

Subphthalocyanine-Fullerene Dyads and Related Systems

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Subphthalocyanines^[1] (SubPcs, Figure 1) are 14- π electron aromatic macrocycles obtained by boron-templated cyclotrimerization of phthalonitriles. Their cone-shaped structure and C_3 symmetry give rise, upon proper peripheral substitution, to helical chirality^[2]. SubPcs have demonstrated very interesting photophysical properties which have been exploited in the fields of nonlinear optics or photonic devices. In the last decade, a lot of attention has been centered on their obtention and synthetic utility as precursors of unsymmetrically substituted phthalocyanines^[3] (Pcs).

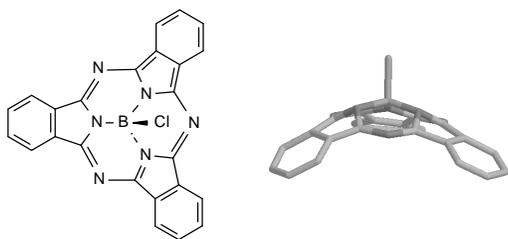


Figure 1

Despite their rich electronic properties, SubPcs have scarcely been coupled into dyads with other interesting electroactive units. Only very recently, a series of SubPc-Pc dyads linked by an ethynyl spacer has been photo- and electrochemically studied.

Unlike their lower homologues, Pcs have enjoyed certain attention on their photo- and electrochemical behaviour in fullerene dyads^[4]. Our group reported the synthesis and electrochemical properties of a zinc phthalocyanine directly linked to a fullerene through a pyrrolidine ring (figure 2).^[4d] The system was studied by cyclic voltammetry and Osteryoung square wave voltammetry and showed inter- and intramolecular electronic interactions between the two electroactive subunits.

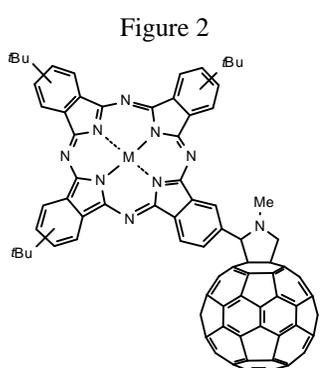
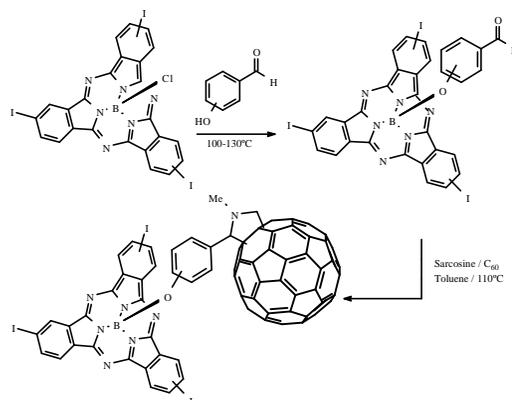


Figure 2

SubPcs are two-photon absorbers and may behave as electron donors in the presence of C_{60} . For these reasons, it seemed very interesting to us to prepare the first SubPc-Fullerene dyads and to perform a detailed photo- and electrochemical study. Our synthetic strategy consisted on preparing a SubPc bearing a reactive benzaldehyde substituent in the axial position. The formyl group allowed the linkage to C_{60} by means of the Prato reaction (Scheme 1).



Scheme 1

The average distance between the two subunits was regulated by the position of the formyl group in the axial phenoxy ligand of the SubPc (*o*-, *m*- or *p*-) (Figure 3).

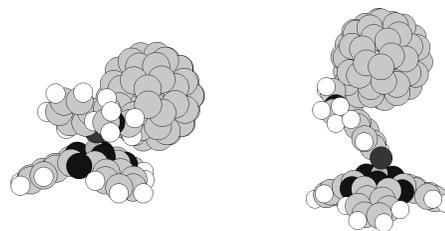


Figure 3

In the present communication, the synthesis and properties of these SubPc- C_{60} dyads are described.

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