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## Fullerene photoactive dyads assembled by axial coordination with metals

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### Abstract

The most promising examples of fullerene dyads assembled by axial coordination with several electron donors, including porphyrins and subphthalocyanines, are reviewed. The review discusses the photophysical properties of such systems based on the structural modifications of the ligands by covalent chemistry. *To cite this article: A. Mateo-Alonso et al., C. R. Chimie 9 (2006).*

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### 1. Introduction

Photoactive systems comprised of an electron-donor and an electron-acceptor, are particularly attractive for conversion of light into electric current [1–5]. In such systems, rapid photoinduced electron transfer (PET) should be followed by diffusional splitting of a charge separated radical pair, mimicking a key step in natural photosynthesis. The inherent properties of C<sub>60</sub>, which can accept reversibly up to six electrons [6,7] together with its low reorganization energy [8–10], offer to this field an exceptional three-dimensional electron-acceptor. On the other hand, macrocycles such as porphyrins, subphthalocyanines and their metallated homologues, can be used as electron donors [3,4]. The advantage of these heterocycles lies in the minimal structural changes when electrons are released from them.

The nature of the linker between the two electroactive units controls the distance, orientation and electro-  
nic coupling and thus, small structural variations can affect the lifetime of the charge-separated state. Since PET between the donor and C<sub>60</sub> can take place through space, they can be connected by means of non-covalent interactions, giving photoactive supramolecular couples. If C<sub>60</sub> is properly functionalized, combined with the presence of central metal ions within the different heterocycles, the two units can be connected directly by metal complexation. The use of non-covalent interactions have shown to be a very useful tool to access very complicated architectures with less effort, including others that otherwise could not be approached through simple covalent chemistry.

In the following article we would like to illustrate the high versatility of axial coordination to produce structurally complex dyads from fairly simple building blocks, focusing on how structural modifications can tune the properties of such systems. The review starts

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with the description of the most popular systems based on pyridine coordination with metal porphyrins. Since this strategy can be applied to other heterocycles, the review continues with some recent examples of axial coordination between aromatic alkoxides and boron subphthalocyanines. The most interesting photophysical properties observed for each system are also described. Detailed reviews in this field have been recently published by D'Souza and Ito [11,12].

## 2. Porphyrin–pyridyl complexes

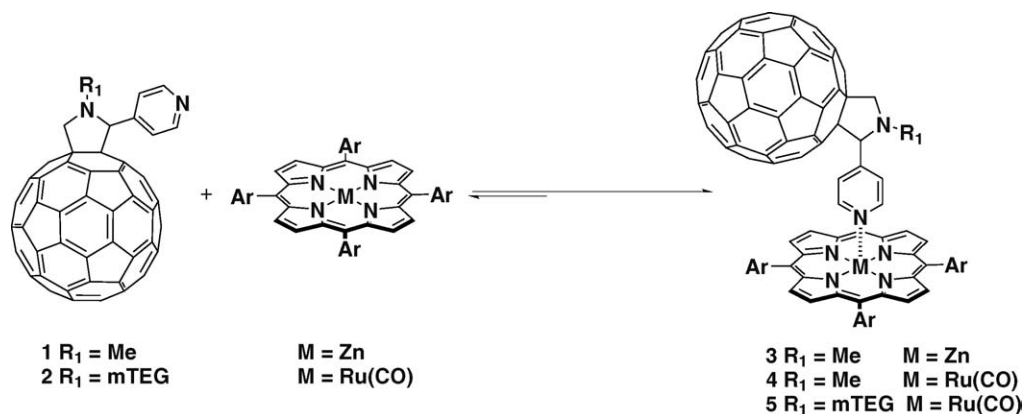
Pyridine is known to coordinate a wide variety of metal porphyrins [13,14]. The efficiency of coordination depends mainly on the metal ion. Following this approach, dyads between fullerenes and metalloporphyrins by axial coordination have been described.

$C_{60}$  was functionalized via [3 + 2] cycloaddition with a pyridyl coordinating group using sarcosine and 4-pyridine aldehyde as the starting materials [15,16] yielding fullerene ligand **1**. Several dyads have been assembled between ligand **1** and zinc and ruthenium tetraphenyl porphyrins (Scheme 1) [17–19]. The difference between both metalloporphyrins relies mainly on the strength of the metal–N coordination bond. In the case of zinc tetraphenylporphyrin (ZnTPP), the coordination with pyridine is weak since the only  $\sigma$  bonding is present. While in the case of ruthenium tetraphenylporphyrin (Ru(CO)TPP)  $\sigma$  bonding is reinforced by  $\pi$  backbonding.

The coordination between ZnTPP and ligand **1** was extensively studied [18,19]. The absorption spectrum of ZnTPP was measured at increasing concentrations of the fullerene ligand **1** in different solvents. In non-coordinating solvents (e.g. toluene, dichloromethane) the spectra revealed a red shift of the Q bands and a broad-

ening of the Soret band, which was attributed to the formation of the complex. In more polar and coordinating solvents (e.g., THF, benzonitrile) such effect was not observed, indicating that there was competition in the coordination of zinc between the fullerene pyridine and the solvent.  $^1\text{H-NMR}$  experiments were carried out with 1:1 mixtures of the ligand **1** and ZnTPP in  $\text{CDCl}_3$ , the pyridine protons showed shifting from 8.4 to 3.6 ppm due to anisotropy effected by porphyrin ring over the pyridine substituent confirming that the coordination with the zinc atom occurred. The photophysics of complex **3** showed intramolecular PET. In dichloromethane, a lifetime of 8.6  $\mu\text{s}$  was observed. While in polar solvents such as benzonitrile very efficient charge separation was detected with lifetimes of several hundreds of microsecond. The differential absorption changes observed in benzonitrile, revealed the participation of two components in the formation of  $C_{60}$  radical-anion. One corresponds to intramolecular PET when the complex is assembled. The other one was assigned to the intermolecular PET between the free ligand and the porphyrin. This effect was also observed in EPR experiments.

Similar experiments were carried out with Ru(CO)TPP (Scheme 1) [19]. Complex **4** showed primarily intramolecular energy transfer (EnT) from the photoexcited porphyrin to the fullerene in toluene. In benzonitrile, in which the increase of polarity enables bond detachment, intramolecular charge-separated states followed by fast recombination were observed. The electrochemical behavior of **4** was studied by cyclic voltammetry (CV) [20]. The cathodic pattern showed eight one-electron reversible reduction waves. Based of CV experiments on ligand **1** and on Ru(CO)TPP, five reductions were assigned to fullerene centered reductions



Scheme 1.

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