JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 844–851
DOI: 10.1002/poc.558

Synthesis and photophysical properties of Zn(II) porphyrin–C_{60} dyad with potential use in solar cells†

M. Elisa Milanesio, Miguel Gervaldo, Luis A. Otero, Leonides Sereno, Juana J. Silber and Edgardo N. Durantini*

Departamento de Química, Universidad Nacional de Río Cuarto, Agencia Postal Nro 3, 5800 Río Cuarto, Argentina

Received 12 March 2002; revised 10 July 2002; accepted 15 July 2002

ABSTRACT: Zn(II) porphyrin–C_{60} dyad (**7**) was synthesized by the coupling reaction between Zn(II) 5-(4-aminophenyl)-10,15,20-tris(4-methoxylphenyl)porphyrin (**4**) and 1,2-dihydro-1,2-methanofullerene[60]-61-carboxylic acid (**6**). The electron-donor capacity of the porphyrin moiety in dyad **7** is enhanced by methoxy group substitution on the macrocycle peripheries and complexation with Zn(II). Spectroscopic studies showed only a very weak interaction between the chromophores in the grown state. The emission of the porphyrin moiety in dyad **7** is strongly quenched by the attached fullerene C_{60} moiety. Thermodynamically, dyad **7** shows a higher capacity to form a photoinduced charge-separated state than the same dyad with free-base porphyrin. This was confirmed by steady-state photolysis in the presence of methylviologen as electron acceptor and *N,N,N′,N′*-tetramethyl-1,1′-naphthidine as electron donor. Dyad **7** sensitizes a tin dioxide (SnO_2) electrode and the generation of photoelectrical effect shows that a large photocurrent is generated for the dyad **7** in the region where C_{60} is mainly responsible for light absorption. Also, dyad **7** produces a higher photoelectric effect than the corresponding amidoporphyrin model. An alternative photoelectric mechanism, other than direct electron injection from the excited porphyrin to SnO_2, could be occurring, probably involving a charge-separated state of dyad **7**. These results indicate that dyad **7** shows interesting properties for possible application in artificial solar energy conversion devices. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: metalloporphyrin; fullerene; metal complex; energy conversion; solar cell; photosensitization

INTRODUCTION

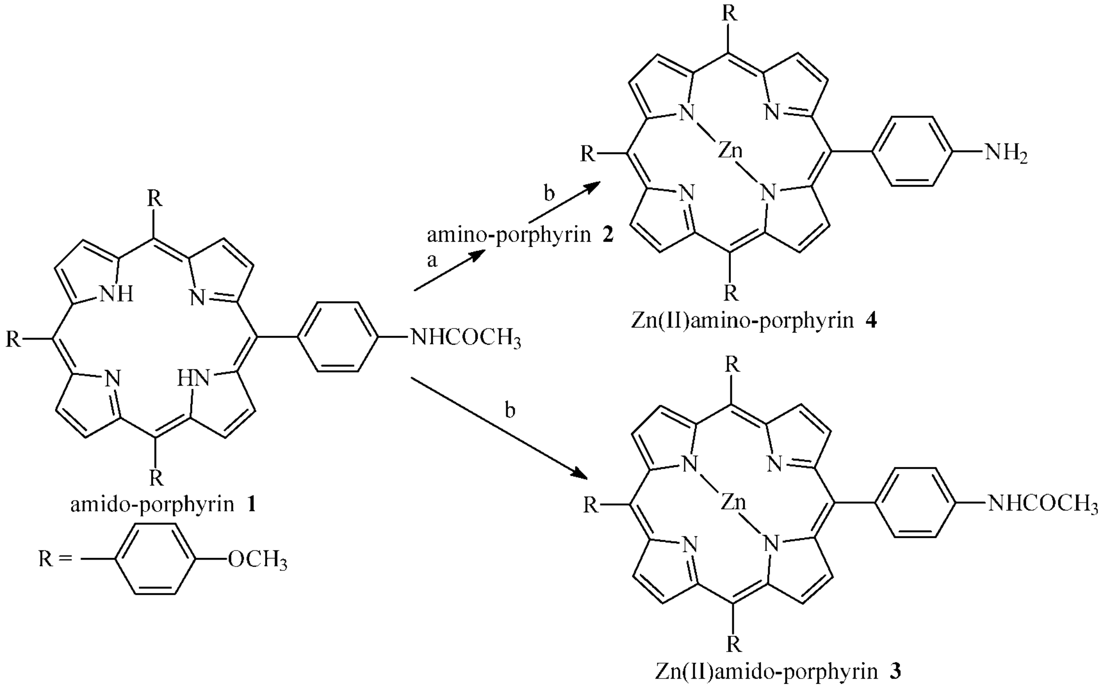
Molecular dyads composed of an energy or electron donor capable of photoinduced energy or electron transfer to a covalently linked acceptor component have been used as mimics of the natural photosynthetic reaction centers and as photochemical molecular devices.[1,2] Porphyrin derivatives are the most frequently employed building blocks as electron donors and sensitizers in artificial photosynthetic models.[3,4] Several related porphyrins have been used as light receptors in solar energy conversion, achieving spectral sensitization of wide bandgap semiconductors.[5–7] In these systems, the energy difference between the conduction band edge of an n-type semiconductor and the oxidation potential of the excited adsorbed dye provides the driving force for photoinduced charge injection.[8] On the other hand, the unique three-dimensional structure of fullerene C_{60} derivatives, and the facile electron acceptability of up to six electrons, make them good candidates as electron acceptors.[3,9–15] The development of covalent chemistry of C_{60} has opened up the possibility of attaching this spherical structure with several electron donors separated by different spacers,[16–21] in which there is light-induced transfer of electrons or energy from a porphyrin donor to a fullerene acceptor.[3]

In previous work we have developed a convenient procedure for the synthesis of *meso*-substituted porphyrins bearing three identical molecular structures B and one different A (AB_3-porphyrins) from *meso*-(substituted) dipyrromethanes.[22–24] Structure A bears a functional group which can be used to link the porphyrin with other molecules, while B are substituted by groups that allow changes of the physical properties of the tetrapyrrolic macrocycle. Several of these porphyrins have been covalently linked to other structures by amide bonds to form dyads with potential use in solar cells.[6,25,26] Particularly interesting is the dyad formed by free-base methoxyphenylporphyrin attached to fullerene C_{60}.[26,27] The generation of photoelectrical effects through the spectral sensitization of an SnO_2 nanostructured electrode by this dyad is around twice as high as the yield of

**Correspondence to:* E. N. Durantini, Departamento de Química, Universidad Nacional de Río Cuarto, Agencia Postal Nro 3, 5800 Río Cuarto, Argentina.
E-mail: edurantini@exa.unrc.edu.ar

[†] Presented in part at the Sixth Latin American Conference on Physical Organic Chemistry (CLAFQO-6), held at Isla Margarita, Venezuela, during December 2001.

Contract/grant sponsor: Consejo Nacional de Investigacioues Científicas y Técnicas (CONICET).
Contract/grant sponsor: Agencia Nacional de Promoción Científica y Técnica.
Contract/grant sponsor: Fundación Antorchas.
Contract/grant sponsor: SECYT de la Universidad Nacional de Río Cuarto.



Scheme 1. Synthesis of Zn(II) amidoporphyrin **3** and Zn(II) aminoporphyrin **4**. a., THF–CH_3OH–KOH, ~70 °C, 18 h; b, $Zn(CH_3COO)_2$–CH_3OH–CH_2Cl_2, room temperature, 30 min

the porphyrin moiety at the same wavelength (Soret band). A mechanism involving the formation of an intramolecular photoinduced charge-transfer state was proposed to explain the efficiency in the generation of photoelectrical effect.[27] Recently, the photoelectrochemical activity of a zinc porphyrin–fullerene dyad, which forms cluster aggregates on nanostructured SnO_2 films, has also been reported.[28]

This paper reports the synthesis of the Zn(II) porphyrin–C_{60} dyad 7, which was designed in order to stabilize the charge-transfer state ($ZnP^{\cdot+}$–$C_{60}^{\cdot-}$). Thus, the porphyrin moiety bears electron-donating methoxy groups and a complex with Zn(II), which stabilize the radical cation. This structure is covalently linked to the electron-acceptor C_{60} moiety by an amide bond. Thermodynamically the ion pair formation ($ZnP^{\cdot+}$–$C_{60}^{\cdot-}$) is favored in dyad **7** with respect to the free-base porphyrin–C_{60} dyad **8**. Preliminary studies of the spectral sensitization of nanostructured wide bandgap semiconductor (SnO_2) electrodes coated with dyad **7** show a visible light-harvesting efficiency that is remarkably improved as compared with the corresponding monomers.

RESULTS AND DISCUSSION

Synthesis

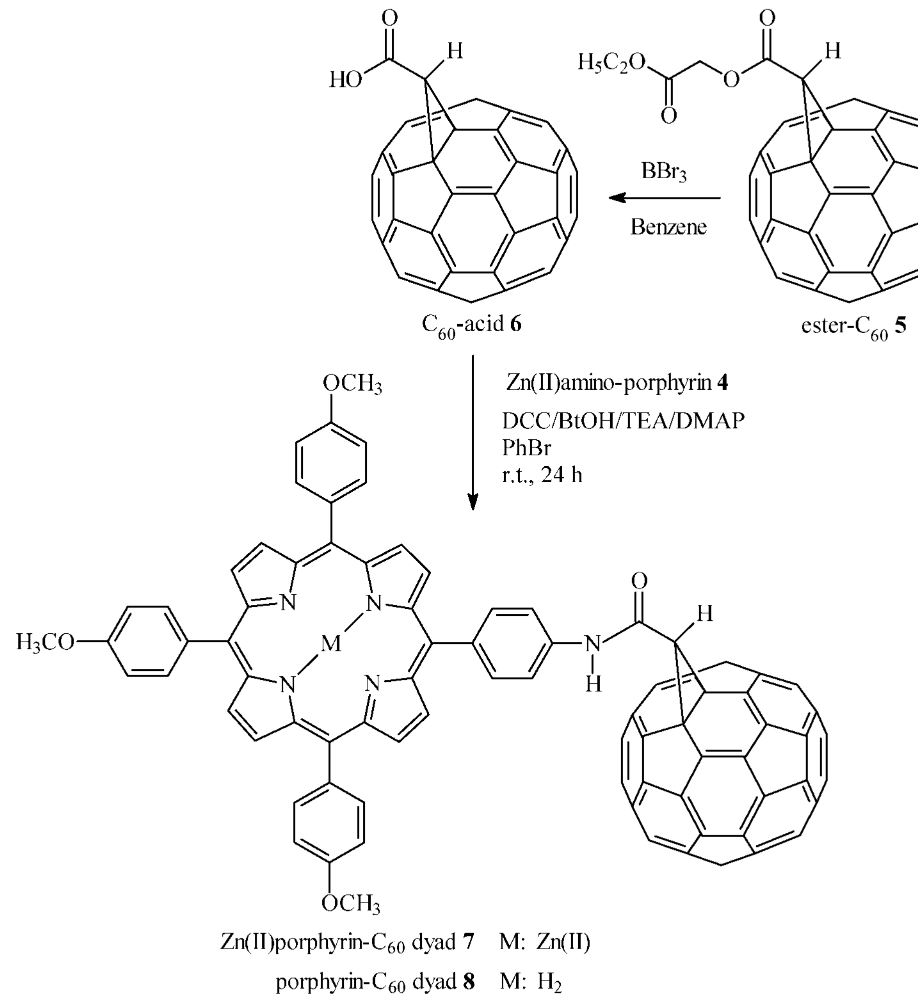
5-(4-Acetamidophenyl)-10,15,20-tris(4-methoxyphenyl)-porphyrin (**1**) was conveniently synthesized in 18% yield from the acid-catalyzed condensation of *meso*-(4-methoxyphenyl)dipyrromethane with an appropriate binary mixture of 4-methoxybenzaldehydes and 4-acetamidobenzaldehyde.[22,26] The basic hydrolysis of amidoporphyrin **1** produced aminoporphyrin **2** in 75% yield by heating in tetrahydrofuran (THF)–methanol–KOH medium (Scheme 1, step a). Treatment of porphyrins **1** and **2** with zinc acetate in dichloromethane (Scheme 1, step b) afforded the corresponding Zn(II) amidoporphyrin **3** (98%) and Zn(II) aminoporphyrin **4** (96%), respectively.

The precursor 1,2-dihydro-1,2-methanofullerene[60]-61-carboxylic acid (**6**) was prepared from (ethoxycarbonyl)methyl-1,2-dihydro-1,2-methanofullerene[60]-61-carboxylate (**5**) according to the method described in the literature.[29]

The dicyclohexylcarbodiimide-mediated condensation of the C_{60}-acid **6**[21,26,29] and the Zn(II) aminoporphyrin **4** produces the Zn(II)porphyrin–C_{60} dyad **7** as shown in Scheme 2. The reaction was performed in the presence of dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (BtOH), triethylamine (TEA) and 4-(dimethylamino)pyridine (DMAP) in bromobenzene (PhBr) at room temperature for 24 h, to yield after work-up the desired dyad **7** in 70% yield.

Absorption spectra

The absorption spectra of the dyad **7** and the corresponding porphyrin model in toluene are shown in Fig. 1. The absorption in the UV region is stronger than that of



Scheme 2. Synthesis of Zn(II) porphyrin–C$_{60}$ dyad **7**

porphyrin owing to the presence of the C$_{60}$ moiety, whereas in the visible region the spectra of the dyads are similar to that of the porphyrin monomer. Also, the porphyrin absorption shows the typical Soret and characteristic Q-bands of a Zn(II) metalloporphyrin. The absorption maxima of the Soret and Q-bands are given in Table 1. The spectrum of dyad **7** is essentially a linear combination of the spectra of the corresponding models **3** and **5**, with only minor differences in wavelength maxima and band shapes [Fig. 1(B)]. Thus the absorption spectra are consistent with only a weak interaction between the moieties in the ground state and the two chromophores retain their individual identities.[10,13,25]

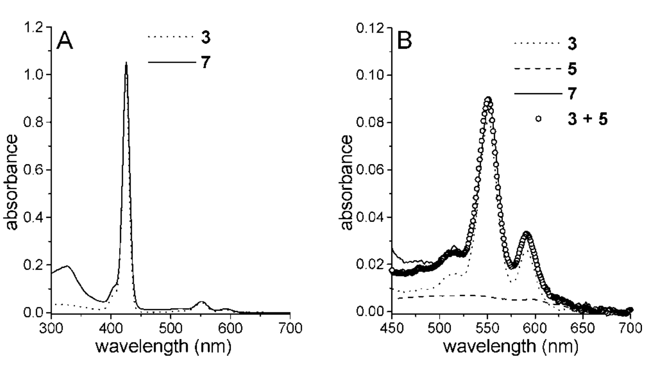


Figure 1. Absorption spectra in toluene of (A) Zn(II) amidoporphyrin **3** (dotted line) and dyad **7** (solid line), 2.7 μM, and (B) Q-band enlargement of Zn(II) amidoporphyrin **3** (dotted line), ester–C$_{60}$ **5** (dashed line), dyad **7** (solid line) and a linear combination of the spectra of **3** and **5** (open circle), 5.1 μM

Steady-state fluorescence spectra

The corrected emission spectra were taken in toluene, exciting the sample at 550 nm [Fig. 2(A); note that the dyad **7** emission is multiplied by 10]. The fluorescence emission maxima are shown in Table 1. A similar Stokes shift of ~10 nm was observed for the porphyrin **3** and dyad **7**. The fluorescence quantum yields (ϕ_F) of these compounds were calculated by the steady-state comparative method using tetraphenylporphyrin (TPP) as a reference (Table 1). Dyad **7** shows only very weak

Table 1. Absorption and fluorescence emission data in toluene

Compound	Absorption λ_{max} (nm) $\epsilon \times 10^{-4}$ ($l\,mol^{-1}\,cm^{-1}$)[a]					Fluorescence λ_{max} (nm)			ϕ_F
3		426 (39.0)	552 (1.71)	593 (0.61)		603	653		0.064
7	325 (7.10)	426 (39.1)	553 (1.75)	594 (0.64)	712	604	654	720	1.5×10^{-3}

[a] The ε values are in parentheses

emission from the porphyrin moiety, indicating strong quenching of the porphyrin excited singlet state (quenching efficiency η_q ≥0.98) by the attached fullerene structure. Similar quenching values have been reported for porphyrin derivatives attached to a fullerene structure.[10,11,14,27] As can be see in Fig. 2(A), dyad **7** shows very weak emission from the C_{60} moiety with a peak maximum at ~720 nm.[9,10] The energy levels of the singlet excited stated of $^1ZnP^*–C_{60}$ and $ZnP–^1C_{60}^*$ were calculated in toluene taking into account the energy of the 0–0 electronic transition, giving 2.07 and 1.73 eV, respectively.[9] These results show that energy transfer from the locally excited porphyrin singlet state to the C_{60} moiety is an exothermic process by 0.34 eV.

In a more polar solvent, THF, practically no fluorescence emission from the C_{60} was detected when the Q-band was excited, where the absorption is mainly due to the porphyrin moiety (result not shown). Fluorescence spectra were also taken in both solvents (toluene and THF), exciting dyad **7** at 426 nm, where both porphyrin and C_{60} moieties absorb [Fig. 2(B)]. Under this condition, fluorescence from the C_{60} moiety was clearly evidenced in toluene, whereas in THF only a very weak emission from the C_{60} structure at ~720 nm is observed. The ϕ_F of dyad **7** is ~1.6 times lower in THF than in toluene. These results suggest that in toluene there is a relaxation pathway mainly from the excited singlet state of the porphyrin to that of the C_{60}, as evidenced by the excitation spectra at 725 nm [see Fig. 2(B), inset]. In a more polar solvent, such as THF, another competitive electron transfer pathway from the porphyrin to the C_{60} could be occurring to produce an ion pair state.[9,10]

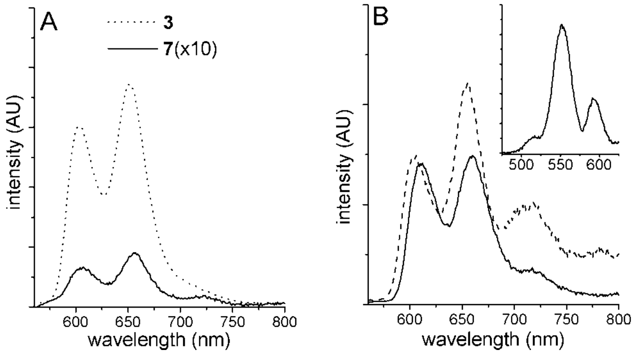
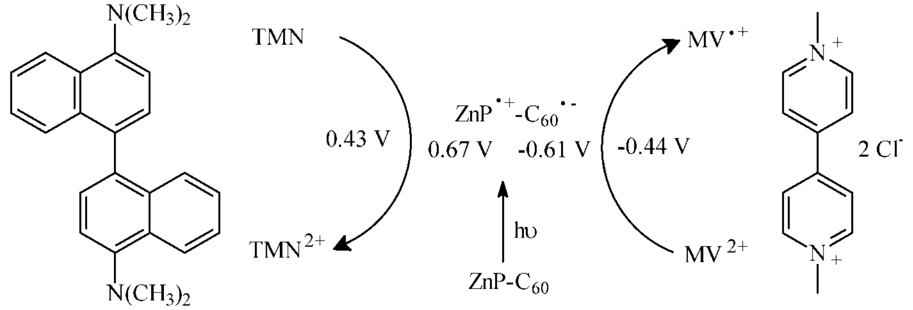


Figure 2. Fluorescence emission spectra of (A) Zn(II) amidoporphyrin **3** (dotted line) and dyad **7** multiplied by 10 (solid line) in toluene, λ_{exc} = 550 nm, 5.1 μM, and (B) dyad **7** in toluene (dashed line) and in THF (solid line), λ_{exc} = 426 nm. Inset: excitation spectrum in toluene, λ_{em} = 725 nm

Steady-state photolysis in the presence of an electron acceptor and an electron donor

The asymmetrical dyad **7** presents mainly two moieties with different electron donor–acceptor properties. The electron-donor character of the tetrapyrrolic macrocycle was enhanced by the presence of methoxy groups in a *para* position on the peripheral phenyl rings. This property was further enlarged in dyad **7** by forming a metal complex with Zn(II). The increase in the extra electron-donor character of the porphyrin was inferred by the oxidation potential of Zn(II) amidoporphyrin **3** (0.67 V), which is 240 mV easier to oxidize than the corresponding 5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (0.91 V), where the free base bears methyl groups instead methoxy groups.[6] Therefore, the structure formed by Zn(II) porphyrin linked to electron acceptor C_{60} makes dyad **7** a good candidate for a photoinduced electron-transfer system.[3] Thermodynamically, dyad **7** presents a high capacity to form a photoinduced charge-separated state. The energy of 1.28 eV for the ion pair state ($ZnP^{\cdot+}–C_{60}^{\cdot-}$) of dyad **7** was calculated considering the first oxidation potential of the porphyrin and the first reduction potential of the C_{60} (−0.61 V) moieties in 1,2-dichloroethane.[27] The formation of this state was confirmed using methylviologen (MV^{2+}) as electron acceptor.[30] A comparison between the one-electron reduction potential of C_{60} (−0.61 V) and the MV^{2+} (−0.44 V) indicated that an electron transfer from $C_{60}^{\cdot-}$ to MV^{2+} is exothermic by 0.17 eV (Scheme 3). Also, an external electron donor, such as *N,N,N′,N′*-tetramethyl-1,1′-naphthidine (TMN),[31] can be added to the system. This molecule has a well-established redox process in two oxidation steps, where the first potential to produce monocation is at 0.43 V, and the second one is easier to oxidize than the first.[31] Therefore, an electron transfer from TMN to $ZnP^{\cdot+}$ (0.67 V) is expected to be exothermic by 0.24 eV. Under this condition, once the charge separation state has been obtained by photoirradiation of the Soret band of dyad **7** in the absence of oxygen, the oxidation of TMN and the reduction of MV^{2+} should be accomplished by a reaction with $ZnP^{\cdot+}$ and $C_{60}^{\cdot-}$, respectively, as illustrated in Scheme 3. The steady-state photolysis of the dyad **7**–TMN–MV^{2+} system deoxygenated with argon in DMF–water (5%)



Scheme 3. Photoreduction of MV^{2+} by dyad **7** in the presence of TMN

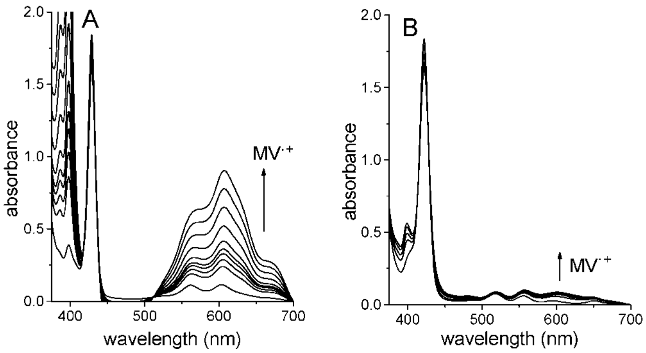


Figure 3. Spectral change observed in the steady-state photolysis of (A) dyad **7** (irradiation times: 0, 10, 15, 20, 25, 35, 55, 85, 115, 145 min) and (B) free-base dyad **8** (irradiation times: 0, 20, 40, 60, 80 min), in DMF–water (5%) containing MV^{2+} (8.0×10^{-4} M) and TMN (4.0×10^{-4} M), $\lambda_{exc} = 425$ nm

produces a progressive increase in the characteristic absorption band of $MV^{\cdot+}$ ($\lambda_{max} \approx 400$ and 610 nm), as shown in Fig. 3(A).[32,33] By contrast, no reaction occurs in the dark or in the absence of the dyad **7** under photoirradiation. Moreover, it is important to note that no reaction occurs on irradiating the dyad **7** when only the electron acceptor MV^{2+} or the electron donor TMN is added.

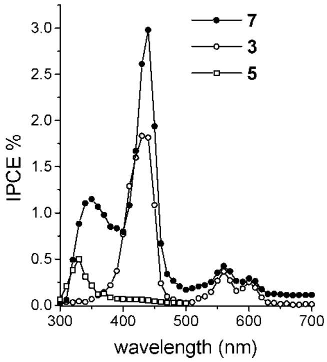


Figure 4. Photocurrent action spectrum of ITO–SnO_2 electrode bearing dyad **7** (solid circles), Zn(II) amidoporphyrin **3** (open circles) and ester–C_{60} **5** (open squares). The spectra are corrected by IPCE of the ITO–SnO_2 electrode

To compare the effect produced by Zn(II) metallation in dyad **7** on photoinduced ion-pair formation, a similar photolysis experiment in the presence of MV^{2+} was performed using the free-base dyad **8** (Scheme 2), where no metal forms a complex with the porphyrin moiety. As can be observed in Fig. 3(B), a considerably lower $MV^{\cdot+}$ concentration is formed in a similar irradiation time when free-base dyad **8** is used instead dyad **7**. This result is to be expected considering the energy of 1.43 eV for the charge-transfer state of free-base dyad **8**,[27] which is ~0.15 eV higher than the ion-pair formation in dyad **7**.

Photoelectrochemistry

Preliminary results on the photoelectrochemical properties of dyad **7** adsorbed over a nanoestructured semiconductor SnO_2 electrode demonstrated that the SnO_2-modified film exhibits photoresponse in the visible region with good light-harvesting capacity (Fig. 4). The incident-photon-to-photocurrent efficiency (IPCE) was obtained through the measure of the generated photocurrent when the electrodes are illuminated with monochromatic light, by using the equation

$$\mathrm{IPCE}(\%) = 100(i_{sc} \times 1240)/(I_{inc}\lambda) \qquad (1)$$

where i_{sc} is the short-circuit photocurrent (A cm^{-2}), I_{inc} is the incident light intensity (W cm^{-2}) and λ is the excitation wavelength (nm).[6,34] The photocurrent action spectrum closely matches the absorption spectrum of the ITO–SnO_2–dyad electrode (Fig. 4). The photoinduced charge separation efficiencies, with maximum IPCE around 1.8 and 3.0%, were found at the Soret band for Zn(II) amidoporphyrin **3** (absorbance 0.16) and dyad **7** (absorbance 0.12), respectively. The fact that there is a close correspondence between the photocurrent action spectrum and the absorption spectrum of the electrodes confirms that light absorption by the dyad **7** is the initial step in the generation of a photoinduced charge-transfer mechanism, as in the natural photosynthetic apparatus.

The charge injection yield (Φ_{inj}) from the excited dye to the semiconductor times the charge collection efficiency (η_c) of the systems at the Soret bands were calculated from IPCE and light-harvesting efficiency ($LHE = 1 - 10^{-A}$, where A is the absorbance of the ITO/SnO_2/dye electrode) of the dyad by using the equation[34]

$$\Phi_{inj}\eta_c = IPCE/LHE \qquad (2)$$

Taking into account the dye light absorption at the Soret band, the product $\Phi_{inj}\eta_c$ yields 0.06 and 0.12 for Zn(II) amidoporphyrin **3** and dyad **7**, respectively. These results indicate that a twofold increase is obtained when using dyad **7** instead porphyrin **3**. Moreover, in control experiments using a ITO–SnO_2–C_{60} electrode, a considerably lower anodic photocurrent with respect to ITO–SnO_2–dyad **7** is observed (Fig. 4) in the spectral region where C_{60} is mainly responsible for the light absorption (λ <380 nm).[35] This indicates that also in this case, instead of direct electron injection from the excited porphyrin to the SnO_2 nanoparticles, another mechanism is involved, probably involving an photoinduced intramolecular charge separation state.

On the other hand, the product $\Phi_{inj}\eta_c$ for dyad **7** is lower than that obtained for the free-base dyad **8** ($\sim$0.20).[27] A possible reason for the lower photocurrent efficiency of the dyad **7** with respect to **8** is back-electron transfer process from the semiconductor to the metalloporphyrin, which is enhanced with respect to the free-base porphyrin.[6,7]

CONCLUSION

The electron-donor nature of the free-base tetraphenylporphyrin was increased by the presence of methoxy groups in the *para* position and by forming a metal complex with Zn(II). This Zn(II) aminoporphyrin **4** was covalently attached to the fullerene structure by a DCC-mediated amidation reaction to form dyad **7**. The amide linkage provides electronic coupling between the chromophores, a good electron-donor porphyrin and an electron-acceptor C_{60}. Hence, dyad **7** has good chance of undergoing intramolecular photoinduced electron transfer. The absorption studies indicate insignificant electronic interaction in the ground state. The quenching of the porphyrin fluorescence in dyad **7** shows a significant interaction between the porphyrin singlet excited state and the fullerene ground state. Thermodynamically, fluorescence quenching of the porphyrin moiety could occur by photoinduced energy transfer and also by electron transfer from porphyrin to the C_{60} structure to yield a charge-separated species ($ZnP^{\cdot+}$–$C_{60}{}^{\cdot-}$). Apparently, in a polar solvent, such as THF, the charge-separated state arises from both the excited singlet state of the porphyrin and the C_{60} moiety. The photoinduced formation of this state was evidenced by the formation of $MV^{\cdot+}$ in the presence of TMN. A considerable higher effect of MV^{2+} reduction is found for dyad **7** with respect to the free-base porphyrin dyad **8**. Probably, the charge-separated state of dyad **7** is involved in photocurrent generation on the SnO_2 semiconductor electrode, producing an increase in the photoelectric effect in comparison with the corresponding monomers. The fact that dyad **7** is less effective in producing photoelectrical effects than the free-base dyad **8** can be explained by considering that the metallized porphyrin enhances the back-electron transfer process.[6,7] An appropriate orientation of the dyad **7**, detaching the ZnP structure from the SnO_2 surface, could help in increasing the photocurrent efficiency because of a decrease in the back-electron transfer process from the semiconductor to metalloporphyrin. Further studies concerning the mechanism of photocurrent generation are in progress.

EXPERIMENTAL

General

Absorption spectra were recorded on a Shimadzu UV-2401PC spectrometer. NMR spectra were taken on a Varian Gemini spectrometer at 300 MHz. Mass spectra were measured with a Varian MAT 312 instrument operating in the electron ionization (EI) mode at 70 eV and with a Vestec Laser Tec Research Instrument by laser desorption time-of-flight mass spectrometry. TLC Uniplate silica gel GHLF (250 μm) thin-layer chromatography plates from Analtech and silica gel (230–400 mesh) for column chromatography from Aldrich were used. Fluorescence spectra were recorded on a Spex FluoroMax fluorimeter. The fluorescence quantum yields (ϕ_f) were calculated by comparison of the area below the corrected emission spectrum in degassed toluene solution with that of TPP ($\phi_f = 0.11$) as a fluorescence standard, with excitation at $\lambda_{ex} = 550$ nm.[36] Cyclic voltammetry (CV) was performed using the previously described equipment,[6] and was carried out in 1,2-dichloroethane containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All the redox potentials are referred to a saturated calomel electrode (SCE).

Starting materials

All chemicals from Aldrich were used without further purification, except for hydroquinone, which was recrystallized from toluene. TMN was synthesized as reported previously from pure naphthidine by a modification of the formaldehyde–borohydride method.[31] Toluene, tetrahydrofuran, dichloromethane and chloroform (GR grade) from Merck were distilled and stored over 4 Å molecule sieves.

Syntheses

5-(4-Acetamidophenyl)-10,15,20-tris(4-methoxylphenyl)porphyrin (**1**), 5-(4-aminophenyl)-10,15,20-tris(4-methoxylphenyl)porphyrin (**2**) and dyad **8** were synthesized as described previously.[26] The precursor 1,2-dihydro-1,2-methanofullerene[60]-61-carboxylic acid (**6**) (C_{60}-acid) was prepared according to the literature.[29]

*Zn(II) 5-(4-acetamidophenyl)-10,15,20-tris(4-methoxylphenyl)porphyrin (**3**).* To a solution of amidoporphyrin **1** (50 mg, 0.066 mmol) in 30 ml of dichloromethane was added 10 ml of a saturated solution of Zn(II) acetate in methanol. The mixture was stirred for 30 min at room temperature. Solvents were evaporated under reduced pressure and flash chromatography (silica gel; dichloromethane–methanol, 2%) yielded 52 mg (96%) of pure Zn(II) amidoporphyrin **3**. TLC (silica gel), R_f (dichloromethane–methanol, 3%) = 0.45. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 2.34 (s, 3H, $COCH_3$); 4.08 (s, 9H, $ArOCH_3$); 7.28 (d, 6H, $J = 8.6$ Hz, 10,15,20-Ar 3,5-H); 7.45 (brs, 1H, Ar-NHCO); 7.87 (d, 2H, $J = 8.0$ Hz, 5 Ar 3,5-H); 8.11 (d, 6H, $J = 8.6$ Hz, 10,15,20-Ar 2,6-H); 8.15 (d, 2H, $J = 8.0$ Hz, 5 Ar 2,6-H); 8.82–8.96 (m, 8H, pyrrole). MS, *m/z* 825 (M^+) (824.6548 calculated for $C_{49}H_{37}N_5O_4Zn$).

*Zn(II) 5-(4-aminophenyl)-10,15,20-tris(4-methoxylphenyl)porphyrin (**4**).* The reaction was performed as described above for Zn(II) amidoporphyrin **3**, using 50 mg (0.069 mmol) of aminoporphyrin **2**. Flash column chromatography (silica gel; dichloromethane–methanol, 1%) yielded 53 mg (98%) of pure Zn(II) aminoporphyrin **4**. TLC (silica gel), R_f (dichloromethane–methanol, 3%) = 0.69. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm): 3.98 (s, brs, 2H, $ArNH_2$); 4.07 (s, 9H, $ArOCH_3$); 7.04 (d, 2H, $J = 8.0$ Hz, 5 Ar 3,5-H); 7.27 (d, 6H, $J = 8.5$ Hz, 10,15,20-Ar 3,5-H); 7.98 (d, 2H, $J = 8.0$ Hz, 5 Ar 2,6-H); 8.10 (d, 6H, $J = 8.5$ Hz, 10,15,20-Ar 2,6-H); 8.78–8.96 (m, 8H, pyrrole). MS, *m/z* 783 (M^+) (782.6443 calculated for $C_{47}H_{35}N_5O_3Zn$).

*Zn(II) porphyrin–C_{60} dyad (**7**).* Zn(II) amino-porphyrin **4** (25 mg, 0.030 mmol) and C_{60}-acid **6** (20 mg, 0.025 mmol) were dissolved in 16 ml of dry PhBr. This mixture was stirred under argon for 15 min, then DCC (6 mg, 0.030 mmol), BtOH (4 mg, 0.030 mmol), TEA (4 µl, 0.030 mmol) and DMAP (4 mg, 0.032 mmol) were added. The reaction mixture was sonicated for 20 min under an argon atmosphere and then, the solution was stirred for 24 h at room temperature. Flash column chromatography (silica gel) using toluene (removal of PhBr) and then dichloromethane as eluent afforded 27 mg (70%) of pure dyad **7**. TLC (silica gel), R_f (dichloromethane) = 0.53. ^{1}H NMR ($CDCl_3$, TMS), δ (ppm) 4.11 (s, 9H, $ArOCH_3$); 4.88 (s, 1H, methine); 7.33 (d, 6H, $J = 8.5$ Hz, 10,15,20-Ar 3,5-H); 7.50 (s, brs, 1H, NHCO); 7.85 (d, 2H, $J = 8.7$ Hz, 5 Ar 2,6-H); 8.12 (d, 6H, $J = 8.5$ Hz, 10,15,20-Ar 2,6-H); 8.22 (d, 2H, $J = 8.7$ Hz, 5 Ar 2,6-H); 8.83–8.99 (m, 8H, pyrrole). MS, *m/z* 1543 (M^+) (1542.6392 calculated for $C_{109}H_{35}N_5O_4Zn$).

Steady-state photolysis

A square quartz cuvette (10 mm i.d.) which contained a deaerated *N,N′*-dimethylformamide (DMF)–water (5%) solution of dyad **7** (3.0×10^{-6} M), MV^{2+} (8.0×10^{-4} M) and TMN (4.0×10^{-4} M) was irradiated with monochromatized light of $\lambda = 425$ nm from a 150 W high-pressure Xe lamp (Photon Technology Instruments, PTI) through a PTI high-intensity grating monochromator. The light intensity was determined as 10.5 mW cm^{-2} with a slit width of 20 nm (Radiometer Laser Mate-Q, Coherent). The photochemical reaction was monitored by measuring the absorption spectra at different irradiation times.

Preparation of SnO_2 nanocrystalline films

The SnO_2 nanostructured film-thin electrodes were prepared by using a modification of Bedja *et al.*'s procedure.[5,37] As base contact optically transparent electrodes of indium tin oxide (ITO, 100 Ω/square, Delta Technologies) were used. The ITO slides were cleaned by the method already described.[25] ITO–SnO_2 electrodes were prepared by spin coating using a Model P6204-A Specialty Coating System. Aliquots of 0.1 ml of SnO_2 colloidal suspension (1.5% SnO_2, particle diameter 20–30 Å, Alfa Chemicals) were spread on clean ITO surfaces with a 3.5 cm^2 area and spun at 3000 rpm for 30 s, then the electrodes were dried for 5 min at 80 °C. Thick films of pristine SnO_2 were obtained by repeating the applications 15 times. The final films were annealed at 450 °C for 1 h. The ITO–SnO_2 electrodes were modified with dye by soaking ITO/SnO_2 films in a saturated *n*-hexane/dichloromethane (7:3) solution of the dye for 2 h. The electrodes were then washed with the same solvent, dried in a nitrogen stream at room temperature and stored in vials. A copper wire was connected to the electrode surface with an indium solder to achieve electrical contact.

Photoelectrochemical measurements

Photoelectrochemical experiments were conducted in an aqueous solution (0.01 M) of hydroquinone, with phosphate buffer (pH 5.2) prepared from 0.05 M NaH_2PO_4 and NaOH. This solution was thoroughly degassed by bubbling with argon and maintained in the top of the cell by a continuous stream. The measurements were carried out in an already described quartz photoelectrochemical cell using a laboratory-made, battery-operated, low-noise potentiostat.[25] Action spectra of ITO–

SnO_2–dye were obtained by illumination of the photoelectrodes with monochromatic light in the front face configuration using the irradiation system described previously.[25,26]

Acknowledgements

The authors thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) of Argentina, Agencia Nacional de Promoción Científica y Técnica, Fundación Antorchas and SECYT de la Universidad Nacional de Río Cuarto for financial support. L.A.O., J.J.S. and E.N.D. are Scientific Members of CONICET.

REFERENCES

1. Gust D, Moore TA, Moore AL. *Acc. Chem. Res.* 2001; **34**: 40–48.
2. Wasielewski MR. *Chem. Rev.* 1992; **92**: 435–461.
3. Imahori H, Sakata Y. *Eur. J. Org. Chem.* 1999; 2445–2457.
4. Steinberg-Yfrach G, Rigaud J-L, Durantini EN, Moore AL, Gust D, Moore TA. *Nature (London)* 1998; **392**: 479–482.
5. Otero L, Osora H, Li W, Fox MA. *J. Porphyrins Phthalocyanines* 1998; **2**: 123–131.
6. Fungo F, Otero L, Durantini EN, Silber JJ, Sereno L. *J. Phys. Chem. B* 2000; **104**: 7644–7651.
7. Koehorst RBM, Boschloo GK, Savenije TJ, Goossens A, Schaafsma TJ. *J. Phys. Chem.* 2000; **104**: 2371–2377.
8. O'Regan B, Gratzel M. *Nature (London)* 1990; **253**: 737–739.
9. Imahori H, Hagiwara K, Aoki M, Akiyama T, Taniguchi S, Okada T, Shirakawa M, Sakata Y. *J. Am. Chem. Soc.* 1996; **118**: 11771–11782.
10. Imahori H, El-Khouly ME, Fujitsuka M, Ito O, Sakata Y, Fukuzumi S. *J. Phys. Chem. A* 2001; **105**: 325–332.
11. Liddell PA, Sumida JP, Macpherson AN, Noss L, Seely GR, Clark KN, Moore AL, Moore TA, Gust D. *Photochem. Photobiol.* 1994; **60**: 537–541.
12. Armaroli N, Marconi G, Echegoyen L, Bourgeois J-P, Diederich F. *Chem. Eur. J.* 2000; **6**: 1629–1645.
13. Paddon-Row MN, Shephard MJ. *J. Phys. Chem. A* 2002; **106**: 2935–2944.
14. Ikemoto J, Takimiya K, Aso Y, Otsubo T, Fujitsuka M, Ito O. *Org. Lett.* 2002; **4**: 309–311.
15. Fong R II, Schuster DI, Wilson SR. *Org. Lett.* 1999; **1**: 729–732.
16. Diederich F, Isaacs L, Philp D. *Chem. Soc. Rev.* 1994; 243–255.
17. Sun Y, Drovetskaya T, Bolskar RD, Bau R, Boyd PD, Reed CA. *J. Org. Chem.* 1997; **62**: 3642–3649.
18. Wedel M, Montforts F-P. *Tetrahedron Lett.* 1999; **40**: 7071–7074.
19. Guldi DM, Luo C, Prato M, Troisi A, Zerbetto F, Scheloske M, Dietel E, Bauer W, Hirsch A. *J. Am. Chem. Soc.* 2001; **123**: 9166–9167.
20. D'Souza F, Deviprasad GR, El-Khouly ME, Fujitsuka M, Ito O. *J. Am. Chem. Soc.* 2001; **123**: 5277–5284.
21. MacMahon S, Fong R II, Baran PS, Safonov I, Wilson SR, Schuster DI. *J. Org. Chem.* 2001; **66**: 5449–5455.
22. Durantini EN, Silber JJ. *Synth. Commun.* 1999; **29**: 3353–3368.
23. Durantini EN. *J. Porphyrins Phthalocyanines* 2000; **4**: 233–242.
24. Durantini EN. *Molecules* 2001; **6**: 533–539.
25. Fungo F, Otero LA, Sereno L, Silber JJ, Durantini EN. *J. Mater. Chem.* 2000; **10**: 645–650.
26. Fungo F, Otero LA, Sereno L, Silber JJ, Durantini EN. *Dyes Pigm.* 2001; **50**: 163–170.
27. Fungo F, Otero L, Borsarelli CD, Durantini EN, Silber JJ, Sereno L. *J. Phys. Chem. B* 2002; **106**: 4070–4078.
28. Himahori H, Hasobe T, Yamada H, Kamat PV, Barazzouk S, Fujitsuka M, Ito O, Fukuzumi S. *Chem. Lett.* 2001; 784–785.
29. Isaacs L, Diederich F. *Helv. Chim. Acta* 1993; **76**: 2454–2464.
30. Fukuzumi S, Imahori H, Okamoto K, Yamada H, Fujitsuka M, Ito O, Guldi DM. *J. Phys. Chem.* 2002; **106**: 1903–1908.
31. Miras MC, Silber JJ, Sereno L. *J. Electroanal. Chem.* 1986; **201**: 367–386.
32. Darwent JR, McCubbin I, Porter G. *J. Chem. Soc., Faraday Trans 2* 1982; **78**: 903–910.
33. Alam MM, Ito O. *J. Phys. Chem. A* 1999; **103**: 1306–1310.
34. Nazeeruddin MK, Kay A, Rodicio I, Humphry-Buker R, Müller E, Liska P, Vlachopoulos N, Grätzel M. *J. Am. Chem. Soc.* 1993; **115**: 6382–6390.
35. Kamat PV, Gevaret M, Vinodgopal K. *J. Phys. Chem. B* 1997; **101**: 4422–4427.
36. Tatman D, Liddel PA, Moore TA, Gust D, Moore AL. *Photochem. Photobiol.* 1998; **68**: 459–466.
37. Bedja I, Hotchandani S, Kamat PV. *J. Phys. Chem.* 1994; **98**: 4133–4140.