A Copper(I) Bis-phenanthroline Complex Buried in Fullerene-Functionalized Dendritic Black Boxes**

Nicola Armaroli,* Corinne Boudon,
Delphine Felder, Jean-Paul Gisselbrecht,
Maurice Gross,* Giancarlo Marconi,
Jean-François Nicoud, Jean-François
Nierengarten,* and Veronica Vicinelli

Dedicated to Prof. Guy Solladié
on the occasion of his 60th birthday

On account of their fascinating structures and properties, dendrimers have attracted increasing attention in the past few years.[1] In the development of procedures to synthesize monodispersed dendrimers,[1, 2] increasing emphasis is being placed on the design and study of functionalized dendrimers.[3–5] For example, because the dendrimer surface may contain multiple copies of a given chromophore, it can be used as an antenna for light harvesting.[4] It is conceivable that a large number of peripheral chromophores could prevent direct photoexcitation at the central core. Whereas dendrimers containing various electro- and photoactive chromophores have been prepared in order to explore the influence of the microenvironment inside the macromolecule on the properties of the functional core,[5] very large surrounding dendritic branches may be able to isolate a central functional core and thus prevent any external contact.

Here we report on the electrochemical and photophysical behavior of dendrimers with a bis(1,10-phenanthroline)copper(I) ($[Cu(phen)_2]^+$) core and peripheral fullerene π chromophores[6] and show how the surrounding fullerene-functionalized dendritic branches are able to isolate the central Cu^I complex. The dendrimers and the parent compounds are depicted in Figure 1.

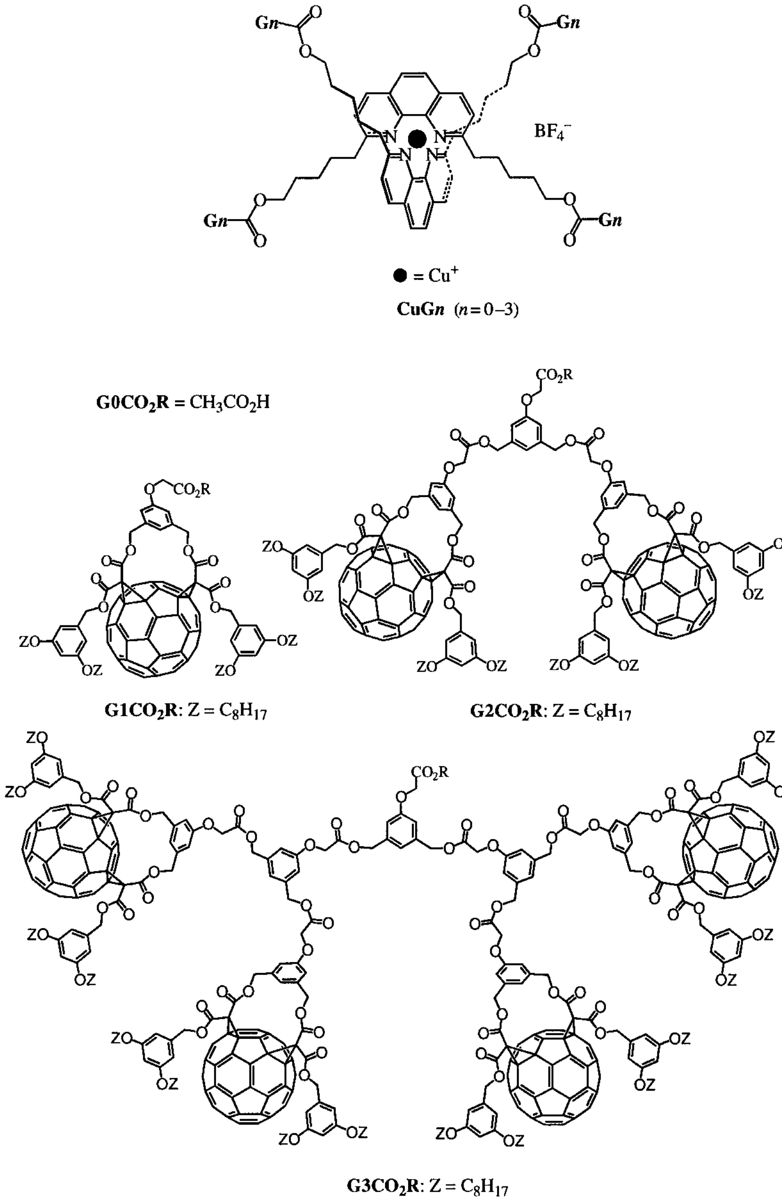

Figure 1. Schematic representation of the investigated dendrimers.

The electrochemical investigations on **GnCO_2tBu** and **CuGn** were carried out by steady-state voltammetry (SSV) on a rotating-disk electrode and cyclic voltammetry (CV) in CH_2Cl_2/0.1 M Bu_4NPF_6 on a glassy carbon electrode.[7a] Both SSV and CV gave identical redox potentials (Table 1). Compound **G1CO_2tBu** showed the characteristic behavior previously reported for fullerene *cis*-2 bis-adducts.[7] Whereas the first reduction at −1.07 V versus ferrocene/ferrocenyl cation (Fc/Fc^+) is reversible, the second reduction at about −1.4 V is irreversible. It was shown that the second electron transfer in *cis*-2 derivatives is followed by a chemical reaction.[7] The similar results that were obtained for reductions of the dendrimers of higher generations **G2CO_2tBu**, **G3CO_2tBu**, and **CuG1–CuG3** show that the peripheral fullerene subunits behave as independent redox centers in all compounds. The Cu^I/Cu^{II} oxidation potential of **CuG1** remains unchanged relative to the parent compound **CuG0**, and this indicates the absence of intramolecular electronic

---

[*] Dr. N. Armaroli, Dr. G. Marconi, Dr. V. Vicinelli
Istituto di Fotochimica e Radiazioni d'Alta Energia del CNR
via Gobetti 101, I-40129 Bologna (Italy)
Fax: (+39) 051-6399844
E-mail: armaroli@frae.bo.cnr.it

Prof. M. Gross, Dr. C. Boudon, Dr. J.-P. Gisselbrecht
Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide
Université Louis Pasteur and CNRS
UMR no. 7512, 4 rue Blaise Pascal, F67008 Strasbourg (France)
Fax: (+33) 3-88-61-15-53
E-mail: gross@chimie.u-strasbg.fr

Dr. J.-F. Nierengarten, D. Felder, Prof. J.-F. Nicoud
Groupe des Matériaux Organiques
Institut de Physique et Chimie des Matériaux de Strasbourg
Université Louis Pasteur and CNRS
23 rue du Loess, F-67037 Strasbourg (France)
Fax: (+33) 3-8810-7246
E-mail: niereng@michelangelo.u-strasbg.fr

[**] This work was supported by the CNRS and the CNR. We are grateful to Dr. Francesco Barigelletti and Dr. Lucia Flamigni for valuable discussions and advice, and also to M. Minghetti for technical assistance.

Table 1. Data on the reduction and oxidation of **G1CO$_2$*t*Bu – G3CO$_2$*t*Bu** and **CuG0 – CuG3** determined by CV on a glassy carbon electrode in CH_2Cl_2/0.1 M Bu_4NPF_6.[a]

Compound	Reduction E_1	Reduction E_2	Oxidation E_1
G1CO$_2$*t*Bu	– 1.07 (75)	– 1.45[b]	+ 1.2[b]
G2CO$_2$*t*Bu	– 1.07 (75)	– 1.45[b]	+ 1.1[b]
G3CO$_2$*t*Bu	– 1.08 (80)	– 1.45[b]	+ 1.1[b]
CuG0	– 2.20[b, c]	–	+ 0.60 (70)
CuG1	– 1.08 (80)	– 1.39[b]	+ 0.60[d, e]
CuG2	– 1.08 (80)	– 1.43[b]	n.o.[f]
CuG3	– 1.07 (70)	– 1.40[b]	n.o.[f]

[a] Values for $(E_{pa} + E_{pc})/2$ [V] vs Fc/Fc^+ and ΔE_{pc} [mV] (in parenthesis) at a scan rate of 0.1 V s^{-1}. [b] Peak potential values at a scan rate v of 0.1 V s^{-1}; irreversible process. [c] Reversible for $v > 0.5$ V s^{-1}. [d] Poorly resolved signal of small amplitude, irreversible process. [e] The slope observed in SSV for this oxidation is ca. 200 mV per log unit, which also indicates an irreversible oxidation process. [f] n.o. = not observed.

communication between the central copper(I) complex and the four surrounding fullerene units in **CuG1**. The amplitude of the fullerene-centered reduction wave is expected to be four times larger than that of the Cu-centered oxidation. Surprisingly, however, the amplitude of the oxidation peak of **CuG1** is smaller than expected.[8] In addition, the metal-centered oxidation became irreversible, which indicates a decrease in the electron-transfer rate, as was previously observed for other electroactive cores in dendrimers.[3] This suggests that the bulky fullerene units around the Cu center partially prevent its approach to the electrode surface and, as a result, oxidation at the central core could not be completed on the timescale of the CV measurement. Consistent with this, the electrochemical oxidation of the Cu site could no longer be observed with dendrimers of the highest generations **CuG2** and **CuG3**. The central electroactive site appears to be totally inaccessible owing to isolation by the bulkier surrounding dendrimer structures. This observation is in full agreement with molecular modeling studies, which show that the interior of the dendrimer in **CuG2** and **CuG3** is virtually inaccessible to external contacts.[9]

The absorption and luminescence spectra of **CuG0**, **G1CO$_2$*t*Bu**, and **CuG1** in CH_2Cl_2 are shown in Figure 2. The absorption spectrum of **CuG0** in CH_2Cl_2 exhibits the typical intense $\pi-\pi^*$ ligand-centered bands in the UV and the much weaker metal-to-ligand charge-transfer (MLCT) bands in the visible region, typical of the $[Cu(phen)_2]^+$-type chromophore.[11] In CH_2Cl_2, **CuG0** displays luminescence from the lowest MLCT excited state[12] both at room temperature ($\lambda_{max} = 718$ nm, $\Phi = 0.0011$, $\tau = 163$ ns, deaerated solution) and at 77 K ($\lambda_{max} = 670$ nm, $\tau = 3.2$ µs). The absorption spectrum of the dimethanofullerene **G1CO$_2$*t*Bu** is less resolved than those of methanofullerenes and plain C_{60}.[13] In the UV region, only one distinct band is present ($\lambda_{max} = 258$ nm, $\varepsilon = 107000\,M^{-1}cm^{-1}$) with two shoulders above 300 nm, in contrast to the two distinct bands observed for the parent compounds in the same spectral region.[13] In the visible region the spectrum is very broad, and the band corresponding to the lowest allowed singlet transition, which is typically very sharp and distinguishable for C_{60},[13] is barely detectable ($\lambda_{max} = 433$ nm, $\varepsilon = 3300\,M^{-1}cm^{-1}$).

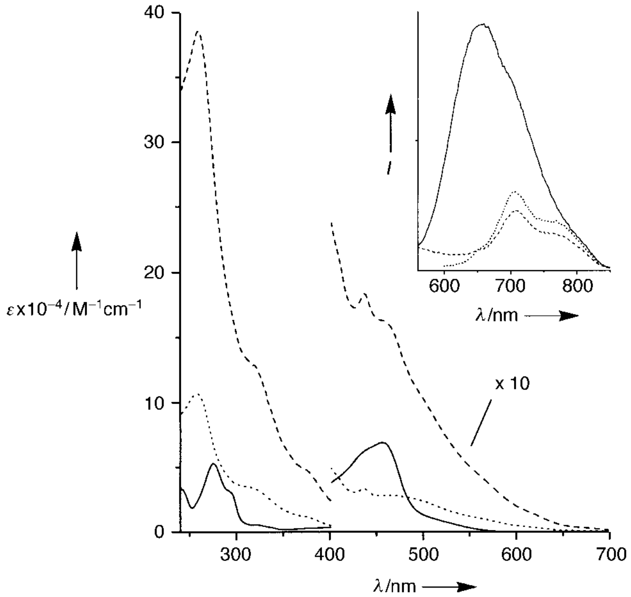

Figure 2. Absorption spectra of **CuG0** (solid line), **G1CO$_2$*t*Bu** (dotted line), and **CuG1** (dashed line). Inset: emission spectra of the same compounds at $\lambda_{exc} = 456$ nm, $A = 0.150$ (CH_2Cl_2, 298 K).

The compound **G1CO$_2$*t*Bu** displays fluorescence at room temperature ($\lambda_{max} = 706$ nm, $\Phi_{em} = 0.0003$, $\tau = 1.5$ ns, CH_2Cl_2) and 77 K ($\lambda_{max} = 704$ nm, $\tau = 2.0$ ns, methylcyclohexane glass). The picosecond time-resolved absorption spectrum of **G1CO$_2$*t*Bu** (Figure 3) shows singlet – singlet ($\lambda_{max} = 560$ and 900 nm) and triplet – triplet ($\lambda_{max} = 705$ nm) absorption features. On a longer timescale the decay of the triplet state can be determined (18 µs, deaerated solution) and is shorter than that of C_{60} (60 µs),[13] as is typical for substituted fullerenes.[14] The absorption spectra of **G2CO$_2$*t*Bu** and **G3CO$_2$*t*Bu** have the same shape as that of **G1CO$_2$*t*Bu**, but the molar extinction coefficients are respectively two and four times larger than those of **G1CO$_2$*t*Bu**. They also exhibit the same luminescence properties.

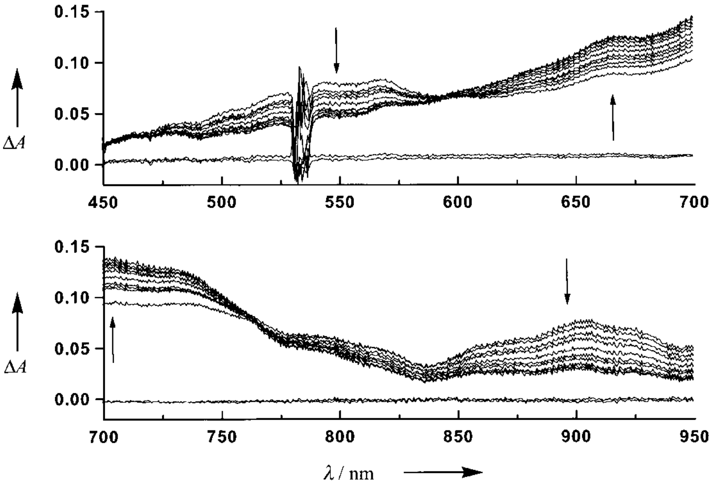

Figure 3. Picosecond transient absorption spectrum of **G1CO$_2$*t*Bu** (CH_2Cl_2; $\lambda_{exc} = 532$ nm; energy: 5 mJ per pulse; $A = 0.220$; time intervals 330 ps).

In an attempt to rationalize the spectroscopic features of the fullerene dendrons, quantum mechanical calculations were performed on **G1CO$_2$*t*Bu** with the ZINDO/S program,[15] with a CI limited to 196 singly excited configurations after optimization of the geometry by the MM+ molecular mechanics procedure. The results of the calculation are in good agreement with the energy of the main peaks in the absorption spectrum. In particular, the lowest singlet transition is calculated to be at 647 nm, with a small oscillator strength ($f = 0.004$) owing to the disruption of the high symmetry of C_{60} (I_h) upon substitution (C_s). The lowest triplet transition is located at 882 nm, that is, a large red shift with respect to the unsubstituted compound ($\lambda(T_1) = 758$ nm for C_{60}). The first allowed singlet transition (T_{1u}) is split into three components at 453, 449 and 445 nm, with a total f value of 0.024, while at higher energies, relevant bands are found at 390 ($f = 0.113$), 308 ($f = 0.083$), and 252 nm ($f = 0.229$), in good agreement with the peaks detected at 372, 312, and 259 nm. The most notable peaks of the transient spectrum (Figure 3) are calculated to lie at 1083, 994, 920, 580 and 526 nm for the singlet manifold ($S_1 \rightarrow S_n$), and at 1263 and 658 nm for the triplet-triplet transitions.

The absorption spectra of the dendrimers **CuG1**–**CuG3** correspond to the sum of the corresponding component units, without appreciable ground-state electronic interactions among them. The increasing number of fullerene units around the Cu^I complex core implies increased shielding of the central core from incident light, especially in the UV region. In this regard, it is noteworthy that the molar extinction coefficient of **CuG3** at 258 nm reaches a value of $1.5 \times 10^6\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$, probably one of the highest ever found for soluble supermolecules, and thus allows a limit of detection below 1 ppm in CH_2Cl_2.

Upon selective excitation of the peripheral units at 600 nm, fullerene fluorescence is observed for all dendrimers **CuG*n***; the corresponding emission quantum yield and excited state lifetimes are identical, within experimental error, to those of the corresponding dendronic subunits **G*n***. Despite the fact that selective excitation of the $[Cu(phen)_2]^+$ central core is not possible, clear evidence for the quenching of the luminescence of such a moiety can be obtained. For instance, by exciting **CuG1** at 456 nm, although the light partition is about 40% (core) and 60% (fullerenes), the MLCT emission of the central core is dramatically quenched in a steady-state experiment (Figure 2). Analogous patterns are shown by **CuG2** and **CuG3**, although the light partition is less favorable for the central core because of the above-mentioned shielding effect. In a time-resolved experiment we did not observe any residual luminescence decay for **CuG1** within the time resolution (20 ns); hence, a rate constant of $k_q > 5 \times 10^7\,\mathrm{s}^{-1}$ can be estimated for the quenching of the luminescence of the central core by the peripheral units.

The photophysics of the dendrimers can be rationalized by means of an energy level diagram with all low-lying electronic levels (Figure 4), that is, the lowest singlet (^{1}G*n*) and triplet (^{3}G*n*) levels centered on the peripheral fullerene fragments and the lowest MLCT excited state of the Cu^I-complexed central core (^{MLCT}Cu). The energy values were obtained from corrected luminescence band maxima at 77 K or, where these were unavailable, as in the case of ^{3}G*n*,[16] from theoretical calculations. It is noteworthy that a new low-energy electronic level is made available in the supramolecular array, namely, the charge-separated state Cu$^+$–G*n*$^-$ at 1.68 eV, as deduced from the electrochemical data. In principle, the quenching of the MLCT excited state (positioned at 1.85 eV) can occur by three pathways:[17]

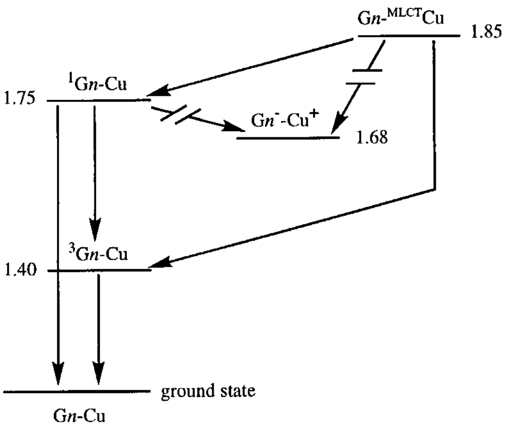

Figure 4. Energy-level diagram describing the excited state deactivation pathways and the intercomponent energy transfer processes of the dendrimers in CH_2Cl_2. On the left are the lowest electronic levels centered on the peripheral fullerene units, and on the right the lowest MLCT level centered on the $[Cu(phen)_2]^+$ core. G*n*$^-$–Cu$^+$ represents the charge-separated state formed upon electron transfer from the electron-donating central core to an electron-accepting fullerene peripheral fragment.

1) Energy transfer to the fullerene centered singlet ^{1}G*n* ($\Delta G = -0.10$ eV)
2) Energy transfer to the fullerene centered triplet ^{3}G*n* ($\Delta G = -0.45$ eV)
3) Electron transfer to the charge separated state ($\Delta G = -0.17$ eV).

We believe that electron transfer (process 3) is not the prevailing phenomenon for at least two reasons: 1) it does not take place from ^{1}G*n* (no quenching of the fluorescence of the fullerene moiety is observed), although a similar thermodynamic driving force ($\Delta G = -0.07$ eV) would be involved, and 2) the quenching of the central core also occurs at 77 K, but electron-transfer in a rigid matrix is usually blocked unless it is exothermic by at least 0.6–0.7 eV[18] (in our case $\Delta G = -0.17$ eV; Figure 4). A straightforward discussion of the energy transfer mechanism involved, that is, dipole–dipole (Förster-type) or exchange (Dexter-type), is made difficult by the fact that the two partners are linked by flexible connections. We calculated the rate of energy transfer according to a Förster mechanism using spectroscopic quantities[13] on the order of $7 \times 10^7\,\mathrm{s}^{-1}$ for components separated by only 5 Å, a distance at which the exchange mechanism can also play a role. The determination of the experimental rate constants by ultrafast luminescence spectroscopy will probably give a better insight into this issue.

Experimental section

All photophysical investigations were carried out in CH_2Cl_2 (Carlo Erba, spectrofluorimetric grade). Absorption spectra were recorded with a Perkin-Elmer λ5 spectrophotometer. Emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter. Details of the correction of emission spectra and the determination of luminescence quantum yields were as reported previously.[14] Luminescence lifetimes on the nanosecond timescale were determined with an IBH single photon counting apparatus ($\lambda_{exc} = 337$ nm) or a single-shot Nd:YAG laser apparatus ($\lambda_{exc} = 532$ nm). Transient absorption spectra and lifetimes with picosecond and nanosecond resolution were obtained with two pump and probe systems based on Nd:YAG lasers; excitation with the second (532 nm) or third harmonic (355 nm) was used. Details of this time-resolved spectroscopy equipment were reported earlier.[14] Experimental uncertainties were estimated to be ±8% for lifetime determination, ±20% for quantum yields, and ±3 nm for emission and absorption peaks.

Received: May 31, 1999
Revised version: July 23, 1999 [Z13491IE]
German version: *Angew. Chem.* **1999**, *111*, 3895–3899

Keywords: copper · dendrimers · electrochemistry · fullerenes · UV/Vis spectroscopy

---

[1] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules: Concepts, Synthesis, Perspectives*, VCH, Weinheim, **1996**.

[2] H.-B. Mekelburger, W. Jaworek, F. Vögtle, *Angew. Chem.* **1992**, *104*, 1609; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1571; J. Issberner, R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413.

[3] F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681; D. K. Smith, F. Diederich, *Chem. Eur. J.* **1998**, *4*, 1353; A. Archut, F. Vögtle, *Chem. Soc. Rev.* **1998**, *27*, 233; H. Frey, *Angew. Chem.* **1998**, *110*, 2313; *Angew. Chem. Int. Ed.* **1998**, *37*, 2193; M. Fischer, F. Vögtle, *Angew. Chem.* **1999**, *111*, 934; *Angew. Chem. Int. Ed.* **1999**, *38*, 884; M. A. Hearshaw, J. R. Moss, *Chem. Commun.* **1999**, 1.

[4] S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto, V. Balzani, *Chem. Eur. J.* **1995**, *1*, 211; A. Bar-Haim, J. Klafter, R. Kopelman, *J. Am. Chem. Soc.* **1997**, *119*, 6197; S. Serroni, A. Juris, M. Venturi, S. Campagna, I. Resino Resino, G. Denti, A. Credi, V. Balzani, *J. Mater. Chem.* **1997**, *7*, 1227; D.-L. Jiang, T. Aida, *Nature* **1997**, *388*, 454; R. Kopelman, M. Shortreed, Z.-Y. Shi, W. Tan, Z. Xu, J. S. Moore, A. Bar-Haim, J. Klafter, *J. Phys. Chem. B* **1997**, *101*, 6318; V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26.

[5] Recent examples: C. J. Hawker, K. L. Wooley, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1993**, *115*, 7638; P. J. Dandliker, F. Diederich, M. Gross, C. B. Knobler, A. Louati, E. M. Sanford, *Angew. Chem.* **1994**, *106*, 1821; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1739; P. J. Dandliker, F. Diederich, J.-P. Gisselbrecht, A. Louati, M. Gross, *Angew. Chem.* **1995**, *107*, 2906; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2725; H.-F. Chow, I. Y.-K. Chan, D. T. W. Chan, R. W. M. Kwok, *Chem. Eur. J.* **1996**, *2*, 1085; E. C. Constable, P. Haverson, M. Oberholzer, *Chem. Commun.* **1996**, 1821; J. P. Collman, L. Fu, A. Zingg, F. Diederich, *Chem. Commun.* **1997**, 193; J. Issberg, F. Vögtle, L. De Cola, V. Balzani, *Chem. Eur. J.* **1997**, *3*, 706; G. R. Newkome, E. He, *J. Mater. Chem.* **1997**, *7*, 1237; X. Camps, H. Schönberger, A. Hirsch, *Chem. Eur. J.* **1997**, *3*, 561; I. Jestin, E. Levillain, J. Roncali, *Chem. Commun.* **1998**, 2655; A. P. H. J. Schenning, R. E. Martin, M. Ito, F. Diederich, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Chem. Commun.* **1998**, 1013; P. R. L. Malenfant, L. Groenendaal, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1998**, *120*, 10990; F. Cardullo, F. Diederich, E. Echegoyen, T. Habicher, N. Jayaraman, R. M. Leblanc, J. F. Stoddart, S. Wang, *Langmuir* **1998**, *14*, 1955; P. Bhyrappa, G. Vaijayanthimala, K. S. Suslick, *J. Am. Chem. Soc.* **1999**, *121*, 262; M. Plevoets, F. Vögtle, L. De Cola, V. Balzani, *New J. Chem.* **1999**, 63; M. Enomoto, T. Aida, *J. Am. Chem. Soc.* **1999**, *121*, 874.

[6] J.-F. Nierengarten, D. Felder, J.-F. Nicoud, *Tetrahedron Lett.* **1999**, *40*, 273.

[7] a) J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 2238; b) J.-F. Nierengarten, C. Schall, J.-F. Nicoud, *Angew. Chem.* **1998**, *110*, 2037; *Angew. Chem. Int. Ed.* **1998**, *37*, 1934; c) R. Kessinger, M. Gomez-Lopez, C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Echegoyen, F. Diederich, *J. Am. Chem. Soc.* **1998**, *120*, 8545.

[8] The decrease in amplitude of redox processes in bulky systems is a complex process that is difficult to rationalize; for a straightforward discussion, see F. A. Armstrong, H. A. O. Hill, N. J. Walton, *Acc. Chem. Res.* **1988**, *21*, 407.

[9] The accessible surface of the central core to the solvent molecules in the **CuG2** dendrimer was calculated with the MSEED program.[10] First we calculated the area of exposure to the solvent for **CuG0** and **G1CO$_2$*t*Bu**, which amounted to 620 Å^2 and 840 Å^2, respectively. Since for **CuG2** the surface available to the solvent is 6710 Å^2, the exposure of the central core amounts, at most, to about 10%. For **CuG3** this can assumed to be less than 5%. If we consider that in the apolar CH_2Cl_2 medium the counterion is likely to be in tight vicinity to the $[Cu(phen)_2]^+$ central core, we can conclude that the interior of the dendrimer is virtually inaccessible to external contact.

[10] G. Perrot, B. Cheng, K. D. Gibson, J. Vila, K. A. Palmer, A. Nayeem, B. Maigret, H. A. Sheraga, *J. Comput. Chem.* **1992**, *13*, 1.

[11] C. C. Phifer, D. R. McMillin, *Inorg. Chem.* **1986**, *25*, 1329.

[12] F. Vögtle, I. Lüer, V. Balzani, N. Armaroli, *Angew. Chem.* **1991**, *30*, 1367; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1333.

[13] N. Armaroli, F. Diederich, C. O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten, J.-P. Sauvage, *Chem. Eur. J.* **1998**, *4*, 406.

[14] N. Armaroli, F. Diederich, L. Echegoyen, T. Habicher, L. Flamigni, G. Marconi, J.-F. Nierengarten, *New J. Chem.* **1999**, 77.

[15] A. D. Bacon, M. C. Zerner, *Theor. Chim. Acta* **1979**, *53*, 21.

[16] Phosphorescence from C_{60} and its derivatives has rarely been reported and only in matrices below 5 K or at 77 K in presence of solvents that contain heavy atoms.

[17] For the calculation of the thermodynamic driving force for electronic excited states from spectroscopic and/or electrochemical parameters, see V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, **1991**, p. 44.

[18] For example, see a) G. L. Gaines III, M. P. O'Neil, W. A. Svec, M. P. Niemeczyk, M. R. Wasielewski, *J. Am. Chem. Soc.* **1991**, *113*, 719; b) F. Scandola, R. Argazzi, C. A. Bignozzi, M. T. Indelli, *J. Photochem. Photobiol. A* **1994**, *82*, 191.

2-Phenylquinoline–Carbohydrate Hybrids: Molecular Design, Chemical Synthesis, and Evaluation of a New Family of Light-Activatable DNA-Cleaving Agents**

Kazunobu Toshima,* Ryusuke Takano, Yutaka Maeda, Masataka Suzuki, Akira Asai, and Shuichi Matsumura

The development of photochemical DNA-cleaving agents, which selectively cleave DNA by irradiation with light with a specific wavelength under mild conditions and without any additives such as metals and reducing agents, is very interest-

---

[*] Prof. Dr. K. Toshima, R. Takano, Y. Maeda, M. Suzuki,
Prof. Dr. S. Matsumura
Department of Applied Chemistry, Faculty of Science
and Technology
Keio University, 3-14-1 Hiyoshi
Kohoku-ku, Yokohama 223-8522 (Japan)
Fax: (+81) 45-563-0446
E-mail: toshima@applc.keio.ac.jp

Dr. A. Asai
Tokyo Research Laboratories, Kyowa Hakko Kogyo Co., Ltd.
3-6-6 Asahi-machi, Machida-shi, Tokyo 194-8533 (Japan)

[**] This research was partially supported by a Grant-in-Aid for Encouragement of Young Scientists from the Ministry of Education, Science, Sports and Culture (Japan).