Polymeric Films Containing Acceptor–Donor Assemblies. Photoelectrodes Based on Irradiation of Inter- and Intramolecular Charge-Transfer Complexes

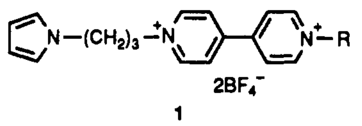
Alain Deronzier* and Mohamed Essakalli

Laboratoire d'Electrochimie Organique et de Photochimie Rêdox (URA CNRS D1210), Universitê Joseph Fourier Grenoble 1, BP 53X, 38041 Grenoble Cêdex, France *(Received: June 27, 1990)*

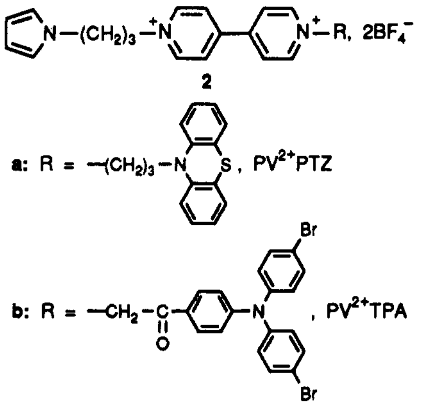
The behavior under visible irradiation of optically transparent electrodes (OTE) modified by thin films of polypyrrole containing several kinds of electron acceptor–donor assemblies has been investigated. Photolysis of electrodes coated by thin films of polypyrrole substituted by a reversible electron acceptor (viologen) in the presence of an irreversible electron donor (benzilate anion) in acetonitrile gives appreciable photocurrents. The photoresponse results from the photoinduced charge separation of the charge-transfer complex created at the interface. The measured photocurrents are markedly larger (up to 5 times) with films of polypyrrole substituted by a reversible electron acceptor (viologen) covalently linked with a donor (phenothiazine, triphenylamine, or benzidine) than with the former ones under similar experimental conditions. The greater efficiency of these materials is attributed to the formation of an intramolecular charge-transfer complex occurring inside films between the two molecular entities. Markedly weaker photocurrents are obtained with polypyrrole films based on bilayers of the two independent components than with films of unimolecular design while films based on copolymers arrangements give moderately weaker photoresponses.

Introduction

Photoconversion processes based on the electron-transfer quenching of molecular excited state are well established. However, the recombination by back electron transfer remains the major hindrance to the long-life storage of the redox energy.[1] One eventual solution to that problem is to construct assemblies of chromophores and quenchers as polymeric films on electrode surfaces with the aim of achieving spatial separation of the photogenerated species.[2] Most of the molecular photoelectrodes described involve a polypyridyl complex of ruthenium(II) associated with an oxidative quencher fixed in a polymeric matrix, and in some cases appreciable photocurrents have been observed.[3] Recently we have demonstrated that a photoresponse can also be obtained from an electrode on which a nonconventional photosensitizer has been immobilized. In this device photocurrent arises from the illumination of a charge-transfer complex (CTC) formed between a reversible electron donor (phenothiazine) deposited as a polypyrrole film on the electrode surface and an irreversible electron acceptor[4] (tropylium cation). In order to develop the possibilities offered by such designs we have investigated the photoelectrochemical properties of films containing other electron acceptor–donor combinations. Since it has been shown that visible irradiation of the charge-transfer complex formed in fluid solution between viologen as a reversible electron acceptor and benzilate anion as an irreversible donor leads to the net buildup of the monoelectronic reduced form of the viologen,[5] we have first studied this sytem immobilized at the electrode surface. Polypyrrole films containing viologens were obtained as previously described[6] by anodic electropolymerization of monomers **1a–b**.



We report also in this paper the photoelectrochemical features of more valuable polypyrrole film assemblies in which several reversible donors (phenothiazine, triphenylamine, benzidine) are covalently linked to an acceptor (viologen). These materials were recently synthesized[7] by electropolymerization of monomers **2a–b**.



We have compared the extent of the resulting photocurrents with those from other types of films containing molecular assemblies (bilayers, copolymers) based on the two independent components. The unimolecular system appears to be the most efficient as a consequence of the formation of an intramolecular charge-transfer complex.

Experimental Section

1. Materials. The preparations of the monomers **1** (PPV^{2+}, PMV^{2+}), **2** ($PV^{2+}PTZ$, $PV^{2+}TPA$), and **4** (PPTZ) were reported elsewhere.[4,6,7] Formula of monomers **3**, **4**, and **5** are given further on in the text.

Monomer **3** ($PV^{2+}NB$) was synthesized by refluxing 4-(4′-pyridyl)-*N*-(3-pyrrol-1-yl-propyl)pyridinium 4-toluenesulfonate[7] (0.200 g, 0.92 mmol), in CH_3CN (20 mL) with a slight excess

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[1] (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244. (b) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389–440. (c) Jurin, A.; Barigelletti, F.; Campagna, S.; Balzani, V.; Beker, P.; Van Zelensky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

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[3] (a) Oyama, N.; Yamaguchi, S.; Kaneko, M.; Yamada, A. *J. Electroanal. Chem.* **1982**, *139*, 215–222. (b) Kaneko, M.; Moriya, S.; Yamada, A.; Yamamoto, H.; Oyama, N. *Electrochim. Acta* **1984**, *29*, 115–118. (c) Hupp, J. T.; Otruba, J. P.; Parus, S. J.; Meyer, T. J. *J. Electroanal. Chem.* **1985**, *190*, 287–291. (d) Kaneko, M. *J. Macromol. Sci. A* **1987**, *24*, 357–365. (e) Hupp, J. T.; Meyer, T. J. *J. Electroanal. Chem.* **1987**, *224*, 59–65. (f) Surridge, N. A.; Hupp, J. T.; McClanahan, S. F.; Gould, S.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 304–313. (g) Hupp, J. T.; Meyer, T. J. *J. Photochem. Photobiol. A* **1989**, *48*, 419–433. (h) Deronzier, A.; Essakalli, M. *J. Chem. Soc., Chem. Commun.* **1990**, 242–244. (i) Downard, A. J.; Surridge, N. A.; Meyer, T. J.; Deronzier, A.; Moutet, J.-C. *J. Phys. Chem.* **1990**, *94*, 6754–6764.

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[6] (a) Bidan, G.; Deronzier, A.; Moutet, J.-C. *J. Chem. Soc., Chem. Commun.* **1984**, 1185–1186. (b) Coche, L.; Deronzier, A.; Moutet, J.-C. *J. Electroanal. Chem.* **1986**, *198*, 187–193.

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TABLE I: Single-Component Film Growth Conditions

monomers	concn, mM	appl potential, V
PMV^{2+}	2.0	0.80
PPV^{2+}	1.0	0.80
PPTZ	2.0	0.85
$PV^{2+}PTZ$	2.0	0.80
$PV^{2+}TPA$	3.0	0.80
$PV^{2+}NB$	2.0	0.90

of 4-nitrobenzyl bromide (0.405 g, 0.93 mmol) for 15 h. After the solution had cooled, the yellow precipitate was filtered off and washed carefully with diethyl oxide. This precipitate was dissolved in a water + ethanol mixture and passed through an ion-exchange column (Amberlite IRA 93) in BF_4^- form. The solvent was removed under vacuum and the product dissolved in a minimum of acetonitrile and dropped into stirred diethyl oxide. The precipitate was collected by suction filtration and dried under vacuum. The yield was 51%. FAB-MS: *m/z*, positive mode $[C^{2+},BF_4^-]^+$ 487. ^1H NMR (CD_3CN): δ (ppm) 2.52 (m, 2 H), 4.12 (m, 2 H), 4.60 (m, 2 H), 5.96 (m, 4 H), 6.64 (t, 2 H, J = 4 Hz), 7.72 (m, 2 H), 8.28 (m, 4 H), 8.42 (m, 2 H), 8.76 (m, 2 H), 9.04 (m, 2 H).

Monomer **5** (PNB) was prepared following an adaptation of the Clauson–Kaas–Tyle[8] method. A mixture of 4.9 g of 4-nitrobenzyl hydrochloride + 3.7 mL of 2,5-dimethoxytetrahydrofuran + 15 mL of glacial acetic acid was refluxed and stirred for 45 min. It was then allowed to cool to room temperature, poured into water, and extracted with CH_2Cl_2. The organic phase was washed first with a saturated Na_2CO_3 aqueous solution and then with water and dried over anhydrous magnesium sulfate. Concentration of the solution under reduced pressure afforded **5** as a brown solid. The yield was 62%. ^1H NMR (CD_3CN): δ (ppm) 5.19 (s, 2 H), 6.15 (t, 2 H, J = 4 Hz), 6.78 (t, 2 H, J = 4 Hz), 7.28 (m, 2 H), 8.15 (m, 2 H).

Tetrabutylammonium benzilate was prepared as previously reported.[5] Triethanolamine (Fluka) puriss was used as received or distilled with the same result.

2. Film Preparations and Photoelectrochemical Measurements. Electrochemical equipment and purification of acetonitrile and tetraethylammonium perchlorate (TEAP) have been previously described.[7] Film preparations and photoelectrochemical measurements were made using a conventional sandwich-type cell[9] and following an experimental procedure reported previously.[10] All potentials were referred to the Ag/Ag^+ (10 mM) in CH_3CN reference electrode.

2.1. Film Preparations. All experiments were run in a drybox (Jaram) under an argon atmosphere. Thin films of polymers were prepared by controlled-potential oxidation using the conditions shown in Table I in CH_3CN containing 0.1 M (TEAP) on a disk-shaped (area 1 cm^2) optically transparent indium oxide electrode (OTE). The auxiliary electrode was a platinum disk mounted parallel without a separating-compartment system. The length of the cell was 1 cm.

After polymerization, the electrolysis solution was removed and the cell flushed with clean CH_3CN. A solution of CH_3CN + 0.1 M TEAP was then introduced and the apparent surface concentration of electroactive species (hence the film thickness) Γ (mol cm^{-2}) was determined by integration under cyclic voltammetric waves for appropriate redox couples.

Electropolymerization of a second layer on top of an initial layer was achieved by using the conditions described above. The content of redox sites in the outer layer was also determined by potential scans. Copolymeric films were prepared by controlled potential electrolysis of solutions containing a mixture of the monomers. The approximate composition of the resulting films were determined by charge measurements as described for single component films.

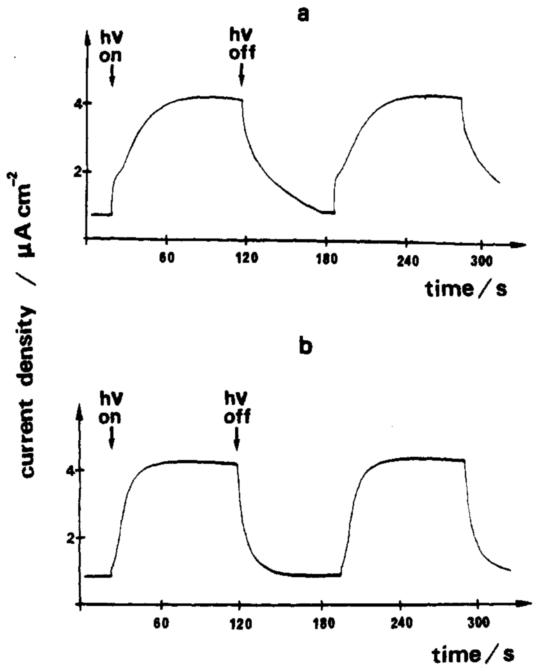

Figure 1. Photocurrent responses of an OTE coated with (a) a poly(PPV^{2+}) film ($\Gamma = 4.5 \times 10^{-8}$ mol cm^{-2}); (b) a poly(PMV^{2+}) film ($\Gamma = 5.2 \times 10^{-8}$ mol cm^{-2}) in the presence of $(C_6H_5)_2C(OH)CO_2^-$ ($C = 5 \times 10^{-3}$ M) in CH_3CN + 0.1 M TEAP solution.

2.2. Photoelectrochemical Measurements. In these experiments a quartz disk was used instead of the platinum disk auxiliary electrode, while a platinum wire served as the auxiliary electrode. The cell was filled up with a standard benzilate–CH_3CN + 0.1 M TEAP solution in the drybox. The polymeric film electrodes were irradiated with a 250-W Hg lamp through UV and IR cutoff filters with a surface light intensity of 150 mW cm^{-2}. Light intensities were measured with a calibrated calorimeter (Scientech 36-0001). The electrode potential was adjusted to 0 V by a potentiostat (PAR 173). The photoresponse was recorded on a *X–t* recorder (Sefram TGM 164). Absorption spectra of films were obtained by using a Beckman Acta CIII UV–visible spectrophotometer. All measurements were performed at room temperature.

Results and Discussion

*1. Photoelectrodes Based on Poly(**1a-b**).* Figure 1 shows typical responses under visible irradiation of OTE/poly (**1a**) and OTE/poly (**1b**) electrodes in the presence of 5×10^{-2} M tetrabutylammonium benzilate $[Bu_4N^+(C_6H_5)_2C(OH)CO_2^-]$ in CH_3CN containing 10^{-1} M TEAP. The electrodes were potentiostated at 0 V. The steady-state values I_s of the anodic photocurrents are moderately stable with time (loss of ~8% after 15 min of irradiation). By analogy with the related system[5] in fluid solution, irradiation of the CTC induces charge separation leading to the buildup of the viologen cation radical in the film (noted $V^{•+}$) and $(C_6H_5)_2C(OH)CO^•$ species. The latter undergoes a rapid irreversible transformation into $(C_6H_5)_2C^•(OH)$ which reacts with V^{2+} by thermal electron transfer to give $(C_6H_5)C{=}O$ and $V^{•+}$. Photochemically and chemically generated $V^{•+}$ species diffusing in the film by electron hopping[11] are oxidized back at the electrode interface in agreement with that demonstrated for a photoelectrochemical cell containing a similar CTC system in solution (quantum yield of $V^{•+}$ photoproduction under monochromatic irradiation was previously measured; ϕ = 0.42 at 405 nm and 0.29 at 436 nm). The mechanism for the anodic photocurrent response can be represented by Scheme I. V^{2+} is complexed again by the excess of $(C_6H_5)_2C(OH)CO_2^-$ and is ready for participation in another photoredox cycle. The induction period required to reach I_s is longer for poly(**1a**) compared to poly(**1b**)

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(9) Gruver, G. A.; Kuwana, T. *J. Electroanal. Chem.* **1972**, *36*, 85–99.

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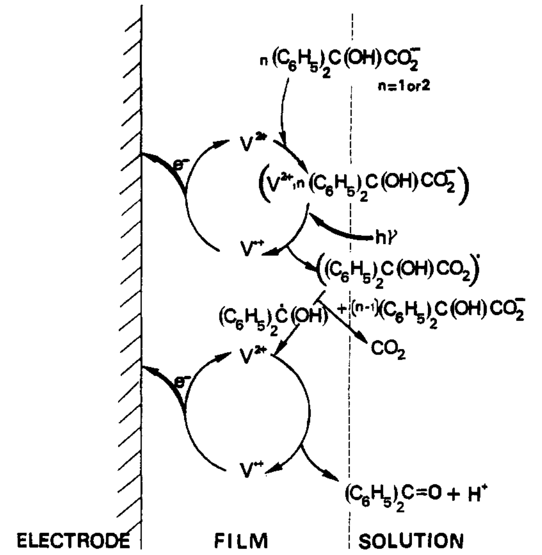
SCHEME I: Schematic Representation of the Events Occurring with the Poly(PMV^{2+}) and Poly(PPV^{2+}) Films following Excitation



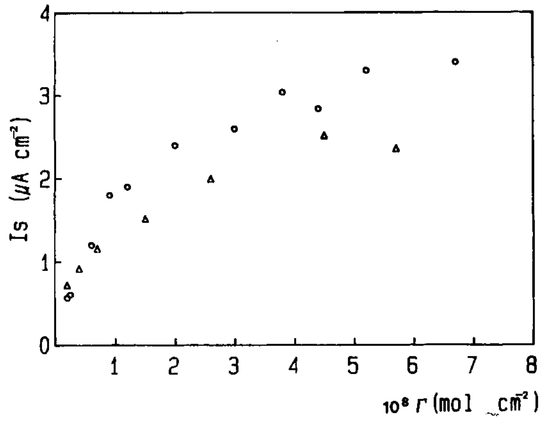


Figure 2. Plots of the steady-state photocurrents I_s vs poly(PMV^{2+}) (○) and poly(PPV^{2+}) (△) thickness. [$(C_6H_5)_2C(OH)CO_2^-$] = 5×10^{-2} M in both cases.

with films having the same thickness. This difference is due mainly to the difference of permeability toward $(C_6H_5)_2C(OH)CO_2^-$ between the two films since poly(**1a**) is a more cross-linked and dense polymer than poly(**1b**).[12] Photolysis in the absence of $(C_6H_5)_2C(OH)CO_2^-$ or of an uncoated OTE in the presence of the irreversible electron donor did not cause any photocurrent. Moreover, if after an irradiation at the polymeric film electrode the same solution is irradiated at a bare OTE electrode, no photocurrent could be detected. This proves that the photocurrent is not due to the presence of some viologen species in solution resulting from a partial break of the polymer.

Variations in benzilate concentration have an important effect on the I_s magnitude. For low concentration ((0–2) $\times 10^{-2}$ M) I_s increases linearly with concentration while I_s reaches an upper limit for benzilate concentrations higher than 5×10^{-2} M. This maximum can be attributed to the absorption of light by $V^{\bullet+}$ above 400 nm, limiting its photoproduction.

Figure 2 shows the evolution of I_s vs the film thickness $\Gamma_{V^{2+}}$ (apparent surface concentration of viologen species) using an identical amount of $(C_6H_5)_2C(OH)CO_2^-$. For thin films, I_s increases first with Γ and reaches an upper limit at $\Gamma = 4.5 \times 10^{-8}$ mol cm^{-2} for poly(**1a**) and at $\Gamma > 6 \times 10^{-8}$ mol cm^{-2} for poly(**1b**). These observations indicate that the photoinduced electron transfer between viologen and benzilate occurs within the bulk polymeric films as well as at the film–solution interface. A previous study[10] of the influence of Γ on photocurrent magnitude using a photosystem based on the irradiation of an electrode coated with a polypyrrole film substituted by a ruthenium(II) tris(bipyridine) complex in the presence of an irreversible electron acceptor has shown that the limiting value was reached for a markedly lower Γ (<10^{-8} mol cm^{-2}). This difference comes probably from the high level of cross-linking in the latter films which involved three pyrrole units per complex. After the limiting value for I_s is reached, I_s decreases slowly as Γ increases for poly(**1a**) while I_s remains identical for poly(**1b**). Increasing the film thickness results in more difficulty for the electrons to propagate by self-exchange from the photogenerated $V^{\bullet+}$ species in the film to the OTE/polymer interface.

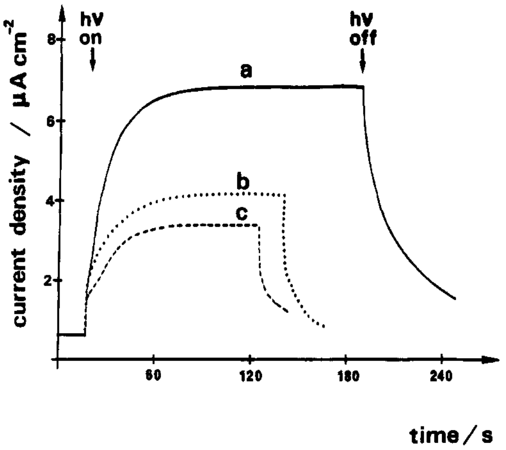
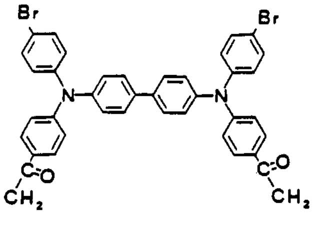


Figure 3. Photocurrent responses of an OTE coated with (a) a poly(PV^{2+}PTZ) film ($\Gamma = 2 \times 10^{-8}$ mol cm^{-2}); (b) a poly(PV^{2+}TPA) film ($\Gamma = 2 \times 10^{-8}$ mol cm^{-2}); (c) a poly(PV^{2+}BZ) film ($\Gamma = 2 \times 10^{-8}$ cm^{-2} with $(C_6H_5)_2C(OH)CO_2^-$ ($C = 5 \times 10^{-2}$ M) in CH_3CN + 0.1 M TEAP solution.

Other experiments were also performed with an OTE/poly(**1b**) in which the conductivity of the polypyrrole chain was previously destroyed by potentiostating the modified electrode at 1.2 V during 20 min.[3i] In that condition I_s is lowered by a third because of the greater difficulty for the electrons to propagate through the film, since it is known[12] that polypyrrole–viologen films are only partially conductive at 0 V.

From all these data it appears that the polypyrrole–viologen,benzilate CTC acts as a more efficient photoelectrochemical device than the one based on polypyrrole–phenothiazine,tropylium CTC.[4] Under optimum conditions, using an identical surface light intensity, the photocurrent magnitude of the former is 7 times higher than that of the latter. These observations are in good agreement with the high quantum yield for buildup of $V^{\bullet+}$ resulting from the irradiation of a solution containing viologen–benzilate CTC.[5]

*2. Photoelectrodes Based on Poly(**2a**–**b**).* Since these materials contain both an electron acceptor and donor site, their application as photoelectrodes in the presence of either an irreversible acceptor or donor could be considered. However, taking into account the results presented in the preceding section, only irradiation with the irreversible donor $(C_6H_5)_2C(OH)CO_2^-$ was investigated. In Figure 3 are shown the photocurrent responses generated by the irradiation of OTE/poly(**2a**) and OTE/poly(**2b**) electrodes for which $\Gamma = 2 \times 10^{-8}$ cm^{-2}. The benzilate concentration was 5×10^{-2} M and the electrode was potentiostated at 0 V. A third curve (curve c) exhibits the response of an OTE/poly(**2c**) (poly(PV^{2+}BZ)) containing as a donor a benzidine unit. This



poly(**2**) unit

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(12) Coche, L.; Moutet, J.-C. *J. Electroanal. Chem.* **1987**, *224*, 111–112.

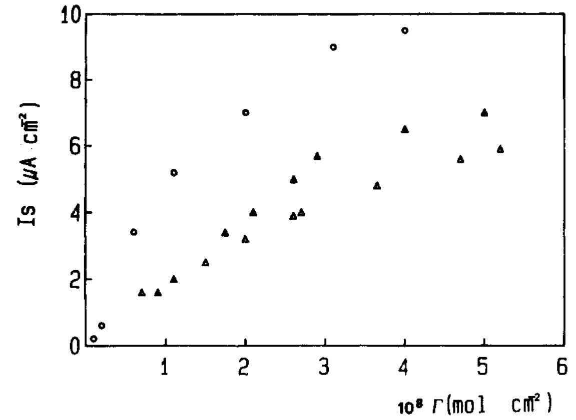


Figure 4. Plots of the steady-state photocurrent I_s vs poly($PV^{2+}PTZ$) (○), poly($PV^{2+}BZ$) (▲) and poly($PV^{2+}TPA$) (△) thickness. $[(C_6H_5)_2C(OH)CO_2^-]$ = 5 × 10^{-2} M in all cases.

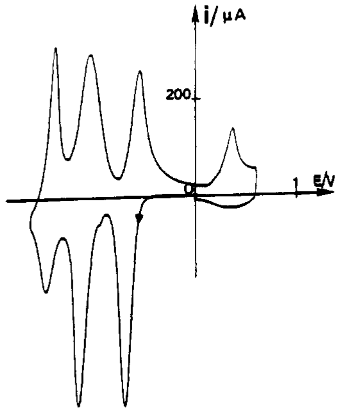


Figure 5. Cyclic voltammogram of a Pt electrode modified by a film of poly($PV^{2+}NB$) (Γ = 3.7 × 10^{-8} mol cm^{-2}) in CH_3CN + 0.1 M TEAP solution; scan rate ν = 0.1 V s^{-1}.

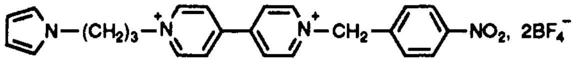
modified electrode is obtained as previously demonstrated by potentiostating the poly(**2b**), benzidine unit resulting from the debromodimerization of the electrogenerated radical cation of the triphenylamine group occurring in the film. For all these films the steady-state value of the photocurrents decreases to ~90% of its original value after half an hour. At the same time the loss of electroactivity is 10% as estimated by cyclic voltammetry experiments. As expected, the I_s magnitude is largely dependent on Γ (Figure 4). By comparison of the data from Figures 2 and 4 it appears that photocurrents arising from poly(**2a–c**) films are remarkably more intense than those observed with poly(**1a–b**) films having the same thickness. This is particularly pronounced with the poly(**2a**) modified electrode. It should be noted that the I_s maximum is not yet reached for Γ = 4 × 10^{-8} mol cm^{-2}.

Two main hypotheses can be formulated to explain this enhancement:

(i) The donor group acts as a spacer between two excited states of CTC, minimizing the self-quenching effects.[13] As a consequence, the efficiency of the photoinduced charge separation and hence the photocurrent intensity, are improved.

(ii) The formation of an intramolecular CTC between V^{2+} species and the electron donor units inside the film.

In order to test the validity of the first hypothesis we have synthesized the monomer **3** ($PV^{2+}NB$) in which the electron donor



3 ($PV^{2+}NB$)

is replaced by a reversible acceptor such as a nitrobenzene group. In poly(**3**) no intramolecular CTC formation can occur while the structure of the polymer remains close to that of poly(**2**). The bulky group nitrobenzene is probably large enough to space two V^{2+} adjacent sites. The corresponding film resulting from the anodic electropolymerization conducted at 0.9 V (electropolymerization yield 66%) exhibits all the expected reversible reduction couples of the molecule ($E_{1/2}(V^{2+}/V^{\bullet+})$ = −0.61 V, $E_{1/2}(V^{\bullet+}/V^0)$ = −1.07 V, $E_{1/2}(NB/NB^{\bullet-})$ = −1.40 V) as well as that of the polypyrrole oxidation ($E_{1/2}$ = 0.34 V) as seen in Figure 5. Photolysis of an OTE/poly(**3**) electrode in the presence of $(C_6H_5)_2C(OH)CO_2^-$ 5 × 10^{-2} M in CH_3CN TEAP 10^{-1} M leads to photocurrent intensities markedly lower than those with OTE/poly(**2a–c**) (Table II). However, they are quite comparable to those arising from the irradiation of an OTE/poly(**1b**) modified electrode, demonstrating that the spacer effect is not the major effect brought about by the donor unit in poly(**1a–c**) films. The examination of the electronic absorption spectrum of a solution of monomer 2 × 10^{-3} M **2a** in CH_3CN reveals a continuous absorption in the visible region with a shoulder at around 450 nm (Figure 6A) which is typical of a CTC formation. In this figure

TABLE II: Comparison of Steady-State Photocurrent Magnitudes I_s for Several Bifunctionalized Polymeric Films[a]

$10^8\Gamma$/mol cm^{-2}	I_s, μA cm^{-2}	$10^8\Gamma$/mol cm^{-2}	I_s, μA cm^{-2}
OTE/poly($PV^{2+}NB$) ($\Gamma_{V^{2+}} = \Gamma_{NB}$)			
1.5	1.4	5.5	4.1
3	2.3		
OTE/poly($PV^{2+}PTZ$) ($\Gamma_{V^{2+}} = \Gamma_{PTZ}$)			
1.1	5.2	4	9.5
3.1	9		
OTE/poly(PMV^{2+}) ($\Gamma_{V^{2+}}$)			
1.2	1.9	5	3.3
3	2.6		

[a] $((C_6H_5)_2C(OH)CO_2^-)$ = 5 × 10^{-2} M in CH_3CN in all cases.

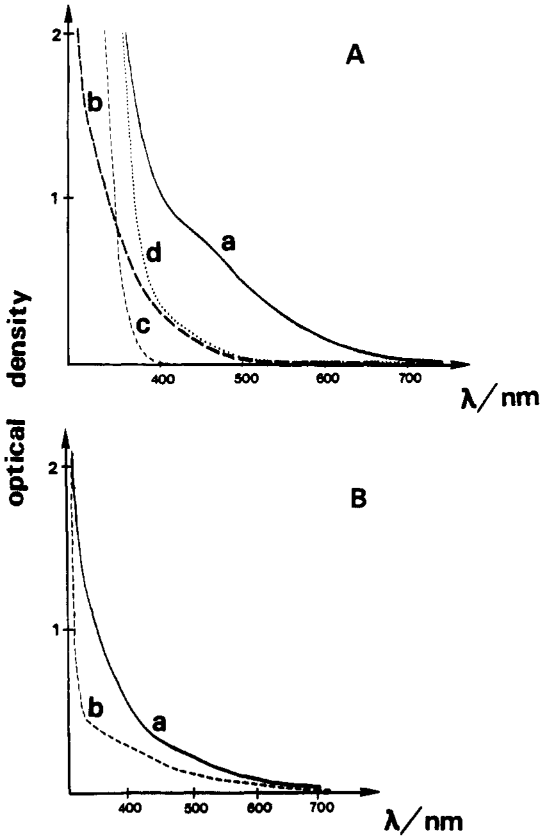


Figure 6. (A) Absorption spectrum of a 2 × 10^{-3} M solution of (a) $PV^{2+}PTZ$, (b) PMV^{2+}, and (c) PPTZ in CH_3CN. Curve d is the spectrum of a mixture of PMV^{2+} and MePTZ (methyl-N-phenothiazine) of the same concentration (2 × 10^{-3} M) in CH_3CN. (B) Absorption spectrum of (a) an OTE/poly($PV^{2+}PTZ$) electrode (Γ = 2 × 10^{-8} mol cm^{-2}) and (b) an OTE/poly(PMV^{2+}) electrode (Γ = 3 × 10^{-8} mol cm^{-2}).

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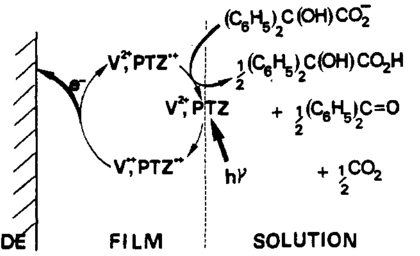
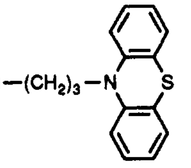
[13] Margerum, L. D.; Meyer, T. J.; Murray, R. W. J. Electroanal. Chem. 1983, 149, 279–285.

SCHEME II: Schematic Representation of the Additional Events Occurring within the Poly($PV^{2+}PTZ$) Film following Excitation



are also exhibited the spectra of the single-component monomer **1b** and **4**, the latter containing a phenothiazine unit (PTZ).



4 (PPTZ)

Moreover, it shows also that the addition of methyl-*N*-phenothiazine to a solution of **1b** does not enhance significantly its absorption intensity in the visible region. The formation of an intermolecular CTC between viologen and phenothiazine group appears less efficient than the intramolecular one. The intramolecular charge-transfer transition can also be detected in the poly(**2a**) film spectrum (Figure 6B).

The greater ability of bifunctionalized films to act as photoelectrodes has its origin in the addition of another photogeneration process of $V^{\bullet+}$ species to that involved in poly(**1**) films (see Scheme I). The visible irradiation of the intramolecular CTC undergoes a charge separation leading to $V^{\bullet+}$ and the cation radical of the donor. The $(C_6H_5)_2C(OH)CO_2^-$ anion diffusing into the film is rapidly oxidized by the donor$^{\bullet+}$ species, leading to the build up of $V^{\bullet+}$ sites in the film; Scheme II summarizes this process. Benzilate anion is known to be oxidized into benzophenone and benzilic acid in acetonitrile at a moderate anodic potential ($E_{1/2} = 0.67$ V).[14] A cyclic voltammetry experiment conducted on a solution of benzilate (2×10^{-3} M) at an electrode modified by a poly(**2a**) film, for example, demonstrated the efficiency of the indirect oxidation of $(C_6H_5)_2C(OH)CO_2^-$ by the electrogenerated $PTZ^{\bullet+}$ species. An enhancement of the anodic peak of the $PTZ^{\bullet+}$ formation is observed while on the reverse scan the corresponding reduction peak is partially suppressed.

As seen above (Table II), the nature of the electron donor group has an influence on the magnitude of the steady-state photocurrent. I_s increases in the following order: poly($PV^{2+}TPA$) < poly($PV^{2+}BZ$) < poly($PV^{2+}PTZ$). The lower the donor oxidation potential, the larger the I_s is ($E_{1/2}(TPA/TPA^{\bullet+}) = 0.96$ V; $E_{1/2}(BZ/BZ^{\bullet+}) = 0.78$ V; $E_{1/2}(PTZ/PTZ^{\bullet+}) = 0.44$ V). This is in good agreement with the statement that the photoinduced charge separation is more efficient for CTC having lower energy.[15]

*3. Photoelectrodes Based on Bilayers and Copolymers from **1a** and **4*.** To demonstrate the advantages offered by the arrangement of the CTC components as bifunctionalized films, we have investigated the photoelectrochemical activity of photoelectrodes based on bilayers and copolymers of the two independent components.

The bilayers were obtained by the electropolymerization of a second layer on top of an initial layer using the conditions described in the Experimental Section. In such a way bilayers OTE/poly(PMV^{2+})/poly(PPTZ) and OTE/poly(PPTZ)/poly(PMV^{2+}) have been synthesized from monomers **1a** and **4**. These abbreviations depict the sequence of the film structures (electrode/inner layer/outer layer). In Figure 7 is shown the cyclic voltammogram of an OTE/poly(PMV^{2+})/poly(PPTZ) bilayer. As previously reported,[16] this voltammogram is the summation of the two single-component films. There is no significant increase in ΔE_p for the $PTZ/PTZ^{\bullet+}$ couple in the outer film compared to the same couple in a film in contact with a bare electrode. At the potential of the $PTZ/PTZ^{\bullet+}$ couple, the conductivity of the inner layer is sufficient to ensure a rapid charge transfer via the polypyrrole skeleton of the inner polypyrrole–PMV^{2+} layer. For the reverse bilayer the cyclic voltammogram also shows the presence of $PTZ/PTZ^{\bullet+}$, $V^{2+}/V^{\bullet+}$, and $V^{\bullet+}/V^0$ couples. However, for the latter system, electronic transfer appears slower in comparison with the former case as a consequence of the weaker conductivity of the poly(PPTZ) film in its reduced form.[16]

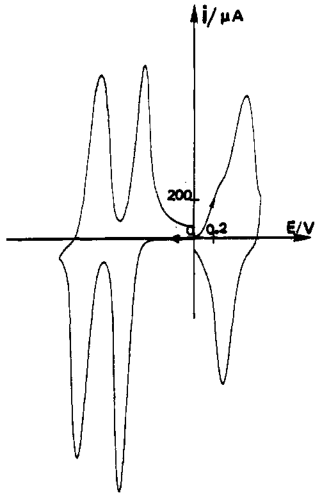


Figure 7. Cyclic voltammetry of an OTE/poly(PMV^{2+}) ($\Gamma = 5 \times 10^{-8}$ mol cm^{-2})/poly(PPTZ) ($\Gamma = 3.6 \times 10^{-8}$ mol cm^{-2}) bilayer in CH_3CN + 0.1 M TEAP solution; scan rate $\nu = 0.05$ V s^{-1}.

TABLE III: Comparison of Steady-State Photocurrent Magnitudes I_s vs Film Thickness for OTE/Poly(PMV^{2+})/Poly(PPTZ) Modified Electrodes[a]

film composition, $10^8\Gamma$/mol cm^{-2}		
inner layer $\Gamma_{V^{2+}}$	outer layer Γ_{PTZ}	I_s, μA cm^{-2}
5	1	1.7
5.7	2.4	2.4
5	3.6	0.7
5.5	4.1	0.6
5	4.8	0.5

[a] ($(C_6H_5)_2C(OH)CO_2^-$) = 5×10^{-2} M in all cases.

TABLE IV: Steady-State Photocurrent Magnitudes I_s vs Film Thickness for OTE/Poly(PPTZ)/Poly(PMV^{2+}) Modified Electrodes[a]

film composition, $10^8\Gamma$/mol cm^{-2}		
inner layer Γ_{PTZ}	outer layer $\Gamma_{V^{2+}}$	I_s, μA cm^{-2}
0.4	4.4	1.4
3	2.4	0.3
3	1	0.2

[a] ($(C_6H_5)_2C(OH)CO_2^-$) = 5×10^{-2} M in all cases.

When solutions containing both the monomers **1b** and **4** are potentiostated at 0.75 V, copolymer films (noted OTE/poly(PMV^{2+}), poly(PPTZ)) are deposited on the electrode. The composition of the resulting copolymeric films depends on the concentration of each monomer. The cyclic voltammograms of these copolymeric films are quite similar to that obtained for the bilayer OTE/PMV^{2+}/PPTZ; however, the rate of electron transfer for the $V^{2+}/V^{\bullet+}$ couple is less than for the $V^{\bullet+}/V^0$ couple in films with a low PMV^{2+}/PPTZ site ratio. When the PMV^{2+} sites are

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(14) Deronzier, A.; Esposito, F. *J. Electroanal. Chem.* **1983**, *146*, 207–209.

(15) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: New York, 1969, and references therein.

(16) Downard, A. J.; Surridge, N. A.; Meyer, T. J.; Cosnier, S.; Deronzier, A.; Moutet, J.-C. *J. Electroanal. Chem.* **1988**, *246*, 321–335.

TABLE V: Steady-State Photocurrent Magnitudes I_s vs Film Thickness for OTE/Poly(PMV^{2+}),Poly(PPTZ) Modified Electrodes[a]

film composition, $10^8\Gamma$/mol cm^{-2}		I_s, μA cm^{-2}
$\Gamma_{PMV^{2+}}$	Γ_{PPTZ}	
3.9	5.8	4.6
4.2	2.5	5.1
5	3	5.5
6	3.5	6.6

[a] $((C_6H_5)_2C(OH)CO_2^-)$ = 5 × 10^{-2} M in all cases.

TABLE VI: Steady-State Photocurrent Magnitudes I_s vs Film Thickness for OTE/Poly(PMV^{2+}),Poly(PNB) Modified Electrodes[a]

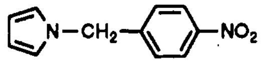
film composition, $10^8\Gamma$/mol cm^{-2}		I_s, μA cm^{-2}
$\Gamma_{V^{2+}}$	Γ_{NB}	
3.5	1.2	1.2
3.5	3	1.3
5	3	1.4
6.2	6	2.2
6.2	8	2

[a] $((C_6H_5)_2C(OH)CO_2^-)$ = 5 × 10^{-2} M in all cases.

diluted, the direct site to site contact required for facile electron transfer is diminished.

Tables III, IV, and V summarize data relative to the magnitude of I_s obtained with these three kinds of films irradiated in the presence of $(C_6H_5)_2C(OH)CO_2^-$ 5 × 10^{-2} M. The bilayer films appear as poorly efficient photoelectrochemical systems. For the bilayer OTE/poly(PMV^{2+})/poly(PPTZ) having a fixed inner film thickness the photocurrent increases as the outer layer thickness increases, but only at low outer layer thickness. The photocurrents generated by the reverse bilayer OTE/poly(PPTZ)/poly(PMV^{2+}) are lower (Table III) since in this design the photogenerated V$^{\bullet+}$ species are spatially isolated from the electrode by the inner layer of poly(PPTZ).

In contrast, the irradiation of copolymeric films leads to large photocurrents (Table V). I_s magnitudes are lower than those arising from bifunctionalized films, but markedly higher than those arising from the photolysis of layers of polypyrrole–viologen. Although there is no clear CTC absorption band in the visible spectrum of copolymeric films, the formation of an intermolecular CTC between viologen and phenothiazine occurring inside films could explain this phenomenon. The forced proximity of the donor and acceptor groups in films facilitates their interaction. In order to verify this hypothesis we have studied the photoelectrochemical response of a copolymeric film containing a reversible acceptor (nitrobenzene group) instead of the phenothiazine electron donor group. Copolymers were prepared by controlled-potential oxidation at 0.82 V of a CH_3CN + 0.1 M TBAP solution of monomers **1b** (PMV^{2+}) and **5** (PNB).



5 (PNB)

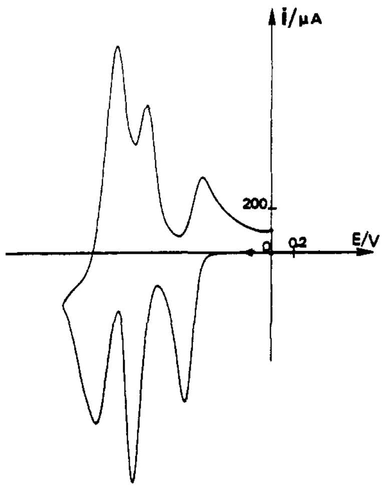


Figure 8. Cyclic voltammetry of an OTE/poly(PMV^{2+}) (Γ = 2.6 × 10^{-8} mol cm^{-2}), poly(PNB) (Γ = 5.8 × 10^{-8} mol cm^{-2}) copolymer film in CH_3CN + 0.1 M TEAP solution; scan rate ν = 0.05 V s^{-1}.

As expected, the cyclic voltammogram of these films exhibits the electroactivity of all the redox couples immobilized at the electrode surface (Figure 8). Data from Table VI demonstrate the poor efficiency of the copolymer poly(PMV^{2+}),poly(PNB) compared to poly(PMV^{2+}),poly(PPTZ) films. On the other hand, photocurrents are less than those observed for a single-component film of poly(PMV^{2+}). As expected, the dilution of V^{2+} sites decreases the propagation rate of the electrons in the polymer.

Conclusion

Bifunctionalized polypyrrole modified electrodes containing both reversible electron acceptor and donor moieties are able to act as photoelectrodes in the presence of an irreversible electron donor. The better efficiency of such materials compared to polypyrrole containing solely an electron acceptor is due to the formation of an intramolecular CTC created in the film by the direct interaction of the acceptor and donor entities. On the other hand, our results demonstrate that the arrangement of the CTC components plays an essential role in the efficiency of the photoresponse. Films based on a unimolecular design produce larger photocurrents than those based on copolymers or bilayers of the two independent components.

Acknowledgment. We thank Professor G. Cauquis for his interest in this work.

Registry No. 1a, 100809-39-0; poly(**1a**), 100779-25-7; **1b**, 94343-60-9; poly(**1b**), 94290-19-4; **2a**, 114703-19-4; poly(**2a**), 114610-62-7; **2b**, 114703-20-7; poly(**2b**), 114593-27-0; poly(**2c**), 131351-98-9; **3**, 131323-16-5; poly(**3**), 131323-17-6; **4**, 109850-28-4; poly(**4**), 109850-29-5; **5**, 107484-31-1; poly(**5**), 131323-18-7; TEAP, 2567-83-1; MePTZ, 1207-72-3; $(C_6H_5)_2C(OH)CO_2^-$, 40145-81-1; CH_3CN, 75-05-8; Pt, 7440-06-4.