Photocurrents at Polymeric Triads: Sensitized Redox Cascades under Forward and Reverse Bias

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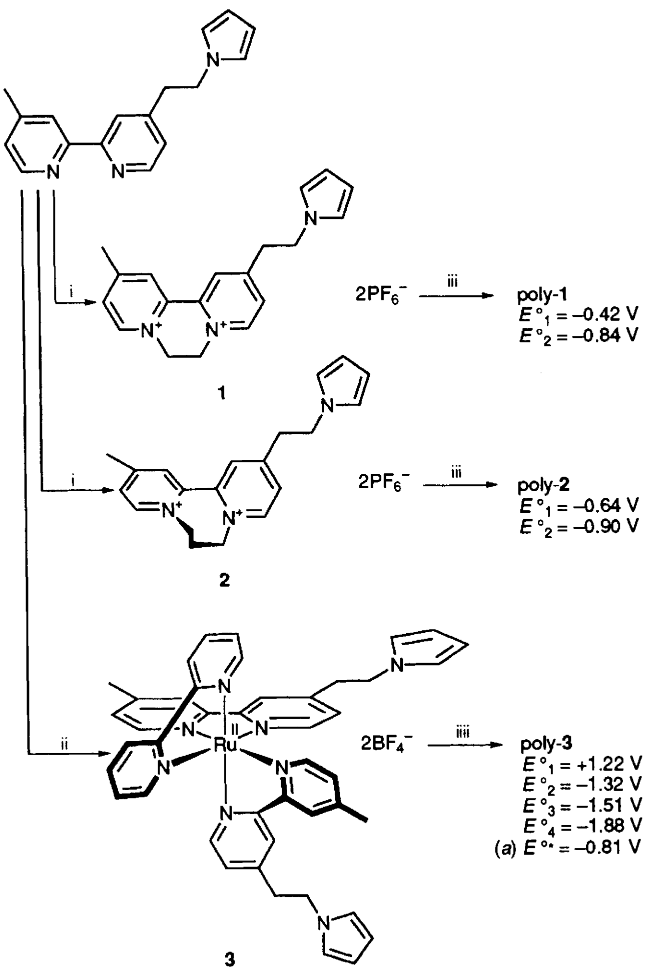
The anodic photocurrents at the 'isomeric' redox-polymer trilayer-film assemblies, {electrode(−0.2 V)/redox$_1$(−0.42 V)/redox$_2$(−0.64 V)/sensitizer(−0.81 V)} and {electrode(−0.2 V)/redox$_2$(−0.64 V)/redox$_1$(−0.42 V)/sensitizer(−0.81 V)} (redox$_{1,2}$ = polymeric diquat homologues, sensitizer = polymeric Ru(bpy)$_3$-derivative), are mainly governed by the sequence of redox$_1$ and redox$_2$, *i.e.* the forward or reverse bias of the intrinsic redox-type diode.

Photoinduced charge separation in (supra)molecular systems requires a photosensitizer, linked to a linear, and conformationally rigid redox cascade, to assure quenching of the excited state, vectorial electron transfer (ET) and a long-lived charge separated state.[1] Principally, the same architecture can be envisaged for the construction of a photoelectrode, *e.g.* a two-dimensional array of sensitized redox cascades, parallel oriented and perpendicular to an electrode surface. Most easily, such assemblies are prepared by the sequential deposition of thin films of the different redox- and photo-active components. So far, reported constructions, based on surface-confined organic redox polymers, include: (*i*) a polymeric film of sensitizer (eventually + quencher) on a semiconductor[2] or conductor,[3] vectorial ET being driven by the Schottky-barrier, the electrode potential and/or an irreversible redox species on the solution side of the assembly; (*ii*) segregated bilayer polymeric films, *i.e.* polymeric diads, such as semiconductor/quencher/sensitizer[4] or conductor/sensitizer/quencher,[5] vectorial ET being also driven by the additional junction; (*iii*) a polymeric film of molecular dyads (sensitizer-quencher) assuring vectorial ET on the level of the molecular subunit, but not necessarily on the scale of the macroscopic assembly.[6] We report here the first polymeric, thin-film triad consisting of conductor/redox$_1$/redox$_2$-(=quencher)/sensitizer with vectorial ET definitely governed by a mild redox$_1$/redox$_2$ interfacial potential of 220 mV.



Scheme 1 Synthesis of the monomers and formation of the redox-polymer films: i, [7]; ii, [8]; iii, anodic electro-co-polymerization (1.34 V *vs.* SCE) on glassy carbon (S = 0.07 cm^2) of **1** (c 1.4 × 10^{-3} mol dm^{-3}, t 60 s) or **2** (c 1.4 × 10^{-3} mol dm^{-3}, t 75 s) + pyrrole (c 0.15 × 10^{-3} mol dm^{-3}) in 0.2 mol dm^{-3} Bu_4NClO_4–MeCN yields poly-**1**′ and poly-**2**′ with incorporated ratios pyrrole/**1** ≈ 2 and pyrrole/**2** ≈ 3 and $1 \times 10^{-8} < \Gamma_{diquat} < 2 \times 10^{-8}$ mol cm^{-2};[8] iii, anodic electropolymerization (1.24 V *vs.* SCE) of **3** (c = 0.6 × 10^{-3} mol dm^{-3}, t 90 s) in 0.2 mol dm^{-3} Bu_4NClO_4–MeCN to yield poly-**3** with $\Gamma_{Ru} \approx 1.5 \times 10^{-8}$ mol cm^{-2}; $E°$s in pure 0.2 mol dm^{-3} Bu_4NClO_4–MeCN (V *vs.* SCE); for bi- and tri-layers, the same polymerisation times were used, and individual Γ in bilayers are in the same range, Γ_3 in a third layer is judged¶ $0.5 \times 10^{-8} < 1.10^{-8}$ mol cm^{-2}; (*a*) $E°(Ru^{III}(bpy)_3/Ru^{II*}(bpy)_3)$ = −0.81 V.[9]

From 4-methyl-4′-(2-pyrrolyl-1-ethyl)-2,2′-bipyridine,[7] the electropolymerizable, homologous diquat derivatives **1** and **2**,[8] as well as the $[Ru(bpy)_3]^{2+}$-based sensitizer **3**, earlier introduced by Cosnier *et al.*,[7] have been prepared (Scheme 1). Anodic electropolymerization of the diquat monomers was accomplished on glassy carbon electrodes (C) from solution of **1** or **2** in the presence of free pyrrole, to yield the redox-polymer monolayer-film modified electrodes C/poly-**1**′ and C/poly-**2**′ ('prime' indicating copolymerization with pyrrole) (Scheme 1).[8] The sensitizer **3**, was electropolymerized in the absence of free pyrrole (Scheme 1). The same procedures, sequentially applied, led to an interesting combination of the three monomers as perfectly segregated bi- and tri-layers, *i.e.* only the current response of the inner-most film, eventually modulated by catalytic charge propagation from or into an outer film, was observed. In pure Bu_4NClO_4–MeCN, the monolayer film modified electrodes C/poly-**1**′ and C/poly-**2**′, exhibit reversible 'diquat' redox chemistry with $E°_1$(poly-**1**′) 220 mV more positive than $E°_1$(poly-**2**′) (Scheme 1).† For the bilayer film modified electrodes, C/poly-**1**′/poly-**2**′ and C/poly-**2**′/poly-**1**′, this small potential difference leads to charge-trapping and diode phenomena, as ET from poly-**2**′ to poly-**1**′ is fast (exergonic ET, forward biased diode) and ET in reverse direction is slowed down (endergonic ET, reverse biased diode).[8]

Table 1 Photocurrent [μA cm^{-2}] at start (i_{start}) and after 6 min ($i_{6\,min}$) of chopped white light illumination for different electrode assemblies with forward (fwd) and reverse (rev.) biased redox-junctions. Electrode potential = −0.2 V (*vs.* SCE).

Electrode assembly	Bias	i_{start}, $i_{6\,min}$
C/poly-**1**′/poly-**2**′/poly-**3**	fwd	3.5, stable
C/poly-**2**′/poly-**1**′/poly-**3**	rev.	0.3, stable
C/poly-**3**	—	0
C/poly-**1**′/poly-**3**	—	2.6, → 1.3
C/poly-**2**′/poly-**3**	—	0.5, ≈ stable
C/poly-**1**′	—	3.9, → 1.6
C/poly-**2**′	—	0.7, stable
C/poly-**1**′/poly-**2**′	fwd	2.5, → 1.7
C/poly-**2**′/poly-**1**′	rev.	0.3, stable

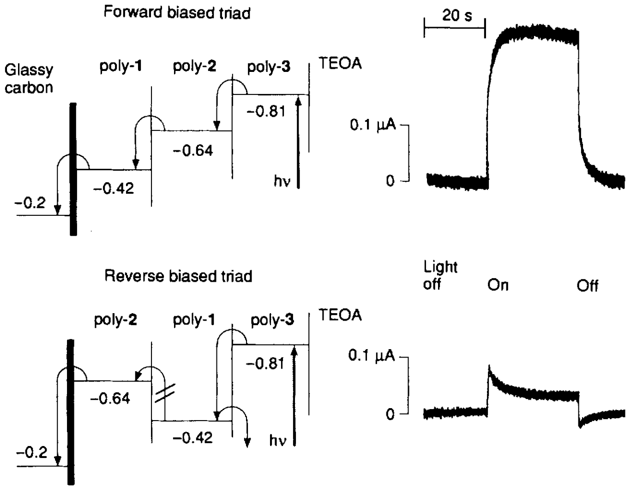


Fig. 1 Experimental photocurrents at two 'isomeric' triads (white light,‡ S = 0.07 cm^2) and mechanistic interpretation in terms of a forward and reverse biased intrinsic diode

If the trilayer C/poly-**1**′/poly-**2**′/poly-**3** with forward biased diode in 0.2 mol dm^{-3} Bu_4NClO_4/0.05 TEOA/MeCN (TEOA = triethanolamine) is potentiostated at −0.2 V *vs.* SCE and illuminated with white light,‡ a stable, anodic photocurrent of 3.5 μA cm^{-2} (average) is observed, the best triad samples reaching 7 μA cm^{-2} (Fig. 1). The average photocurrent drops to 0.7 μA cm^{-2} if blue light of 30 mW cm^{-2} surface light intensity is used.‡ For the triad C/poly-**2**′/poly-**1**′/poly-**3** with build-in reverse biased diode, the current reaches only one tenth of the C/poly-**1**′/poly-**2**′/poly-**3** assembly. This difference is definitely related to the redox diode, poly-**1**′/poly-**2**′. The blank experiments were all done under the same experimental conditions using white light illumination, but different polymer assemblies (Table 1). Both diads, C/poly-**1**′/poly-**3** and C/poly-**2**′/poly-**3** show photocurrents, whereas C/poly-**3** is not active. Astonishingly, the assemblies without poly-**3** layer, *i.e.* without $Ru(bpy)_3$-based sensitizer, exhibit also photocurrents (last four entries in Table 1). Here, sensitization is due to a charge-transfer (CT) complex between TEOA and poly-**1**′ or TEOA and poly-**2**′.§ Typically, the CT complex based photocurrents decay faster, probably because of hindered diffusion of fresh TEOA into the polymer layer or irreversible reactions of $TEOA^{+\cdot}$ with diquat-subunits. However, even in the case of CT complex sensitization, the redox-junction is active, *i.e.* the photocurrent for the forward biased diode, C/poly-**1**′/poly-**2**′ is much larger than for the reverse biased assembly C/poly-**2**′/poly-**1**′. The photocurrent with C/poly-**1**′/poly-**2**′ being larger than with C/poly-**2**′ is probably due to the forward biased junction poly-**1**′/poly-**2**′ assisting charge separation, rather than due to excitation of a TEOA-poly-**1**′ CT complex, as TEOA (*c* 0.05 mol dm^{-3} on the solution side, E_p = 0.88 V) in the case of C/poly-**1**′/poly-**2**′ is essentially not detectable at the electrode-poly-**1**′ interface by cyclic voltammetry.

Notably, our redox cascade can assist (or slow down) photoinduced charge separation in sensitized thin film assemblies, the potential drop over the cascade (220 mV) representing a good compromise between efficient charge separation and acceptable half-cell photovoltage. The conceptual advantage of the triad C/poly-**1**′/poly-**2**′/poly-**3** with build-in charge separator over the diad C/poly-**2**′/poly-**3** (prone to back-ET) should show up with a reversible redox couple on the solution side.

We thank the Swiss National Science Foundation for financial support and K. Pfanner, Institute of Inorganic and Physical Chemistry, University of Berne, for the light intensity measurements.

Received, 28th July 1993; Com. 3/04510B

Footnotes

† The excited state reduction potential of poly-**3** is expected to be similar to that of $[Ru(bpy)_3]^{2+}$, $E°(Ru^{III}/Ru^{II*})$ = −0.81 V,[9] and thus, poly-**1**′ ($E°_1$ = −0.42 V) and poly-**2**′ ($E°_1$ = −0.64 V) are both potential oxidative quenchers (Scheme 1). $E°_1$(poly-**1**′)-$E°_1$(poly-**2**′) = 220 mV is related to the additional methylen group in **2**, that translates into a larger torsional angle between the pyridinium groups.

‡ White light: the electrode was illuminated through the bottom of a cell (320 nm cut-off) with the focused light from a halogen lamp (30 W input). Blue light: the same light source with a 450 nm band-pass filter (70 nm width) was used, yielding a surface light intensity of 30 mW cm^{-2}.

§ **1** ($K_{1\text{-TEOA}}$ = 96 dm^3 mol^{-1}, $\lambda_{1\text{-TEOA}}$ = 544 nm) and **2** ($K_{2\text{-TEOA}}$ = 42 dm^3 mol^{-1}, $\lambda_{2\text{-TEOA}}$ = 522 nm) form blue coloured CT complexes with TEOA in MeCN. Homogeneous donor/4,4′-bipyridinium[10] and surface confined CT complexes[11] have been used as sensitizer–quencher systems in photoelectrochemical cells, and the not-intended CT formation between surface-confined 4,4′-bipyridinium and TEOA in solution has been reported.[12]

¶ Individual surface coverages (Γ) in mono- and bi-layers have been determined by integration of cyclic voltammograms; Γ_{Ru} in an outer layer is not accessible by this method, but can be judged from the charge consumed during electropolymerisation.

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