Synthesis and Electrochemical Properties of Phthalocyanine – Fullerene Hybrids

Andreas Gouloumis,[a] Shen-Gao Liu,[b] Ángela Sastre,[a] Purificación Vázquez,[a] Luis Echegoyen,*[b] and Tomás Torres*[a]

Abstract: Phthalocyanines linked to C_{60} have been synthesized by two general strategies. One of them involves the addition of an azomethine ylide prepared in situ from a formyl phthalocyanine to C_{60}, and the other one involves a statistical condensation of two substituted phthalonitriles, one of them bearing the C_{60} moiety covalently attached. These new phthalocyanine-fullerene dyads have been studied by cyclic voltammetry and Osteryoung square wave voltammetry, and inter- and intramolecular electronic interactions between the two electroactive subunits have been demonstrated.

Keywords: electrochemistry · fullerenes · optical properties · phthalocyanines

Introduction

Monofunctionalized fullerenes linked to interesting electro- or photoactive species have attracted much attention in the last few years for the design of devices capable of performing complex functions, as in molecular switches, receptors, and as photoconductors in photoactive dyads.[1] The excellent electron-accepting properties of C_{60}, together with its low reorganization energy makes this molecule and its derivatives interesting building blocks of more complex systems for the conversion of light into electricity or fuels.[2]

On the other hand, phthalocyanines (Pcs)[3] are porphyrin analogues which exhibit a number of unique properties that make them of great interest in many different scientific and technological areas.[4] These compounds are therefore interesting chromophores to link covalently to a fullerene system to study their possible electronic interactions. Although much attention has been paid to the study of linked porphyrin-fullerene hybrids,[5] up to now just three examples of Pc-C_{60} derivatives have been described by Hanack et al. and Hirsch et al.[6a,b] and ourselves.[6c] However, in all of these cases no influence of the electron-withdrawing properties of the fullerene moiety was detected in the ground state, probably due to the presence of long and nonconjugated spacers. The reported synthesis and study of covalently linked porphyrin-C_{60} adducts through a pyrrolidine spacer[5c] that present extremely rapid interchromophore singlet–singlet energy and photoinduced electron transfer, and their potential use as building blocks for molecular-scale photovoltaic and/or optoelectonic systems,[7] prompted us to design a general strategy for the preparation of related phthalocyanine-C_{60} dyads which would be useful for studying the influence of the phthalocyanine ring close to the sphere. The approach would consist of the preparation of a stable and soluble formyl phthalocyanine (compound **5**) and, following Prato's method, the attachment of this aldehyde derivative to C_{60} through a pyrrolidine ring.[8]

Our group has been involved in the synthesis of metal and metal-free unsymmetrically substituted phthalocyanines carrying a wide variety of substituents[4, 9] such as amino, alkoxy, sulfone, nitro, cyano, alkyl, ethynyl, and styryl groups. The main goal of attaching these peripheral substituents is to create push–pull substituted systems for studying the second- and third-order nonlinear optical properties of these materials.[3c, 10] Although almost every type of organic functionality has been attached to the phthalocyanine ring,[3] to the best of our knowledge formyl-substituted phthalocyanines are still unknown.[11] The incompatibility of the aldehyde group with the standard cyclotetramerization conditions of phthalonitriles,[3b] evident from preliminary experiments, discouraged the use of

[a] Prof. T. Torres, A. Gouloumis, Dr. Angela Sastre,[+] Prof. P. Vázquez
Departamento de Química Orgánica (C-I)
Universidad Autónoma de Madrid
Canto Blanco, 28049 Madrid (Spain)
Fax: (+34) 91-3973966
E-mail: tomas.torres@uam.es

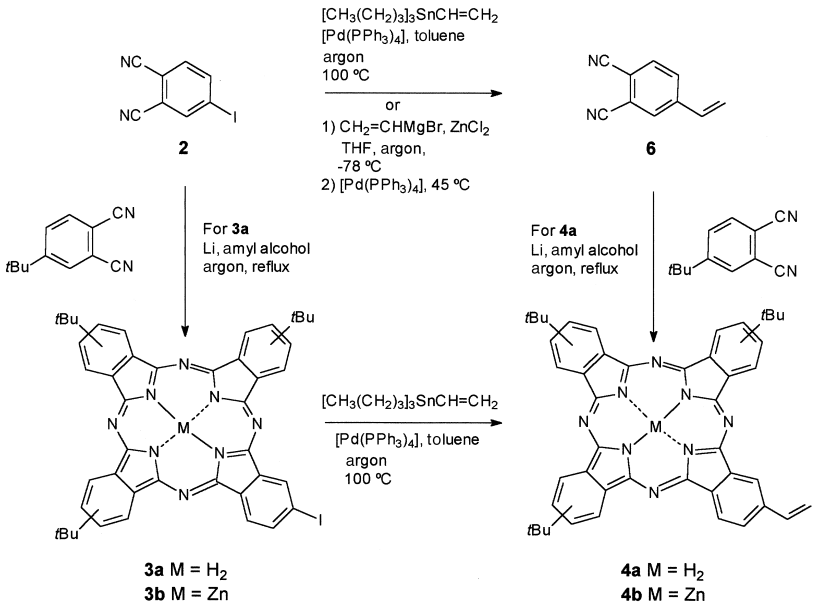
[b] Prof. L. Echegoyen, S.-G. Liu
Department of Chemistry
University of Miami
Coral Gables, Florida 33124 (USA)
Fax: (+1) 305-284-4571
E-mail: echegoyen@miami.edu

[+] Current address:
Departamento de Ciencia y Tecnología de Materiales
Universidad Miguel Hernández
Avda. del Ferrocarril S/N
Elche-03202 (Alicante) (Spain)
Fax: (+34) 96-6658793

0947-6539/00/0619-3600 $ 17.50+.50/0

4-formylphthalonitrile (**7**) in a mixed condensation reaction with other kinds of phthalonitrile for the preparation of formylphthalocyanines like **5**.

Herein, we describe two general strategies for the preparation of phthalocyanine-C_{60} derivatives **1** (see Scheme 2). It is noteworthy that one stategy involves the synthesis of formylphthalocyanines **5**, and a vinylphthalocyanine **4** (see Scheme 1), which should be considered as important intermediates for the preparation of other Pc compounds. Compounds **1**[12] have been electrochemically characterized, and the electronic interaction between the two electroactive subunits have been detected for the first time.



Scheme 1. Synthesis of iodophthalocyanines **3a**, **b** and vinylphthalocyanines **4a**, **b**.

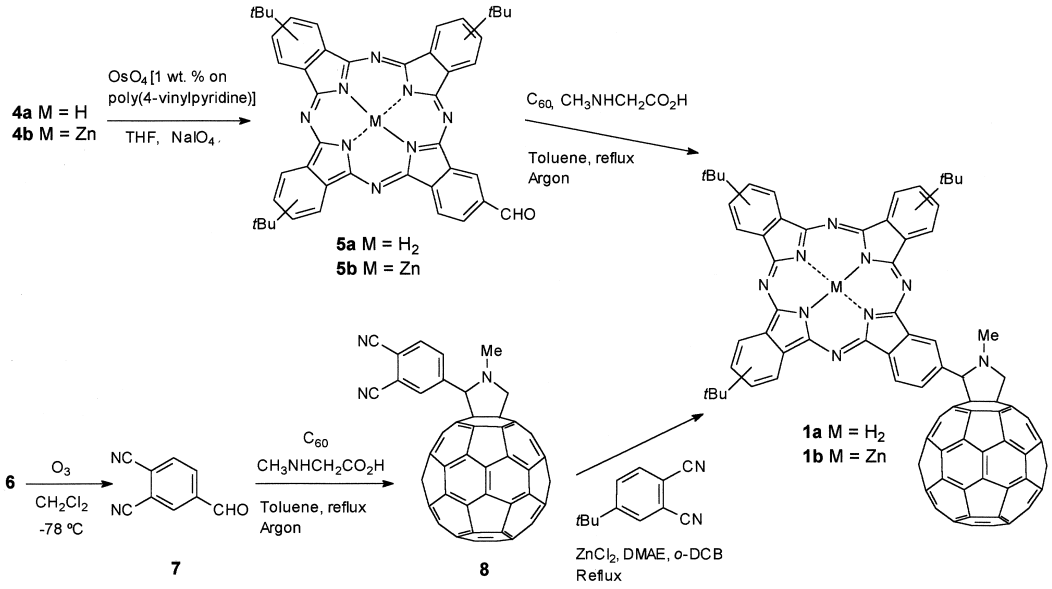
Results and Discussion

The synthesis of the Pc-C_{60} systems **1** was carried out following two different pathways depicted in Scheme 2. One of these involves the addition of an azomethine ylide, prepared in situ from the corresponding formyl derivative **5**, across a fullerene 6:6 ring juncture, and the other involves the statistical condensation of two different substituted phthalonitriles, one of them (**8**) bearing the C_{60} moeity covalently attached. Both approaches require unsymmetrically substituted phthalocyanines.[13]

For these purposes, metal-free tri-*tert*-butyl-iodophthalocyanine (**3a**) and tri-*tert*-butyl-iodophthalocyaninatozinc(II) complex (**3b**)[4a, 14] were prepared from the condensation reaction of 4-*tert*-butylphthalonitrile with 4-iodophthalonitrile (**2**) under the appropriate conditions (Scheme 1). A Stille coupling reaction of both compounds using tributyl(vinyl)tin with $[Pd(PPh_3)_4]$ as a catalyst[15] afforded tri-*tert*-butyl-vinylphthalocyanines **4a** and **4b**[14] in 90% yield. The metal-free vinylphthalocyanine **4a** could also be prepared by condensation of 4-vinylphthalonitrile (**6**) with 4-*tert*-butylphthalonitrile, using lithium metal in amyl alcohol. However, the similarity between alkyl and vinyl groups made the separation of all the phthalocyanines produced in the statistical condensation somewhat difficult, thus resulting in substantially reduced yields (11%). Formylphthalocyanines **5a**, **b** were synthesized by means of an oxidative cleavage reaction of **4a**, **b**, using polymer-supported osmium tetroxide and sodium periodate,[16] or ozone at $-78\,^{\circ}C$ in dichloromethane as solvent,[17] as oxidizing agents (Scheme 2). Higher yields were obtained when the oxidation process was carried out by the first method (75%) than when the ozonolysis procedure was employed (8–10%). The subsequent functionalization of C_{60} was based on the 1,3-dipolar cycloaddition of the azomethine ylide generated in situ from **5**. The reaction of C_{60} with tri-*tert*-butyl-formylphthalocyanines **5a**,**b** in the presence of an excess of *N*-methylglycine (sarcosine), in refluxing toluene, afforded the fulleropyrrolidine–phthalocyanines **1a** and **1b** in 43 and 40% yield, respectively (73 and 63% based on recovered C_{60}). The dyads **1a**,**b** were separated from C_{60} and the bisadducts by flash chromatography on silica gel using toluene as eluent.

In the second approach to prepare Pc-C_{60} systems **1**, 4-vinylphthalonitrile (**6**) was synthesized by using a different procedure to that previously described by Hanack et al.[18] Compound **6** was prepared from 4-iodophthalonitrile (**2**) by reaction of vinylzinc in the presence of Pd^0 as catalyst, or by means of the same Stille conditions used in the preparation of tri-*tert*-butyl-vinylphthalocyanines **4** (Scheme 1). The latter method gives a quantitative yield. Oxidative cleavage of compound **6** by ozonolysis gave rise to 4-formylphthalonitrile (**7**) in high yield (90%). Reaction of **7** with C_{60} and sarcosine yielded the phthalonitrile fulleropyrrolidine derivative **8** in 24% (63% based on C_{60} conversion). Condensation of phthalonitrile **8** with 4-*tert*-butylphthalonitrile (1:10 molar relation), in the presence of zinc chloride, afforded the fullerene–phthalocyaninatozinc(II) complex **1b** (Scheme 2). The crude reaction mixture contained only tetra-*tert*-butylphthalocyanine and compound **1b**, with no di- and mono-*tert*-

Abstract in Spanish: *Se han sintetizado ftalocianinas unidas a C_{60} siguiendo dos estrategias generales. Una de ellas implica la adición de un iluro de azometino preparado in situ a partir de la correspondiente formilftalocianina, y la otra utiliza la condensación estadística de dos ftalonitrilos sustituidos, uno de los cuales está unido covalentemente a la unidad de C_{60}. Estas nuevas diadas de ftalocianina-fullereno se han estudiado por voltametría cíclica y voltametría de onda cuadrada de Osteryoung, habiéndose puesto de manifiesto la existencia entre ambas subunidades electroactivas de interacciones electrónicas, inter- e intramoleculares.*



Scheme 2. Synthesis of fulleropyrrolidinphthalocyanines **1a**, **b**.

butyl compounds. This was probably due to the steric hinderance of two closely spaced C_{60} units inhibiting the macrocyclization. Despite the purification advantage, this second method is not efficient for the preparation of the fulleropyrrolidine Pc-C_{60} systems because of the low yields obtained.

All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, FTIR, and UV/Vis spectroscopy, and by mass spectrometry (FAB or MALDI-TOF; see Experimental Section). It is remarkable that the characteristic formyl resonance of compounds **5** appears at about the same position as for the precursor, formylphthalonitrile (**7**) ($\delta = 10.1$). The UV/Vis spectra of compounds **5** reveal a strong blue shift of the Q bands in comparison with those of their precursors **4**, as a consequence of the electron-withdrawing character of the aldehyde group. Protonated isotopic patterns at *m/z* 1458 and 1521 are observed for **1a** and **1b**, respectively, in the LSIMS and MALDI-TOF spectra, along with the corresponding $[M - C_{60}]^+$ fragments, as major species. The ^{1}H NMR spectra of the dyads **1** are complicated due to the presence of several regioisomers; however, signals corresponding to the pyrrolidine ring at $\delta = 5.5$, 5.1, and 4.4 in compound **1a** can be clearly observed.

The UV/Vis spectrum in *o*-ODCB of compound **1a** shows a split Q band at 670 and 702 nm, and a Soret band at 343 nm (Figure 1). A weak absorption at 432 nm is characteristic of the [6,6] monoadduct of C_{60}. There was little difference when compared with the UV/Vis of the metal-free phthalocyanine **9a**, as a reference compound (Q band at 666 and 702 nm), thus indicating insignificant electronic interactions between the chromophores in the ground state. This is illustrated for the metal-free compound in Figure 1. Similarly, a minimal red shift of the Q band is observed on going from **9b** (681 nm) to **1b** (683 nm) (Figure 1). Comparable effects have been found in related porphyrin-C_{60} systems.[5c, 5h] However, the UV/Vis spectra of the Zn-free compounds **1a** and **9a** are significantly red-shifted by about 20 nm with respect to their Zn-complexed analogues, especially the Q_{max} values ($\Delta\lambda_{\mathbf{9a-9b}} = 21$ and

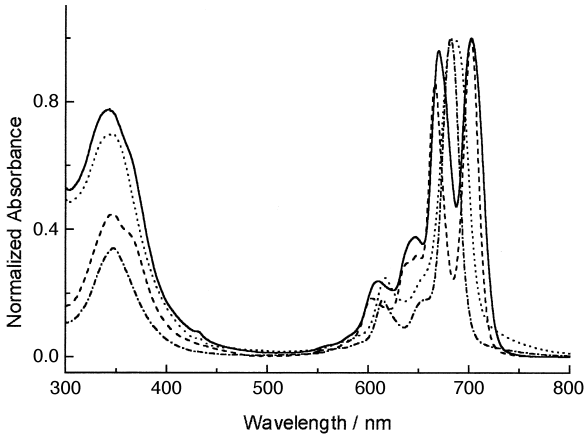
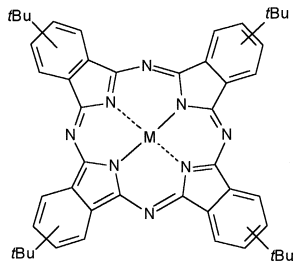
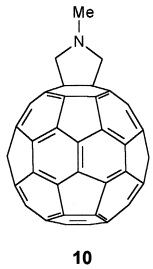


Figure 1. Electronic spectra of: **1a** (solid line), **1b** (dotted line), **9a** (dashed line), and **9b** (broken line) in *o*-ODCB. Concentration about 1×10^{-5} mol L^{-1}.





$\Delta\lambda_{\mathbf{1a-1b}} = 19$ nm in *o*-ODCB). This is in good agreement with the differences between the HOMO–LUMO gap of the phthalocyanine, as measured by electrochemistry (see Table 1). Additionally, the small red shifts in the UV/Vis spectra (ca. 2–4 nm) in the ground state between the phthalocyanines and their fullerene dyads are consistent with the electrochemical studies detailed below.

0947-6539/00/0619-3602 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 19

The solution electrochemistry of the dyads **1a**, **b** was studied using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV). The results measured for **1a**, **b** were compared with those of the model substituted phthalocyanines **9a, b** and the fulleropyrrolidine model compound **10** (see Scheme 3). The voltammetric results are presented in Figure 2 and the potential data are collected in Table 1 .

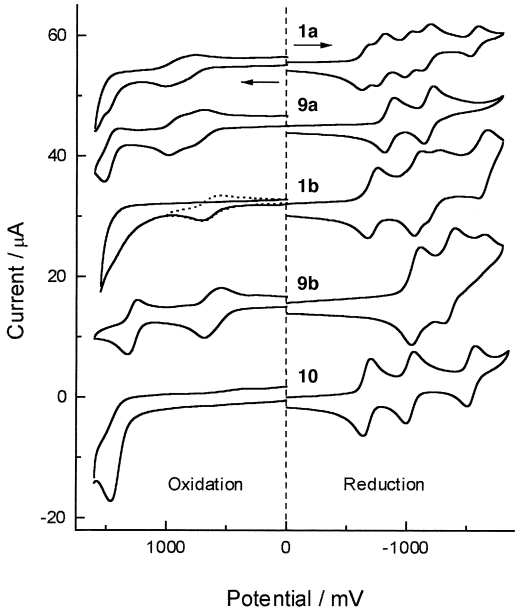


Figure 2. Cyclic voltammograms (sweep rate 0.1 $V s^{-1}$) for **1a**, **9a**, **1b**, **9b**, and **10** in the *o*-ODCB-$TBAPF_6$ system at room temperature.

Model compounds **9a**, **b**, exhibit two, one-electron reversible reduction peaks on the cathodic scan (Figure 2). ΔE_p values for these two reductions are less than 80 mV for both **9a** ($\Delta E_p^1 = 79$ and $\Delta E_p^2 = 72$ mV), and **9b** ($\Delta E_p^1 = 70$ and $\Delta E_p^2 = 75$ mV). For **9b**, a third chemically irreversible ($\nu = 100-600\ mV s^{-1}$) reduction wave was observed at around 1622 mV (Figure 2). However, for **9a**, no more reduction processes beyond -1.2 V could be detected even when the sweep was extended to -1.8 V. Thus, the third irreversible reduction peak for **9b** is probably not Pc-based, and may originate from a decomposition product, or an impurity present in the system. In the anodic scan (Figure 2), **9a** shows two, one-electron, poorly resolved quasi-reversible oxidation waves, and an electrochemically irreversible ($\nu = 100-600\ mV s^{-1}$) oxidation wave at 1523 mV (E_{pa} at $100\ mV s^{-1}$) associated with a corresponding re-reduction peak at around 1414 mV ($\Delta E_p = 109$ mV). For **9b**, the first two one-electron oxidation processes are even more poorly resolved at 20–600 mV s^{-1}, exhibiting what appears to be an electrochemically irreversible two-electron oxidation ($\Delta E_p = 133$ mV). However, the third oxidation of **9b** was a quasi-reversible process at 1283 mV ($E_{1/2}$) with ΔE_p values of 82 mV. On the whole, the cyclic voltammograms of **9a** and **9b** have similar shapes and characteristics in both cathodic and anodic sweep directions. This suggests that the redox processes for **9b** involve the phthalocyanine ligand rather than the metal center. As expected,[19] the presence of the Zn center in **9b** results in a 100–300 mV cathodic shift of the Pc reduction (vs. **9a**) and a similar shift for the oxidations (**9b** is therefore easier to oxidize). The fulleropyrrolidine model compound **10** showed the same electrochemical behavior as previously reported with a cathodic shift (ca. 100 mV) relative to pure C_{60}, but retaining the general sequential pattern.[20] The observed chemically irreversible ($\nu = 100-600\ mV s^{-1}$) oxidation peak at around 1.46 V may be due to the oxidation of the nitrogen atom in the pyrrolidine group attached to the surface of the buckyball, because no oxidations were detected with pure C_{60} under the same experimental conditions.

The cyclic voltammograms of Pc-C_{60} dyads **1a**, **b** are similar to those of **9a**, **b** (Figure 2). Both **1a** and **1b** are electrochemically active in both anodic and cathodic sweeping directions between +1.6 and -1.8 V. Furthermore, the electrochemistry of both species **1a**, **b** is almost the exact sum of the behavior of the independent components: the Pc and the C_{60} portions. Thus, in the anodic direction (0–1.6 V), **1a** shows two, poorly resolved, Pc-based, one-electron quasi-reversible oxidation waves, and a chemically irreversible ($\nu = 100-600\ mV s^{-1}$) pyrrolidine-based oxidation peak at about 1482 mV (E_{pa} at $100\ mV s^{-1}$). For **1b**, the first two Pc-based one-electron oxidations are hardly resolved and electrochemically irreversible ($\nu = 100-600\ mV s^{-1}$); see the oxidation wave at around 700 mV (E_{pa} at $100\ mV s^{-1}$) with a ΔE_p value of 138 mV ($\nu = 100\ mV s^{-1}$) (Figure 2, dotted line of **1b**). The third Pc-based oxidation is chemically irreversible ($\nu = 100-600\ mV s^{-1}$) and is located at about 1438 mV ($\nu = 100\ mV s^{-1}$) (Figure 2, solid line of **1b**). In the cathodic direction between 0 and -1.8 V, **1a** shows five reversible reduction waves ($\Delta E_p < 80$ mV) associated with the corresponding oxidation peaks, and **1b** shows four reversible, or quasi-reversible reduction waves with ΔE_p values between 56 and 105 mV. These reduction waves are based on either the C_{60} or Pc moieties, and can be easily assigned when compared to those of **9a**, **b** and **10** (Table 1). In ad-

Table 1. Electrochemical data (mV vs. Ag/AgCl) of the redox processes of compounds **1a**, **b**, **9a**, **b**, **10**, and two 1:1 molar mixtures **9a** + **10** and **9b** + **10** detected by OSWV in *o*-ODCB solution (0.05 mol dm^{-3} $TBAPF_6$) at room temperature under identical experimental conditions. Errors are estimated at less than 2 mV in all OSWV measurements.

	E_{red}^1[a]	E_{red}^2[b]	E_{red}^3[a]	E_{red}^4[b]	E_{red}^5[a]	E_{red}^6	E_{ox}^1[b]	E_{ox}^2[b]
1a	−664	−792	−1024	−1176	−1576	−2047[a]	853	957
9a		−856		−1184		−2088[b]	744	937
10	−660		−1020		−1532	−1968[a]	1446[c]	
9a + **10**	−660	−844	−1024	−1172	−1536	−1994[a]	772	956
1b	−707	−1068[d]	−1068	−1218	−1632	−2112[a]	669[e]	1324
9b		−1084		−1376	−1616[f]		601[g] 617[g]	1261
9b + **10**	−705	−1064[d]	−1064	−1376	−1580	−2016[a]	700[e]	1348

[a] C_{60}-based reduction. [b] Pc-based redox process. [c] Pyrrolidine-based oxidation. [d] The first Pc-based reduction wave was overlapped with the second C_{60}-based one. [e] Unresolved, two-electron process. [f] Unable to assign. [g] A mid-point value for **9b** at 609 mV was used.

  0947-6539/00/0619-3603 $ 17.50+.50/0

dition, all of the voltammetric processes for both **1a** and **1b** are diffusion-controlled.

In the anodic scan (0 – 1.6 V), comparison of the cyclic voltammograms of the Pc-C_{60} dyads **1a**, **b** with those of the model compounds **9a**, **b** and **10**, leads to the following general observations: 1) the resolution of the oxidation waves for both **1a** and **1b** are worse than those of the corresponding substituted phthalocyanine model compounds, indicating that electronic interactions do exist between the Pc and the C_{60} in **1a**, **b** (see below for details). Furthermore, the voltammetries of the Zn containing compounds are worse resolved than those of their Zn free analogues; 2) the oxidation potentials of the Zn containing compounds occur at more negative potentials with respect to their Zn-free analogues, indicating that the Zn containing compounds are easier to oxidize; 3) all oxidations appear to be Pc-based, not metal-based, as judged from the similarities of the voltammetric responses.

Comparison of the cathodic processes between 0 and – 1.8 V of the dyads **1a**, **b** with those of the model compounds **9a**, **b** and **10** (Figure 2), leads to the following assignments. In the case of **1a**, the first, third and fifth reduction waves are C_{60}-based and the other (the second and fourth) are Pc-based (Table 1). In the case of **1b**, the second reduction process is likely to be the sum of a C_{60}-based reduction, plus one based on the substituted phthalocyanine group. Therefore, the first, second, and fourth reductions are C_{60}-based and the two Pc-based reductions are the second and third ones. This assignment is in good agreement with that of the Diels – Alder adducts of [60]fullerene with phthalocyanines reported by Hirsch and Hanack et al., where the waves were assigned to the corresponding reduction steps by spectroelectrochemistry.[6a,b] These again support the notion that both **1a** and **1b** essentially retain the electronic properties of the C_{60} and of the substituted metal-free or metal-Pc. The observed C_{60}-based reduction potentials ($E_{1/2}$) of both **1a** and **1b** are shifted to more negative values when compared to those of the parent C_{60}. This is typical of most C_{60} monoadducts which show small shifts (ca. 100 mV) due to the partial loss of conjugation upon derivatization.[20],[21]

While cyclic voltammetric experiments were unable to detect a fourth C_{60}-based reduction wave for both **1a** and **1b** in the accessible potential range at room temperature (cf. Figure 2), OSWV revealed such processes easily (cf. Figure 3). Thus, an additional C_{60}-based electron reduction at around -2000 ± 50 mV was detected at room temperature (see Figure 3).

The main interest in these studies was the search for possible intra- and/or intermolecular electronic interactions between the C_{60} and the Pc in the ground state. Upon careful comparison of the redox potentials of **1a**, **b**, **9a**, **b**, and **10** (Table 1), we found that the Pc-based oxidation and reduction potentials are positively shifted in the dyads. For example, for **1a** (vs. **9a**), there is a 109 mV positive shift for the first oxidation, and a 64 mV positive shift for the first reduction peak (Table 1). In the case of **1b**, a positive shift of about 60 mV was measured for both the first and second oxidations with respect to those of **9b** (Table 1). For the reductions of **1b**, the first Pc-based reduction wave was positively shifted by about 16 mV, probably due to the overlap with the second

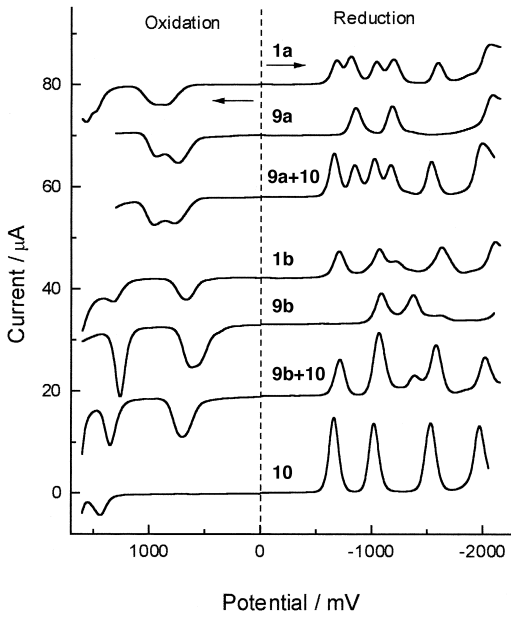


Figure 3. OSWVs for **1a**, **9a**, **1b**, **9b**, **10**, **9a** + **10** (1:1), and **9b** + **10** (1:1) in the *o*-ODCB-$TBAPF_6$ system at room temperature.

reduction of the fullerene moiety. The second Pc-based reduction was positively shifted by 158 mV (Table 1).

Conversely, the C_{60}-based reduction potentials for both dyads **1a**, **b**, are negatively shifted with respect to those of **10**, especially the third and fourth C_{60}-based reduction processes. Furthermore, the shift for **1b** is generally larger than that for **1a**. In the case of **1b**, $\Delta E_{1/2}$ values ($\Delta E_{1/2} = E_{1/2}^{\mathbf{1b}} - E_{1/2}^{\mathbf{10}}$) between **1b** and **10** for the corresponding C_{60}-based reductions are about – 47, – 44, – 48, and – 144 mV for the four successive C_{60}-based reduction waves, respectively (Table 1). These shifts for **1a** were found to be around – 4, – 4, – 44, and – 79 mV, respectively, with respect to **10**.

All of the measurements discussed above show that the redox potentials of the fullerene and the phthalocyanine moieties in **1a** and **1b** changed significantly when compared to those of the model compounds, indicating some degree of charge transfer (intra- and/or intermolcular) from the donating phthalocyanine to the acceptor fullerene at ambient conditions. Since UV/Vis measurements did not show appreciable intramolecular interactions in the ground state (see above), further discussion is presented.

In an attempt to assign the effects to intra- or intermolecular interactions, the cyclic voltammograms and OSWVs of 1:1 molar mixtures **9a** + **10** and **9b** + **10** were recorded and then carefully compared with those of the single compounds **1a**, **b**, **9a**, **b**, and **10**. All the results are shown in Figure 3 and Table 1. In the case of **9a** + **10**, the two Pc-based oxidations of the mixture show a small but measurable positive shift by about 23 ± 5 mV with respect to **9a**. This difference is smaller than that measured between **1a** and **9a**, especially for the first oxidation (Table 1). The C_{60}-based reductions of the mixture are almost identical to those of **10** in both shape and potential, especially for the first three successive reduction processes with potential differences of about -2 ± 2 mV. Interestingly and significantly, a slightly larger negative shift (– 26 mV) was observed for the fourth C_{60}-based reduction peak. For the two

0947-6539/00/0619-3604 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 19

Pc-based reductions, a small positive shift was observed of around 12 mV in comparison with those of **9a**, again smaller than that measured between **1a** and **9a** (Table 1). The same trend was observed for the mixture of **9b** and **10**, but the shifts were generally larger. All Pc-based redox waves (except the second reduction, for which no shift was observed) are positively shifted by about 85 ± 5 mV (oxidations) and 20 mV for the first Pc-based reduction. All four C_{60}-based reductions show significant negative shifts by about 46 ± 2 mV with respect to **10**. All of these results indicate that intermolecular interactions are present between the donating substituted phthalocyanine model compounds **9a** or **9b**, and the accepting fulleropyrrolidine model compound **10**. The interactions are larger in the case of the Zn-Pc compared with the Zn-free analogue. This is consistent with the results obtained from the covalently linked dyads **1a** and **1b**. However, it should be noted that the potential shifts due to intermolecular interactions in these physical mixtures are smaller than those observed in the covalently linked dyads **1a**, **b**, indicating that intramolecular interactions, to some extent, must also be contributing to the observed shifts, as shown in Figure 4. This

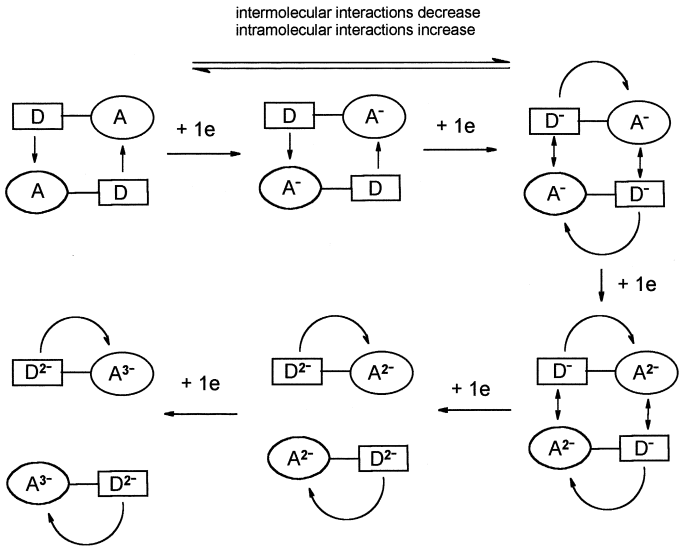


Figure 4. Schematic representation of the inter- and intramolecular interactions between and within the dyads.

is actually consistent with the results for ferrocenyl fulleropyrrolidines reported by Prato et al.,[22] and the results of dimethylaniline-substituted dithienylethyl fulleropyrrolidine recently reported by our group,[23] in which small intramolecular interactions were observed. Figure 4 presents a schematic interpretation of the results, where intramolecular electronic interactions become more prevalent as the reduction state of the compound increases sequentially.

Conclusion

Phthalocyanine-C_{60} dyads **1a, b** in which the C_{60} moiety is close to the macrocycle have been prepared. The most straightforward approach to these compounds involves formyl phthalocyanine derivatives **5a**, **b** which have been synthesized for the first time. The 1,3-dipolar cycloadditions of the azomethine ylide generated from **5a**, **b** to C_{60} proceeds in good yields. On the contrary, lower overall yields of the fulleropyrrolidine – phthalocyanine systems were obtained by using a statistical condensation method from adequately substituted phthalonitriles. Electrochemical properties of two new Pc-C_{60} dyads **1a**, **b** were studied and compared to those of the model compounds. The results of both **1a** and **1b** show that the electrochemical properties of these Pc-C_{60} dyads essentially retain the electronic properties of both C_{60} and substituted metal-free or metal-complexed phthalocyanine. The observed C_{60}-based reduction potentials of both **1a** and **1b** are shifted to more negative values when compared to those of fulleropyrrolidine **10**, especially for the Zn-complexed dyad **1b**, whose C_{60}-based reduction potentials are all shifted to more negative values by about 44 – 144 mV. In contrast, all the phthalocyanine-based redox (both reductions and oxidations) processes in **1a**, **b** were positively shifted with respect to those of model phthalocyanines **9a**, **b**. After comparing with the electrochemical results of 1:1 molar mixtures of **9a** (or **9b**) and **10**, we conclude that both inter- and intramolecular electronic interactions between the covalently bonded substituted phthalocyanine and the C_{60} ball in the dyads **1a** and **1b** contribute to the observed potential shifts. The intramolecular effect is much more pronounced as the system is sequentially reduced and, not surprisingly, becomes very noticeable after the third reduction.

Experimental Section

Melting points were determined on a Bchi apparatus and are uncorrected. Infrared spectra were recorded on a Bruker (FT-IR) spectrophotometer. The ^{1}H NMR spectra were obtained on a Bruker AC-200 (200 MHz), AC-300 (300 MHz) and DRX-500 (500 MHz), and the ^{13}C NMR spectra were obtained on a Bruker DRX-500 (125 MHz) spectrometer. UV/Vis spectra were recorded on a Perkin Elmer 8453 spectrophotometer. The mass spectra were determined on a VG AutoSpec spectrometer. Elemental analyses were performed on a Perkin Elmer 2400 CHN elemental analyzer.

Tri-*tert*-butyl-(*N*-methyl-3,4-fulleropyrrolidin)phthalocyanine (1a): A well-stirred mixture of tri-*tert*-butyl-formylphthalocyanine (**5a**) (40 mg, 0.056 mmol), C_{60} (40 mg, 0.056 mmol), and sarcosine (12.5 mg, 0.14 mmol) in toluene (50 mL) was refluxed under argon for 24 h. After flash chromatography (SiO_2 toluene increasing to toluene/ethyl acetate 95:5) **1a** (35 mg, 43 %) (73 % based on fullerene) was isolated as a green solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.8 - 8.6$, 8.4 – 7.9 (br, 12H; arom H), 5.6 – 4.9, 5.2 – 5.0, 4.6 – 4.3 (br, 3H; pyrrolidine H), 3.3 – 2.8 (br, 3H; N-CH_3), 1.9 – 1.6 (br s, 27H; C(CH_3)$_3$), (– 0.8) – (– 1.8) (br s, NH); UV/Vis ($CHCl_3$): λ_{max} (log ε) = 339 (5.0), 426 (3.7), 607 (4.3), 648 (4.6), 668 (5.0), 700 nm (5.0); MS: MALDI-TOF: *m/z*: 1458 [$M + H^+$], 1457 [M^+], 738 [$M - C_{60}$]$^+$.

Tri-*tert*-butyl-(*N*-methyl-3,4-fulleropyrrolidin)phthalocyaninatozinc(II) (1b)

Method A: Following the same procedure described for the preparation of **1a**, starting with **5b** (28 mg, 0.036 mmol), fullerene (26 mg, 0.036 mmol) and sarcosine (5 mg, 0.056 mmol), **1b** was obtained as a green solid, (22 mg, 40 %) (63 % based on fullerene). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.5 - 7.6$ (br, 12H; arom H), 5.6 – 5.4, 5.2 – 5.0, 4.6 – 4.3 (br, 3H; pyrrolidine H), 3.4 – 2.8 (br, 3H; N – CH_3), 2.0 – 1.5 (br s, 27H; C(CH_3)$_3$); UV/Vis ($CHCl_3$): λ_{max} (log ε) = 348 (4.9), 429 (3.9), 614 (4.3), 681 nm (5.1); MS: MALDI-TOF: *m/z*: 1521 [$M + H^+$], 800 [$M - C_{60}$]$^+$.

Method B: 4-*Tert*-butylphthalonitrile (19 mg, 0.11 mmol), *N*-methylpyrrolidine derivative **8** (10 mg, 0.011 mmol), Cl_2Zn (14 mg, 0.1 mmol) dissolved in a mixture of dimethylaminoethanol (DMAE; 1 mL) and *ortho*-

dichlorobenzene (ODCB; 1 mL) were refluxed under argon overnight. After flash chromatography (SiO_2, toluene) the fulleropyrrolidine–phthalocyanine derivative **1b** was afforded. MS (FAB): *m/z*: 1521 $[M+H^+]$, 800 $[M-C_{60}]^+$, 720 $[C_{60}]^+$.

Tri-*tert*-butyliodophthalocyanine (3a): Lithium metal (37 mg, 5.33 mmol) in 1-pentanol (1 mL) under an argon atmosphere was refluxed for 15 min. The suspension was cooled down to room temperature and 4-iodophthalonitrile (127 mg, 0.5 mmol) and 4-*tert*-butylphthalonitrile (553 mg, 3 mmol) in amyl alcohol (1 mL) were added and the mixture was refluxed overnight. The solvent was evaporated and the crude product obtained was purified by chromatography (Al_2O_3, hexane/dioxane 5:1) to yield **3a** (69 mg, 17%) as a blue solid. M.p. > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.0-7.3$ (m, 12H; arom H), 1.9–1.7 (m, 27H; $C(CH_3)_3$), (−3.7)–(−4.5) (m, 2H; NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 153.5$, 153.4, 128.1, 122.5, 119.2, 36.5, 36.4, 32.6, 32.5, 32.4, 32.3; IR (KBr): $\tilde{\nu} = 3416$, 3290, 2954, 2865, 1616, 1503, 1482, 1392, 1318, 1257, 1091, 1008, 749 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 343 (4.9), 609 (4.4), 641 (4.6), 666 (5.1), 695 nm (5.0); MS (FAB): *m/z*: 809 $[M+H^+]$; $C_{44}H_{41}N_8I$ (808.76): calcd: C 65.34, H 5.11, N 13.85; found: C 65.07, H 4.99, N 13.64.

Tri-*tert*-butylvinylphthalocyanine (4a)

Method A: A mixture of tri-*tert*-butyl-iodophthalocyanine (**3a**) (69 mg, 0.085 mmol) and $[Pd(PPh_3)_4]$ (5 mg, 0.0043 mmol) in toluene (50 mL) was stirred under argon. Then tributyl(vinyl)tin (50 μL, 0.17 mmol) was added. The reaction mixture was heated at 100 °C for 10 h. The solvent was evaporated and the solid residue was triturated with methanol, filtered, and chromatographed (Al_2O_3, hexane/dioxane 5:1) to afford **4a** (54 mg, 90%) as a blue solid. M.p. > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.0-7.5$ (m, 12H; arom H), 7.1–6.8 (several m, 1H; vinyl H), 6.2–5.9 (several dd, 1H; vinyl H), 5.65–5.4 (several m, 1H; vinyl H), 1.9–1.7 (m, 27H, $C(CH_3)_3$), −3.1– −3.6 (m, 2H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 153.4$, 153.3, 137.9, 135.5, 133.3, 127.8, 122.3, 118.9, 115.2, 36.4, 32.5; IR (KBr): $\tilde{\nu} =$ 3417, 3290, 2955, 2903, 2865, 1616, 1503, 1482, 1465, 1392, 1318, 1257, 1091, 1008, 828, 749 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 344 (4.8), 607 (4.3), 647 (4.6), 668 (5.0), 702 nm (5.1); MS (FAB): *m/z*: 709 $[M+H^+]$; $C_{46}H_{44}N_8$ (708.91): calcd: C 77.94, H 6.26, N 15.81; found: C 77.64, H 6.02, N 15.61.

Method B: Lithium metal (11 mg, 1.6 mmol) was dissolved under an argon atmosphere in amyl alcohol (1 mL) and the mixture was refluxed for 15 min. After cooling, 4-*tert*-butylphthalonitrile (166 mg, 0.9 mmol) and 4-vinylphthalonitrile (**6**) (16 mg, 0.1 mmol) were added and the mixture was refluxed overnight. Column chromatography (two SiO_2 columns, CH_2Cl_2/hexane 2:1 and CH_2Cl_2/hexane 1:1) gave **4a** (8 mg, 11%).

Tri-*tert*-butylvinylphthalocyaninatozinc(II) (4b): To a stirred solution of tri-*tert*-butyliodophthalocyaninatozinc(II) (**3b**) (44 mg, 0.05 mmol), $[Pd(PPh_3)_4]$ (3 mg, 0.0026 mmol) in toluene (50 mL) under an argon atmosphere, tributyl(vinyl)tin (44 μL, 0.15 mmol) was added and the solution heated at 100 °C for 10 h. The solvent was evaporated and the residual solid was triturated with methanol, filtered, and chromatographed (SiO_2, hexane/dioxane 4:1) to yield **4b** (35 mg, 91%) as a blue solid. M.p. > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.7-7.3$ (br, 12H; arom H), 7.0–6.7 (br, 1H; vinyl H), 6.0–5.7 (br, 1H; vinyl H), 5.5–5.35 (br, 1H; vinyl H), 1.7–1.5 (br, 27H; $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 153.5$, 139.0, 138.0, 128.0, 125.9, 122.5, 36.1, 32.3; IR (KBr):$\tilde{\nu} =$ 3416, 2953, 2901, 2863, 1614, 1489, 1392, 1331, 1256, 1089, 923, 747 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 354 (4.7), 616 (4.2), 682 (5.0), 718 (sh) nm (4.6); MS (FAB): *m/z*: 771 $[M+H^+]$; $C_{46}H_{42}N_8Zn$ (772.27): calcd: C 71.54, H 5.48, N 14.51; found: C 71.24, H 5.59, N 14.23.

Tri-*tert*-butylformylphthalocyanine (5a) and tri-*tert*-butylformylphthalocyaninatozinc(II) (5b)

Method A: To a suspension of OsO_4 (200 mg; 1% wt. of poly(4-vinylpyridine)) and tri-*tert*-butylvinylphthalocyanine (**4a**) (54 mg 0.076 mmol) or tri-*tert*-butyl-vinylphthalocyaninatozinc(II) (**4b**) (54 mg, 0.07 mmol) in THF (100 mL) was added dropwise a saturated aqueous solution of $NaIO_4$ (30 mL) at room temperature. The reaction mixture was stirred at this temperature for 16 h, then filtered over celite, and after the solvents were evaporated under reduced pressure, the crude products were purified by flash chromatography (SiO_2, hexane/ethyl acetate 9:1 changing to 6:1).

5a: Yield: (40 mg, 74%) as a blue solid; m.p. > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.09$ (br s, 1H; CHO), 9.6–9.1, 8.5–7.3 (m, 12H; arom H), 1.75–1.5 (m, 27H; $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 192.2$, 191.8, 153.3, 153.2, 153.1, 138.3, 134.8, 134.4, 133.0, 131.8, 130.8, 127.5, 123.8, 122.2, 120.4, 119.1, 36.2, 36.1, 32.5, 32.3; IR (KBr): $\tilde{\nu} =$ 3423, 2956, 1697, 1610, 1488, 1394, 1257, 1181, 1085, 747 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 344 (4.7), 621 (4.3), 643 (4.5), 680 (4.9), 693 nm (5.0); MS (FAB): *m/z*: 711 $[M+H^+]$; $C_{45}H_{42}N_8O$ (710.88): calcd: C 76.03, H 5.96, N 15.76; found: C 76.28, H 6.14, N 15.51.

5b: Yield: (41 mg, 76%) as a blue solid; m.p. > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.1$ (br s, 1H; CHO), 9.5–8.7, 8.5–7.3 (br, 12H; arom H), 1.7–1.5 (br, 27H; $C(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 187.3$, 153.4, 138.5, 131.8, 128.2, 123.8, 36.0, 32.3; IR (KBr): $\nu =$ 3416, 2955, 2903, 1697, 1611, 1486, 1392, 1331, 1278, 1256, 1180, 1085, 1047, 747 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 353 (4.8), 610 (4.3), 639 (4.4), 670 (5.0), 698 nm (5.0); MS (FAB): *m/z*: 773 $[M+H^+]$; MALDI-TOF: *m/z*: 773 $[M+H^+]$; $C_{45}H_{40}N_8OZn$ (774.24): calcd: C 69.81, H 5.21, N 14.47; found: C 69.65, H 5.38, N 14.23.

Method B: A solution of tri-*tert*-butyl-vinylphthalocyanine (**4a**) (47 mg, 0.066 mmol) or tri-*tert*-butyl-vinylphthalocyaninatozinc(II) (**4b**) (40 mg, 0.052 mmol) in CH_2Cl_2 (30 mL) was cooled at −78 °C, and then an excess of ozone was passed through the mixture for 3 min (the solution turned dark green and then light brown). After the reaction mixture was purged with argon for 30 min at −78 °C, it was treated with dimethyl sulfide (3 mL). The cold bath was removed and the mixture was allowed to stir at room temperature for 2 h. Removal of the solvents under reduced pressure provided a residual solid which was purified by chromatography as in Method A.

5a: Yield: (3.8 mg, 8%).

5b: Yield: (4 mg, 10%).

4-Vinylphthalonitrile (6)

Method A: To a stirred solution of 4-iodophthalonitrile (101 mg, 0.4 mmol) and $[Pd(PPh_3)_4]$ (21 mg, 0.02 mmol) in toluene (25 mL) under argon atmosphere, tributyl(vinyl)tin (0.24 mL, 0.8 mmol) was added. The mixture was heated at 100 °C for 12 h. After removal of the solvent under reduced pressure, dichloromethane (20 mL) was added and the solution was washed with water, dried, and the solvent was evaporated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2/hexane 2:1) to give **6** (60 mg, yield: 97%) as a white solid. M.p. 61 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.82$ (d, ^4J(H,H) = 1.6 Hz, 1H; arom H), 7.80 (d, ^3J(H,H) = 8.2 Hz, 1H; arom H), 7.74 (dd, ^4J(H,H) = 1.6, ^3J(H,H) = 8.2 Hz, 1H; arom H), 6.74 (dd, ^2J(H,H) = 10.8, ^3J(H,H) = 17.6 Hz, 1H), 5.96 (d, ^3J(H,H) = 17.6 Hz, 1H), 5.62 (d, ^2J(H,H) = 10.8 Hz, 1H); $C_{10}H_6N_2$ (154.17): calcd: C 77.91, H 3.92, N 18.17; found: C 77.66, H 4.13, N 18.01.

Method B: Vinylmagnesium bromide (4 mL, 4 mmol, 1M THF), $ZnCl_2$ (8 mL, 4 mmol, 0.5M THF) and dry THF (10 mL) were added at −78 °C to a three-neck flask equipped with a reflux condenser, and the mixture was warmed up to 0 °C over 30 min. Then, a solution of 4-iodophthalonitrile (1 g, 3.94 mmol), and a catalytic amount of $[Pd(PPh_3)_4]$ in freshly distilled THF was added by cannula and the mixture heated to 45 °C overnight. Water (100 mL) was added and the mixture was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried, filtered through a plug of silica, and reduced under pressure to obtain a white-yellowish solid, which upon purification by flash chromatography (SiO_2, CH_2Cl_2/hexane 4:1) afforded **6** (425 mg, 70%).

4-Formylphthalonitrile (7): A solution of 4-vinylphthalonitrile (**6**) (63 mg, 0.41 mmol) in CH_2Cl_2 (8 mL) was cooled at −78 °C, an excess of ozone was passed through the mixture (the solution becomes deep blue in color when saturated with ozone). After the reaction mixture was purged with argon for 30 min at −78 °C, it was treated with dimethyl sulfide (0.2 mL). The cold bath was removed and the mixture was allowed to stir at room temperature for 30 min. Removal of the solvents provided crude formylphthalonitrile, which was purified by flash chromatography (SiO_2, CH_2Cl_2/hexane 4:1) to furnish **7** (58 mg, 90%); m.p. 138 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 10.1$ (s, 1H; CHO), 8.25 (d, ^4J(H,H) = 1.53 Hz, 1H), 8.18 (dd, ^4J(H,H) = 1.53, ^3J(H,H) = 7.96 Hz, 1H), 7.97 (d, ^3J(H,H) = 7.96 Hz, 1H); ^{13}C NMR (65 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 188.2$ (CHO), 138.8, 134.5, 133.7, 133.2, 120.2, 117.2, 114.5 (CN), 114.3 (CN); IR (KBr): $\tilde{\nu} = 3106$, 3071, 3047, 2878 (CHO), 2233 (C≡N), 1709 (C=O), 1567, 1381, 1149, 1096, 850, 752 cm^{-1}; MS (EI) *m/z* (%): 156 (61) $[M^+]$, 155 (100) $[(M-H)^+]$, 127 (40) $[(M-CHO)^+]$; $C_9H_4N_2O$ (156.14): calcd: C 69.23, H 2.58, N 17.94; found: C 69.03, H 2.26, N 17.68.

0947-6539/00/0619-3606 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 19

4-(N-Methyl-3,4-fulleropyrrolidin)phthalonitrile (8): C_{60} (72 mg, 0.1 mmol), sarcosine (27 mg, 0.3 mmol), and 4-formylphthalonitrile (**7**) (78 mg, 0.5 mmol) were refluxed in toluene (50 mL) under an argon atmosphere for 6 h. Flash chromatography (SiO_2, toluene) afforded *N*-methylpyrrolidine derivative **8** (22 mg, 24 %; 63 % based on C_{60} conversion). M.p. > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3/CS_2$, 25 °C, TMS) δ = 8.1 – 8.4 (m, 2H), 7.89 (d, ^3J(H,H) = 8.1 Hz, 1H), 5.05 (s, 1H; pyrrolidine H), 5.04 (d, ^2J(H,H) = 9.6 Hz, 1H; pyrrolidine H), 4.34 (d, ^2J(H,H) = 9.6 Hz, 1H; pyrrolidine-H), 2.81 (s, 3H; N-CH_3); ^{13}C NMR (125 MHz, $CDCl_3/CD_3COCD_3$, 25 °C, TMS): δ = 155.63, 155.32, 152.06, 151.19, 147.28, 147.24, 146.28, 146.17, 146.09, 145.93, 145.88, 145.63, 145.58, 145.56, 145.38, 145.36, 145.32, 145.25, 145.22, 145.17, 145.15, 145.11, 144.69, 144.43, 144.40, 144.25, 143.76, 143.12, 143.05, 142.71, 142.64, 142.60, 142.52, 142.17, 142.14, 142.07, 142.03, 142.00, 141.91, 141.87, 141.79, 141.69, 141.60, 140.30, 140.23, 140.08, 139.62, 137.42, 136.26, 136.17, 135.57, 133.84, 133.63, 115.76 (CN), 114.79 (CN), 81.62 (CH), 76.45 (sp^3 C), 69.67 (CH_2), 68.96 (sp^3 C), 39.61 (NMe); MS (FAB): *m/z*: 904 ($M-H)^+$, 720 (C_{60}); IR (KBr): $\tilde{\nu}$ = 2922, 2851, 2782, 2231, 1600, 1509, 1464, 1424, 1261, 1180, 1099, 1033, 805 cm^{-1}.

Electrochemistry: Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) were performed on a Windows-driven BAS 100 w electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) at room temperature with a three-electrode configuration in *o*-dichlorobenzene (*o*-ODCB) solution containing the substrate (typically about 1 mmol dm^{-3}) and the supporting electrolyte. A platinum (∅1 mm) or glassy carbon (∅3 mm) disc served as the working electrode, a platinum wire (∅1 mm) and a commercial Ag/AgCl aqueous electrode being the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The surface of the working electrode was polished with commercial Alpha Micropolish Alumina No. 1C (Aldrich) with a particle size of 1.0 micron. Tetrabutylammonium hexafluorophosphate ($n$$Bu_4NPF_6$) purchased from Fluka (> 99 %) was recrystallized twice from ethanol and dried under vacuum overnight prior to use and was employed as the supporting electrolyte in 0.1 mol dm^{-3} concentration. Solutions were stirred and deaerated by bubbling argon for a few minutes prior to each voltammetric measurement. The scan rate was 100 mV s^{-1} unless otherwise specified. OSWVs were obtained by using a sweep width of 25 mV, a frequency of 15 Hz, a step potential of 4 mV, and a quiet time of 2 s. Experimental uncertainty on all measured potentials by OSWV reported in this paper are estimated less than 2 mV.

Acknowledgements

This work was supported by CICYT and Comunidad de Madrid (Spain) through grants MAT-99-0180, and 07N/020/98. A Graduated Research Fellowship of the Ministerio de Educación y Cultura to A. G. is gratefully acknowledged. S-G.L. and L.E. greatly appreciate the National Science Foundation (grant CHE-9816503) for generous support of this work.

[1] a) H. Imahori, Y. Sakata, *Adv. Mater.* **1997**, *9*, 537 – 546; b) N. Martín, L. Sánchez, B. Illescas, I. Pérez, *Chem. Rev.* **1998,** *98*, 2527 – 2547.

[2] V. Balzani, F. Scandola, *Supramolecular Photochemistry*; Ellis Horwood, New York, **1991**.

[3] a) *Phthalocyanines: Properties and Applications, Vols. 1 – 4* (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, Weinheim, **1989**, **1993**, **1996**; b) M. Hanack, H. Heckmann, R. Polley in *Methods in Organic Chemistry (Houben-Weyl), Vol. E 9d* (Ed.: E. Schaumann), Thieme, Stuttgart, **1998**, pp. 717 – 833; c) G. de la Torre, M. Nicolau, T. Torres in *Phthalocyanines: Synthesis, Supramolecular Organization and Physical Properties* (*Handbook of Advanced Electronic and Photonic Materials*) (Ed.: H. S. Nalwa), Wiley, Chichester, **2000**, *in press.*

[4] For recent papers of our group in this field see: a) E. M. Maya, P. Vázquez, T. Torres, *Chem. Eur. J.* **1999**, *5*, 2004 – 2013; b) A. González, P. Vázquez, T. Torres, *Tetrahedron Lett*. **1999**, *40*, 3263 – 3266; c) G. de la Torre, M. V. Martínez-Díaz, P. Ashton, T. Torres, *J. Org. Chem*. **1998**, *63*, 8888 – 8893; d) F. Fernández-Lázaro, T. Torres, B. Hauschel, M. Hanack, *Chem. Rev.* **1998**, *98*, 563 – 575; e) U. Keller, B. del Rey, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux, J. Zyss, T. Torres, *J. Am. Chem. Soc*. **1998**, *120*, 12808 – 12817.

[5] a) P. A. Liddell, J. P. Sumida, A. N. Macpherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore, D. Gust, *Phtochem. Photobiol*. **1994**, *60*, 537 – 541; b) H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada, Y. Sakata, *Chem. Lett*. **1995**, 265 – 266; c) T. Drovetskaya, C. A. Reed, P. Boyd, *Tetrahedron Lett.* **1995**, *36*, 7971 – 7974; d) H. Imahori, Y. Sakata, *Chem. Lett*. **1996**, 199 – 200; e) M. G. Ranasinghe, A. M. Oliver, D. F. Rothenfluh, A. Salek, M. N. Paddon-Row, *Tetrahedron Lett.* **1996**, *27*, 4797 – 4800; f) T. Akiyama, H. Imahori, A. Ajawakom, Y. Sakata, *Chem. Lett*. **1996**, 907 – 908; g) H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, Y. Sakata, *J. Am. Chem. Soc*. **1996**, *118*, 11771 – 11782; h) R. Fong II, D. I. Schuster, S. R. Wilson, *Org. Lett*. **1999**, *1*, 729 – 732.

[6] a) T. G. Linssen, K. Dürr, M. Hanack, A. Hirsch, *J. Chem. Soc. Chem. Commun.*, **1995**, 103 – 104; b) K. Dürr, S. Fiedler, T. Linssen, A. Hirsch, M. Hanack, *Chem. Ber*. **1997**, *130*, 1375 – 1378; c) Á. Sastre, A. Gouloumis, P. Vázquez, T. Torres, V. Doan, B. J. Schwartz, F. Wudl, L. Echegoyen, J. Rivera, *Org. Lett.* **1999**, *1,* 1807 – 1810.

[7] D. Kuciauskas, S. Lin, G. R. Seely, A. L. Moore, T. A. Moore, D. Gust, T. Drovetskaya, C. A. Reed, P. D. W. Boyd, *J. Phys. Chem.* **1996**, *100*, 15926 – 15932.

[8] M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519 – 526 and references therein.

[9] a) A. Sastre, T. Torres, M. Hanack, *Tetrahedron Lett*. **1995**, *36*, 8501 – 8504; b) A. Sastre, B. del Rey, T. Torres, *J. Org. Chem.* **1996**, *61*, 8591 – 8597; c) G. de la Torre, T. Torres, *J. Phorph. Phthalocy.* **1997**, *1*, 221 – 226; d) E. M. Maya, P. Vázquez, T. Torres, *Chem. Commun*. **1997**, 1175 – 1176.

[10] G. de la Torre, P. Vázquez, F. Agulló-López, T. Torres, *J. Mat. Chem.* **1998**, *8*, 1671 – 1683; b) G. de la Torre, T. Torres, F. Agulló, *Adv. Matter.* **1997**, *9*, 265 – 269.

[11] The first example of a Pc analogue bearing an aldehyde function has been recently reported in a modified Pc in which the formyl group is not directly linked to an isoindole subunit. R. Jung, K.-H. Schweikart, M. Hanack, *Eur. J. Org. Chem.* **1999**, 1687 – 1691.

[12] Compounds **1** are actually mixtures of positional isomers (relative to *tert*-butyl groups position), but the conclusions of this article do not depend on having pure isomers since given the planar character of the Pc and the spherical nature of C_{60} the relative orientation of both moieties should not be affected since the electronic interactions Pc – C_{60} are equivalent in all isomers.

[13] Unsymmetrically substituted phthalocyanines are usually not difficult to prepare, but arduous to separate from the statistical mixture obtained in the condensation of two different substituted units. The lack of an effective regioselective procedure for the preparation these compounds[3] lead to the systematic use of the mixed condensation method for the preparation of this kind of compounds.

[14] H. Ali, J. E. Van Lier, *Tetrahedron Lett*. **1997**, *38*, 1157 – 1160.

[15] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504 – 519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508 – 524.

[16] G.Cainelli, M. Contento, F. Manescalchi, L. Plessi, *Synthesis* **1989**, 47 – 48.

[17] Z. Cohen, E. Keinan, Y. Mazur, A. Ulman, *J. Org. Chem.* **1976**, *41*, 2651 – 2652.

[18] A. Beck, M. Hanack, *Chem. Ber.* **1993**, *126*, 1493 – 1494.

[19] a) A. R. Özkaya, A. I. Okur, A. Gül, Ö. Bekaroglu, *J. Coord. Chem*. **1994**, *33*, 311 – 318; b) A. R. Özkaya, I. Yilmaz, Ö. Bekaroglu, *J. Porphyrins Phthalocyanines* **1998**, *2*, 483 – 492.

[20] M. Prato, *J. Mater. Chem*. **1997**, *7*, 1097 – 1109.

[21] L. Echegoyen, L. E. Echegoyen, *Acc. Chem. Res.* **1998**, *31*, 593 – 601.

[22] M. Maggini, A. Karlsson, G. Scorrano, G. Sandonà, G. Farnia, M. Prato, *J. Chem. Soc. Chem. Commun*. **1994**, 589 – 590.

[23] S. G. Liu, L. H. Shu, J. Rivera, H. Y. Liu, J.-M. Raimundo, J. Roncali, A. Gorgues, L. Echegoyen, *J. Org. Chem*. **1999**, *64*, 4884 – 4886.

Received: January 28, 2000 [F2267]