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# Convex–convex and concave–convex interactions between C<sub>60</sub> and non-planar aromatic subphthalocyanine macrocycle in both covalent and supramolecular arrays

Christian G. Claessens, David González-Rodríguez, Rodrigo S. Iglesias, T. Torres \*

*Departamento de Química Orgánica, Universidad Autónoma de Madrid, Campus de Cantoblanco, Madrid, Spain*

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## Abstract

Subphthalocyanines are curved aromatic macrocycles that are being synthesized and studied for their excellent photophysical and electrochemical properties. The curvature of this C<sub>3</sub> symmetrical molecule defines very interesting concave and convex  $\pi$ -surfaces. This review article gives an updated overview of the efforts made in our research group in the synthesis of covalent and non-covalent ensembles that bring together the convex  $\pi$ -surface of C<sub>60</sub> fullerene and the convex or concave aromatic surfaces of a subphthalocyanine moiety. *To cite this article: C.G. Claessens et al., C. R. Chimie 9 (2006).*

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## 1. Introduction

Despite the long standing fascination for non-planar  $\pi$ -extended molecules, many questions concerning these systems remain still open: can they have an aromatic behavior, how do they interact with other  $\pi$ -systems, what is the influence of the curvature on their electronic characteristics, do their concave and convex faces give rise to different properties?

C<sub>60</sub> is one of these non-planar systems that behaves as both an aromatic and a non-aromatic system depending on the way it is studied. This question has generated a huge amount of work, and only recently, it was demonstrated theoretically that C<sub>60</sub> does show weak inner

and outer spherical currents that justify its ambiguous behavior [1].

On the other hand, subphthalocyanine [2] (SubPcs, Fig. 1) represents a peculiar non-planar aromatic heteromacrocycle composed of three diminoisindole units *N*-fused around a boron atom presenting a 14- $\pi$ -electron system. The singular structure of subphthalocyanines confers them very interesting electronic and optical properties that may be useful in the construction of artificial photosynthetic systems: (i) they are excellent antenna units that absorb in the 550–650-nm region with extinction coefficients on the order of  $\sim 50\,000\text{ M}^{-1}\text{ cm}^{-1}$  and excitation energies above 2.0 V, (ii) their rigid non-planar core affords small Stokes shifts and low reorganization energies [3], and (iii) their redox characteristics may be tuned by the introduction of different peripheral substituents.

\* Corresponding author.

*E-mail address:* [tomas.torres@uam.es](mailto:tomas.torres@uam.es) (T. Torres).

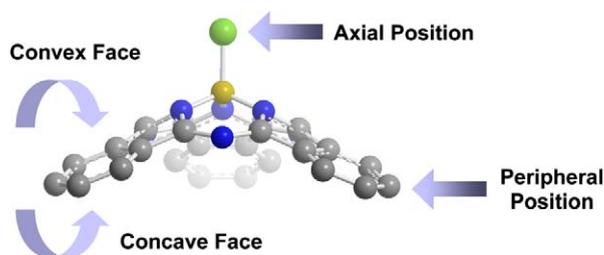


Fig. 1. Ball and stick representation of boronchlorosubphthalocyanine.

Due to their handy chemistry, the assembly of SubPcs into multicomponent photo- and electroactive systems may be performed via different routes involving peripheral [4] or axial functionalization as illustrated in Fig. 1 [5]. This versatility allowed the study of the interactions between photoactive and/or electroactive moieties such as  $C_{60}$  with both concave and convex faces of the SubPc macrocycle.

## 2. Convex–convex interactions in subphthalocyanine– $C_{60}$ covalent assemblies

The photophysical properties of a series of SubPc– $C_{60}$  dyads, in which the fullerene fragment was attached via the axial position of the macrocycle and thus, interacts through the **convex face** of the SubPc, have been recently studied by us [6]. Two main modifications were performed in these systems (Fig. 2): (i) the distance between the two components was modified through isomeric *ortho*-, *meta*- or *para*-substituted phenoxy spacers, and (ii) the macrocyclic unit was equipped with different peripheral groups (i.e. fluorine or iodine atoms and ether or amino groups), while the intercomponent distance was kept unchanged.

The synthesis of the SubPc units **3a–c** was carried out by the usual condensation reaction of the corresponding phthalonitriles **2a–c** in the presence of boron trichloride and subsequent substitution of the axial chlorine atom with *o*-, *m*- or *p*-hydroxybenzaldehyde led to **o-4b**, **m-4a–c** and **p-4b** (Scheme 1). The preparation of SubPcs bearing electron-donating groups **m-4c** and **m-4d** initially represented a synthetic challenge, since boron halides show a strong tendency to react with amines or ether groups. We found, however, that the diphenylether moiety is stable enough to boron trichloride in the reaction conditions employed and SubPc **m-4c** could be obtained in moderate yields (39%). On the other hand, the introduction of amine groups was successfully accomplished by a palladium-

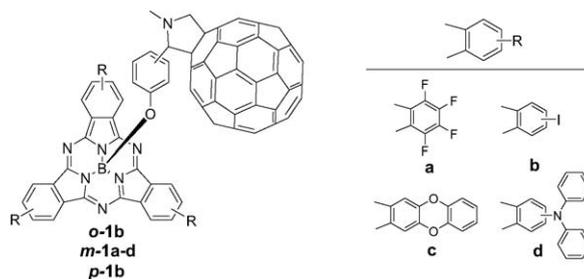
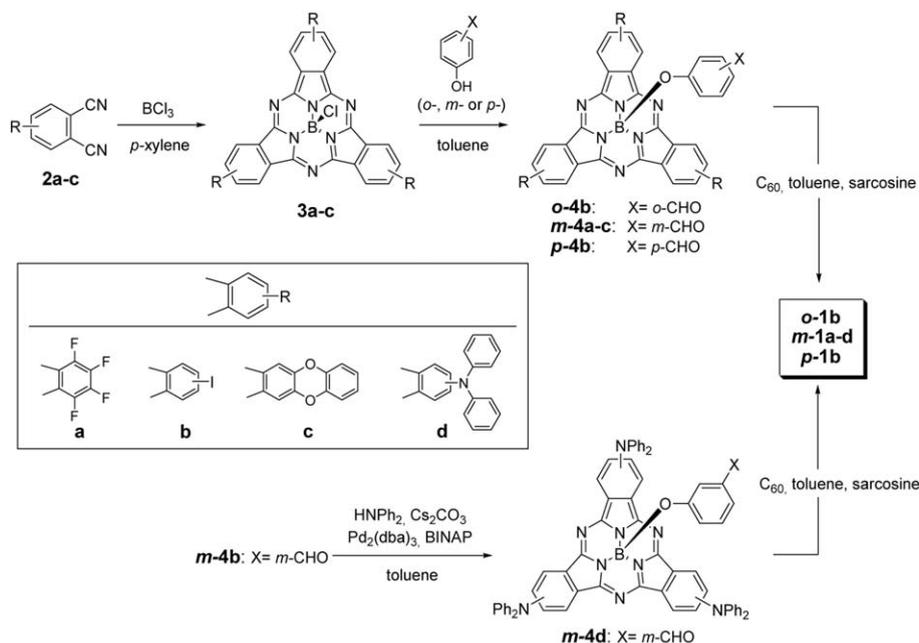
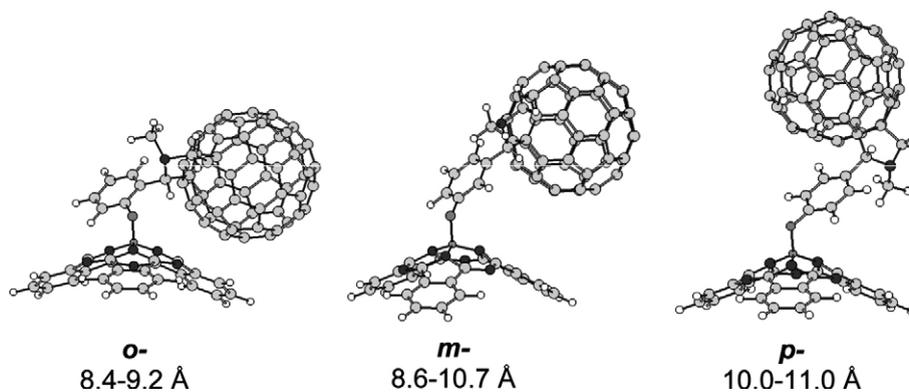


Fig. 2. Structure of SubPc– $C_{60}$  dyads **o-1b**, **m-1a–d** and **p-1b**.

catalyzed cross-coupling methodology between diphenylamine and triiodoSubPcs, leading to compound **m-4d** in good yields. In a last step, the SubPc– $C_{60}$  dyads **o-1b**, **m-1a–d** and **p-1b** were prepared by a 1,3 dipolar cycloaddition reaction between formyl-substituted SubPcs **o-4b**, **m-4a–d** and **p-4b** and  $C_{60}$  in the conditions described by Prato and Maggini [7]. Mono-addition products were isolated in moderate yields (~45%) and, in all cases, a small amount of bisadducts (~8%) was also obtained.

The intrinsic flexibility of the phenoxy spacer, having two torsional angles that lead to multiple conformations, makes that, in solution, the  $C_{60}$  and subphthalocyanine units in the dyads are not restrained at fixed relative positions. The structural modeling of the *o*-, *m*- and *p*-systems, using molecular mechanics and AM1 semiempirical methods, allowed the evaluation of the maximum and minimum distance between the two moieties in each isomeric dyad (Fig. 3).

A first inspection of the absorption spectra of these systems already revealed small, but notable intercomponent ground-state interactions. In fact, the Q band of the SubPc shows a small red-shift and a broadening in the dyads when compared to the reference compounds. When comparing **o-1b**, **m-1b** and **p-1b**, the magnitude of this red-shift was found to be dependent on the distance between the two components, reaching a maximum for compound **o-1b**. Cyclic voltammetry experiments showed, however, that **m-1b** is the easiest to reduce and also the easiest to oxidize in this series, thus indicating the weakest ground state interaction between the donor and acceptor groups. Therefore, in the ground state, the electronic effects that dominate the different redox processes occur through-bond and not through-space, since they follow the expected (and similar) behavior for the *ortho* and *para*, and the weakest electronic coupling for the *meta* isomer. On the other hand, the first oxidation process of the macrocycle gradually shifts to lower potentials (by ca. 200 mV) in the

Scheme 1. Synthesis of SubPc-C<sub>60</sub> dyads **o-1b**, **m-1a-d** and **p-1b**.Fig. 3. AM1 models and intercomponent distance range for *o*-, *m*- and *p*-isomeric SubPc-C<sub>60</sub> dyads.

series **a** > **b** > **c** > **d**, as the electron-donor character of the substituents on the SubPc increased.

The detailed photophysical characterization of these systems provided the comprehension of the different mechanistic scenarios occurring in the dyads upon initial light irradiation. Selective photoexcitation of the SubPc unit in dyads **m-1a**, **o-1b**, **m-1b** or **p-1b**, or in dyad **m-1c** in a non-polar environment, gave rise to a sequence of exergonic photophysical events that involve: (i) nearly quantitative singlet-singlet energy transfer to the C<sub>60</sub> moiety, (ii) fullerene-centered intersystem crossing, and (iii) triplet-triplet energy transfer back to the SubPc. The efficiencies of these energy transfer processes were found to increase as the dis-

tance between the two components decreased. On the contrary, the stabilization of the SubPc<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> radical pair state in more polar media or by lowering the redox gap between the donor and acceptor units caused charge transfer to dominate. In the case of **m-1c** in benzonitrile, the thus formed radical pair decayed in 0.65 ns to yield the SubPc triplet excited state. Further stabilization was achieved for dyad **m-1d**, whose charge-transfer state lies now below both triplets. As a result, the charge-transfer state lifetime increased in more than two orders of magnitude (~100 ns) with respect to **m-1c** and showed a significant stabilization in less polar solvents, a clear attribute of the inverted region of the Marcus parabola.

### 3. Convex–convex interactions in subphthalocyanine dimer–C<sub>60</sub> covalent assemblies

SubPcs are not only prone to axial functionalization, the peripheral extension of their curved aromatic surface is another possibility that has been investigated as well, which leads to SubPc analogues with substantially red-shifted absorption wavelengths. Compounds of this type include subnaphthalocyanines [8], and, more recently described, subphthalocyanine fused dimers (hereafter referred simply as *Dimers*) and trimers [9]. SubPc *Dimers* are prepared by condensation of a phthalonitrile along with tetracyanobenzene. Due to the SubPc cone-shaped geometry, the *Dimers* exist as two topoisomers, *anti* and *syn*, which have been isolated and unambiguously characterized. In contrast with the analogous phthalocyanine fused dimers [10], the SubPc *Dimers* present a distinct and highly-red shifted (ca. 120 nm) Q-band with respect to its “monomeric” counterpart.

The SubPc *Dimers*, while bearing two axial positions, allow a double connection to a C<sub>60</sub>-fullerene unit (in the case of the *syn* isomer). This double connection from the **convex face** of the *Dimer* permits an “anchoring” of the C<sub>60</sub> suitable for through-space interactions between the acceptor C<sub>60</sub> and donor SubPc *Dimer* units.

This *Dimer*–C<sub>60</sub> dyad **5** (Fig. 4) was prepared [11] employing the same two-step above-mentioned procedure (axial functionalization with an aldehyde group, followed by cycloaddition to the C<sub>60</sub>-fullerene) used for the preparation of SubPc–C<sub>60</sub> axially-linked dyads. This procedure applied to the *syn* topoisomer **7** yields the expected doubly-connected *Dimer*–C<sub>60</sub> dyad **5** in 14% yield. The <sup>1</sup>H NMR spectrum of the dyad **5** shows several broad signals corresponding to the multiple regioisomers and diastereoisomers (simple molecular

modeling indicates that at least 20 could be formed) and the dynamic processes occurring within them. Photophysical studies reveal that the *Dimer*–C<sub>60</sub> dyad undergoes a series of energy transfer events similar to those observed in the SubPc–C<sub>60</sub> analogues *m-1a*, *o-1b*, *m-1b* or *p-1b*—after photoexcitation of the donor unit (*Dimer*), follows a singlet–singlet energy transfer to the acceptor fullerene, which decays by inter system crossing to the C<sub>60</sub> triplet state, ending with the energy back-transfer to the *Dimer* triplet state. In contrast with the SubPc–C<sub>60</sub> dyad, the singlet–singlet transfer in the *Dimer*–C<sub>60</sub> dyad occurs between nearly isoenergetic states, as the *Dimer* S<sub>1</sub> state lies at a significantly lower energy (1.77 eV) than that of SubPc (2.1 eV), thus being very close to the S<sub>1</sub> state of C<sub>60</sub>-fullerene (1.76 eV).

### 4. Concave–convex interactions in a subphthalocyanine–C<sub>60</sub> non-covalent assembly

Finally, we thought it would be very interesting to investigate the interactions between the **concave face** of a SubPc macrocycle and the complementary convex surface of a C<sub>60</sub> molecule. In order to do that, we designed a self-assembled C<sub>60</sub> receptor **8** (Fig. 5) composed of two subphthalocyanine units connected by three pyridine–Pd(II)–pyridine linkages so that their concave surfaces would face each others and form a hollow capsule [12].

Reaction of SubPc **3b** (Scheme 2) with 3,5-ditertbutylphenol in toluene at reflux yielded the axially functionalized SubPc **9** in 80% yield. Triethynyl-3-pyridyl-substituted subphthalocyanine **10** was obtained by standard Sonogashira cross-coupling reaction from triiodo SubPc **9** in 70% yield. Cage compound **8** was quantitatively self-assembled (Scheme 2) by mixing stoichiometric

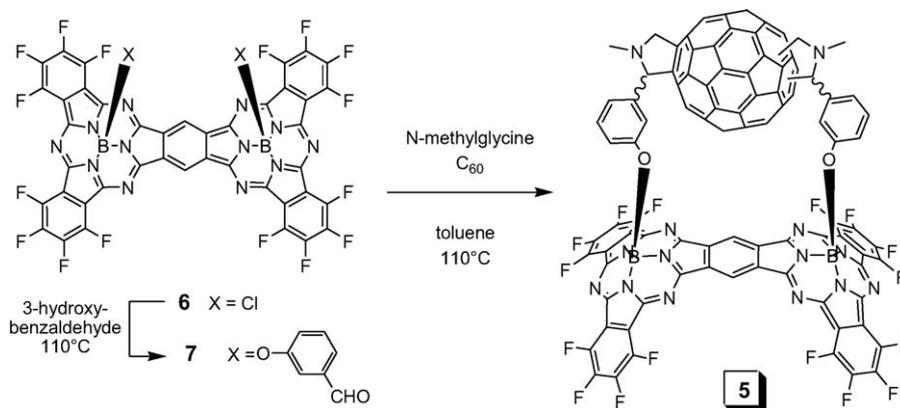


Fig. 4. Synthesis of subphthalocyanine dimer–C<sub>60</sub> dyad.

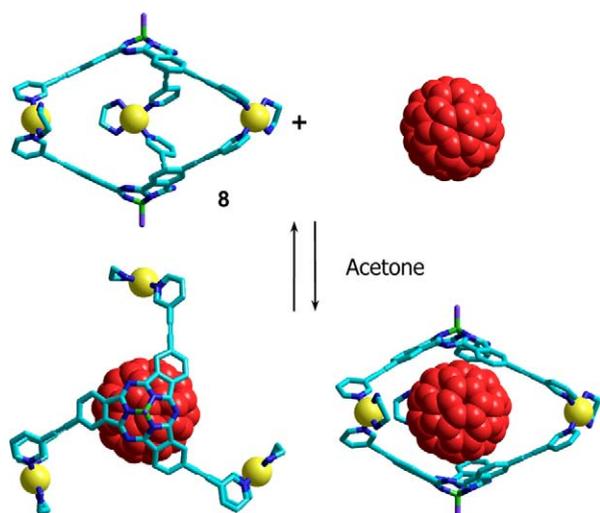


Fig. 5. Complexation of a  $C_{60}$  molecule within the self-assembled subphthalocyanine cage **8**.

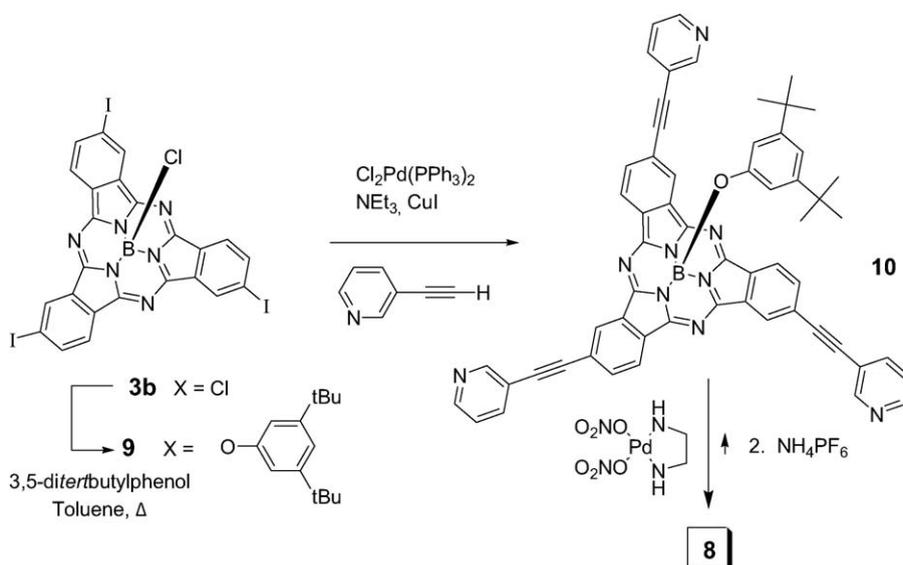
amounts of SubPc **10** and the palladium(II) complex (en)  $Pd(NO_3)_2$  in a 1:1:1 mixture of water/methanol/acetonitrile followed by anion exchange with an excess of ammonium hexafluorophosphate. The fullerene complex was prepared by adding 5 equivalents of  $C_{60}$  to a solution of capsule **8** in *d*<sub>6</sub>-acetone.  $^{13}C$  NMR spectrum of this mixture showed a broadening of the signals corresponding to the  $M_3L_2$  cage **8** and the appearance of a peak at 140.1 ppm attributed to  $C_{60}$ . In sharp contrast,  $^{13}C$  NMR of pure  $C_{60}$  in the same conditions does not show any signal since fullerene is not soluble enough in acetone (1 mg ml<sup>-1</sup>) [13]. Further evidence for the encapsulation of  $C_{60}$  was obtained from elec-

troscopy mass spectrometry in the same solvent that showed peaks at  $m/z = 1154.8$ , 829.7, 634.5 and 505.5 corresponding to  $[[C_{60} \subset \mathbf{8}] \cdot 3PF_6]^{3+}$ ,  $[[C_{60} \subset \mathbf{8}] \cdot 2PF_6]^{4+}$ ,  $[[C_{60} \subset \mathbf{8}] \cdot PF_6]^{5+}$  and  $[C_{60} \subset \mathbf{8}]^{6+}$ , respectively, that compare well with theoretical exact mass values at 1153.2, 828.7, 633.9 and 504.1, respectively. Thus, in this way, one metallocupramolecular capsule **8** can extract a  $C_{60}$  molecule from the solid state and stabilize it in between the two concave surfaces of the subphthalocyanine halves. In addition to the magnetic interactions between the two components as evidenced by NMR spectroscopy, further photophysical studies are underway in order to deepen our understanding of the communication between the two  $\pi$ -extended surfaces.

## 5. Conclusions and outlook

Subphthalocyanines are shown to be extremely promising photo- and electroactive molecular building blocks for the construction of multicomponent assemblies in combination, for example, with  $C_{60}$  moieties. Photoinduced energy and electron transfer events take place in this kind of SubPc– $C_{60}$  dyads following initial photoexcitation of the SubPc chromophore. On the other hand, they also represent ideal non-planar aromatic systems in which both convex and concave faces are accessible following covalent and supramolecular strategies.

This chemically versatile macrocycle is only beginning to emerge as a relevant molecule in the fields of photophysics, supramolecular chemistry and non-linear



Scheme 2. Synthesis of the  $M_3L_2$  subphthalocyanine capsule **8**.

optics [14]. We are certain that there is still plenty of room for many useful applications of subphthalocyanines and subphthalocyanine derivatives.

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