Pergamon

Tetrahedron Letters 40 (1999) 273–276

TETRAHEDRON
LETTERS

Phenanthroline Ligands Substituted with Fullerene-Functionalized Dendritic Wedges and Their Copper(I) Complexes.

Jean-François Nierengarten*, Delphine Felder and Jean-François Nicoud

Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg,
Université Louis Pasteur et CNRS, 23 rue du Loess, 67037 Strasbourg, France

Received 9 October 1998; accepted 5 November 1998

Abstract: Fullerene-functionalized dentritic wedges with a carboxylic acid function have been attached to a phenanthroline diol derivative. Assembling of the resulting phenanthroline ligands around a copper(I) center gives the corresponding dendritic complexes with 4, 8 or 16 peripherical C_{60} groups.

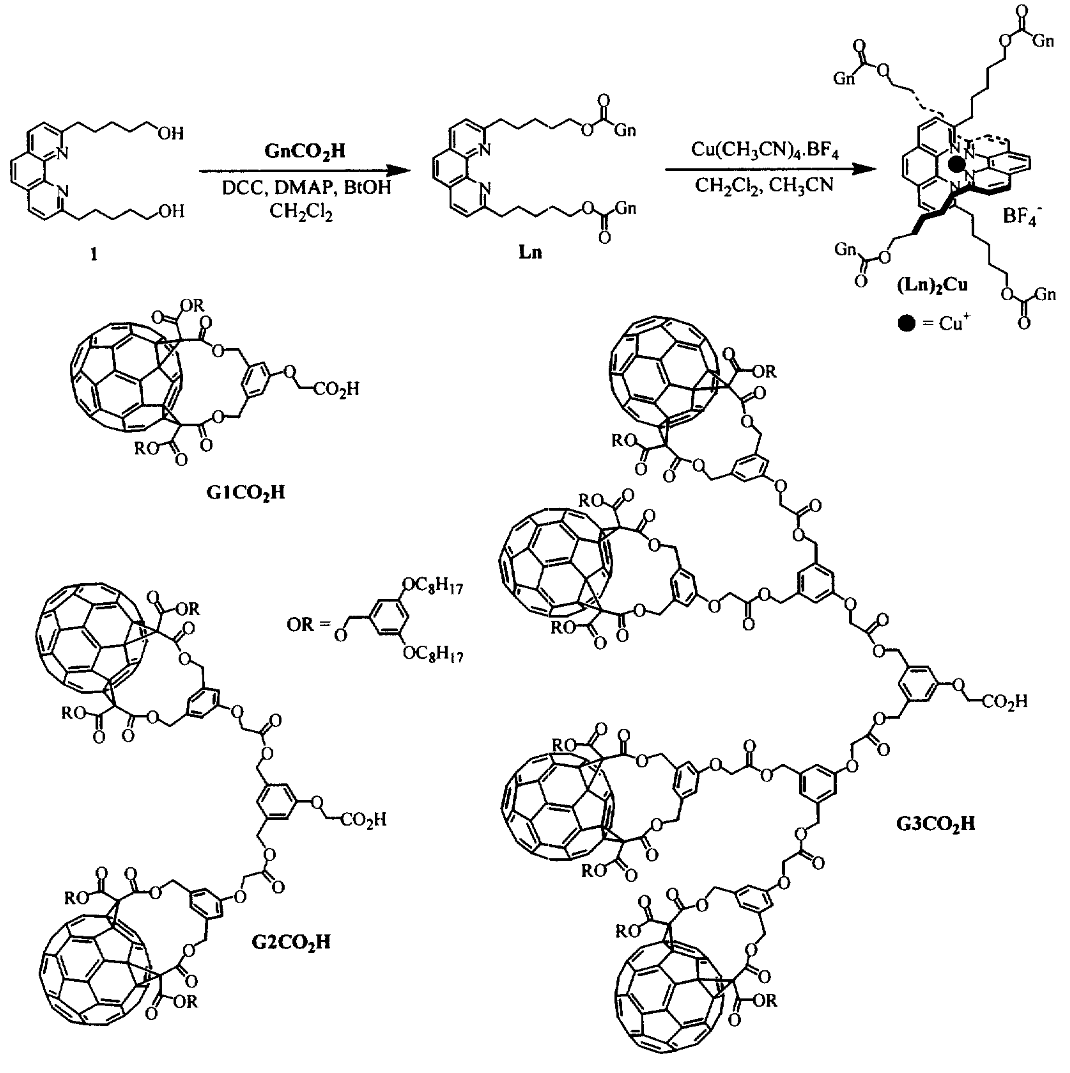
In light of their unique structures and properties, dendrimers have attracted increasing attention in the past decade[1] and the use of dendrimer building blocks for the self-assembly of larger nano- and mesoscopic supramolecular structures appears as an emerging area with unlimited possibilities for fundamental new discoveries and practical applications.[1,2] Dendrimers containing various electro- and photoactive chromophores have been prepared in order to explore influences of the microenvironment inside the macromolecule on the properties of the functional core.[1,2] On the other hand, because a dendrimer surface may contain multiple copies of a given functional group, it can be used for example as a platform for amplification of substrate binding[3] or as an antenna for light harvesting.[4] In this paper we report the preparation of new dendrimers with a bis(1,10-phenanthroline)copper(I) core and fullerene π chromophores at the periphery. The largest dendritic copper(I) complex reported herein [**(L3)$_2$Cu**] contains 16 peripherical C_{60} groups. Photoinduced intramolecular processes such as electron or energy transfer between the peripheral C_{60} subunits and the central copper(I) complex are expected to occur.[5] Furthermore such processes should become more efficient for the complexes of highest generations due to the increasing number of fullerene units (antenna effect).

Diol **1** was prepared according to the literature procedure[6] and allowed to react with the dendrons **G1-3CO$_2$H**[7] under DCC-mediated esterification conditions to give the corresponding ligands **L1-3** (Scheme 1). In a typical procedure, DCC (1 equiv.) was added to a stirred solution of **G1CO$_2$H** (500 mg), diol **1** (0.45

Fax: 33 388 10 72 46, E-mail: niereng@michelangelo.u-strasbg.fr

0040-4039/99/$ - see front matter © 1998 Published by Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)02379-X

equiv.), 4-dimethylaminopyridine (DMAP, 0.2 equiv.) and 1-hydroxybenzotriazole (BtOH, 0.2 equiv.) in CH_2Cl_2 (20 ml) at 0°C and the solution was allowed to warm slowly to room temperature (1 h). After stirring for 24 hrs, the mixture was filtered and concentrated. Column chromatography (SiO_2, CH_2Cl_2 containing 5% MeOH) followed by gel permeation chromatography (Biorads, Biobeads SX-1, toluene) yielded **L1** (370 mg, 75% yield). Ligand **L2** was prepared from **$G2CO_2H$** in 48% yield under similar conditions, and **L3** from **$G3CO_2H$** in 24% yield.



Scheme 1. Synthesis of **L1-3** and of the corresponding copper(I) complexes **(L1-3)$_2$Cu**.

The copper(I) complexes **(L1-3)$_2$Cu** were obtained by treatment of the corresponding ligands **L1-3** (1 equiv.) with $Cu(CH_3CN)_4.BF_4$ (0.6 equiv.) in CH_2Cl_2/CH_3CN (2/1) at room temperature. **(L1-3)$_2$Cu** were thus formed in good yields; however, due to difficulties encountered during their purification, the isolated yields were low [56% for **(L1)$_2$Cu**, 35% for **(L2)$_2$Cu** and 33% for **(L3)$_2$Cu**]. Partial decomposition of the complexes was observed on Al_2O_3 (also on SiO_2); effectively, a part of the product stuck all along the column (this could be easily observed because of the compound's dark red color) and could not be eluted any more.

Whereas the coordination of the ligands **L1-3** to the copper(I) cation could not be easily observed by apparition of the metal-to-ligand charge transfer (MLCT) band characteristic of bis(2,9-dialkyl-1,10-phenanthroline)copper(I) derivatives at *ca.* 450 nm[8] since it is masked by the fullerene absorption in this region, the ^{1}H-NMR spectra of **(L1-3)$_2$Cu** provide good evidence for their formation.[9] Effectively, the methylene group directly attached to the phenanthroline core observed at *ca.* 3.2 ppm in the ligands **L1-3** is shifted to *ca.* 2.6 in the corresponding complexes **(L1-3)$_2$Cu**. This particular behavior is highly specific of such copper(I) complexes[10] and is the result of the ring current effect of one phenanthroline subunit on the 2,9-substituents of the second one in the complex. Furthermore, the FAB-MS confirmed the structure of **(L1)$_2$Cu** with signals at m/z = 7872.7 and 3967.6 corresponding to $[M - BF_4^-]^+$ (calc. for $C_{532}H_{400}O_{60}N_4Cu$: 7872.6) and $[M - \mathbf{L1} - BF_4^-]^+$ (calc. for $C_{266}H_{200}O_{30}N_2Cu$: 3968.1), respectively. In the FAB-MS spectra of **(L2)$_2$Cu**, only the peak corresponding to $[M - \mathbf{L2} - BF_4^-]^+$ could be observed at m/z = 7908.1 (calc. for $C_{530}H_{392}O_{66}N_2Cu$: 7908.5). It should be pointed out that no peaks corresponding to defected dendrons were observed in the FAB-mass spectra of **(L1-2)$_2$Cu**, thus providing clear evidence for their monodispersity. In the FAB-MS of **(L3)$_2$Cu**, no characteristic peak could be observed. Due to the presence of the 64 surrounding long alkyl chains, **(L3)$_2$Cu** aggregates strongly and high energy is required for dissociation during FAB-MS analysis, therefore fragmentation occurs, especially on the fragile benzylic ester functions; furthermore its molecular mass is quite high (31601.8). Nevertheless, the NMR and UV/Vis data obtained for **(L3)$_2$Cu** and comparison with **(L1-2)$_2$Cu** provide very good evidence for the proposed structure.

In this paper, we have shown that the dendrons **G1-3CO$_2$H** described in the previous communication are useful building blocks for the preparation of monodisperse dendrimers of high molecular weight and up to 16 fullerene π chromophores have been assembled around a bis(phenanthroline) copper(I) core. The electrochemical and photophysical behavior of those new compounds are currently under investigation in order to see how the surrounding fullerene groups affect the properties of the central copper(I) complex.

Acknowledgements: We thank A. Van Dorsselaer and R. Hueber for recording the mass spectra and Hoechst AG for Samples of C_{60}.

References and Notes

1) Newkome, G. R.; Moorefield, C. N.; Vögtle, F.; *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH, Weinheim, **1996**.

2) a) Zeng, F.; Zimmerman, S. C.; *Chem. Rev.* **1997**, *97*, 1681-1712 and references cited therein; b) Smith, D. K.; Diederich, F.; *Chem. Eur. J.* **1998**, *4*, 1353-1361.
3) a) Roy, R.; Zanini, D.; Meunier, S. J.; Romanowska, A.; *J. Chem. Soc., Chem. Commun.* **1993**, 1869-1872; b) Aoi, K.; Itoh, K.; Okada, M.; *Macromolecules* **1995**, *28*, 5391-5393.
4) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M.; *Acc. Chem. Res.* **1998**, *31*, 26-34.
5) A rotaxane made from a bis-phenanthroline copper(I) complex and two C_{60} units acting as stoppers has been already reported and photoinduced intramolecular processes have been observed in this multicomponent molecular system, see: Armaroli, N.; Diederich, F.; Dietrich-Buchecker, C. O.; Flamigni, L.; Marconi, G.; Nierengarten, J.-F.; Sauvage, J.-P.; *Chem. Eur. J.* **1998**, *4*, 406-416.
6) Nierengarten, J.-F.; Dietrich-Buchecker, C. O.; Sauvage, J.-P.; *New J. Chem.* **1996**, *20*, 685-693.
7) Nierengarten, J.-F.; Felder, D.; Nicoud, J.-F.; *Tetrahedron Lett.* **1999**, *40*, 269-272.
8) a) Alonso-Vante, N.; Ern, V.; Chartier, P.; Dietrich-Buchecker, C. O.; McMillin, D. R.; Marnot, P. A.; Sauvage, J.-P.; *Nouv. J. Chim.* **1983**, *7*, 3-5; b) Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Sauvage, J.-P.; *Inorg. Chem.* **1989**, *28*, 4070-4072.
9) Selected spectroscopic data: **L2**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, J = 7, 48 H), 1.20-2.10 (m, 204 H), 3.20 (br t, J = 6.5, 4 H), 3.83 (t, J = 6.5, 32 H), 4.25 (t, J = 6.5, 4 H), 4.65 (s, 4 H), 4.70 (s, 8 H), 5.08 (d, J = 13, 8 H), 5.22 (s, 8 H), 5.28 (s, 16 H), 5.72 (d, J = 13, 8 H), 6.34 (t, J = 2, 8 H), 6.45 (d, J = 2, 16 H), 6.77 (br s, 8 H), 6.91 (br s, 4 H), 7.00 (br s, 2 H), 7.13 (br s, 4 H), 7.50 (d, J = 8, 2 H), 7.70 (s, 2 H), 8.12 (d, J = 8, 2 H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (178000), 320 (sh, 53500), 375 (sh, 59300), 436 (17200), 467 nm (14000); **L3**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, J = 7, 96 H), 1.20-2.10 (m, 396 H), 3.18 (t, J = 6.5, 4 H), 3.83 (t, J = 6.5, 64 H), 4.23 (t, J = 6.5, 4 H), 4.62 (s, 4 H), 4.69 (s, 24 H), 5.06 (d, J = 13, 16 H), 5.19 (s, 24 H), 5.28 (s, 32 H), 5.71 (d, J = 13, 16 H), 6.34 (br s, 16 H), 6.45 (br s, 32 H), 6.77 (br s, 16 H), 6.88 (br s, 12 H), 6.90 (br s, 2 H), 6.99 (br s, 4 H), 7.12 (br s, 8 H), 7.46 (d, J = 8, 2 H), 7.70 (s, 2 H), 8.12 (d, J = 8, 2 H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (207000), 320 (sh, 64000), 375 (sh, 122000), 436 (36500), 467 nm (29500); **$(L2)_2Cu$**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, J = 7, 96 H), 1.20-2.00 (m, 408 H), 2.65 (br t, J = 6.5, 8 H), 3.70 (br t, J = 6.5, 8 H), 3.83 (t, J = 6.5, 64 H), 4.50 (s, 8 H), 4.71 (s, 16 H), 5.08 (d, J = 13, 16 H), 5.23 (s, 16 H), 5.28 (s, 32 H), 5.72 (d, J = 13, 16 H), 6.34 (br s, 16 H), 6.45 (br s, 32 H), 6.79 (br s, 16 H), 6.89 (br s, 8 H), 7.00 (br s, 4 H), 7.13 (br s, 8 H), 7.79 (d, J = 8, 4 H), 8.03 (s, 4 H), 8.56 (d, J = 8, 4 H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (323000), 320 (sh, 97500), 375 (sh, 103000), 436 (35300), 467 nm (29300); **$(L3)_2Cu$**: ^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 0.88 (t, J = 7, 192 H), 1.20-2.00 (m, 792 H), 2.68 (br t, J = 6.5, 8 H), 3.68 (t, J = 6.5, 8 H), 3.85 (t, J = 6.5, 128 H), 4.63 (br s, 56 H), 5.08 (d, J = 13, 32 H), 5.12 (br s, 48 H), 5.28 (br s, 64 H), 5.72 (d, J = 13, 32 H), 6.34 (br s, 32 H), 6.45 (br s, 64 H), 6.78 (br s, 32 H), 6.85 (br s, 28 H), 6.98 (br s, 8 H), 7.13 (br s, 16 H), 7.77 (d, J = 8, 4 H), 8.01 (s, 4 H), 8.50 (d, J = 8, 4 H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (360000), 320 (sh, 121000), 375 (sh, 158000), 436 (50500), 467 nm (41600).
10) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P.; Kintzinger, J.-P.; Maltese, P.; *Nouv. J. Chim.* **1984**, *8*, 573-582.