Synthesis and Binding Properties of Dendritic Oxybathophenanthroline Ligands towards Copper(II)

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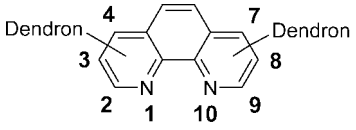
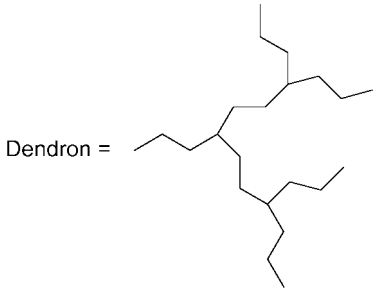
Dendritic oxybathophenanthroline ligands (generation 0 to 3) have been synthesized by treatment of 4,7-bis(4′-hydroxyphenyl)-1,10-phenanthroline with the corresponding Fréchet-type dendrons carrying a benzylic bromide function at the focal point. The complexation of copper(II) has been studied by liquid–liquid extraction using the radioisotope ^{64}Cu and time-resolved laser-induced fluorescence spectroscopy (TRLFS) in organic media indicating the formation of 1:3 complexes (Cu:dendritic ligand). Electronic and EPR spectroscopy were used to characterize the copper(II) chromophore, which is shown to have the expected distorted square-planar geometry with two phenanthroline donors coordinated to the copper(II) center. The third dendritic ligand therefore is proposed to be bound by secondary interactions. The stability constants of the 1:3 complexes were found to be in the order of log $K \approx 16$ in $CHCl_3$. On the other hand, increasing generation of the dendritic Fréchet-type branches leads to enhanced shielding of the copper ion from the environment. Additional information about this behaviour was obtained by the fluorescence lifetimes, which are much less influenced upon addition of copper(II) salt to solutions of the higher generation ligands.

Introduction

Derivatives of 1,10-phenanthroline and their metal complexes are of considerable interest in bioinorganic chemistry, biology and medicine.[1] Oxidative substitutions of 1,10-phenanthroline give versatile 5,6-disubstituted intermediates for the introduction of less bulky groups into the chelating unit. Such 5,6-substituted phenanthrolines play an important role as hydrophobic DNA intercalators (dipyridophenazine[2]), and most representatives of chromophore-containing derivatives base on this substitution pattern.[3] Also, metallodendrimers consisting of ruthenium(II) complexes with bisphenanthroline ligands bridged in the 5,6-positions have been described as robust, structurally rigid and well-defined nanoscopic complexes.[4] Dendritic modifications gain in importance as they open the way for tailoring nano dimension, solubility or complexation behaviour (complex stability, kinetics of formation) in manifold directions.[5] Due to steric reasons, the attachment of highly branched units particularly in the 4,7- and 3,8-positions of the 1,10-phenanthroline core seems to be suited in this respect (Scheme 1). In addition Fréchet-type dendrons being attached adjacent to the metal coordination centre (2,9-positions) have also been presented.[6]





Scheme 1. Suitable positions for dendritic modification of 1,10-phenanthroline.

Ruthenium(II) complexes containing 4,7-bis(benzyloxy)-1,10-phenanthroline units[7] and also dendritic rutheni-

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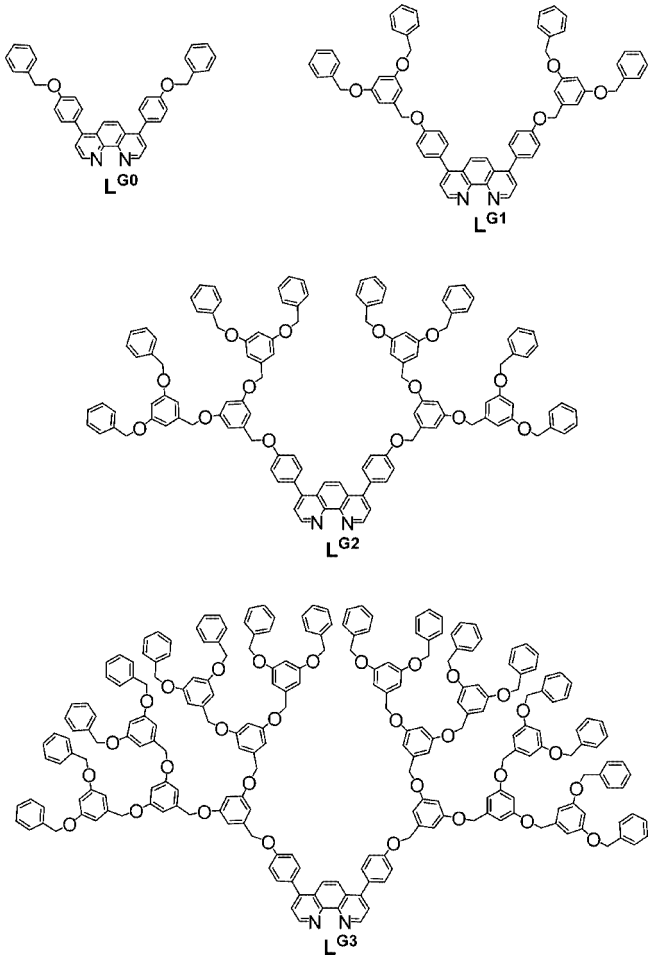
um(II) complexes bearing bis-substituted 2,2′-bipyridine moieties have been reported to exhibit interesting luminescence and redox properties.[8] Ruthenium(II) dendrimers containing carbazole-based chromophores as branches in the 4,7-positions of phenanthroline exhibit significant absorption and luminescence characteristics.[9] Complexation of appropriate metals with phenanthroline ligands carrying branched units in the 3,8-positions induces the formation of supramolecular self-assemblies with tuneable coordination geometry.[10] In this respect, we are interested to characterize the self-assembly system involving novel dendritic compounds and copper(II). Here, we report the synthesis of 1,10-phenanthroline ligands $\mathbf{L^{G0}}$–$\mathbf{L^{G3}}$ with attached Fréchet-type dendrons (generation 0 to 3) in the 4,7-positions (Scheme 2). The complexation behaviour of these hydrophobic dendritic oxybathophenanthroline derivatives towards Cu^{II} has been studied by liquid-liquid extraction experiments, time-resolved laser-induced fluorescence spectroscopy and electronic as well as EPR spectroscopy.

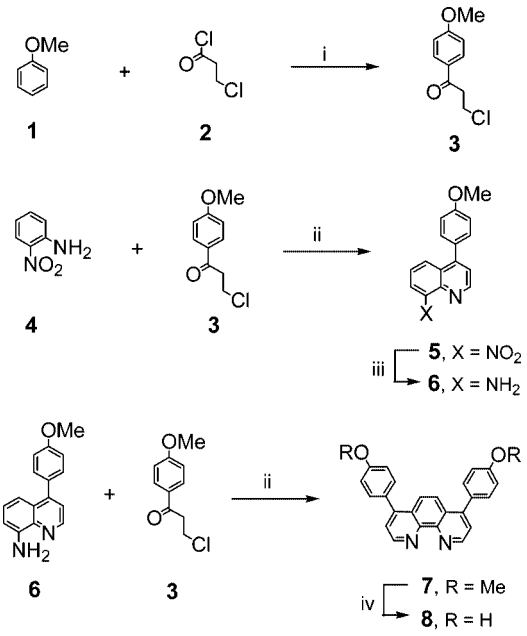


Scheme 2. Constitutions of the investigated dendritic OBP ligands $\mathbf{L^{G0}}$–$\mathbf{L^{G3}}$.

Results and Discussion

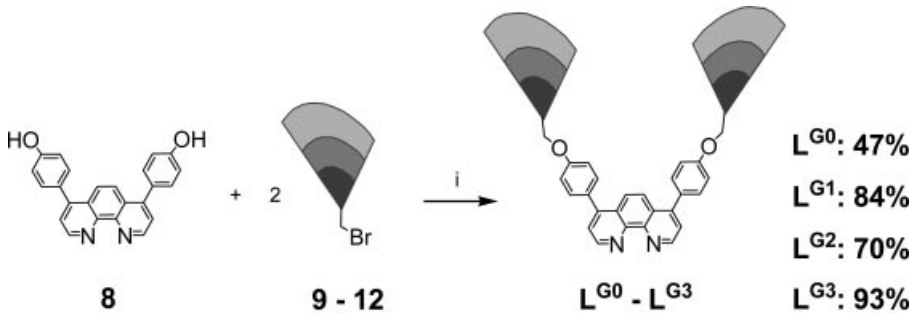
Syntheses

The parent phenanthroline ligand **8** with two *p*-hydroxyphenyl groups in the positions 4 and 7 was synthesized in a multi-step sequence (Scheme 3).[11] The β-chloro ketone **3** was prepared by a Friedel–Crafts acylation of 3-chloropropionyl chloride (**2**) and anisole (**1**) in dry 1,2-dichloroethane at 0 °C in the presence of anhydrous aluminum chloride to yield a colourless solid. The reaction of the β-chloro ketone **3** with *o*-nitroaniline (**4**) under the conditions of the Yale modification of the Skraup quinoline synthesis, gave the 4-substituted 8-nitroquinoline **5** as a yellow solid. The nitro group was subsequently reduced with tin(II) chloride dihydrate in dry ethanol under reflux conditions to form the 4-(4′-methoxyphenyl)-8-aminoquinoline **6** as a yellow solid. The 4,7-disubstituted 1,10-phenanthroline **7** was obtained by a second Skraup reaction of aminoquinoline **6** and β-chloro ketone **3** using again the conditions of the Yale modification. Demethylation of the bisanisyl-1,10-phenanthroline (**7**) was performed in dry dichloromethane at –20 °C by treatment with boron tribromide to yield the phenanthroline building block **8** carrying two hydroxy functions to which the various dendritic wedges could be attached.[12]



Scheme 3. Preparation of the 4,7-bis(*p*-hydroxyphenyl)-1,10-phenanthroline (**8**); (i) 0 °C, 3 h, 1,2-dichloroethane; (ii) addition of **3** at 100–120 °C, aq. As_2O_5 (80%), concd. H_3PO_4, 140 °C, 1 h, (iii) $SnCl_2{\cdot}2H_2O$, reflux, 4 h, EtOH, (iv) addition of BBr_3 at –20 °C, 2 h, room temp., CH_2Cl_2.

The dendritic oxybathophenanthroline (OBP) ligands $\mathbf{L^{G0}}$–$\mathbf{L^{G3}}$ were synthesized according to Scheme 4. Thus, 1 equiv. of 4,7-bis(4′-hydroxyphenyl)-1,10-phenanthroline (**8**) was dissolved in DMF and deprotonated by treatment with sodium hydride. Addition of 2 equiv. of benzyl bromide (**9**) or the corresponding dendritic benzyl bromides[13] **10**–**12** followed by purification on silica gel gave the products in medium to high yields as colourless solids in the case of the benzyl derivative, or as viscous oils for the higher generations. The medium yield for the benzyl-substituted derivative $\mathbf{L^{G0}}$ may be explained by the formation of a *N*,*O*-



Scheme 4. Schematic representation for the preparation of the dendritic oxybathophenanthroline (OBP) ligands; (i) NaH (60% in paraffin), room temp., 1 d, DMF.

dibenzyl derivative, in which one nitrogen of the phenanthroline unit is substituted by a benzylic moiety.[14] Due to the small size of benzyl bromide such a cyclohexa-2,5-dienone derivative can be formed in higher quantities. But for the dendritic generations with an increased steric demand this side reaction seems to be less favoured and leads therefore to higher yields. Additionally, the purification of $\mathbf{L^{G0}}$ on silica gel was more difficult as a result of the higher polarity of the phenanthroline unit. Substitution of the phenanthroline building block **8** with dendritic units of a various size leads to an increased lipophilicity of the ligands and thus to easier purification by column chromatography. The structures of all new oxybathophenanthroline ligands could be readily deduced from ^1H and ^{13}C NMR spectra as well as from mass spectrometric analysis.

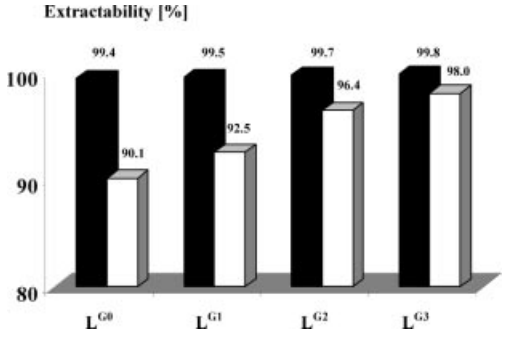


Figure 1. Extractability of copper(II) by dendritic OBP ligands $\mathbf{L^{G0}}$–$\mathbf{L^{G3}}$; black bars $c_{Cu(NO_3)_2} = 1\times10^{-4}$ M, $c_{HPic} = 5\times10^{-3}$ M, pH = 5.3 (MES/NaOH); white bars $c_{Cu(NO_3)_2} = 1\times10^{-4}$ M, pH = 5.3 (MES/NaOH); $c_{\text{dendritic ligand}} = 1\times10^{-3}$ M in $CHCl_3$, time = 30 minutes.

Liquid–Liquid Extraction

1,10-Phenanthroline is known to form strong complexes with copper(II). Depending on the experimental conditions, the resulting complexes may have 1:1, 1:2 or 1:3 stoichiometry (metal/ligand), and show different coordination geometries.[15] Due to the Jahn–Teller lability 1:3 stoichiometry (pseudo-octahedral coordination geometry) is unlikely with the rigid phenanthroline-type chelates. By virtue of the high lipophilicity of the dendritic oxybathophenanthrolines, liquid–liquid extraction experiments have been chosen to characterise the binding properties of the OBP ligands $\mathbf{L^{G0}}$–$\mathbf{L^{G3}}$ towards Cu^{II} in the aqueous-organic system $Cu(NO_3)_2$/buffer/H_2O/dendritic ligand/$CHCl_3$. Precise data of the efficiency of complex formation and the stoichiometry of the copper(II) complexes with the ligands investigated were obtained using the radiotracer technique with ^{64}Cu as radioisotope.[16] First extraction experiments have been performed in the presence of the lipophilic picrate anion (Figure 1). In this case the extractability of Cu^{II} is almost quantitative for all ligands. But also in the absence of the picrate anion, Cu^{II} is very efficiently extracted into the organic phase. Here, a dendritic effect is clearly visible caused most likely by the increasing lipophilicity of the complexes formed.

Interestingly, a rapid attainment of extraction equilibrium (within few minutes) was observed. Even in the case of the most bulky ligand $\mathbf{L^{G3}}$ the equilibrium was attained after 10 minutes.[17] As expected, the Cu^{II} extraction is enhanced with increasing pH accompanied by decreasing protonation of the chelating moiety.[18] Information about the overall stoichiometry of the complexation was obtained by measuring the distribution ratio D_{Cu}[19] as a function of the ligand concentration in the organic solvent (Figure 2).

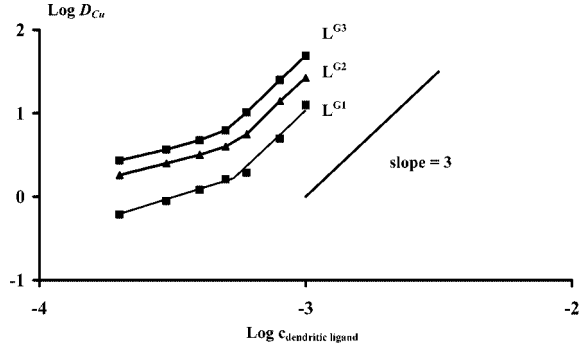


Figure 2. Variation of log D_{Cu} with ligand concentration for the extraction of copper(II) with dendritic OBP ligands $\mathbf{L^{G1}}$–$\mathbf{L^{G3}}$; $c_{Cu(NO_3)_2} = 1\times10^{-4}$ M, pH = 5.3 (MES/NaOH), time = 30 minutes, $c_{\text{dendritic ligand}} = 2\times10^{-4}$ M to 1×10^{-3} M in $CHCl_3$.

Surprisingly, in all cases, the slopes of the lines in the log D_{Cu}/logc_{ligand} plots were 3 if the ligand excess is high enough compared to the copper concentration. This finding indicates the formation of 1:3 complexes (Cu^{II}: dendritic ligand).[20] However, this is not an indication for three phenanthroline donors, coordinated to the copper(II) centers (see below).[21]

Luminescence Characteristics

The fluorescence properties of the ligands $\mathbf{L^{G0}}$–$\mathbf{L^{G3}}$ are summarized in Table 1. The time-resolved fluorescence spectrum of $\mathbf{L^{G0}}$ is shown in Figure 3 as an example.

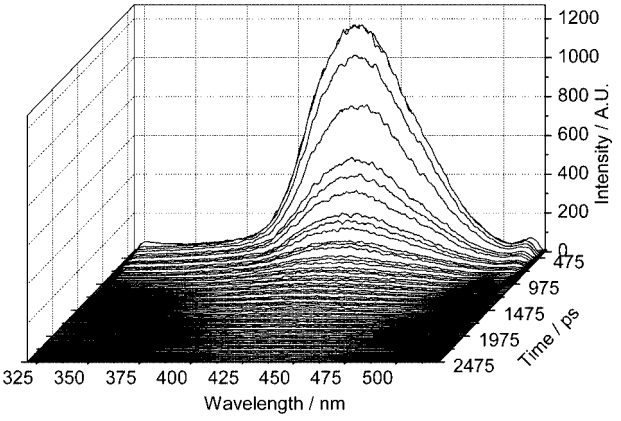


Figure 3. Time-resolved fluorescence spectrum of the dendritic OBP ligand $\mathbf{L^{G0}}$, $c_{dendritic\ ligand} = 1 \times 10^{-5}$ M in $CHCl_3$.

For all four ligands a two-exponential fluorescence decay behaviour was observed in the absence of Cu^{II}. The component with the shorter fluorescence decay time shows the higher fluorescence intensity. The maximum of this fluorescence emission is located at ca. 430 nm. The fluorescence maximum for the second emitting component was found at ca. 420 nm. Additionally the fluorescence decay time of this component depends on the size of the dendritic wedges. Going to higher generations the fluorescence decay times decrease. This may be due to an increasing number of deactivation channels.

Addition of copper(II) to the solution of the ligands leads to a decrease in fluorescence intensity (static fluorescence quenching). As expected, the complexes formed do not show any fluorescence. The fluorescence with the shorter fluorescence lifetime was mainly influenced by the formation of the complexes (see Table 1 in the Supporting Information; for details see the footnote on the first page of this article). At Cu^{II}/ligand ratios of 1:3 the fluorescence of the 430 nm component disappears. This behaviour is in agreement with the results of the liquid–liquid extraction (1:3 complexes). The ligand $\mathbf{L^{G2}}$ shows a somewhat different behaviour. Here, the fluorescence disappears at a 1:2 ratio of Cu^{II} to ligand. In a separate measurement with a metal to ligand ratio of 1:3 only a monoexponential fluorescence decay with the longer fluorescence lifetime was observed. This is strong evidence that also a 1:3 adduct is formed.

In addition the fluorescence intensities were used to confirm complex formation. Due to the observation that mainly the fluorescence intensity of the component with the shorter fluorescence lifetime is influenced by the complex formation these data were evaluated for the stability of the complexes. The species concentration can be calculated from the fluorescence intensities of the free ligand. The resulting stability constants are summarized in Table 2.

Table 2. Stability constants of the formed Cu^{II} complexes.

Ligand	Metal	Stoichiometry	log K	Solvent
$\mathbf{L^{G0}}$	Cu^{II}	3:1	16.4 ± 0.8	$CHCl_3$
$\mathbf{L^{G1}}$	Cu^{II}	3:1	17.5 ± 0.9	$CHCl_3$
$\mathbf{L^{G2}}$	Cu^{II}	3:1	15.6 ± 0.7	$CHCl_3$
$\mathbf{L^{G3}}$	Cu^{II}	3:1	16.6 ± 0.7	$CHCl_3$

It was found that the fluorescence decay times of the longer decay component decrease with increasing size of the dendritic branches if no copper(II) is added. The addition of copper(II) influences the fluorescence lifetime (Supporting Information, Table 2). However, this effect decreases with increasing size of the dendritic wedge. The longer fluorescence lifetime as function of the cooper(II) concentration shows no clear behaviour. For the ligand $\mathbf{L^{G0}}$ a clear dynamic quench effect was observed, which is much less remarkable for the ligand $\mathbf{L^{G1}}$. The ligand $\mathbf{L^{G2}}$ shows an increase of the fluorescence lifetime. For the ligand $\mathbf{L^{G3}}$ addition of copper(II) resulted in much less influence. However, also intermediate deviations from this trend were observed. A profound explanation of this behaviour is not possible at this time. The fluorescence lifetime of the second component with the shorter lifetime is also influenced by the addition of Cu^{II}. This behaviour can be explained by a less pronounced dynamic quenching effect of the Cu^{II} or in reverse, that the increasing generation of the dendritic structure leads to an increased shielding effect on the deexcitation channels of the copper(II).

Geometry of the Copper(II) Chromophores

Due to the Jahn–Teller lability of the d^9 copper(II) ions the formation of stable $[Cu(L)_3]^{2+}$ complexes, where L is a

Table 1. Fluorescence properties of the dendritic OBP ligands.

Ligand	Center of gravity (1) nm	Fluorescence decay time (1) ps	Center of gravity (2) nm	Fluorescence decay time (2) s	Intensity ratio (1)/(2)	Intensity relative to L^0
$\mathbf{L^{G0}}$	430.1	160 ± 2	423.7	1860 ± 10	22.6	1
$\mathbf{L^{G1}}$	430.3	270 ± 2	417.0	1080 ± 10	3.3	1.45
$\mathbf{L^{G2}}$	431.8	240 ± 2	419.9	990 ± 10	3.6	1.57
$\mathbf{L^{G3}}$	430.1	260 ± 2	417.2	890 ± 10	3.3	1.05

bidentate ligand, is not likely, specifically with L = 1,10-phenanthroline derivatives. One would rather expect the stabilization of a distorted square planar (tetragonally distorted octahedral or square pyramidal) chromophore derived from $[Cu(L)_2(X)_n]^{2+}$, where X may be OH_2 and n = 0, 1, 2. The third dendritic phenanthroline ligand found in the extraction and luminescence experiments may then be bound by secondary interactions (outer sphere coordination) to the distorted square-planar complex. The type of chromophore was analyzed by electronic and EPR spectroscopy and supported by molecular mechanics modeling.

Solutions for the UV/Vis-NIR and EPR spectra ($\mathbf{L^{G0}}$ and $\mathbf{L^{G3}}$) were prepared as those for the liquid–liquid extractions ($[Cu(trif)_2]^{2+}$, H_2O/L, $CHCl_3$; $[Cu^{2+}] \approx 1.0$ mM, $[Cu^{2+}]$:[L] = 1:3). The electronic spectra (Supporting Information) show two broad transitions centered at approx. 708 nm and 925 nm for $\mathbf{L^{G0}}$, and 734 nm and 925 nm for $\mathbf{L^{G3}}$, respectively. The lower energy band is due to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition and was not well resolved in our spectra (relatively low concentration), the feature at higher energy is due to transitions from d_{xy}, d_{xz}, d_{yz} and therefore is, as expected, very broad. While $[Cu(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) was reported to have transitions at 680 nm and 1250 nm,[22] $[Cu(phen)_2(OH_2)_n]^{2+}$ (n = 0, 1, 2) has transitions at 750–800 nm and ca. 980 nm.[22,23] Addition of up to 3 equiv. of phen did not change the spectroscopic parameters. The assignment of these transitions to CuN_4O_n (n = 0, 1, 2) chromophores is supported by EPR spectra (identical solutions, T = 100 K). The analysis of the spin Hamiltonian parameters (g_x = 2.06, g_y = 2.08, g_z = 2.22, $A_x = A_y$ = 45 G, A_z = 128 G) supports this conclusion (experimental and simulated spectra are given in the Supporting Information): the major features are similar to those reported for the EPR spectra of distorted square planar $[Cu(phen)_2]^{2+}$-type chromophores,[24] the minor features are similar to those of $[Cu(phen)_2(OH_2)](NO_3)_2$ (g_x = 2.02, g_y = 2.13, g_z = 2.23).[25]

The conclusion that the extracted copper(II) species are $[Cu(L)_2(OH_2)_n]^{2+}\cdot L$ is supported by strain energy minimized structures, using the MOMEC program[26] and force field[27] (for structural data and plots of the optimized structures see Supporting Information). The optimized structures ($[Cu(L)_2(OH_2)_2]^{2+}$) have Cu–N distances (ca. 1.97 Å) and tetrahedral distortions of the CuN_4 chromophores (ca. 42°) which are very similar to those of reported $[Cu(phen)_2(OH_2)_n]^{2+}$-type structures.[28]

Conclusions

An efficient synthetic strategy has been developed for the preparation of new dendritic ligands consisting of a 1,10-phenanthroline core unit to which hydrophobic polybenzyl ether dendrons are attached in the 4,7-positions. These oxybathophenanthroline ligands rapidly form very stable 1:3 adducts in organic media with Cu^{II}. Electronic and EPR spectroscopy suggest that two of the ligands are coordinated to copper(II) by the phenanthroline donors, the third ligand probably is bound by secondary interactions. The dendritic ligands are capable to extract Cu^{II} with high efficiency. For extraction experiments a dendritic effect was found most likely caused by the increasing lipophilicity when going to higher generations. As obtained by titration experiments using TRLFS, the dendritic ligands $\mathbf{L^{G0}}$–$\mathbf{L^{G3}}$ form strong 1:3 adducts with copper(II) in $CHCl_3$ ($\log K \approx$ 16). Studies of the fluorescence lifetimes show an increased shielding effect with increasing generation of the dendritic wedge attached to the phenanthroline unit. The results obtained for the copper(II) complexation with hydrophobic dendritic phenanthroline ligands have encouraged us to develop water-soluble analogues having targeting units at the periphery in view of binding and selective transport of the diagnostically and therapeutically relevant radioisotopes ^{64}Cu and ^{67}Cu.

Experimental Section

General Remarks: All starting materials were purchased from commercial sources and used without further purification. The dendritic bromides[13] **9**–**12** and the 4,7-(bisanisyl)phenanthroline[11] (**7**) have been prepared according to literature. The solvents were dried using standard techniques. Reactions were monitored by thin-layer chromatography using TLC plates pre-coated with silica gel $60F_{254}$ (Merck) and compounds detected by UV light (254 nm). Column chromatography was carried out using silica gel (Merck 15101). Melting points were determined with a Reichert Thermovar microscope and were not corrected. ^1H and ^{13}C NMR spectra were recorded using Avance 300 and AM 400 MHz Bruker instruments; the solvent signal was used for internal calibration. Mass spectra were recorded using a MS-50 from A.E.I., Manchester, GB (EI), a Concept 1H from Kratos Analytical Ltd., Manchester, GB (FAB), or a MALDI-TofSpec-E from MICROMASS, GB (MALDI). Electronic spectra were recorded with a JASCOV-570 UV/Vis-NIR spectrophotometer and EPR spectra were obtained from a Bruker ELEXSYS-E-500 instrument (X-band); spin-Hamiltonian parameters were obtained by simulation of the spectra with XSophe (version 1.1.4).[29]

3-Chloro-1-(4′-methoxyphenyl)propan-1-one (3): To a suspension of powdered aluminum chloride (7.23 g, 54.2 mmol) in dry 1,2-dichloroethane (40 mL) were added slowly 3-chloropropionyl chloride (**2**) (4.55 mL, 47.4 mmol) at 0 °C and anisole (**1**) (4.91 mL, 45.2 mmol) under cooling with water. The orange solution was stirred at room temp. for 3 h and left standing for about 12 h. The dark orange solution was poured onto ice (50 g), the organic phase separated and the aqueous phase extracted two times with CH_2Cl_2. The collected organic phases were washed with water, several times with aqueous NaOH (2%, 50 mL) until the organic phase did not turn back to yellow, and then twice with water. The organic phase was dried with $MgSO_4$ and the solvent removed under reduced pressure. Purification by gradient column chromatography [SiO_2, CH_2Cl_2/petroleum ether (40/60), 20:1 to CH_2Cl_2] gave 9.23 g (97% yield) of a colourless solid. R_f = 0.68 (CH_2Cl_2); m.p. 63–64 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.29 (t, J = 7 Hz, 2 H, CH_2Cl), 3.75 (s, 3 H, OCH_3), 3.80 (t, J = 7 Hz, 2 H, $COCH_2$), 6.82 (AA′ part of the AA′BB′ system, 2 H, H_{ar}), 7.82 (BB′ part of the AA′BB′ system, 2 H, H_{ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 39.0, 40.9, 55.5, 113.9, 129.6, 130.4, 163.9, 195.2 ppm. MS (EI, 70 eV): m/z (%) = 198 (12) [$M^{+\cdot}$].

4-(4′-Methoxyphenyl)-8-nitroquinoline (5): To a solution of *o*-nitroaniline (**4**) (1.38 g, 10.0 mmol), aq. As_2O_5 (3.37 g, 80%) and concd. H_3PO_4 (9 mL) was added portionwise β-chloro ketone **3** (2.48 g, 12.5 mmol) at 100 °C in 10 min so that the temperature is not rising above 120 °C. The solution was stirred at 120 °C for 5 min and then heated to 140 °C for 1 h. The deep red solution was cooled to room temp., poured onto CH_2Cl_2 (150 mL) and water (100 mL), and neutralized with aq. KOH (30%). The aqueous phase was extracted several times with CH_2Cl_2, the collected organic phase dried with $MgSO_4$, and the solvent removed under reduced pressure. Column chromatography (SiO_2, CH_2Cl_2) gave 1.56 g (56%) of a yellow coloured solid. R_f = 0.40 (CH_2Cl_2); m.p. 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.95 (s, 3 H, CH_3), 7.09 (AA′ part of the AA′BB′ system, 2 H, H_{ar}), 7.41 (BB′ part of the AA′BB′ system, 2 H, H_{ar}), 7.43 (d, J = 4 Hz, 1 H, H_{ar}), 7.55 (dd, J = 9, J = 8 Hz, 1 H, H_{ar}), 7.98 (dd, J = 8, J = 1 Hz, 1 H, H_{ar}), 8.17 (dd, J = 9, J = 1 Hz, 1 H, H_{ar}), 9.02 (d, J = 4 Hz, 1 H, H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 55.6, 114.5, 122.9, 123.4, 125.1, 128.1, 129.2, 130.2, 131.0, 140.2, 148.7, 149.0, 152.1, 160.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 280 (100) [$M^{+\cdot}$].

8-Amino-4-(4′-methoxyphenyl)quinoline (6): A solution of nitrochinoline **5** (1.15 g, 4.1 mmol) and tin(II) chloride dihydrate (2.78 g, 12.3 mmol) in dry ethanol (30 mL) was refluxed for 4 h. The solution was cooled to room temp. and made alkaline with concd. ethanolic NaOH. The precipitate was filtered off, and the solvent removed under reduced pressure. Purification by gradient column chromatography (SiO_2, CH_2Cl_2 to CH_2Cl_2/methanol, 30:1) gave 0.91 g (89%) of a yellow solid. R_f = 0.18 (CH_2Cl_2); m.p. 148–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.78 (s, 3 H, CH_3), 4.95 (br. s, 2 H, NH_2), 6.81 (dd, J = 6, J = 3 Hz, 1 H, H_{ar}), 6.93 (AA′ part of the AA′BB′ system, 2 H, H_{ar}), 7.16 (m, 3 H, H_{ar}), 7.24 (BB′ part of the AA′BB′ system, 2 H, H_{ar}), 8.62 (d, J = 4 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 55.4, 109.9, 114.0, 114.2, 121.7, 127.2, 127.6, 130.8, 131.0, 138.9, 144.3, 147.0, 148.1, 159.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 250 (100) [$M^{+\cdot}$].

4,7-Bis(4′-methoxyphenyl)-1,10-phenanthroline (7): To a solution of the aminoquinoline **6** (1.43 g, 5.7 mmol), aq. As_2O_5 (1.61, 80%) and concd. H_3PO_4 (9 mL) was added portionwise the β-chloro ketone **3** (1.58 g, 7.1 mmol) at 100 °C in 10 min so that the temperature is not rising above 120 °C. The solution was stirred at 120 °C for 5 min and then heated to 140 °C for 1 h. The deep red reaction mixture was cooled to room temp., poured onto CH_2Cl_2 (150 mL) and water (100 mL) and neutralized with aqueous NaOH (20%). The aqueous phase was extracted several times with CH_2Cl_2, the collected organic phase dried with $MgSO_4$ and the solvent removed under reduced pressure. Column chromatography (SiO_2, CH_2Cl_2) yielded a brownish solid (1.50 g, 67%). R_f = 0.35 (CH_2Cl_2/MeOH, 5:1); m.p. 208–209 °C. ^{1}H NMR (400 MHz, 1:1 $CDCl_3$/CD_3OD, 25 °C): δ = 2.41 (s, 6 H, CH_3), 5.58 (AA′ part of the AA′BB′ system, 4 H, H_{ar}), 5.95 (BB′ part of the AA′BB′ system, 4 H, H_{ar}), 6.10 (d, J = 5 Hz, 2 H, H_{ar}), 6.40 (s, 2 H, H_{ar}), 7.62 (d, J = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 54.9, 114.0 123.6, 123.9, 126.5, 129.7, 130.8, 146.2, 148.6, 149.1, 160.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 392 (100) [$M^{+\cdot}$].

4,7-Bis(4′-hydroxyphenyl)-1,10-phenanthroline (8): To a solution of 4,7-bis(4′-methoxyphenyl)-1,10-phenanthroline (**7**) (6.77 g, 17.3 mmol) in dry dichloromethane (90 mL) was added dropwise boron tribromide (4.91 mL, 51.8 mmol) at –20 °C. The red suspension was stirred at room temp. for 2 h, poured onto ice and let stand still for 30 min. The solution was neutralized with aq. KOH (5%), the organic phase separated and the aqueous phase extracted several times with 10:1 CH_2Cl_2/MeOH. The collected organic phase was dried with $MgSO_4$ and the solvent removed under reduced pressure. The remaining solid was three times suspended in CH_2Cl_2 and filtered. The solid was dried to yield a yellow solid (3.20 g, 47%). M.p. 285–288 °C. ^{1}H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 6.98 (AA′ part of the AA′BB′ system, 4 H, H_{ar}), 7.41 (BB′ part of the AA′BB′ system, 4 H, H_{ar}), 7.65 (d, J = 5 Hz, 2 H, H_{ar}), 7.92 (s, 2 H, H_{ar}), 9.08 (d, J = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C): δ = 116.1, 124.0, 124.3, 126.3, 128.0, 131.5, 145.9, 148.7, 149.5, 158.6 ppm. MS (EI, 70eV): *m*/*z* (%) = 392 (100) [$M^{+\cdot}$].

General Procedure for the Preparation of Dendritic OBP Ligands (L^{G0}–L^{G3}): To a suspension of 4,7-bis(4′-hydroxyphenyl)-1,10-phenanthroline (**8**) (0.1 mmol) in dry DMF (10 mL) was added NaH (0.22 mmol, 60% in paraffin). The reaction mixture turned to red. After 5 min a solution of the corresponding bromides[13] **9**–**12** (0.21 mmol) in dry DMF (5 mL) was added, and the suspension stirred for 1 d at room temp. The residual NaH was deactivated by slow addition of water at 0 °C. CH_2Cl_2 (30 mL) was added, the suspension neutralized with aq. HCl (2 N), and the aqueous phase extracted several times with CH_2Cl_2. The collected organic phase was washed with concd. aq. $NaHCO_3$, water, dried with $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel.

4,7-Bis(4′-benzyloxyphenyl)-1,10-phenanthroline (L^{G0}): 4,7-Bis(4′-hydroxyphenyl)-1,10-phenanthroline (**8**) (100.0 mg, 0.27 mmol), benzyl bromide **9** (98.6 mg, 0.58 mmol), NaH (24.2 mg, 0.60 mmol, 60% in paraffin) in dry DMF (15 mL). Column chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1 to 20:1) gave a colourless solid (69.8 mg, 47%). R_f = 0.42 (CH_2Cl_2/MeOH, 5:1); m.p. 230–231 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.12 (s, 4 H, OCH_2), 7.10 (AA′ part of the AA′BB′ system, 4 H, H_{ar}), 7.30–7.47 (m, 14 H, H_{ar}), 7.52 (d, J = 5 Hz, 2 H, H_{ar}), 7.85 (s, 2 H, H_{ar}), 9.16 (d, J = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.2, 115.1, 123.5, 124.0, 126.5, 127.5, 128.1, 128.7, 130.6, 131.0, 136.7, 147.0, 148.1, 149.7, 159.2 ppm. MS (FAB, NBA): *m*/*z* (%) = 545.2 ([M + H]$^+$, 100), 454.1 (12), 307.0 (18).

4,7-Bis{4′-[3′′,5′′-bis(benzyloxy)benzyloxy]phenyl}-1,10-phenanthroline (L^{G1}): 4,7-Bis(4′-hydroxyphenyl)-1,10-phenanthroline (**8**) (120.0 mg, 0.33 mmol), dendritic Fréchet-type G1 bromide **10** (256.1 mg, 0.69 mmol), NaH (29.0 mg, 0.73 mmol, 60% in paraffin) in dry DMF (15 mL). Column chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1 to 20:1) gave a brownish viscous oil (269.5 mg, 84%). R_f = 0.55 (CH_2Cl_2/MeOH, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.05 (s, 8 H, OCH_2), 5.08 (s, 4 H, OCH_2), 6.58 (t, J = 2 Hz, 2 H, H_{ar}), 6.72 (d, J = 2 Hz, 4 H, H_{ar}), 7.10 (AA′-part of the AA′BB′-system, 4 H, H_{ar}), 7.26–7.47 (m, 24 H, H_{ar}), 7.51 (d, J = 5 Hz, 2 H, H_{ar}), 7.90 (s, 2 H, H_{ar}), 9.18 (d, J = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.1, 70.2, 101.7, 106.5, 115.1, 123.5, 124.0, 126.5, 127.6, 128.6, 130.6, 131.0, 136.8, 139.3, 147.0, 148.1, 149.7, 159.1, 160.3 ppm. MS (FAB, NBA): *m*/*z* (%) = 969.5 ([M + H]$^+$, 60), 307.1 (100).

4,7-Bis(4′-{3′′,5′′-bis[3′′′,5′′′-bis(benzyloxy)benzyloxy]benzyl}-phenyl)-1,10-phenanthroline (L^{G2}): 4,7-Bis(4′-hydroxyphenyl)-1,10-phenanthroline (**8**) (70.0 mg, 0.19 mmol), dendritic Fréchet-type G2 bromide **11** (325.9 mg, 0.40 mmol), NaH (16.9 mg, 0.42 mmol, 60% in paraffin) in dry DMF (15 mL). Column chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1 to 20:1) gave a brownish viscous oil (246.0 mg, 70%). R_f = 0.51 (CH_2Cl_2/MeOH, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.86 (s, 8 H, OCH_2), 4.89 (s, 16 H, OCH_2), 4.96 (s, 4 H, OCH_2), 6.58 (t, J = 2 Hz, 6 H, H_{ar}), 6.57 (d, J = 2 Hz, 8 H, H_{ar}), 6.59 (d, J = 2 Hz, 4 H, H_{ar}), 7.00 (AA′ part of the AA′BB′ system, 4 H, H_{ar}), 7.17–7.28 (m, 40 H, H_{ar}), 7.12 (BB′

part of the AA′BB′ system, 4 H, H_{ar}), 7.40 (d, J = 5 Hz, 2 H, H_{ar}), 7.88 (s, 2 H, H_{ar}), 9.08 (d, J = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.0, 70.1, 70.2, 101.7, 101.7, 106.5, 106.6, 115.2, 123.6, 124.0, 126.5, 127.6, 128.1, 128.3, 128.6, 130.6, 131.1, 136.8, 136.9, 139.3, 139.4, 147.0, 148.1, 149.8, 159.1, 160.1, 160.2 ppm. MS (FAB, NBA): m/z (%) = 1818.6 ([M + H]$^+$, 17), 303.1 (100).

4,7-Bis[4′-(3′′,5′′-bis{3′′′,5′′′-bis[3′′′′,5′′′′-bis(benzyloxy)benzyloxy]benzyloxy}benzyl)phenyl]-1,10-phenanthroline (L^{3G}): 4,7-Bis(4′-hydroxyphenyl)-1,10-phenanthroline (**8**) (40.0 mg, 0.11 mmol), dendritic Fréchet-type G3 bromide **12** (381.9 mg, 0.23 mmol), NaH (9.7 mg, 0.24 mmol, 60% in paraffin) in dry DMF (15 mL). Column chromatography (SiO_2, CH_2Cl_2/MeOH, 50:1 to 20:1) gave a brownish viscous oil (360.0 mg, 93%). R_f = 0.55 (CH_2Cl_2/MeOH, 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.86 (s, 16 H, OCH_2), 4.89 (s, 8 H, OCH_2), 4.92 (s, 32 H, OCH_2), 4.95 (s, 4 H, OCH_2), 6.49 (m, 12 H, H_{ar}), 6.61 (m, 26 H, H_{ar}), 6.65 (d, J = 2 Hz, 4 H, H_{ar}), 7.03 (AA′ part of the AA′BB′ system, 4 H, H_{ar}), 7.18–7.34 (m, 80 H, H_{ar}), 7.36 (BB′ part of the AA′BB′ system, 4 H, H_{ar}), 7.42 (d, J = 5 Hz, 2 H, H_{ar}), 7.84 (s, 2 H, H_{ar}), 9.11 (d, J = 5 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.0, 70.1, 70.2, 70.3, 101.6, 101.7, 101.8 106.5, 106.6, 106.8, 115.2, 123.6, 124.0, 126.5, 127.6, 128.0, 128.6, 130.6, 131.1, 136.9, 139.3, 139.4, 139.5, 147.0, 148.1, 149.8, 159.1, 160.1, 160.2, 160.3 ppm. MS (MALDI-TOF, DHB): m/z = 3515.9 (34) [M + H]$^+$, 1940.7 (24), 1621.5 (100).

Liquid–Liquid Extraction Procedure: Extraction studies were performed at 25 ± 1 °C in 2 cm^3 microcentrifuge tubes by mechanical shaking. The phase ratio $V_{(org)}$:$V_{(w)}$ was 1:1 (0.5 cm^3 each); the shaking period was 30 min. The extraction equilibrium was achieved during this period. All samples were centrifuged after extraction. The copper concentration in both phases was determined radiometrically using γ-radiation [^{64}Cu, NaI(Tl) scintillation counter Cobra II/Canberra Packard]. The aqueous solution was adjusted using 0.05 mol·dm^{-3} 2-[*N*-morpholino]ethanesulfonic acid (MES)/ NaOH (pH = 5.3–5.9).

Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS): Fluorescence measurements were carried out by use of a spectrometer system described elsewhere.[30] The ligands (L^{0G}–L^{3G}) were dissolved in $CHCl_3$. The total concentration of the ligand was $1 \cdot 10^{-5}$ mol·dm^{-3}. The fluorescence of solutions with increasing concentration of added Cu^{II} trifluoromethanesulfonate were measured. The ligand to Cu^{II} ratio was varied from 10:1 to 1:1. The fluorescence of the non-complexed ligand was excited by 130 fs laserpulses at 266 nm. The repetition rate of the laser system was 1 kHz. The emitted fluorescence was focussed into a 270 mm spectrograph (Acton Research) and the spectrum was measured by an intensified CCD (charged coupled device) camera (LaVision). The gate of the camera system was set to be 120 ps and the observed wavelength range was set from 350 nm to 510 nm. The range for time-resolved measurements was limited from 0 to 4000 ps with steps of 25 ps.

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