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Encapsulation of phthalocyanine- C_{60} fullerene conjugates into metallosupramolecular subphthalocyanine capsules: a turn of the screw

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Abstract: In this communication, encapsulation studies between metallosupramolecular capsule **1**, formed by 2 subphthalocyanines (SubPcs) coordinated to 3 metallic centers, and phthalocyanine (Pc)- C_{60} fullerene conjugates **2–5** have been carried out. It was shown that the encapsulation of the C_{60} moiety by the SubPc cage occurred exclusively for dyads **2–4**, whereas it was not observed in the case of triad **5**. The rigidity of the linker between the Pc and the fullerene unit proved to have an important impact in the complex formation. Complex formation was tested in 2 different solvents, where the importance of solvophobic effects was highlighted. The resulting multicomponent supramolecular systems represent a unique combination of photoactive moieties where covalent and supramolecular chemistry coexist.

Key words: Phthalocyanines, subphthalocyanines, C_{60} fullerene, metallosupramolecular chemistry, host–guest complexes

1. Introduction

Phthalocyanines (Pcs)^{1–3} and subphthalocyanines (SubPcs)^{4,5} are aromatic macrocycles obtained by condensation of phthalonitriles and formed by 4 and 3 *N*-fused 1,3-diiminoisoindoline units, respectively (Figure 1). In the case of SubPcs, the presence of a boron Lewis acid during the synthesis is essential for templating the condensation of only 3 precursors.

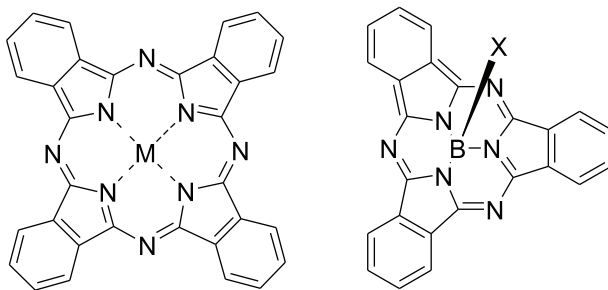


Figure 1. Molecular structures of a Pc (left) and a SubPc (right).

The intense absorption of these compounds in the visible region of the solar spectrum, as well as their photophysical properties, have rendered them an interesting platform for the study of photoinduced energy and

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electron transfer in donor–acceptor (D–A) conjugates.^{6–9} In addition, they have found applications in many optoelectronic devices.^{10–13}

SubPcs also possess a concave π -system due the presence of a sp^3 boron atom in their cavity. This curved structure has been previously exploited for the construction of metallosupramolecular capsules.^{14–16} Furthermore, the π -surface of SubPcs is perfectly adapted from a geometric point of view to the shape of C_{60} fullerene. In fact, adequately substituted SubPcs as well as the SubPc-based metallosupramolecular capsules are able to form inclusion complexes with fullerenes in solution.^{14,17} Photoinduced energy transfer from the SubPc to the encapsulated fullerene has been observed in these supramolecular systems by femtosecond transient spectroscopy.^{14,17}

In this communication, 4 Pc- C_{60} conjugates have been tested as new guests for SubPc-based capsules. The aim of this work is to go one step further in the construction of photoactive supramolecular SubPc-fullerene ensembles.

2. Results and discussion

SubPc-based metallosupramolecular capsule **1** and Pc- C_{60} dyads **2–4** (Figure 2) were prepared as previously described.^{14,18,19} Details for the synthesis and characterization of triad **5** are reported in the experimental section.

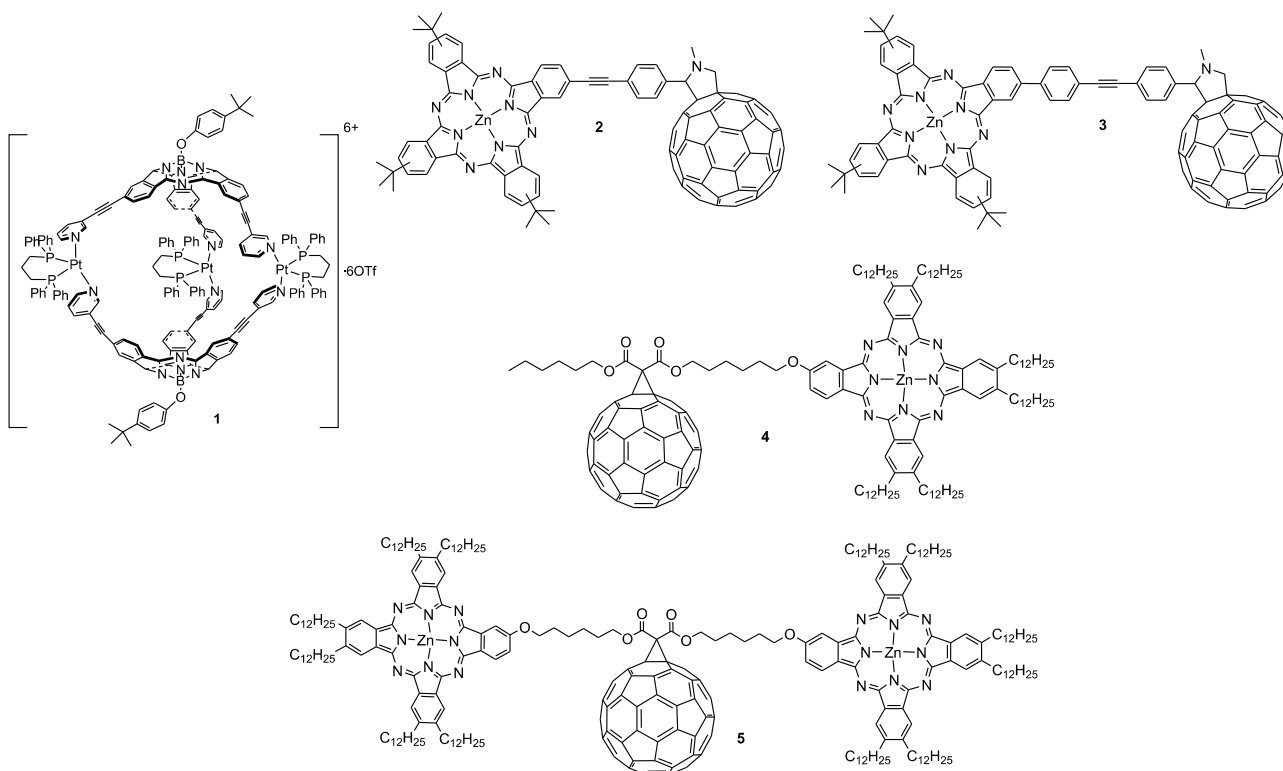


Figure 2. Molecular structures of SubPc capsule **1** host and Pc- C_{60} ensembles **2–5** chosen as potential guests.

The presence of phosphine ligands in SubPc-based capsule **1** helped to easily follow the C_{60} encapsulation process in solution by ^{31}P NMR. Moreover, it is known that the host–guest equilibrium of SubPc capsules and

fullerenes is slow compared to the NMR time-scale, thus allowing the calculation of the binding constants by integration of the phosphorous signals of the free cage and the complex in the ^{31}P NMR spectra. In analogy with previous studies of C_{60} -PCBM encapsulation by SubPc-capsules,¹⁴ the stoichiometry of the complexes between the SubPc capsule and the Pc- C_{60} conjugates was assumed to be 1:1.

Thus, the methodology followed for probing the inclusion of the C_{60} moiety of the Pc- C_{60} ensembles **2–5** into the cavity of SubPc capsule **1** was the preparation of 1:1 solutions of both components in either deuterated chloroform (where conjugated **2–5** are not soluble) or deuterated THF. ^{31}P NMR of these mixtures showed peaks corresponding to free capsule **1** as well as to the inclusion complex (Figure 3).

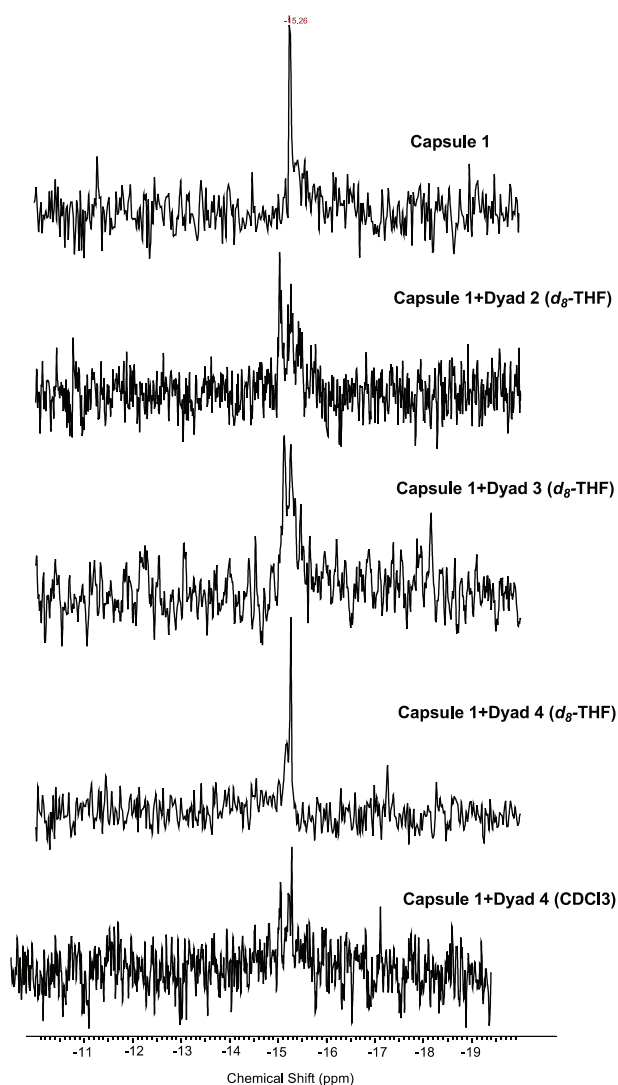


Figure 3. ^{31}P NMR spectra of capsule **1** (top) and 1:1 mixtures with dyads **2** and **3** (in d_8 -THF) and **4** (in CDCl_3 and d_8 -THF).

Binding constants were calculated from the integration of the phosphorous signals in ^{31}P NMR, considering that the sum of the concentrations of free capsule and complex equals the initial concentration of compound **1**. The association constants obtained are listed in the Table. Dyad **4** was the only one that could be

encapsulated both in CDCl_3 and d_8 -THF. From the values of the binding constants obtained we infer that the solvophobic effect plays an important role in the formation of these complexes. It is apparent that the enhanced rigidity of the linker in dyads **2** and **3** provides better encapsulation, having binding constants slightly higher than for the flexible compound **4**. Compound **5** did not form any complex with capsule **1**, probably due to the presence of the 2 Pc units, which made difficult the encapsulation of the C_{60} moiety.

Table. Binding constants between capsule **1** and dyads **2-4** in CDCl_3 ^(a) and d_8 -THF^(b).

Pc- C_{60} dyad	K_{eq} (M^{-1}) – ^{31}P NMR
4	1.7×10^3 ^(a)
	8.5×10^2 ^(b)
3	1.10×10^3 ^(b)
2	2.73×10^3 ^(b)

As an additional experiment, size-exclusion chromatography of the mixtures containing SubPc capsule **1** and Pc guests **4** or **5** was performed. Surprisingly, the host-guest complex **1:4** eluted separately from the uncomplexed species **1** and **4** in size-exclusion column chromatography as a first compound, which was easily identified as a dark-blue band. The blue color results from the combined absorption of SubPc, at 580 nm pink, and the Pc, at 700 nm green, for all complexes, as can be observed for example in the UV-visible absorption spectrum of **1+2** (Figure 4). In contrast, when the mixture of **1** and **5** was subjected to size-exclusion chromatography, the first compound to elute was the Pc- C_{60} triad, showing that encapsulation had not occurred.

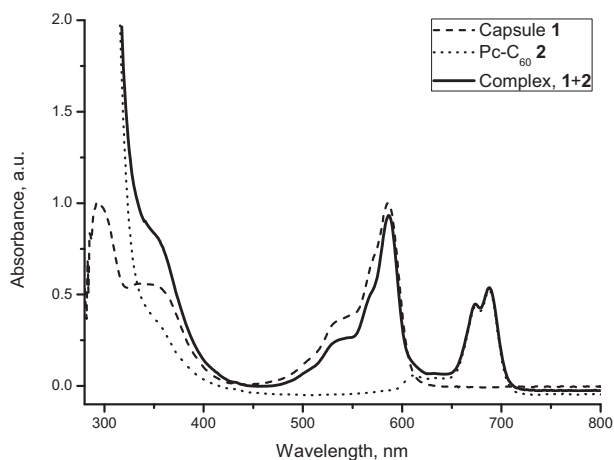


Figure 4. Comparison of UV-Vis absorption spectra of capsule **1**, compound **2**, and the complex they form in THF.

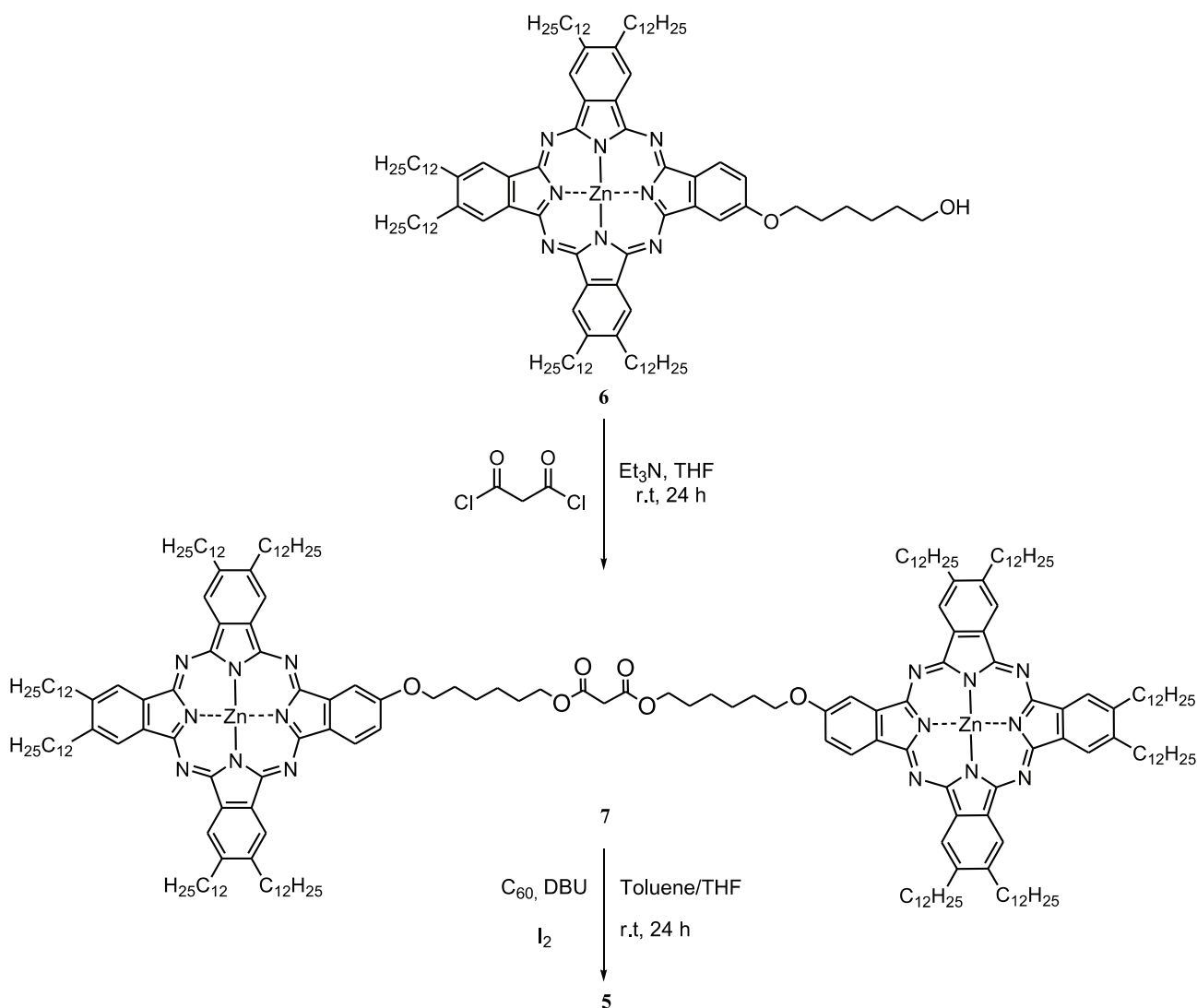
In conclusion, we have successfully shown the potential of SubPc-based capsules for encapsulating fullerenes functionalized with chromophores. The importance of the solvophobic effect and rigidity of the linker within the Pc- C_{60} guest is highlighted. These preliminary studies are a first step towards building complex photoactive systems based on the combination of supramolecular and covalent binding of SubPcs and Pcs. In addition, the potential of these chromophores as building-blocks in D-A systems is shown. The well-known photophysical properties of Pcs, SubPcs, and fullerenes are expected to ease the future study of photoinduced processes in the complexes discussed here.

3. Experimental

UV-Vis spectra were recorded with a JASCO V-660 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded with Bruker AC-300 equipment. Chemical shifts, δ , are indicated in ppm, using the residual solvent peak as reference. Column chromatographies were carried out on permeation gel Bio Beads S-X1 (200–400 mesh) and TLC on aluminum sheets coated with silica gel 60 F254 (Merck). Chemicals were purchased from Aldrich Chemical Co. and Alfa Aesar and were used as received without further purification.

3.1. Synthesis of $(\text{Pc})_2\text{C}_{60}$ **5**

The synthesis of $(\text{Pc})_2\text{C}_{60}$ **5** and its malonate precursor **7** is depicted in the Scheme. The hydroxy-Pc **6** was prepared and purified according to a published procedure.¹⁸ Condensation of Pc **6** with malonyl chloride yielded malonate derivative **7**, which was linked to C_{60} by a Bingel reaction to give $(\text{Pc})_2\text{C}_{60}$ **5**.



Scheme. Synthesis of $(\text{Pc})_2\text{C}_{60}$ **5**.

3.2. Pc dimer **7**

To a solution of Pc **6**¹⁸ (50 mg, 0.029 mmol) and malonyl chloride (1.4 μ L, 0.014 mmol) in THF (5 mL), a solution of Et₃N (4.04 μ L, 0.029 mmol) in THF (2 mL) was added dropwise. The mixture was stirred at room temperature overnight, and then evaporated to dryness. Purification of the solid residue by column chromatography (toluene/THF 10:1) afforded pure compound **7** (25 mg, 49%).

¹H NMR (*d*₈-THF, 300 MHz): δ = 9.08 (s, 2H, ArH), 9.03 (s, 2H, ArH), 8.76 (d, *J* = 9, 2H, ArH), 8.68 (s, 2H, ArH), 8.62 (s, 2H, ArH), 8.58 (s, 2H, ArH), 8.48 (s, 2H, ArH), 8.39 (s, 2H, ArH), 7.58 (d, *J* = 9, 2H, ArH), 4.67 (t, *J* = 6 Hz, 4H, OCH₂), 4.50 (t, *J* = 6 Hz, 4H, CH₂O), 3.65 (s, 2H, O₂CCH₂CO₂), 3.4–3.3 (m, 12H, alkylH), 3.2–3.1 (m, 12H, alkylH), 2.26–1.3 (m, 256H, alkylH), 1.1–0.9 (m, 36H, alkylH); IR (KBr): ν (cm⁻¹) = 2928, 2847, 1738, 1603, 1464, 1342, 1234, 1103, 1090, 870; UV/Vis (THF): λ_{max} (log ϵ) = 678 (5.28), 632 (5.03), 343 (5.15); MS (MALDI, dithranol), *m/z*: 3469.5 (M-H)⁺; HRMS (MALDI-TOF, dithranol): calc. for C₂₂₃H₃₄₄N₁₆O₆Zn₂: [M]⁺: *m/z*: 3470.5682, found 3470.5236.

3.3. (Pc)₂C₆₀ **5**

To a solution of C₆₀ fullerene (14.51 mg, 0.02 mmol) in dry toluene (5 mL), a solution of Pc **7** (35 mg, 0.01 mmol) in THF (1 mL), I₂ (2.5 mg, 0.01 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 μ L, 0.02 mmol) was added. The mixture was stirred at room temperature overnight and then evaporated to dryness. Purification of the solid residue by silica gel column chromatography [first with toluene and then with toluene/THF (10:1)] followed by size-exclusion column chromatography (THF) afforded pure (Pc)₂C₆₀ **5** (5 mg, 12%).

¹H NMR (*d*₈-THF, 300 MHz): δ = 9.06 (m, 2H, ArH), 9.17–8.90 (m, 4H, ArH), 8.82–8.34 (m, 10H, ArH), 7.58 (m, 2H, ArH), 4.94–4.84 (m, 2H, OCH₂), 4.81–4.54 (m, 6H, OCH₂), 3.59–3.32 (m, 12H, alkylH), 3.31–3.02 (m, 12H, alkylH), 2.24–1.3 (m, 256H, alkylH), 1.1–0.9 (m, 36H, alkylH); IR (KBr): ν (cm⁻¹) = 3442, 2956, 2920, 2851, 1750, 1646, 1609, 1466, 1432, 1339, 1105; UV/Vis (THF): λ_{max} (log ϵ) = 679 (5.2), 632 (5.0), 339 (5.1); MS (MALDI, dithranol), *m/z*: 4188.6 (M)⁺; HRMS (MALDI-TOF, dithranol): calc. for C₂₈₃H₃₄₂N₁₆O₆Zn₂: [M]⁺: *m/z*: 4188.5526, found 4188.5649.

3.4. Samples for ³¹P NMR study

Capsule **1** (2 mg, 0.45 mmol), and the corresponding Pc-C₆₀ conjugate (0.45 mmol) were dissolved in CDCl₃ or *d*₈-THF. An aliquot from each of these mixtures was taken after 1 h to ensure equilibrium conditions and a ³¹P NMR spectrum was recorded.

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