

A Multi-O₂ Complex Derived from a Copper(I) Dendrimer

Robertus J. M. Klein Gebbink,^[a] Anton W. Bosman,^[b] Martinus C. Feiters,^{*[a]}
E. W. Meijer,^{*[b]} and Roeland J. M. Nolte^{*[a]}

Abstract: The high-pressure reaction of 2-vinylpyridine with the primary amines of four consecutive generations of poly(propylene imine) dendrimers (DAB-dendr-(NH₂)_n) (*n* = 4, 8, 16, 32) yielded dendrimers with bis[2-(2-pyridyl)ethyl]-amine (PY2) ligands. The complexation of the new dendrimers with metal ions was investigated by a variety of techniques. The reaction of the first- and fourth-generation dendrimers (*n* = 4 and 32, respectively) with Zn^{II}(ClO₄)₂ was studied by ¹H NMR titration, and

the complexation of all new dendrimers with Cu^I(ClO₄)₂ was investigated by UV/Vis and EPR spectroscopy. Quantitative coordination of one metal ion per PY2 group was demonstrated in all cases. A UV/Vis titration of the fourth-generation dendrimer DAB-dendr-(PY2)₃₂ in dichloromethane with [Cu^I(CH₃CN)₄](ClO₄) in acetonitrile re-

vealed that approximately 30 Cu^I ions were bound. Low-temperature UV/Vis spectroscopy of this complex in dichloromethane at -85 °C in the presence of dioxygen showed that approximately 60–70% of the copper centers can bind dioxygen, corresponding to 10–11 of these molecules per dendrimer molecule. This complex can be considered a synthetic analogue of hemocyanin, the copper-containing oxygen transport protein from the hemolymph of molluscs and arthropods.

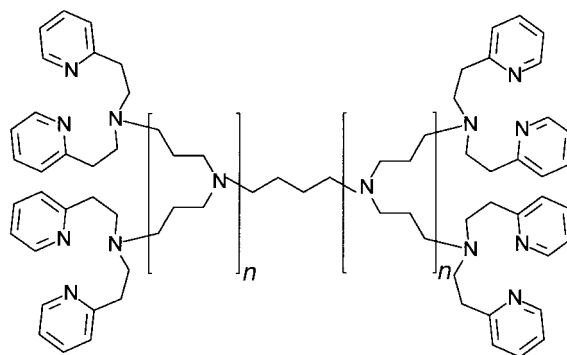
Keywords: copper • dendrimers • dioxygen complexes • N ligands • zinc

Introduction

The remarkable O₂-binding properties of the binuclear copper protein hemocyanin (Hc) have stimulated many groups to develop biomimetic copper complexes with various Cu:O₂ stoichiometries and different binding modes for the O₂ ligand.^[1] In the enzyme tyrosinase, it has been suggested that O₂ activation takes place at a binuclear copper site similar to that in Hc.^[2a] In the copper enzymes dopamine β-hydroxylase and ascorbate oxidase, this activation occurs at one of two mononuclear copper sites^[2b] and at a trinuclear copper site,^[2c] respectively. Analogues for these copper sites may be expected to catalyze oxidation reactions with molecular oxygen as the oxidant. The complexes reported by Karlin et al.^[1c,d] and Kitajima et al.^[1b,3] have been very helpful in predicting the μ-η²:η² peroxo binding mode for the O₂ ligand in oxy-Hc. Hc molecules are known to assemble into large aggregates under the influence of protons and of certain alkali

and alkaline earth metal ions.^[4] In this way a complex is formed which binds many O₂ molecules. This behavior of Hc inspired us to design a multicopper complex which is similarly capable of binding a large number of O₂ molecules.

The current interest in star-shaped, highly branched polymers (so-called dendrimers) has led to the synthesis of metallodendrimers such as metal-based dendritic polymers^[5] and multimetal dendrimer complexes.^[6] Dendritic Fe-porphyrin complexes were prepared by Jiang and Aida as well as by Collman, Diederich et al., and were shown to have a very high affinity for O₂ and CO.^[7] Catalytically active metallodendrimers have been described by the groups of van Koten, Reetz, and Suslick, amongst others.^[8] Here we report on the preparation of four generations of dendrimers, possessing 4, 8, 16, and 32 bis[2-(2-pyridyl)ethyl]amine (PY2) ligands at their peripheries (compounds **1**, **2**, **3**, and **4**,



n: DAB-dendr-(PY2)_{2⁽ⁿ⁻¹⁾}; *n* = 1, 2, 3, 4

[a] Dr. M. C. Feiters, Prof. R. J. M. Nolte, Dr. R. J. M. Klein Gebbink
Department of Organic Chemistry, NSR Center
University of Nijmegen
Toernooiveld, NL-6525 ED Nijmegen (The Netherlands)
Fax: (+31) 24-3652929
E-mail: tijdink@sci.kun.nl

[b] Prof. E. W. Meijer, A. W. Bosman
Laboratory for Macromolecular and Organic Chemistry
Eindhoven University of Technology
P.O. Box 513, NL-5600 MB Eindhoven (The Netherlands)
Fax: (+31) 40-2451036
E-mail: tgotbm@chem.tue.nl

respectively). The polypyridine dendrimer **4** is found to bind approximately 32 Cu^I or Cu^{II} ions in its PY2 groups, and the Cu₃₂^I complex in turn can bind 10 or more molecules of O₂.

Results and Discussion

Synthesis and characterization of (DAB-dendr-(PY2)_n): Recently we showed that poly(propylene imine) dendrimers (DAB-dendr-(NH₂)_n)^[9] are capable of forming multimetal complexes in which the metals are sited selectively at the dendrimer periphery.^[10] In order to obtain a multiligand system designed to complex Cu^I ions, we had to modify the primary amines of the poly(propylene imine) dendrimers with PY2 groups. We have also described a very efficient high-pressure procedure for the modification of primary amines with PY2-type pyridine ligands by a Michael-type reaction.^[11] To explore the applicability of the high-pressure procedure in the synthesis of PY2-functionalized dendrimers, we first synthesized the first-generation analogue **1**. Under a pressure of 15 kbar and at 50 °C the starting tetraamine DAB-dendr-(NH₂)₄ was completely converted within 16 h into the desired pyridine compound DAB-dendr-(PY2)₄ with acetic acid as a catalyst. Analytically pure **1** was successfully isolated in 64% yield after column chromatography, by which the oligo- and polyvinylpyridine side products were removed.

These procedures applied to the dendrimers DAB-dendr-(NH₂)_n (*n* = 8, 16, 32) with vinylpyridine yielded very viscous orange-brown oils, which were purified by precipitation in the case of DAB-dendr-(PY2)₈ (**2**) and DAB-dendr-(PY2)₁₆ (**3**), and by dialysis in the case of DAB-dendr-(PY2)₃₂ (**4**). FT-IR

Abstract in Dutch: De hoge druk-reactie van 2-vinylpyridine met de primaire amines van vier opeenvolgende generaties van poly(propyleen-imine) dendrimeren (DAB-dendr-(NH₂)_n) (*n* = 4, 8, 16, 32) leverde dendrimeren op met bis[2-(2-pyridyl)ethyl]amine (PY2) liganden. De complexering van de nieuwe dendrimeren met metaalionen werd onderzocht met een aantal technieken. De reactie van de 1e en 4e generatiedendrimeren met Zn^{II}(ClO₄)₂ werd bestudeerd door middel van een ¹H NMR titratie, en de complexering van alle nieuwe dendrimeren met Cu^{II}(ClO₄)₂ werd onderzocht door middel van UV-zichtbaar licht spectrofotometrie en EPR. Kwantitatieve coordinatie van 1 metaal-ion per PY2 groep werd in alle gevallen aangetoond. Een spectrofotometrische titratie van het 4e generatie dendrimeer DAB-dendr-(PY2)₃₂ in dichloormethaan met [Cu^I(CH₃CN)₄](ClO₄) in acetonitril gaf als resultaat dat ongeveer 30 Cu^I ionen werden gebonden. Op basis van spectrofotometrische metingen bij -85 °C aan dit complex in dichloormethaan in aanwezigheid van zuurstof kon geconcludeerd worden dat ongeveer 60–70% van de kopercentra betrokken was bij zuurstofbinding, wat correspondeert met 10–11 moleculen zuurstof per dendrimeermolecuul. Dit complex kan beschouwd worden als een synthetisch analogon van hemocyanine, het koperhoudende zuurstoftransporteiwit uit de haemolymphe van weekdieren en geleedpotigen.

and ¹³C NMR analysis showed that all the primary amine groups had reacted, although some dispersity of the number of residual primary amine groups in **4** could not be completely ruled out.^[12] Broadened resonances were observed in the ¹H NMR spectrum of **4**. The relative intensities of the signals were in agreement with the expected polypyridine dendrimer structure. For **1–3**, ESI-MS spectra confirmed the complete functionalization of the dendrimers. Both ESI and MALDI-TOF mass analysis revealed a very broad ion cluster of low intensity between 7500 and 10500 amu for **4**. This range corresponds to the calculated molecular mass (10242 amu) of the monocation of a completely reacted polyamine. The origin of the broadening of the peak is not yet clear: it may be the result of fragmentation during the analysis, although incomplete conversion cannot be excluded.

Zn^{II} and Cu^{II} complexes of (DAB-dendr-(NH₂)_n): An uptake of four Cu^{II} ions per molecule of **1** was revealed by UV/Vis spectroscopic titration of **1** with Cu(ClO₄)₂ in methanol, in which the increase in the d–d absorption band of the resulting complex at 664 nm was plotted against the number of Cu^{II} ions added per ligand. ¹H NMR titration of **1** with Zn^{II}(ClO₄)₂ in a mixture of deuterated methanol and acetonitrile was carried out to obtain more structural information. Addition of Zn^{II} to **1** resulted in a new set of pyridine signals at lower field (Figure 1), indicating the coordination of the PY2 donor

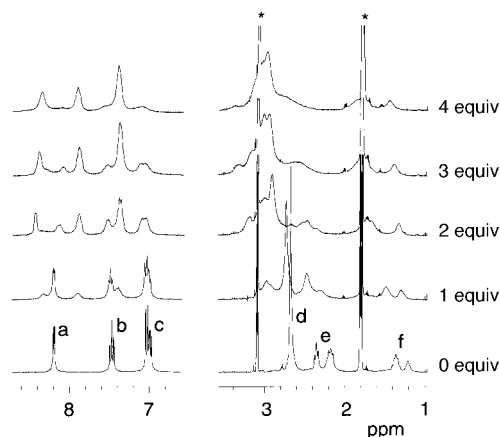


Figure 1. ¹H NMR titration of **1** with Zn(ClO₄)₂.

centers to a transition metal. Downfield shifts were also observed for protons of the ethylene spacer and for some of the methylene protons adjacent to tertiary amine nitrogen atoms of **1**, but no shifts were observed for the β-methylene protons in the dendrimer core. Analysis of the NMR titrations showed that four Zn^{II} ions were bound per molecule of **1**, consistently with identical binding of Zn^{II} and Cu^{II} by the PY2 ligand set.

The tetranuclear copper complex [1(Cu₄^{II})](ClO₄)₈ was isolated in 42% yield by simply adding a methanol solution of the appropriate amount of Cu^{II}(ClO₄)₂ · 6H₂O to a stirred solution of **1** in methanol, then warming the mixture to reflux temperature, and precipitation. The elemental analysis was in agreement with the proposed structure, and MALDI-TOF mass spectrometry showed a strong peak at *m/z* = 1710, attributed to the tetranuclear copper complex with three

perchlorate counterions. FT-IR analysis in the solid state showed that the perchlorate is noncoordinating ($\tilde{\nu}(\text{ClO}_4^-) = 1097, 623 \text{ cm}^{-1}$). In methanol solution this complex behaved as an 8:1 electrolyte ($A_m = 1116 \text{ S cm}^2 \text{ mol}^{-1}$), indicating the complete dissociation of the perchlorate counterions. A frozen methanol solution of the complex at 130 K displayed a typical axial EPR spectrum ($g_{\perp} = 2.07, g_{\parallel} = 2.25, A_{\parallel} = 170 \text{ G}$), which might be explained by the weak axial coordination of solvent molecules to the copper centers. The EPR linewidth was small and there was no indication of the presence of more than a single type of copper center. All of these observations strongly supported the formation of tetranuclear complexes in which the metal centers are complexed by the PY2 parts of the ligand and are further weakly coordinated by solvent molecules. There was no evidence for participation of the tertiary amine N atoms of the dendrimer core in the complexation.

UV/Vis and EPR titrations showed that the pyridine dendrimers **2**, **3**, and **4** readily bind copper ions as well. The UV/Vis spectroscopic titration curves of **2**, **3**, and **4** with $\text{Cu}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in a MeOH/CH₃CN (1:1, v/v) mixture revealed inflection points at 8, 16, and 32 copper ions per dendrimer, respectively. The EPR spectra of various mixtures of **4** and $\text{Cu}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in pure methanol are presented in Figure 2. A typical axial spectrum, resembling the spectrum

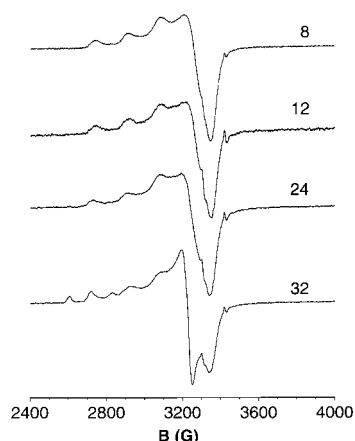


Figure 2. EPR titration of **4** with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in MeOH (130 K, 2 mW); see text for experimental details.

recorded for the tetranuclear complex derived from **1**, was obtained for the 8:1 mixture of $\text{Cu}^{\text{II}}(\text{ClO}_4)_2$ and **4** ($g_{\perp} = 2.07, g_{\parallel} = 2.25, A_{\parallel} = 185 \text{ G}$). Further addition of Cu^{II} did not change the spectrum much initially; only after 32 equivalents of Cu^{II} had been added did signals due to free Cu^{II} in solution emerge. During this titration neither the g -tensor values nor the copper hyperfine coupling constant underwent large changes, implying high homogeneity of the copper centers. A ^1H NMR titration of dendrimer **4** with $\text{Zn}(\text{ClO}_4)_2$ in a CD₃OD/CD₃CN (1:1, v/v) mixture was also carried out. Shifts comparable with those in the titration with **1** were observed (vide supra). The results of the UV/Vis, EPR, and ^1H NMR titrations indicated that the fourth-generation dendrimer **4** was completely functionalized with PY2 ligands, and that the expected number of Cu^{II} and Zn^{II} ions could be bound.

Binding of Cu^{I} and O_2 by dendrimer **4:** To investigate whether the dendritic ligand **4** behaved in a comparable way toward Cu^{I} ions, we performed a UV/Vis spectroscopic titration by adding $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ in acetonitrile to a solution of **4** in dichloromethane under oxygen-free conditions (Figure 3). Dendritic ligand **4** was selected for this purpose, as it was expected to give a metallo-dendrimer in which the number of Cu^{I} ions was comparable with that in a typical deoxy-Hc assembly. The titration revealed the uptake of approximately 30 Cu^{I} ions per molecule of **4**. This is considered to be in agreement, within experimental error, with the number of PY2 ligands (32) in **4**, and thus matches the number of Cu^{II} ions bound by this ligand.

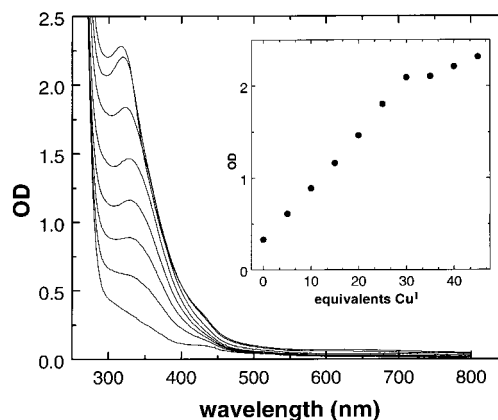


Figure 3. UV/Vis spectra of **4** in dichloromethane in the absence of dioxygen, upon titration with $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ in acetonitrile. Top to bottom: 35, 30, 25, 20, 15, 10, 5, and 0 equiv Cu^{I} added. Inset: Optical density (OD) at 335 nm.

Complex $[\mathbf{4}(\text{Cu}^{\text{I}})_{32}](\text{ClO}_4)_{32}$ was synthesized and isolated by simple mixture of solid $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ with a solution of the polypyridine dendrimer in CH₂Cl₂, followed by concentration and precipitation by diethyl ether. The choice of the perchlorate counterion was expected to result in highly reactive, three-coordinate Cu^{I} complexes, which are known to be formed from PY2-based ligands and $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{ClO}_4$.^[13] The complex $[\mathbf{4}(\text{Cu}^{\text{I}})_{32}](\text{ClO}_4)_{32}$ was characterized by ^1H NMR and UV/Vis spectroscopy. Downfield shifts were observed for the pyridine protons and for the methylene protons adjacent to some of the tertiary amine N atoms of **4**, indicating the coordination of the PY2 donor centers to a transition metal. No shifts were observed for the β -methylene protons in the dendrimer backbone. The UV/Vis spectrum showed no absorption corresponding to Cu^{II} d–d transitions, but instead displayed a very strong feature at 340 nm (Figure 4). This spectrum strongly resembles those of other Cu^{I} complexes in which the copper ion is coordinated by the PY2 unit.^[11, 13] The extinction coefficient ϵ of the 340 nm band amounts to approximately $3250 \text{ m}^{-1} \text{ cm}^{-1}$ per Cu atom. This value corresponds well to that reported by Karlin et al. for $[\text{Cu}_2\text{N}_4](\text{ClO}_4)_2$, a Cu^{I} complex derived from a tetramethylene-linked bis-PY2 ligand,^[13] and to those we reported for related molecular host complexes ($\epsilon = 1750 \text{ m}^{-1} \text{ cm}^{-1}$ and $2500\text{--}3000 \text{ m}^{-1} \text{ cm}^{-1}$ per Cu^{I} –PY2 unit, respectively).^[11] These observations indicate that the copper ions are coordi-

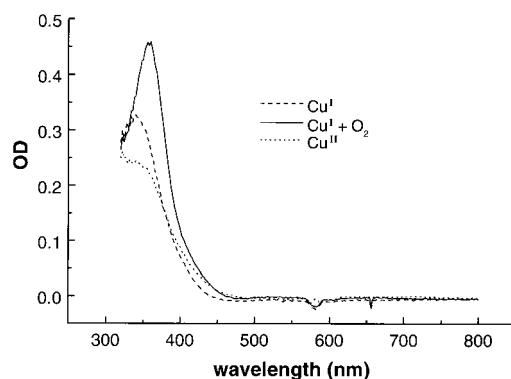


Figure 4. UV/Vis spectra in CH_2Cl_2 . Broken line: the $\text{Cu}^{\text{I}}\text{ClO}_4$ complex of **4**; solid line: its O_2 complex; dotted line: the O_2 complex after warming to ambient temperature.

nated at the dendrimer periphery only, and that the amine functions in the core of the dendrimer are not involved in the Cu^{I} coordination.

The ability of $[\mathbf{4}(\text{Cu}^{\text{I}})_{32}](\text{ClO}_4)_{32}$ to bind dioxygen was studied by low-temperature UV/Vis spectroscopy. When predried dioxygen was bubbled through a CH_2Cl_2 solution of this complex at -85°C , a strong absorption band was formed at 360 nm (Figure 4). This band indicates the formation of dioxygen complexes in which the dioxygen molecule is bound as a bent $\mu\text{-}\eta^2\text{:}\eta^2$ peroxo ligand between two Cu^{II} centers.^[13] The absence of additional absorption bands around 430 nm excludes the formation of bis(μ -oxo) species.^[14] The extinction coefficient of the 360 nm band amounted to $145\,300\text{ M}^{-1}\text{ cm}^{-1}$ per $(\text{Cu})_{32}$ complex. This value corresponds to $\epsilon = 9100\text{ M}^{-1}\text{ cm}^{-1}$ per Cu_2O_2 unit, assuming that all the copper ions are involved in O_2 binding. For the O_2 adduct formed by Karlin's $[\text{Cu}_2\text{N}_4](\text{ClO}_4)_2$ complex, the extinction coefficient of the 360 nm band is $14\,000\text{ M}^{-1}\text{ cm}^{-1}$.^[13] For the same band $\epsilon = 12\,800\text{--}13\,100\text{ M}^{-1}\text{ cm}^{-1}$ in the O_2 complexes of the molecular host compounds that we reported previously.^[11] It appears likely, therefore, that 65–70% of all copper centers of $[\mathbf{4}(\text{Cu}^{\text{I}})_{32}](\text{ClO}_4)_{32}$ are involved in dioxygen binding; this corresponds to a total of 10–11 molecules of dioxygen per Cu^{I} dendrimer. That not all the copper ions are involved in dioxygen binding may be the result of restrictions placed on the structure of the complex by the highly branched nature of the dendrimer backbone. Another explanation would be that 16 dioxygen molecules are bound, involving all the copper ions of the dendritic complex, but that the individual Cu_2O_2 moieties in the resulting complex have a relatively low extinction coefficient ($\epsilon = 9100\text{ M}^{-1}\text{ cm}^{-1}$). When the complex was left to stand at low temperature and subsequently warmed to room temperature, green Cu^{II} complexes were formed (Figure 4), showing that no additional stabilization of the copper dioxygen species in the dendritic complex occurred. In any case, this dendritic dioxygen complex may be regarded as a 'hot' species as it contains at least approximately 10–11 highly activated dioxygen molecules at its copper-covered periphery, resulting in a high local concentration of oxygenating equivalents. The oxidizing properties of the dendritic oxygen complex are under investigation.

Experimental Section

Materials and methods: $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ was synthesized according to Kubas.^[15] Poly(propylene imine) dendrimers were a generous gift from DSM Research. 2-Vinylpyridine was purified before use by flash chromatography over Silica 60 with diethyl ether as the eluent. All other chemicals were purchased commercially and used as received. Solvents were dried and distilled before use, except methanol, which was HPLC grade and used as received. Diethyl ether was distilled from sodium/benzophenone. Dichloromethane and acetonitrile were distilled from calcium hydride. The dichloromethane used in the handling of the Cu^{I} complexes was stirred with concentrated sulfuric acid for two days, and neutralized by washing with ammonia and with water before distillation. The air-sensitive Cu^{I} samples were prepared by standard Schlenk techniques. Solvents were deoxygenated by repeated freeze–thaw cycles or by bubbling dinitrogen through them (20 min).

TLC analyses were performed on precoated aluminum oxide 150F₂₅₄ (type T) plates (Merck). Flash chromatography was carried out using neutral aluminum oxide (70–200-mesh; Across), brought to activity III.^[16] Regenerated cellulose dialysis tubing (pore size 24 Å), swollen in water for 1 h, was used for dialysis. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer.

Low-temperature UV/Vis spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer driven by a Compaq Deskpro 386S computer using a software system written by On-Line Instrument Systems, Inc. The spectrophotometer was equipped with a Kontes KM-611772 variable-temperature UV/Vis Dewar cell with quartz windows. The low temperature inside the Dewar assembly was achieved by circulation, by an external cooling unit (Neslab CC-100II cryocool immersion cooler, Agitainer A with circulation pump), of cold methanol through a copper tubing coil inside the methanol-filled Dewar cell. The cuvette assembly consisted of a quartz cuvette fused to one end of a glass tube. The other end was attached to a high-vacuum stopcock and a 14/20 ground glass joint. The temperature inside the Dewar assembly was monitored by an Omega Model 651 resistance thermometer probe. The spectrum of the solvent was also recorded for each set of experiments. After a solution of $[\mathbf{4}(\text{Cu}^{\text{I}})_{32}](\text{ClO}_4)_{32}$ in dichloromethane had been placed in the Dewar assembly, the temperature was allowed to equilibrate for 10 min and the spectrum was then recorded. The volume of the cuvette assembly had been previously calibrated against the height of the solution in the tube; this height at low temperature was noted to determine the concentration. Oxygenation of the chilled solutions was effected by direct bubbling of dry, precooled dioxygen through a syringe needle. The spectra were recorded at set intervals; after the solutions had been warmed to room temperature, the spectra were recorded again.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument. Chemical shifts are referred to TMS. EPR spectra were recorded at X-band frequency using a Bruker ER200D SRC spectrometer. The temperature was set at 130 K by a Bruker ER411 variable-temperature unit. MALDI-TOF-MS spectrometry was performed on a PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer at the Institute for Mass Spectrometry, University of Amsterdam. ESI-MS spectra were recorded on an API 300 MS/MS mass spectrometer (PE-Sciex) with a mass range of 3000. FT-IR spectra were recorded on a Biorad FTS-25 instrument. Elemental analyses were performed on a Carlo Erba EA1108 instrument. Melting points were measured on a Reichert–Jung hot stage mounted on a microscope, and are reported uncorrected.

Syntheses

DAB-dendr-(PY2)₄ (1): A Teflon high-pressure capsule was filled with a solution of DAB-dendr-(NH_2)₄ (1.10 g, 3.47 mmol), 2-vinylpyridine (4.08 g, 38.9 mmol), and acetic acid (1.7 g, 28 mmol) in methanol (total volume 15 mL) and was kept at 50°C and 15 kbar for 16 h. The resulting reddish solution was dissolved in CH_2Cl_2 ; this solution was washed twice with an equal volume of aqueous 15% NaOH and once with an equal volume of water. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The excess vinylpyridine was removed by leaving the resulting brown oil under vacuum on a rotary evaporator for several hours. Yield: 4.9 g crude product. Purification was performed portionwise by column chromatography (neutral alumina (activity III), $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (97/3, v/v)). Yellowish oil; typical yield: 209 mg (64%) from 400 mg crude

oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 1.35$ (m, 4H), 1.56 (m, 8H), 2.33 (t, $J = 7.2$ Hz, 12H), 2.54 (t, $J = 7.4$ Hz, 8H), 2.91 (s, 12H), 7.06 (ddd, $J = 1.1$, 4.8, 7.3 Hz, 8H), 7.09 (d, $J = 7.7$ Hz, 8H), 7.52 (dt, $J = 2.3$, 9.9 Hz, 8H), 8.49 (ddd, $J = 1.0$, 4.8 Hz, 8H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 25.5$, 25.7, 36.6, 52.7, 52.8, 54.6, 121.6, 124.0, 136.8, 149.8, 161.4; FT-IR (KBr): $\tilde{\nu} = 3067$, 3007 (ArH), 2943, 2803 (CH_2), 1591, 1568, 1473, 1434 (C=C, C=N), 1362 (CH_2), 1302, 1248, 1211 (C-N), 1145, 1113, 1082, 1049, 992 (C-C), 749 cm^{-1} (Ar); FAB-MS: $m/z = 1158$ [(M+H) $^+$]; $\text{C}_{72}\text{H}_{96}\text{N}_{14} \cdot \text{MeOH}$: calcd. C 73.70, H 8.47, N 16.48; found C 73.64, H 8.19, N 16.10.

DAB-dendr-(PY2) $_8$ (2): The procedure was identical to that described for **1**, using DAB-dendr-(NH $_2$) $_8$ (334 mg, 0.43 mmol), 2-vinylpyridine (1.34 g, 12.2 mmol), and acetic acid (415 mg, 69 mmol) in methanol (total volume 7.5 mL). Purification was by precipitation of a concentrated dichloromethane solution of the crude product in hexane. Brownish orange oil; yield: 922 mg (87%); $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 1.35$ (m, 4H), 1.52 (brm, 24H), 2.32 (t, 20H), 2.35 (brm, 16H), 2.53 (t, 16H), 2.88 (s, 64H), 7.05 (m, 32H), 7.50 (m, 16H), 8.47 (m, 16H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 25.2$, 25.4, 36.7, 52.7, 52.9, 54.1, 54.7, 121.7, 124.0, 136.8, 149.9, 161.4; FT-IR (KBr): $\tilde{\nu} = 3067$, 3007 (ArH), 2942, 2803 (CH_2), 1590, 1568, 1474, 1434 (C=C, C=N), 1365–1250 (C-N), 1150–990 (C-C), 749 cm^{-1} (Ar); ESI-MS: m/z : 2456 [(M+H) $^+$].

DAB-dendr-(PY2) $_{16}$ (3): The procedure was identical to that described for **1**, using DAB-dendr-(NH $_2$) $_{16}$ (374 mg, 0.22 mmol), 2-vinylpyridine (2.00 g, 18.2 mmol), and acetic acid (426 mg, 71 mmol) in methanol (total volume 7.5 mL). Purification was by precipitation of a concentrated dichloromethane solution of the crude product in hexane. Brownish orange oil; yield: 1.02 g (91%); $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 1.35$ (brm, 4H), 1.52 (brm, 56H), 2.32 (brt, 52H), 2.35 (brm, 32H), 2.51 (t, 32H), 2.87 (s, 128H), 7.05 (m, 64H), 7.47 (m, 32H), 8.46 (m, 32H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 25.0$, 25.5, 36.7, 52.6, 52.8, 52.9, 53.2, 54.1, 54.6, 121.6, 124.0, 136.8, 149.8, 161.4; FT-IR (KBr): $\tilde{\nu} = 3067$, 3007 (ArH), 2942, 2803 (CH_2), 1590, 1568, 1474, 1434 (C=C, C=N), 1365–1250 (C-N), 1150–990 (C-C), 749 cm^{-1} (Ar); ESI-MS: m/z : 5052 [(M+H) $^+$].

DAB-dendr-(PY2) $_{32}$ (4): The procedure was identical to that described for **1**, using DAB-dendr-(NH $_2$) $_{32}$ (114 mg, 0.32 mmol), 2-vinylpyridine (430 mg, 4.10 mmol), and acetic acid (132 mg, 22 mmol) in methanol (total volume 7.5 mL). After workup a brown oil was obtained. Yield: 414 mg. Purification was by three dialysis runs against methanol/water (500 mL; 95:5, v/v). Brownish orange oil; yield: 330 mg (100%); $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta = 1.3$ (br, 4H), 1.52 (brm, 124H), 2.30 (brt, 64H), 2.37 (brm, 116H), 2.49 (brt, 64H), 2.85 (brs, 256H), 7.02 (brm, 128H), 7.46 (brm, 64H), 8.44 (brm, 64H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta = 24.8$, 25.3, 36.5, 52.5, 52.8, 53.1, 54.5, 121.7, 124.0, 136.8, 149.7, 161.3; FT-IR (KBr) $\tilde{\nu} = 3067$, 3007 (ArH), 2942, 2803 (CH_2), 1590, 1568, 1474, 1434 (C=C, C=N), 1365–1250 (C-N), 1150–990 (C-C), 749 cm^{-1} (Ar); MALDI-TOF-MS: m/z : 7500–10500 (calcd. 10242.8); $\text{C}_{632}\text{H}_{880}\text{N}_{126} \cdot \text{MeOH}$: calcd. C 74.00, H 8.67, N 17.18; found C 74.42, H 8.58, N 16.85.

[I(Cu $^{\text{II}}$) $_4$](ClO $_4$) $_8$: To a solution of ligand **1** (45 mg, 0.04 mmol) in MeOH (10 mL) was added dropwise a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (57.6 mg, 0.16 mmol) in MeOH (1 mL). A dark green precipitate was formed immediately upon addition of the copper salt. After the addition was completed, the reaction mixture was heated quickly to reflux. This resulted in a clear, dark green solution, which was set aside and allowed to come to room temperature. The dark green precipitate formed was collected by filtration, then dried in vacuo. Pale, dark green powder; yield: 36 mg (42%); m.p. 168 °C (decomp); $A_m(\text{acetonitrile}) = 1116 \text{ Scm}^2 \text{ mol}^{-1}$; UV/Vis (acetonitrile): $\lambda_{\text{max}} = 261$ ($\epsilon = 26300$), 307 (sh, 13700), 390 (sh, 3640), 664 nm ($750 \text{ M}^{-1} \text{ cm}^{-1}$); FT-IR (KBr): $\tilde{\nu} = 3474$ (H_2O), 3084 (ArH), 2957, 2848 (CH_2), 1612, 1572, 1489, 1448 (C=C, C=N), 1320 (C-N), 1097, 623 (noncoord. ClO $_4^-$), 769 cm^{-1} (Ar); MALDI-TOF-MS: m/z : 1710 [(1+4Cu+3ClO $_4$) $^+$], 1546 [(1+3Cu+2ClO $_4$) $^+$], 1383 [(1+2Cu+ClO $_4$) $^+$], 1221 [(1+Cu) $^+$]; $\text{C}_{72}\text{H}_{96}\text{N}_{14}\text{Cu}_4\text{Cl}_8\text{O}_{32} \cdot 4\text{H}_2\text{O}$: calcd. C 37.94, H 4.60, N 8.60; found C 37.72, H 4.89, N 8.53.

[4(Cu $^{\text{I}}$) $_{32}$](ClO $_4$) $_{32}$: To solid $\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_2\text{ClO}_4$ (50.2 mg, 0.16 mmol, 32 equiv) a solution of **4** (49.1 mg) in CH_2Cl_2 (35 mL) was added dropwise under continuous stirring. After 2 h the resulting orange solution had turned somewhat cloudy. Filtration yielded an orange powder, which was discarded, and a clear orange solution, which was concentrated in vacuo before an excess of diethyl ether was added to induce precipitation of an orange-brown powder. After storage at -20 °C overnight the supernatant

was decanted and the precipitate was dried in vacuo. The pale yellow-brown product was isolated after another precipitation. Yield: not determined; $^1\text{H NMR}$ (CD_3NO_2 , 300 MHz): $\delta = 1.59$ (brs, 124H), 2.30–2.70 (brm, 244H), 2.89 (brs, 256H), 7.33 (brs, 128H), 7.81 (brs, 64H), 8.59 (brs, 64H); UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 340$ nm ($\epsilon = 104600 \text{ M}^{-1} \text{ cm}^{-1}$).

Acknowledgments

This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). The authors thank DSM Research for an unrestricted research grant. Prof. K. D. Karlin (Johns Hopkins University, Baltimore, MD, U.S.A.) and Dr. R. A. J. Janssen (Eindhoven) are acknowledged for the use of low-temperature UV/Vis and EPR facilities, respectively, and for helpful discussions. Dr. R. Fokkens (University of Amsterdam) for help with the MALDI-TOF-MS, and Mr. J. L. J. van Dongen (Eindhoven) for help with the ESI-MS. Mr. R. W. M. Aben and Dr. J. W. Scheeren (Nijmegen) are thanked for help with the high-pressure reaction facility.

- [1] For selected reviews see: a) T. N. Sorrell, *Tetrahedron* **1989**, *45*, 3–68; b) N. Kitajima, *Adv. Inorg. Chem.* **1992**, *39*, 1–77; c) K. D. Karlin, Z. Tyeklar, A. D. Zuberbühler in *Bioinorganic Catalysis* (Ed.: J. Reedijk, Marcel Dekker, New York, **1993**, pp. 261–315); c) S. Fox, K. D. Karlin in *Active Oxygen in Biochemistry* (Eds.: J. S. Valentine, C. S. Foote, A. Greenberg, J. F. Liebman), Chapman and Hall, Glasgow, **1995**, pp. 188–231.
- [2] a) E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.* **1996**, *96*, 2563–2605; b) J. P. Klinman, *Chem. Rev.* **1996**, *96*, 2541–2561; c) A. Messerschmidt, A. Rossi, R. Ladenstein, R. Huber, M. Bolognesi, G. Gatti, A. Marchesini, R. Petruzelli, A. Finazzi-Agró, *J. Mol. Biol.* **1989**, *206*, 513–529.
- [3] N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 1277–1291.
- [4] K. A. Magnus, H. Ton-That, J. E. Carpenter, *Chem. Rev.* **1994**, *94*, 727–735, and references therein.
- [5] a) S. Achar, J. J. Vittal, R. J. Puddephatt, *Organometallics* **1996**, *15*, 43–50; b) W. T. S. Huck, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1995**, *117*, 8293–8294.
- [6] a) M. Slany, M. Bardaji, M.-J. Casanove, A.-M. Caminade, J. P. Majoral, B. Chaudret, *J. Am. Chem. Soc.* **1995**, *117*, 9764; b) P. Lange, A. Schier, H. Schmidhauer, *Inorg. Chem.* **1996**, *35*, 637.
- [7] a) D.-L. Jiang, T. Aida, *Chem. Commun.* **1996**, 1523–1524; b) J. P. Collman, L. Fu, A. Zingg, F. Diederich, *Chem. Commun.* **1997**, 193–194.
- [8] a) J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijckens, D. M. Grove, G. van Koten, *Nature (London)* **1994**, *372*, 659–663; b) M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem.* **1997**, *109*, 1559–1562; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1526–1529; c) P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *J. Am. Chem. Soc.* **1996**, *118*, 5708–5711.
- [9] E. M. M. de Brabander-van den Berg, E. W. Meijer, *Angew. Chem.* **1993**, *105*, 1370–1372; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1308–1310.
- [10] A. W. Bosman, A. P. H. J. Schenning, R. A. J. Janssen, E. W. Meijer, *E. W. Chem. Ber./Recueil* **1997**, *130*, 725–728.
- [11] R. J. M. Klein Gebbink, C. F. Martens, M. C. Feiters, K. D. Karlin, R. J. M. Nolte, *Chem. Commun.* **1997**, 389–390.
- [12] J. C. Hummelen, J. L. J. van Dongen, E. W. Meijer, *Chem. Eur. J.* **1997**, *3*, 1489–1493.
- [13] a) K. D. Karlin, M. S. Haka, R. W. Cruse, G. J. Meijer, A. Farooq, Y. Gultneh, J. C. Hayes, J. Zubieta, *J. Am. Chem. Soc.* **1988**, *110*, 1196–1207; b) K. D. Karlin, Z. Tyeklar, A. Farooq, M. S. Haka, P. Ghosh, R. W. Cruse, Y. Gultneh, J. C. Hayes, P. J. Toscano, J. Zubieta, *Inorg. Chem.* **1992**, *31*, 1436–1451.
- [14] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. Pan, X. Wang, V. G. Young, Jr., C. J. Cramer, L. Que, Jr., W. B. Tolman, *J. Am. Chem. Soc.* **1996**, *118*, 11555–11574.
- [15] G. J. Kubas, *Inorg. Synth.* **1979**, *19*, 90–92
- [16] H. Brockman, H. Schrodder, *Ber. Dtsch. Chem. Ges.* **1941**, *74B*, 73–78.

Received: June 8, 1998 [F1194]