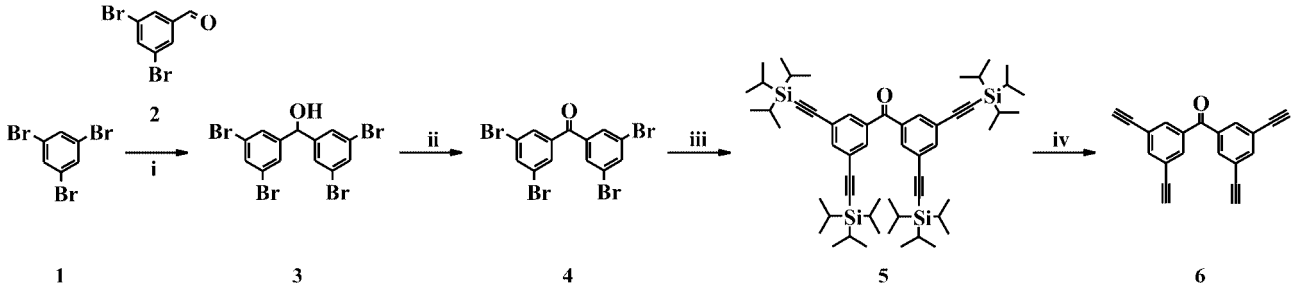
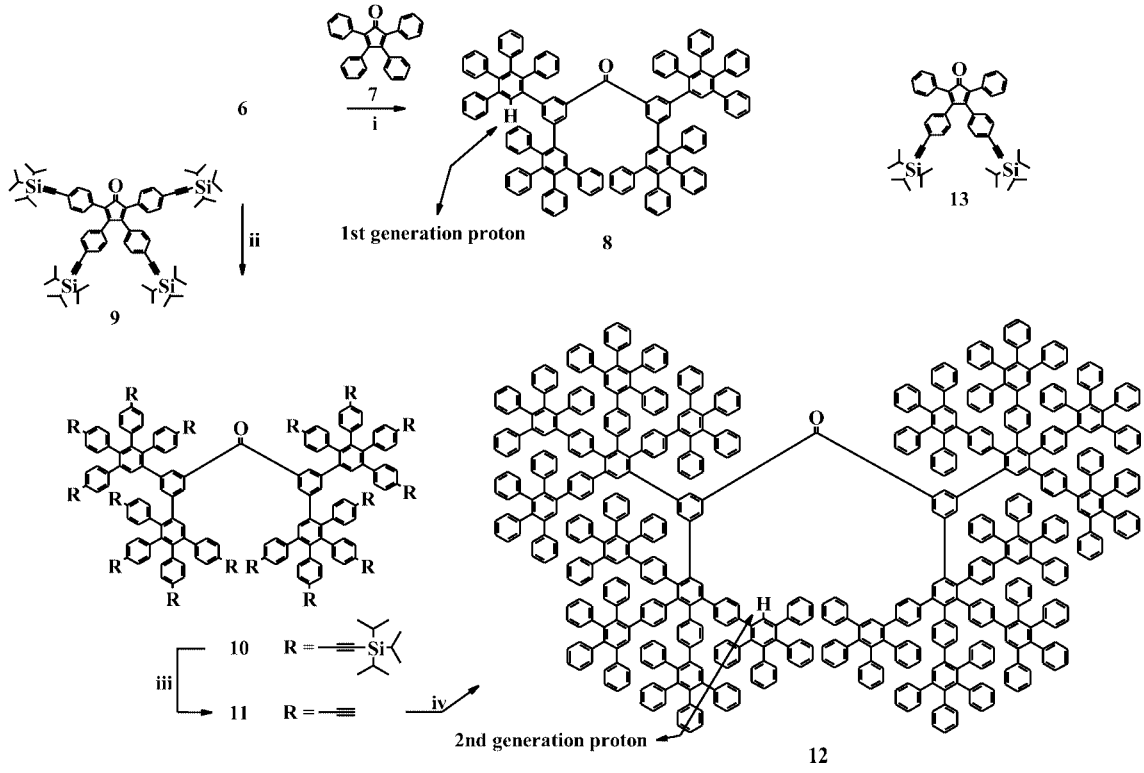
none (**6**). The synthesis of monodisperse, structurally well-defined polyphenylene dendrimers consisted of two steps. Firstly, the [4+2] cycloaddition of a (tetraphenyl)cyclopentadienone branching unit to an ethynyl-substituted core or dendrimer, and secondly, the deprotection of the TIPS protecting groups, which activates the molecule for further growth.[10] The first-generation dendrimer **8** was obtained from the Diels–Alder cycloaddition of (tetraphenyl)cyclopentadienone (**7**) with the benzophenone core **6** (Scheme 2).

To increase the isolation of the benzophenone core, the branching unit **9** was used for the synthesis of the second-generation dendrimer **12**. This building block possesses four active sites for further dendrimer growth (A_4B) and therefore provides a significantly denser dendrimer shell than the parent branching unit **13**, which carries only two protected ethynyl groups (A_2B).[10b] Subsequent cleavage of the TIPS protecting groups in dendrimer **10** generated the first-generation dendrimer **11** with 16 peripheral ethynyl groups. The Diels–Alder cycloaddition of **11** with (tetraphenyl)cyclopentadienone (**7**) yielded the second-generation dendrimer **12**, where the benzophenone core is surrounded already by 100 benzene rings.

The monodispersity of the dendrimers **8** and **12** was proven by MALDI-TOF mass spectrometry showing single distinctive signals for the product mass. The NMR spectroscopy displayed generation-dependent chemical shifts of the protons on the pentaphenyl repeating units (Scheme 2). To derive some knowledge about the shape and size of the synthesized dendrimers, force-field calculations were carried out.[11] Figure 1 shows the three-dimensional structures of (a) the first- and (b) the second-generation dendrimers **8** and **12**, respectively.



Scheme 1. Synthesis of the benzophenone core 3,3′,5,5′-(tetraethynyl)benzophenone (**6**). (i) *n*-butyllithium, –78 °C, 80%; (ii) oxalyl chloride, DMSO, triethylamine, CH_2Cl_2, –78 °C, 85%; (iii) 6 equiv. (triisopropylsilyl)ethyne, $[Pd(PPh_3)_2]Cl_2$, PPh_3, CuI, toluene/triethylamine, 80 °C, 60%; (iv) TBAF, THF, 67%.



Scheme 2. Synthesis of the first- and second-generation dendrimers **8** and **12**, (i) 6 equiv. **7**, *o*-xylene, 150 °C, 77%. (ii) 6 equiv. **9**, *o*-xylene, 160 °C, 76%; (iii) TBAF, THF, 78%; (iv) 48 equiv. **7**, *o*-xylene, 170 °C, 85%.

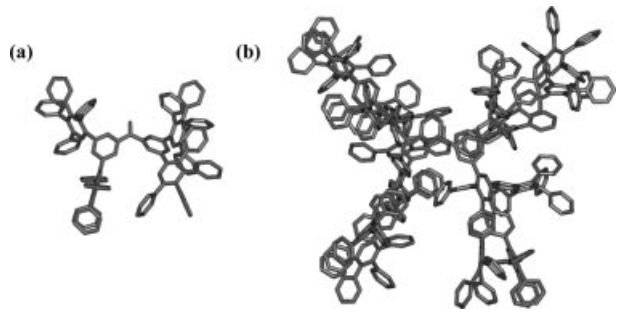


Figure 1. Molecular model of (a) the first-generation dendrimer **8** and (b) the second-generation dendrimer **12**. For reasons of clarity, the hydrogen atoms have been omitted. Radii were measured as largest carbon–carbon distances between the carbonyl carbon and peripheral benzene rings.

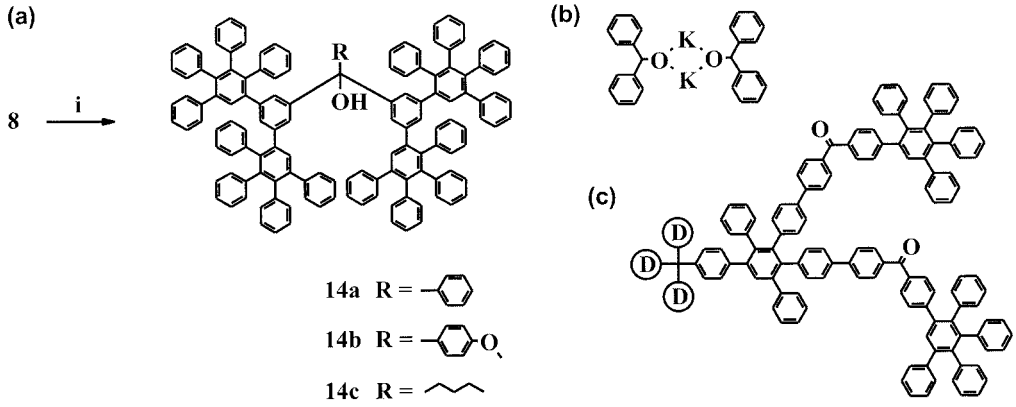
The shape of **8** is strongly influenced by the substitution pattern of the benzophenone core, resulting in a bent dumb-bell-like structure. Contrary, in the second-generation dendrimer **12**, the high number of branching points arising from the A_4B branching unit **9**, and the additional dendrimer layer produced an increased encapsulation of the core. Additionally, due to the dense polyphenylene shell provided by the A_4B branching unit **9**, compound **12** possesses a more spherical shape. From the models, the radii were determined to be 2.2 nm for **8** and 3.6 nm for **12** (largest carbon–carbon distance between the carbonyl carbon and peripheral benzene rings).

Chemical Functionalizations: Applying the synthetic concept recently presented,[6] aryl- and alkyllithium reagents were used for the functionalization of the dendrimer core. When the first-generation dendrimer **8** was treated with phenyllithium, the alcoholic product **14a** could be obtained in good yield (Scheme 3). The reaction of **8** with the Grignard reagent (4-methoxyphenyl)magnesium bromide yielded the dendrimer **14b**. Residual amounts of starting material had to be separated from the product in both cases. When larger reagents, e.g. biphenyllithium, obtained from the halogen–lithium exchange of 3-bromobiphenyl, were treated with **8**, only the starting material **8** was recovered. Likewise as for **8**, the reaction of phenyllithium with the second-generation dendrimer **12** yielded starting material and alcoholic product. No side-product, coming from the possible Grignard reduction, could be detected. Due to the small difference in polarity, the second-generation alcoholic product could not be separated from the mixture, however, NMR spectra suggested less than 10% of unreacted **12**. Also in the case of **12**, no product was formed during the reaction with biphenyllithium. To extend the postsynthetic concept to alkyllithium reagents, **8** was treated with *n*-butyllithium to give the alcoholic product **14c**. Surprisingly, even in that case, residual starting material was obtained.

The functionalization of the benzophenone core was obviously possible only with reagents smaller than biphenyl. Furthermore, contrary to polyphenylene dendrimers possessing multiple benzophenones in their scaffold (Scheme 3c),[6] no quantitative conversion could be achieved for both dendrimers, **8** and **12**. An explanation for these results is the different substitution pattern of the benzophenones. The benzophenones in the dendritic scaffold were connected to the dendrimer backbone by their *para*-positions. This allowed the introduction of even large nucleophiles like pyrene. The herein presented dendrimers **8** and **12** were grown from a fourfold *meta*-substituted benzophenone core. This substitution pattern obviously produced an enhanced spatial shielding, thus only reagents of the size of benzene or smaller could react with the carbonyl function.

Further proof for the encapsulation of the benzophenone core was derived from the alkali-metal reduction of **8** and **12**. The reduction of dendrimers **8** and **12** was performed on a potassium mirror under high vacuum in THF solution.[12] UV/Vis and EPR spectroscopy were used to follow the state of reduction.

Upon contact of a solution of dendrimer **8** with the potassium mirror, two increasing absorption bands at $\lambda \approx 350$



Scheme 3. (a) Chemical functionalizations of the first-generation dendrimer **8** with aryl- and alkyllithium and Grignard reagents. (b) Potassium-bridged biradical of benzophenone. (c) Schematic draw of a polyphenylene dendrimer functionalized with eight benzophenones in the scaffold.[6] One arm is drawn out fully. The three other arms are identical with the one shown but are abbreviated as a circled-D for ease of visualization. (i) **14a**: 60 equiv. phenyllithium, THF, 70 °C, 70%. **14b**: 25 equiv. (4-methoxyphenyl)magnesium bromide, THF, 70 °C, 66%. **14c**: 100 equiv. *n*-butyllithium, THF, 70 °C, 70%.

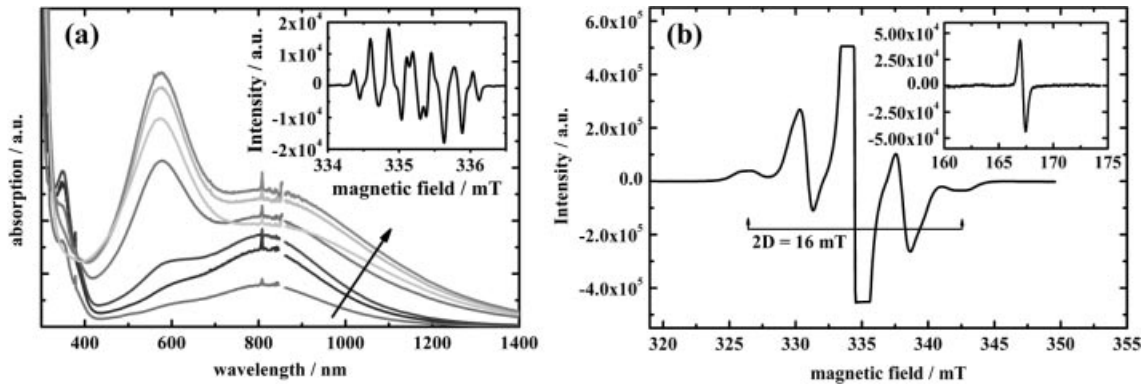


Figure 2. (a) UV/Vis absorption spectra of dendrimer **8** in THF in the order of further reduction. (K, THF, room temp.) Inset: EPR spectrum of dendrimer **8** at the maximum amount of radical monoanion. (b) EPR spectra of the radical anion of **8** in THF at ca. 120 K, zero-field splittings and half-field transition (inset).

and 825 nm were observed in the UV/Vis spectra (Figure 2a). They can be assigned to the formation of the radical anion of the phenyl-substituted benzophenone core, with the absorption maxima bathochromically shifted as compared to those of the parent benzophenone radical monoanion (λ_{max} = 336 and 560 nm).[13] The bathochromic shift ($\Delta\lambda_{max} \approx$ 14 nm, first absorption maximum) was smaller than the shift observed for the radical anions of *para*-phenyl-substituted benzophenones (Scheme 3c, $\Delta\lambda_{max} \approx$ 75 nm).[6] Reason for this is the less efficient delocalization of the charge/spin into the neighboring phenyl rings in the case of the *meta*-phenyl-substituted benzophenone core **6**. At a maximum intensity of the radical anion bands, the solution EPR spectra (inset in Figure 2a) displayed a somewhat resolved signal with several lines. The computer simulation of experimental spectra yielded the proton hyperfine couplings of a_H (*para*) = 0.35 mT and a_H (*ortho*) = 0.25 mT very close to those of known benzophenones.[14] Thus, the detected hyperfine couplings can be assigned to the four *ortho*-protons and the two *para*-protons carrying the largest spin-density, whereas further phenyl rings block the *meta*-positions of the benzophenone radical monoanion. The frozen-state EPR spectra ($T \approx$ 120 K) surprisingly showed characteristic zero-field splittings of $2D \approx$ 16 mT (Figure 2b), which are of similar size as usually found for potassium-bridged benzophenone anions (Scheme 3b, $2D \approx$ 18–20 mT).[13,15] In addition to the typical Δms = 1 signals for the zero-field splittings, also a relatively strong half-field transition at $g \approx$ 4 was found (Δms = 2), further demonstrating the triplet character of these biradicals (inset in Figure 2b). For the second-generation dendrimer **12**, reduction experiments have been performed under the same conditions. The UV/Vis and EPR spectra in solution were similar to those of the first-generation dendrimer **8**. Contrary to **8**, the EPR spectra of a frozen solution of **12** displayed no zero-field splittings and half-field transition, ruling out the formation of potassium-bridged biradicals from two anions of **12**.

The different results from the frozen-state EPR measurements can be attributed to two reasons: Firstly, the diameter of **12** is significantly larger than that of **8**, thus keeping the radical centers separate. Secondly, using the A_4B branching-unit **9** during the synthesis of dendrimer **12** afforded a dense polyphenylene shell, which efficiently encapsulated the core. For both dendrimers **8** and **12**, continued reduction on the potassium mirror resulted in the decrease of the absorption band of the radical monoanion ($\lambda \approx$ 350 and 825 nm). A new absorption band at $\lambda \approx$ 575 nm increased in intensity (Figure 2a) and can be attributed to the absorption of the benzophenone dianion.[13] EPR showed a signal of very low intensity, however, the signal did not disappear even after longer reaction time. Upon further reduction, the increase of an intense sharp EPR signal was observed due to highly mobile extra charges in the polyphenylene shell.[6]

Conclusions

First- and second-generation polyphenylene dendrimers with a single active carbonyl group in the core were prepared by the divergent approach. Chemical functionalizations of the core with aryl-/alkyllithium and Grignard reagents were limited to molecules smaller than biphenyl due to spatial shielding. The alkali-metal reduction of the benzophenone core produced the corresponding radical monoanion species. Potassium-bridged benzophenone anions could only be detected for the first-generation dendrimer **8**, due to the larger and denser dendrimer shell of the second-generation dendrimer **12**, that led to an isolation of the radical anion species. Molecular modelling showed an efficient encapsulation of the core for the second-generation dendrimer, supporting the results obtained from the reduction and the postsynthetic functionalization of the benzophenone core.

The herein presented approach enables the synthesis of shape-persistent and monodisperse nanoparticles with a single isolated active site in the interior. With the postsynthetic concept, the introduction of functional groups in the core of polyphenylene dendrimers is simplified, however the size of the nucleophile was found to be a limiting factor. This concept should also allow the introduction of tempera-

ture-labile functions, which are not stable under the conditions of the Diels–Alder cycloaddition (≈ 150 °C), and represents therefore a significant step forward in the synthesis of monofunctional well-defined nanoobjects.

Experimental Section

General Remarks. General Procedures: All starting materials were obtained from commercial suppliers (Aldrich, Fluka, Fischer, Strem, Acros) and were used without purification. Solvents were used in HPLC-grade purity as purchased. All atmosphere-sensitive reactions were performed under argon using Schlenk techniques. Column chromatography was carried out with silica gel 60 (230–400 mesh) from E. Merck. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX250 spectrometer, a Bruker AC300 spectrometer, a Bruker AMX500 NMR spectrometer and a Bruker 700Ultrashield NMR spectrometer by using residual proton resonance of the solvent or the carbon signal of the deuterated solvent as the internal standard. Abbreviation Bp = benzophenone. FD mass spectra were performed with a VG-Instruments ZAB 2-SE-FDP. MALDI-TOF mass spectra were measured with a Bruker Reflex II and dithranol as matrix (molar ratio dithranol/sample, 250:1). EPR spectra were recorded with a CW X-band ESP 300 equipped with an NMR gauss meter (Bruker ER 035), a frequency counter (Bruker ER 041 XK) and a variable-temperature-control continuous-flow N_2 cryostat (Bruker B-VT 2000). The elemental analysis was carried out by the Microanalytical Laboratory of the University of Mainz, Mainz, Germany. Because of the high carbon content in some molecules, the combustion may have been incomplete (sooting) resulting in lower values than expected for the carbon content.

Bis(3,5-dibromophenyl)methanol (3): 1,3,5-Tribromobenzene (2.6 g, 8.3 mmol) was placed in dry diethyl ether (150 mL) at –78 °C under argon. Within 60 min *n*-butyllithium (5.07 mL, 8.3 mmol, 1.6 M in hexane) was added dropwise, and the solution stirred for 2 h at this temperature. 3,5-Dibromobenzaldehyde (2.4 g, 9.1 mmol) was dissolved in diethyl ether (30 mL) and added to the solution within 5 min. The reaction mixture was stirred for another 2 h at –78 °C and then allowed to reach room temperature. Methanol (100 mL) was added and the solution stirred for 30 min. The organic layer was concentrated under reduced pressure and the crude product purified by column chromatography (petroleum ether/CH_2Cl_2) to afford **3** as a white solid. Yield: 3.3 g (6.6 mmol) 80%. ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 353 K): δ = 7.88 (s, 2 H, 4-H, 4′-H), 7.69 (s, 4 H, 2-H, 2′-H, 6-H, 6′-H) ppm. ^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 353 K): δ = 146.5 (C-1, C-1′), 134.1 (C-4, C-4′), 128.6 (C-2, C-2′, C-6, C-6′), 123.7 (*C*–Br), 74.2 (*C*–OH) ppm. FD mass (8 kV): *m*/*z* (%) = 499.8 (100) $[M]^+$. $C_{13}H_8Br_4O$ (499.8): calcd. C 31.24, H 1.61; found C 31.33, H 1.62.

3,3′,5,5′-(Tetrabromo)benzophenone (4): Dry CH_2Cl_2 (25 mL) was placed in a flask under argon and cooled to –78 °C. Oxalyl chloride (1.1 mL, 2.15 mmol) was added through a septum and the solution was stirred for 15 min. Afterwards DMSO (0.31 mL, 4.41 mmol), dissolved in CH_2Cl_2 (2 mL), was added and after 15 min of stirring, compound **3** (1 g, 2.0 mmol), dissolved in CH_2Cl_2 (2 mL), was added and the solution stirred for another 15 min. Thereafter, triethylamine (1.41 mL, 10.0 mmol) was added and the solution allowed to reach room temperature. Subsequent extraction with brine, 1% H_2SO_4, H_2O and 5% $NaHCO_3$ gave the crude product which could be purified by recrystallisation from EtOH to give **4** as a white solid. Yield: 846 mg (1.7 mmol), 85%. ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 353 K): δ = 7.89 (s, 4 H, 2-H, 2′-H, 6-H, 6′-H), 7.74 (s, 2 H, 4-H, 4′-H) ppm. ^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 353 K): δ = 190.8 (*C*=O), 139.7 (C-1, C-1′), 138.6 (C-4, C-4′), 131.4 (C-2, C-2′, C-6, C-6′), 123.8 (*C*–Br) ppm. FD mass (8 kV): *m*/*z* (%) = 497.9 (100) $[M]^+$. $C_{13}H_6Br_4O$ (497.8): calcd. C 31.37, H 1.21; found C 31.38, H 1.26.

3,3′,5,5′-Tetrakis(triisopropylsilanylethynyl)benzophenone (5): Compound **4** (3.6 g, 7.23 mmol) was suspended in triethylamine (60 mL) and toluene (20 mL). Bis(triphenylphosphane)palladium(II) dichloride (1.02 g, 1.45 mmol), copper(I) iodide (550 mg, 2.89 mmol), and triphenylphosphane (1.02 g, 1.45 mmol) were added, and the flask evacuated and flushed with argon for several times. Under stirring the reaction mixture was heated to 60 °C and triisopropylsilylethyne (9.65 mL, 43.4 mmol) was injected through a septum. After 15 min stirring at this temperature the reaction was heated to 80 °C and stirred overnight under argon. After cooling the reaction mixture was diluted with CH_2Cl_2 and extracted with H_2O. The organic phase was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (petroleum ether/CH_2Cl_2) to afford **5** as a white solid. Yield: 3.87 g (4.3 mmol), 60%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.78–7.79 (m, 6 H, $H_{arom.}$), 1.14 (s, 84 H, -C*H*, -CH_3) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2, 300 K): δ = 193.9 (*C*=O), 139.1 (C-4, C-4′), 137.8 (C-1, C-1′), 133.0 (C-2, C-2′, C-6, C-6′), 124.8 (*C*–C≡), 105.2 (*C*≡C–Si), 93.6 (C≡*C*–Si), 18.9 (*C*H$_3$), 11.8 (*C*H) ppm. FD mass (8 kV): *m*/*z* (%) = 902.8 (100) $[M]^+$). $C_{57}H_{90}OSi_4$ (903.7): calcd. C 75.76, H 10.04; found C 76.07, H 10.08.

3,3′,5,5′-(Tetraethynyl)benzophenone (6): Compound **5** (500 mg, 0.55 mmol) was dissolved in dry THF (10 mL) and reacted with TBAF (175 mg, 0.5 mmol) under argon for 5 min. The reaction was quenched with H_2O. Purification was performed by column chromatography (petroleum ether/CH_2Cl_2) to afford **6** as a white solid. Yield: 103 mg (0.37 mmol), 67%. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ = 7.82 (s, 6 H, 2-H, 2′-H, 4-H, 4′-H, 6-H, 6′-H), 3.77 (s, 4 H, ≡C*H*) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2, 300 K): δ = 192.9 (*C*=O), 139.3 (C-4, C-4′), 138.6 (C-1, C-1′), 133.5 (C2, C-2′, C-6, C-6′), 124.3 (*C*–C≡), 82.1 (*C*≡CH), 81.0 (≡*C*H) ppm. FD mass (8 kV): *m*/*z* (%) = 278.4 (100) $[M]^+$). $C_{21}H_{10}O$ (278.3): calcd. C 90.63, H 3.62; found C 90.70, H 3.89.

8: A mixture of **6** (75 mg, 0.27 mmol) and **7** (620 mg, 1.61 mmol) was dissolved in *o*-xylene (6 mL) and refluxed at 150 °C for 16 h under argon. The solvent was removed under reduced pressure and the crude product purified by column chromatography (petroleum ether/CH_2Cl_2) to afford **8** as a white solid. Yield: 0.35 g (0.2 mmol), 77%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.25 (s, 2 H, 4-H_{Bp}, 4′-H_{Bp}), 7.20–7.17 (m, 22 H, $H_{arom.}$), 7.04 (s, 4 H, 2-H_{Bp}, 2′-H_{Bp}, 6-H_{Bp}, 6′-H_{Bp}), 6.95–6.70 (m, 62 H, $H_{arom.}$) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2, 300 K): δ = 196.5 (*C*=O) 142.2, 142.0, 141.6, 141.3, 140.7, 140.4, 140.1, 134.0, 139.6, 137.4, 135.6, 131.8, 131.8, 131.6, 130.3, 129.0, 127.4, 127.2, 127.0, 126.7, 126.2, 126.0, 125.8 ppm. FD mass (8 kV): *m*/*z* (%) = 1704 (100) $[M]^+$. $C_{133}H_{90}O$ (1704): calcd. C 93.74, H 5.32; found C 93.84, H 5.34.

10: A mixture of **6** (50 mg, 0.18 mmol) and **9** (1.2 g, 1.09 mmol) was dissolved in *o*-xylene (6 mL) and refluxed at 160 °C for 20 h under argon. The solvent was removed under reduced pressure and the crude product purified by column chromatography (petroleum ether/CH_2Cl_2). Precipitation from methanol afforded **10** as a white solid. Yield: 625 mg (136 μmol), 76%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.33–7.06 (m, 50 H, $H_{arom.}$), 6.80–6.64 (m, 24 H, $H_{arom.}$), 1.14–1.09 (m, 336 H, -C*H*, -CH_3) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2, 300 K): δ = 194.5 (*C*=O), 141.6, 141.5, 141.4, 140.8, 140.5, 140.3, 140.2, 140.0, 139.4, 139.3, 137.1, 133.8, 131.9,

131.8, 131.6, 131.4, 131.1, 130.2, 129.4 (all $C_{arom.}$), 122.3, 121.8, 121.7, 121.5 (all *C*–C≡), 107.3, 107.2 (all *C*≡C–Si), 91.3, 91.2 (all ≡*C*–Si), 19.0, 18.9, 18.9 (all *C*H$_3$), 11.2 (*C*H) ppm. MALDI TOF mass: *m/z* (%) = 4552 (50), [M – 43, isopropyl]$^+$, 4595 (100), [M]$^+$, 4618 (20), [M + Na]$^+$, 4633 (40) [M + K]$^+$. $C_{309}H_{410}OSi_{16}$ (4590): calcd. C 80.86, H 9.00; found C 80.94, H 7.11.

11: Compound **10** (350 mg, 76.2 μmol) was dissolved in dry THF (10 mL) and treated with TBAF (385 mg, 1.22 mmol) under argon for 5 min. The reaction was quenched with H_2O. Purification was performed by precipitation from methanol/H_2O to afford **11** as a white solid. Yield: 125 mg (60 μmol), 78%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.33–7.31 (m, 12 H, $H_{arom.}$), 7.17 (s, 2 H, 4-H_{Bp}, 4′-H_{Bp}), 7.11–7.03 (m, 28 H, $H_{arom.}$), 6.98–6.96 (d, $^3J_{H,H}$ = 8.2 Hz, 8 H, $H_{arom.}$), 6.79–6.77 (d, $^3J_{H,H}$ = 8.2 Hz, 8 H, $H_{arom.}$), 6.71–6.70 (d. $^3J_{H,H}$ = 8.2 Hz, 8 H, $H_{arom.}$), 6.67–6.65 (d, $^3J_{H,H}$ = 8.2 Hz, 8 H, $H_{arom.}$), 3.13–2.99 (4s, 16 H, ≡C*H*) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2, 300 K): δ = 195.3 (*C*=O), 141.9, 141.3, 141.3, 140.8, 140.6, 140.4, 140.4, 140.3, 139.3, 139.2, 137.3, 135.3, 132.0, 131.7, 131.6, 131.5, 131.4, 131.3, 131.2, 130.2, 129.2 (all $C_{arom.}$), 120.9 120.3, 120.1 (all *C*–C≡), 83.5, 83.6, (all *C*≡CH) 78.1, 78.0, 77.7, 77.7 (all ≡*C*H) ppm. MALDI TOF mass: *m/z* (%) = 2090 (100) [M]$^+$, 4182 (10) [2 M]$^+$ ($C_{165}H_{90}O$ calcd. 2089).

12: A mixture of **11** (60 mg, 28.7 μmol) and **7** (530 mg, 1.38 mmol) was dissolved in *o*-xylene (4 mL) and refluxed at 170 °C for 3 days under argon. The solvent was removed under reduced pressure and the crude product purified by column chromatography (petroleum ether/CH_2Cl_2). Precipitation from methanol afforded **12** as a white solid. Yield: 190 mg (24.4 μmol), 85%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.43–7.39 (m, 20 H, $H_{1st+2nd\ generation}$), 7.26 (s, 4 H, $H_{arom.}$), 7.13 (m, 370 H, $H_{arom.}$), 6.54–6.34 (s, 16 H, $H_{arom.}$) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2, 300 K): δ = 196.4 (*C*=O), 142.2, 142.2, 142.1, 142.1, 142.0, 142.0, 141.2, 141.1, 141.0, 141.0, 140.8, 140.6, 140.6, 140.5, 140.4, 139.7, 139.6, 139.6, 139.4, 139.3, 131.9, 131.5, 131.5, 131.4, 130.3, 130.3, 130.2, 130.2, 129.7, 129.6, 127.9, 127.8, 127.8, 127.2, 127.1, 127.1, 126.9, 126.9, 126.5, 126.5, 126.0, 125.9, 125.6, 125.5 ppm. MALDI TOF mass: *m/z* = 7792 (100) [M]$^+$, 7819 (40) [M + Na]$^+$, 7898 (45) [M + Ag]$^+$. $C_{613}H_{410}O$ (7792): calcd. C 94.49, H 5.30; found C 94.46, H 5.33.

14a: Compound **8** (110 mg, 64.5 μmol) was dissolved in dry THF (5 mL) under argon. A solution of phenyllithium (2 mL, 3.8 mmol, 1.8–2.1 M) in cyclohexane/ether (70:30) was added through a septum and the mixture heated at 70 °C for 16 h. Then H_2O (5 mL) was added, the mixture extracted with CH_2Cl_2/H_2O and the organic solvent removed under reduced pressure. The crude product was purified by column chromatography (petroleum ether/CH_2Cl_2) and precipitation from methanol to afford **14a** as a white solid. Yield: 80 mg (45 μmol), 70%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.21 (s, 4 H, $H_{1st\ generation}$), 7.16–7.11 (m, 20 H, $H_{arom.}$), 6.99–6.62 (m, 65 H, $H_{arom.}$), 6.53 (s, 4 H, 2-H_{Bp}, 2′-H_{Bp}, 6-H_{Bp}, 6′H_{Bp}), 6.47–6.46 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, 4-H_{Bp}, 4′-H_{Bp}), 1.89 (s, 1 H, O*H*) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ = 146.6, 145.6, 142.1, 141.1, 141.0, 140.8, 140.5, 140.3, 139.8, 139.6, 131.9, 131.8, 131.8, 131.3, 130.6, 130.3, 128.2, 128.1, 128.0, 127.9, 127.3, 127.2, 126.9, 126.7, 125.9, 125.7, 81.6 (*C*–OH) ppm. FD mass (8 kV): *m/z* (%) = 1783.7 (100), [M]$^+$, 892.3 (85) [M]$^{2+}$. $C_{139}H_{96}O$ (1782.3): calcd. C 93.67, H 5.43; found C 93.67, H 5.48.

14b: Compound **8** (100 mg, 58.7 μmol) was placed in a Schlenck tube under argon. (4-Methoxyphenyl)magnesium bromide (3 mL, 1.5 mmol, 0.5 M in THF) was added and the reaction mixture refluxed at 70 °C for 24 h. After cooling, H_2O (5 mL) was added and the solution stirred for another 30 min. Extraction with CH_2Cl_2/H_2O and concentration of the organic layer under reduced pressure gave the crude product, which was further purified by column chromatography (petroleum ether/CH_2Cl_2) and precipitation from methanol to afford **14b** as a white solid. Yield: 70 mg (39 μmol), 66%. ^{1}H NMR (700 MHz, CD_2Cl_2, 300 K): δ = 7.21 (s, 4 H, $H_{1st\ generation}$), 7.18–7.11 (m, 20 H, $H_{arom.}$), 6.99 (s, 2 H, 4-H_{Bp}, 4′-H_{Bp}), 6.93–6.92 (m, 12 H, $H_{arom.}$), 6.86–6.83 (m, 22 H, $H_{arom.}$), 6.78–6.75 (m, 16 H, $H_{arom.}$), 6.68–6.67 (m, 4 H, $H_{arom.}$), 6.63–6.61 (m, 8 H, $H_{arom.}$), 6.53–6.52 (2s, 4 H, 2-H_{Bp}, 2′-H_{Bp}, 6-H_{Bp}, 6′-H_{Bp}), 6.35–6.34 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H_{arom}), 3.80 (s, 3 H, CH_3), 1.87 (s, 1 H, O*H*) ppm. ^{13}C NMR (175 MHz, CD_2Cl_2, 300 K): δ = 158.6, 146.8, 142.1, 142.0, 141.2, 141.1, 141.0, 140.8, 140.5, 140.4, 139.7, 139.6, 138.1, 132.0, 131.9, 131.8, 131.4, 130.6, 130.3, 129.8, 128.2, 127.9, 127.8, 127.2, 126.9, 126.7, 126.0, 125.9, 125.7, 113.3, 81.3 (*C*–OH), 55.6 (*C*H$_3$) ppm. FD mass (8 kV): *m/z* (%) = 1815.2 (100) [M]$^+$, 1797.8 (30) [M – 17 = OH]$^+$. $C_{140}H_{98}O_2$ (1812.3): calcd. C 92.78, H 5.45; found C 92.43, H 5.38.

14c: Compound **8** (96 mg, 56.3 μmol) was dissolved in dry THF (5 mL) under argon. A solution of *n*-butyllithium (2 mL, 3.2 mmol, 1.6 M) in hexane was added through a septum and the mixture heated at 70 °C for 16 h. Afterwards H_2O (5 mL) was added, the mixture extracted with CH_2Cl_2/H_2O and the organic solvent removed under reduced pressure. The crude product was purified by column-chromatographie (petroleum ether/CH_2Cl_2) and precipitation from methanol to afford **14c** as a white solid. Yield: 70 mg (39 μmol), 70%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ = 7.24 (s, 4 H, $H_{1st\ generation}$), 7.17–7.12 (m, 20 H, $H_{arom.}$), 6.96–6.69 (m, 63 H, $H_{arom.}$), 6.61 (s, 4 H, 2-H_{Bp}, 2′-H_{Bp}, 6-H_{Bp}, 6′-H_{Bp}), 1.28–1.24 (m, 4 H, α-CH_2, β-CH_2), 1.15–1.06 (sept, 2 H, $^3J_{H,H}$ = 7.4 Hz, γ-CH_2), 0.81 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ = 146.5 (C_{Bp}-1, C_{Bp}-1′), 142.0, 141.9, 141.1, 141.0, 140.9, 140.8, 140.4, 139.6, 139.5, 131.9, 131.8, 131.7, 131.3, 130.3, 129.9, 127.8, 127.2, 127.1, 126.8, 126.6, 125.9, 125.6, 77.5 (*C*–OH), 40.9 (α-*C*H$_2$), 25.4 (β-*C*H$_2$), 23.3 (γ-*C*H$_2$), 14.2 (*C*H$_3$) ppm. FD mass (8 kV): *m/z* (%) = 1761.5 (100) [M]$^+$. $C_{137}H_{100}O$ (1762.3): calcd. C 93.37, H 5.72; found C 93.04, H 5.61.

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