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Phenylene Alkylene Dendrons with Site-Specific Incorporated Fluorescent Pyrene Probes

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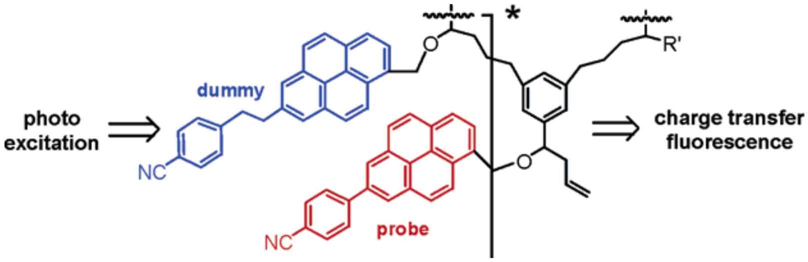

This report deals with the synthesis and the spectroscopic properties of two second generation (G2) dendrons with site-specific incorporated phenyl pyrene derivatives as solvatochromic fluorescent probes. The generations that do not carry the probe are equipped with volume dummies, pyrene moieties that do not show a solvatochromic effect. Two complementary G2 phenylene alkylene dendrons were synthesized using Suzuki−Miyaura cross coupling. Most of the reactions used in the 10-step sequence generating the target compounds proceeded in good yields. The incorporated probes can be selectively photoexcited and show solvatochromic shifts that are of the same magnitude as for the free probes in a homogeneous solvent environment. In addition to the charge-transfer fluorescence, a broad emission band is observed that is assigned to an intramolecular exciplex formation between the aryl pyrene chromophores.

Introduction

The investigation of the photophysical properties of dendrimers with incorporated chromophores has been the subject of considerable interest in recent years.[1] Because of the unique molecular architecture of dendrimers, especially the encapsulation effects of active core functionalities and their potential as light-harvesting antennas and as framework for redox-active functionalities, they have received great attention.[2−4] However, many details of the influence of the structure of the dendrimers in solution on these processes remain an open question. Because of their flexibility, many dendrimers can exist in numerous low-energy conformations. Solvation is a crucial parameter that determines if the dendrimers exist in more extended or collapsed structures.[5,6] Furthermore

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smaller dendrimers can be expected to form more open structures in contrast to larger molecules that should have more spherical shapes with a denser packing. As a consequence, site isolation by encapsulation, for example, strongly depends on the solvent properties.[7] Structural and solvent effects can also be expected to have a strong influence on the efficiency of excimer-like interactions as well as energy and electron transfer, processes that strongly rely on the relative positions and energies of the photoexcited states of the involved chromophores and redox-active groups, respectively.[8]

The attachment of functional probes has facilitated the detailed investigation of these properties.

A generation-dependent accessibility was shown for dendrons by incorporating anthracene as a single fluorescent probe unit in a specific location and studying the accessibility of these locations using an intermolecular photoinduced electron-transfer-based fluorescence quenching process.[9] Especially pyrene has been applied as a probe due to its well-known fluorescence characteristics. The relative structural permeabilities of a single pyrenyl residue attached to an amine within a series of symmetric poly(amido) dendrimers was investigated by quenching experiments. The increasing blocking of a pyrenyl residue with the growing dendrimer network could be shown.[10] Pyrene photoactive cores were used as probes to investigate the isolation of the core functionality by fluorescence quenching, energy transfer, and solvatochromic methods. With increasing chain length as well as solvent polarity enhanced site isolation was found.[5] Pyrene moieties in poly(propylene imine) dendrimers were used to probe the extent of steric crowding. More excimer emission was observed for higher generations with little evidence of interdendrimer interactions.[11] Pyrenes were also used for studies of the energy transfer in dendrimers. Energy transfer from pyrene units at the periphery to a diphenylanthracene core was observed for dendrons in solution and particles of dendrimer aggregates.[12] Excimer emission was also observed as the predominant fluorescence in a series of pyrene-capped dendrons that can be effectively quenched when a suitable donor group is attached at the focal point. These results indicate substantial electronic coupling between the appended chromophores and a suitable donor as the core unit.[13]

A more detailed knowledge of generation-specific solvent effects should contribute to the basic understanding of dendrimers. However, the possible variation of the solvent density inside a dendrimer that could strongly affect the microenvironment and especially the local polarity at each site has not received much attention. If the density of a dendrimer gradually decreases from its interior to its exterior as, e.g., SANS measurements[6,14] and computational studies[6,15] indicate, the local polarity created by generation-specific penetration of polar solvent molecules would be expected to increase in the same direction resulting in a polarity gradient, especially for spherical dendrimers with a high degree of symmetry. A similar polarity gradient has been supposed to have an effect on the charge-transfer efficiency of photoexcited polyelectrolyte multilayer systems.[16] Such an effect could be applied for dendritic systems that are equipped with electron acceptors at defined generations to realize a stepwise electron transfer through the dendritic framework. A different stabilization of the formed radical anions[17] after charge separation due to different degrees of solvation in each generation could provide the free-energy gradient as the necessary driving force.

In our concept, we will apply fluorescent polarity probes to study the possible polarity gradient in dendritic structures with the probes incorporated at specific generations.[18] Because of the bulkiness of such probes in comparison to the dendrimer skeleton, the concept involves so-called volume dummies. They will be attached to those generations that do not carry the probes in order to maintain the same sterical and solvation situation in comparable generations of a set of dendrimers, Figure 1a.

In this project, the cyano-substituted phenyl pyrene derivative **1** (Figure 1b) will be applied as fluorescence probe. **1** was found to be a suitable probe due to its strong solvatochromic effect and sufficient fluorescence quantum yield.[19] For mixtures of **1** and **2**, it was already shown that **1** fulfills the requirement to be exclusively photoexcitable in the presence of the volume dummy **2**.[19]

The tuning of the properties of dendrimers is commonly achieved by derivatization of the peripheral end groups or the core moiety. Contrary to this approach, the internal functionalization of the volume between is pursued with less activity.[20] Especially the site-specific incorporation of functional groups by premodified branching units seems to be a valuable goal, since there are only a handful of examples known at present.[21]

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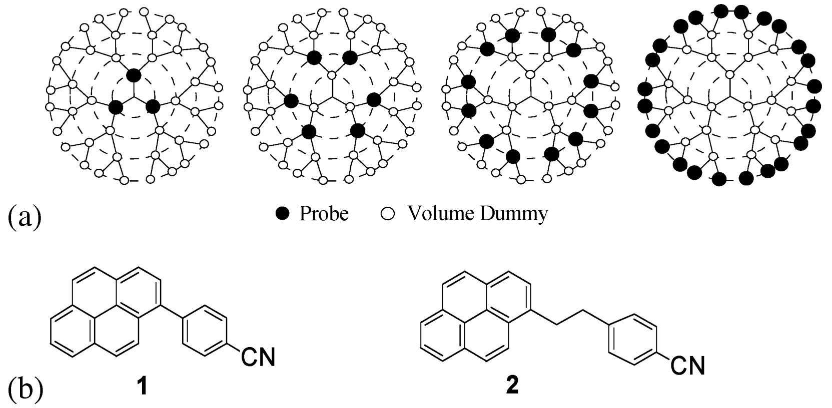


FIGURE 1. (a) Dendrimers with generation-specific incorporated polarity probes and volume dummies. (b) Structures of the parent molecules of polarity probe **1** and the corresponding volume dummy **2**.

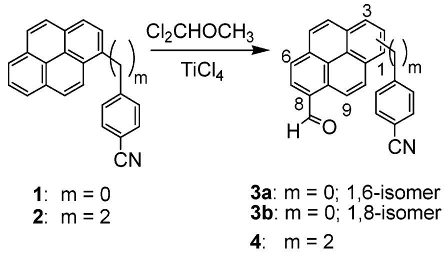
Here we report on the initial convergent synthesis[22] of a set of two G2 dendrons with generation-specific attached solvation probes and volume dummy molecules based on AB_2-type building blocks obtained by derivatization of the phenyl pyrenes **1** and **2**. The dendrimer backbone consists of phenylene and alkylene units and is generated by applying Suzuki−Miyaura cross-coupling conditions, i.e., coupling of in situ prepared alkylboranes and aromatic halides.[23,24] This strategy allows for accelerated convergent construction of all-hydrocarbon dendrons because formation of one generation can be achieved in a single preparative step. The UV absorption and photoemission properties of the two G2 dendrons are investigated and discussed in regard to solvatochromic effects and intramolecular interaction of the incorporated chromophores.

Results and Discussion

Syntheses. To attach the probe **1** and the volume dummy **2** covalently to a dendritic skeleton, they have to be equipped with functional groups. Their incorporation can be realized either on the benzonitrile part or the pyrene part. The latter approach is subject of this report.

Since Ti(IV)-catalyzed formylation of pyrene selectively gives the monoformyl product in high yields, this reaction was chosen for the second substitution step.[19,25,26] Reaction of pyrenes **1** and **2** with dichloromethoxymethane in the presence of $TiCl_4$ gave the corresponding aldehydes

SCHEME 1



3 and **4** in yields of 62 and 90%, respectively (Scheme 1), as the mixture of their isomers. The ratio of the 3-, 6-, and 8-regioisomers was about 1:2:2, revealed by ^{1}H NMR spectroscopy. Repeated recrystallization instead of column chromatography was the most efficient way to remove the 3-isomer from the mixture of the isomers. The remaining mixture of the 6- and 8-isomers **3a/3b** was used in the following steps.

Small amounts of the pure samples of **3a** and **3b** were obtained for their characterization by repeated fractionated recrystallization. In 2D heteronuclear multiple quantum coherence (HMQC) NMR experiments, all signals of the ^{1}H and ^{13}C NMR spectra could be assigned. The large downfield shifts of H-5 (**3a**) and H-9 (**3b**) are caused by the strong deshielding of the neighboring carbonyl group. This was confirmed by single-crystal X-ray diffraction of **3b** which represents one of the few examples of a pyrene derivative single-crystal X-ray structure with two acyclic carbon substituents in the ortho (1-, 3-, 6-, and 8-) positions known to present.[27] The carbonyl group lies in the pyrene plane with a deviation of 2°. The carbonyl oxygen points toward the proton H-9. The O−H-9 distance of 2.32 Å is significantly shorter than the sum of the van der Waals radii (2.60 Å). Since the distance O−C-9 is 2.96 Å and the angle C-9−H-9−O amounts to 125°, one can interpret such an arrangement as an attractive intramolecular C−H···O bonding.[28] These values match very well with other hydrogen bonds of the same kind. The dihedral angle of the phenyl group

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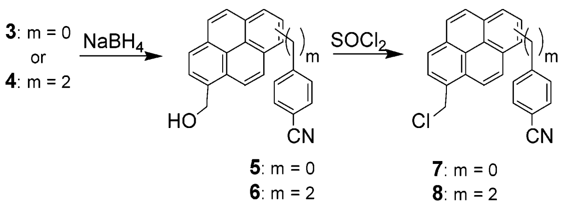
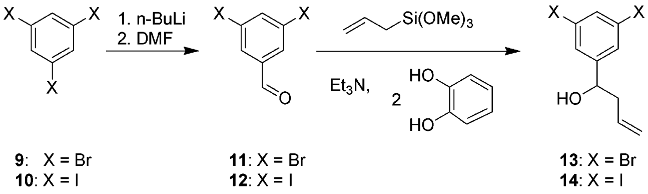
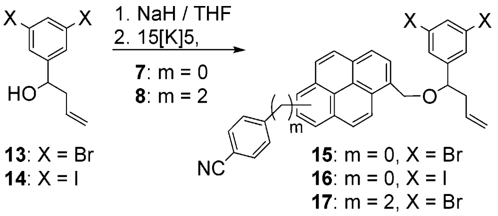
SCHEME 2



SCHEME 3



SCHEME 4



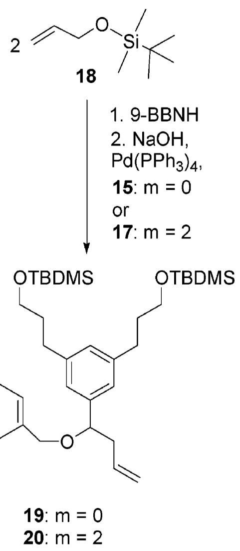
and the pyrene plane is 62°, which corresponds to the calculated value of 61° for phenyl pyrene.[27,29]

Aldehydes **3** and **4** were quantitatively (thin-layer chromatography, TLC) reduced to benzyl alcohols **5** and **6** with $NaBH_4$, and the hydroxy goups converted into the corresponding benzyl chlorides **7** and **8** with thionyl chloride on a multigram scale (Scheme 2). Because of their low stability on silica gel, the benzyl chlorides were purified by recrystallization from the reaction mixture.

3,5-Dibromo and diiodo homoallyl benzenes were shown to act as AB_2 monomers in the convergent synthesis of dendrons by Suzuki−Miyaura cross coupling.[23] To apply this strategy to the present probe and dummy concept, the related compounds **13** and **14** were synthesized, which carry a benzylic hydroxy function for subsequent attachments (Scheme 3). 1,3,5-Tribromobenzene (**9**) was monolithiated with butyllithium in diethyl ether at −78 °C, and the resulting lithium organyl intermediate was trapped with dimethylformamide (DMF) to give aldehyde **11**.[30] The 1,3,5-triiodobenzene (**10**) was lithiated in toluene at room temperature and subsequently reacted with DMF to prevent multiple lithiation and formation of butylated byproducts. Both aldehydes **11** and **12** were allylated under mild conditions with allyl trimethoxy silane in the presence of catechol and triethylamine to give the butenols **13** and **14** in yields of about 85%.[31]

Butenols **13** and **14** were coupled to the benzyl chlorides **7** and **8**, respectively, by modified Williamson conditions to afford the AB_2 monomers **15**−**17** (Scheme 4). Various conditions for the ether bond formation of a secondary alkoxide with chloro methyl pyrene were tested. The best result was obtained when an excess of the alcohol was deprotonated with sodium hydride in THF and benzyl chloride was added along with catalytic amounts of crown ether 15[K]5.[32] The yields of the isolated ethers **15**−**17** ranged between 82 and 89%.

SCHEME 5



The monomers **15** and **16** carry the fluorescent probe, compound **17**, the volume dummy. To convergently construct dendrons with the probe unit at a specific site, peripheral units were synthesized by converting the halogens of the monomers **15**−**17** into propyl TBDMS ethers. Incorporation of a peripheral functionality allows a flexible subsequent derivatization of the dendrimers. The TBDMS group as a hydroxy-protecting group was chosen because of its mild cleavage conditions. In the present system, the pyrene moieties are attached to the hydrocarbon skeleton of the dendron by two hydrolytically sensitive benzylic functions. Allyl TBDMS ether **18** was therefore in situ hydroborated with 9-BBN−H and reacted with monomers **15** and **17** in the presence of Pd-$[(PPh)_3]_4$ in a homogeneous THF/aqueous base system to give the peripheral building blocks **19** and **20** in an isolated yield of 52 and 58%, respectively (Scheme 5). The comparatively low yields were due to a loss of product in the column chromatography purification step because the monocoupling products and the desired compounds **19** and **20** exhibit very similar R_f values (TLC). All precursor molecules with an ethylene bridge between the pyrene and the benzonitrile unit showed a higher propensity to solidify than the phenyl pyrene analogue. This trend culminated in the observation that the volume dummy molecule **20** is an amorphous solid, whereas the probe molecule **19** is an oil.

Repetition of the procedure, i.e., hydroboration of the terminal olefin at the focal point of the peripheral units **19** and **20** and cross coupling with the opposing monomers **17** or **15**/**16**, respectively, resulted in both G2 dendrons **21** and **22** (Schemes 6 and 7). They carry the solvatochromic probe molecule either in the second (outer) or in the first (inner) generation. The side products, i.e., the monocoupling product and the excess

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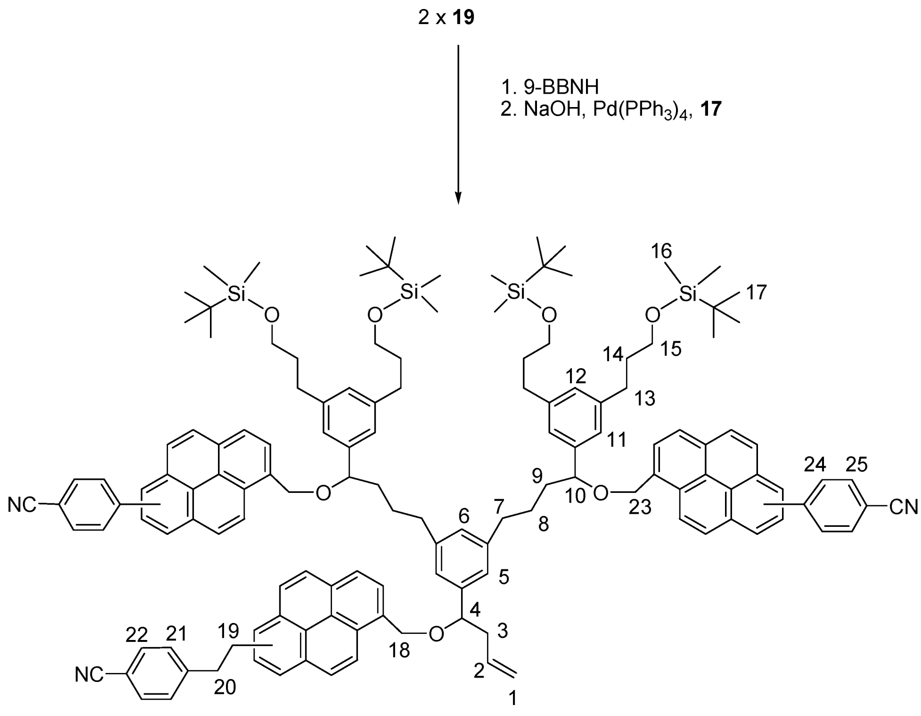
SCHEME 6



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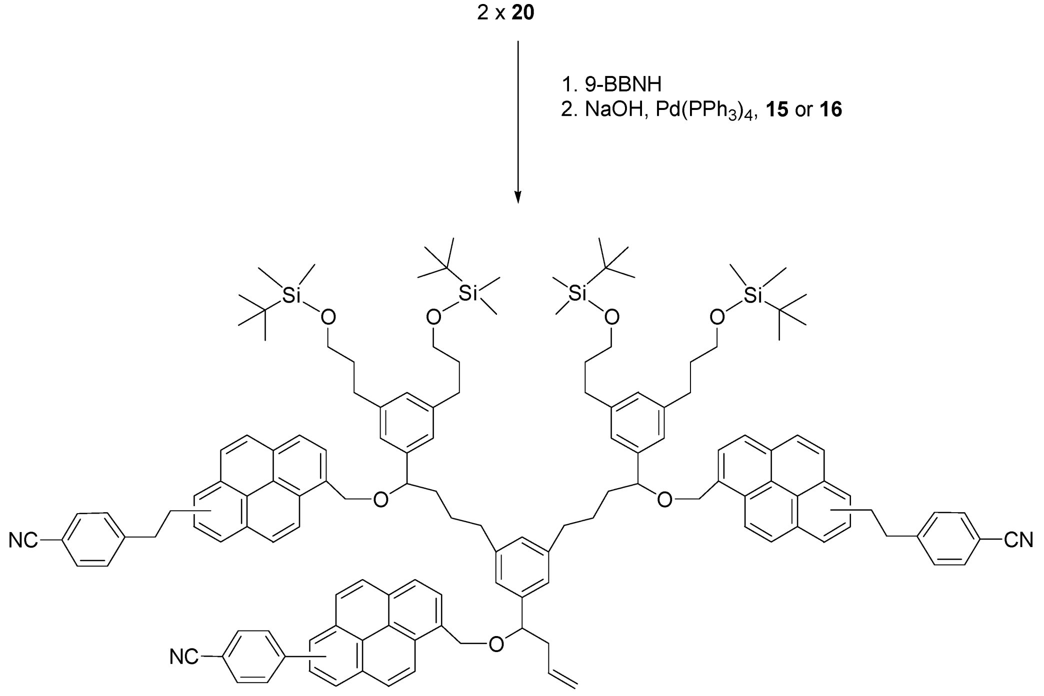
SCHEME 7



22

of 25% of the hydroborated G1 dendron, could not be removed quantitatively by column chromatography. Purification was finally achieved by preparative gel permeation chromatography (GPC) separation. Because of the multistep workup procedure, the isolated yields of the G2 dendrons **21** and **22** were as small as 11 and 50%, respectively.

The target compounds were obtained as analytically pure materials, and their structures have unequivocally been characterized. All ^{1}H NMR signals besides the pyrenyl protons could be assigned (Figure 2). Formation of the product is indicated by the new resonances for the protons H-7 to H-9 compared to the spectra of the starting material. Interestingly, the absorptions for the aromatic

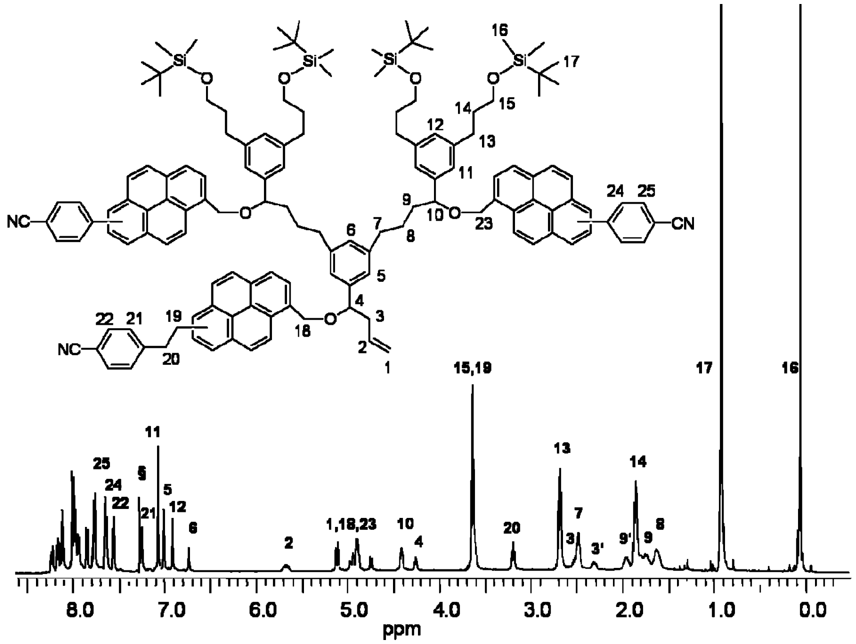


FIGURE 2. ^{1}H NMR spectrum of G2 dendron **21** (§: $CHCl_3$).

protons of the branching benzene units are all separated with a maximum difference of 0.33 ppm from H-6 to H-11. The signals of H-3, H-9, H-18, and H-23 all show a large diastereotopic splitting, although partly superimposed with other signals. The matrix-assisted laser desorption−ionization time-of-flight (MALDI TOF) mass spectrometric analyses displayed intense peaks for the molecular ion of sodium and potassium adducts. Their isotope distribution fits the calculated data.

Spectroscopic Properties. The UV absorption and fluorescence properties of the dendrons **21** and **22** with incorporated probe units in the first and second generation, respectively, were investigated in comparison to the free cyano-substituted phenyl pyrene derivative **1**[19] as model probe and the corresponding dummy **2** with an ethyl group as a tether between the pyrene and the benzonitrile moiety. Besides the change of the microenvironment of the incorporated probes, the influence of the dendritic backbone, especially in regard to possible intramolecular interactions between the chromophores, was of special interest.

The normalized UV absorption and fluorescence spectra of the dendrons **21** and **22** are given in Figure 3. As it was shown for mixtures of the free probe **1** and the dummy **2**,[19] a selective excitation of the incorporated probes in **21** and **22** can be realized for excitation wavelengths >360 nm.

The UV absorption spectra of **21** and **22** show the main maximum at about 352 nm, Table 1. In contrast to the free probe, the maxima are red shifted by about 10 nm and a fine structure with multiple maxima is observed independent of the solvent polarity. The fluorescence spectra in the nonpolar solvent methylcyclohexane (MCH) have a maximum at about 410 nm for both compounds. In acetonitrile (ACN), the spectra are considerably red shifted with maxima at 432 nm for **21** and 437 nm for **22**. This solvatochromic effect indicates that a certain charge-transfer (CT) character is present in the excited states, with the pyrene moiety as the donor and the benzonitrile group as the acceptor unit.[19]

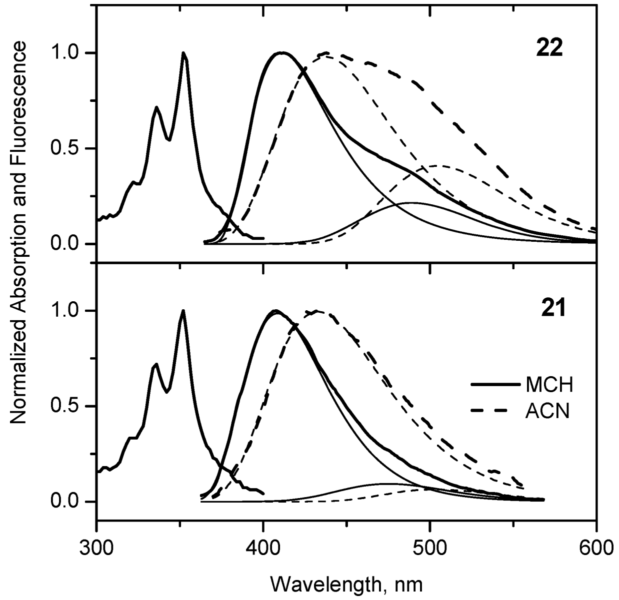


FIGURE 3. UV absorption in MCH and fluorescence spectra of the dendrons **21** and **22** in MCH and ACN. The thin lines represent the decomposed fluorescence spectra.[33]

Interestingly, in addition to the CT band, a red-shifted shoulder between 470 and 505 nm appears in the emission spectra of the dendrons and the intensity of the shoulder with respect to the main peak is higher for **22** than for **21**, Figure 3. In the case of **22**, the relative intensity of the shoulder is higher in ACN than in MCH.

The Stokes shifts were calculated as the difference of the energies of the absorption and fluorescence maxima, determined after deconvolution of the superimposed spectra,[33] with values of about 4000 cm^{-1} in MCH and

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(33) Using the program: Peakfit 4.06 ed.; SPSS Inc.: 1995.

TABLE 1. UV Absorption and Fluorescence Maxima, Stokes Shifts, and Fluorescence Quantum Yields of the Free Probe 1, the Dummy Molecule 2, and the Dendrons with Incorporated Probes in the First or Second Generation

compd	solvent	λ_{abs}, nm	λ_{flu}, nm[a]	ν_{ST}, cm^{-1} [b]	Φ_{fl}[b]	τ_{fl}, ns[c]
1	MCH	343	391, 406	4050	0.69	5.8
	ACN	344	427	5650	0.81	2.7
2	MCH	344	378, 389	3000	0.042	7.3
	ACN	344	378, 388	2950	0.063	7.2
21	MCH	352	409	4950	0.38	
			475 sh[d]	7350	0.043	
	ACN	352	432	5250	0.28	
			503 sh[d]	8500	0.015	
22	MCH	352	411	4100	0.36	2.4
			489 sh[d]	7950	0.096	31.3[e]
	ACN	352	437	5550	0.24	1.7
			505 sh[d]	8600	0.10	13.6[e]

[a] Fluorescence maxima of **21** and **22** from the deconvoluted spectra.[33] [b] Error about 10%. [c] Error about 5%, excitation at 357 nm and detection at the fluorescence maxima. [d] Shoulder. [e] Detection at 550 nm to minimize contribution of the CT emission.

5400 cm^{-1} in ACN for the CT band and values between 7000 and 8600 cm^{-1} for the red-shifted emission, Table 1. The fluorescence quantum yields were calculated for both emission bands from the decomposed fluorescence spectra with higher values for the CT than for the red-shifted emission. The values for the CT bands are slightly lower in comparison to the values of the free probe **1**, Table 1. The solvatochromic shifts and the quantum yields for the CT bands of **21** and **22** are of the same magnitude as the values reported for **1**. These two measures have been the key parameters in the selection of **1** as suitable probe molecule.[19] This indicates that the attachment of the pyrene moiety of the probe to the dendritic backbone does not affect the formation of the photoexcited CT state that is combined with a geometrical relaxation of the pyrene and benzonitrile subunits of the probe. As expected, no significant differences have been found in the spectroscopic parameters of the dendrones **21** and **22** probably due to the small size and the flexibility of these dendritic subunits that levels out any differences in the microenvironment of the incorporated probes.

The fluorescence decay times have been measured for **1**, **2**, and **22** in MCH and ACN with the shorter lifetimes in the highly polar solvent, Table 1. In comparison to the main CT emission, fluorescence lifetimes of more than one magnitude higher have been determined for the species that is assigned to the red-shifted shoulder.

The observed shoulder in the range of 470−505 nm indicates the existence of a second emissive state. Pyrenes are well known for the ability to form excimers in solutions of concentrations higher than 10^{-5} M with typically broad and red-shifted emission bands, where the interacting chromophores are arranged in a sandwich-like structure.[34] In principle, such an intermolecular interaction could also be the reason for the formation of the second emission band observed for **21** and **22**. In this case, a concentration dependence of the relative intensities of the CT band vs the shoulder in the fluorescence spectra would be expected. However, such dependence was not found for the spectra of **22** in the range of the measured sample concentrations (10^{-7}−10^{-6} M).

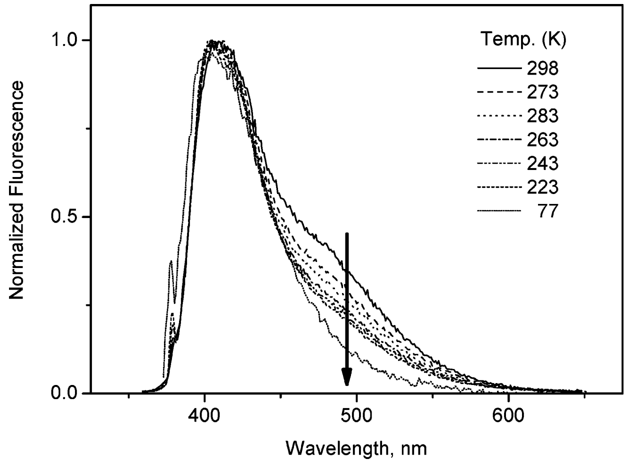

FIGURE 4. Decrease of the shoulder at 490 nm of **22** in MCH relative to the main fluorescence peak with decreasing temperature. The appearance of a new small peak at 375 nm at low temperature can be assumed to indicate the formation of a pure locally excited state of the probe chromophore.[37]

Interactions between different chromophores could also occur intramolecularly for **21** and **22**. In this case, it can be assumed that a geometrical reorientation between the subunits of the molecules must take place. It is well known that such processes are affected by a change of the solvent viscosity.[35,36] A significant decrease of the intensity of the shoulder relative to the main peak by lowering the temperature was observed for **22** in MCH and butyronitrile. At 77 K, the red-shifted emission band disappears completely, i.e., the reorientation process that leads to the formation of this excited state is completely frozen out, Figure 4. This observed temperature effect strongly supports the assumption of an intramolecular exciplex formation.

After excitation of the probe chromophore in **1**, **21**, or **22** and initial population of the Franck−Condon state a geometrically relaxed fluorescent CT state is formed as it was described for other phenyl pyrene derivatives.[19,37] In the cases of **21** and **22**, a subsequent interaction between the chromophores of the photoexcited probe and the dummy moiety that requires a change of the conformation of several single bonds in the dendron leads to the formation of the exciplex as illustrated in Scheme 8.

This is consistent with the results of the lifetime measurements for **22** where the relatively long fluorescence lifetimes (31 and 14 ns) of the red-shifted exciplex emission in contrast to the values for the CT emission of about 2 ns can be explained by the stronger electronic coupling between the donor and acceptor moiety in the latter case due to the shorter distance between both units.[38] However, the short fluorescence lifetime of the

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(34) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Company: Menlo Park, CA, 1978.

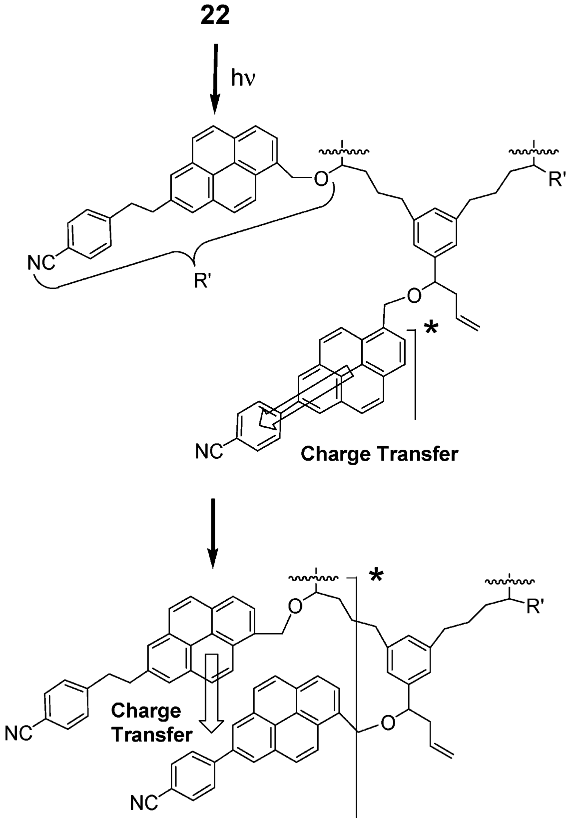
(35) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899−4031.

(36) Zhang, B.-W.; Cao, Y.; Bai, J.-W.; Chen, J.-R. *J. Photochem. Photobiol. A* **1997**, *106*, 169−175. (b) Kawakami, J.; Furuta, T.; Nakamuru, J.; Uchida, A.; Iwamura, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 47−54.

(37) Weigel, W.; Rettig, W.; Dekhtyar, M.; Modrakowski, C.; Beinhoff, M.; Schlueter, A. D. *J. Phys. Chem. A* **2003**, *107*, 5941−5947.

(38) Kawakami, J.; Nakamura, J.; Iwamura, M. *J. Photochem. Photobiol., A* **2001**, *140*, 199−206.

SCHEME 8. Charge Transfer within the Probe Unit after Photoexcitation of 22 and Subsequent Exciplex Formation with the Dummy Moiety as the Donor and the Photoexcited Probe as Acceptor



CT state in the nanosecond range should be long enough to allow reorientation of the chromophores involved in the exciplex formation at least from those ground-state conformations that are close to the proposed exciplex structure. The intramolecular exciplex formation also explains the observed higher intensity of the shoulder in the fluorescence spectra of **22** compared to **21** since the probability for exciplex formation between the photoexcited probe and the pyrene chromophore of the dummy is higher in **22** due to the better probe/dummy ratio of 1:2 vs 2:1 in **21**.

Conclusions

In summary, we have presented the initial convergent synthesis of a set of two G2 dendrons with generation-specific attached solvatochromic probes and volume dummies. The site-specific incorporation of functional groups was achieved by derivatization of phenyl pyrenes to obtain premodified branching units. The phenylene alkylene dendrimer backbone was constructed in an accelerated manner by applying Suzuki−Miyaura cross-coupling conditions where one generation can be synthesized in a single preparative step. The incorporated probes can be selectively photoexcited and the strong solvatochromic shifts observed in the same magnitude as for the parent probe molecules in a homogeneous solvent environment can be explained by the high charge transfer character of the excited states. This solvatochromic effect will be used as a tool to probe the microenvironment in regard to the solvent density in the interior of larger dendrimers those synthesis is under way. In contrast to the free probe molecules, the G2 dendrons show an additional broad emission band in the fluorescence spectra that is assigned to the formation of an exciplex between the aryl pyrene chromophores. The exciplex formation requires a geometrical reorientation between the subunits of the G2 dendrons that are highly flexible due to their relatively small size and can be frozen out at low temperatures.

Experimental Section

X-(4-Benzonitrile)-pyrene-1-carbaldehyde, Three Isomers (X = 3, 6, 8) (3). To a solution of 4-pyren-1-yl-benzonitrile **1** (11.51 g, 37.91 mmol) and dichloro methyl methyl ether (4.30 mL, 47.54 mmol, 1.25 equiv) in CH_2Cl_2 (250 mL), titanium(IV)chloride (11.5 mL, 104.9 mmol, 2.77 equiv) was added within 30 min at 0 °C. The dark mixture was stirred at room temperature overnight. Water (100 mL) was added, the phases separated, and the aqueous one was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (CH_2Cl_2). Yield: 62% (7.79 g) of **3** as a mixture of regioisomers (3-, 6-, and 8-formyl isomer). By recrystallization of suitable fractions pure (^{1}H NMR), samples of the 6- and the 8-isomers **3a** and **3b** were obtained; their structures were elucidated by 2D HMQC NMR experiments. The structure of 8-isomer **3b** was solved by X-ray analysis.

[X-(4-Benzonitrile)-pyren-1-yl]-methanol, Two Isomers (X = 6 and 8) (5). Aldehyde **3** (11.95 g, 36.06 mmol) was solved in THF (500 mL), and 2-propanol (1000 mL) was added. After addition of sodium borohydride (7.25 g, 191.65 mmol, 5.32 equiv), the reaction mixture was stirred for 2 h at ambient temperature. The unreacted sodium borohydride was hydrolyzed by dropwise addition of diluted hydrochloric acid to the ice-cooled mixture until no more hydrogen evolution occurred. The organic solvents were distilled off, and the residue was extracted with dichloromethane. The combined organic layers were dried and filtered, and the solvent evaporated. Column chromatography (CH_2Cl_2, then CH_2Cl_2:methanol = 20:1) gave 11.80 g (98%) of a mixture of two regioisomers of [X-(4-benzonitrile)-pyren-1-yl]-methanol **5**.

1-Chloromethyl-X-(4-benzonitrile)-pyrene, One Isomer (X = 6 or 8) (7). To a suspension of alcohol **5** (9.87 g, 29.61 mmol) in CH_2Cl_2 (350 mL) a solution of thionyl chloride in CH_2Cl_2 (50 mL) was added dropwise at room temperature (40 min). The clear solution was stirred until gas evolution stopped (3 h). To the ice-cooled solution, aqueous NaOH (1 M, 150 mL) was added carefully, and the phases were separated. The aqueous one was extracted with CH_2Cl_2, the combined organic layers were dried over $MgSO_4$ and filtered, and the solvent evaporated. The resulting brownish residue was recrystallized from CH_2Cl_2:methanol to give 8.60 g (83%) of **7** as an amorphous solid. The reaction proceeded quantitatively as the TLC showed no alcohol. The reduced yield may be due to the loss of product in the recrystallization step. It was found that the benzyl chloride was not stable on silica gel (2D TLC).

3,5-Diiodobenzaldehyde (12). To a suspension of 1,3,5-triiodobenzene **10** (17.39 g, 38.15 mmol) in toluene (650 mL), a 1.6 M solution of *n*-butyllithium in hexane (28.00 mL, 44.80 mmol, 1.17 equiv) was added within 60 min at room temperature. After 3 days, *N*,*N*-dimethyl formamide (10.0 mL, 119.0 mmol, 3.12 equiv) was added all at once and the mixture was stirred for an additional 1 day with a mechanical stirrer. Water (200 mL) was added, the phases were separated, and the aqueous one was extracted with toluene twice. The combined organic layers were dried over $MgSO_4$, and the filtrate evaporated. Chromatographic separation through silica gel (hexanes:EtOAc = 10:1) gave 9.02 g (66%) of **12** as colorless crystals. When Et_2O or THF at −78 °C was used instead of toluene, the product was accompanied by butylated side-products.

1-(3,5-Dibromo-phenyl)-but-3-en-1-ol (13). Allyl-trimethoxysilane (18.00 mL, 106.83 mmol, 1.53 equiv) was added dropwise to a suspension of 18.50 g (70.10 mmol) 3,5-dibromobenzaldehyde **9**, 23.01 g (208.97 mmol, 2.98 equiv) catechol, and triethylamine (50 mL, 358.73 mmol, 5.12 equiv). The mixture was stirred at 70 °C for 24 h. The acidified (25% hydrochloric acid) suspension was extracted with dichloromethane (5×), the combined organic phases were washed with brine and dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexanes/EtOAc = 10:1), and the product was distilled in vacuo to give 17.96 g (84%) of 84 as a colorless liquid.

1-(4-Benzonitrile)-X-[1-(3,5-dibromo-phenyl)-but-3-enyloxymethyl]-pyrene, Two Isomers (X = 6, 8) (15). To a suspension of sodium hydride (0.332 g of a 60% suspension in mineral oil, 8.65 mmol, 2.03 equiv) in THF (5 mL) was added carefully a solution of 1-(3,5-dibromo-phenyl)-but-3-en-1-ol **13** (2.57 g, 8.40 mmol, 1.97 equiv) in THF (5 mL). After 1 h 1-chloromethyl-X-(4-benzonitrile)-pyrene **7** (1.50 g, 4.26 mmol), [15]-crown-5 (0.094 g, 0.43 mmol, 0.1 equiv), and THF (50 mL) were added, and the solution was stirred overnight. A small amount of silica gel was added, and the solvent was removed. The residue was purified by column chromatography on silica gel (CH_2Cl_2) to yield 2.21 g (83%) of **15** as greenish glassy material that could not be recrystallized.

1-(1-{3,5-Bis-[3-(*tert*-butyl-dimethyl-silanyloxy)-propyl]-phenyl}-but-3-enyl oxymethyl)-X-(4-benzonitrile)-pyrene, Two Isomers (X = 6, 8) (19). Allyloxy-dimethyl-*tert*-butylsilane **18** (1.33 mL, 6.26 mmol, 2.99 equiv) was added to a solution of 9-BBN−H (12.55 mL of a 0.5 M solution in THF, 6.28 mmol, 3.00 equiv) at 0 °C, and the solution was stirred for 18 h at ambient temperature. After addition of aqueous sodium hydroxide (1 M, 20 mL), **15** (1.30 g, 2.09 mmol), the catalyst precursor $Pd(PPh_3)_4$ (0.15 g, $1.3 \cdot 10^{-4}$ mol, 3.1 mol-% per coupling) and additional THF (20 mL), the suspension was stirred for 17 h at 60 °C. Extractive workup with diethyl ether and column chromatography on silica gel (CH_2Cl_2) gave 0.88 g (52%) of **19** as a highly viscous oil.

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Supporting Information Available: General experimental methods, synthesis of compounds **4**, **6**, **8**, **14**, **16**, **17**, **20**, **21**, and **22**, analytical data of all compounds, ^1H NMR spectra of **3a** and **3b**, crystallographic data, including an ORTEP plot, tables with crystal data, structure refinement, figures of crystal lattice and unit cell, the CIF file of compound **3b**, and the concentration dependent fluorescence spectra of **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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