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1a R=H 1b R=SC₆H₁₃, OC₄H₉, OC₅H₁₁

2a R=H 2b R=C₁₂H₂₅ 2c R=OC₁₂H₂₅





3 R=H, C₁₂H₂₅

4a R=C₁₂H₂₅ 4b R=OC₁₂H₂₅



Scheme 1. Polycyclic aromatic hydrocarbons 1-6.

dimensional superstructures that are attracting considerable attention in the field of charge transfer processes.^[1-4] The deposition of monomolecular layers, a central step for using such disklike molecules in nanoelectronic devices, can be performed by evaporating PAHs in ultrahigh vacuum (UHV) and, in case of alkyl-substituted soluble derivatives, also by deposition from solution. However, both preparation procedures cannot be applied to larger PAHs which have recently been synthesized.^[5–8] We therefore present a method to produce PAHs, for example, hexabenzocoronene, directly by a thermally induced cyclodehydrogenation route starting from a precursor molecule adsorbed on a Cu(111) surface. This new synthetic route is based on the following concept:

Template-Mediated Synthesis of Polycyclic Aromatic Hydrocarbons: Cyclodehydrogenation and Planarization of a Hexaphenylbenzene Derivative at a Copper Surface**

Klaus Weiss, Gunda Beernink, Florian Dötz, Alexander Birkner, Klaus Müllen, and Christof H. Wöll*

Polycyclic aromatic hydrocarbons (PAHs) such as triphenylene (1a), hexa-*peri*-hexabenzocoronene (HBC, 2a), and its higher homologue 3 (Scheme 1) form two- and three-

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First a precursor **4b** of the target compound **5** is synthesized and deposited in monolayers on a Cu surface. On heating this adsorbate layer, **4b** is completely dealkylated and converted by cyclodehydrogenation into the planar product **5**. The PAH **5** does not exist in solution, but is stabilized through the interaction of the oxygen atoms with the Cu surface, which also hinders its desorption.

We used near edge X-ray absorption fine structure (NEX-AFS) spectroscopy for the characterization of molecules adsorbed on metal surfaces and for the analysis of products formed by chemical modifications. This method allows a determination of the molecular orientation and provides detailed information on the electronic structure of the molecules. Scanning tunneling microscopy (STM) provides additional information on the lateral order of the molecular adsorbate.

The synthetic route to hexaether **4b** is shown in Scheme 2. Starting from commercially available 4-iodophenol (**7**), etherification with 1-bromodecane affords 4-(dodecyloxy)iodobenzene (**8**), which is then coupled to (trimethylsilyl)acetylene



Scheme 2. Synthesis of the precursor molecule **4b**. $R = OC_{12}H_{25}$.

(TMSA) by using the method developed by Hagihara, Sonogashira et al.^[9] Deprotection of the trimethylsilyl group with KF in DMF afforded the acetylene **9**, which, after renewed Hagihara–Sonogashira coupling with **8** was converted into 4,4'-di(dodecyloxy)diphenylacetylene (**10**). The cyclotrimerization of **10** with $[Co_2(CO)_8]$ in dioxane finally gives the precursor **4b**.^[10] The key step on the path to the PAH **2c** is the oxidative cyclodehydrogenation of the oligophenylene precursors. Optimization of the appropriate cyclization conditions finally proved FeCl₃ to be superior to all other Lewis acids on the way to hexaalkyl-substituted HBCs. In a typical cyclization experiment the precursor 4a is dissolved in dichloromethane, and a solution of FeCl₃ in nitromethane is added dropwise at room temperature. After the starting material had disappeared (TLC) the mixture was precipitated in methanol, and purified by column chromatography or recrystallization. However, in the case of 4b this synthetic protocol did not give the desired compound 2c but the quinone 6 (Scheme 1) in 96% yield. Oxidative dealkylation and dehydrogenation leads to an extended quinonoid system which also incorporates the central aromatic ring. It is well known that compounds such as 4b undergo reactions in the presence of Lewis acids which involve both ether cleavage and oxidation to quinonoid aromatic structures as well as formation of new carbon-carbon bonds between adjacent phenyl rings.^[11, 12] Which of the two reactions occurs first depends on the system.^[12]

The thermogravimetric analysis of **4b** shows that this substance is stable up to temperatures of 490 K; in the temperature range between 490 K and 570 K about 1 % loss in weight can be observed. Monolayers of **4b** with a film thickness of about 3 Å were deposited at a temperature of T = 540 K from a stainless steel Knudsen cell onto a clean, structurally well-defined Cu(111) surface. The deposition rate of 3 Å min⁻¹ was controlled by a quartz crystal microbalance. The samples were heated for 5-10 min to different temperatures and subsequently investigated by NEXAFS spectroscopy. For each temperature the layer thickness was determined by relating the height of the edge jump to the signal intensity at 280 eV.^[13] The results reveal that the amount of molecules present on the surface is essentially unchanged.

Figure 1 shows a series of NEXAFS spectra recorded at the C(1s) absorption edge at normal and grazing photon inci-



Figure 1. C(1s) NEXAFS spectra of **4b** monolayers adsorbed on Cu(111) and heated for 5-10 min to different temperatures. The spectra were recorded for normal and grazing photon incidence, where the angle between the electric field vector of the linearly polarized synchrotron light and the surface normal is 90° and 30°, respectively. The spectra are normalized to the absorption step at 325 eV and focus on the NEXAFS spectral features in close proximity to the absorption edge which is located at around 291 eV. The bottom spectrum was recorded for **4b** deposited from solution.

dence. The spectra recorded for 4b heated to 500 K reveal a well-defined resonance at 285.1 eV, which is assigned to an excitation of C(1s) core level electrons into the lowest unoccupied π^* orbital of the phenyl subunits. Following previous studies on linear saturated hydrocarbons^[14] an additional weak resonance R at 287.4 is attributed to excitations of C(1s) electrons into Rydberg(R) orbitals of the alkyl chains. The comparison with spectra recorded for 4b deposited from solution shows that most of the alkyl chains were removed during evaporation. For the sample heated to temperatures above 500 K the spectra of **4b** recorded at normal and grazing incidence are virtually identical. This absence of dichroism is consistent with a wide distribution of phenyl orientation angles as expected from the nonplanar structure of the molecules. In contrast, spectra recorded for the surface heated to higher temperatures reveal an increasing amount of dichroism, which provides direct evidence for a thermally induced planarization of the molecule 4b.[15] Since such a planarization is-because of steric constraints-not possible for the unmodified molecule, this observation provides strong evidence for the onset of dehydrogenation. This effective planarization is completed after heating the sample to 710 K, at which temperature essentially all molecules are oriented coplanar with the surface.

A more detailed investigation of the NEXAFS spectra reveals that the occurrence of the dichroism is accompanied by two thermally induced effects. The significant broadening of the phenylene π^* -resonance is attributed to the interaction of the phenyl groups with the Cu(111) surface and indicates a direct interaction of all ring systems with the surface. This is a general feature in NEXAFS spectra of π -electron systems in direct contact with metal surfaces and has previously been seen for benzene adsorbed on Cu substrates.^[16, 17] The disappearance of the resonance at 287.4 eV at temperatures above 570 K supports the complete dealkylation of the hexaether on the Cu surface. This finding is supported by the results of a detailed X-ray photoelectron spectroscopy (XPS) study, where in addition-due to the formation of a O-Cu bond - a significant O(1s) binding energy shift has been observed.[18]

To obtain independent information on the products of this temperature-induced reaction we have carried out STM measurements on submonolayers of 4b using a UHV-based instrument. No stable imaging was observed directly after deposition of the molecule. This behavior is expected since the as-deposited molecules are bound to the surface only through weak van der Waals forces and the molecules should thus be very mobile. Reproducible STM results were only obtained after heating the samples above 500 K; typical STM topographs are presented in Figure 2. After the samples had been heated to 570 K, the STM data reveal the formation of well-ordered islands of adsorbed molecules. The diameter of the spherical objects within these islands (bright areas) amounts to 17 ± 1 Å, which within the error bars agrees with the diameter of a single hexaphenylbenzene unit. At this stage the height of the islands amounts to 2.1 Å (see Figure 2). When the samples were heated further, the STM images reveal a substantial reduction in contrast and a significant decrease of the island heights from 1.8 Å (after heating to

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Figure 2. STM images $(300 \text{ Å} \times 300 \text{ Å})$ of **4b** submonolayers adsorbed on Cu(111) and heated for 10–15 min to different temperatures. Right: Line profiles which were taken along the white lines indicated in the images. All images were recorded in the constant current mode. No filtering procedures were used. The images (a)–(c) were recorded with a tip bias voltage of -0.3 V and a tunneling current of 0.03 nA. Image (d) was recorded with a tip bias voltage of -1.0 V and a tunneling current of 0.5 nA.

620 K) to 1.5 Å (after heating to 670 K) and then to 1.2 Å (after heating to 720 K).

The results of our NEXAFS and STM studies provide very strong evidence for the reaction scenario depicted in Figure 3.



Figure 3. Schematic representation of the stepwise planarization of the hexaphenylbenzene unit of **4b** by thermally induced cyclodehydrogenation. The molecule is anchored through the oxygen atoms to the Cu(111) surface. The formation of hexabenzocoronene unit **5** (shown at the bottom, right) is completed at 710 K.

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Heating 4b to a temperature of 470 K leads to sublimation accompanied by substantial dealkylation, and a physisorbed film is deposited on the substrate at room temperature. Heating the substrate to temperatures above 570 K leads to complete dealkylation followed by the formation of an O-Cu bond. A very similar reaction mechanism has been found in a recent study on the temperature-induced reaction of hexabutyloxytriphenylene with a Cu(111) surface.^[19] In this case the cleavage of the alkyl-O bond and the formation of a O-Cu bond was also found to occur at 570 K. At this temperature the height of the islands is 2.1 Å, which is consistent with the presence of the unmodified hexaphenylbenzene unit. The NEXAFS data demonstrate that the structure of the phenyl rings is unmodified at this temperature.

Although the lateral mobility of the molecules is expected to decrease significantly as a result of the formation of covalent O-Cu bonds, the high degree of lateral order seen in the STM topographs demonstrates the presence of a mobility which is sufficiently high to allow the formation of wellordered islands. The NEXAFS data (shape and polarization dependence of the π^* -resonance) as well as the STM measurements (height of the islands) reveal that the dehydrogenation/planarization process is completed at 710-720 K. The substrate is covered with hexabenzocoronene units, which are bound (as shown in 5) through oxygen atoms to the surface. The importance of graphite segments and molecularly defined graphitic structures suggests the transfer of this novel strategy, namely the surface-induced PAH synthesis, to considerably larger oligophenylenes.^[6, 8]

Experimental Section

The NEXAFS measurements were recorded at the synchrotron radiation facility BESSY I (Berlin) using beamline HE-TGM2^[20] and a multichamber UHV system operated in the low 10⁻¹⁰ mbar pressure range. The spectra were recorded in partial electron yield (PEY) detection mode by using a channeltron with a retarding voltage of -150 V. After calibrating the photon energy scale with respect to the NEXAFS data for highly oriented pyrolytic graphite and correcting the spectra for the monochromator transmission function by division through the spectrum of the clean Cu(111) surface, the spectra were normalized to the edge jump at 325 eV.^[21] The STM data were recorded at room temperature with a UHV Omicron Micro STM (base pressure lower than 1×10^{-11} mbar) in the constant current mode with tip bias voltages of -0.3-1.0 V and tunneling currents of 0.03-0.5 nA. Imaging was performed with a scanning speed of 900 Å s⁻¹. In both UHV systems the Cu(111) surface was cleaned by extensive Ar⁺ sputtering (ion energy 1 keV) and annealing cycles prior to the experiments. Measurements using thermogravimetry were carried out using a Mettler TG 50 thermobalance.

8: 4-Iodophenol (7) (100.01 g, 454.59 mmol), 1-bromododecane (226.82 g, 910.08 mmol), and potassium carbonate (125.72 g, 911.01 mmol) were dissolved in dimethylformamide (DMF) (500 mL) and refluxed for 3 h. The solution was then diluted with water, hydrochloric acid (2N), and extracted with dichloromethane. The combined extracts were washed with aequeous sodium bicarbonate, sodium chloride, and dried (MgSO₄). Evaporation of the solvent in vacuo and column chromatography (petroleum ether/ dichloromethane) of the crude product yielded a colorless solid (149.56 g, 85%,). M.p. 37°C; ¹H NMR (200 MHz, CDCl₃): $\delta = 7.56$ (d, ³J(H,H) = 8.0 Hz, 2H; 3-H, 5-H), 6.68 (d, ³J(H,H) = 8.0 Hz, 2H; H-2, 6-H), 3.39 (t, ${}^{3}J(H,H) = 7.0 \text{ Hz}, 2H; \text{ OCH}_{2}, 1.90 - 1.70 \text{ (m, 2H; OCH}_{2}CH_{2}), 1.60 - 1.10$ (m, 18H; H_{alkyl}), 0.91 (t, ${}^{3}J(H,H) = 7.9$ Hz, 3H; CH₃); ${}^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 159.56$ (C-1), 138.64, 117.47 (C_{arene}), 82.88 (C-4), 68.65 (OCH₂), 32.43, 30.15, 30.09, 29.87, 29.68, 26.51, 23.20 (all Calkyl), 14.61 (CH₃); MS (FD, 8 kV): m/z (%): 388.3 (100) [M^+] (calcd for C₁₈H₂₉OI = 388.3).

4-Dodecyloxy(trimethylsilylethynyl)benzene: 4-(Dodecyloxy)iodobenzene (8) (70.02 g, 180.31 mmol), triphenylphosphane (2.36 g, 9.03 mmol), copper(i) iodide (1.71 g, 8.98 mmol), and trans-[Pd(PPh₃)₂Cl₂] (1.90 g, 2.71 mmol) were dissolved in piperidine (700 mL) under an argon atmosphere. TMSA (19.51 g, 197.92 mmol) was added dropwise, and the mixture stirred for 6 h and then cooled to room temperature. The mixture was then washed with aqueous ammonium chloride, extracted with dichloromethane, and the combined extracts were washed again with aqueous ammonium chloride and water, and dried over MgSO4. After removal of the solvent in vacuo, the crude product was purified by column chromatography (petroleum ether/ethyl acetate) to give a colorless oil (58.76 g, 92 %). ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 7.43 \text{ (d}, {}^{3}J(\text{H},\text{H}) = 8.5 \text{ Hz},$ 2H; 3-H, 5-H), 6.82 (d, ${}^{3}J(H,H) = 8.5$ Hz, 2H; 2-H, 6-H), 3.94 (t, ${}^{3}J(H,H) =$ 6.4 Hz, 2H; OCH₂), 1.80 (m, 2H, OCH₂CH₂), 1.33-1.21 (m, 18H; H_{alkyl}), 0.96 (t, 3H, ${}^{3}J(H,H) = 6.3$ Hz; CH₃), 0.23 (s, 9H; SiCH₃); ${}^{13}C$ NMR (50 MHz, CDCl₃): $\delta = 159.90$ (C-1), 133.84, 115.69 (C-2), 114.84, 105.97 (Ar-C=C), 92.60 (Ar-C=C), 68.47 (OCH₂), 32.48, 30.20, 30.15, 29.93, 29.75, 26.56, 23.23, (all C_{alkyl}), 14.62 (CH₃), 0.61 (SiCH₃); MS (FD, 8 kV): m/z (%): 358.2 (100) [M^+] (calcd for C₂₃H₃₈OSi = 358.6).

9: 4-Dodecyloxy(trimethylsilylethynyl)benzene (37.83 g, 105.48 mmol) was dissolved in DMF (450 mL), and a solution of potassium fluoride (18.61 g, 321 mmol) in water (65 mL) was added. The solution was stirred for 3 h, diluted with water, and extracted with toluene. The combined extracts were washed with water, dried over MgSO4, and the solvent evaporated in vacuo. Column chromatography (petroleum ether/ethyl acetate) afforded 9 as a colorless oil (30.06 g, 98 %). ¹H NMR (200 MHz, CDCl₃): δ = 7.46 (d, ${}^{3}J(H,H) = 9.0 Hz, 2H; 3-H, 5-H), 6.85 (d, {}^{3}J(H,H) = 9.0 Hz, 2H; 2-H, 6-H),$ 4.95 (t, ${}^{3}J(H,H) = 7.4$ Hz, 2H; OCH₂), 3.01 (s, 1H; ≡CH), 1.81 (m, 2H; OCH₂CH₂), 1.34-1.21 (m, 18H; H_{alkyl}), 0.98 (t, 3H, ${}^{3}J(H,H) = 7.1$ Hz; CH₃); ¹³C NMR (50 MHz, CDCl₃): $\delta = 160.09$ (C-1), 134.01, 114.95 (C-4), 114.66, 84.30 (Ar-C=C), 76.21 (Ar-C=C), 68.51 (OCH₂), 32.55, 30.28, 30.02, 29.81, 26.63, 23.29 (all C_{alkyl}), 14.65 (CH₃); MS (FD, 8 kV): *m/z* (%): 286.1 (100) $[M^+]$ (calcd for $C_{20}H_{30}O = 286.5$).

10: 4-(Dodecyloxy)iodobenzene (8) (33.55 g, 86.40 mmol), copper(1) iodide (1.64 g, 8.63 mmol), and [Pd(PPh₃)₄] (1.36 g, 1.72 mmol) were dissolved in piperidine (350 mL) under an argon atmosphere. 4-(Dodecyloxy)ethynylbenzene 9 was also dissolved in piperidine (100 mL), added, and the mixture was stirred for 3 h. The resulting mixture was diluted with water (300 mL), extracted with dichloromethane, and dried over Na_2SO_4 . The organic solvent was removed in vacuo and the residue was purified by chromatography with petroleum ether to yield a colorless solid (46.12 g, 97%,). M.p. 97°C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.42$ (d, ³J(H,H) = 8.4 Hz, 4H; 2-H, 2'-H, 6-H, 6'-H), 6.85 (d, ${}^{3}J$ (H,H) = 8.4 Hz, 4H; 3-H, 3'-H, 6-H, 6'-H), 4.98 (t, ${}^{3}J(H,H) = 6.2$ Hz, 4H; OCH₂), 1.80 (m, 4H; OCH₂CH₂), 1.60–1.20 (m, 36H; H_{alkyl}), 0.92 (m, 6H; CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 159.09 (C-4, C-4'), 133.03, 116.08 (C-1, C-1'), 115.02, 84.00 (C=C), 68.58 (OCH₂), 32.41, 30.13, 29.88, 29.73, 26.52, 23.17 (all C_{alkyl}), 14.57 (CH₃); MS (FD, 8 kV): m/z (%): 547.1 (100) [M^+] (calcd for C₃₈H₅₈O₂ = 546.9).

4b: 4,4'-(Dodecyloxy)diphenylacetylene (10) (30.50 g, 54.95 mmol) and $[\mathrm{Co}_2(\mathrm{CO})_8]$ (0.51 mg, $1.49\times10^{-3}\,\mathrm{mmol})$ were dissolved in 1,4-dioxane (600 mL) under an argon atmosphere and refluxed for 4 h. Solvent was removed in vacuo and the brown residue purified by column chromatography (petroleum ether/dichloromethane) to give a yellowish solid (26.72 g, 89%). M.p. 52°C; ¹H NMR (250 MHz, CD₂Cl₂): $\delta = 6.68$ (d, ³J(H,H) = 8.5 Hz, 12 H; H meta to O), 6.40 (d, ${}^{3}J(H,H) = 8.5$ Hz, 12 H; H ortho to O), 4.74 (t, ${}^{3}J(H,H) = 6.6$ Hz, 12H; OCH₂), 1.64 (m, 12H; OCH₂CH₂), 1.45 – 1.15 (m, 108H; H_{alkyl}), 0.87 (m, 18H; CH₃); ¹³C NMR (75 MHz, CDCl₃): $\delta = 156.80$ (C_{arene}-O), 140.75, 134.05, 132.95, 113.38 (all C_{arene}), 68.24 (OCH₂), 32.45, 30.09, 29.96, 29.82, 26.53, 23.16 (all C_{alkyl}), 14.57 (CH₃); MS (FD, 8 kV): m/z (%): 1639.5(100) [M^+] (calcd for C₁₁₄H₁₇₄O₆ = 1639.3).

6: Hexaphenylbenzene (4b) (1.01 g, 0.62 mmol) was dissolved in dichloromethane (150 mL) in a Schlenk flask under an argon atmosphere. Throughout the whole reaction a constant stream of argon was bubbled through the mixture to remove HCl formed in situ. A solution of FeCl₂ (1.80 g, 11.10 mmol) in nitromethane was added dropwise and the mixture stirred for 30 min at room temperatue. Methanol (100 mL) was added and a beige solid precipitated which was filtered and dried in vacuo (768 mg, 96%). M.p. 178°C; ¹H NMR (500 MHz, [D₆]DMSO, 393 K): $\delta = 7.32$ (d, ${}^{3}J(H,H) = 8.4 \text{ Hz}, 4 \text{ H}; H_{\text{arene}}), 7.04 \text{ (d, } {}^{3}J(H,H) = 8.4 \text{ Hz}, 4 \text{ H}; H_{\text{arene}}), 6.75$ $(dd, {}^{3}J(H,H) = 4.4 Hz, {}^{4}J(H,H,) = 1.0 Hz, 2H; ortho-H_{auinone}), 6.70 (d,$

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 $\label{eq:3.1} \begin{array}{l} {}^{3}J(\mathrm{H},\mathrm{H})=9.8~\mathrm{Hz},\,4\,\mathrm{H};\,\mathrm{H}_{\mathrm{arene}}),\,6.60~(\mathrm{d},\,{}^{4}J(\mathrm{H},\mathrm{H})=1.0~\mathrm{Hz},\,2\,\mathrm{H};\,ortho-\mathrm{H}_{\mathrm{quinone}}),\,6.37~(\mathrm{d},\,{}^{3}J(\mathrm{H},\mathrm{H})=4.4~\mathrm{Hz},\,2\,\mathrm{H};\,meta-\mathrm{H}_{\mathrm{quinone}}),\,6.14~(\mathrm{d},\,{}^{3}J(\mathrm{H},\mathrm{H})=9.8~\mathrm{Hz},\,4\,\mathrm{H};\,\mathrm{H}_{\mathrm{arene}}),\,1.91(\mathrm{m},\,4\,\mathrm{H};\,\mathrm{OCH}_2,\,1.75~(\mathrm{m},\,4\,\mathrm{H};\,\mathrm{OCH}_2\mathrm{CH}_2),\,1.62~(\mathrm{m},\,4\,\mathrm{H};\,\mathrm{OCH}_2\mathrm{CH}_2\mathrm{C},\,1.58-1.32~(\mathrm{m},\,68\,\mathrm{H};\,\mathrm{H}_{\mathrm{alkyl}}),\,1.04-0.94~(\mathrm{m},\,12\,\mathrm{H};\,\mathrm{CH}_3);\,1^{3}\mathrm{C}$ NMR (125~MHz, [D_8]THF): $\delta=185.98~(\mathrm{C}_{\mathrm{quinone}}),\,161.75~(\mathrm{C}_{\mathrm{arene}}-\mathrm{O}),\,161.36~(\mathrm{C}_{\mathrm{arene}}-\mathrm{O}),\,147.32,\,145.05,\,140.90,\,137.00,\,135.94~130.60~(\mathrm{all}~\mathrm{C}_{\mathrm{arene}}),\,58.57~(\mathrm{OCH}_2),\,34.08,\,31.82,\,31.45,\,28.25,\,24.75~(\mathrm{all}~\mathrm{C}_{\mathrm{alkyl}}),\,15.63~(\mathrm{CH}_3);\,\mathrm{MS}~(\mathrm{FD},\,8~\mathrm{kV}):\,m/z~(\%):\,1300.4~(100)~[M^+]~(\mathrm{calcd}~\mathrm{for}~\mathrm{C}_{90}\mathrm{H}_{122}\mathrm{O_6}=1300.0);\,\mathrm{IR}~(\mathrm{KBr~pellet}):~\tilde{\nu}~[\mathrm{cm}^{-1}]=3062(\mathrm{w}),\,3041(\mathrm{w}),\,2918(\mathrm{s}),\,2847(\mathrm{s}),\,1663~[(\mathrm{CO})_{\mathrm{st}},\mathrm{reteh}],\,1603(\mathrm{m}),\,1495(\mathrm{m})~[v(\mathrm{C=C})_{\mathrm{arene}}],\,1244(\mathrm{s})~[(\mathrm{Ar-O-R})],\,1170(\mathrm{m}),\,825(\mathrm{m});~\mathrm{UV/Vis}~(\mathrm{CHCl}):\,\lambda[\mathrm{nm}]~(\mathrm{lg}\varepsilon~[\mathrm{L}~\mathrm{mol}^{-1}\mathrm{cm}^{-1}]):\,314~(\mathrm{sh},\,4.52),\,330~(4.69),\,347~(4.74).\end{array}$

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Fluorescence Detection from Single Dendrimers with Multiple Chromophores**

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Following the pioneering studies of Moerner and Kador as well as Orrit and Bernard^[1] a wealth of experiments have been performed using high-resolution single-molecule spectroscopy (SMS) at low temperature.^[2] Single molecules that are immobilized on and in thin polymer films and gels, as well as on glass, have been investigated at room temperature with various types of optical microscopies.^[3, 4] The spectroscopic study of single molecules in solution has attracted substantial attention and is currently being developed as a new tool in analytical chemistry.^[5]

In the majority of the SMS studies the single molecules are investigated through their fluorescence properties. One of the most prominent observations in SMS studies is the occurrence of sudden changes in fluorescence intensity, often called the on-off behavior of a single molecule. This is in contrast to bulk measurements where the fluorescence intensity decreases exponentially with irradiation time as a result of photobleaching. Herein we investigate the difference between SMS of a single chromophore and of multichromophoric systems with the emphasis on the passage from the typical on-off behavior of a single molecule to the behavior of the ensemble. To this end a system has to be synthesized in which chromophores can be placed at a specific distance without being coupled through bonds. One way to obtain multiple chromophores in a well arranged environment is based on dendrimer synthesis.

We have recently introduced a new type of dendrimers and hyperbranched 3-dimensional polyphenylenes consisting of penta- or hexaphenylbenzene building blocks with strongly twisted benzene units.^[6, 7] The polyphenylene dendrimers are synthesized by repetitive Diels – Alder reactions using ethynylsubstituted aromatic cores such as 3,3',5,5'-tetraethynylbiphenyl (1) and the cyclopentadienone derivative 2 as the branching (A₂B-type) reagent. The stepwise approach to

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