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Fullerohelicates: a new class of fullerene-containing supermolecules†

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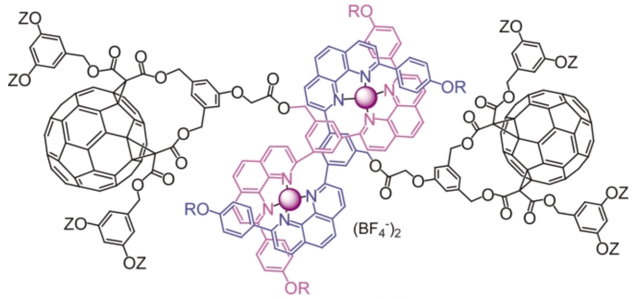
Received (in Cambridge, UK) 30th March 2004, Accepted 7th May 2004
First published as an Advance Article on the web 17th June 2004

A multicomponent array made of a bis-copper(I) helicate core and two peripheral fullerene subunits has been prepared and electron transfer from the photoexcited Cu(I)-complexed unit to C_{60} occurs.

Owing to their chirality and their structural analogy with DNA, double helices have fascinated chemists for decades. In the last twenty years, numerous examples of polymetallic double-stranded helical coordination compounds have been reported.[1] Such systems, named *helicates* by Lehn,[2] have been widely explored to understand the metal-directed self-assembly processes leading to the supramolecular helical systems.[1] Furthermore, the structural features of helicates have been beautifully exploited by Sauvage and Dietrich-Buchecker as templates for the synthesis of topologically non-trivial compounds such as molecular knots[3] and doubly-interlocked [2]catenanes.[4] It has also been shown by Ziessel and co-workers that a helicate core can behave as a mesogenic unit, thus providing an original chiral scaffold for the preparation of new liquid crystals.[5] One of the challenges of this chemistry is now to incorporate helicates in new supramolecular functional devices. In this regard, systems constructed by coordination of Cu(I) cations with oligo-bipyridine or -phenanthroline ligands are of particular interest. The long-lived metal-to-ligand charge transfer (MLCT) excited state of these complexes has a marked reducing character[6] making them good candidates for the construction of helicate-acceptor arrays which might undergo photoinduced electron transfer. We became therefore interested in the synthesis of bis-copper(I) helicate $Cu_2(\mathbf{1})_2$ with C_{60} as electron acceptor. In the design of this compound, we have selected a *m*-phenylene-bis-phenanthroline core known to form a double-stranded helicate upon complexation to copper(I).[7] This ligand has actually been functionalized with a hydroxy group to allow the attachment of a fullerene carboxylic acid derivative *via* an esterification reaction.

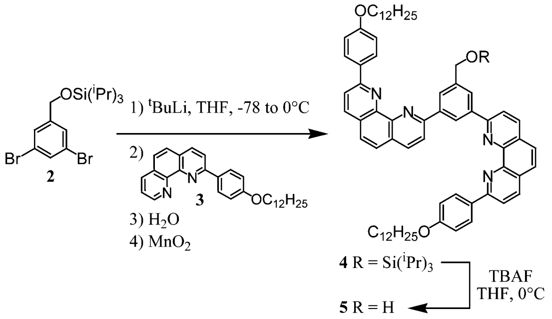


$Cu_2(\mathbf{1})_2$ (R = $C_{12}H_{25}$, Z = C_8H_{17})

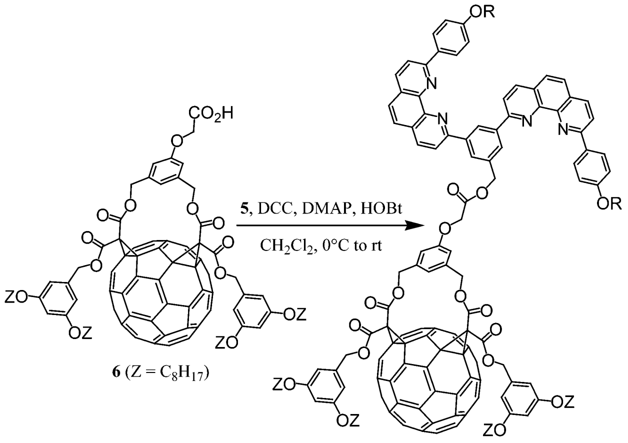
The preparation of the bis-phenanthroline precursor is depicted in Scheme 1. Compound **2** was obtained by $LiAlH_4$ reduction of the commercially available 3,5-dibromobenzaldehyde followed by reaction of the resulting 3,5-dibromobenzylic alcohol with triisopropylsilyl chloride in DMF in the presence of imidazole. Treatment of **2** with *t*-BuLi followed successively by addition of the resulting organolithium derivative to **3**[8] (0.5 equiv.), hydrolysis and rearomatisation with MnO_2 gave **4** in 31% yield. Alcohol **5** was then obtained in 88% yield by treatment with tetra-*n*-butylammonium fluoride (TBAF) in THF at 0 °C.

The synthesis of the C_{60}-substituted ligand **1** was achieved from **5** and **6**[9] under esterification conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) and 1-hydroxybenzotriazole (HOBt) (Scheme 2). The corresponding copper(I) complex $Cu_2(\mathbf{1})_2$ was then obtained in 75% yield by treatment of ligand **1** with $Cu(CH_3CN)_4BF_4$ in CH_2Cl_2–CH_3CN at room temperature. It can be added that the copper(I) helicate $Cu_2(\mathbf{4})_2$ was prepared under similar conditions from **4** and $Cu(CH_3CN)_4BF_4$. The latter compound has been used as reference compound for the photophysical studies.

The structure and purity of all new compounds were confirmed by ^1H- and ^{13}C-NMR spectroscopy, mass spectrometry and elemental analysis. In particular, the ^1H-NMR spectrum of **1** shows all the characteristic features of the C_s symmetrical 1,3-phenylenebis(methylene)-tethered fullerene *cis-2* bis-adduct substituent.[9] Effectively, an AB quartet and a singlet are observed for the



Scheme 1 Preparation of bis-phenanthroline **5**.



6 (Z = C_8H_{17})

1 (R = $C_{12}H_{25}$, Z = C_8H_{17})

Scheme 2 Preparation of the C_{60}-substituted ligand **1**.

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† Electronic supplementary information (ESI) available: ^1H-NMR spectra of **1** and $Cu_2(\mathbf{1})_2$. See http://www.rsc.org/suppdata/cc/b4/b404742g/

DOI: 10.1039/b404742g

diastereotopic benzylic CH_2 groups and an AX_2 system is revealed for the aromatic protons of the 1,3,5-trisubstituted bridging phenyl ring. The spectrum is also characterized by three sets of signals in a typical pattern for a disymmetrically 2,9-disubstituted-1,10-phenanthroline, an A_2X system for the aromatic protons of the bridging phenyl unit and an AA′XX′ system for the aromatic protons of the two 4-dodecyloxyphenyl rings (Fig. S1†). Upon complexation to copper(I), dramatic changes are observed for the chemical shift of the signals corresponding to the protons belonging to the bis-phenanthroline moiety due to the stacking of the aromatic subunits in the helicate (Fig. S2†). Importantly, the ^{1}H-NMR also provided clear evidence for the formation of a chiral complex, *i.e.* a helical system. In particular, the two equivalent fullerene *cis*-2 bis-adduct moieties have lost their plane of symmetry. For this reason, the protons that were enantiotopic in ligand **1** are not equivalent any longer in complex $Cu_2(\mathbf{1})_2$ and give rise to a more complicated set of signals (Fig. S3†). Finally, the structure of $Cu_2(\mathbf{1})_2$ was confirmed by mass spectrometry. The FAB-MS of $Cu_2(\mathbf{1})_2$ is characterized by a singly charged peak at *m*/*z* 5734.0 and a doubly charged ion peak at *m*/*z* 2824.7 which can be assigned to $Cu_2(\mathbf{1})_2$ after loss of one and two tetrafluoroborate counteranions, respectively.

The electronic absorption spectrum of $Cu_2(\mathbf{1})_2$ in CH_2Cl_2 is reported in Fig. 1 and well corresponds to the sum of the absorption spectra of its component units (**6** and $Cu_2(\mathbf{4})_2$). This is in contrast with what recently observed for a Cu(I)-bisphenanthroline complex sandwiched between two fullerenes, where the absorption spectrum reveals electronic interactions among the subunits.[10] In the present case a spacer is located between the inorganic core and the organic units. Thus, although the system is relatively flexible, the interchromophoric distance is kept long enough to prevent significant electronic interactions. The absorption and luminescence properties of fullerene **6** have been already reported[10] and those of $Cu_2(\mathbf{4})_2$ are in line with analogous Cu(I) complexes of 2,9-diphenylphenanthroline ligands.[11] **6** exhibits the characteristic weak fluorescence band of C_{60} fullerenes (λ_{max} = 770 nm, τ = 1.5 ns, and Φ_{em} = 3.0 × 10^{-4}).[10] In $Cu_2(\mathbf{4})_2$ an emission band attributed to the deactivation of a thermally equilibrated manifold of the lowest singlet and triplet metal-to-ligand charge-transfer states (^{1}MLCT and ^{3}MLCT), is detected (λ_{max} = 720 nm, τ = 130 ns and Φ_{em} = 5.1 × 10^{-4} in oxygen-free CH_2Cl_2 solution).

Selective excitation of a specific component in $Cu_2(\mathbf{1})_2$ is not possible (Fig. 1). We chose to excite at 540 nm where the light partitioning among the Cu(I) chromophores and carbon spheres in $Cu_2(\mathbf{1})_2$ is 1 : 1.[10] Under these conditions the quenching of the metal-complexed core is complete, and only the C_{60} fluorescence band (50% intensity relative to **6**) is detected with unchanged lifetime (Fig. 1). A 50% decrease of the fullerene triplet yield is measured, by means of the intensity of the sensitized singlet oxygen emission band (Fig. 1).[10] From these results it is possible to conclude that (i) the metal complexed core undergoes photoinduced quenching not attributable to energy transfer because no sensitization of the fullerene singlet and triplet states occur; (ii) following light excitation, the fullerene moieties of $Cu_2(\mathbf{1})_2$ behave in the same way as **6**. The energy level diagram in Fig. 2 reports the relevant electronic excited levels of the two types of chromophores. In principle electron transfer may occur from both the Cu(I) and the C_{60} moiety, but only the former is effective in promoting charge separation. This is related to the CT nature of the corresponding excited state that facilitates the electron transfer process from the kinetic point of view.[10] The localized and short-lived $^1\pi\pi^*$ level of C_{60} is comparably less effective in promoting the same process and regular internal deactivation takes place prior to photoinduced electron transfer.

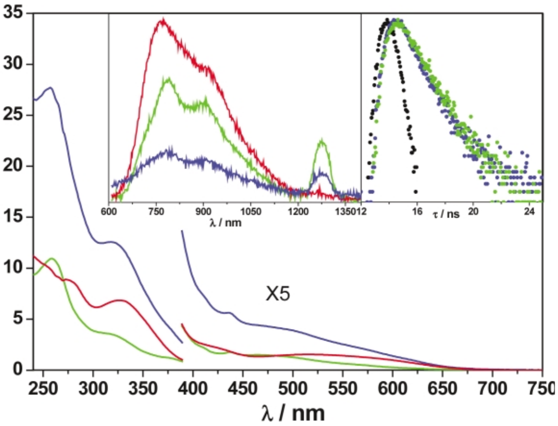

Fig. 1 Absorption spectrum of $Cu_2(\mathbf{1})_2$ (blue), $Cu_2(\mathbf{4})_2$ (red), and **6** (green). Left-hand side inset: uncorrected luminescence spectra in CH_2Cl_2 including the sensitized singlet oxygen luminescence peak at 1270 nm. CH_2Cl_2 solution, λ_{exc} = 540 nm, A = 0.700 for all samples. Right-hand side inset: emission decays of $Cu_2(\mathbf{1})_2$ (blue) and **6** (green) at λ_{exc} = 465 nm and λ_{em} > 700 nm; black trace: laser decay.

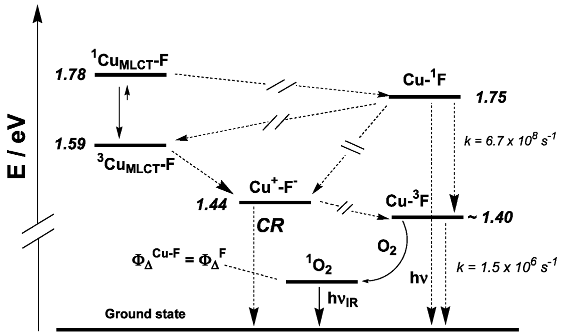

Fig. 2 Energy level diagram for $Cu_2(\mathbf{1})_2$ and photoinduced processes upon excitation of both chromophores (**Cu** and **F** denote a metal complex and a fullerene moiety, respectively). The excited state energies are determined as in ref. 10.

In conclusion a novel fullerohelicate architecture has been synthesized in which two chromophores are potentially able to trigger electron transfer. However only for the inorganic unit the process is competitive toward intrinsic deactivation. Further synthetic efforts are now under way to prepare optically active fullerohelicates to obtain new systems with original chiroptical properties.

Work supported by CNR, CNRS, EU (RTN Contract HPRN-CT-2002-00171), French Ministry of Research (ACI Jeunes Chercheurs to J-.F.N.). This paper is dedicated to Dr C. O. Dietrich-Buchecker in recognition of her seminal work in this field and for her support and enthusiasm in the early stage of our career.

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