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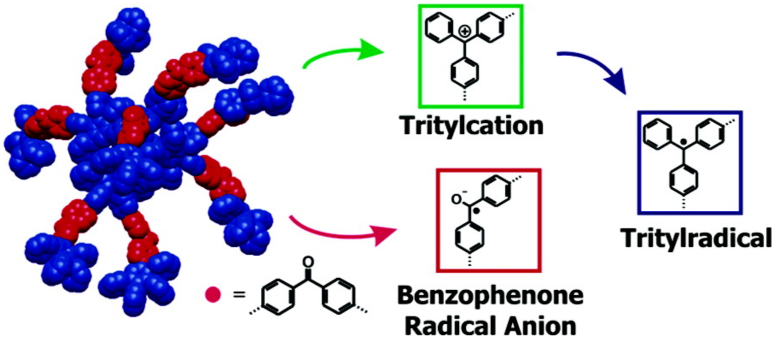

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Multiple Functionalization of Benzophenones Inside Polyphenylene Dendrimers − Toward Entrapped Ions and Radicals

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Abstract: Polyphenylene dendrimers possessing a defined number of keto groups in the dendritic scaffold have been synthesized by using a benzophenone-functionalized tetraphenylcyclopentadienone branching unit. A postsynthetic functionalization of the polyphenylene backbone was achieved by reacting the entrapped keto groups with organolithium reagents yielding monodisperse alcohol products. To investigate the accessibility and reactivity of the embedded groups, many functions of different size and nature, for example, the chromophore pyrene, were introduced. Moreover, suitable precursors for the synthesis of dendrimer entrapped species, trityl cations, trityl radicals, and ketyl radical anions, were obtained. To gain insight into the structure of these newly functionalized dendrimers, UV/vis, EPR, and NMR measurements have been performed. They showed a delocalization of the charge/spin into the polyphenylene dendritic arms leading to a stabilization of the ions/radicals. Remarkably, for the ketyl radicals, EPR measurements indicated the occurrence of intermolecular metal-bridged biradicals. They suggest the existence of a dendritic radical network of the dendrimers themselves.

Introduction

Throughout the last years, there has been an increasing interest in the synthesis of three-dimensional architectures bearing multiple spin and/or charge carrying functions.[1] In this regard, dendritic structures with their unique properties, for example, monodispersity and mesoscopic dimension, have been functionalized with suitable groups that allowed the synthesis of novel nanoobjects. For instance, Rajca et al.[2] combined dendritic macrocycles with spatially well-defined polarized π-spins to achieve organic magnetic materials on the nanoscale. However, the experimental examination and quantification of radical species is often difficult because of their high reactivity and thus short lifetime. To circumvent these problems, Ballester et al. introduced perchlorinated triphenylmethyl radicals possessing high chemical and thermal stability.[1i] The investigation of the monomer−dimer equilibrium of the parent triphenylmethyl radical showed that phenyl substituents are very powerful stabilizing substituents, mainly due to resonance. In addition to electronic effects, bulky substituents can produce steric hindrance keeping the radicals apart from each other.[3]

To obtain defined nanostructures,[4] many functions have been introduced in the core[5] or in the periphery[6] of dendrimers. However, only few examples of a regiospecific covalent functionalization of the interior dendrimer backbone are known.[7] In general, two possibilities exist for the functionalization of

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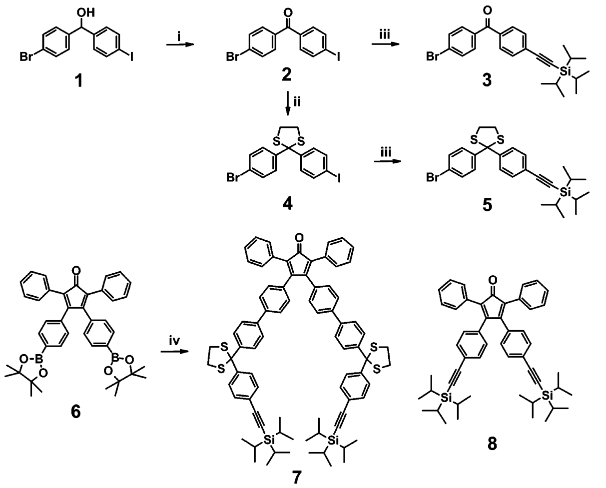
inner dendrimer generations: (i) the use of a branching unit carrying the desired function (a priori) or (ii) a postsynthetic approach (a posteriori). The latter offers a larger flexibility because once the dendrimer has been synthesized, the functionalization can easily be varied. Recently, Majoral and Caminade et al.[8] introduced phosphorus dendrimers, in which a layer-specific grafting of different reagents has been achieved. Schlüter et al.[9] presented a concept based on internal aryl bromo functions that could be reacted using Suzuki cross-coupling.

Polyphenylene dendrimers have attracted great attention, as they possess stiff and shape-persistent dendrons,[10] which allowed the efficient shielding of core moieties[11] as well as the topologically defined placement of functions on the surface.[12] Up to now, however, defined postsynthetic functionalizations in the scaffold of polyphenylene dendrimers are still elusive.

In this paper, we present the synthesis of a benzophenone-substituted tetraphenylcyclopentadienone branching unit that was employed in a Diels−Alder cycloaddition to build up polyphenylene dendrimers with a defined number of incorporated keto groups. Because keto groups are known to be important substrates for several reactions, for example, Aldol- and Claisen-condensation or Grignard-reactions,[13] they exhibit both prerequisites for a postsynthetic reaction, high reactivity as well as high selectivity. A postsynthetic functionalization was therefore applied by reacting the dendrimers with organolithium reagents. In that way, suitable precursors for the synthesis of trityl radicals and trityl cations were obtained. Moreover, because the direct reduction of benzophenone with potassium is known to form the ketyl radical anion,[14] this was also tested for the benzophenone bearing dendrimers. Entrapping radicals or charged species in polyphenylene dendrons was expected to lead to a delocalization of their charge/spin into the all-phenyl backbone. Moreover, the intramolecular recombination or dimerization of radical centers should be avoided due to the hindered motion of the shape-persistent dendritic arms. EPR and NMR techniques were used to investigate the role of the polyphenylene shell upon the accessibility and the chemical properties of the charge/spin carrying centers.

Scheme 1. Synthesis of the Branching Unit 3,4-Bis-[4-(2-{4-[(triisopropylsilylethynyl)-ethynyl]-phenyl}-[1,3]dithiolan-2-yl)-phenyl]-2,5-diphenylcyclopentadienone (**7**)[a]



[a] (i) Oxalyl chloride, DMSO, triethylamine, CH_2Cl_2, −78 °C, 93%; (ii) ethane-1,2-dithiole, $BF_3{\cdot}OAc_2$, CH_2Cl_2, 95%; (iii) **2**/**4**, 1.1 equiv of triisopropylsilylethyne, $[Pd(PPh_3)_2]Cl_2$, PPh_3, CuI, toluene/triethylamine, 97/96%; (iv) 3 equiv of **5**, $Pd(PPh_3)_4$, K_2CO_3, toluene/ethanol, 80 °C, 78%.

Results and Discussion

Synthesis of the Scaffold-Functionalized Polyphenylene Dendrimers. A key reagent for the construction of polyphenylene dendrimers with embedded keto groups is a tetraphenylcyclopentadienone branching unit, carrying benzophenones, and, in addition, ethynyl groups allowing further growth in a Diels−Alder cycloaddition. Recently, we have shown that the boronic acid-functionalized tetraphenylcyclopentadienone **6** is a versatile building block, as bromo- or iodo-substituted aromatic compounds with the desired functionality can easily be introduced.[15] Therefore, the asymmetric benzophenone derivative **3** was synthesized in which the bromo function was designed for the coupling with **6** (Scheme 1).

After mono-lithiation of 1,4-diiodo-benzene, the reaction was quenched with 4-bromo-benzaldehyde to afford (4-bromo-phenyl)-(4-iodo-phenyl)-methanol (**1**) in 80% yield.[16] Subsequent Swern oxidation[17] generated **2** in almost quantitative yield. The desymmetrization of the benzophenone made sure that the following Hagihara−Sonogashira cross-coupling[18] with triisopropylsilylethyne could be carried out selectively on the iodo function to obtain a single product in high yield. Unfortunately, the Suzuki cross-coupling[19] of **3** with **6** gave the desired benzophenone-functionalized tetraphenylcyclopentadienone (structure not shown) in only 20% yield, even when different catalyst/base systems were employed. However, after the introduction of a dithiolane protecting group,[20] the reaction of **5** with **6** furnished the tetraphenylcyclopentadienone **7** in 78% yield

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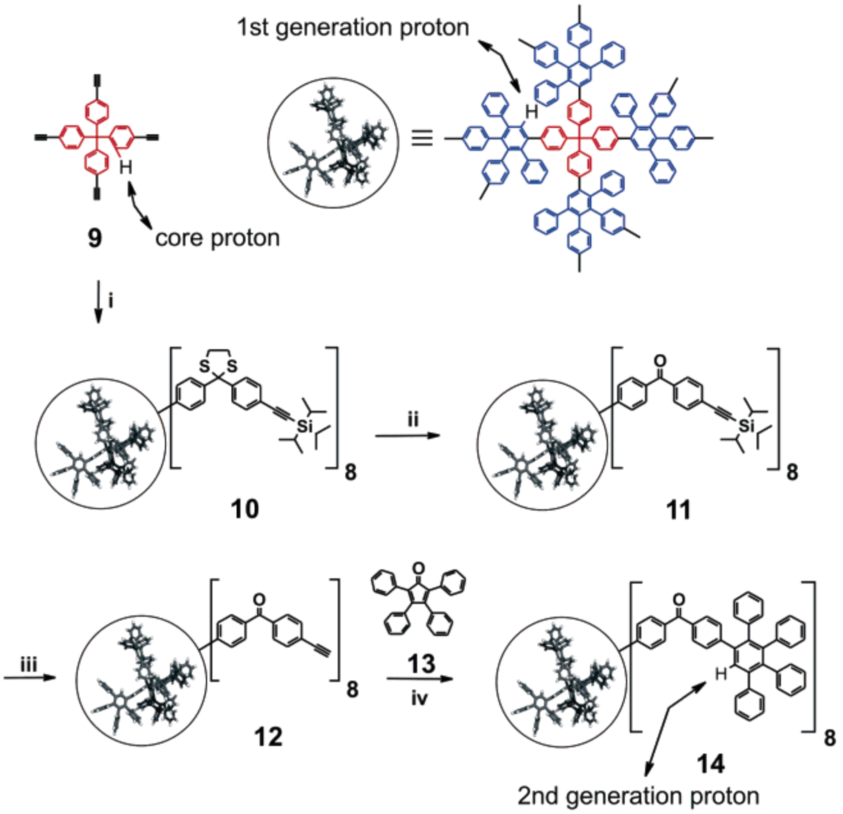
Scheme 2. Synthesis of the Benzophenone-Functionalized Polyphenylene Dendrimer **14**[a]



[a] (i) 6 equiv of **7**, *o*-xylene, 155 °C, 98%; (ii) *t*-butylbromide, DMSO, 75 °C, 94%; (iii) 8 equiv of TBAF, THF, 96%; (iv) 16 equiv of **13**, *o*-xylene, 160 °C, 97%.

(Scheme 1). The key step in the synthesis of structurally well-defined polyphenylene dendrimers is the repeated [4+2] cycloaddition of the branching unit to an ethynyl-substituted core or dendrimer and subsequent deprotection of the triisopropylsilyl (TIPS) protected ethynyl groups, which activates the molecule for further growth. To place the functional groups in the inner dendritic scaffold, **7** was used in the first step of dendrimer growth to give the first-generation dendrimer **10** (Scheme 2).

The monodispersity of the ketone bearing polyphenylene dendrimers could easily be proven by means of MALDI-TOF mass spectrometry. In the case of **10**, no product mass signal could be detected due to fragmentation of the dithiolane protecting groups. However, the absence of the ethynyl ^{1}H NMR proton signal of the core **9** indicated quantitative conversion. To enable MALDI-TOF mass spectrometry for the higher generation dendrimers, the deprotection of the benzophenones was accomplished using *tert*-butylbromide and DMSO to give **11**.[21] The ethynyl-functionalized first-generation dendrimer **12** was obtained by quantitative desilylation of the TIPS protecting groups with tetrabutylammonium fluoride (TBAF). Subsequent Diels−Alder cycloaddition of **12** and tetraphenylcyclopentadienone **13** gave the second-generation dendrimer **14** in 97% yield. The herein described dendrimers possess good solubility in common organic solvents (CH_2Cl_2, toluene, or THF, e.g., **11** even in hexane), which allowed their purification by column chromatography as well as their complete characterization by standard spectroscopic techniques. ^{1}H NMR spectroscopy showed well-separated and clearly assignable signals for some of the aromatic protons as well as for the protons of the dithiolanyl, ethynyl, or TIPS groups. The relative intensities of aromatic and aliphatic signals corresponded well with the expected values. An additional proof of structure could be obtained because characteristic signals of the core protons were found (Scheme 2). Further, the protons on the pentaphenyl repeating units showed generation-dependent chemical shifts in the ^{1}H NMR spectra. To obtain an impression of the shape and size of the synthesized dendrimers, molecular mechanics calculations were carried out by applying the MMFF method.[22] Figure 1 shows as an example the three-dimensional structure of the second-generation dendrimer **14** functionalized with eight keto groups in its scaffold.

As the benzophenone-functionalized branching unit **7** possesses elongated branching arms, the calculated diameter of **14** (5.8 nm) is significantly bigger than that for the corresponding second-generation polyphenylene dendrimer (4.4 nm),[23] constructed from the parent branching unit **8** (Scheme 2). The three-dimensional structure of **14** suggested that even in the scaffold of the second-generation dendrimer the benzophenones (red) are not shielded completely. This would allow reaction partners to approach the keto groups, which might therefore become accessible toward chemical transformations. This point was investigated by further chemical transformations. A well-investigated π-system is the trityl cation, which is generated immediately when the corresponding triphenylmethanol derivative is reacted with a stong acid, such as trifluoroacidic acid

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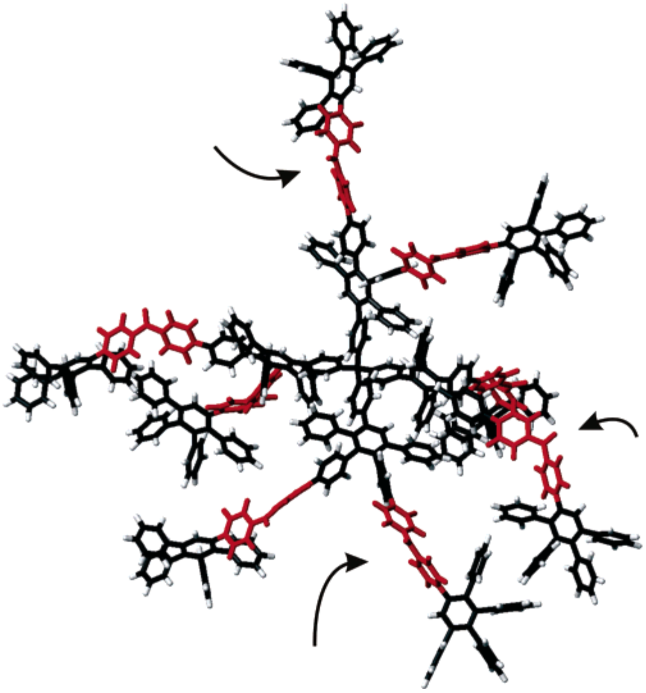
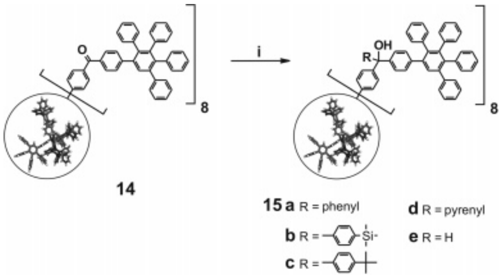


Figure 1. Molecular model of the second-generation dendrimer **14** with eight benzophenones (red).

Scheme 3. Reaction of the Benzophenone-Functionalized Dendrimer **14** with Lithium Reagents[a]

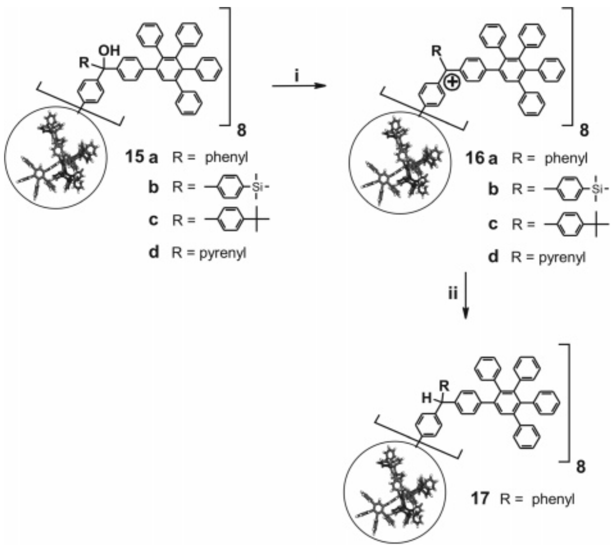


[a] (i) **15a** 100 equiv of C_6H_5Li, THF, 70 °C, 97%; **15b**−**d** *tert*-butyllithium, 1-bromo-4-trimethylsilyl-(TMS)-benzene/1-bromo-4-*tert*-butylbenzene/1-bromopyrene, respectively, THF, 70 °C, 96%, 78%, and 76%, respectively; **15e** 170 equiv of $LiAlH_4$, THF, 70 °C, 80%.

(TFA).[24] Because keto groups are known to be highly reactive toward organolithium reagents, multiple triphenylmethanol groups should be available by the reaction of the benzophenone bearing dendrimer **14** with, for example, phenyllithium. Accordingly, an excess of phenyllithium was reacted with **14** in refluxing THF, yielding the eight times substituted product **15a** in 97% yield (Scheme 3).

Purification of **15a** was easily achieved by repetitive precipitation from methanol. No side products could be observed by NMR spectroscopy, elemental analysis, and mass spectrometry. The ready availability of the polyalcohol **15a** qualified it as an attractive precursor for the synthesis of a dendrimer with multiple entrapped trityl cations. When **15a** was reacted with trifluoroacidic acid (TFA) in CH_2Cl_2, the reaction mixture immediately turned deep blue, indicating the formation of the corresponding trityl cations (Scheme 4).

Scheme 4. Formation of the Trityl Cations **16a**−**d** and Hydride Abstraction of **16a**[a]



[a] (i) TFA/BF_3·OEt_2, respectively, CH_2Cl_2; (ii) **16a**, triethylsilane, CH_2Cl_2, 0 °C, 90%.

A detailed spectroscopic characterization of the trityl cations is given below. When borontrifluoride diethyl etherate (BF_3·OEt_2) was used as the acid, the octacation **16a** could be isolated as the dark-blue trifluoroborate salt. The solid showed no degradation when stored under an argon atmosphere at room temperature for months. Hydrolysis of **16a** regenerated the triphenylmethanol precursor as indicated by identical NMR spectra of the hydrolysis product and **15a**. To achieve an independent structure proof, the reduction of **16a** was carried out using triethylsilane as a hydride donor[25] (Scheme 4). A solution of **16a** in CH_2Cl_2 at 0 °C was reacted with triethylsilane, whereupon the color of the reaction mixture faded away immediately. The desired single product **17** could be verified by NMR as well as by MALDI-TOF mass spectrometry. The stability and therefore easy handling of the trityl cation-functionalized dendrimer **16a** was expected to make it an ideal candidate for the synthesis of a dendrimer bearing multiple trityl radicals. A variety of procedures involving the reduction of a triarylmethyl carbenium ion and the thermal or photolytic decomposition of a suitable precursor are known.[26] The dimerization of triphenylmethyl radicals can be inhibited by bulky para substituents; for example, the tris(*p*-*tert*-butylphenyl)methyl radical is thought to be fully dissociated in solution.[27] To suppress the possible intramolecular recombination of the dendrimer embedded trityl radicals, 1-bromo-4-*tert*-butylbenzene was converted via halogen−metal exchange into its lithiumreagent. Subsequent reaction with **14** in the same way as described before yielded dendrimer **15c** (Scheme 3). Similarly to **15a**, **15c** was converted into its corresponding trityl cation derivative **16c**. The synthesis of **15a** and **15c** demonstrated the use of imbedded keto groups for the regiospecific postsynthetic

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(27) Colle, K. S.; Glaspie, P. S.; Lewis, E. S. *J. Chem. Soc., Chem. Commun.* **1975**, 266−267. However, the fact that crystalline head-to-head dimers can be obtained from solutions of tris(2,6-di-*tert*-butyl-4-diphenyl)methyl radicals (Stein, M.; Winter, W.; Rieker, A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 692−694) and of tris(3,5-di-*tert*-butyl-4-diphenyl)methyl radicals (Kahr, B.; Vanengen, D.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 8305−8307) raises the possibility of head-to-head association in solution.

functionalization of the interior dendrimer backbone. To show the possibility of a more challenging functionalization, a trimethylsilyl (TMS) group was introduced analogously to the above-described *p-tert*-butyl group to give **15b** (Scheme 3). TMS groups can easily be converted into iodides,[28] which would then allow further functionalization of the inner dendritic structure via Suzuki or Hagihara−Sonogashira cross-coupling. Unfortunately, the reaction of iodine monochloride with **15b** did not proceed quantitatively.

To test the accessibility of the benzophenones toward even larger nucleophiles, the introduction of the sterically demanding chromophore pyrene was considered. Pyrene is one of the best studied chromophores with well-known fluorescence properties.[29] When two pyrene molecules are in close proximity, excimers are formed leading to a characteristic emission in the UV/vis spectrum,[29c] thus making pyrene ideally suited to study aggregation phenomena. Accordingly, the UV/vis spectra of a monodisperse dendrimer bearing multiple pyrene units in its dendritic scaffold were expected to give information about the spatial arrangement of the introduced pyrenes. Thus, 1-bromopyrene was lithiated and reacted with the keto groups in the second-generation dendrimer **14** (Scheme 3). After prolonged reaction time, the 8-fold functionalization yielding **15d** could be proven by NMR and MALDI-TOF mass measurements, showing that the outer polyphenylene shell did not hamper the penetration of a molecule as large as pyrene.[30] **15b** and **15d** were converted into their corresponding trityl cation derivatives **16b** and **16d** similarly to the before described **16a** (Scheme 4). To show further derivatizations of encapsulated benzophenone functions, we tried to reduce the keto groups via hydrogenation. The reaction of **14** with an excess of $LiAlH_4$ was carried out in refluxing THF and afforded after hydrolysis and precipitation from methanol **15e** as a single product in good yield (Scheme 3). Despite the rigorous reaction conditions, no degradation of the dendrons was observed underlining the chemical inertness of polyphenylene dendrimers.

Spectroscopic Properties of the Charge and Spin Carrying Dendrimers. In the following section, the in depth spectroscopic characterization of the charge and spin carrying dendrimers is presented. High-resolution ^{1}H and ^{13}C NMR data for **16a−d** were recorded to quantify the number of charged centers. Single distinctive peaks for the positively charged carbon of **16a−d** were found in the ^{13}C NMR spectra proving the quantitative conversion of all eight triphenylmethanol groups into the corresponding trityl cations. ^{13}C NMR spectra of **16a−c** showed shifts of $\Delta\delta = 121.8$ ppm (C−OH, 81.8 ppm; C$^+$, 203.6 ppm) for **16a−b** and $\Delta\delta = 120.1$ ppm (C−OH, 81.7 ppm; C$^+$, 201.8 ppm) for **16c**. For the pyrenyl-substituted dendrimer **16d**, a downfield shift by $\Delta\delta = 112.0$ ppm (C−OH, 83.6 ppm; C$^+$, 195.6 ppm) was found. The transformation of the parent triphenylmethanol into the corresponding trityl cation induced a downfield shift of the methyl carbon by $\Delta\delta = 134.4$ ppm (C−OH, 77.2 ppm; C$^+$, 211.6 ppm).[31] **16d** showed the smallest downfield shift due to the conjugated π-system of pyrene. The shift was even lower than for the reference (1-pyrenyl)-diphenylmethyl cation $\Delta\delta = 117.5$ ppm (C−OH, 83.9 ppm; C$^+$, 201.4 ppm).[3] The smaller downfield shift of the trityl cations embedded in the dendritic structures **16a−d** as compared to the parent trityl cation can be attributed to the delocalization of the positive charge into the π-system of the neighboring dendritic phenyl rings. Characterization of the octatrityl cations **16a−d** by ^{1}H NMR spectroscopy displayed well-separated signals for the aromatic triphenylmethyl protons. The chemical shifts of **16a−d** were derived from H,H-COSY and H,H-NOESY experiments and are shown in Figure 2 (see also Supporting Information).

For comparison, the spectra of the polyalcohol precursors **15a−d** are shown as well. The signal patterns of the triphenylmethyl cation units of **16a−c** were similar to those of tetra- and hexatrityl cations, obtained by Rathore et al.,[24a] as well as to those of the parent trityl cation.[33] The peak assignment for the protons of the pyrenyl units in **16d** agreed with published data[32] and is given as an inset in Figure 2. A generation-dependent chemical shift of the protons located on the pentaphenylunits of the polyalcohol precursors **15a−d** was observed (Scheme 2). For the protons of the first generation, singlets occurred at $\delta = 7.65$ ppm (**15a**) and 7.60 ppm (**15b−d**), respectively. The protons of the second generation were located at $\delta = 7.58$ ppm (**15a**), 7.52 ppm (**15b**, **15c**), and 7.56 ppm (**15d**). Generating the octatrityl cations **16a−d** resulted in a downfield shift of the first- and second-generation proton resonances due to the delocalization of the positive charge into the adjacent phenyl rings supporting the results from the ^{13}C NMR spectra. In this regard, the first-generation protons were downfield shifted by $\Delta\delta = 0.14$ ppm for **16a−c** and $\Delta\delta = 0.13$ ppm for **16d**. The second-generation protons displayed a larger downfield shift of $\Delta\delta = 0.22$ ppm for **16a−c** and 0.18 ppm for **16d**, respectively. Probably this is due to the smaller distance between the positively charged carbon and the second-generation proton (∼6.6 Å) as compared to the larger distance (∼12.3 Å) between the first-generation proton and the cationic center.[34] Different from high-resolution NMR data, the optical absorption spectra of **16a−c** were quite similar with a strong absorption at $\lambda \approx 600$ nm red shifted as compared to the parent trityl cation (twin band, $\lambda_{max} = 410$ and 432 nm).[35] **16d** possesses an additional strong absorption band at $\lambda = 742$ nm, which is similar to the reference (1-pyrenyl)diphenylmethyl cation.[36] The optical absorption spectra are included in the Supporting Information. The strong bathochromic shifts seen for the dendrimer embedded trityl cations **16a−c** indicate a delocalization of the positive charge into the neighboring phenyl rings supporting the results from the ^{1}H and ^{13}C NMR measurements. Furthermore, UV/vis spectra with similar absorption bands were found for highly conjugated systems

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(30) However, the prolonged reaction time was probably not only a result of the size of the nucleophile but also of the delocalization of the negative charge in the pyrene moiety.

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(34) Distances were derived from three-dimensional structures calculated by the MMFF method.[22]

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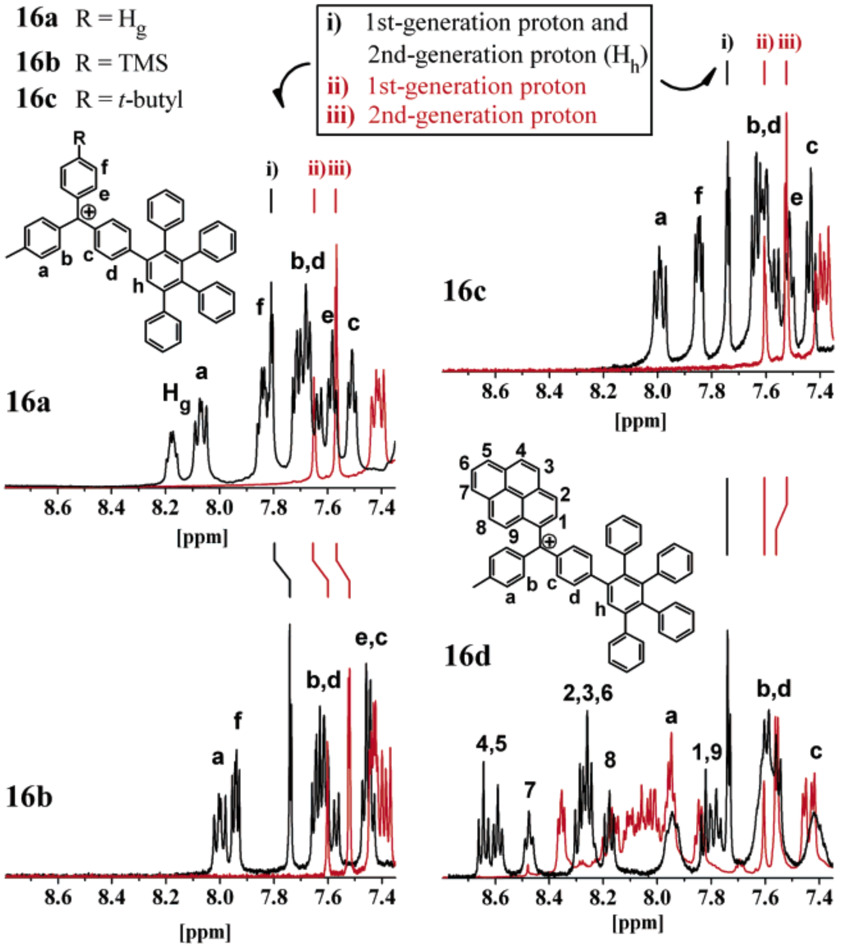
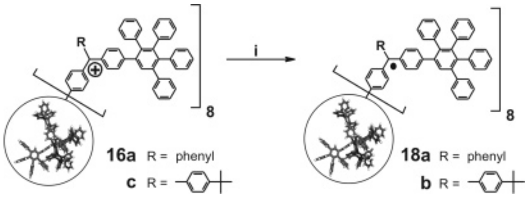


Figure 2. ^{1}H NMR spectra of **16a**−**d** trifluoroacidic acid salts (black line and assignment) and of their corresponding precursors **15a**−**d** (red line and assignment) (500 MHz, CD_2Cl_2/*d*-TFA, 300 K).

consisting of a central triphenylmethyl cation with attached oligo(1,4-phenylenevinylene)s.[24b]

The 8-fold pyrenyl-functionalized dendrimer **15d** was obtained from the postsynthetic functionalization of **14** (Scheme 3). Its absorption spectrum showed signal patterns comparable to that of unsubstituted pyrene (Supporting Information) except for additional strong absorptions at short wavelengths belonging to the dendritic polyphenylene backbone.[37] The introduced pyrenes are bound via a sp^3 carbon; thus their conjugation with the polyphenylene dendrons is interrupted. Only small bathochromic shifts of the pyrene absorption ($\Delta\lambda_{max} = 11$ nm) were therefore induced in contrast to 1,3,6,8-tetraphenylpyrene ($\Delta\lambda_{max} = 43$ nm).[38] The extinction coefficient ϵ of **15d** (2.47×10^4 m^2 mol^{-1}, 348 nm) was approximately the 8-fold value as for monomer pyrene (3.17×10^3 m^2 mol^{-1}, 337 nm), further supporting the 8-fold incorporation of pyrene into the dendritic backbone of **15d**. Unsubstituted pyrene exhibits a strong characteristic excimer fluorescence at $\lambda = 475$ nm arising from the close proximity of two pyrene molecules.[29c] No excimer fluorescence was observed for the embedded pyrenes in **15d**. A spatially separated arrangement of the pyrene moieties inside the dendrimer backbone can therefore be suggested, mainly due to the stiff and shape-persistent polyphenylene dendrons.[10]

Scheme 5. Reduction of the Octatrityl Cations **16a** and **16c** Yielding the Trityl Radical Bearing Dendrimers **18a**,**b**[a]



[a] (i) CH_2Cl_2, $SnCl_2$.

The stable trityl cation bearing dendrimers **16a** and **16c** was used as starting materials for the synthesis of polyphenylene dendrimers containing multiple trityl radicals in the dendritic scaffold (Scheme 5).

In a sealed glass tube, **16a** was dissolved in CH_2Cl_2 and reduced with $SnCl_2$ to give the dendrimer **18a** bearing multiple trityl radicals. The reaction was followed using UV/vis and EPR spectroscopy. After some hours of mixing, the blue solution of the trityl cations slowly became green and one strong absorption band at ~400 nm with a shoulder at ~370 nm appeared in the UV/vis spectra (Supporting Information). As compared to the parent trityl radical possessing two absorption maxima ($\lambda_{max} = 332$, 515 nm),[39] only the absorption signal at ~400 nm could clearly be detected, while the one at longer wavelength (~570

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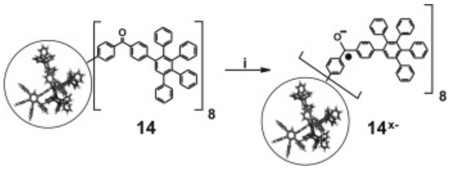
Scheme 6. Formation of Ketyl Radical Anion Bearing Dendrimers **14**$^{x-}$ Starting from **14**^{a}



^{a} (i) Potassium mirror, THF.

nm) was hidden in the strong absorption of the cation. The first absorption of **18a** is shifted by 70 nm as compared to the parent trityl radical and is thus very similar to other phenyl-substituted trityl radicals, for example, 4,4′-diphenyltrityl ($\Delta\lambda_{\max} = 55$ nm).[3b] Accordingly, an efficient delocalization of the spin density into the adjacent phenylene units of **18a** can be assumed. This suggests a similar stabilizing effect of the polyphenylene dendrons for the embedded trityl cations **16a**−**d**, trityl radicals, and the benzophenone radical anions to be discussed later. As $SnCl_2$ is not soluble in CH_2Cl_2, the heterogeneous reduction proceeded very slowly. Even after prolonged reaction times (several days), however, the absorption band of the octatrityl cation **16a** ($\lambda_{\max} \approx 620$ nm) only decreased but did not disappear. It might be suggested that the remaining cation absorption band still hampered the detection of the bathochromically shifted second absorption band of the polyphenylene-substituted trityl radicals. The same behavior was found for the trityl radical derivative **18b**. The EPR spectrum of **18a** showed at least 15 resolved lines (seven lines between the two maxima). Due to the asymmetric nature of the trityl sites, already the proton couplings with the ortho-protons of the three phenyl rings should be different. Furthermore, the neighboring phenyl rings possess some spin density rendering a full analysis of the hyperfine coupling constants difficult. As the para-position of the trityl radicals in **18b** is blocked by a *tert*-butyl group, a reduced number of 13 lines was observed in its EPR-spectrum (five lines between the maxima), indicating the loss of the coupling with the para-proton of the phenyl ring. From the recorded UV/vis and EPR spectra, it thus becomes evident that dendrimer entrapped trityl cations have been converted into their analogous trityl radicals. Upon standing, the initial green color of the solutions became colorless. Similarly, the color faded away immediately when the sealed glass tubes were opened. Obviously, the multitrityl systems **18a**,**b** were less stable than, for example, the perchlorinated triphenylmethyl radicals.[1i]

Extensive studies have been performed on the formation of stable radical anions by the reaction of ketones and aldehydes with metals.[14] This chemistry should be tested for the benzophenones being embedded in the dendritic structure, because we had already shown their accessibility for various chemical transformations. The reduction of the benzophenone bearing polyphenylene dendrimer **14** was performed on a potassium mirror under high vacuum in THF solution (Scheme 6) using a technique previously described.[40]

UV/vis and EPR spectroscopy were applied to monitor the reduction. Upon contacting the solution of the benzophenone bearing dendrimer **14** with the potassium mirror, two increasing absorption bands at $\lambda \approx 410$ and 950 nm were observed in the UV/vis spectra (Figure 3).

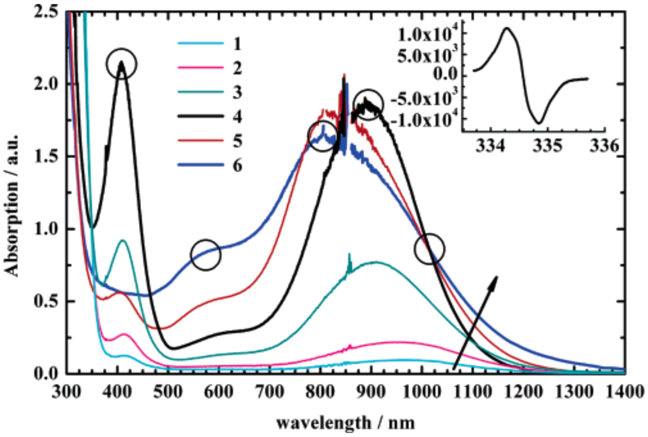


Figure 3. UV/vis absorption spectra of dendrimer **14** in THF (1−6) in the order of further reduction. Inset: EPR spectrum at the maximum intensity of the radical monoanion absorption band ($\lambda = 950$ nm) in THF at 300 K.

These bands can be assigned to the formation of the radical anions of benzophenones in the dendritic scaffold, and the bathochromic shift as compared to the signals of the parent benzophenone anion ($\lambda_{\max} = 336$ and 560 nm)[35] can be attributed to some delocalization of the charge and spin density into the adjacent phenyl rings of the polyphenylene dendrons. At a maximum intensity of these bands, the EPR spectra displayed a broad signal with four shoulders ($a_H \approx 0.27$ mT; see inset in Figure 3). Their hyperfine coupling can be assigned to the four ortho-protons carrying the largest spin density, while the para-positions of the benzophenone radical monoanion are blocked by further phenyl rings. Upon continued reduction on the potassium mirror, the absorption bands of the radical monoanion ($\lambda = 410$ and 950 nm) disappeared and two new absorption bands at $\lambda = 575$ and 800 nm were displayed. They can be attributed to the absorption bands of the benzophenone dianions in the dendrimer.[41] Further, an isosbestic point was observed at $\lambda = 1013$ nm, which indicated that the radical monoanions were transformed into the corresponding dianions without any side reactions. EPR showed a signal of very low intensity; however, no complete diamagnetic state could be achieved even after extended reaction times. The UV/vis signals broadened with prolonged contact times. These findings can be explained by additional charging of the phenylene shell, where these extra charges are not localized on any defined bi- or triphenyl units,[42] but just delocalize by electron hopping over many phenylene units. Thus, while the ketyl species could be generated quantitatively, a well-defined reduction to the benzophenone dianions was not possible, before charging of the polyphenylene shell resulted in dendrimers possessing differently charged species.

The alkali metal reduced ketyl radical anions are well known to form metal (counterion)-bridged dimers, which can be identified as biradicals in the triplet state.[14b,d,41,43] Therefore, also the frozen state EPR spectra were recorded at maximum intensity of the radical monoanion. These EPR spectra displayed characteristic large zero-field splittings of $2D = 15$−17 mT

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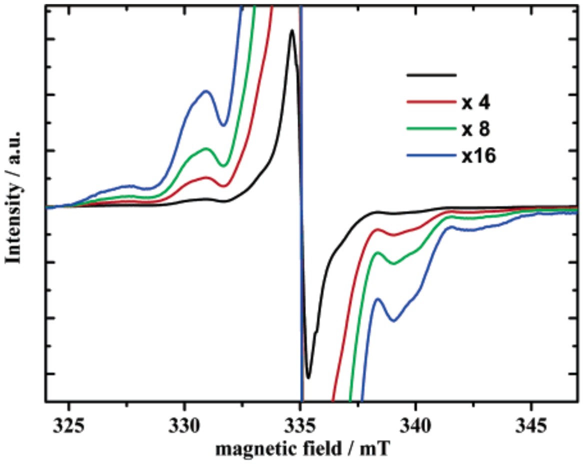

Figure 4. EPR spectra of the radical anion $\mathbf{14}^{x-}$ in THF at ~120 K; zero-field splittings enlarged upon enhanced scale of spectrum.

(Figure 4), which are of size similar to what is usually found for benzophenone anion dimers ($2D \approx 18-20$ mT).[14b,d,41,43]

In addition to the typical signals for the zero-field splittings, which exceeded the spectral width of the anisotropic hyperfine interaction of the monoradicals, also a relatively strong half-field transition at $g \approx 4$ was found ($\Delta m_s = 2$), further demonstrating the triplet character of these biradicals. According to a point dipole evaluation,[44] the observed zero-field splittings correspond to a distance of 0.55−0.57 nm between the radical centers. The intramolecular distances between two benzophenones in the dendritic structure, on the other hand, were found to be 1.2−1.5 nm[34] and should therefore give only small zero-field splittings of $2D < 3.2$ mT for intramolecularly interacting radicals in $\mathbf{14}^{x-}$. Such tiny splittings could unfortunately not be resolved due to the broad radical monoanion signal. Thus, the large zero-field splittings can only be explained by intermolecular penetration of dendritic arms, arranging the ketyl radicals in such a close proximity that metal-bridged biradicals are formed (see Figure 5).

The formation of metal-bridged biradicals is obviously not hindered by the outer phenylene shell, which is in line with the impression gained from the three-dimensional model structure of **14** (Figure 1) displaying larger voids in the dendritic structure. Further, the outer shell is para-substituted to the benzophenone units, thus producing only little steric hindrance around the radical center. Therefore, one can safely suggest the formation of a radical network of the dendrimers, originating from the interlocking of different dendrimers $(\mathbf{14}^{x-}\cdot\mathbf{K}^+)_y$.

Conclusion

The benzophenone-substituted tetraphenylcyclopentadienone **7** was used to synthesize monodisperse polyphenylene dendrimers, bearing a defined number of keto groups in their backbone. These dendrimers turned out to be suitable substrates for a perfect postsynthetic functionalization of the inner dendrimer using organolithium reagents. Even large reaction partners such as pyrene could be introduced quantitatively, allowing the easy and versatile modification of the dendritic scaffold. This postsynthetic procedure should enable even the introduction of functionalities, which are not stable under the conditions of the Diels−Alder cycloaddition ($T \approx 430$ K). Further proof for the accessibility of the inner keto groups was achieved as trityl cations, trityl radicals, and ketyl species could be generated throughout the dendritic scaffold. Thereby, the stiff and shape-persistent polyphenylene dendrons ensured the formation of spatially separated and thus stabilized functions. However, only the trityl cation derivatives were stable under ambient conditions. Particular attention should be drawn to the radical anion bearing dendrimers where the formation of intermolecular biradicals was observed, suggesting the existence of interlocked dendritic arms. It thus became obvious that benzophenone units only shielded by one dendrimer generation are highly accessible to many chemical transformations even with bulky substituents. Therefore, we are currently exploring the formation of biradicals in polyphenylene dendrimers with a higher steric congestion where the benzophenone is used as the core system.

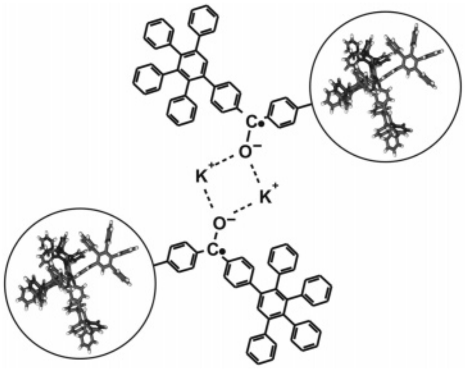

Figure 5. Schematic illustration of the biradical formation of radical anion bearing dendrimers.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft (SFB 625) is gratefully acknowledged. We thank C. Beer for synthetic support.

Supporting Information Available: Additional UV/vis and EPR spectra. Synthesis details and characterization (by NMR and FD/MALDI-TOF mass techniques) of the described dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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