A Water-Soluble Calix[4]arene-Based Podand Incorporating 4,4′-Dicarboxy-2,2′-bipyridine Chelating Units − Synthesis and Complexation Properties towards Copper Ions

Nicolas Psychogios,[a] Jean-Bernard Regnouf-de-Vains,*[a] and Helen M. Stoeckli-Evans[b]

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A water-soluble calix[4]arene-based podand has been prepared by incorporation, at the lower rim, of two 4,4′-dicarboxy-2,2′-bipyridine units in opposite positions. The association between its coordination and hydrophilic properties were beneficial to the complexation and solubilization of copper(I) in water, even in the presence of bovine serum albumin. The ligand and its corresponding Cu^{I} complex have been fully characterized, but attempts to crystallize them have been unsuccessful so far. For this reason, the dinuclear $ZnCl_2$ complex of the organic solvent soluble tetraester intermediate has been crystallized, and subjected to X-ray diffraction analysis, confirming the expected podand-like structure of the ligand.

Introduction

The transition from organic to aqueous solubility of the calixarenes, and their corresponding properties, is gaining attention as demonstrated by a rapid on-line survey on *water-soluble calixarenes*, and recent review literature.[1] The introduction of carboxylic acid functionalities at the lower[2] and upper rims,[3,4] or sulfonyl,[5,6] phosphonate,[7] and alkylamino groups[8] at the upper rim have been the main routes for making calixarenes water soluble. Many structural modifications have been carried out on these water-soluble structures, leading to new ligands for various metal cations.

With the aim of conducting, in water, some complexation experiments, that we have previously developed with lipophilic calixarene-based heterocyclic podands,[9−17] and in anticipation of future biological investigations, we attempted to synthesize a hydrophilic ligand able to complex the relatively unstable Cu^{I} cation in this medium. A number of very rare examples of water-soluble copper(I) coordination complexes have been described involving a sulfonated phosphane ligand,[18] or calix[6]-[19] and calix[4]arene[20−22] heterocyclic derivatives illustrating, in part, the difficulty of protecting this cation from disproportionation in water, and thus limiting investigations on its properties in aqueous media. The fact that the copper(I) complexes are diamagnetic and colored (metal-to-ligand charge transfer band at ca. 450 nm) should allow a convenient analysis of the complexation processes by NMR and UV spectroscopy.

In this report, we describe (a) the multi-step synthesis of the water-soluble calix[4]arene-based heterocyclic podand **6** in which the 2,2′-bipyridine arms exhibit both chelating and hydrophilic behavior, (b) its complexation properties towards Cu^{I} and Cu^{II} ions in water, and (c) the synthesis and characterization of the copper(I) complex **7**. Attempts to obtain crystals of **6** and **7** suitable for X-ray analysis did not succeed, but were successful for the dinuclear $ZnCl_2$ complex of the organic-solvent soluble tetraester intermediate **4**, allowing a preliminary structural investigation.

Results and Discussion

Ligand Syntheses

The calixarene podand species **4**−**7** were prepared according to Scheme 1. The starting calix[4]arenetetrol was synthesized as described previously.[23−26]

The bipyridine arms were introduced to the calixarene platform via the bromomethyl intermediate **3**, which was prepared according to Scheme 2 The starting bipyridine **1** was prepared following the Ni^{0}-mediated procedure of Alpha et al.,[27] from methyl 2-methyl-6-[(*p*-tolylsulfonyl)oxy]-pyridine-4-carboxylate. For the latter, the toxic and expensive pyridine generally used as base and solvent for the tosylation reaction was replaced by triethylamine and

[a] GEVSM, UMR 7565 CNRS-Université Henri Poincaré, Faculté de Pharmacie,
5, rue Albert Lebrun, BP 403, 54001 Nancy Cedex, France
Fax: (internat.) +33-3-83682345
E-mail: jean-bernard.regnouf@pharma.uhp-nancy.fr
[b] Laboratoire de Cristallographie, Institut de Chimie, Université de Neuchâtel,
51, C.P. 2, 2007 Neuchâtel, Switzerland
Fax: (internat.) +41-32-7182511
E-mail: Helen.Stoeckli-Evans@unine.ch

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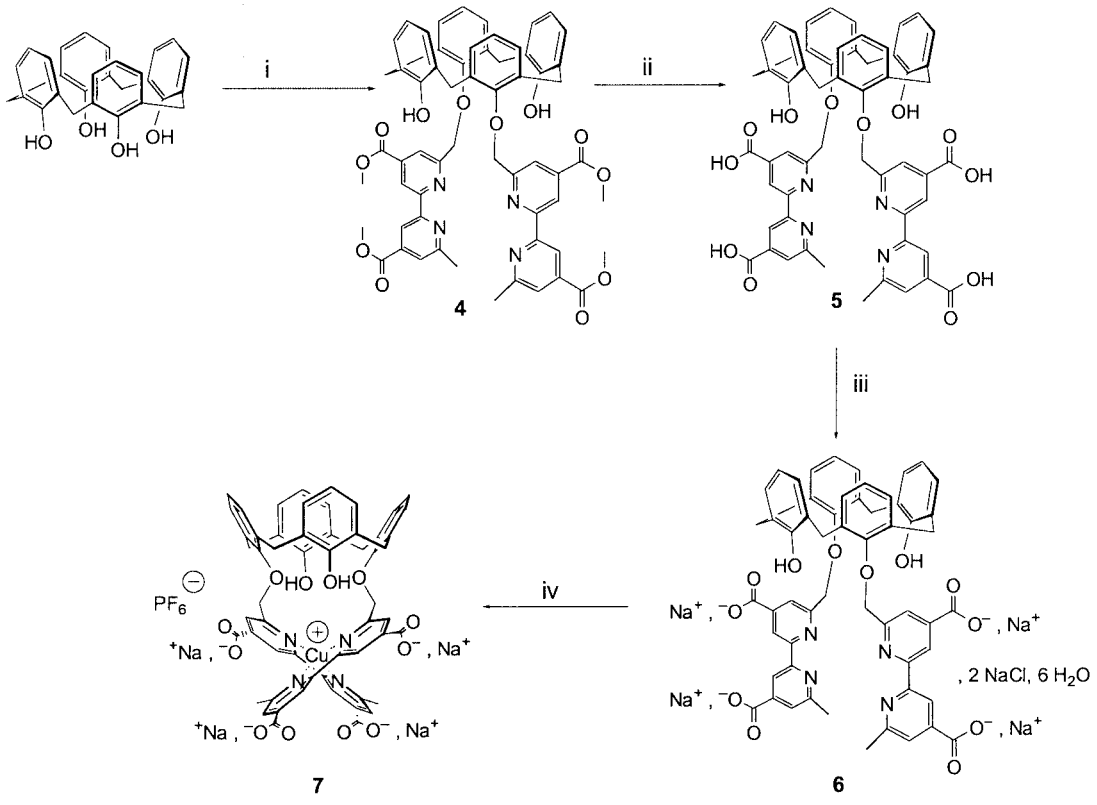
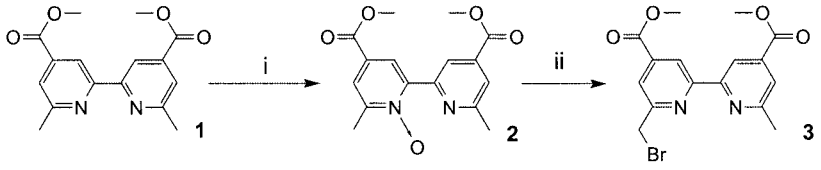


Scheme 1. i) **3**, MeCN, K_2CO_3, reflux, 83%; ii) a) NaOH, H_2O, EtOH, reflux; b) HCl, pH 3−4, 80%; iii) NaOH, H_2O, pH 7, 100%; iv) $Cu(MeCN)_4PF_6$, MeCN, H_2O



Scheme 2. i) *m*CPBA, CH_2Cl_2, 90%; ii) a) $(CF_3CO)_2O$; b) LiBr, THF, DMF, 55%

CH_2Cl_2.[28] This safe and economical procedure afforded the tosyl derivative in a yield of 90%.

The introduction of a single active bromomethyl functionality at the 6-position of **1** was performed via a three step process including a controlled *N*-oxidation, a Boeckelheide rearrangement, and a *pseudo*-halogen exchange. Compound **1** was initially treated in CH_2Cl_2 with 1 equiv. of *m*CPBA at 0 °C, then at room temperature to afford the mono-*N*-oxide **2**, mixed with ca. 5% of the corresponding di-*N*-oxide, and ca. 5% of unchanged bipyridine **1**. An analytical sample of **2** was obtained by chromatography on Al_2O_3 (CH_2Cl_2) but, unstable on this support, and in order to avoid dismutation, the above-mentioned raw mixture was frozen or directly transformed.

The second step was a modified Boekelheide rearrangement. This process initially described with picoline *N*-oxides[29−30] allows the functionalization, by an active carbonyl compound via a radical or ionic mechanism, of the methyl group in the α-position of the *N*-oxide function. With acetic anhydride, this leads to an acetate-protected hydroxymethyl functionality, a key compound for further transformations. This reaction was employed successfully to prepare more sophisticated activated heterocyclic systems, notably with 6,6′-dimethyl-2,2′-bipyridine and its analogues.[27,31−35]

The presence of the two ester functions in **1**, both of which are prone to hydrolysis, led us to employ a more sensitive pathway involving a labile trifluoroacetate derivative, which exhibits, in the alkyl[36] and arylalkyl series,[32,34] the interesting characteristic of being directly substituted by bromine in polar aprotic solvent, and at room temperature via a pseudo-halogen exchange with LiBr.

Thus, the raw mono-*N*-oxide **2** was heated to reflux in CH_2Cl_2 in the presence of an excess of trifluoroacetic anhydride. After evaporation of the solvent the solid residue, which contains the dimethyl 6-trifluoroacetyl-6′-methyl-2,2′-bipyridine-4,4′-dicarboxylate, was dissolved in dry DMF and dry THF in the presence of an excess of anhy-

drous LiBr, itself dried under vacuum at 150 °C. The resultant monobromide **3** was obtained pure in a yield of 55%. The dibromomethyl analogue[27] was also isolated in a yield of 12%, and the bipyridine **1** (ca. 15%) was recovered. Their formation was explained by the partial dismutation of **2** under the given conditions of the reaction.[35]

A similar but longer process involving the consecutive formation of the trifluoroacetate, the alcohol, the mesylate, and then the bromide was also described for the *tert*-butyl ester analogue of **3**,[37] as well as another procedure involving a radical bromination.[38]

Following the procedure previously reported by Beer et al.[39] for the unsubstituted bipyridine, the monobromide **3**, calix[4]arenetetrol, and K_2CO_3 were heated to reflux in MeCN to give the podand **4** in a yield of 83% after chromatography (SiO_2, CH_2Cl_2). The four ester functions of **4** were saponified in an aqueous alcoholic NaOH solution at reflux. Acidification to pH 3−4 resulted in the precipitation of the tetraacid **5**, which was recovered in a yield of 80%. A controlled neutralization of **5** with NaOH afforded the tetrasodium carboxylate **6** in almost quantitative yield (Scheme 1).

Complexation Studies

The formation of the copper(I) complex **7** was initially studied by UV-visible spectroscopy in water (Figure 1). The addition of $[Cu(MeCN)_4]PF_6$ to a solution of **6** resulted in the immediate appearance of the expected MLCT band at 470 nm (red color), characteristic of tetrahedral copper(I) complexes. The evolution of this band, as well as the new ligand-centered band at ca. 300 nm, was complete upon addition of 1 equiv. of metal, confirming the formation of a mononuclear complex.

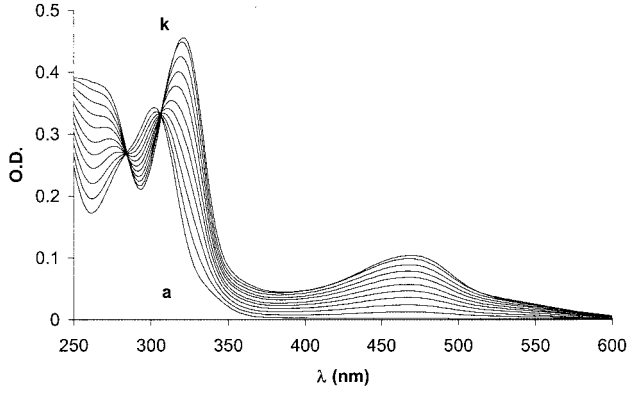


Figure 1. UV-visible titration of **6** with $[Cu(MeCN)_4]PF_6$: a) **6**, [2 mL; 1.71×10^{-5} M in H_2O]; from b) to k): addition of 1 equiv. of $[Cu(MeCN)_4]PF_6$ [$10 \times 4\mu L$; 9.98×10^{-4} M in MeCN]

The air-stable red complex **7** was prepared quantitatively by addition of 1 equiv. of $[Cu(MeCN)_4]PF_6$ in acetonitrile to an aqueous solution of **6**, followed by evaporation to dryness. Attempts to crystallize **7** for an X-ray structural analysis were unsuccessful.

Since the redox properties of copper are favorable for the doubly charged species, we have followed the complexation of $CuCl_2$ by UV-visible spectroscopy in water (Figure 2). The presence of two isosbestic points at 304 nm (0 to 1 equiv.) and 316 nm (1 to 2 equiv.) revealed the formation of two consecutive complex species, namely [$CuCl_2$/**6**] and [$(CuCl_2)_2$/**6**]. In order to prepare a sample of the corresponding final complex, the addition of 2 equiv. of $CuCl_2$ in water to an aqueous solution of **6** resulted in a brown-green coloration, nevertheless immediately followed by formation of a gel then precipitation. The solvent was removed by filtration and the residue was dried under high vacuum to give **8** as a green-brown powder. Surprisingly, the solid thus obtained remained insoluble in common solvents, even in DMSO. This behavior led us to believe that the water solubilizing carboxylate groups were in fact engaged in a chelating interaction with copper(II), giving oligomeric or polymeric chelate species resulting in loss of solubility of the material. No relevant mass analysis has been obtained.

An elemental analysis of the copper(II) complex **8** was consistent with the formula $C_{56}H_{40}ClCu_2N_4NaO_{12}\cdot 4.5H_2O$, corresponding to the loss of 3 equiv. of NaCl thus suggesting an ionic interaction between copper and the carboxylate groups. Such an interaction should involve a bridging mode of the copper ions between two calixarene moieties, in a linear polymeric network. Nevertheless, IR spectroscopy (KBr) did not show relevant modifications in the carbonyl region with regards to the ligand **6**. Attempts to improve this structure are under current investigation.

The bimetallic copper(II) complex [$(CuCl_2)_2 \subset$ **6**] formed during the UV titration experiment was subjected to reduction by ascorbate (Figure 3). The complex was fully reduced after the addition of 0.5 equiv. of ascorbate, as deduced by the appearance of the expected MLCT band at 470 nm, characterized by an ε value of 5500 $mol\cdot L^{-1}\cdot cm^{-1}$, similar to that of complex **7**. The addition of more ascorbate did not result in any further change in the absorption pattern.

In order to make a biological assessment of the complex **7**, competition experiments with bovine serum albumin were monitored by UV-visible spectroscopy (Figure 4). The results show that the presence of 1 equiv. or 10 equiv. of BSA relative to **7** did not change the absorption profile of the latter, the MLCT band being conserved even after 24 or 48 hours. Under the same conditions, the copper(I) complex of the corresponding free bipyridine decomposed. In parallel, we have verified that no absorption band of the MLCT type was generated by the interaction between BSA and $[Cu(MeCN)_4]PF_6$. This confirmed that the copper(I) ion is strongly maintained in a tetrahedral coordination by **6** under these conditions.

In contrast to, a similar test carried out with [$(CuCl_2)_2 \subset$ **6**] (Figure 5) resulted in the loss of the ligand-centered band at 322 nm, which was concomitant with the appearance of a new band at 312 nm (1 equiv. BSA), the latter being found again as a shoulder with 10 equiv. of BSA. After 1 day, the absorption pattern was found to be similar to the free ligand **6** ($\lambda_{max.}$ = 304 nm). No specific absorption bands were observed during the reaction between BSA and $CuCl_2$.

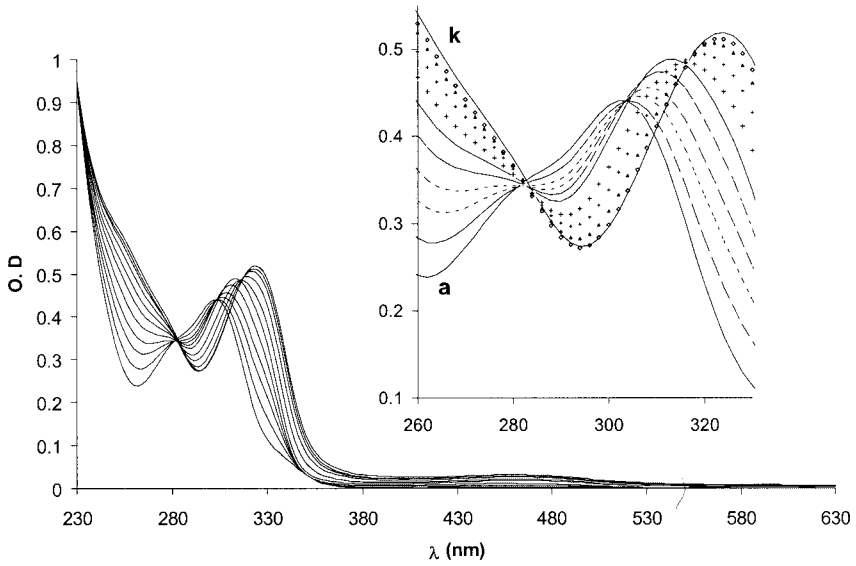


Figure 2. UV-visible titration of **6** by $CuCl_2{\cdot}2H_2O$: a) **6**, [2 mL; 2.0×10^{-5} M in H_2O]; from b) to k): addition of 2 equiv. of $CuCl_2{\cdot}2H_2O$ [10×8 μL; 1.00×10^{-3} M in H_2O]

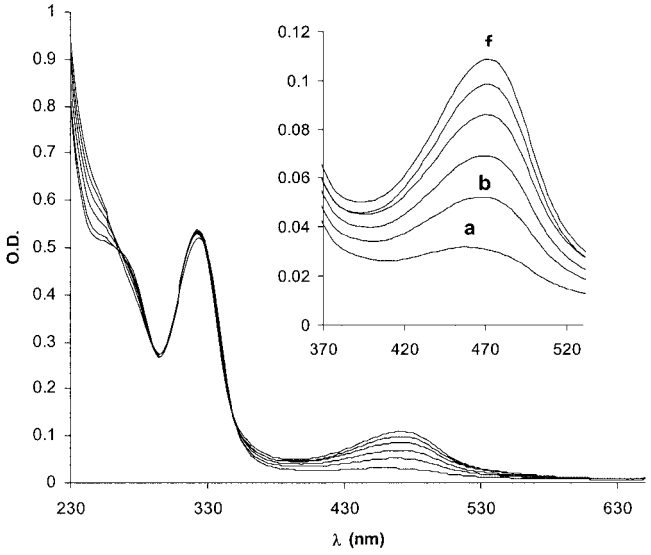


Figure 3. UV-visible titration of [$(CuCl_2)_2 \subset$ **6**] by ascorbic acid: a) [$(CuCl_2)_2 \subset$ **6**], [2 mL; 2.0×10^{-5} M in H_2O]; from b) to f): addition of 0.5 equiv. of ascorbic acid [5×4μL; 1.00×10^{-3} M in H_2O]

Compounds **2**−**7** gave satisfactory elemental, IR, MS and NMR analyses.

In particular, a preliminary elemental analysis performed on **6** dried with P_2O_5 showed the presence of 2 molecules of NaCl and 3 molecules of H_2O, but the instability of the mass during the weighing process suggested logically that **6** was hygroscopic. After equilibration under ambient conditions, the analysis of **6** was consistent with the presence of 2 molecules of NaCl and 6 molecules of H_2O. Argon plasma emission spectrophotometric analyses were consistent with the presence of 5 sodium ions for one ligand **6**, 5 sodium, and 1 copper ion for one complex **7**. Dialysis experiments performed with cellulose ester membranes (cut-off mol. wt. = 100) on aqueous solutions of **6** and **7** did not result in satisfactory removal of sodium chloride, the residual solutions giving precipitates of silver chloride upon addition of silver nitrate. Attempts to evaluate the water content in **6** and **7** by mass-coupled thermogravimetric analysis were not successful, the loss of water being observed over a wide range of temperatures (20−250 °C). Nevertheless, **6** showed a clean loss of four CO_2 molecules between 420 and 540 °C.

NMR Analyses

According to de Mendoza et al,[40,41] ^{13}C NMR spectroscopic analyses showed that **4**, **5** and **6** exist in the cone conformation.

The cone conformation of **6** was also demonstrated by ^1H NMR spectroscopy in D_2O, with the Ar-CH_2-Ar AB system located at δ = 3.18−3.96 ppm (J_{AB} = 15 Hz). 2D-COSY experiments allowed the full assignment of resonance signals. In the aromatic region, the ligand exhibits four perfectly well resolved bipyridyl singlets together with two doublets and two triplets for the calixarene moiety, which confirmed the expected structure. The terminal methyl groups and the methoxy linkers appear as singlets at δ = 2.53 and 5.33 ppm, respectively.

The ^1H NMR spectrum of the copper(I) complex **7** in D_2O (Figure 6) exhibits broad resonance signals in all the relevant frequency domains, except for the aromatic calixarene protons, which appear as well resolved doublets and triplets. The presence of more than the four expected bipyridyl resonance signals is in accordance with the probable presence of more than one species under these conditions. Addition of [D_6]DMSO to the aqueous solution resulted in the increasing of one of the signals, and a general sharpening of all signals. At the concentration used in the NMR experiments, it is possible to suggest that oligomeric or

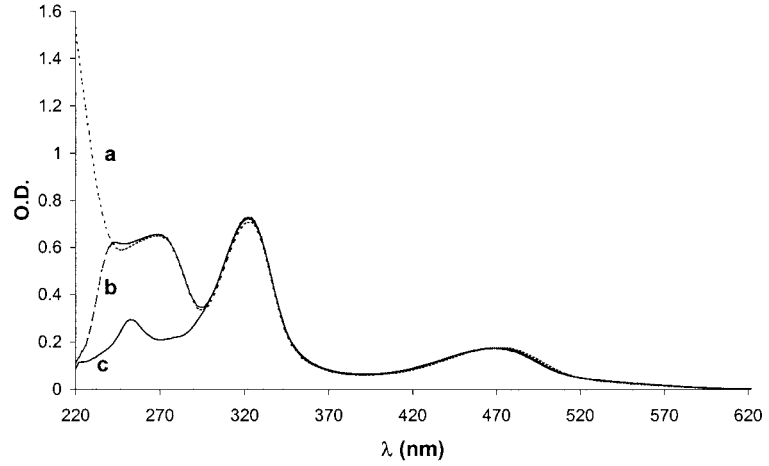


Figure 4. UV-visible analysis of **7** in the presence of bovine serum albumin: a) **7**, [1.6×10^{-5} M in H_2O]; b) 1 equiv. of BSA; c) 10 equiv. of BSA

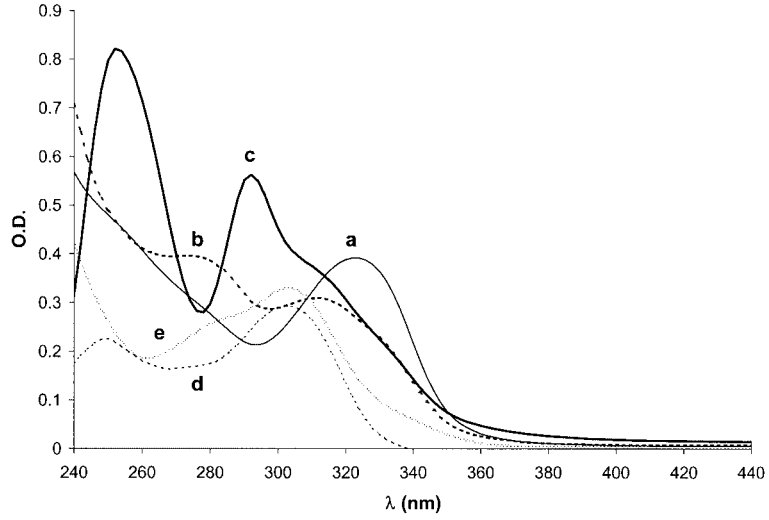


Figure 5. UV-visible analysis of [$(CuCl_2)_2 \subset$ **6**] in the presence of bovine serum albumin: a) [$(CuCl_2)_2 \subset$ **6**], [1.6×10^{-5} M in H_2O]; b) 1 equiv. of BSA; c) 10 equiv. of BSA; d) 10 equiv. of BSA, one day; e) **6** [1.6×10^{-5} M in H_2O]

polymeric complex species can be formed involving, due to the lack of steric hindrance at the upper rim, conic or non-conic calixarene platforms, that could correspond to the presence of multiple signals. The addition of DMSO may modify the solvation of these flexible species, resulting in the recovery of a conic conformer. Finally, pure [D_6]DMSO gave a well resolved NMR spectrum resulting in the presence of the expected cone conformer as the major compound with, notably, the presence of the four bipyridyl singlets, the aromatic succession of calixarene doublets and triplets, and the appearance of two AB systems at $\delta = 3.27$ and 4.24 ppm ($J_{AB} = 12$ Hz), and 5.31 and 6.27 ppm ($J_{AB} = 11$ Hz), which can be attributed to the Ar-CH_2-Ar and OCH_2-bpy spin systems, respectively. According to the results obtained with parent hydrophobic complexes ,[11,13] the presence of the Ar-CH_2-Ar AB system confirmed the cone conformation, and the OCH_2-bpy AB system confirmed the complexation of copper(I) in a prohelicoidal tetrahedral mode.

Mass Spectrometry

The mass analyses of ligand **6** and complex **7** were performed with the electrospray technique in the positive or negative mode. In the positive mode, **6** exhibited the mono-(sodium) and the doubly charged bis(sodium) derivatives at 1076.0 and 549.3 a.m.u. (base peak), respectively, accompanied by other entities, which were not well analyzed. Conversely, the negative mode analysis resulted in the exhibition of three groups of doubly charged (481.2, 492.2 and 503.2 a.m.u.), triply charged (327.8 and 320.5 a.m.u.), and tetra-charged (240.0 a.m.u.) species resulting from the loss of 2, 3 or 4 sodium ions compensated, when necessary, by replacement with 1 or 2 protons. The base peak appearing

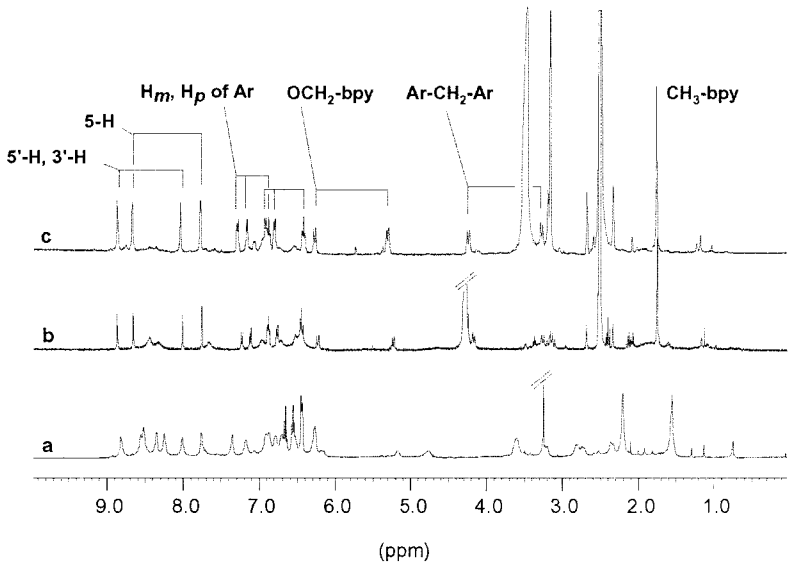


Figure 6. ^{1}H NMR spectrum of the copper(I) complex **7** (a: D_2O, b: D_2O + [D_6]DMSO, c: [D_6]DMSO; 400 MHz, room temp.)

in this case at 320.5 a.m.u. was attributed to the triply charged species [**6**−4Na^+ + H^+]$^{3-/3}$.

The copper(I) complex **7** gave no relevant information in the positive mode. In the negative mode, three groups of signals were observed. As for the ligand, the loss of 1, 3, and 4 sodium ions compensated by addition of protons when necessary, resulted in doubly charged species located at 544.1, 523.2, and 512.2 a.m.u. The loss of 4 sodium ions resulted in a triply charged species located at 341.3 a.m.u. Finally, the hexafluorophosphate anion appeared as a pure entity at 144.9 a.m.u. (base peak), and as an adduct with $NaPF_6$ at 312.9 a.m.u.

X-ray Crystallography

Attempts to obtain single crystals of the ligand **6**, its Cu^I complex **7**, and other transition metal complexes of **6** suitable for X-ray diffraction analyses were unsuccessful. In order to ascertain the podand structure, and considering that on the basis of NMR results, the general structure of **6** should not be different from the organic-solvent soluble tetraester intermediate **4**, we tried to prepare various metal complexes of the latter and good results were obtained with zinc(II). In particular, the reaction of **4** with $ZnCl_2$ gave the conic complex **9** which was characterized by 1D and 2D ^{1}H NMR spectroscopic experiments, mass spectrometry, and elemental analysis. Crystals of **9** suitable for X-ray diffraction analysis were obtained as yellow plates by slow diffusion of hexane into a dichloromethane solution of the complex.

Compound **9** crystallizes with 2 independent molecules, C and D, per asymmetric unit, hence the molecular formula is [Cl_2Zn**6**ZnCl_2]·2.25CH_2Cl_2.

The molecular structure without the solvent is illustrated in the PLATON[42] drawing (Figure 7) along with a partial crystallographic numbering scheme.

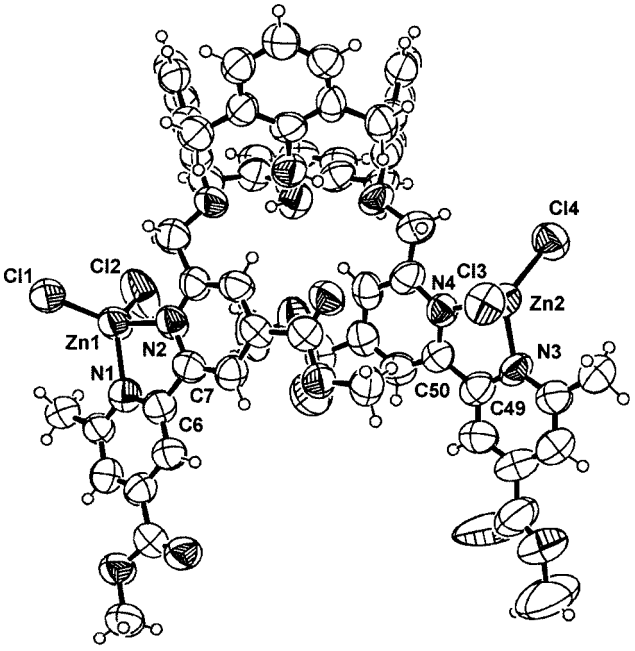


Figure 7. ORTEP side-view of complex **9**, molecule C

As expected, the calixarene subunit of **9** is in the cone conformation and substituted in alternate positions of the lower rim by two dimethyl 6-methyl-2,2′-bipyridyl-4,4′-dicarboxylate arms tethered to the platform by a 6′-methyleneoxy linker. Each bipyridyl unit coordinates via its nitrogen atoms to a tetrahedral Zn^{II} cation, with the two remaining coordination positions occupied by two chloride anions, as already observed.[43]

In the two independent molecules C and D, the [bpyZnCl_2] units are opposed to each other, facing outward

Table 1. Selected torsion angles [°] around the zinc center in complex **9**

N2−Zn1−N1−C6	1.5(5)	N4−Zn2−N3−C50	−10.8(5)
N1−Zn1−N2−C7	2.1(5)	N3−Zn2−N4−C49	+8.0(5)
N1−C6−C7−N2	6.4(10)	N3−C50−C49−N4	−4.9(10)
N22−Zn21−N21−C66	4.5(8)	N24−Zn22−N23−C111	−7.9(6)
N21−Zn21−N22−C67	−1.0(8)	N23−Zn22−N24−C110	7.7(6)
N21−C66−C67−N22	6.5(17)	N24−C110−C111−N23	−0.3(12)

Table 2. Selected bond lengths [Å] and angles [°] around the zinc center in complex **9**

Zn1−N1	2.059(7)	N1−Zn1−N2	80.5(3)	N3−Zn2−N4	80.3(3)
Zn1−N2	2.083(7)	N1−Zn1−Cl2	116.2(2)	N3−Zn2−Cl4	119.0(2)
Zn1−Cl2	2.197(3)	N2−Zn1−Cl2	108.07(18)	N4−Zn2−Cl4	114.00(19)
Zn1−Cl1	2.204(3)	N1−Zn1−Cl1	114.61(19)	N3−Zn2−Cl3	108.8(2)
Zn2−N3	2.048(7)	N2−Zn1−Cl1	113.4(2)	N4−Zn2−Cl3	110.02(18)
Zn2−N4	2.074(6)	Cl2−Zn1−Cl1	117.88(13)	Cl4−Zn2−Cl3	118.47(10)
Zn2−Cl4	2.196(2)				
Zn2−Cl3	2.201(2)				
Zn21−N21	2.065(12)	N21−Zn21−N22	81.4(6)	N23−Zn22−N24	79.8(4)
Zn21−N22	2.134(16)	N21−Zn21−Cl21	114.5(3)	N23−Zn22−Cl23	115.0(3)
Zn21−Cl21	2.174(3)	N22−Zn21−Cl21	113.0(4)	N24−Zn22−Cl23	114.8(3)
Zn21−Cl22	2.190(4)	N21−Zn21−Cl22	110.5(3)	N23−Zn22−Cl24	110.0(2)
Zn22−N23	2.036(7)	N22−Zn21−Cl22	106.1(3)	N24−Zn22−Cl24	108.9(2)
Zn22−N24	2.100(9)	Cl21−Zn21−Cl22	123.32(16)	Cl23−Zn22−Cl24	120.9(2)
Zn22−Cl23	2.179(3)				
Zn22−Cl24	2.214(4)				

from the calixarene main axis, and orienting the chlorine atoms in the direction of the calixarene platform. A rotation of 90 ° around the C_2 axis shows that these two units are quasi parallel.

Looking more precisely at the complex subunits of molecules C and D, shows that the bipyridine units are planar, with N−C−C−N torsion angles between −4.9 and 6.5 ° (Table 1). The zinc(II) centers are in strongly distorted tetrahedral coordination environments, with N−Zn−N angles of ca. 80 °, Cl−Zn−Cl angles of ca. 120 °, and N−Zn−Cl between 106 and 119° (Table 2).

The Zn−N and ZnCl distances (Table 2) are consistent with those measured in a non-carboxylated analogue,[43] suggesting a poor influence of the electroactive ester substituents on the complex geometry.

Conclusion

A new water-soluble calix[4]arene-based bipyridyl podand **6** has been synthesized and subjected to complexation studies with copper(I) and copper(II) species in water. The copper(I) complex **7** exhibits considerable stability, even in the presence of bovine serum albumin, promising interesting behavior in biological media. It was fully characterized as a mononuclear species, involving probably a pro-helicoidal pseudo-tetrahedral complexation mode between the chelating bipyridines and the metallic center, as already observed for organic-solvent soluble analogues. No crystals of either water-soluble ligand **6** or the copper(I) complex **7** could be obtained, but the lipophilic tetra methyl ester intermediate **4** reacted with zinc(II) chloride to give a monocrystalline dinuclear complex **9** which was characterized by X-ray diffraction, thus confirming the expected podand-like structure of the ligand. The evaluation of the complexing ability of **6** with various transition metal cations in water and biological media, as well as their potent antimicrobial activities are under current investigation.

Experimental Section

General Remarks: Melting points (°C, uncorrected) were determined with an Electrothermal 9200 Capillary apparatus. ^{1}H, ^{13}C and ^{15n} NMR spectra were recorded with a Bruker DRX 400 (chemical shifts in ppm) instrument. Mass spectra (electronic ionization − EI, and electrospray − ES) were recorded with a Nermag R-1010C apparatus or a Micromass Platform II apparatus, respectively, at the Service Commun de Spectrométrie de Masse Organique, Nancy. Infrared spectroscopy was performed with a Mattson 5000 FT apparatus (KBr, $\tilde{\nu}$ in cm^{-1}) and UV spectra were recorded using a SAFAS UV mc^2 apparatus, $\lambda_{max.}$ in nm, ε in $dm^3 \cdot mol^{-1} \cdot cm^{-1}$. Elemental analyses were performed at the Service de Microanalyse, Nancy. Merck TLC plates were used for chromatographic analyses (SiO_2, ref 1.05554; Al_2O_3, ref 1.05581). Sodium and copper concentrations were determined by argon plasma emission spectrophotometry on a Spectrascan 7 Spectrametrics apparatus. Mass-coupled thermogravimetric analyses were performed with a Netzch STA 409 C apparatus.

All commercially available products were used without further purification unless otherwise specified.

***N*-Oxide 2:** To a solution of dimethyl 6,6′-dimethyl-2,2′-bipyridine-4,4′-dicarboxylate (**1**) (1 g, 3.30 mmol) in CH_2Cl_2 (20 mL) at 0 °C under argon, was added dropwise a solution of *m*-chloroperbenzoic acid (0.685 g, 3.96 mmol; from 0.975 g of 70% commercial

*m*CPBA) in CH_2Cl_2 (10 mL). The mixture was then stirred at room temp. for 2.5 h (TLC monitoring; Al_2O_3, CH_2Cl_2/hexane, 90:10). The solvent was evaporated to dryness at 25 °C, and the residue was triturated with Et_2O to remove *m*CBA and unchanged *m*CPBA. The resultant solid, which contained 90% of the mono *N*-oxide, traces of di-*N*-oxide, and unchanged bipyridine was retained at −20 °C. (1.025 g). A small analytical sample of **2** was obtained by rapid chromatography (Al_2O_3; CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ = 2.62 (s, 3 H, *Me*bpy), 2.74 (s, 3 H, *Me*bpy), 3.98 (s, 3 H, COO*Me*), 3.99 (s, 3 H, COO*Me*), 7.82 (s, 1 H), 7.94 (d, *J* = 2.7 Hz, 1 H), 8.61 (d, *J* = 2.7 Hz, 1 H), 9.05 (s, 1 H) (3-H, 3′-H, 5-H, 5′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.80 (*Me*bpy), 24.99 (*Me*bpy), 53.22 (−O*Me*), 122.00, 123.75, 126.00, 126.38 (C3, C3′, C5, C5′), 125.74, 138.45, 147.61, 150.53, 150.77, 159.82 (C2, C2′, C4, C4′, C6, C6′), 164.96, 166.11 (*C*OOMe) ppm. $C_{16}H_{16}N_2O_5$·0.1H_2O (318.11): calcd. C 60.41, H 5.13, N 8.80; found C 60.17, H 4.98, N 8.57.

Bromide 3: Compound **2** (1 g, 5.0 mmol) was dissolved at room temp. in dry CH_2Cl_2 (10 mL), and trifluoroacetic anhydride (10 mL) was added. The solution was brought to reflux under argon over 1.5 h, during which time it became orange. The solvents were then evaporated to dryness. The raw material containing the trifluoroacetic ester was dissolved at room temp. in a 1:1 mixture of dry DMF and dry THF (15 mL), then anhydrous LiBr (2 g, 23 mmol, dried at 180 °C over 1 h) was added. The resultant yellow mixture was stirred under argon for 4 h (TLC monitoring, SiO_2, CH_2Cl_2), and the solvents were evaporated to dryness (2 torr, 70 °C). The residue was washed with water (3 × 20 mL) then chromatographed (SiO_2, CH_2Cl_2) to give the monobromide **3** (1 g, 55%), the dibromide (0.25 g, 12%), and unchanged **1**. White powder, m.p. 160−162 °C. IR: ṽ = 1565.8 (C=N), 1731.3 (COOMe). UV-vis (CH_2Cl_2): λ = 310 nm (16700). ^{1}H NMR ($CDCl_3$): δ = 2.75 (s, 3 H, *Me*bpy), 4.02 (s, 3 H, COO*Me*), 4.03 (s, 3 H, COO*Me*), 4.72 (s, 2 H, C*H*$_2$Br), 7.79 (d, *J* = 0.5 Hz, 1 H), 8.06 (d, *J* = 1.1 Hz, 1 H), 8.79 (d, *J* = 0.5 Hz, 1 H), 8.91 (d, *J* = 1.3 Hz, 1 H, 3-H, 3′-H, 5-H, 5′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 24.99 (*Me*bpy), 33.78 (Br*C*H$_2$), 53.12, 53.25 (O*Me*), 118.25, 120.32, 123.37, 123.46 (C3, C3′, C5, C5′), 139.16, 140.63, 155.83, 157.02, 157.97, 159.75 (C2, C2′, C4, C4′, C6, C6′), 165.79, 166.38 (*C*OOMe) ppm. MS (EI): *m*/*z* = 380−378 [**3**]$^+$, 322−320 [**3** − COOMe]$^+$; 299 [**3** − Br]$^+$. $C_{16}H_{15}BrN_2O_4$·0.1CH_2Cl_2 (387.7): calcd. C 49.88, H 3.95, N 7.23; found C 50.00, H 3.95, N 7.23.

Calixarene Tetraester 4: A suspension of calix[4]arene (1 g; 2.35 mmol) and K_2CO_3 (0.305 g; 2.35 mmol) in anhydrous CH_3CN (50 mL) was heated to reflux under argon for 30 min. The bromide **3** (1.88 g; 4.95 mmol) was then added and reflux was continued for 4 h (TLC monitoring; SiO_2, CH_2Cl_2/MeOH, 95:5). The solvent was evaporated to dryness, and the residue was washed with Et_2O and water before being chromatographed (SiO_2, CH_2Cl_2) to give **4** (2 g; 83%). White powder, m.p. 268−270 °C (dec.). IR: ṽ = 1567.9 (C=N), 1732.1 (COOMe). UV (CH_2Cl_2): λ = 310 nm (23200). ^{1}H NMR ($CDCl_3$): δ = 2.77 (s, 6 H, *Me*bpy), 3.48−4.43 ("q", AB, J_{AB} = 13 Hz, 8 H, Ar-C*H*$_2$-Ar), 3.55 (s, 6 H, −O*Me*), 3.99 (s, 6 H, −O*Me*), 5.47 (s, 4 H, −OC*H*$_2$bpy), 6.71 (t, *J* = 7.4 Hz, 2 H, 4-H of Ar-OH), 6.86 (t, *J* = 7.8 Hz, 2 H, 4-H of Ar), 7.00 (d, *J* = 7.6 Hz, 4 H, 3-H and 5-H of Ar), 7.12 (d, *J* = 7.4 Hz, 4 H, 3-H and 5-H of Ar-OH), 7.77 (d, *J* = 1 Hz, 2 H, 3′-H or 5′-H of bpy), 8.18 (s, 2 H, ArO*H*), 8.71 (d, *J* = 1.0 Hz, 2 H, 5′-H or 3′-H of bpy), 8.84 (d, *J* = 1.1 Hz, 2 H, 3-H or 5-H of bpy), 9.12 (d, *J* = 1 Hz, 2 H, 5-H or 3-H of bpy) ppm. ^{13}C NMR ($CDCl_3$): δ = 25.04 (*Me*bpy), 31.98 (Ar-*C*H$_2$-Ar), 52.63 (−O*Me*), 53.05 (−O*Me*), 78.77 (−O*C*H$_2$bpy), 117.95, 119.50, 120.11, 121.98, 123.28, 126.24 (C3, C3′, C5, C5′ of bpy, C_p of Ar), 128.98, 129.69 (C_m of Ar), 128.12, 133.52, 139.06, 139.82, 152.26, 153.88, 156.18, 156.25, 158.73, 159.82 (C2, C2′, C4, C4′, C6, C6′ of bpy; $C_{i,o,p}$ of Ar), 165.58, 166.43 (*C*OOMe) ppm. MS (ES, positive mode): *m*/*z* = 1020 [**4**]$^+$, 703 [**4** − OCH$_2$Bpy(COOMe)$_2$]$^+$. $C_{60}H_{52}N_4O_{12}$ (1021.07): calcd. C 70.58, H 5.13, N 5.49; found C 70.48, H 5.45, N 5.34.

Calixarene Tetraacid 5 and Calixarene Tetraacid Sodium Salt 6: A suspension of **4** (1 g; 0.98 mmol) in a solution of NaOH (0.4 g; 10 mmol) in MeOH (110 mL) and H_2O (90 mL) was heated to reflux under argon for 24 h. After cooling to room temp., the solution was acidified to pH 3−4 with 1 M HCl. The resultant precipitate of tetraacid **5** was filtered, washed with H_2O (4 × 30 mL), then dispersed in H_2O (50 mL) and dissolved by careful addition of 1 M NaOH up to pH 7.0. The resultant solution was evaporated to dryness to give **6** (0.97 g; 80%). **6:** White powder, m.p. 270−280 °C (dec.). IR: ṽ = 1555.8 (C=N), 1604.3 (COONa). UV (H_2O): λ = 302 nm (21600). ^{1}H NMR (D_2O): δ = 2.54 (s, 6 H, *Me*bpy), 3.18−3.96 ("q", J_{AB} = 15 Hz, 8 H, Ar-C*H*$_2$-Ar), 5.34 (s, 4 H, −OC*H*$_2$bpy), 6.41 (t, *J* = 7.5 Hz, 2 H, 4-H of Ar1), 6.63 (d, *J* = 7.4 Hz, 4 H, 3-H and 5-H of Ar1), 6.66 (t, *J* = 7.4 Hz, 2 H, 4-H of Ar2), 7.03 (d, *J* = 7.7 Hz, 4 H, 3-H and 5-H of Ar2), 7.53 (s, 2 H, 3′-H or 5′-H of bpy), 7.65 (s, 2 H, 5′-H or 3′-H of bpy), 7.96 (s, 2 H, 3-H or 5-H of bpy), 8.22 (s, 2 H, 5-H or 3-H of bpy) ppm. ^{13}C NMR (D_2O): δ = 23.29 (*Me*bpy), 30.79 (Ar-*C*H$_2$-Ar), 78.25 (−O*C*H$_2$), 119.24, 120.59, 121.68, 123.32, 124.07, 126.18 (C3, C3′, C5, C5′ of bpy; C_p of Ar), 128.46, 133.71 ($C_o$of Ar), 129.40 ($C_m$of Ar), 147.49, 147.64, 150.87, 152.09, 155.42, 156.00, 156.38, 159.68 (C2, C2′, C4, C4′, C6, C6′ of bpy; C_p of Ar), 172.93, 173.60 (COO^-) ppm. ES-MS: (positive mode, 30 V): *m*/*z* = 1075.98 [**6** + Na^+]$^+$, 549.27 [**6** + 2 Na^+]$^{2+/2}$; (negative mode, 20 V): *m*/*z* = 503.24 [**6** − 2 Na^+]$^{2-/2}$, 492.23 [**6** − 3 Na^+ + H^+]$^{2-/2}$, 481.22 [**6** − 4 Na^+ + 2 H^+]$^{2-/2}$, 327.87 [**6** − 3 Na^+]$^{3-/3}$, 320.53 [**6** − 4 Na^+ + H^+]$^{3-/3}$, 240.04 [**6** − 4 Na^+]$^{4-/4}$. $C_{56}H_{40}N_4Na_4O_{12}$·2NaCl·6$H_2O$ (1277.87): calcd. C 52.63, H 4.10, N 4.38; found C 52.88, H 3.82, N 4.24.

A solution of **6** (0.925 g, 0.724 mmol) in water (50 mL) (pH = 7.38) was carefully acidified to pH = 3.11 with 1 M HCl. The resultant yellow suspension was washed with CH_2Cl_2 (4 × 30 mL) before the residual organic solvent was removed under vacuum. The yellow precipitate was filtered off, washed with H_2O, CH_3OH and CH_2Cl_2, then dried under vacuum. (**5**; 0.65 g, 93%). M.p. 235 °C (dec.). IR: ṽ = 1568.1 (C=N), 1720.6 (COOH). ^{1}H NMR ([D$_6$]DMSO): δ = 2.67 (s, 6 H, *Me*bpy), 3.48−4.27 ("q", J_{AB} = 13 Hz, 8 H, Ar-C*H*$_2$-Ar), 5.41 (s, 4 H, C*H*$_2$O), 6.61 (t, *J* = 7.5 Hz, 2 H, H_p of Ar), 6.86 (t, *J* = 7.5 Hz, 2 H, H_p of Ar), 7.09 (d, *J* = 7.6 Hz, 4 H, $H_m$of Ar), 7.17 (d, *J* = 7.6 Hz, 4 H, $H_m$of Ar), 7.73 (d, *J* = 1 Hz, 2 H), 8.47 (s, 2 H), 8.62 (s, 4 H), 8.93 (s, 2 H, 3-H, 3′-H, 5-H, 5′-H of bpy and ArO*H*) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 25.03 (*Me*bpy), 31.59 (Ar-*C*H$_2$-Ar), 78.78 (−O*C*H$_2$), 118.02, 119.64, 119.81, 122.61, 123.74, 126.50 (C3, C3′, C5, C5′ of bpy, C_p of Ar), 128.13, 134.43 (C_o of Ar), 129.46, 129.99 (C_m of Ar), 140.49, 140.91, 152.75, 153.87, 155.77, 155.86, 158.79, 159.89 (C2, C2′, C4, C4′, C6, C6′ of bpy; C_{ipso} of Ar), 166.65, 167.19 (COOH) ppm. ES-Ms (pos. mode): *m*/*z* = 965.35 [**5** + H^+]$^+$, 483.30 [**5** + 2 H^+]$^{2+/2}$. $C_{56}H_{44}N_4O_{12}$·2.5H_2O (1010.01): calcd. C 66.59, H 4.89, N 5.55; found C 66.89, H 4.83, N 5.10.

Copper(I) Complex 7: A solution of [Cu(MeCN)$_4$]PF_6 (0.076 g, 0.205 mmol) in MeCN was added to a solution of **6** (0.3 g, 0.204 mmol) in H_2O (10 mL). The resultant deep red solution was stirred at room temp. for 10 min, and the solvents were evaporated to dryness to give **7** as a brown-red powder. (0.34 g, 100%). IR: ṽ = 855 (PF_6^-), 1555.4 (C=N), 1608.7 (COO^-). UV: λ = 320 (22780), 470 nm (5210; MLCT). ^{1}H NMR ([D$_6$]DMSO): δ = 1.76

(s, 6 H, *Me*bpy), 3.27−4.24 ("q", J_{AB} = 12 Hz, 4 H, Ar-CH_2-Ar), 5.31−6.27 ("q", J_{AB} = 11.0 Hz, 4 H, CH_2O), 6.42 (t, J = 7.0 Hz, 2 H, H_p of Ar1), 6.80 (d, J = 7.4 Hz, 2 H, H_m of Ar1), 6.87 (t, J = 7.0 Hz, 2 H, H_p of Ar2), 6.92 (d, J = 7.6 Hz, 2 H, H_m of Ar1), 7.16 (d, J = 7.0 Hz, 2 H, H_m of Ar2), 7.28 (d, J= 7.0 Hz, 4 H, H_m of Ar2), 7.78 (s, 2 H, 5-H or 3-H bpy), 8.04 (s, 2 H, 5′-H or 3′-H bpy), 8.67 (s, 2 H, 3-H or 5-H bpy), 8.87 (s, 2 H, 3′-H or 5′-H bpy) ppm. ES-MS (neg. mode, 30 V): m/z = 544.4 [**6** + Cu^+ − Na^+ − 2 H^+]$^{2-/2}$, 523.20 [**6** + Cu^+ − 3 Na^+]$^{2-/2}$, 512.19 [**6** + Cu^+ − 4 Na^+ + H^+]$^{2-/2}$, 341.25 [**6** + Cu^+ − 4 Na^+]$^{3-/3}$, 312.83 [$NaPF_6$ + PF_6^-]$^-$, 144.87 [PF_6^-]$^-$. $C_{56}H_{40}N_4Na_4O_{12}$·$CuPF_6$·NaCl·4$H_2O$ (1391.91): calcd. C 48.32, H 3.48, N 4.03; found C 48.18, H 3.71, N 4.00.

Copper(ii) Complex 8: A solution of ligand **6** (0.1 g; 0.0783 mmol) in H_2O (3 mL) was mixed with a solution of $CuCl_2(H_2O)_2$ (0.0267 g; 0.156 mmoles) in H_2O (2 mL) at room temp., resulting in the immediate formation of a green-brown gelatinous precipitate. The solvent was evaporated to dryness under high vacuum without heating. The resultant solid was then triturated with H_2O (3 × 2 mL) and filtered to give **8**. (0.094 g; 98%). Deep-brown solid. IR: $\tilde{\nu}$ = 1559.20 (C=N), 1611.12 (COO^-). $C_{56}H_{40}Cu_2ClN_4NaO_{12}$·4.5$H_2O$ (1227.54): calcd. C 54.79, H 4.02, N 4.56; found C 54.70, H 3.83, N 4.65.

Zinc(ii) Complex 9: A solution of ligand **4** (0.05 g; 0.045 mmol) in CH_2Cl_2 (5 mL) was mixed with $ZnCl_2$ (0.06 g; 0.44 mmol) at room temp. under Ar. The resultant solvents were evaporated to dryness, twice dissolved in CH_2Cl_2 and filtered then evaporated to dryness. The residue was dissolved in CH_2Cl_2 (5 mL) and precipitated in an excess of Et_2O to give **9** as a light yellow powder (0.056 g; 95%). UV: λ = 338 nm (34650). ^{1}H NMR (CD_2Cl_2): δ = 3.11 (s, 6 H, *Me*bpy), 3.57 (s, 6 H, COO*Me*), 3.67, 4.36 (AB, J_{AB} = 13.5 Hz, 8 H, Ar-CH_2-Ar), 4.14 (s, 6 H, COO*Me*), 5.83 (s, 4 H, OCH_2bpy), 6.77 (t, J = 7.4 Hz, 2 H, H_p of Ar1), 6.99 (t, J = 7.4 Hz, 2 H, H_p of Ar2), 7.12 (d, J = 7.6 Hz, 4 H, H_m of Ar2), 7.20 (d, J = 7.6 Hz, 4 H, H_m of Ar1), 7.90 (s, 2 H, O*H*), 8.24 (s, 2 H, 3-H or 5-H of Mepy), 8.77 (s, 2 H, 3-H or 5-H of OCH_2py), 8.89 (s, 2 H, 3-H or 5-H of CH_3py), 9.90 (s, 2 H, 3-H or 5-H of OCH_2py) ppm. ES-MS (pos. mode, 100 V): m/z = 1315.3 [**4** + 2 $ZnCl_2$ + Na^+]$^+$, 1257.3 [**4** + $ZnCl_2$ + ZnCl]$^+$, 1179.4 [**4** + $ZnCl_2$ + Na^+]$^+$, 1043.4 [**4** + Na^+]$^+$, base peak. $C_{60}H_{52}Cl_2N_4O_{12}Zn_2$ (1293.63): calcd. C 55.71, H 4.05, N 4.39; found C 55.76, H 4.08, N 4.37.

X-ray Crystallographic Study: The intensity data were collected at 153 K (−120 °C) with a Stoe Mark II-Image Plate Diffraction System[44] equipped with a two-circle goniometer using Mo-K_α graphite-monochromated radiation. Image plate distance 100 mm, ω rotation scans 0−180° at φ 0°, and 0−21° at φ 90°, step Δω = 1.2°, 2θ range 2.29−59.53°, $d_{max.} - d_{min.}$ = 17.799−0.716 Å.

The structure was solved by direct methods using the program SHELXS-97.[45] The refinement and all further calculations were carried out using SHELXL-97.[46] The H-atoms were either located from Fourier difference maps and refined isotropically or included in calculated positions, and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

An empirical absorption correction was applied using the DIFABS routine in PLATON.[42] Transmission factors $T_{min.}/T_{max.}$ were 0.091 and 0.550, respectively. A considerable amount of disordered solvent was present and the SQUEEZE routine in PLATON revealed the presence of 380 electrons for a volume of 1559 Å^3. This could be equated to 9 molecules of CH_2Cl_2 per unit cell and the *hkl* file was modified accordingly.

Details for the experimental conditions, cell data, structure, and refinement data are given in Table 3.

Table 3. Crystal data and structural refinement of **9**

Empirical formula	$C_{62.25}H_{56.5}Cl_{8.5}N_4O_{12}Zn_2$ [$C_{14}Zn_2(C_{60}H_{52}N_4O_{12})$]·2.25($CH_2Cl_2$)]
Formula mass	1484.68
Temperature	153(2) K
Crystal system, Space group	triclinic, $P\bar{1}$
Unit cell dimensions	
a [Å]	11.6265(9)
b [Å]	16.3888(13)
c [Å]	36.039(3)
α [°]	80.222(6)
β [°]	89.128(6)
γ [°]	84.924(6)
V [Å^3]	6740.7(9)
Z	4
$D_{calcd.}$ [g·cm^{-3}]	1.463
Linear absorption coefficient [mm^{-1}]	1.110
F(000)	2656
Crystal size [mm]	0.50 × 0.24 × 0.10
θ Range for data collection [°]	1.15 to 24.10
Limiting indices	$-12 \le h \le 13$ $-18 \le k \le 18$ $-41 \le l \le 41$
Reflections collected/unique	43707/20350
Number of observed reflections	8602
Max./min. transmission	0.550 and 0.091
Data/restraints/parameters	20350/0/1468
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0854, $wR2$ = 0.2138
R indices (all data)	$R1$ = 0.1575, $wR2$ = 0.2493
Densities (max./min.) [e·Å^3]	0.465/−0.865

CCDC-213363 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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