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Phthalocyanine–Azacrown–Fullerene Multicomponent System: Synthesis, Photoinduced Processes, and Electrochemistry[#]

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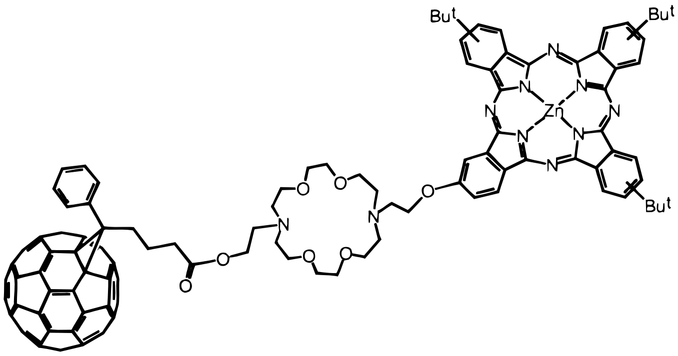
ABSTRACT



The first phthalocyanine–fullerene system having a flexible bridge containing an azacrown subunit has been synthesized, and investigations of its excited state processes through femtosecond flash photolysis experiments and of its electrochemical properties have been carried out.

Synthesis of porphyrin-linked-fullerene (C_{60}) hybrids have received considerable attention recently in order to study their photophysical properties.[1] Photoinduced electron transfer (PET) generally takes place easily in this kind of system. In some cases, these dyads can be considered as biomimetic model compounds for artificial photosynthesis with potential application in solar energy conversion systems.[2]

Taking into account the particular electronic characteristics of the phthalocyanines (Pcs)[3] and their great versatility, C_{60}−bridge−phthalocyanine systems should be an excellent

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[#] Dedicated to Professor José Elguero on the occasion of his 65th birthday.

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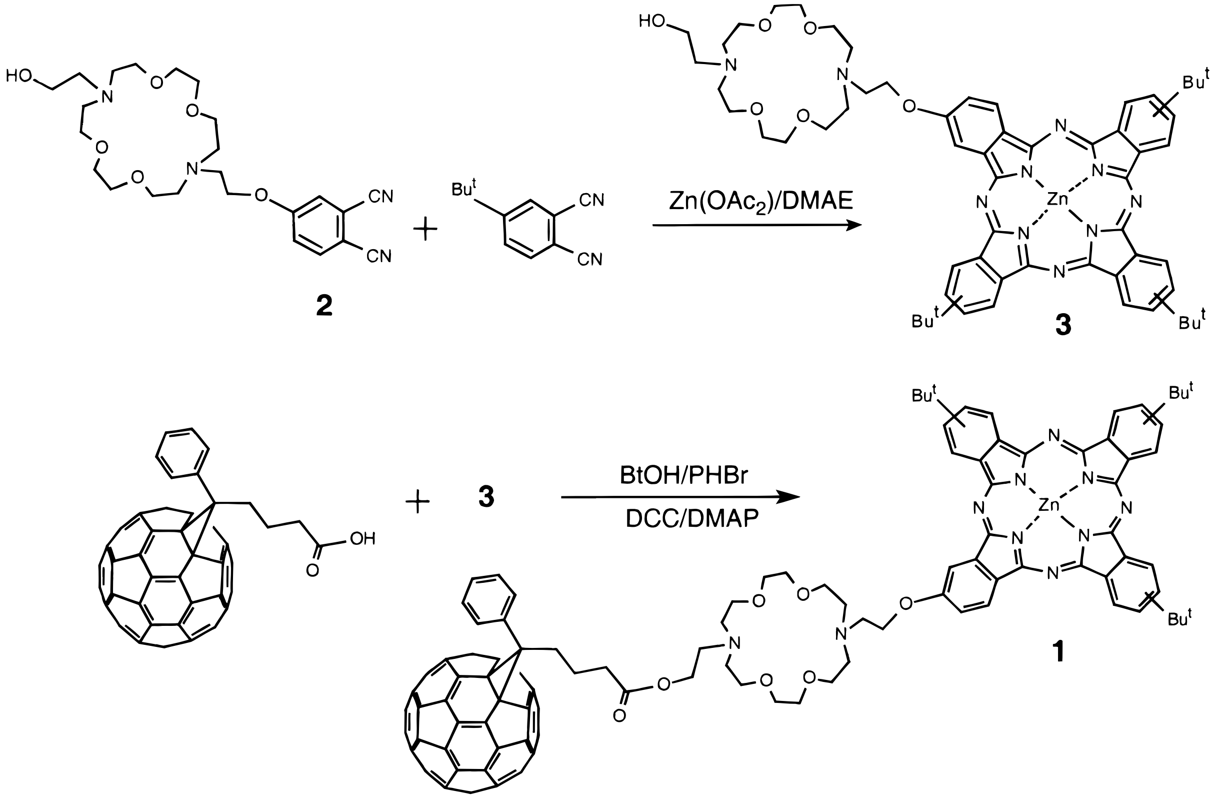
Scheme 1. Synthesis of Compound **1**



paradigm for studying the dynamics of electron and energy transfer processes between the C_{60} ball and the Pc macrocycle under controlled conditions. Surprisingly, despite the high scientific and technological interest of Pcs to date, just a couple of phthalocyanine−C_{60} arrays having only rigid linkers have been synthesized[4] and, to the best of our knowledge, no PET studies have been undertaken with these compounds.

We report here the synthesis of phthalocyanine−C_{60} hybrid **1** having a flexible linker containing an azacrown subunit. The nature of the linker could induce conformational changes in the multicomponent system in the presence, for example, of alkaline ions, potentially allowing external control over the electronic interaction between the C_{60} and the phthalocyanine.[1b] The alkali metal cation modulated redox properties of fullerene−crown ether conjugates have been reported very recently.[5a] Femtosecond flash photolysis and electrochemistry experiments have also been carried out in order to determine possible intramolecular or intermolecular electron or energy transfer between the Pc and the C_{60} in compound **1**.[5b]

For the preparation of **1** (Scheme 1) a modular approach employing a Pc building block (**3**) bearing an azacrown functionalized with a hydroxyalkyl chain was used. This compound was esterified with an appropriate C_{60} functionalized with a carboxylic group.

Phthalonitrile **2** was prepared for the first time in 55% yield by *ipso* substitution on 4-nitrophthalonitrile with *N*,*N′*-bis(hydroxyethyl)diaza-18-crown-6[6] using potasium carbonate as the base. The unsymmetrically substituted phthalocyanine compound **3** was synthesized, as a mixture of eight positional isomers, using a statistical method.[7] The conclusions of this paper do not depend on having a pure isomer; thus no further purification was attempted. One equivalent of compound **2** and three equivalents of 4-*tert*-butylphthalonitrile were allowed to react with zinc acetate in *N*,*N*-dimethylaminoethanol under reflux. The phthalocyaninate zinc complex **3** was separated from other phthalocyanines by chromatography on silica gel with chloroform/methanol as the mobile phase as a dark green solid in 21% yield. Phthalocyanine−azacrown ether−C_{60} system **1** was synthesized through a coupling[8] between the 1-(3-carboxypropyl)-1-phenyl-[6,6]-C_{61}[9] and the unsymmetrical phthalocyanine **3**, in the presence of 1-hydroxybenzotriazole (BtOH), dicyclohexylcarbodiimide (DCC), and 4-(dimethylamino)pyridine (DMAP) in bromobenzene as solvent. The crude product was purified by alumina and silica gel chromatographies succes-

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sively, to obtain a dark green powder in 25−30% yield. Compounds **1** and **3** were characterized by NMR, IR, FAB-MS,and UV−vis.[10]

Compounds **1** and **3** are quite soluble either in polar or in nonpolar organic solvents (hexane, CH_2Cl_2, MeOH). The UV−vis spectrum in $CHCl_3$ of the unsymmetrical zinc phthalocyanine **3** shows a Q-band at 680 nm and a Soret band at 351 nm. Despite the breadth of the Q-band, the splitting characteristic for the unsymmetrically substituted phthalocyanines[11] is too weak to be resolved. No shifts or splittings of the Q-band are observed in the UV−vis of the fullerene−azacrown−phthalocyanine system **1** in $CHCl_3$ in comparison with its precursor **3**. In accordance with previous data,[4] the UV−vis spectrum of compound **1** is a superposition of those of a zinc phthalocyanine and a typical 1,2 methanofullerene[8] product reflected by the absorption at 430 nm. This result shows that the fullerene has no influence on the electronic structure of the phthalocyanine ring in the ground state (Figure 1).

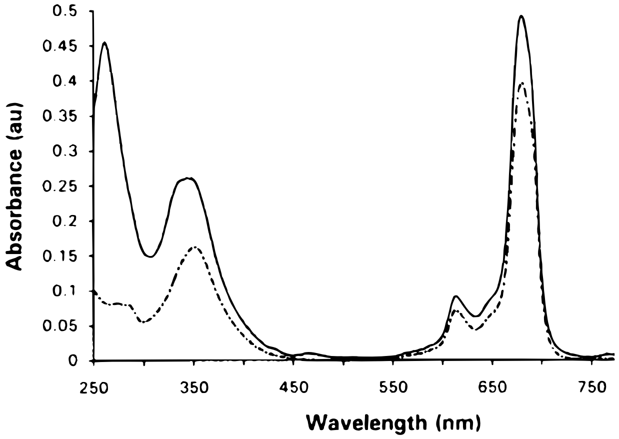

Figure 1. UV−vis spectra ($CHCl_3$) of compounds **1** (solid line) and **3** (dashed line).

Aggregation phenomena typical of Pcs can have great influence on the intermolecular photoinduced processes expected in compound **1**. Aggregation in phthalocyanine systems is easily detected from optical absorption studies resulting in a decrease of the maximum extinction coefficient and a blue shift of the Q-band. The effect of solvent ($CHCl_3$, THF, MeOH) and alkali cations (Na^+, K^+, Rb^+, Cs^+) on the aggregation of compounds **1** and **3** has been studied in the usual way.[12] Surprisingly no observable changes in the UV−vis were found. This lack of aggregation is probably due to the steric hindrance of the bulky peripheral groups of the Pc, which prevent an effective $\pi-\pi$ interaction between the phthalocyanine subunits.[13] It is remarkable that when the UV−vis spectrum of compound **3** was measured in a water−methanol (95:5) mixture at concentrations as high as 10^{-4} M, the peak corresponding to the monomer at 680 nm is still evident.[14] This nonaggregative behavior could have important advantages not only for studying intramolecular processes in compounds such as **1** but also for the application of these compounds in photodynamic therapy.[15]

Femtosecond flash photolysis studies were carried out on both compounds **1** and **3** to determine the nature of the excited state and the possible effects of electron transfer. Experiments were carried out exciting both at 680 nm (the Pc Q-band, see Figure 1) and at 400 nm (excitation localized predominantly on the substituted C_{60} moiety) to search for possible electron or hole transfer. Excited state absorption was then recorded as a function of time at both 800 nm (where the Pc cation is expected to strongly absorb)[16] and 1070 nm (where the fullerene anion is expected to absorb).[17] The decay of the excited state absorption for compound **3** is 1.8 ns; the excited state for compound **1** clearly has a shorter lifetime, with the kinetic trace fitting a biexponential decay with 40 ps and 1.3 ns lifetimes (Figure 2).

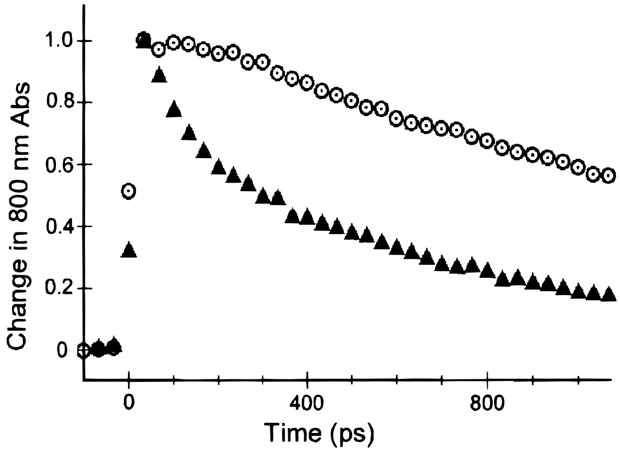

Figure 2. Femtosecond flash photolysis kinetic traces (800 nm) for compounds **1** (triangles) and **3** (circles) following excitation at 400 nm.

One possibility for the shorter excited state lifetime of compound **1** compared to **3** is hole transfer from the fullerene

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(10) Selected data for **1**: yield 25−30%; mp > 200 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 9.7−9.3 (m, 6Harom-Pc), 8.3−8.0 (m, 3Harom-Pc), 7.9−7.5 (m, 2Harom-Pc, 2Harom-Ph), 7.5−7.2 (m, 1Harom-Pc, 3Harom-Ph), 4.2−4.0 (m, 2H, Pc-OCH_2), 3.8−1.5 (broad signals, CH_2O, CH_2N, CH_2CH_2, *t*-Bu) ppm; FAB-MS (NOBA) 1972 $[(M + H)^+]$; FT-IR (KBr) ν 3440, 2956, 2925, 2857, 1733, 1610, 1489, 1454, 1392, 1330, 1258, 1090, 1047, 921, 829, 803, 749, 526 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log $\epsilon/dm^3\ mol^{-1}\ cm^{-1}$) 680 (4.1), 614 (3.35), 469 (3.32), 430 (sh), 344 (3.8) nm. Selected data for **3**: yield 21%; mp > 200 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 9.7−9.3 (m, 6Harom-Pc), 8.3−8.0 (m, 3Harom-Pc), 7.8−7.2 (3 × m, 3Harom-Pc), 4.2−4.0 (m, 2H, Pc-OCH_2), 3.8−2.5 (broad s, CH_2O, CH_2N), 1.8−1.6 (m, 9H, *t*-Bu) ppm; FAB-MS (NOBA) *m/z* 1115 $[(M + Na)^+]$, 1093 $[(M + H)^+]$; FT-IR (KBr) ν 3264, 2960, 2886, 2820, 2233, 1600, 1353, 1319, 1294, 1105, 942, 909, 754, 728, 707 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log $\epsilon/dm^3\ mol^{-1}\ cm^{-1}$) 680 (5.13), 614 (4.39), 351 (4.75) nm.

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(13) Tetra-*tert*-butylphthalocyanine zinc complex, for example, does not present aggregation either in polar (MeOH, DMF) or in moderate polar organic solvents (THF, $CHCl_3$) at 10^{-4} M concentration.

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to the Pc in **1**. To check this possibility, we also probed at 1070 nm where the C_{60} anion is reported to absorb.[17] The expected signal for hole transfer would be a complementary increase in absorption with time as charge transfer builds electron density on the fullerene moiety. The observed kinetics at 1070 nm, however, are identical to those at 800 nm, and the magnitude of the absorbance is significantly smaller. This suggests that the excited state produced by 400 nm excitation is characterized by a broad absorption band, and there appears to be no evidence for charge transfer or localization (of course, it is possible that the signature fulleride anion absorption is shifted away from 1070 nm upon substitution).

The excited state dynamics of compounds **1** and **3** were also explored following excitation of the Pc Q-band at 680 nm. Again, the observed kinetics were identical to those presented in Figure 2 with excitation at 400 nm. Additional experiments measuring the kinetics after the addition of potassium salts showed no significant changes in the excited state dynamics. This is in accordance with the UV−vis experiments which suggest that no significant changes upon complexation nor aggregation take place despite the presence of the ionophilic bridge. The photolysis data suggest that the presence of the fullerene group can modify the excited state lifetime of the Pc by energy transfer or some other nonradiative process, but evidence for charge transfer in **1** cannot be inferred.

The Osteryoung square wave voltammogram of compound **1** is shown in Figure 3. The large and sharp three waves observed correspond to the C_{60} group at $E_{1/2}$ of −1.06, −1.73, and −1.93 V, respectively, versus Fc/Fc^+. The two small waves between the second and third fullerene-based wave are assigned to the Pc group and have $E_{1/2}$ of approximately −1.60 and −1.70 V versus ferrocene. For compound **3**, these waves appear around $E_{1/2}$ values of −1.52 and −1.73 V.

To probe the possible observation of an intramolecular cation-mediated interaction between the C_{60} and the phthalocyanine moieties, K^+ was added to the solutions of **1** and **3** (ranging from 1 equiv to saturation), but no significant change was observed in the electrochemistry. The addition of K^+ or Na^+ to phthalocyanines has also been reported to have negligible effects in peak potentials and peak separations.[18] Addition of cryptand [2.2.2] to solutions of **1** did not induce any changes in the electrochemical behavior.

The anodic scan of compound **1** shows two poorly resolved waves due to the Pc group, but it was not possible to calculate the $E_{1/2}$ values. For compound **3**, a single reversible sharp wave is observed with $E_{1/2}$ of 0.00 V versus Fc/Fc^+.

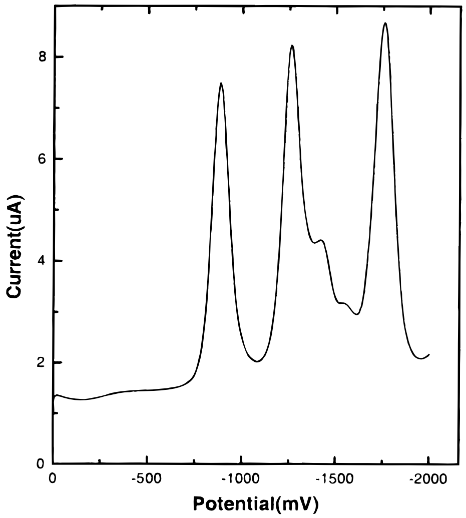

Figure 3. Osteryoung square wave voltamogram (OSWV) of compound **1** (scan rate: 100 mV s^{-1}; pseudoreference electrode Ag/Ag^+).

In summary, the electrochemical data seem to indicate that there is no significant interaction between the C_{60} and the Pc group in compound **1**. This is in accord with the small difference observed in the excited state lifetimes between compounds **1** and **3** in the flash photolysis studies, indicating no evidence of charge transfer between the two groups.

In conclusion, compound **1** represents the first flexible model of the dyad C_{60}−Pc for studying electron and excitation transfer processes. Additional photophysical experiments are needed for determining the exact nature of the observed interactions between the C_{60} and the Pc and the role of the azacrown linker. These are in progress to provide a better insight into the mechanisms involved in this model system and will be presented later.

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