

Towards Collective Physical Properties in Supramolecular Organized Phthalocyanine- C_{60} Fullerene Conjugates[⊗]Giovanni Bottari^{@1} and Tomás Torres^{@2}*Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco 28049 Madrid, Spain*^{@1}Corresponding author E-mail: giovanni.bottari@uam.es^{@2}Corresponding author E-mail: tomas.torres@uam.es

The organization of phthalocyanine- C_{60} fullerene conjugates is emerging as a powerful tool for the development of novel collective physical properties. This highlight presents the pioneering approaches on this topic.

Keywords: Donor-acceptor systems, fullerene, phthalocyanine, supramolecular organization.

Phthalocyanines (Pcs)^[1,2] are aromatic macrocycles which present a rich redox chemistry coupled to an intense absorption in the red/near infrared (IR) region of the solar spectrum with high extinction coefficients and fluorescence quantum yields.

The unique physicochemical features of these macrocycles make them ideal molecular components for the preparation of photoactive, donor-acceptor (D-A) ensembles. In such systems, the Pcs' role is twofold: first, they function as antennas, due to their excellent optical absorption in the visible region of the emission solar spectrum; and second, once photoexcited, they act as an electron donor.^[3,4]

Among the acceptor moieties that have been chosen as molecular partner for Pcs, C_{60} fullerene has a privileged position. This spherical carbon nanostructure in fact possesses an extraordinary electron acceptor property,^[5-7] which coupled with its small reorganization energy and its ability for promoting fast charge separation and slow charge recombination, have prompted its incorporation in Pc-based materials.

In this context, a few molecular and supramolecular architectures incorporating both Pc and C_{60} fullerene moieties have been prepared^[8-10] and the photophysical properties of these systems studied both in solution^[11,12] and in the solid state. In the majority of the cases the formation of long-lived charge-separated species was observed for these photo- and electroactive systems, thus paving the way for the utilization of these materials as active components of devices such as organic solar cells.^[13-15]

However, the successful utilization of these systems into devices is strongly related to the possibility to control the spatial arrangement of these molecules with respect to each other, since a high degree of order of these molecules at the molecular level is often accompanied by an improvement in the device's performance.

To achieve this goal then, it is necessary to carefully design and prepare Pc- C_{60} systems capable to self-organize

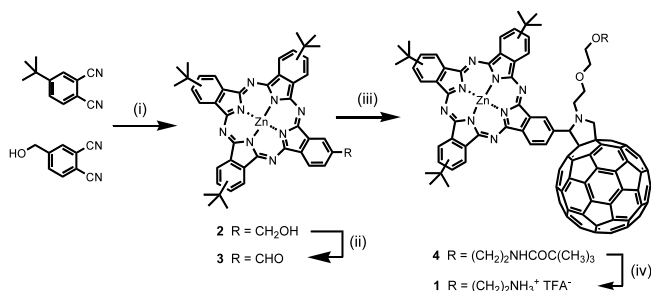
spontaneously into highly-ordered supramolecular structures.

Although Pcs, owing to their flat aromatic surface, can spontaneously interact with each other by π - π stacking interactions,^[16-20] the formation of long-range, ordered Pc-based systems, either in the term of discrete supramolecular architectures or infinite ill-defined aggregates, still remains a challenging task^[21,22] and often requires the introduction of additional recognition motifs such as the cation complexation as in crowned-Pcs,^[23-25] the use of hydrogen-bonding^[26-30] and metal-ligand^[31,32] interactions and/or the introduction of adequate substituents at the Pc periphery to promote a mesomorphic behavior.^[33-36]

Somehow more complicate is the case when such organization is sought for Pc- C_{60} conjugates, probably due to the presence of the bulky spherical carbon moiety, as reflected by the scarce number of reports on this topic.

Up to date, few examples have been reported in which a Pc- C_{60} dyad has been organized through supramolecular interactions.

The first example is represented by Pc- C_{60} dyad **1** (Scheme 1).^[37] The synthesis of this dyad starts with a statistical crossover condensation of 4-*tert*-butylphthalonitrile and 4-hydroxymethylphthalonitrile (the latter one prepared *via* reduction of 4-formylphthalonitrile)



Scheme 1. General reaction conditions for the preparation of the amphiphilic Pc- C_{60} dyad **1**. i) $Zn(OAc)_2$, dimethylaminoethanol, reflux. ii) SO_3 -pyridine complex, NEt_3 , dry dimethylsulfoxide, argon, 50 °C. iii) C_{60} fullerene, *tert*-butylcarbamate-protected, N-functionalized glycine, toluene, reflux. iv) trifluoroacetic acid, CH_2Cl_2 , RT.

⊗ This contribution is dedicated to professor Vasilij Fedorovich Borodkin on the occasion of his 100th Anniversary.

⊗ Статья посвящена 100-летию юбилею профессора Василия Фёдоровича Бородинкина.

in the presence of $\text{Zn}(\text{OAc})_2$ leading to the hydroxymethyl-functionalized $\text{Zn}^{\text{II}}\text{Pc}$ **2**, which was isolated in 22% yield. **Pc 2** was then subjected to an oxidative treatment with an excess of a SO_3 -pyridine complex in the presence of NEt_3 in dry dimethylsulfoxide, affording formylPc **3** in 84% yield.

Finally, the 1,3-dipolar cycloaddition reaction of an azomethine ylide, generated *in situ* from formylPc **3** and a *tert*-butylcarbamate-protected, *N*-functionalized glycine, to C_{60} fullerene (also known as “Prato reaction”), afforded Pc- C_{60} dyad **4**. Such reaction, which results in the formation of a pyrrolidine group, represents one of the most used synthetic strategies used nowadays for the functionalization of fullerenes. The carbamate protecting group in **4** was finally converted into an ammonium group by treatment with an excess of trifluoroacetic acid to afford Pc- C_{60} salt **1**. Due to the presence of the positively charged end groups, compound **1** could be dispersed in aqueous solutions giving rise to the formation of aggregates as demonstrated by UV-vis analysis. Transmission electron microscopy (TEM) analysis revealed that the amphiphilic Pc- C_{60} dyad **1** is able to form, when dispersed in water, perfectly ordered 1-D nanotubes due to a combination of solvophobic and π - π stacking interactions (Figure 1).

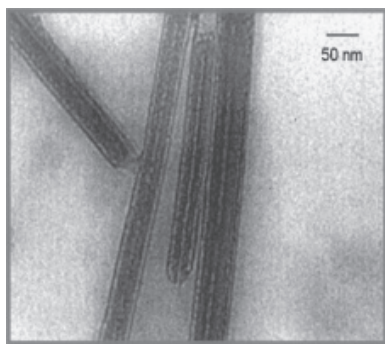
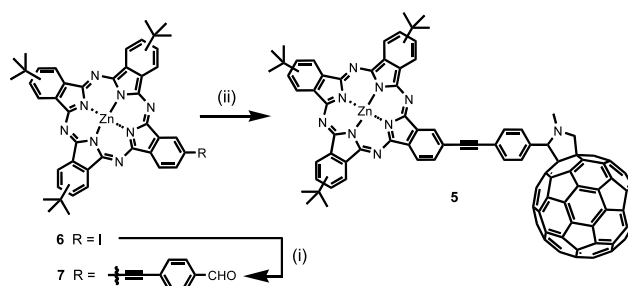


Figure 1. TEM image of the supramolecular nanotubes formed by dispersing Pc- C_{60} dyad **1** in water. The TEM image is reprinted with permission from reference 37. Copyright 2005, American Chemical Society.

A considerable change in the photophysical properties of the one-dimensional, self-organized Pc- C_{60} salt **1** with respect to the molecularly dispersed compound was also observed. Photophysical studies (*i.e.*, steady-state/time-resolved fluorescence experiments and transient absorption measurements) in fact revealed that the photoreactivity of these tubular nanostructures is remarkable, in terms of both ultrafast charge separation (*i.e.*, $\sim 10^{12} \text{ s}^{-1}$) and ultraslow charge recombination (*i.e.*, $\sim 10^3 \text{ s}^{-1}$), and it results in an impressive stabilization of the charge separated species $\text{Pc}^{\bullet+}\text{-C}_{60}^{\bullet-}$ of six orders of magnitude relative to the Pc- C_{60} dyad **4**.

Somehow different, and probably to some extent more complex, is the case when such organization of Pc- C_{60} conjugates is sought on substrates, since in this latter case the interactions between the molecules and the surface itself should also be taken into account.

Up to date, the only example of a Pc- C_{60} conjugate organized on a surface is represented by dyad **5** (Scheme 2).^[38]



Scheme 2. Synthesis of the structurally-rigid, Pc- C_{60} conjugate **5**. i) 4-ethynylbenzaldehyde, CuI, $\text{PdCl}_2(\text{PPh}_3)_2$, NEt_3 , dry toluene, reflux. ii) C_{60} fullerene, *N*-methylglycine, dry toluene, reflux.

The structurally-rigid Pc- C_{60} dyad **5** was prepared starting from the iodo-containing Pc **6** which was then coupled to 4-ethynylbenzaldehyde via a palladium-catalyzed Sonogashira coupling reaction affording the formylPc **7** in 92% yield. This latter compound was then reacted with C_{60} fullerene and *N*-methylglycine affording dyad **5** in 36% yield. The organization properties of the covalently-linked conjugate **5** on highly ordered pyrolytic graphite (HOPG) and graphite-like surfaces were also investigated by using atomic force microscopy (AFM). These studies showed that, on such surfaces, the D-A ensemble **5** is able to self-organize forming fibers and films (Figure 2). The electrical properties of these self-assembled nanostructured architectures were also probed by conductive-AFM (C-AFM). C-AFM is a powerful tool for measuring electrical properties in nanostructured architectures, since it allows the electrical mapping (usually with a spatial resolution of the order of the C-AFM tip radius, ca. 30 nm) of a sample as a metal-coated AFM tip is passed over it.

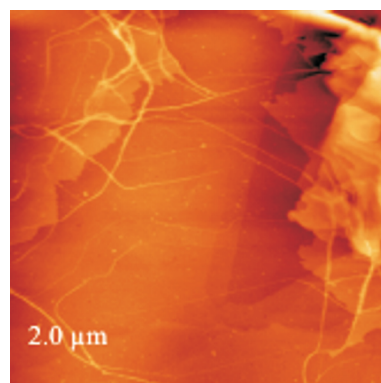


Figure 2. AFM topographic image of Pc- C_{60} dyad **5** drop-casted on highly oriented pyrolytic graphite (HOPG). The AFM image is reprinted with permission from reference 38. Copyright 2008, Wiley-VCH.

These C-AFM studies revealed outstanding electrical conductivity values for both supramolecular fibers and films, which resulted to be related to the extremely high degree of molecular order of the Pc- C_{60} conjugates within the nanostructures.

Very recently, the first example of mesogenic Pc- C_{60} dyads has been reported.^[39] In such systems, a favourable combination of the length of the linker with the length of peripheral substituents on the Pc, allows the bulky C_{60} moiety to be accommodated in the liquid-crystalline phase.

Detailed analysis of this supramolecular organization, as well as deeper insight in the structure-property relationships of these dyads, will be the subject of a separate publication.

The above mentioned studies clearly demonstrate that the supramolecular organization of Pc-C₆₀ systems, either in solution or a solid substrate, is able to considerably affect some of the dyad's physical properties, giving rise to the appearance of collective physical phenomena.

In this context, the preparation of easy-to-assemble, supramolecular nanostructures in which photo- and redox-active units, such as Pcs and C₆₀ fullerenes, respectively excellent donor and acceptor moieties, are molecularly self-assembled across multiple length scales is extremely promising, since it opens up the possibility of using these D-A conjugates for relevant technological applications such as nano-optoelectronics and photovoltaics. It can be easily envisaged that both scanning force and tunneling microscopies will play an important part in the study and implementation of such systems, providing some valuable guidelines about these systems' supramolecular organization, information that are of paramount importance for the optimization of resulting devices.

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