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Convergent Synthesis of Noncovalent Metallodendrimers Containing Hydrophobic Dendrons at the Periphery

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The noncovalent synthesis of “layer-block” metallodendrimers containing hydrophobic shells of covalent dendritic wedges at the periphery is described. Starting from first- and second-generation Fréchet wedges having phosphines at their focal point, convergent dendritic growth yields third- and fourth-generation metallodendrimers in which the coordination of nitriles, pyridines, and phosphines to SCS Pd^{II} pincers is used as the assembly motif. In this convergent growth, the number of terminal hydrophobic phosphine wedges increases with generation. The solubility of the dendritic structures in apolar organic solvents such as chloroform and dichloromethane increases accordingly, in contrast to previously reported metallodendrimers. All dendritic structures were characterized by ^{1}H and ^{31}P NMR spectroscopy, elemental analysis, and MALDI-TOF mass spectrometry.

Introduction

Coordination chemistry is increasingly utilized in the rapidly expanding field of self-assembly, e.g., in the construction of discrete structures with nanosize dimensions.[1] Notable examples include Fujita’s 10-component interlocked cages (Pd^{II}−pyridine coordination),[2] Beer’s cavitand trimer and tetramer (Zn^{II}−dithiocarbamate coordination),[3] and Lehn’s circular helicates (Fe^{II}−bipyridine coordination).[4] In nanotechnology,[5] functionalization of such nanosize assemblies is exploited in order to introduce properties that allow them to be addressed individually (by photons, electrons, etc.) and to obtain functional machines at the molecular level.[6] One class of molecules that might be used as components in nanotechnology are *dendrimers*,[7] highly branched globular macromolecules of low polydispersity that emanate from a central core. *Metallodendrimers*[8] represent a subclass of dendrimers. They may have interesting photoactive or redoxactive properties, and their coordination chemistry facilitates the synthesis, e.g., via self-assembly. In metallodendrimers, metals can be incorporated either in the core,[9] the periphery,[10] or at each branching point.[11] Dendrimers containing metals as the “glue” between building block have also been investigated.[12] In our group, we have exploited the coordination chemistry of Pd^{II} for the noncovalent assembly of metallodendrimers using building blocks **A**, **B**, and **C** depicted in Chart 1. The coordination of cyano groups to Pd^{II} was first used in the *divergent* assembly of metallo-

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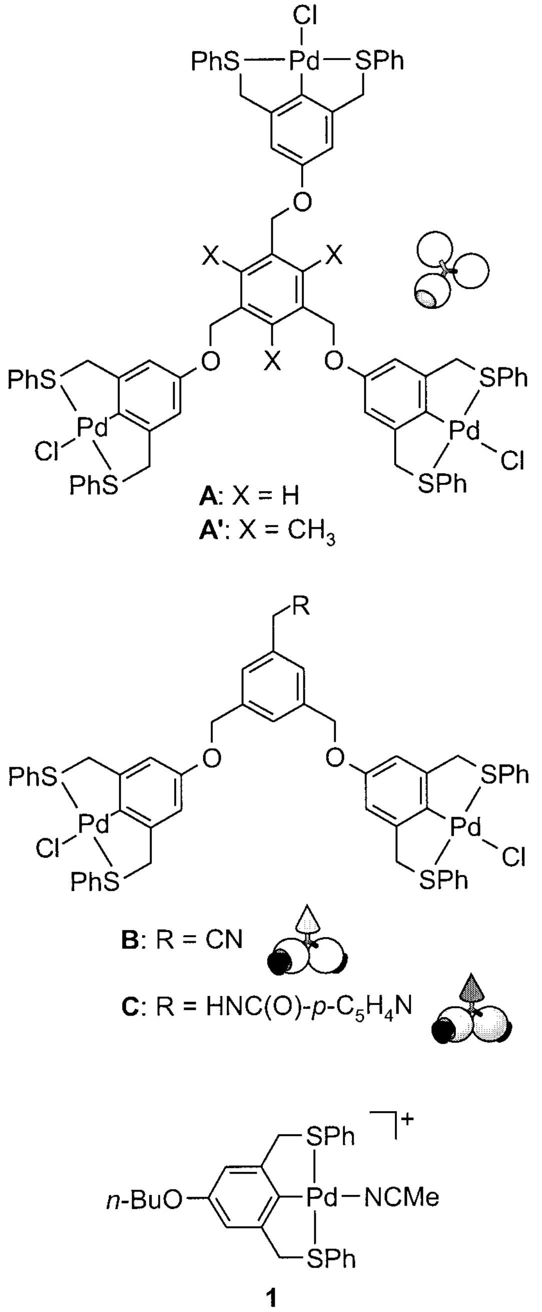
Chart 1. Building Blocks (and Their Schematic Representations) Used in the Construction of Metallodendrimers



dendrimers up to generation five.[13] For convergent synthesis, we combined nitrile and pyridine coordination.[14] The stronger coordination of pyridine was exploited for the synthesis of dendrons containing free cyano groups at the focal point, and these were subsequently coupled to the Pd^{II} pincer moieties of the core.

Many of these polycationic metallodendrimers suffer from a low solubility in apolar organic solvents, due to the presence of SCS Pd^{II} pincers at the periphery of the metallodendrimers. To increase the metallodendrimer solubility, we have now introduced a hydrophobic layer of covalently synthesized dendrons, e.g., the aryl ether dendritic wedges first reported by Hawker and Fréchet.[15] The resulting assembly is a novel example of a "layer-block"[16] dendritic architecture, i.e., a noncovalently assembled metallodendritic interior surrounded by covalently synthesized dendrons. This structure requires that the metallodendrimers are assembled convergently, which means that ligands are needed that are stronger than pyridines. We have recently described that phosphines are such ligands,[17] and here, we report the successful incorporation of phosphine dendritic wedges into our convergent metallodendrimer assembly process,[18] producing high yields of hybrid covalent−noncovalent metallodendrimers in which three different ligand types are employed to hold the metallodendrimers together.

Results and Discussion

Synthesis of Covalent Dendritic Phosphine-Functionalized Wedges. First- and second-generation Fréchet-type dendritic wedges **D** and **E** (Scheme 1) functionalized at the focal point with phosphines were synthesized.[19] 3,5-(Benzyloxy)benzylamine[20] **2** was coupled to 4-(diphenylphosphino)benzoic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBt) to afford the first-generation phosphine wedge **D** in nearly quantitative yield. Second-generation phosphine wedge **E** (Scheme 1) was prepared and characterized as reported recently.[21] Wedge **D** was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, FAB mass spectrometry, and elemental analysis. It displays a signal at −5.6 ppm in the ^{31}P NMR spectrum, which is very close to triphenylphosphine (−5.5 ppm). In the positive FAB mass spectrum, a signal corresponding to $[M + H]^+$ was found at an *m/z* value of 608.6. In addition a

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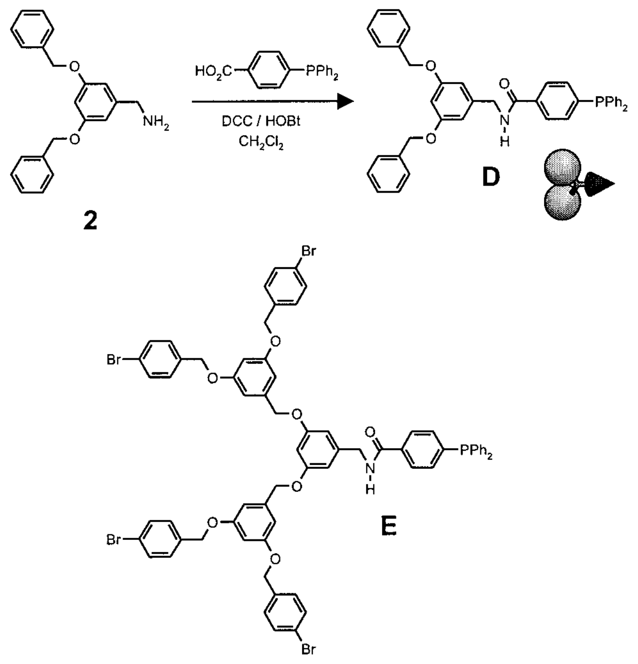
Scheme 1. Synthesis and Structure of Phosphine Wedges D and E, Respectively



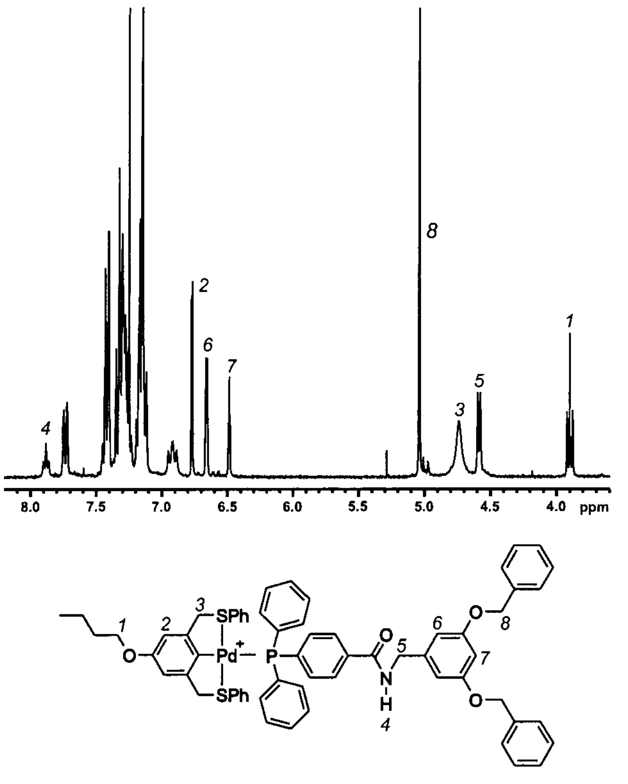


Figure 1. Part of the ^{1}H NMR spectrum (CDCl$_3$, 298 K) of the complex **1·D**.

small signal was observed corresponding to the oxidized molecule, most likely formed inside the spectrometer since phosphine oxidation was not evident from both ^{1}H and ^{31}P NMR spectroscopy.

Coordination of Phosphine Wedges to SCS Pd^{II} Pincer Systems. As we have reported recently, phosphines are able to coordinate to SCS Pd^{II} pincer systems.[17] Moreover, it was shown that triphenylphosphine completely suppresses the coordination of pyridines, thus enabling the uncoordinated pyridine ligand to bind to other SCS Pd^{II} pincers.

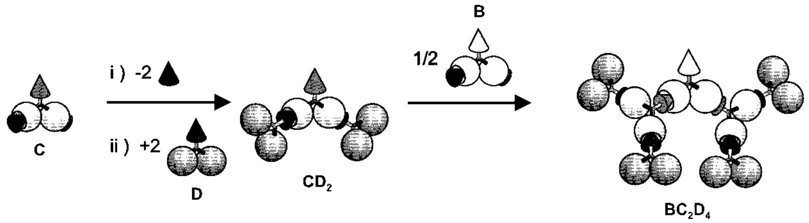
Coordination of wedges **D** and **E** to model SCS Pd^{II} pincer **1** (Chart 1) was investigated by exchange experiments. Upon addition of 1 equiv of dendritic phosphine wedge **D** or **E** to **1**, the coordinated acetonitrile ligand was quantitatively replaced by the phosphine, as shown by ^{1}H NMR spectroscopy. The signal from the acetonitrile methyl protons shifted from 2.08 (coordinated) to 1.99 (uncoordinated) ppm. Furthermore, a characteristic doublet was observed for the aromatic protons of the cyclopalladated aromatic ring (6.77 ppm), which arises from ^{1}H$-$^{31}P coupling ($J = 2.2$ Hz, see Figure 1). The coordination of phosphine to Pd^{II} was also evident from the ^{31}P NMR spectrum, in which a diagnostic shift from -5.6 to 13.7 ppm was observed.[17]

Convergent Metallodendrimer Growth Starting from Phosphine Wedge D. The organometallic building blocks required for convergent synthesis of a full metallodendrimer are depicted in Chart 1, along with their schematic representations. First, pyridine building block **C** was reacted in CH$_2$Cl$_2$ with 2 equiv of AgBF$_4$ to remove the two chlorides coordinated to the Pd^{II} centers (which precipitated as AgCl), and subsequently, 2 equiv of phosphine wedge **D** were added (Scheme 2). After the mixture was stirred for 10 min and filtered over Hyflo, dendron **CD$_2$** was obtained as a yellow solid in 89% yield. The stronger coordination strength of phosphine over pyridine prevents the coordination of the pyridine moiety to Pd^{II}. The ^{1}H NMR spectrum unequivocally shows the absence of a broadening and upfield shift of the signal for the pyridine α-protons, features due to coordination to Pd^{II}.[14] The ^{1}H NMR spectrum displays *three* doublets between 4.2 and 4.6 ppm for the CH$_2$N protons. However, only *two* doublets are expected (one from **C** and one from **D** in a 1:2 integral ratio) on the basis of the (alleged) symmetry of **CD$_2$**. The combined integrals of the three doublets correspond to the expected six protons. The relative intensities of the doublets vary as a function of solvent (in CD$_2$Cl$_2$ three doublets of almost equal intensity are observed, whereas in CDCl$_3$/CD$_3$NO$_2$ 4:1 one large and two small doublets are found). Also, heating the sample (up to 50 °C) resulted in different intensities of the doublets. These data suggest hindered rotation of the phosphine wedges around the Pd^{II}$-$P bond, resulting in different rotational isomers with different symmetries.

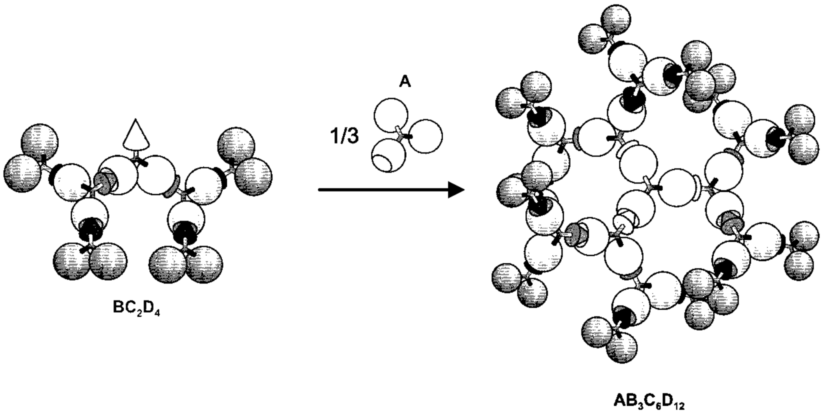
In the ^{31}P NMR spectrum of **CD$_2$**, only one signal was observed (at 13.6 ppm), indicating complete (>98%) coordination of the phosphines of **D** to the Pd^{II} pincers of **C** (within the limitations of the ^{31}P NMR technique). Subsequently, the pyridine moiety of **CD$_2$** was used for coordination to two Pd^{II} centers of nitrile building block **B**. The two chlorides of **B** were removed by AgBF$_4$, and 2 equiv of **CD$_2$** were added to produce the third-generation metallodendrimer wedge **BC$_2$D$_4$** (Scheme 2). Coordination of the pyridine moieties was confirmed by ^{1}H NMR spectroscopy, as very broad signals were observed in the region around 8.0 ppm.[14] Furthermore, the successful formation of this wedge was proven by MALDI-TOF mass spectrometry (vide infra).

Finally, three dendritic wedges **BC$_2$D$_4$** were coordinated to deprotected **A** to produce the full hybrid covalent$-$noncovalent metallodendrimer **AB$_3$C$_6$D$_{12}$** (Scheme 3). Figure 2 displays one dendritic branch of the dendritic structure obtained in this way, whereas the other two branches are represented by cones. The ^{1}H NMR spectrum (Figure 3a, CD$_2$Cl$_2$, 298 K) of this dendrimer re-

Scheme 2. Schematic Representation of the Convergent Synthesis of Metallodendritic Wedge BC_2D_4



Scheme 3. Schematic Representation of the Coupling of Dendrons BC_2D_4 to the Core A to Produce the Hybrid Covalent−Noncovalent Metallodendrimer $AB_3C_6D_{12}$



veals broad signals, most likely due to slow tumbling times and restricted mobility of the nanosize metallodendrimer (molecular weight 20.3 kDa) in solution. Similar signal broadening has been observed for other metallodendrimers.[14] Evidence for the dendritic structure was obtained from other analytical techniques. First, in the ^{31}P NMR spectrum the signal at 13.6 ppm was still present as the only peak. Furthermore, in the MALDI-TOF mass spectrum only a signal at 20.27 kDa (corresponding to $[M - BF_4]^+$) was observed in the region 5−45 kDa, indicating the presence of a monodisperse metallodendrimer (vide infra). Finally, the correct molecular composition was determined by elemental analysis of $\mathbf{AB_3C_6D_{12}}$. Remarkably, in going from the wedge $\mathbf{CD_2}$ to the dendrimer $\mathbf{AB_3C_6D_{12}}$ the products become increasingly soluble in apolar solvents such as dichloromethane and chloroform, and $\mathbf{AB_3C_6D_{12}}$ displays a very high solubility at r.t. in these solvents. This is in sharp contrast to some of our metallodendrimers reported before, which displayed limited solubility in nitromethane or mixtures thereof with chlorinated solvents, even when heated.[14] This difference must be due to the increasing number of hydrophobic phosphine wedges at the periphery of the dendrimers. Controlling the solubility properties of dendrimers by judicious choice of the peripheral groups is very common in dendrimer chemistry.[22,23]

Convergent Metallodendrimer Growth Starting from Phosphine Wedge E. A metallodendrimer with a thicker hydrophobic shell was obtained by the convergent growth starting from the second-generation phosphine wedge **E**. First, pyridine building block **C** was deprotected by $AgBF_4$, and subsequently, 2 equiv of phosphine wedge **E** were coordinated to Pd^{II}. The resulting wedge $\mathbf{CE_2}$ was characterized by ^1H and ^{31}P NMR spectroscopy, MALDI-TOF mass spectrometry (vide infra), and elemental analysis. Two of these wedges were coordinated to deprotected nitrile building block **B** to produce the dendritic wedge $\mathbf{BC_2E_4}$. This wedge was characterized by the same analytical techniques as $\mathbf{CE_2}$. Finally, coordination of three of these wedges around the core **A** was performed in an attempt to assemble the covalent−noncovalent metallodendrimer $\mathbf{AB_3C_6E_{12}}$. However, the product gave no signal in the expected region in the MALDI-TOF mass spectrum. This might indicate that the size of the wedge $\mathbf{BC_2E_4}$ prevents the nitriles at the focal points from coordination to the Pd^{II} centra in **A**. Coupling of large dendritic wedges to a rather small core is one of the major problems in convergent dendrimer synthesis. However, evidence for the coordination of dendritic wedges $\mathbf{BC_2E_4}$ to the slightly modified dendritic core **A′** (Chart 1) could be obtained by ^1H NMR spectroscopy. The modified core **A′** contains three methyl groups instead of protons at its central benzene unit. These methyl groups display a signal around 2.4 ppm in the ^1H NMR spectrum, a region devoid of other metallodendrimer proton signals. This makes it an ideal diagnostic probe for the dendrimer conformation by measuring its T_1 relaxation time constant. It has been shown that proton T_1 relaxation rates of methyl protons in substituted aromatic molecules are sensitive to the steric environment.[24] Hecht and Fréchet[25] found that the T_1 relaxation time constants of methylene protons near the dendrimer core increase with increasing dendrimer generation. This was attributed to a more extended confor-

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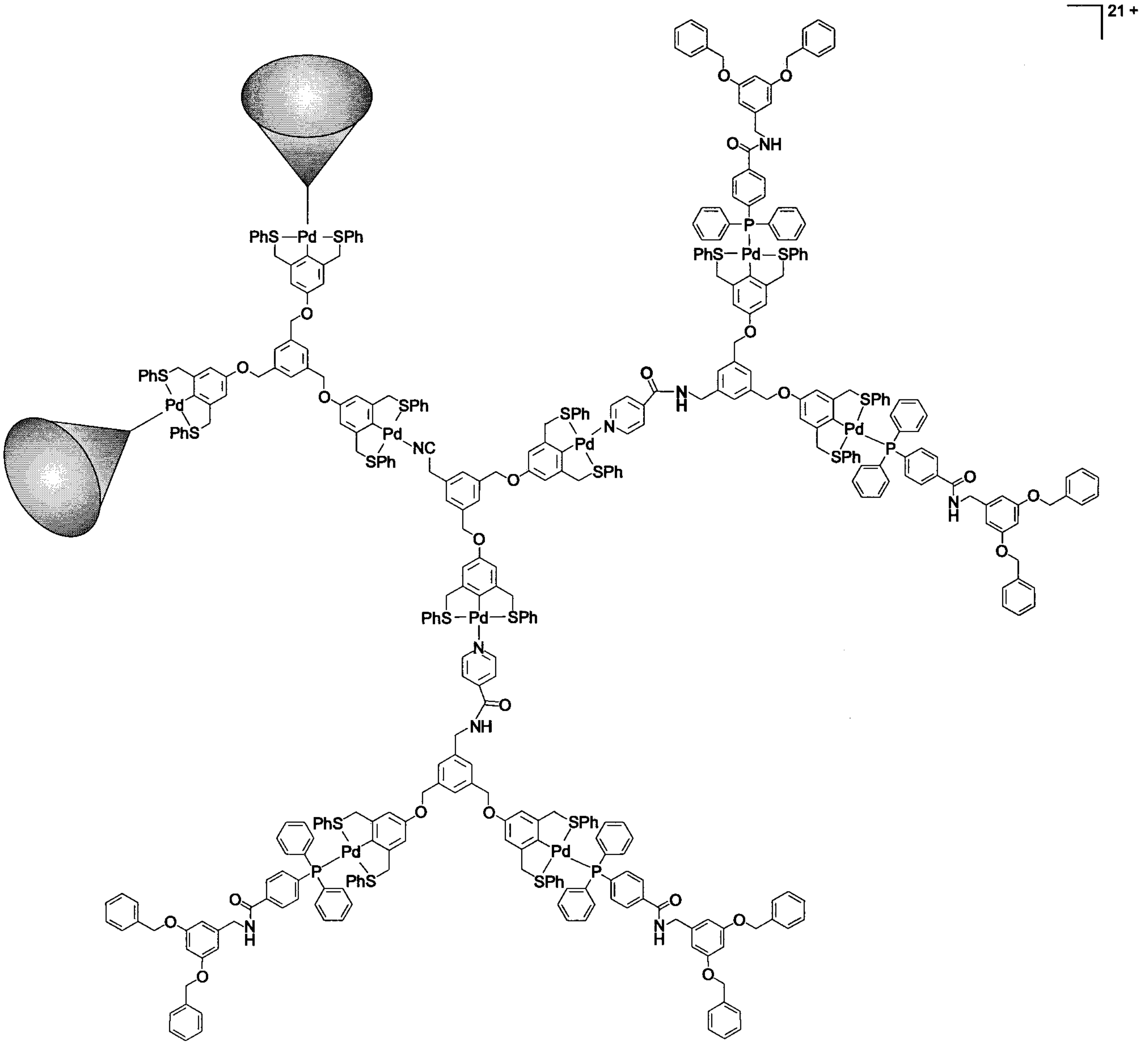
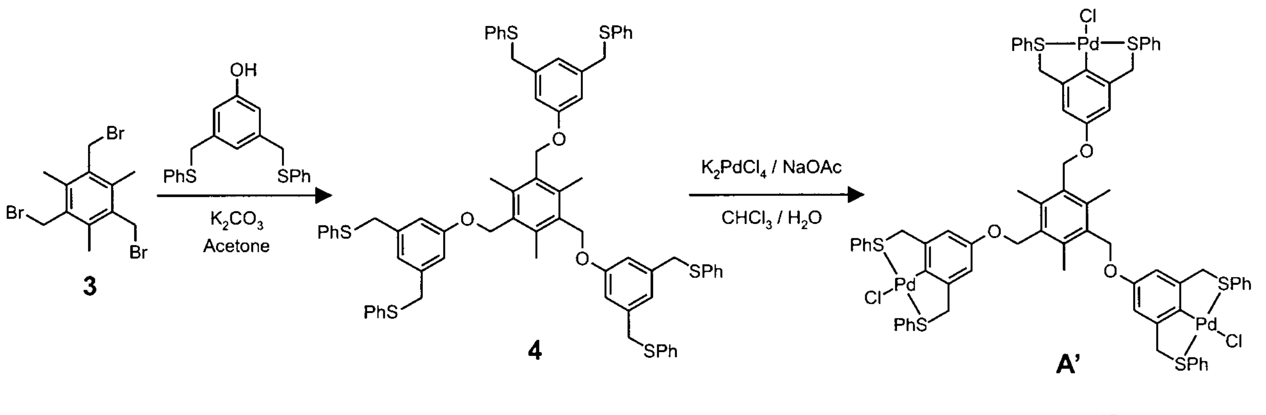


Figure 2. Dendritic structure of $AB_3C_6D_{12}$. Only one branch is fully drawn; the other two identical branches are represented by schematic cones.

Scheme 4. Synthesis of Modified Dendrimer core A′



mation of the core as the steric bulk of the dendrimer wedges increases, which leads to more conformational freedom of the methylene protons and thereby an increasing T_1 value.

A′ was synthesized starting from 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene[26] (**3**) by triple alkylation with 3,5-bis(phenylthiamethyl)phenol,[27] followed by cyclopalladation of the three pincer ligands of **4** with

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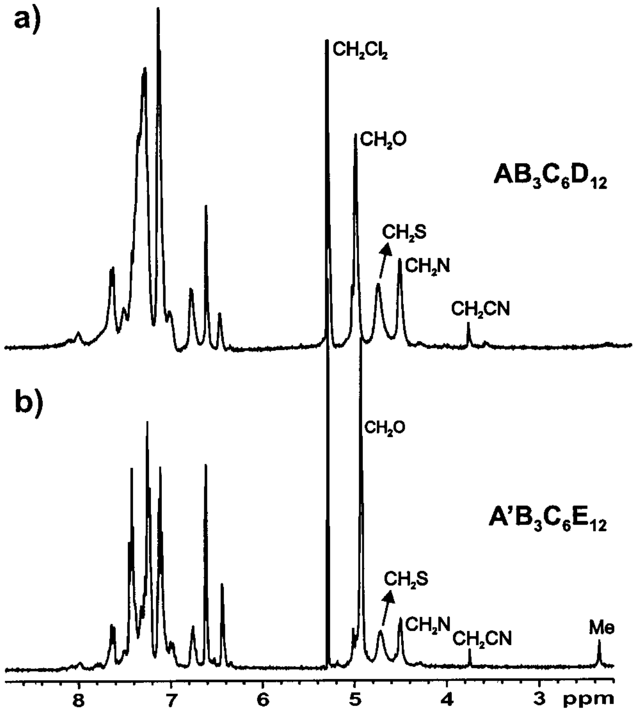

Figure 3. ^1H NMR spectra (CD_2Cl_2, 298 K) of metallodendrimers $\mathbf{AB_3C_6D_{12}}$ and $\mathbf{A'B_3C_6E_{12}}$.

K_2PdCl_4/NaOAc in a refluxing two-phase mixture of chloroform and water (Scheme 4).[28]

Characterization of $\mathbf{A'B_3C_6E_{12}}$ and Measurements of Methyl Proton Relaxation Rate Constants. Using the modified core **A′**, the influence of several ligands on the T_1 relaxation rate constant of the core methyl groups was investigated by ^1H NMR spectroscopy. The core **A′** was deprotected using 3 equiv of $AgBF_4$, and subsequently, 3 equiv of PPh_3, $\mathbf{CE_2}$, or $\mathbf{BC_2E_4}$ were added in order to produce assemblies of varying size. Measurements of methyl proton relaxation rate constants were performed on these assemblies at low concentration (e.g., 0.4 mM for $\mathbf{A'B_3C_6E_{12}}$) in CD_2Cl_2. The T_1 values of the methyl protons were found to increase in the ligand series Cl (0.70 ± 0.01 s) < PPh_3 (0.83 ± 0.01 s) < $\mathbf{CE_2}$ (1.03 ± 0.01 s) < $\mathbf{BC_2E_4}$ (1.10 ± 0.01 s), reflecting the increase in steric bulk in this series. These results imply that a similar phenomenon is occurring in the metallodendrimers as in the covalent dendrimers studied by Fréchet, namely the formation of more extended core conformations with increasing dendrimer generations. Moreover, the T_1 values show that the largest metallodendrimer $\mathbf{A'B_3C_6E_{12}}$ has indeed been assembled successfully. Its ^1H NMR spectrum (CD_2Cl_2, 298 K) is shown in Figure 3b. In contrast to $\mathbf{AB_3C_6E_{12}}$, for which a signal in the expected region of the MALDI-TOF mass spectrum was not observed, MALDI-TOF mass spectrometry of metallodendrimer $\mathbf{A'B_3C_6E_{12}}$ revealed the presence of a small but significant signal at *m/z* 29.3 kDa, which is in the expected range for $\mathbf{A'B_3C_6E_{12}}$.[29] Finally, the correct molecular composition was determined by elemental analysis. It is noteworthy that nearly all metallodendrons and metallodendrimers reported herein lack the presence of solvent in the analytical samples, in contrast to previously reported metallodendrimers, which were found to include substantial amounts of nitromethane in the solid samples.[13,14] The growth strategy reported here avoids the use of nitromethane.

Table 1. Characterization of Metallodendrimers by MALDI-TOF Mass Spectrometry

compd	fragment	obsd mass (Da)	calcd mass (Da)
$\mathbf{CD_2}$	$[M - BF_4]^+$	2426.3	2426.3
$\mathbf{BC_2D_4}$	$[M - BF_4]^+$	6140.6	6142.0
$\mathbf{AB_3C_6D_{12}}$	$[M - BF_4]^+$	20271.5	20283.1
$\mathbf{CE_2}$	$[M - BF_4]^+$	3908.7	3908.5
$\mathbf{BC_2E_4}$	$[M - BF_4]^+$	9107.2	9102.3
$\mathbf{A'B_3C_6E_{12}}$	$[M]^+$	29332.4	29315.6

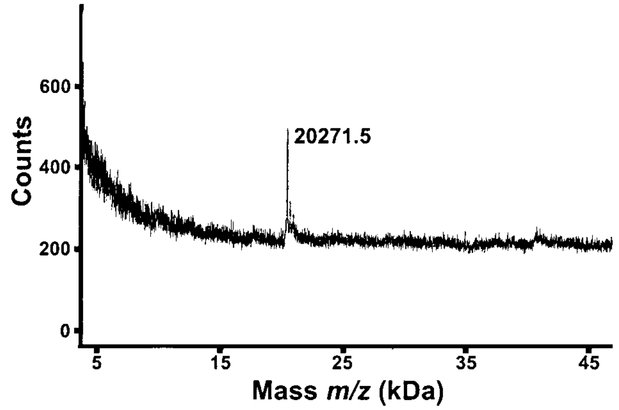

Figure 4. MALDI-TOF spectrum of $\mathbf{AB_3C_6D_{12}}$.

In view of the similarity between the cores **A** and **A′**, it can also be concluded from these results that the convergent assembly of $\mathbf{AB_3C_6E_{12}}$ using the original core **A** has been successful as well, although a signal in the expected region of the MALDI-TOF mass spectrum was not observed in that case.

MALDI-TOF Mass Spectrometry of Metallodendrimers. The determination of the molecular masses of dendrimers has become one of the most powerful techniques in their characterization. This is in part due to the symmetrical nature of dendrimers, which might hamper complete structure assignment by NMR spectroscopy. Particularly, ESI (electrospray ionization) and MALDI (matrix-assisted laser desorption ionization) mass spectrometry have recently been applied intensively to dendritic systems.[7b] Previously, we have also characterized metallodendrimers by either one of these techniques.[13,14] The dendritic structures reported here were all characterized by MALDI-TOF mass spectrometry. Table 1 displays the results of these measurements, and the spectrum of $\mathbf{AB_3C_6D_{12}}$ is displayed in Figure 4. From Table 1, it is evident that all found *m/z* values of the metallodendrimers except $\mathbf{A'B_3C_6E_{12}}$ correspond to the loss of only one BF_4 anion, a characteristic feature which we have also observed in previously reported metallodendrimers.[14] This is in contrast to ES-MS spectra of similar metallodendrimers, which display a preferential loss of a number of anions (up to 39 BF_4 anions for a fourth-generation metallodendrimer).[13] In the case of

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[28] Cyclopalladation using $Pd[MeCN]_4(BF_4)_2$ as the palladium source was found to cleave the benzylic ether bonds, a phenomenon that does not occur in **A**. Obviously, the three methyl moieties render the benzylic ethers more labile towards the HBF_4 that is released upon cyclopalladation with $Pd[MeCN]_4(BF_4)_2$.

[29] In addition to the signal at 29.33 kDa, larger signals are present at *m/z* 14.61, 10.11, 7.35, and 4.97 kDa, corresponding to various substructures of $\mathbf{A'B_3C_6E_{12}}$ formed by fragmentation in the mass spectrometer.

$A'B_3C_6E_{12}$, the broad signal in the MALDI-TOF spectrum centers around 29.33 kDa, which corresponds to $[M]^+$ instead of $[M - BF_4]^+$.

Conclusions

Both covalent and noncovalent syntheses of dendritic structures have been combined here in the assembly of "layer-block" metallodendrimers containing hydrophobic dendrons at their periphery. First- and second-generation Fréchet wedges functionalized at their focal point with phosphines were shown to coordinate to SCS Pd^{II} pincers, and their coordination was combined with the coordination of nitriles and pyridines to convergently assemble noncovalent metallodendrimers in high yields. All metallodendrimers were fully characterized by ^1H and ^{31}P NMR spectroscopy, elemental analysis, and MALDI-TOF mass spectrometry. The introduction of hydrophobic dendrons at the periphery of metallodendrimers significantly increases their solubility in apolar organic solvents, compared to metallodendrimers lacking these dendrons. Currently, research on these dendrimers is focused on the introduction of a fluorescent switch at the dendritic core, with the ultimate aim of manipulating single molecules of nanosize dimensions.

Experimental Section

General Comments. Melting points were determined with a Reichert melting point apparatus and are uncorrected. CH_2Cl_2 and hexane were freshly distilled from $CaCl_2$. CH_3CN (p.a. from Merck) was stored over molecular sieves (4 Å). Other solvents (EtOH, $CHCl_3$, acetone) were used as received (p.a. from Merck). All reagents were purchased from Aldrich and used without further purification. All solution manipulations with phosphines were performed in degassed solvents. NMR spectra were recorded in $CDCl_3$ (unless stated otherwise) at 298 K on a Varian Unity 300 locked to the deuterated solvent at 300.1 (^1H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz, respectively. Chemical shifts are given relative to tetramethylsilane (TMS). FAB mass spectra were recorded on a Finnigan MAT 90 mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as the matrix. Matrix-assisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectra[30] were recorded using a Perkin-Elmer/PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer (PerSeptive Biosystems, Inc., Framingham, MA) equipped with delayed extraction.[31] A 337 nm UV nitrogen laser producing 3 ns pulses was used. and the mass spectra were obtained in the linear and reflectron mode. Samples were prepared by mixing 10 μL of chloroform solution of the sample with 30 μL of a solution of 0.5 mg/L hydroxybenzylidene malononitrile (HBM) and 0.5 mg/L dithranol (DIT) in chloroform/liquid poly(ethylene glycol). One μL of the solution was loaded on a gold-sample plate, the solvent was removed in warm air, and the sample transferred to the vacuum of the mass spectrometer for analysis. Elemental analyses were performed using a Carlo Erba EA1106. The presence of solvents in the analytical samples was confirmed by ^1H NMR spectroscopy. Column chromatography was performed using silica gel (SiO_2, E. Merck, 0.040−0.063 mm, 230−240 mesh). 3,5-(Benzyloxy)benzylamine **2**,[20] 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene,[26] and 3,5-bis(phenylthiamethyl)phenol[27] were prepared according to literature procedures.

Phosphine-Functionalized First-Generation Dendrimer Wedge (D). To a mixture of 3,5-bis(benzyloxy)benzylamine **2** (0.24 g, 0.75 mmol), 4-(diphenylphosphino)benzoic acid (0.21 g, 0.69 mmol), and 1-hydroxybenzotriazole hydrate (HOBt, 0.09 g, 0.67 mmol) in $CHCl_3$ (50 mL) was added 1,3-dicyclohexylcarbodiimide (DCC, 0.16 g, 0.78 mmol), and the resulting solution was stirred at room temperature under an argon atmosphere for 3.5 h. The solution was subsequently washed with saturated aqueous solutions of $NaHCO_3$ and NaCl and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography (SiO_2; eluent: CH_2Cl_2) to afford pure dendritic wedge **D** as a white solid: yield 0.50 g (quant); mp 164−166 °C; ^1H NMR δ 7.74 (d, $J = 7.0$ Hz, 2 H), 7.47−7.33 (m, 22 H), 6.63 (d, $J = 2.2$ Hz, 2 H), 6.60 (t, $J = 2.2$ Hz, 1 H), 6.35 (t, $J = 5.5$ Hz, 1 H), 5.36 (s, 4 H), 4.63 (d, $J = 5.5$ Hz, 2 H); ^{13}C NMR δ 166.5, 159.7, 141.7, 139.9, 136.2, 135.8, 133.7, 133.5, 133.2, 132.9, 128.6, 128.2, 128.1, 127.5, 127.0, 126.4, 126.3, 106.4, 100.7, 69.6, 43.6; ^{31}P NMR δ −5.6; FAB-MS *m/z* 608.6 ($[M + H]^+$, calcd 608.7). Anal. Calcd for $C_{40}H_{34}NO_3P{\cdot}H_2O$: C, 76.78; H, 5.80; N, 2.24. Found: C, 76.68; H, 5.55; N, 2.44.

A′ Precursor (4). A mixture of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.25 g, 0.63 mmol), 3,5-bis(phenylthiamethyl)phenol (0.63 g, 1.86 mmol), K_2CO_3 (0.51 g, 3.69 mmol), and 18-crown-6 (0.05 g, 0.19 mmol) in acetone (60 mL) was refluxed overnight under an argon atmosphere. After evaporation of the solvent in vacuo, the resulting paste was taken up in CH_2Cl_2 (100 mL) and washed with brine. The organic phase was dried over $Na_2SO_{,4}$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (using CH_2Cl_2/hexane 65:35 (v/v) as the eluent), affording a white solid: yield 0.52 g (71%); mp 77−79 °C; ^1H NMR δ 7.32−7.17 (m, 30 H), 6.88 (s, 3 H), 6.76 (s, 6 H), 4.92 (s, 6 H), 4.05 (s, 12 H), 2.33 (s, 9 H); ^{13}C NMR δ 158.7, 138.7, 135.6, 131.1, 129.7, 128.3, 126.0, 121.5, 113.4, 64.4, 38.6, 15.4; FAB-MS *m/z* 1170.5 ($[M]^+$, calcd 1170.3). Anal. Calcd for $C_{72}H_{66}O_3S_6{\cdot}0.2H_2O$: C, 73.58; H, 5.69; S, 16.37. Found: C, 73.36; H, 5.59; S, 16.25.

A′. A solution of K_2PdCl_4 (0.29 g, 0.89 mmol) and NaOAc (73 mg, 0.89 mmol) in water (100 mL) was added to a solution of **3** (0.29 g, 0.25 mmol) in $CHCl_3$ (100 mL). The two-phase mixture was refluxed for 2 h and subsequently cooled to rt. After filtration of the mixture over Hyflo, the organic phase was washed with brine and dried over anhydrous Na_2SO_4. As TLC and ^1H NMR indicated incomplete cyclopalladation, the crude product was subjected to the same reaction conditions once more. After workup, the crude product was purified by column chromatography (using CH_2Cl_2/MeOH 97:3 (v/v) as the eluent), which afforded a yellow solid: yield 85 mg (22%); mp 191−193 °C; ^1H NMR δ 7.86−7.83 (m, 12 H), 7.39−7.35 (m, 18 H), 6.66 (s, 6 H), 4.97 (s, 6 H), 4.57 (br s, 12 H), 2.38 (s, 9 H); ^{13}C NMR δ 156.4, 151.5, 149.7, 138.8, 131.8, 131.0, 129.4, 129.1, 108.3, 64.5, 51.4, 15.4; FAB-MS *m/z* 1555.2 ($[M - Cl]^+$, calcd 1555.0). Anal. Calcd for $C_{72}H_{63}Cl_3O_3Pd_3S_6$: C, 54.24; H, 3.98; S, 12.07. Found: C, 54.32; H, 3.84; S, 12.15.

General Procedure for the Convergent Growth of Metallodendritic Wedges and Dendrimers. Building block, wedge, or core (1−6 μmol) was dissolved in CH_2Cl_2, and the required amount of $AgBF_4$ was added as a concentrated solution (0.10−0.20 M) in water. After the mixture was stirred for 5 min, the required amount of other building block or wedge was added in one portion. The mixture was vigorously stirred for 15 min, and subsequently CH_2Cl_2 and H_2O were removed under reduced pressure. The crude product was again dissolved in CH_2Cl_2, and AgCl was removed by filtration over Hyflo. After evaporation of the solvent, the product was obtained as a yellow solid.

CD_2. Pyridine building block **C** (3.6 mg, 3.0 μmol) was deprotected with $AgBF_4$ (6.0 μmol, 35 μL of a 0.1699 M solution), and subsequently phosphine wedge **D** (3.7 mg, 6.0 μmol) was added: yield 6.8 mg (89%); ^1H NMR (CD_2Cl_2) δ 8.60 (d, $J = 6.0$ Hz, 2 H), 7.75 (d, $J = 6.0$ Hz, 2 H), 7.63 (d, $J = 7.0$ Hz, 4 H), 7.47−7.22 (m, 43 H), 7.16−7.00 (m, 24 H), 6.83 (t, $J = 5.5$ Hz, 1 H), 6.79−6.47 (m, 10 H), 5.01 (s, 8 H), 4.97 (s, 4 H), 4.73 (br s, 8 H), 4.57 (d, $J = 5.5$ Hz, 1.5 H), 4.53 (d, $J = 5.5$ Hz, 2.5 H), 4.47 (d, $J = 5.5$ Hz, 2 H); ^{31}P NMR (CD_2Cl_2) δ 13.6; MALDI-TOF MS *m/z* 2426.3 ($[M - BF_4]^+$, calcd 2426.3). Anal.

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[30] Karas, M.; Bachmann, D.; Bahr, U.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Process.* **1987**, *78*, 53−68.

[31] Vestal, M. L.; Juhasz, P.; Martin, S. A. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 1044−1050.

Calcd for $C_{135}H_{114}B_2F_8N_4O_9P_2Pd_2S_4$: C, 64.52; H, 4.57; N, 2.23; S, 5.10. Found: C, 64.41; H, 4.27; N, 2.09; S, 5.10.

BC$_2$D$_4$. Nitrile building block **B** (2.1 mg, 1.9 μmol) was deprotected with $AgBF_4$ (3.8 μmol, 33 μL of a 0.1145 M solution), and subsequently dendritic wedge **CD$_2$** (9.2 mg, 3.8 μmol) was added: yield 10.6 mg (92%); ^{1}H NMR (CD_2Cl_2) δ 7.99 (very br s, 4 H), 7.61 (d, J = 7.0 Hz, 8 H), 7.49 (br s, 4 H), 7.42−6.94 (m, 157 H), 6.79−6.45 (3 × m, 24 H), 5.01 (s, 4 H), 4.97 (s, 8 H), 4.96 (s, 16 H), 4.73 (br s, 24 H), 4.50 (br d, 12 H), 3.74 (s, 2 H); ^{31}P NMR (CD_2Cl_2) δ 13.6; MALDI-TOF MS *m/z* 6140.6 ([M − BF_4]$^+$, calcd 6142.0). Anal. Calcd for $C_{320}H_{269}B_6F_{24}N_9O_{20}P_4Pd_6S_{12}$: C, 61.71; H, 4.35; N, 2.02; S, 6.18. Found: C, 61.46; H, 4.52; N, 1.75; S, 6.27.

AB$_3$C$_6$D$_{12}$. Dendrimer core **A** (2.1 mg, 1.4 μmol) was deprotected with $AgBF_4$ (4.3 μmol, 40 μL of a 0.1077 M solution), and subsequently dendritic wedge **BC$_2$D$_4$** (25.9 mg, 4.2 μmol) was added: yield 24.0 mg (85%); ^{1}H NMR (CD_2Cl_2) δ 8.0 (very br s, 12 H), 7.6 (d, J = 7.0 Hz, 24 H), 7.5−6.9 (m, 516 H), 6.75 (br d, 42 H), 6.6 (br s, 24 H), 6.4 (br s, 12 H), 4.95 (br s, 90 H), 4.65 (br s, 84 H), 4.45 (br s, 36 H), 3.7 (s, 6 H); ^{31}P NMR (CD_2Cl_2) δ 13.6; MALDI-TOF MS *m/z* 20271.5 ([M − BF_4]$^+$, calcd 20283.1). Anal. Calcd for $C_{1029}H_{864}B_{21}F_{84}N_{27}O_{63}P_{12}Pd_{21}S_{42}\cdot CH_2Cl_2$: C, 60.42; H, 4.26; N, 1.85; S, 6.58. Found: C, 60.10; H, 4.21; N, 1.85; S, 6.26.

CE$_2$. Pyridine building block **C** (4.7 mg, 3.9 μmol) was deprotected with $AgBF_4$ (7.9 μmol, 35 μL of a 0.2255 M solution), and subsequently phosphine wedge **E** (10.6 mg, 7.9 μmol) was added: yield 14.5 mg (92%); ^{1}H NMR (CD_2Cl_2) δ 8.56 (d, J = 6.0 Hz, 2 H), 7.73 (d, J = 6.0 Hz, 2 H), 7.62 (d, J = 7.0 Hz, 4 H), 7.46−6.97 (m, 79 H), 6.73−6.40 (m, 22 H), 4.98 (s, 4 H), 4.92 (s, 16 H), 4.85 (s, 8 H), 4.67 (br s, 8 H), 4.55 (d, J = 5.5 Hz, 1.8 H), 4.50 (d, J = 5.5 Hz, 2.9 H), 4.43 (d, J = 5.5 Hz, 1.3 H); ^{31}P NMR (CD_2Cl_2) δ 13.6; MALDI-TOF MS *m/z* 3908.7 ([M − BF_4]$^+$, calcd 3908.5). Anal. Calcd for $C_{191}H_{156}B_2Br_8F_8N_4O_{17}P_2Pd_2S_4$: C, 57.45; H, 3.89; N, 1.40; S, 3.21. Found: C, 57.60; H, 4.24; N, 1.68; S, 2.86.

BC$_2$E$_4$. Nitrile building block **B** (1.2 mg, 1.1 μmol) was deprotected with $AgBF_4$ (2.2 μmol, 19 μL of a 0.1145 M solution), and subsequently dendritic wedge **CE$_2$** (8.8 mg, 2.2 μmol) was added: yield 8.3 mg (82%); ^{1}H NMR (CD_2Cl_2) δ 7.70 (br s, 4 H), 7.60 (d, J = 7.0 Hz, 8 H), 7.4−6.9 (m, 181 H), 6.75−6.35 (3 × br s, 48 H), 4.9 (br s, 60 H), 4.65 (br s, 24 H), 4.5−4.4 (br d, 12 H), 3.7 (s, 2 H); ^{31}P NMR (CD_2Cl_2) δ 13.6; MALDI-TOF MS *m/z* 9107.2 ([M − BF_4]$^+$, calcd 9102.3). Anal. Calcd for $C_{432}H_{349}B_6Br_{16}F_{24}N_9O_{36}P_4Pd_6S_{12}$: C, 56.44; H, 3.87; N, 1.37; S, 4.19. Found: C, 56.63; H, 4.12; N, 1.25; S, 3.88.

A′B$_3$C$_6$E$_{12}$. Dendrimer core **A′** (1.4 mg, 0.9 μmol) was deprotected with $AgBF_4$ (2.7 μmol, 24 μL of a 0.1128 M solution), and subsequently dendritic wedge **BC$_2$E$_4$** (23.9 mg, 2.7 μmol) was added: yield 22.1 mg (87%); ^{1}H NMR (CD_2Cl_2) δ 8.0 (very br s, 12 H), 7.6 (d, J = 7.0 Hz, 24 H), 7.5−6.9 (m, 603 H), 6.75 (br s, 42 H), 6.6 (br s, 72 H), 6.4 (br s, 36 H), 4.90 (br s, 186 H), 4.65 (br s, 84 H), 4.5 (br s, 36 H), 3.7 (s, 6 H), 2.4 (s, 9 H); ^{31}P NMR (CD_2Cl_2) δ 14.1; MALDI-TOF MS *m/z* 29332.4 ([M]$^+$, calcd 29315.6). Anal. Calcd for $C_{1368}H_{1110}B_{21}Br_{48}F_{84}N_{27}O_{111}P_{12}Pd_{21}S_{42}$: C, 56.05; H, 3.82; N, 1.29; S, 4.59. Found: C, 56.04; H, 4.15; N, 1.20; S, 4.33.

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