
From Solution to Surfaces: Synthesis, Physical Properties, and Materials Applications of Novel Fullerene and Porphyrin Derivatives

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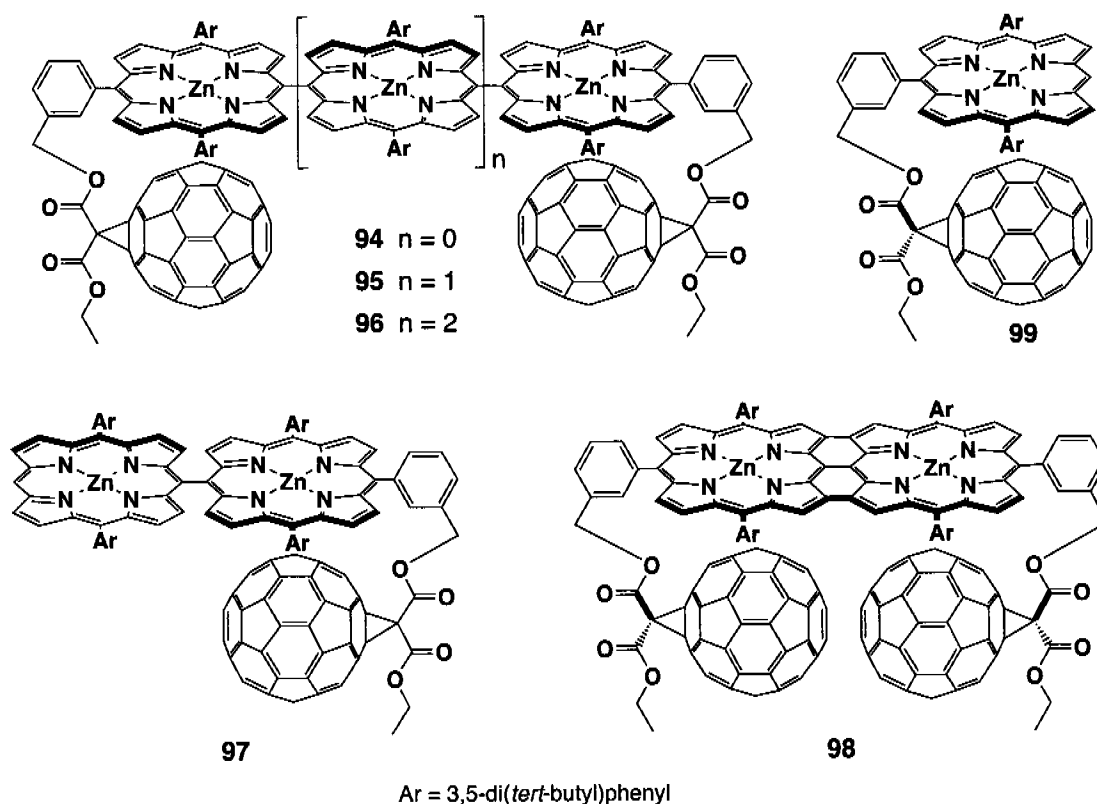
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Abstract

Recent achievements in the organic derivatization of C_{60} with other functional molecules have made the utilization of its unique optical and electronic properties in materials applications the major area of investigations in fullerene chemistry. In particular, the ability of the carbon sphere to reversibly accommodate up to six electrons and to participate efficiently in photoinduced electron transfer processes have animated many scientists to develop novel fullerene-based optoelectronic devices. In this respect, the functionalization of C_{60} with other redox-active species, *e.g.* porphyrins, and the modification of semiconductive or metallic surfaces with fullerene-containing thin films holds promise for materials with new exceptional properties and applications in a variety of technological fields.

In the first part of *Chapter 1*, the reader is given a short account on the discovery of C_{60} as well as its main electronic, spectroscopic, and other physical properties. This Section is concluded by a description of the most important chemical reactions utilized to prepare methanofullerenes. In the second part of *Chapter 1*, some significant and recent examples of functionalized [60]fullerenes employed in materials applications are reported.



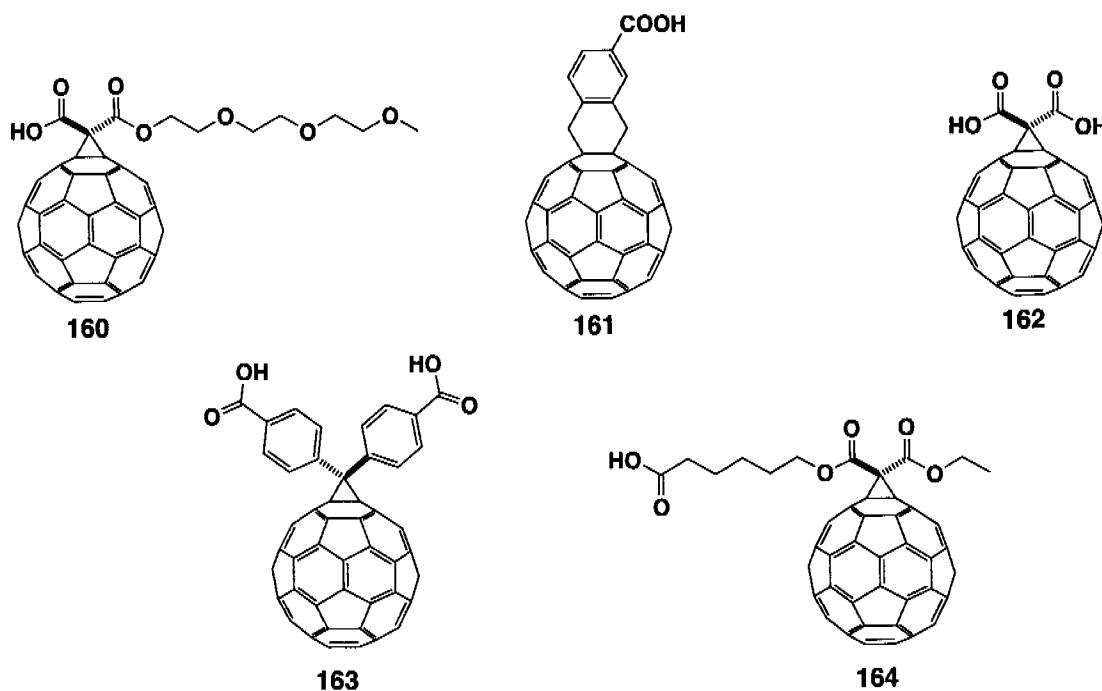
The first part of the present doctoral work is described in *Chapter 2*, where the syntheses of fullerene-derived porphyrins **94-99** are reported. Evidence for the successful synthesis of compounds **94-99** was obtained by ^1H - and ^{13}C -NMR spectroscopy and high-resolution *Fourier*-transform ion-cyclotron-resonance matrix-assisted laser-desorption-ionization (HR-FT-ICR-MALDI) mass spectrometric experiments, which revealed the molecular ion as the only peak. In all the dyads prepared in the course of this work, the relative position of the fullerene moiety with respect to the nearest porphyrin ring – *i.e.* the carbon sphere sits atop the porphyrin plane – was unambiguously established by ^1H - and ^{13}C -NMR spectroscopy. In contrast, no evidence for a tangential contact between the carbon sphere and the fused tetrapyrrolic macrocycle in compound **98** could be detected by ^1H -NMR spectroscopy.

In collaboration with the group of *Prof. Luis Echegoyen (Clemson University)*, detailed electrochemical studies were performed in order to investigate the electronic properties of all porphyrins and [60]fullerene-porphyrin conjugates synthesized in the context of this work (first part of *Chapter 3*). *meso,meso*-Linked porphyrin arrays were shown to feature only weak π -interactions between neighboring porphyrin units. In contrast, triply linked “diporphyrin”-type dimers showed a full π -delocalization over the two porphyrin units. Although the changes in potentials of the fullerene- and porphyrin-centered redox processes are small, a weak electronic interaction between the chromophoric components in dyads **94-99** was observed at the ground state. Moreover, both *meso,meso*-linked porphyrin-[60]fullerene conjugates **94-97** and triply linked porphyrin-[60]fullerene **98** were shown to have an exceptional multicharge storage capacity because of the large number of electrons that can be reversibly exchanged.

In collaboration with the group of *Dr. Nicola Armaroli (ISOF Bologna)*, full studies of the photophysical properties of all fullerene-porphyrin conjugates were performed (second part of *Chapter 3*). Strong CT interactions are clearly evidenced in the excited state using time-resolved absorption spectroscopy. All the CT states detected in the synthesized porphyrin-[60]fullerene conjugates are luminescent, and their emission bands are located in the NIR region. The photophysical dynamics of their CT states were investigated in solvents of different polarities. Interestingly, the energy level of the CT state is decreased upon increasing the solvent polarity along the series $\text{PhMe} \rightarrow \text{Et}_2\text{O} \rightarrow \text{THF}$. The dramatic drop of the luminescence quantum yield in polar solvents was ascribed to the lowering of the CT energy level and to the location of the CR process in the *Marcus* inverted region. Despite the fact that triply linked porphyrin dimers are much better electron donors than simple porphyrins, their low-lying and very short-lived (4.5 ps) singlet state offers an extremely

competitive pathway for the deactivation of the higher-energy singlet excited state of C₆₀. Remarkably, it was observed that the photoinduced processes of triply linked porphyrin conjugate **98** (fullerene → porphyrin energy transfer) are completely different from those of the biaryl-type biporphyrin conjugate **94** (porphyrin → fullerene electron transfer) while, notably, both molecules are NIR emitters.

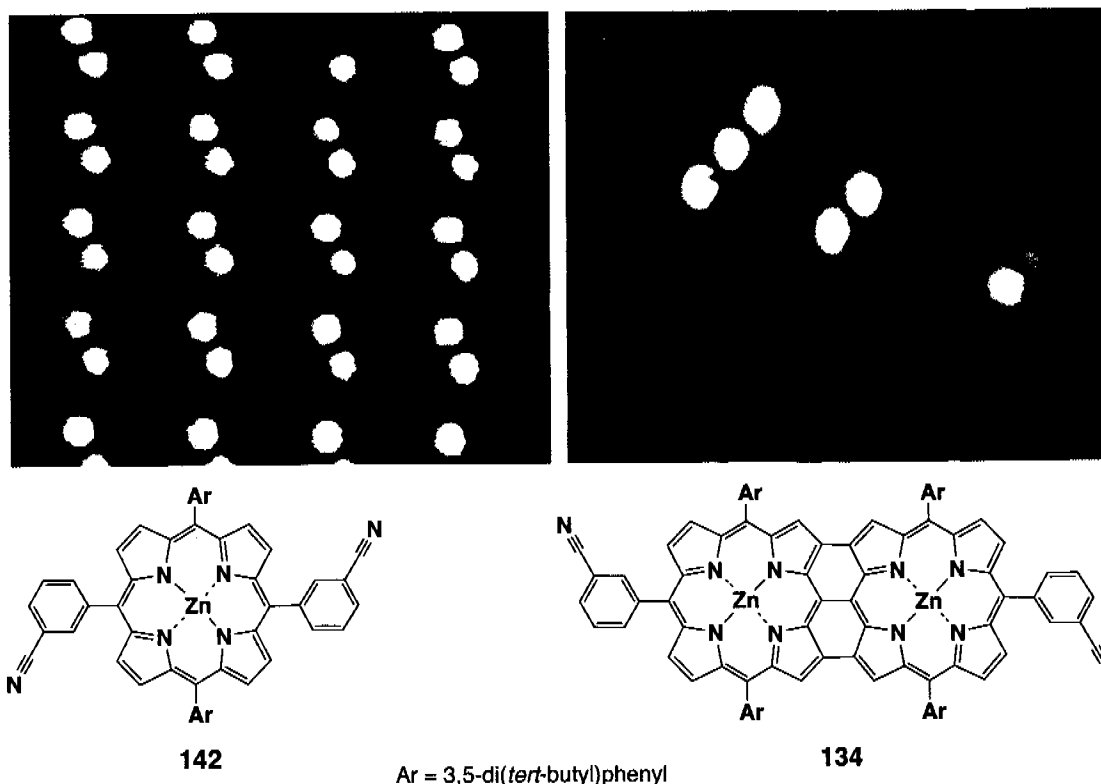
As a part of our efforts to prepare fullerene derivatives for materials applications, *Chapter 5* describes the design and synthesis of fullerene-derived carboxylic acids **160-164** and their subsequent adsorption on semiconductor surfaces such as (*n*- and *p*-type) GaAs and ZnO. The work is the fruit of a joint effort with *Adi Salomon* from the group of *Prof. D. Cahen (Weizmann Institute of Science)*. The fullerene-derived carboxylic acids have differently sized and shaped linkers between the C₆₀ moiety and the surface-binding carboxy groups to allow investigation of the effects resulting from changes in distance and orientation between the carbon sphere and the surface. The semiconductor surfaces modified with fullerene-containing monolayers of **160-164** were prepared and characterized by a variety of techniques (*Fourier* transform infrared spectroscopy, water contact angle measurements, ellipsometry, and atomic force microscopy). Specifically, all the fullerene-containing *n*-GaAs surfaces display high lipophilicity and, depending on the fullerene-derived carboxylic acid, different topographic images were observed by means of AFM.



In addition, fullerene clustering and a lack of order within the monolayers were observed. In the second part of *Chapter 5*, the modification of the electronic properties of *p*- and *n*-type

GaAs surfaces have been investigated in great detail, showing a strong influence of the electron-accepting fullerene moieties on the electronic properties of the semiconductor, *e.g.* work function and band bending. Evidence for a fullerene-centered electron trapping on the fullerene-containing GaAs surfaces was obtained from SPV (surface photovoltage) and CPD (contact potential difference) measurements. An opposite behavior was observed with fullerene-modified ZnO surfaces. In particular, an electron injection from the carbon sphere to the ZnO conduction band via HOMO-LUMO excitation of the C₆₀ molecule followed by a LUMO-CB(ZnO) transition was observed. These studies showed the first example of direct electronic modification of semiconductor properties mediated by superficially adsorbed C₆₀ derivatives.

Chapter 6 presents the “bottom-up” fabrication of patterned surfaces based on unprecedented two-dimensional addressable supramolecular assemblies composed of porphyrins and C₆₀. The experimental work was performed in collaboration with *Dr. Hannes Spillmann* from the group of *Dr. Thomas Jung* at the *University of Basel*.



The first scanning tunneling microscopy studies on monolayers of triply linked and monomeric porphyrins show that **134** and **142** self-organize into ordered molecular bilayers upon co-deposition with C₆₀. The arrangement of the fullerene molecules on the patterned layer can be controlled by the porphyrin structure. The observed mode of self-assembly is

the results of a delicate balance between the fullerene-porphyrin interaction and the conformational motion within the underlying porphyrin layer. Repositioning experiments conducted with the STM tip demonstrate that the C₆₀ molecules are weakly adsorbed on the porphyrin monolayers and they can be easily relocated without disrupting the underlying layer. These systems provide an exceptional example for the potential of the supramolecular approach in the fabrication of laterally addressable molecular devices, which are hardly imaginable using established miniaturizing methods such as the 'lithographic' techniques.