ChemPubSoc Europe

DOI: 10.1002/chem.201500138

CHEMISTRY
A European Journal
Full Paper

Dendrimers |*Hot Paper*|

# Synthesis of Onion-Peel Nanodendritic Structures with Sequential Functional Phosphorus Diversity

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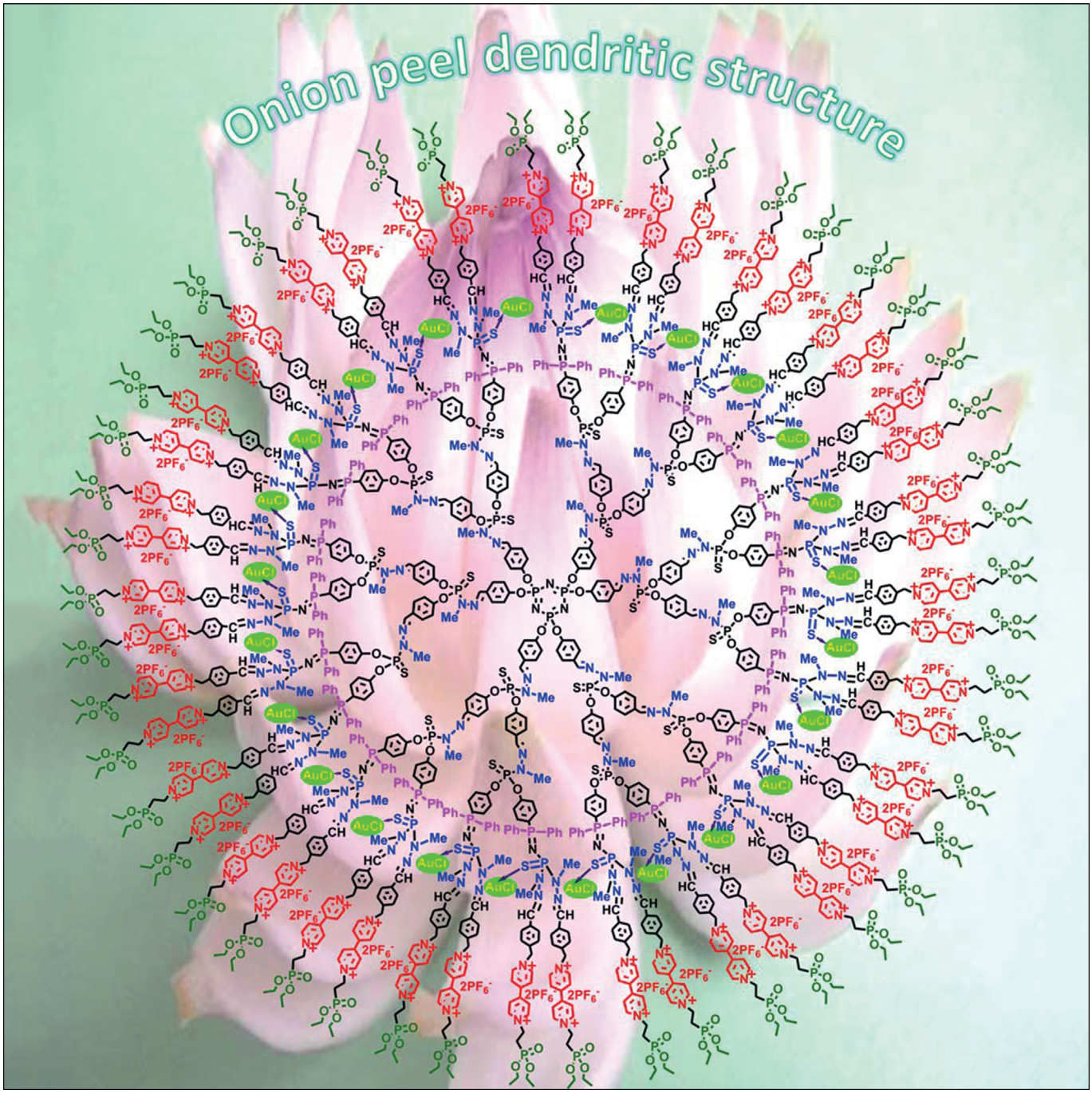
*Dedicated to Prof. Dr. Michael Veith on the occasion of his 70th birthday*



**Abstract:** The preparation of novel families of phosphorus-based macromolecular architectures called "onion peel" phosphorus nanodendritic systems is reported. This construct is based on the versatility of methods of synthesis using several building blocks and on the capability of these systems to undergo regioselective reactions within the cascade structure. Sustainable metal-free routes such as the Staudinger reaction or Schiff-base condensation, involving only water and nitrogen as byproducts, allow access to several dendritic macromolecules bearing up to seven different phosphorus units in their backbone, each of them featuring specific reactivity. The presence of the highly aurophilic P=N–P=S fragment enables selective ligation of $Au^{I}$ within the dendritic framework.

## Introduction

Nanomedicine is defined as the application of nanotechnology in making a medical diagnosis or in the treatment and/or prevention of disease. Nowadays, nanomedicine encompasses several diverse domains, such as detection of nanoparticles (materials at nanometer scale), drug delivery systems, or nanofabrication of biomaterials. Thus, in the domain of the nanocarriers, the main objective of nanomedicine is the development of nano-objects as drug delivery systems (major use) or drugs per se (minor use) to tackle various diseases, thus providing opportunity to decrease suffering and death resulting from diseases such as cancers, Alzheimer's and Parkinson's diseases, tuberculosis, or HIV. Among the vast array of molecules used in nanomedicine, dendrimers, pertaining to the large family of polymers, appear among the most efficient classes of nanodevices to fight efficiently against these diseases. Indeed, it was already demonstrated that some dendrimers are nanoparticles of choice for drug delivery when they are used as cargo for one or (more scarcely) multiple cytotoxic drugs, for example.[1] In parallel, dendrimers are known to be very active themselves as efficient transfecting agents, anti-prion, anti-inflammatory, or antitumor drugs, to name a few, or for diagnosis.[2]

Dendrimers also play a key role in several other fields of research, such as the design and assembly of a variety of novel functional nanomaterials with the formation of nanotubes (exclusively made with dendrimers), microcapsules, fibers, or mesoporous materials,[3] or in catalysis whereby a positive "dendritic effect" and very high enantioselectivities have been reported.[4]

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So large a number of properties and applications can be explained by the possibility to use well-defined buildings blocks to tailor at will the construction of these monodisperse polymers. This allows control of the internal structure of the dendrimers (both core and branches) with the possibility to build a hydrophobic or hydrophilic interior, thereby tuning their supramolecular chemistry, and also to graft a variety of functional groups onto their outer shells.[5]]

Within the dendrimer family, phosphorus dendrimers are of paramount interest due to the remarkable versatility of the phosphorus chemistry, which enables: a) a large scope for original methodologies for the synthesis of new dendrimers, b) access to several different types of phosphorus dendritic structures, each having their own chemical properties, and c) many applications, spanning from nanomedicine to materials science.[6]

Consequently, there is continuous interest in extending the chemical skeleton feature of dendrimers in general and of phosphorus dendrimers in particular. This prompted us to design new dendritic phosphorus species offering diverse possibilities for their respective backbone chemical structures, including the core, branching points, internal branches, and outer shell. This structural diversity provides extensive possibilities to perform regioselective chemical reactions allowing, for example, the covalent incorporation of drugs, metals, or fluorophores for medicinal or material purposes. Our efforts were turned towards the design of unprecedented "onion peel" nanodendritic phosphorus structures, in which a large variety of different phosphorus units can be regioselectively incorporated stepwise, each of them bringing the possibility to increase the functionalities of the final macromolecules or affording new perspectives for development. In addition, the repeating branches of each generation are generally not identical. In a recent pioneering work, Roy and co-workers reported an "onion peel strategy" for the divergent construction of biologically active glycodendrimers using different building blocks at each level.[7,8]

We report herein a general strategy for the straightforward preparation of various onion-peel nanodendritic structures, incorporating up to seven different types of phosphorus units, which, to our knowledge, is unprecedented for all classes of macromolecules and polymers. Due to the numerous possible applications of viologen units in different fields, such as electron- and charge-storing devices, electron sponges, antimicrobial and antiviral agents, or sequential complexation agents as guest anions and for molecular recognition purposes,[5a,9–11]

branches incorporating these active linkages were also added stepwise. As a first example of application, regioselective reaction complexation with $Au^{I}$ within the cascade structure of these onion-peel structures is also reported. The selection of $Au^{I}$ originates from known medical and material applications.[12]

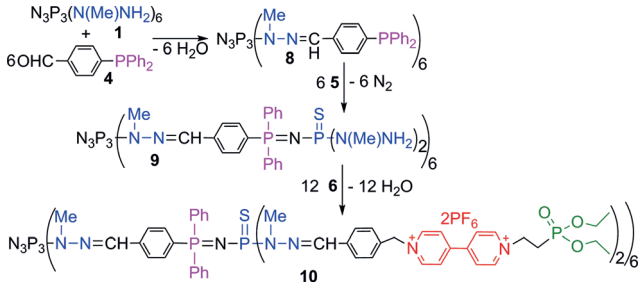
## Results and Discussion

The choice of the different layers and building blocks that constitute these onion-peel dendritic structures is crucial. Indeed, each layer should bring additional properties in comparison with a "classical uniform dendrimer". The fundamental requisite for such multistep design is the selection of an available core that is hydrophobic, multifunctional, and easily tailored. Consequently, we directed our strategy towards the use of the hexachlorocyclotriphosphazene ($P_3N_3Cl_6$) to prepare three different cores (**1–3**) bearing either hydrazine, phosphine or aldehyde groups (Figure 1). All of them are chemically stable and


**Figure 1.** Cores and building blocks.

their functional groups easily accessible for further diverse reactions. The second goal was to select the constitution of the internal branches. We decided to incorporate three different motifs within the cascade structure: a) the O–$C_6H_4$–CH=N–$N(CH_3)$–P(S) hydrophobic linkage with stable hydrazidothiophosphine moieties; b) the P=N–P=S moieties, which permit regioselective reactions inside the dendrimer due to the strong polarization of the $P^{+}$–N=P–$S^{-}$ fragment (e.g, alkylation, complexation to sulfur); c) functionalized viologens, which might bring interesting properties as previously reported [9–11] for pure viologen monomers, polymers, and dendrimers.

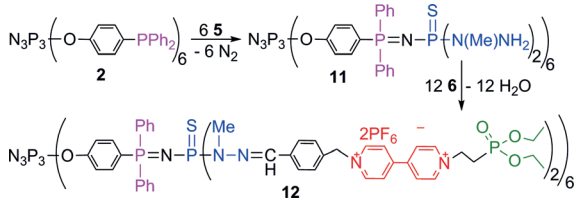
To address these issues, four different types of building blocks (**4–7**) were prepared according to procedures already reported by our group[13,14] (Figure 1). The first step of our synthetic strategy dealt with the Schiff-base reaction involving aldehyde **4** and hexahydrazinocyclotriphosphazene **1**,[13] leading to dendrimer **8** (generation 0) bearing six identical phosphino units.[14] Subsequent Staudinger reaction between **8** and the azidothiobishydrazinophosphine **5** afforded dendrimer **9** (generation 1) decorated with 12 methylhydrazino groups and incorporating six P=N–P=S linkages. The reaction proceeded in mild conditions and was monitored by $^{31}P$ NMR spectroscopy, showing the disappearance of the signals of the phosphino group of **8** (singlet at $\delta = -5.8$ ppm) and of the azido derivative **5** (singlet at $\delta = 82.6$ ppm), alongside the appearance of two doublets at $\delta = 14.4$ (P=N), and 73.0 ppm (P=S; $^{2}J(P,P) = 16.6$ Hz) due to the formation of the P=N–P=S linkages. **9** is therefore comprised of two different layers and the presence of hydrazino end groups allows for another Schiff-base reaction with the aldehyde **6**, incorporating in its structure a viologen unit and a phosphonate group. The Schiff-base reaction proceeded smoothly giving rise in near-quantitative yield to the onion-peel polycationic dendritic structure **10**, formed by three different layers (Scheme 1). This synthetic methodology is characterized by the regioselective incorporation of three




**Scheme 1.** Synthesis of generation 1 onion-peel phosphorus dendritic system **10**.

layers in high yields without the use of protection/deprotection reactions and with the formation of water or nitrogen as the only byproducts of the reaction. In addition, this has allowed the selective introduction to the structure, alongside viologen units, of five phosphorus groups in different environments: the $P_3N_3$ core, the P=N–P=S moieties, the terminal phosphonate, and the counter-anion $PF_6$, each allowing further diverse chemical reactions. The presence of these five different phosphorus group types is nicely corroborated by $^{31}P$ NMR with the presence of a singlet at $\delta = 18.5$ ppm ($P_3N_3$ core), two doublets at $\delta = 11.7$ (P=N) and 56.0 ppm (P=S) with $^{2}J(P,P) = 26.0$ Hz (P=N–P=S unit), a singlet at $\delta = 23.8$ ppm ($P(O)(OEt)_2$), and a heptuplet at $\delta = -144.4$ ppm ($PF_6$ anion) with a coupling constant of $^{1}J(P,F) = 709.0$ Hz.

The construction of these phosphorus nanodevices with five different phosphorus moieties opens the way towards new perspectives. The conception of such tailored systems and their high chemical structure diversification can also be illustrated by the synthesis of the onion dendrimers **11** and **12** (Scheme 2). In this case, we simply change the first steps of the methodology based on the reactivity of the hexachlorocyclotriphosphazene core. In this particular case, the core was treated with the 4-hydroxyphenylphosphine **7** to give the hexafunctionalized core **2** in good yield. Direct condensation of **2** with the azido phosphine **5** leads to the generation 1 dendrimer **11**, possessing 12 hydrazino end groups. Similarly to the last step in the preparation of the dendrimer **9** from the den-



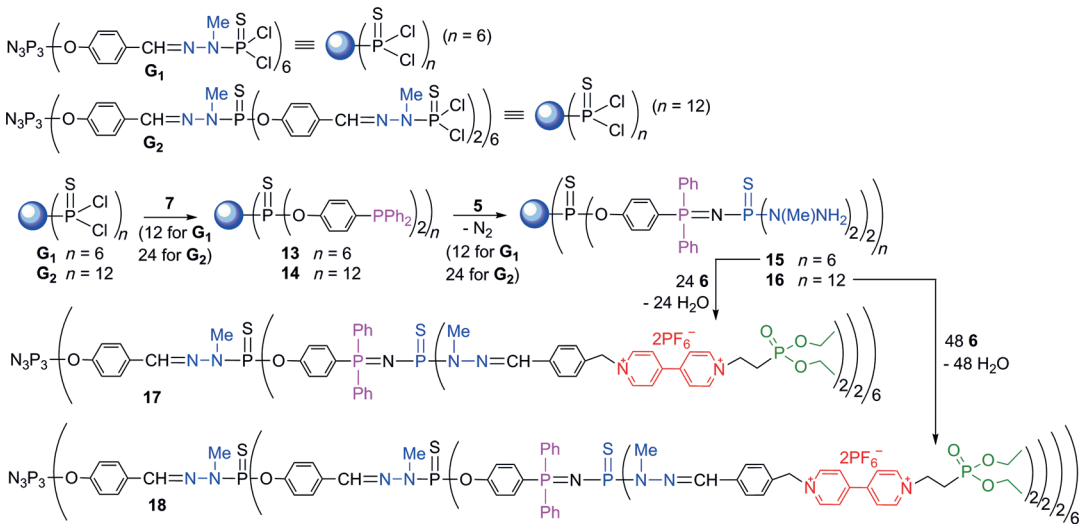

**Scheme 2.** Synthesis of generation 1 onion-peel phosphorus dendritic system **12**.

drimer **8** and viologen **6**, the condensation reaction between the aldehyde **6** and the dendrimer **11** afforded another new onion-peel dendritic structure **12**, thus illustrating the versatility of the method of preparation of these dendritic derivatives, by simply modifying the nature of the core (hexaphosphinocyclotriphosphazene for the synthesis of **12** versus hexahydrazinocyclotriphosphazene for the synthesis of **10**). Again, yields were nearly quantitative and the same byproducts (water and nitrogen) were formed and easily removed.

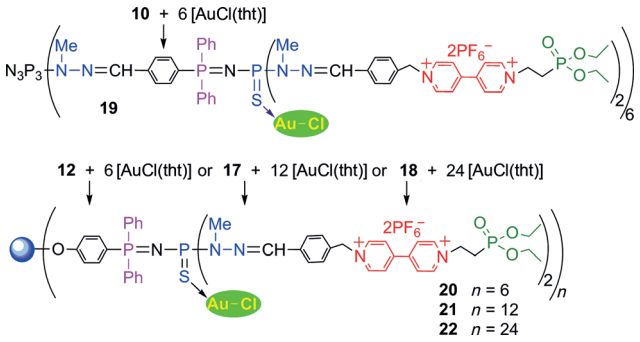
Having demonstrated the efficiency of these tools for the construction of "small" onion-peel dendritic structures (generations 0 and 1), the next goal of this study was to investigate the possibility to prepare higher-generation dendritic structures incorporating more than three different layers, each able to bring additional properties for the final onion-peel derivatives. This strategy is based on the preparation of "classical" phosphorus dendrimers of generations 1 and 2, decorated on their surfaces with 12 or 24 $P(S)Cl_2$ moieties, respectively. The synthesis of these macromolecules comprises the reiteration of a sequence of two reactions, condensation and substitution reactions between thiophosphorhydrazides and aldehydes.[15] Nucleophilic substitution of the $P(S)Cl_2$ end groups of the dendrimers with the 4-hydroxyphenylphosphine **7** afforded the macromolecular surface-decorated polyphosphines **13** and **14** (Scheme 3). The Staudinger-type reaction between these polyphosphines and the azide **5** led quantitatively to the polyhydrazino dendrimers **15** and **16**, respectively. The final steps consisted of a condensation reaction of **15** and **16** with the viologen aldehyde **6**, allowing the installation of photo-reactive bipyridinium units within the newly prepared onion-peel dendritic structures **17** and **18** of generations 2 and 3, respectively, in 82 and 78% yield, respectively (Scheme 3). Once again, no activating agents were needed and the byproducts were water for the condensation and nitrogen for the Staudinger reaction. $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopic analysis gave good evidence for the complete reactions. $^{31}P$ NMR spectroscopy appears to be the most powerful technique for this purpose. For example, the condensation reaction between **15** and **6** is characterized by the disappearance of the two doublets due to the P=N–P=S fragments in **15**, at $\delta = 12.2$ (P=N) and 70.85 ppm (P=S; $^2J(P,P) = 17.0$ Hz), alongsife the appearance of two new doublets at $\delta = 11.2$ (P=N) and 56.4 (P=S; $^2J(P,P) = 26.3$ Hz) for the final derivative.

Based on these syntheses, important features of the dendritic structures **17**, **18** include the incorporation of 3 or 4 layers for **17** and **18**, respectively, of different constitution, length, stability and reactivity, alongside the fact that **17** and **18** are the first examples of polymeric macromolecules bearing a so large variety of different phosphorus groups; six for the generation 2 dendrimer **17** and seven for the generation 3 dendrimer **18**. Interestingly, most of these phosphorus linkages offer the possibility to perform further reactions. For example, ring-opening polymerization of the $P_3N_3$ core can be conducted, as was recently shown with classical phosphorus dendrimers;[16] the internal P=N–P=S linkages can be protonated, alkylated, or complexed with metals; easy anion exchange of $PF_6^-$ can be conducted, thus allowing dramatically changes to the solubility of the resulting derivatives (**17** and **18** with bromide or chloride counter anions, instead of $PF_6$, are water soluble); terminal phosphonate groups can be transformed into phosphonic units or bridged to transition metals (e.g., P–O–Ti bridges) to afford novel extended hybrid mesostructures.

In a preliminary experiment to illustrate the versatility of these onion-peel dendritic structures, four of them, **10** (hexahydrazino cyclotriphosphazene core, generation 1), **12**, **17** and **18** (hexaphenoxy cyclotriphosphazene core, generations 1 to 3) were treated with [AuCl(tht)] (tht = tetrahydrothiophene) at room temperature for two hours. In all cases, complexation took place exclusively at the sulfur atom of the strongly polarized P=N–P=S linkage, affording the dendritic complexes **19**, **20**, **21**, and **22**, respectively (Scheme 4). The most salient evidence of this selective complexation was drawn from $^{31}P$ NMR spectroscopy. Indeed, no changes were observed in the chemical shifts of the core $P_3N_3$ group ($\delta = 18.5$ ppm), of the terminal




**Scheme 3.** Synthesis of generation 2 and 3 onion-peel phosphorus dendritic structures.




**Scheme 4.** Regioselective complexation of $Au^{I}$ within the onion-peel structures **10**, **12**, **17**, and **18**.

phosphonate groups ($\delta = 23.8$ ppm), or that of $PF_6^-$ ($\delta = -144.3$ ppm), whereas, for example, the doublets corresponding to the P=N–P=S linkage were dramatically affected; those for **10** moved from $\delta = 11.7$ (P=N) and 55.9 ppm (P=S; $^2J(P,P) = 26.0$ Hz) to 15.5 (P=N) and 44.9 ppm (P=S; $^2J(P,P) = 19.1$ Hz) for complex **19**. Similar modifications were observed for the complexations of **12**, **17**, and **18**, giving rise to the Au complexes **20**, **21**, and **22**. We observed a slight deshielding effect for the P=N chemical shift when moving from **17** to **21** (from $\delta = 11.2$ to 15.2 ppm) and a strong shielding effect for the P=S chemical shift of the P=N–P=S linkage (from $\delta = 56.4$ to 45.0 ppm), the $^2J(P,P)$ coupling constant varying from 15.2 to 20.5 Hz. Similar trends were observed during the Au complexation of the onion-peel structures **12** and **18**, leading to complexes **20** and **22** (Figure 2).

## Conclusion

In summary, we have proposed several simple and effective strategies for the preparation of unprecedented onion-peel nanodendritic structures of generations 0–3, bearing up to seven different phosphorus groups. These metal-free, sustainable strategies afford high product yields with only water and nitrogen as byproducts. In addition, the strategies presented herein allow the preparation of macromolecular systems with high modular reactivity, as demonstrated in preliminary experiments by the regioselective incorporation of $Au^{I}$ within the dendritic structure (P=N–P=S linkage). Work is underway in our group to illustrate the potential of these novel nanostructures in various fields, such as medicinal chemistry, catalysis, or design of new nanomaterials based on our previous works using classical phosphorus dendrimers.[3–5]

## Experimental Section

All reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulation. Solvents were purified with the MBRAUN SBS-800 purification system, except for acetonitrile, which was distilled over $CaH_2$. NMR spectra were recorded with Bruker AV 300, AV 400 and HD 400 spectrometers. All spectra were measured at 25 °C in the indicated deuterated solvents. References for NMR chemical shifts are $H_3PO_4$ (85%) for $^{31}P$ NMR, and $SiMe_4$ for $^1H$ and $^{13}C$ NMR spectroscopy. $^1H$, $^{13}C$ and $^{31}P$ chemical shifts ($\delta$) are reported in ppm and coupling constants ($J$) are reported in Hertz (Hz). The signals in the spectra are described as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad resonances). Assignment was carried out thanks to two-dimensional experiments when necessary (COSY, HMBC, HMQC). Compounds **1**,[17] **4**,[18] **5**,[19] **6**,[20] **7**,[21] ***Gn***, ($n = 1, 2$)[22] and [AuCl(tht)][23] were prepared according to previously reported procedures. The numbering used for NMR assignment is shown in Figure 3.

### Syntheses

**Compound 2**: Cesium carbonate (1120 mg, 3.45 mmol) was added to a solution of **7** (504 mg, 1.80 mmol) and hexachlorocyclotriphosphazene (50 mg, 0.29 mmol) in THF (15 mL). The mixture was stirred overnight at room temperature, then filtered and the solvent was removed under reduced pressure and the crude product purified by column chromatography (eluent = 20:80 dichloromethane/pentane) to give the desired compound **2** as a white powder (194 mg, 75% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 6.91$ (d, $^3J(H,H) = 8.3$ Hz, 12H, $C_0{}^2H$), 7.15 (dd, $^3J(H,H) = 8.4$, $^3J(P,H) = 7.1$ Hz, 12H, $C_0{}^3H$), 7.23–7.34 ppm (m, 60H, $PPh_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 120.0$ (dd, $^3J(C,P) = 7.3$ Hz, $^3J(P,C) = 5.0$ Hz, $C_0{}^2$), 128.5 (d, $^3J(P,C) = 6.9$ Hz, $C_m$), 128.8 ($C_p$), 133.5 (d, $^2J(P,C) = 19.8$ Hz, $C_o$), 134.3 (d, $^1J(P,C) = 12.3$ Hz, $C_0{}^4$), 135.0 (d, $^2J(P,C) = 20.8$ Hz, $C_0{}^3$), 137.1 (d, $^1J(P,C) = 11.4$ Hz, $C_i$), 150.9 ppm (dd, $^4J(P,C) = 2.4$ Hz, $^2J(P,C) = 4.9$ Hz, $C_0{}^1$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = -6.8$ (s, $PPh_2$), 8.3 ppm (s, $N_3P_3$).

**Dendrimer 8**: To a solution of **1** (60 mg, 0.148 mmol) in THF (5 mL) was added a solution of **4** (258 mg, 0.888 mmol) in THF (2 mL). The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the crude product was washed with pentane/$CH_2Cl_2$ (9:2; 2×40 mL) to afford dendrimer **8** as a white powder (196 mg, 65% yield).$^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 3.32$ (s.br, 18H, $CH_3$), 5.56 (d, $^3J(H,H) = 7.6$ Hz, 12H, $C_0{}^2H$), 7.24 (t, $^3J(P,H) = {}^3J(H,H) = 7.6$ Hz, 12H, $C_0{}^3H$), 7.29–7.40 (m, 60H, $PPh_2$), 7.58 ppm (s.br, 6H, CH=N); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 32.7$, 32.8 (2d, $^2J(P,C) = 5.7$ Hz, $CH_3$), 126.9 (d, $^2J(P,C) = 7.0$ Hz, $C_0{}^2$), 129.0 (d, $^3J(P,C) = 6.9$ Hz, $C_m$), 129.3 (s, $C_p$), 134.2 (d, $^2J(P,C) = 19.7$ Hz, $C_o$), 134.3 (d, $^2J(P,C) = 19.7$ Hz, $C_0{}^3$), 136.7 d, $^4J(P,C) = 5.6$ Hz, $C_0{}^1$), 136.8 (d, $^3J(P,C) = 5.6$ Hz, CH=N), 137.5 (d, $^1J(P,C) = 80.0$ Hz, $C_i$), 138.0 ppm (d, $^1J(P,C) = 22.4$ Hz, $C_0{}^4$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = -5.80$ (s, $PPh_2$), 17.3 ppm (s, $N_3P_3$).

**Dendrimer 9**: To a mixture of dendrimer **8** (200 mg, $0.98.10^{-4}$ mol) and azide **5** (143 mg, 0.73 mmol) was added a minimum amount of $CH_2Cl_2$ to dissolve both reagents (4 mL). The resulting solution was stirred at room temperature for 2 days (monitored by $^{31}P$ NMR spectroscopy). The mixture was washed with pentane/$CH_2Cl_2$ (5:1; 2×50 mL) to afford dendrimer **9** as a white powder (224 mg, 75% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 2.65$ (d, $^3J(P,H) = 11.9$ Hz, 36H, $CH_3$), 3.14–3.20 (m, 24H, $NH_2$), 3.29 (s.br, 18H, $CH_3$), 7.44–7.78 ppm (m, $C_0{}^2H$, $C_0{}^3H$, CH=N, $PPh_2$, 90H); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 32.9$–33.0 (m, $CH_3$), 39.8 (d, $^2J(P,C) = 7.2$ Hz, $CH_3$), 126.7 (d, $^2J(P,C) = 13.0$ Hz, $C_0{}^2$), 129.1 (d, $^3J(P,C) = 12.8$ Hz, $C_m$), 129.9 (dd, $^1J(P,C) = 106.0$ Hz, $^3J(P,C) = 2.7$ Hz, $C_0{}^4$), 130.6 (dd, $^1J(P,C) = 106.5$ Hz, $^3J(P,C) = 3.2$ Hz, $C_i$), 132.9 (d, $^4J(P,C) = 3.0$ Hz, $C_p$), 133.3 (d, $^2J(P,C) = 10.7$ Hz, $C_o$), 133.7 (d, $^2J(P,C) = 11.0$ Hz, $C_0{}^3$), 136.2–136.4 (m, CH=N), 140.3 ppm (d, $^4J(P,C) = 3.1$ Hz, $C_0{}^1$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = 14.4$ (d, $^2J(P,P) = 16.6$ Hz, $PPh_2$), 18.8 (s, $N_3P_3$), 73.0 ppm (d, $^2J(P,P) = 16.6$ Hz, P=S); IR (neat): $\nu = 3306$ $cm^{-1}$ (NH).

**Dendrimer 10**: To a solution of **9** (20 mg, $6.845.10^{-6}$ mol) in methylene chloride (1 mL) was added a solution of **6** (60 mg,

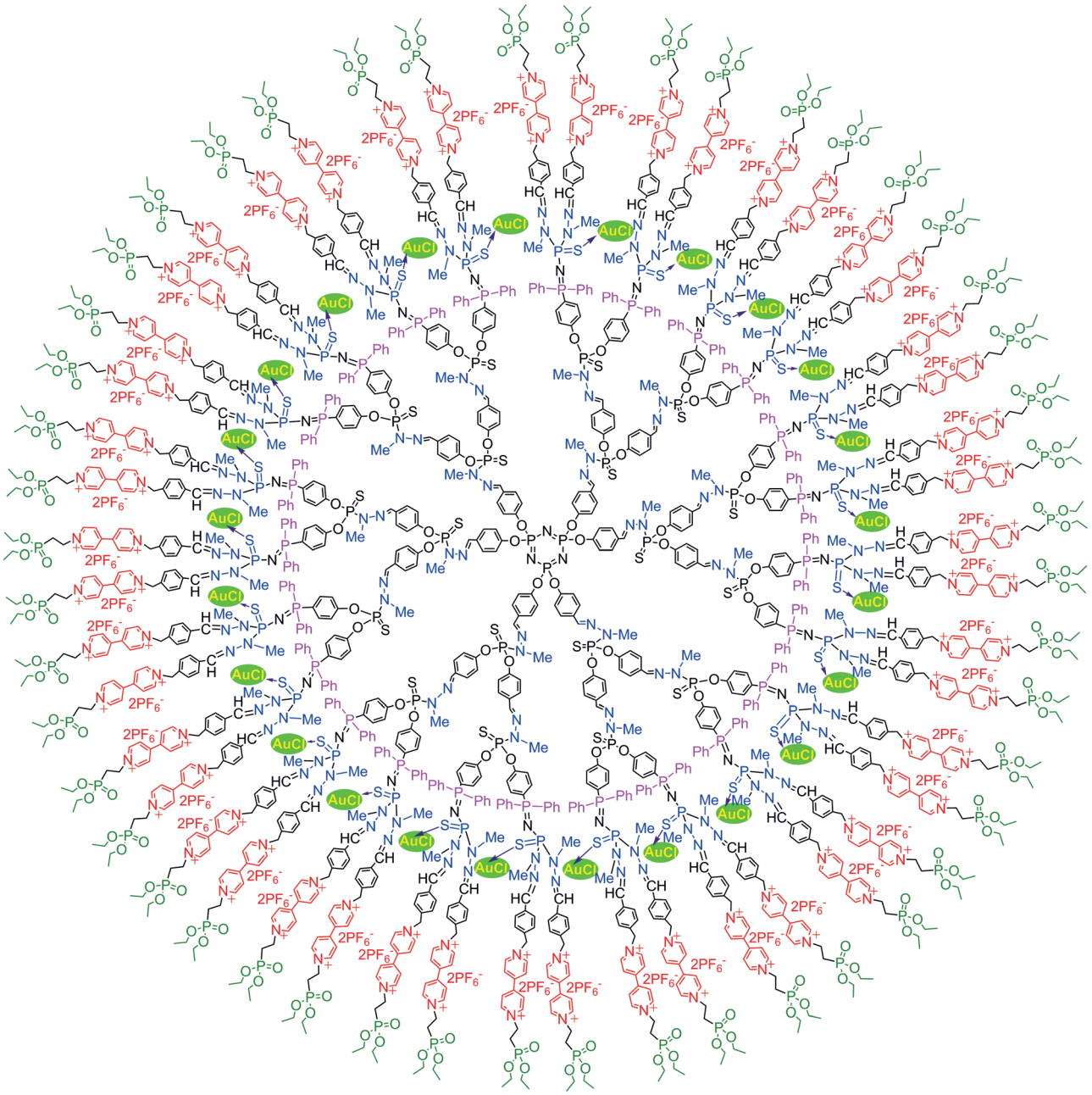


**Figure 2.** Structure of the onion-peel nanodendritic gold complex **22**.

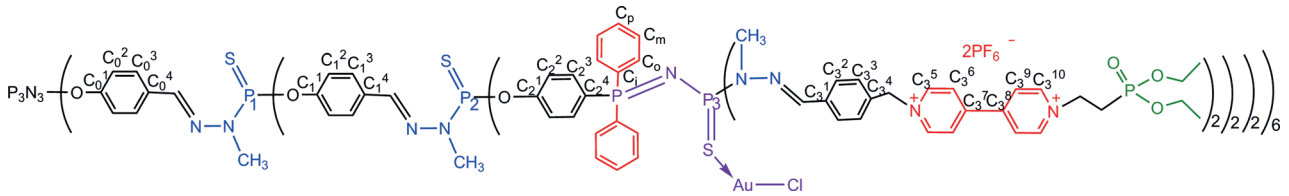


**Figure 3.** Numbering used for NMR peak assignment.

$8.214.10^{-5}$ mol) in acetone (3 mL). This mixture was stirred at room temperature for 2 days (monitored by $^{31}P$ NMR). The mixture was washed with pentane/acetone (8:3; 4×20 mL) to afford dendrimer **10** as an orange powder (60 mg, 75% yield). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CD_3CN$): $\delta = -144.4$ (hept, $^{1}J(P,F) = 709.0$ Hz, $PF_6$), 11.7 (d, $^{2}J(P,P) = 26.0$ Hz, $PPh_2$), 18.5 (s, $N_3P_3$), 23.8 (s, $P(O)(OEt)_2$), 56.0 ppm (d, $^{2}J(P,P) = 26.0$ Hz, P=S); $^{1}H$ NMR (400 MHz, $CD_3CN$): $\delta = 1.26$ (t, $^{3}J(H,H) = 6.8$ Hz, 72H, $OCH_2$-$CH_3$), 2.52–2.62 (m, 24H, $CH_2$-$CH_2P$), 3.16 (d, $^{3}J(P,H) = 10.1$ Hz, 36H, N-$CH_3$), 3.28 (s.br, 18H, N-$CH_3$), 3.89–4.18 (m, 48H, $OCH_2$-$CH_3$), 4.67–4.94 (m, 24H, $CH_2$-$CH_2P$), 5.78 (s,

24H, $C_1^4$-$CH_2$), 7.23–7.79 (m, 150H, $C_0^2$H, $C_0^3$H, $C_1^2$H, $C_1^3$H, CH=N, $PPh_2$), 8.40 (s.br, 48H, $C_1^6$H, $C_1^8$H), 9.01 ppm (s.br, 48H, $C_1^5$H, $C_1^{10}$H); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_3CN$): $\delta = 15.7$ (d, $^3J(P,C) = 5.9$ Hz, $OCH_2$-$CH_3$), 26.5 (d, $^1J(P,C) = 140.7$ Hz, $CH_2$-$CH_2$-P), 32.4, 32.5 (N-$CH_3$), 56.6 ($CH_2$-$CH_2$-P), 62.4 (d, $^2J(P,C) = 6.3$ Hz, $OCH_2$-$CH_3$), 64.4 ($C_1^4$-$CH_2$), 126.1 ($C_0^2$), 126.85, 126.9 ($C_1^2$, $C_1^9$), 127.4 ($C_1^6$), 128.7, 128.8 ($C_0^3$, $C_m$), 129.7 ($C_1^3$), 131.8, 132.6, 132.7 ($C_1^1$, $C_o$, $C_p$), 134.0 ($C_1^4$), 138.2 (CH=N), 145.5, 146.1 ($C_1^7$, $C_1^8$), 150.12 ppm ($C_0^1$); IR (neat): $\nu = 1638$ cm$^{-1}$ (C=N) .

**Dendrimer 11**: To a mixture of dendrimer **2** (240 mg, 0.13 mmol) and azide **5** (169 mg, 0.866 mmol) was added a minimum amount of $CH_2Cl_2$ to solubilize both reagents (2 mL). The resulting solution was stirred at room temperature for 24 h (monitored by $^{31}P$ NMR). The mixture was washed with pentane/$CH_2Cl_2$ (10:1; 3×60 mL) to afford dendrimer **11** as a white powder (250 mg, 68% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 2.65$ (d, $^3J(H,P) = 11.8$ Hz, 36H, Me), 3.70–3.74 (m, 24H, $NH_2$), 7.23 (dd, $^3J(H,H) = 8.6$, $^4J(P,H) = 2.4$ Hz, 12H, $C_0^2$H), 7.43–7.47 (m, 24H, $C_o$H), 7.57 (dd, $^3J(H,H) = 8.6$, $^3J(H,P) = 7.6$ Hz, 12H, $C_0^3$H), 7.69–7.74 ppm (m, 42H, $C_m$H, $C_p$H, CH=N); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 39.3$ (d, $^2J(P,C) = 7.2$ Hz, $CH_3$), 120.8 (d, $^3J(P,C) = 13.5$ Hz, $C_0^2$), 127.2 (d, $^1J(P,C) = 106.4$ Hz, $C_0^4$), 128.6 (d, $^3J(P,C) = 13.6$ Hz, $C_m$), 129.7 (dd, $^1J(P,C) = 107.1$, $^3J(P,C) = 3.3$ Hz, $C_i$), 128.7 (s, $C_p$), 132.7 (d, $^3J(P,C) = 10.7$ Hz, $C_o$), 134.9 (d, $^2J(P,C) = 12.6$ Hz, $C_0^3$), 153.3 ppm ($C_0^1$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = 6.7$ (s, $N_3P_3$), 11.9 (d, $^2J(P,P) = 17.1$ Hz, $PPh_2$), 70.8 ppm (d, $^2J(P,P) = 17.1$ Hz, P=S); IR (neat): $\nu = 3193$ cm$^{-1}$ (NH).

**Dendrimer 12**: To a solution of **11** (20 mg, $7.14.10^{-6}$ mol) in methylene chloride (1 mL) was added a solution of **6** (63.0 mg, $0.86.10^{-6}$ mol) in acetone (3 mL). This mixture was stirred at room temperature for 2 days (monitored by $^{31}P$ NMR). The mixture was washed with pentane/acetone (4:1; 4×20 mL) to afford dendrimer **12** as an orange powder (57 mg, 70% yield). $^1H$ NMR (400 MHz, [$D_6$]acetone): $\delta = 1.09$–$1.38$ (m, 72H, $OCH_2$-$CH_3$), 2.74–3.31 (m, 60H, $CH_2$-$CH_2$P, N-$CH_3$), 3.97–4.32 (m, 48H, $OCH_2$-$CH_3$), 5.08–5.26 (m, 24H, $CH_2$-$CH_2$P), 6.08 (s, 24H, $C_1^4$-$CH_2$), 7.09–8.11 (m, 144H, $C_0^2$H, $C_0^3$H, $C_1^2$H, $C_1^3$H,CH=N, $PPh_2$), 8.59–8.98 (m, 48H, $C_1^6$H, $C_1^8$H), 9.28–9.65 ppm (m, 48H, $C_1^5$H, $C_1^{10}$H); $^{13}C\{^1H\}$ NMR (101 MHz, [$D_6$]acetone): $\delta = 15.8$ (d, $^3J(P,C) = 5.8$ Hz, $OCH_2$-$CH_3$), 26.7 (d, $^1J(P,C) = 140.8$ Hz, $CH_2$-$CH_2$-P), 32.4 (N-$CH_3$), 56.7 ($CH_2$-$CH_2$-P), 62.2 ($OCH_2$-$CH_3$), 64.3 ($C_1^4$-$CH_2$), 125.2 ($C_0^2$), 127.0 ($C_1^2$, $C_1^9$), 127.5 ($C_1^6$), 128.7, 128.9 ($C_0^3$, $C_m$), 129.6 ($C_1^3$), 132.7 (s.br, $C_1^1$, $C_o$, $C_p$), 135.2 ($C_1^4$), 138.3 (CH=N), 145.8, 146.5 ($C_1^7$, $C_1^8$), 150.2 ppm ($C_0^1$); $^{31}P\{^1H\}$ NMR (162 MHz, [$D_6$]acetone): $\delta = -144.3$ (hept, $^1J(P,F) = 709.0$ Hz, $PF_6$), 7.4 (s, $N_3P_3$), 11.2 (s.br, $PPh_2$), 24.2 (s, P(O)$(OEt)_2$), 56.4 ppm (s.br, P=S); IR (neat): $\nu = 1637$ cm$^{-1}$ (C=N).

**Dendrimer 13**: Cesium carbonate (500 mg, 1.30 mmol) was added to a solution of **7** (190 mg, 0.68 mmol) and **Gc1** (100 mg, $0.53.10^{-4}$ mmol) in THF (10 mL). The mixture was stirred overnight at room temperature, then filtered under argon and the filtrate was evaporated to dryness. The resulting oil was dissolved in $CH_2Cl_2$ (1 mL) and this solution was added to a mixture of pentane/$Et_2O$ (8:1; 50 mL) to allow dendrimer **13** to precipitate. **13** was obtained as a white powder (200 mg, 80% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 3.28$ (d, $^3J(P,H) = 10.3$ Hz, 18H, $CH_3$), 7.00 (d, $^3J(H,H) = 8.3$ Hz, 12H, $C_0^2$H), 7.17–7.31 (m, 168H, $C_1^2$H, $C_1^3$H, $PPh_2$), 7.52–7.55 ppm (m, 18H, CH=N, $C_0^3$H); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 32.8$ (d, $^2J(P,C) = 12.5$ Hz, $CH_3$), 121.1 (s, $C_0^2$), 121.4 (dd, $^3J(P,C) = 7.1$ Hz, $^3J(P,C) = 5.0$ Hz, $C^2_1$), 128.2 (s, $C_0^3$), 128.6 (d, $^3J(P,C) = 7.1$ Hz, $C_m$), 128.8 (s, $C_p$), 132.0 ($C_0^4$), 133.6 (d, $^2J(P,C) = 19.7$ Hz, $C_o$), 134.5 (dd, $^1J(P,C) = 12.3$ Hz, $^5J(P,C) = 1.7$ Hz, $C_1^4$), 135.0 (d, $^2J(P,C) = 20.8$ Hz, $C_1^3$), 137.0 (d, $^1J(P,C) = 11.3$ Hz, $C_i$), 139.0 (d, $^3J(P,C) = 15.0$ Hz, CH=N), 151.1–151.2 ppm (m, $C_0^1$, $C_1^1$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = -6.6$ (s, $PPh_2$), 8.1 (s, $N_3P_3$), 61.7 ppm (s, $P_1$=S).

**Dendrimer 14**: Cesium carbonate (653 mg, 2.00 mmol) was added to a solution of **7** (290 mg, 1.04 mmol) and **Gc2** (200 mg, 0.42 mmol) in THF (10 mL). The mixture was stirred overnight at room temperature, then filtered and the filtrate was evaporated to dryness. The resulting oil was dissolved in $CH_2Cl_2$ (3 mL) and this solution was added to a mixture of pentane/$Et_2O$ (9:1; 100 mL) to allow dendrimer **14** to precipitate. **14** was obtained as a white powder (335 mg, 75% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 3.21$ (d, $^3J(P,H) = 10.1$ Hz, 18H, $CH_3$), 3.27 (d, $^3J(P,H) = 10.3$ Hz, 36H, $CH_3$), 6.97 (d, $^3J(H,H) = 8.5$ Hz, 12H, $C_0^2$H), 7.13–7.28 (m, 360H, $C_1^2$H, $C_2^2$H, $C_2^3$H, $PPh_2$), 7.52–7.55 ppm (m, 54H, CH=N, $C_0^3$H, $C_1^3$H); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 32.9$ (d, $^2J(P,C) = 12.5$ Hz, $CH_3$), 121.4 (dd, $^3J(P,C) = 7.3$ Hz, $^3J(P,C) = 4.8$ Hz, $C_2^2$), 121.7, 121.8 ($C_0^2$, $C_1^2$), 128.2, 128.3 ($C_0^3$, $C_1^3$), 128.6 (d, $^3J(P,C) = 7.0$ Hz, $C_m$), 128.8 (s, $C_p$), 132.3 ($C_0^4$, $C_1^4$), 133.6 (d, $^2J(P,C) = 19.7$ Hz, $C_o$), 134.4 (dd, $^1J(P,C) = 12.5$ Hz, $^5J(P,C) = 1.8$ Hz, $C_2^4$), 135.0 (d, $^2J(P,C) = 20.8$ Hz, $C_2^3$), 137.0 (d, $^1J(P,C) = 11.3$ Hz, $C_i$), 139.0 (d, $^3J(P,C) = 14.8$ Hz, CH=N), 151.1–151.3 (m, $C_0^1$, $C_1^1$, $C_2^1$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = -6.7$ (s, $PPh_2$), 8.3 (s, $N_3P_3$), 61.7 (s, $P_2$=S), 62.4 ppm (s, $P_1$=S).

**Dendrimer 15**: To a mixture of dendrimer **13** (150 mg, 0.032 mmol) and azide **5** (85 mg, 0.435 mmol) was added a minimum amount of $CH_2Cl_2$ to solubilize both reagents (4 mL). The resulting solution was stirred at room temperature for 2 days (monitored by $^{31}P$ NMR). The mixture was washed with pentane/$CH_2Cl_2$ (10:3; 2×80 mL) to afford dendrimer **15** as a white powder (183 mg, 85% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 2.65$ (dd, $^3J(P,H) = 11.8$ Hz, $^5J(P,H) = 1.9$ Hz, 72H, $CH_3$), 3.35 (d, $^3J(P,H) = 10.3$ Hz, 18H, $CH_3$), 7.05 (d, $^3J(H,H) = 7.6$ Hz, 12H, $C_0^2$H), 7.42–7.52 (m, 24H, $C_1^2$H), 7.53–7.61 (m, 36H, $C_0^3$H, $C_1^3$H), 7.66–7.82 ppm (m, 120H, $PPh_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 33.0$ (s.br, $CH_3$), 39.3 (d, $^2J(P,C) = 7.5$ Hz, $CH_3$), 121.0 ($C_0^2$), 121.4 (dd, $^3J(P,C) = 7.1$ Hz, $^3J(P,C) = 5.0$ Hz, $C^2_1$), 128.4 ($C_0^3$), 128.6 (d, $^3J(P,C) = 12.9$ Hz, $C_m$), 129.7 (d, $^1J(P,C) = 106.9$ Hz, $C^4_1$), 131.8 ($C_0^4$), 132.3 (d, $^1J(P,C) = 99.7$ Hz, $C_i$), 132.4 ($C_p$), 132.7 (d, $^2J(P,C) = 10.7$ Hz, $C_o$), 134.8 (d, $^2J(P,C) = 12.1$ Hz, $C_1^3$), 139.8–140.1 (m, CH=N), 151.4 (s, $C_0^1$), 153.7 ppm (s, $C_1^1$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = 7.6$ (s, $N_3P_3$), 12.2 (d, $^2J(P,P) = 17.0$ Hz, $PPh_2$), 60.8 (s, $P_1$=S), 70.9 ppm (d, $^2J(P,P) = 17.0$ Hz, $P_2$=S); IR (neat): $\nu = 3311$ cm$^{-1}$ (NH).

**Dendrimer 16**: To a mixture of dendrimer **14** (150 mg, 0.014 mmol) and azide **5** (90 mg, 0.46 mmol) was added a minimum amount of $CH_2Cl_2$ to solubilize both reagents (3 mL). The resulting solution was stirred at room temperature for 4 days (monitored by $^{31}P$ NMR). The mixture was washed with pentane/$CH_2Cl_2$ (10:3; 3×80 mL) to afford dendrimer **16** as a white powder (165 mg, 80% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta = 2.65$ (d, $^3J(P,H) = 11.8$ Hz, 144H, $CH_3$), 3.34 (d, $^3J(P,H) = 9.4$ Hz, 54H, $CH_3$), 7.15–7.79 ppm (m, 426H, $C_0^2$H $C_0^3$H, $C_1^2$H, $C_1^3$H, $C_2^2$H, $C_2^3$H, CH=N, $PPh_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): $\delta = 33.0$ (d, $^2J(P,C) = 12.3$ Hz, $CH_3$), 39.3 (d, $^2J(P,C) = 7.5$ Hz, $CH_3$), 121.3 (d, $^3J(P,C) = 7.3$ Hz, $C_1^2$), 121.5 (d, $^3J(P,C) = 7.3$ Hz, $C_2^2$), 121.8 ($C_0^2$), 127.0 (d, $^1J(P,C) = 105.9$ Hz, $C_2^4$), 128.4 ($C_0^3$, $C_1^3$), 128.6 (d, $^3J(P,C) = 12.8$ Hz, $C_m$), 129.7 (d, $^1J(P,C) = 106.8$ Hz, $C_i$), 132.45 ($C_p$), 132.7 (d, $^2J(P,C) = 10.7$ Hz, $C_o$), 132.9 (s.br, $C_0^4$, $C_1^4$), 134.7 (d, $^2J(P,C) = 12.0$ Hz, $C_2^3$), 140.0 (s.br, CH=N), 151.4 ($C_0^1$), 153.4, 153.7 ppm (s.br, $C_1^1$, $C_2^1$); $^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): $\delta = 8.1$ (s, $N_3P_3$), 12.3 (s.br, $PPh_2$), 60.63 (s, $P_2$=S), 62.5 (s, $P_1$=S), 70.7 ppm (s.br, $P_3$=S); IR (neat): $\nu = 3307$ cm$^{-1}$ (NH) .

**Dendrimer 17**: To a solution of **15** (20 mg, $2.97.10^{-6}$ mol) in methylene chloride (0.5 mL) was added a solution of **6** (100 mg, $0.137.10^{-6}$ mol) in acetone (5 mL). This mixture was stirred at room temperature for 3 days (monitored by $^{31}P$ NMR). The mixture was washed with pentane/acetone (8:3; 5×20 mL) to afford dendrimer **17** as an orange powder (58 mg, 82% yield). $^1H$ NMR (400 MHz, [$D_6$]acetone): $\delta = 1.17$–$1.34$ (m, 144H, $OCH_2$-$CH_3$), 2.70–2.86 (m,

48H, $CH_2$-$CH_2$P), 3.08 (sbr, 90H, N-$CH_3$), 4.02–4.15 (m, 96H, O$CH_2$-$CH_3$), 5.06–5.24 (m, 48H, $CH_2$-$CH_2$P), 6.04 (s, 48H, $C_2^4$-$CH_2$), 7.27–7.80 (m, 318H, $C_0^2$H, $C_0^3$H, $C_1^2$H, $C_1^3$H, $C_2^2$H, $C_2^3$H, CH=N, $PPh_2$), 8.70–8.80 (m, 96H, $C_2^6$H, $C_2^8$H), 9.33–9.50 ppm (m, 96H, $C_2^5$H, $C_2^{10}$H); $^{13}C\{^1H\}$ NMR (101 MHz, [D$_6$]acetone): $\delta = 15.8$ (d, $^3J(P,C) = 5.9$ Hz, $OCH_2$-$CH_3$), 26.7 (d, $^1J(P,C) = 140.4$ Hz, $CH_2$-$CH_2$-P), 32.4 (d, $^2J(P,C) = 8.7$ Hz, N-$CH_3$), 56.6 ($CH_2$-$CH_2$-P), 62.3 (d, $^2J(P,C) = 6.3$ Hz, $OCH_2$-$CH_3$), 64.4 ($C_2^4$-$CH_2$), 121.46 ($C_0^2$), 127.0 ($C_1^2$), 127.1 ($C_2^2$, $C_2^9$), 127.5 ($C_2^6$), 128.7, 128.81 ($C_0^3$, $C_1^3$, $C_m$), 129.6 ($C_2^3$), 132.3, 132.6, 132.77, 133.8 ($C_0^1$, $C_1^1$, $C_o$, $C_p$), 134.9, 135.0 ($C_0^4$, $C_1^4$), 138.3 (CH=N), 145.8, 146.5 ($C_2^7$, $C_2^8$), 150.2 ($C_1^1$), 153.8 ppm ($C_0^1$); $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]acetone): $\delta = -144.3$ (hept, $^1J(P,F) = 709.0$ Hz, $PF_6$), 8.3 (s, $N_3P_3$), 11.19 (d, $^2J(P,P) = 26.3$ Hz, $PPh_2$), 24.4 (s, P(O)$(OEt)_2$), 56.4 (d, $^2J(P,P) = 26.3$ Hz, $P_2$=S), 61.0 ppm ($P_1$=S); IR (neat): $\nu =$ 1638 $cm^{-1}$ (C=N).

**Dendrimer 18**: To a solution of **16** (20 mg, $1.37.10^{-6}$ mol) in methylene chloride (0.5 mL) was added a solution of **6** (48 mg, $0.066.10^{-6}$ mol) in acetone (4 mL). This mixture was stirred at room temperature for 6 days (monitored by $^{31}$P NMR). The mixture was washed with pentane/acetone (5:2; 6×20 mL) to afford dendrimer **18** as an orange powder (52 mg, 78% yield). $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta = 1.25$ (s.br, 288H, $OCH_2$-$CH_3$), 2.82–2.95 (m, 96H, $CH_2$-$CH_2$P), 3.18 (s.br, 198H, N-$CH_3$), 4.05–4.15 (m, 192H, O$CH_2$-$CH_3$), 5.16 (s.br, 96H, $CH_2$-$CH_2$P), 6.05 (s, 96H, $C_3^4$-$CH_2$), 7.27–7.97 (m, 666H, $C_0^2$H, $C_0^3$H, $C_1^2$H, $C_1^3$H, $C_2^2$H, $C_2^3$H, $C_3^2$H, $C_3^3$H, CH=N, $PPh_2$), 8.55–8.95 (m, 192H, $C_3^6$H, $C_3^8$H), 9.22–9.63 ppm (m, 192H, $C_3^5$H, $C_3^{10}$H); $^{13}C\{^1H\}$ NMR (101 MHz, [D$_6$]acetone): $\delta = 15.8$ (d, $^3J(P,C) = 5.7$ Hz, $OCH_2$-$CH_3$), 26.7 (d, $^1J(P,C) = 139.9$ Hz, $CH_2$-$CH_2$-P), 32.6 (N-$CH_3$), 56.8 ($CH_2$-$CH_2$-P), 62.1 (d, $^2J(P,C) = 6.3$ Hz, $OCH_2$-$CH_3$), 64.4 ($C_3^4$-$CH_2$), 121.5 ($C_0^2$, $C_1^2$), 126.9 ($C_2^2$, $C_2^2$, $C_3^9$), 127.4 ($C_3^6$), 128.7, 128.5, 128.8 ($C_0^3$, $C_1^3$, $C_2^3$,$C_m$), 129.6 ($C_3^3$), 132.3, 132.6, 132.7, 133.9 ($C_0^1$, $C_1^1$, $C_2^1$, $C_o$, $C_p$), 134.9, 135.0, 135.1 ($C_0^4$, $C_1^4$, $C_2^4$), 138.3 (CH=N), 145.8, 146.5 ($C_3^7$, $C_3^8$), 150.1 ($C_1^1$, $C_2^1$), 153.8 ppm ($C_0^1$); $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]acetone): $\delta = -144.3$ (hept, $^1J(P,F) = 709.0$ Hz, $PF_6$), 11.3 (d, $^2J(P,P) = 24.8$ Hz, $PPh_2$), 24.1 (s, P(O)$(OEt)_2$), 56.4 (d, $^2J(P,P) = 24.8$ Hz, $P_3$=S), 61.1 (s, $P_2$=S), 62.4 ppm (s, $P_1$=S); IR (neat): $\nu =$ 1638 $cm^{-1}$ (C=N).

**Dendrimer 19**: To solution of dendrimers **10** (20.0 mg, $1.73.10^{-6}$ mol) in acetone (5.0 mL) was added a solution of [AuCl(tht)] (10.0 mg, $3.11.10^{-5}$ mol) in THF (1.0 mL) at room temperature. The colorless solution instantaneously turned pale yellow. The mixture was stirred for 2 h and the solvent was removed under reduced pressure. The residue was washed with dichloromethane (2×4 mL) to remove the excess [AuCl(tht)] and gave the dendrimer **19** as a pale yellow powder (20 mg, 90% yield). $^1$H NMR (400 MHz, [D$_6$]acetone)): $\delta = 1.26$ (t, $^3J(H,H) = 7.1$ Hz, 72H, $OCH_2$-$CH_3$), 2.52–2.62 (m, 24H, $CH_2$-$CH_2$P), 3.31 (s.br, 36H, N-$CH_3$), 3.46 (s.br, 18H, N-$CH_3$), 3.98–4.17 (m, 48H, O$CH_2$-$CH_3$), 5.11–5.36 (m, 24H, $CH_2$-$CH_2$P), 6.10 (s, 24H, $C_1^4$-$CH_2$), 7.48–7.92 (m, 150H, $C_0^2$H, $C_0^3$H, $C_1^2$H, $C_1^3$H, CH=N, $PPh_2$), 8.77 (s.br, 48H, $C_1^6$H, $C_1^8$H), 9.33–9.53 ppm (m, 48H, $C_1^5$H, $C_1^{10}$H); $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]acetone): $\delta = -144.4$ (hept, $^1J(P,F) = 709.0$ Hz, $PF_6$), 15.5 (d, $^2J(P,P) = 19.1$ Hz, $PPh_2$), 17.5 (s.br, $N_3P_3$), 24.0 (s, P(O)$(OEt)_2$), 44.9 ppm (d, $^2J(P,P) = 19.1$ Hz, P=S); IR (neat): $\nu = 1638$ $cm^{-1}$ (C=N).

**Dendrimer 21**: To solution of dendrimers **17** (10 mg, $4.2.10^{-7}$ mol) in acetone (4 mL) was added a solution of [AuCl(tht)] (3.0 mg, $9.36.10^{-6}$ mol) in THF (1 mL) at room temperature. The colorless solution instantaneously turned pale yellow. The mixture was stirred for 3 h and the solvent was removed under reduced pressure. The residue was washed with dichloromethane (3×4 mL) to remove the excess [AuCl(tht)] and gave the dendrimer **21** as a pale yellow powder (10 mg, 90% yield). $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta =$ 1.26 ($^3J(H,H) = 7.0$ Hz, 144H, $OCH_2$-$CH_3$), 2.70–2.86 (m, 48H, $CH_2$-$CH_2$P), 3.28 (s.br, 90H, N-$CH_3$), 3.92–4.24 (m, 96H, O$CH_2$-$CH_3$), 5.02–5.25 (m, 48H, $CH_2$-$CH_2$P), 6.09 (s, 48H, $C_2^4$-$CH_2$), 7.38–8.00 (m, 318H, $C_0^2$H, $C_0^3$H, $C_1^2$H, $C_1^3$H, $C_2^2$H, $C_2^3$H, CH=N, $PPh_2$), 8.70–8.88 (m, 96H, $C_2^6$H, $C_2^8$H), 9.30–9.52 ppm (m, 96H, $C_2^5$H, $C_2^{10}$H); $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]acetone): $\delta = -144.3$ (hept, $^1J(P,F) = 709.0$ Hz, $PF_6$), 8.2 (s.br, $N_3P_3$), 15.2 (d, $^2J(P,P) = 20.3$ Hz, $PPh_2$), 24.0 (s, P(O)$(OEt)_2$), 45.0 (d, $^2J(P,P) = 20.3$ Hz, $P_2$=S), 60.8 ppm (s.br, $P_1$=S); IR (neat): $\nu =$ 1638 $cm^{-1}$ (C=N) .

**Dendrimer 22**: To solution of dendrimers **18** (15.0 mg, $3.08.10^{-7}$ mol) in acetone (3.0 mL) was added a solution of [AuCl(tht)] (5.0 mg, $1.56.10^{-6}$ mol) in THF (1.0 mL) at room temperature. The colorless solution instantaneously turned pale yellow. The mixture was stirred for 3 h, and the solvent was removed under reduced pressure. The residue was washed with dichloromethane (4×3 mL) to remove the excess [AuCl(tht)] and gave the dendrimer **22** as a pale yellow powder (16 mg, 95% yield). $^1$H NMR (400 MHz, [D$_6$]acetone): $\delta = 1.25$ ($^3J(H,H) = 6.9$ Hz, 288H, $OCH_2$-$CH_3$), 2.82–2.95 (m, 96H, $CH_2$-$CH_2$P), 3.29 (s.br, 198H, N-$CH_3$), 3.96–4.18 (m, 192H, O$CH_2$-$CH_3$), 5.17 (s.br, 96H, $CH_2$-$CH_2$P), 6.07 (s, 96H, $C_3^4$-$CH_2$), 7.31–7.97 (m, 666H, $C_0^2$H, $C_0^3$H, $C_1^2$H, $C_1^3$H, $C_2^2$H, $C_2^3$H, $C_3^2$H, $C_3^3$H, CH=N, $PPh_2$), 8.63–8.88 (m, 192H, $C_3^6$H, $C_3^8$H), 9.23–9.54 ppm (m, 192H, $C_3^5$H, $C_3^{10}$H); $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]acetone): $\delta = -144.3$ (hept, $^1J(P,F) = 709.0$ Hz, $PF_6$), 15.2 (s.br, $PPh_2$), 24.0 (s, P(O)$(OEt)_2$), 45.0 (s.br, $P_3$=S), 61.0 ppm (s.br, $P_1$=S and $P_2$=S); IR (neat): $\nu = 1638$ $cm^{-1}$ (C=N).

## Acknowledgements

Thanks are due to the CNRS (France) and to the Euro-Mediterranean University of Fes (Morocco) for financial support.

**Keywords:** dendrimers · gold · nanostructures · phosphorus · viologens

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Received: January 13, 2015
Published online on March 5, 2015