Thin layer cyclic voltammetry: an efficient tool to determine the redox characteristics of large dendrimers

Yannick Rio,[a] Gianluca Accorsi,[b] Nicola Armaroli,*[b] Delphine Felder,[a] Eric Levillain*[c] and Jean-François Nierengarten*[a]

[a] Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, Université Louis Pasteur et CNRS, 23 rue du Loess, 67037, Strasbourg Cedex, France.
E-mail: niereng@ipcms.u-strasbg.fr

[b] Istituto per la Sintesi Organica e la Fotoreattività, Laboratorio di Fotochimica, Consiglio Nazionale della Ricerche, via Gobetti 101, 40129, Bologna, Italy. E-mail: armaroli@frae.bo.cnr.it

[c] Ingénierie Moléculaire et Matériaux Organiques, Université d'Angers et CNRS, 2, bd Lavoisier, 49045, Angers Cedex, France. E-mail: eric.levillain@univ-angers.fr

Dendrimers with an electroactive bis(phenanthroline) copper(I) core have been prepared and thin layer cyclic voltammetry (TLCV) found to be an efficient tool to determine their redox characteristics in spite of the slow electron transfer kinetics observed for the largest compounds.

In light of their unique structures and properties, dendrimers have been extensively studied in recent years.[1] Of particular current interest is the use of such architectures to mimic globular proteins owing to the ability of a dendritic framework to surround active core molecules, thus creating specific site-isolated microenvironments capable of affecting the properties of the core moiety.[2] Such dendritic effects can be conveniently analysed by cyclic voltammetry (CV) measurements. However, increasingly slow electron transfer kinetics have been observed for large electroactive dendrimers and the shielding of the central core is so effective in some cases that charge transfer could not be detected by classical CV measurements.[2–4] This kinetic effect appears to be a severe limitation for the determination of the redox characteristics of large dendrimers. In this paper, we show that thin layer cyclic voltammetry (TLCV) is an efficient alternative tool for such a purpose.

Dendrimers with an electroactive bis(phenanthroline)copper(I) core substituted with Fréchet-type[5] dendrons have been used for the present study (Fig. 1). The synthesis of the corresponding ligands **L0-4** is shown in Scheme 1. Compound **L0** was obtained from 2,9-dimethyl-1,10-phenanthroline (neocuproine) by deprotonation of the methyl groups with LDA to generate the corresponding dicarbanionic species, followed by reaction with benzyl bromide.

Compound **1** was prepared under similar conditions from neocuproine and p-[(t-butyldimethylsilyl)oxy]benzyl bromide. Treatment of **1** with tetra-n-butylammonium fluoride (TBAF) and subsequent reaction of the resulting diphenol **2** with the benzylic bromides GnBr in the presence of K$_2$CO$_3$ and 18-crown-6 (18-C-6) in refluxing acetone yielded the corresponding dendritic ligands **Ln**. Finally, treatment of **L0-4** with Cu(CH$_3$CN)$_4$·BF$_4$ in CH$_2$Cl$_2$ at room temperature afforded the corresponding copper(I) complexes (**L0-4**)$_2$Cu$^+$ in quantitative yields. The coordination of the ligands **L0-4** to the copper(I) cation was easily shown by ^{1}H-NMR spectroscopy. Effectively, the signal corresponding to the methylene groups directly attached to the phenanthroline moiety observed at ca. 3.4 ppm in the ligands **L0-4** is shifted to ca. 2.9 ppm in the complexes. This behaviour is characteristic of such compounds[6] and originates from the ring current effect of one phenanthroline moiety on the 2,9-substituents of the second one in the complex. The dendritic copper(I) complexes were also characterized by mass spectrometry. In all the cases, the pseudo-molecular ion peak corresponding to $[M - BF_4]^+$ is observed as the base peak providing clear evidence for the monodispersity of the com-
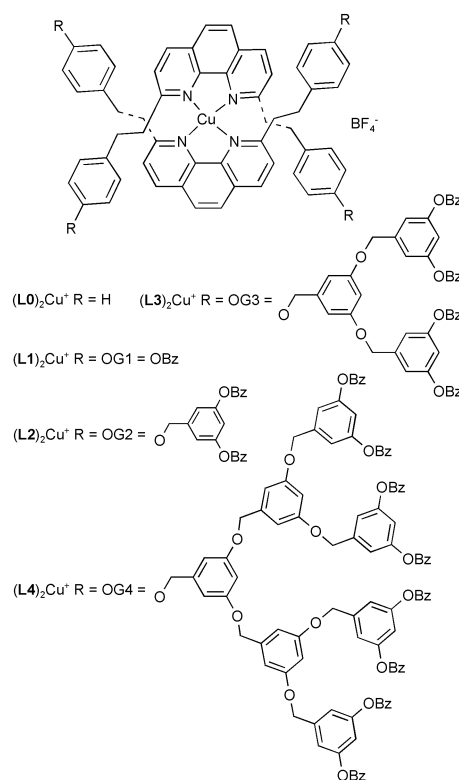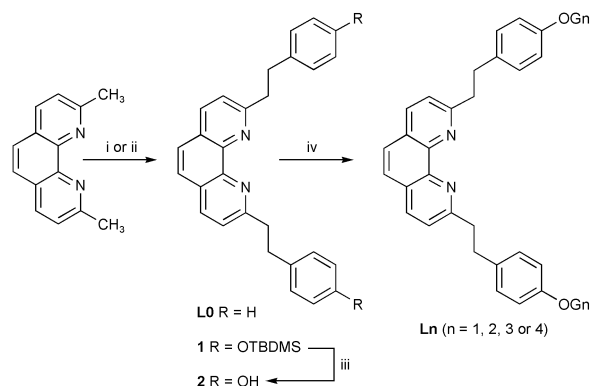

Fig. 1 Dendrimers (**Ln**)$_2$Cu$^+$ (Bz = benzyl).

Scheme 1 Reagents and conditions: (i) LDA, THF, −78 °C, 3 h then benzyl bromide, −78 °C to rt, 12 h (**L0**: 55%); (ii) LDA, THF, −78 °C, 3 h, then p-[(tert-butyldimethylsilyl)oxy]benzyl bromide, −78 °C to rt, 3 h (36%); (iii) TBAF, THF, 0°C, 3 h (97%); (iv) GnBr, K$_2$CO$_3$, 18-C-6, Δ, 48 h (n = 1: 76%; n = 2: 95%, n = 3: 96%, n = 4: 99%).

pounds.† The absorption spectra of the complexes $(\mathbf{Ln})_2\mathrm{Cu}^+$ recorded in CH_2Cl_2 exhibit the intense π–π* ligand-centered bands in the UV and the much weaker and broad metal-to-ligand charge-transfer (MLCT) bands with a maximum at 456 nm, typical of bis(2,9-dialkylphenanthroline)copper(I) chromophores.[7] In room temperature CH_2Cl_2 solutions, all the copper(I) complexes exhibit luminescence from the thermally equilibrated lowest singlet and triplet MLCT excited states.[7,8] The luminescence characteristics (λ_{max} = 714 nm; Φ_{em} = 0.0011 ± 0.0002; τ = 220 ± 20 ns) have been found to be substantially independent of the generation number under these conditions (CH_2Cl_2, air-free solutions).

The CV‡ of $(\mathbf{L0})_2\mathrm{Cu}^+$, performed at 0.1 V s^{-1} in semi-infinite diffusion conditions in CH_2Cl_2/0.5 M n-Bu$_4$PF$_6$, exhibits a classical signal for a reversible one-electron process corresponding to the oxidation of the copper cation[9] at 0.62 V $vs.$ Fc$^+$/Fc. By increasing the size of the dendritic shell, the electron transfer kinetic is attenuated as judged by a decrease in the peak current and an increase in the peak potential differences (Fig. 2). The electron transfer kinetics of the highest generation compound $(\mathbf{L4})_2\mathrm{Cu}^+$ is estimated to be close to 5×10^{-4} cm s^{-1}, compared to 5×10^{-3} cm s^{-1} for $(\mathbf{L0})_2\mathrm{Cu}^+$. The latter kinetic effect has been observed for several examples of dendrimers with an electroactive core and illustrates the dendritic shell effect that leads to a more hindered approach of the core to the electrode.[3,4]
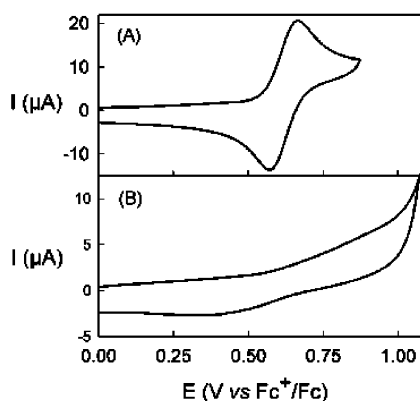

Fig. 2 Voltammograms of the $(\mathbf{L0})_2\mathrm{Cu}^+$ (A) and $(\mathbf{L4})_2\mathrm{Cu}^+$ (B) in CH_2Cl_2/n-Bu$_4$PF$_6$ (0.5 M) at 100 mV s^{-1}.

An investigation has been performed by CV in finite diffusion conditions‡ (TLCV)[10] in order to observe the electrochemical behaviour of these dendrimers at low scan rates. Fig. 3 displays the results obtained in TLCV at 2 mV s^{-1} for $(\mathbf{L4})_2\mathrm{Cu}^+$.
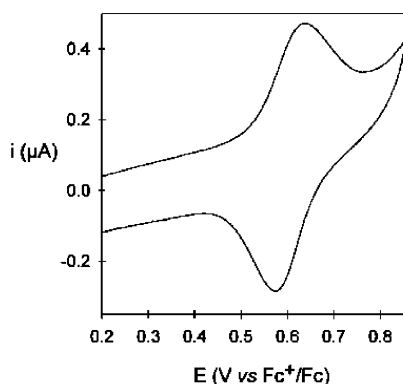

Fig. 3 Voltammogram of the dendrimer $(\mathbf{L4})_2\mathrm{Cu}^+$ in CH_2Cl_2/n-Bu$_4$PF$_6$ (0.5 M) at 2 mV s^{-1} in TLCV.

Surprisingly, the copper(I) bis-phenanthroline core of the largest compound $(\mathbf{L4})_2\mathrm{Cu}^+$ presents a nice and well-resolved signal characteristic of a reversible one-electron process (Fig. 3). Indeed, the voltammograms are similar for all the compounds under these experimental conditions and reveal identical redox potentials (0.62 V $vs.$ Fc$^+$/Fc) for all the copper(I) complexes $(\mathbf{Ln})_2\mathrm{Cu}^+$.

In conclusion, we have shown that the very weak electroactivity observed for the copper(I) bis-phenanthroline core of dendrimer $(\mathbf{L4})_2\mathrm{Cu}^+$ in classical CV can be enhanced by TLCV (note that experimentally, in TLCV with scan rates close to 1 mV s^{-1}, it can be expected to observe a reversible process with an electron transfer kinetic up to 10^{-6} cm s^{-1}). Therefore, TLCV is an efficient tool to determine the redox characteristics of large electroactive dendrimers.

Notes and references

† Selected data for $(\mathbf{L3})_2\mathrm{Cu}^+$: ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.54 (m, 8H), 2.93 (m, 8H), 4.86 (s, 8H), 4.94 (s, 16H), 5.00 (s, 32H), 6.04 (d, J = 8 Hz, 8H), 6.40 (d, J = 8 Hz, 8H), 6.56 (m, 12H), 6.61 (d, J = 2 Hz, 8H), 6.68 (d, J = 2 Hz, 16H), 7.29 (m, 80H), 7.68 (d, J = 8 Hz, 4H), 7.97 (s, 4H), 8.46 (d, J = 8 Hz, 4H). FAB-MS: m/z 3809 ([M − BF$_4$]$^+$, calcd. for C$_{252}$H$_{216}$N$_4$O$_{28}$Cu: 3808.5). Anal. Calcd. for C$_{252}$H$_{216}$N$_4$O$_{28}$CuBF$_4$.H$_2$O (3898.85): C 77.27, H 5.61, N 1.43%. Found: C 77.09, H 5.46, N 1.25%. For $(\mathbf{L4})_2\mathrm{Cu}^+$: ^{1}H-NMR (CDCl$_3$, 200 MHz): δ 2.49 (m, 8H), 2.89 (m, 8H), 4.77 (s, 8H), 4.93 (m, 16H), 5.99 (d, J = 8 Hz, 8H), 6.37 (d, J = 8 Hz, 8H), 6.53 (m, 28H), 6.61 (d, J = 2 Hz, 8H), 6.64 (d, J = 2 Hz, 48H), 7.29 (m, 160H), 7.59 (d, J = 8 Hz, 4H), 7.90 (s, 4H), 8.37 (d, J = 8 Hz, 4H). MALDI-TOF-MS: m/z 7203 ([M − BF$_4$]$^+$, calcd. for C$_{476}$H$_{408}$N$_4$O$_{60}$Cu: 7201.8). Anal. Calcd. for C$_{476}$H$_{408}$N$_4$O$_{60}$CuBF$_4$ H$_2$O (7294.82): C 77.79, H 5.68, N 0.76%. Found C 77.72, H 5.64, N 0.57%.

‡ CV has been performed in a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area and a platinum wire counter electrode. A silver wire served as quasi-reference electrode and its potential has been checked against the ferrocene/ferricinium couple (Fc$^+$/Fc) before and after each experiment. The electrolytic media involved CH_2Cl_2 and 0.5 mol L^{-1} of n-Bu$_4$PF$_6$. All experiments have been performed in a glove box containing dry, oxygen-free (<1 vpm) argon, at room temperature. Electrochemical experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation. Based on repetitive measurements, absolute errors on potentials have been found to be around ± 5 mV.

The setup for the TLCV experiments is described in ref. 10.

1 G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendrimers and Dendrons: Concepts, Syntheses, Applications*, VCH, Weinheim, 2001; J. M. J. Fréchet and D. A. Tomalia, *Dendrimers and other Dendritic Polymers*, Wiley, Chichester, 2001.
2 S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2001, **40**, 74 and references therein; C. B. Gorman and J. C. Smith, *Acc. Chem. Res.*, 2001, **34**, 60.
3 C. S. Cameron and C. B. Gorman, *Adv. Funct. Mater.*, 2002, **12**, 17.
4 P. J. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati and E. M. Sanford, *Angew. Chem., Int. Ed.*, 1994, **33**, 1739; P. J. Dandliker, F. Diederich, J.-P. Gisselbrecht, A. Louati and M. Gross, *Angew. Chem., Int. Ed.*, 1995, **34**, 2725; K. W. Pollak, J. W. Leon, J. M. J. Fréchet, M. Maskus and H. D. Abruna, *Chem. Mater.*, 1998, **10**, 30; N. Armaroli, C. Boudon, D. Felder, J.-P. Gisselbrecht, M. Gross, G. Marconi, J.-F. Nicoud, J.-F. Nierengarten and V. Vicinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 3730; D. K. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1563; C. M. Cardona, T. D. McCarley and A. E. Kaifer, *J. Org. Chem.*, 2000, **65**, 1857; N. Solladié, M. Gross, J.-P. Gisselbrecht and C. Sooambar, *Chem. Commun.*, 2001, 2206.
5 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.
6 C. O. Dietrich-Buchecker, P. A. Marnot, J.-P. Sauvage, J.-P. Kintzinger and P. Maltese, *Nouv. J. Chimie*, 1984, **8**, 573.
7 N. Armaroli, *Chem. Soc. Rev.*, 2001, **30**, 113.
8 D. Felder, J. F. Nierengarten, F. Barigelletti, B. Ventura and N. Armaroli, *J. Am. Chem. Soc.*, 2001, **123**, 6291; R. M. Everly and D. R. McMillin, *J. Phys. Chem.*, 1991, **95**, 9071.
9 P. Federlin, J.-M. Kern, A. Rastegar, C. O. Dietrich-Buchecker, P. A. Marnot and J.-P. Sauvage, *New J. Chem.*, 1990, **14**, 9.
10 F. Gaillard and E. Levillain, *J. Electroanal. Chem.*, 1995, **398**, 77.