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Donor/Conductor/Acceptor Triads Spatially Organized on the Micrometer-Length Scale: An Alternative Approach to Photovoltaic Cells

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Abstract: We have used porous anodised Al_2O_3 membranes as inert matrix for constructing and organizing spatially ternary donor/conductor/acceptor (DCA) systems exhibiting photovoltaic cell activity on the micrometric-length scale. These DCA triads were built stepwise by first growing a conducting polymer inside the membrane pores, thus forming nanorods that completely fill the internal pore space of the membrane. Then, an electron donor and an electron acceptor were adsorbed one on each side of the membrane, so that they were separated by a distance equal to the membrane thickness (ca. 60 μm), but electronically connected through the conductive polymer. When this device was placed between two electrodes and irradiated with visible light, electrons jumped from the donor molecule, crossed the membrane from side to side through the conductive polymer (a journey of about 60 μm!) until they finally reach the acceptor molecule. In so doing, an electric voltage was generated between the two electrodes, capable of maintaining an electric current flow from the membrane to an external circuit. Our DCA device constitutes the proof of a novel concept of photovoltaic cells, since it is based on the spatial organization at the micrometric scale of complementary, but not covalently linked, electron-donor and electron-acceptor organic species. Thus, our cell is based in translating photoinduced electron transfer between donors and acceptors, which is known to occur at the molecular nanometric scale, to the micrometric range in a spatially organised system. In addition our cell does not need the use of liquid electrolytes in order to operate, which is one of the main drawbacks in dye-sensitised solar cells.

Keywords: conducting materials · donor–acceptor systems · membranes · photovoltaic cells · polymers

Introduction

Charge separation by transferring a single electron from a donor (D) to an acceptor (A) molecule is one of the simplest elementary processes in chemistry.[1] When this charge separation is promoted photochemically, the process can serve to transform light energy into chemical reactivity or even into electric current provided that electrons are efficiently collected by an external electrode and the charge-separated state does not decay by back electron transfer. Considerable fundamental research has been focused on increasing the efficiency of the charge separation by minimization of prompt annihilation that occurs when the geminate electron/hole pair generated in the photophysical event recombines.[1] From this basic research it has become clear that the distance between the donor and the acceptor and the electronic interaction between them are key factors controlling the lifetime of the charge-separated state. Aimed at increasing the distance between the donor and acceptor termini, while still having sufficient electronic interaction that permits electron transfer, a fruitful line of research has focused on the design and synthesis of molecular entities in which electron donor and acceptor units ("diads") are covalently linked through a spacer. More sophisticated molecules containing three ("triads") or more substructures involved in the photoinduced electron transfer have also been synthesised.[2,3] Fullerene derivatives covalently linked to porphyrins constitute representative examples of these molecular devices.[4,5] The outcome of this research is that the efficiency of charge separation, minimization of back electron transfer and increase of charge separation lifetime can be achieved by increasing the distance between the donor and

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the acceptor substructures, while preserving their electronic interaction. It has been shown that these molecular diads can serve to develop photovoltaic cells.[6,7] Herein, we have developed an alternative concept of a photovoltaic cell based on contacting nanometric thin films of D and A through a conducting polymer and organizing spatially the system using a macroporous membrane.

Results and Discussion

The first step in the realization of the spatially organised donor/conductor/acceptor (DCA) triad was the preparation of a conductive polymer inside the pores of an anodised Al_2O_3 membrane (Whatman ANODISC 25). For this purpose, we used poly(3,4-ethylenedioxy thiophene) (PEDOT), which is one of the most robust and widely used conducting polymers for nanotechnology applications. Good polymerization is the crucial factor to attain a high electric conductivity between both sides of the membrane and, thus, a good performance of the DCA triad as photovoltaic cell. For the preparation of PEDOT inside the membrane pores (0.2 μm wide), we adapted the method previously reported by Han and Foulger,[8] but we found that better conductivities between both sides of the membrane can be attained if the concentration of the $FeCl_3$ catalysts is increased up to 9 M. This is because when the concentration of $FeCl_3$ is 9 M, PEDOT nanorods sufficiently long and large to completely fill the membrane pores are formed. Once the PEDOT was prepared inside the membrane pores, the photovoltaic device was completed by spin-coating either $[Ru(bpy)_3]^{2+}$ or the Solaronix ruthenium complex “Black-Dye” (RuBD) from a solution in ethanol on one side of the membrane, and subsequently an aqueous solution of methylviologen chloride ($[MV]^{2+}$) on the other side. These two molecules act as electron donors and acceptors, respectively.

Figure 1a shows a SEM image of the anodised alumina membranes. The structure of these membranes is formed by pores of about 200 nm in diameter and relatively uniform in size, running continuously (albeit with some tortuosity and width variations) from one side to the other. The length of these pores is of about 60 μm (as deduced from the corresponding side-view images of the membranes). These pores are all oriented normal to the flat surface of the membrane. Figure 1b shows the SEM image corresponding to PEDOT rods formed upon polymerization of the monomer inside the membrane pores and recovered by dissolving the inorganic alumina with aqueous HF. This image shows that the polymerization procedure leads to PEDOT rods of uniform diameter and length that are in accordance with the diameter and length of the membrane pores. Thus, electron microscopy evidences that our polymerization has succeeded in forming PEDOT rods from side-to-side of the membrane, with the alumina walls acting as submillimetric moulds for the growing polymer.

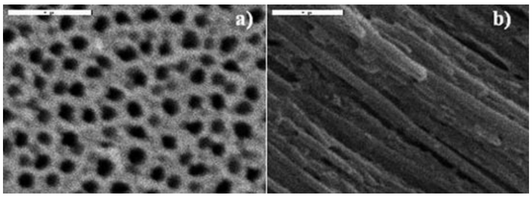

Figure 1. Scanning electron micrograph representative of a) the anodised Al_2O_3 membrane and b) the PEDOT nanorods formed inside the membrane pores.

The Raman spectra can be easily recorded for the membranes with PEDOT-filled pores without destroying or altering them. These Raman spectra were compared with that of an authentic commercial sample of PEDOT. Both Raman spectra are shown in Figure 2 and show remarkable coincidence. Apparently, encapsulation inside the pores of the inorganic membrane does not interfere in the Raman spectrum of PEDOT; this result indicates that the Al_2O_3 membrane acts only as a rigid matrix for the conductive organic polymer.

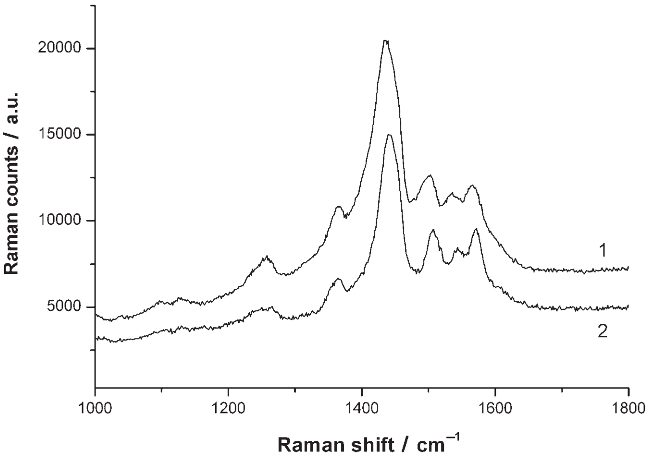

Figure 2. Raman spectra of a PEDOT-containing membrane (spectrum 1) and a commercial PEDOT sample (spectrum 2).

Electric resistance of the PEDOT-containing membranes was determined from the slope of the corresponding *I-V* plots. As expected, the starting alumina membrane has an *I-V* curve typical of an insulating material, and the current flow is negligible in the voltage range studied (−0.4 to +0.5 V). In contrast, PEDOT-containing membranes show a significant conductivity, indicating that the conducting property of PEDOT is manifested on the conductivity of the modified alumina membrane. As it can be seen in Figure 3, these *I-V* plots are straight lines passing through the origin of co-ordinates obeying the Ohm law. Importantly, the resistance of the PEDOT-modified membranes depends upon the concentration of the iron catalyst used, since this concentration is the main parameter influencing PEDOT polymer formation. The lowest conductivity value was 18 kΩ measured for the PEDOT-containing membrane prepared with 9 M $FeCl_3$ solution. It must be taken into account that this resistance reflects the overall contribution of a number

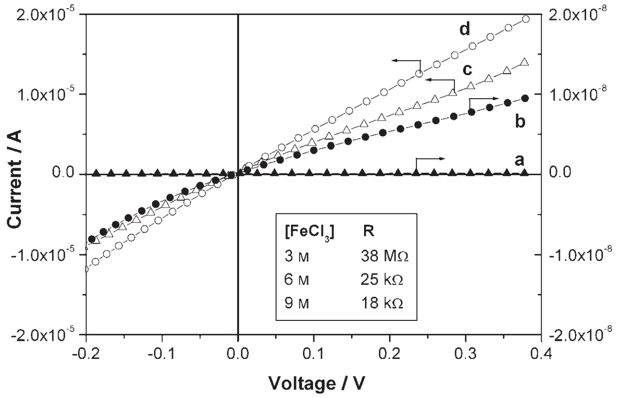

Figure 3. *I-V* curves of a pristine Al_2O_3 membrane (curve a) and PEDOT-containing membranes prepared with $FeCl_3$ solutions of increasing concentration: 3 (curve b), 6 (curve c) and 9 M (curve d). For the sake of clarity, curves c and d are plotted on a different vertical scale with respect to curves a and b. The electric resistance obtained from the slope of the *I-V* plot are presented in the textbox.

of factors, including the electric properties of the polymer itself and the external electric contacts between the membrane and the electrodes. Thus what is important is that our results imply that PEDOT fibers act as "nanocables" connecting electrically both sides of the alumina membrane.

Films of the electron donor (RuBD or $[Ru(bpy)_3]^{2+}$) and the acceptor ($[MV]^{2+}$) were spin-coated on each side of the alumina membrane without interfering one with another. The conductivity of the complete device with a RuBD or $[Ru(bpy)_3]^{2+}$ layer on one side and MV^{2+} on the other decreases below measurable values, thus indicating that PEDOT is covered by the donor and acceptor layers.

Interaction at the molecular level and electronic connectivity between $[Ru(bpy)_3]^{2+}$ and the conducting polymer can be firmly proved by photoluminescence measurements. Thus, in acetonitrile, the characteristic $[Ru(bpy)_3]^{2+}$ phosphorescence appearing at 620 nm observed, when $[Ru(bpy)_3]^{2+}$ is adsorbed on the anodised membrane, is completely quenched and unobserved for those membranes that contain PEDOT inside the pores. Figure 4 shows some emission images showing phosphorescence quenching of $[Ru(bpy)_3]^{2+}$ films when the anodised Al_2O_3 membranes contain PEDOT. Also, solution quenching studies revealed that the emission of $[Ru(bpy)_3]^{2+}$ in efficiently inhibited by dissolved PEDOT.

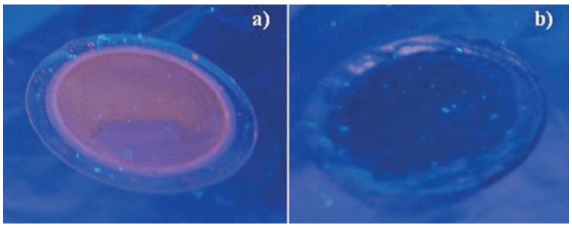

Figure 4. Fluorescence images of the anodised Al2O32 membrane containing a) $[Ru(bpy)_3]^{2+}$ and b) $[Ru(bpy)_3]^{2+}$/PEDOT.

The photovoltaic response of the DCA membrane was tested by exposing the cells to a 355 nm laser flash (5 mJ × pulse^{-1}) and monitoring the temporal profile of the voltage with an oscilloscope. For these measurements each face of the cell was simply connected to the oscilloscope with a cable. The results are presented in Figure 5.

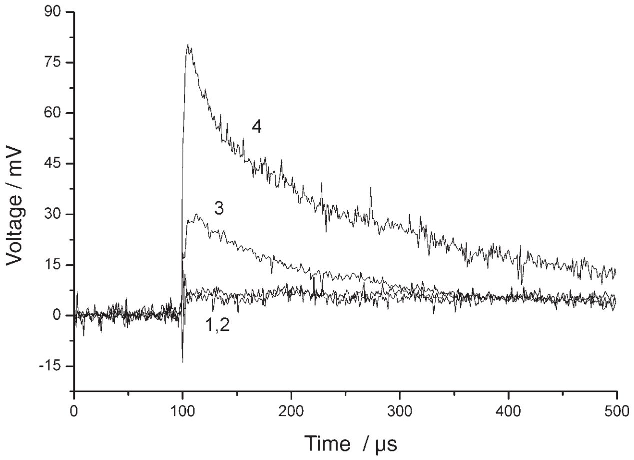

Figure 5. Temporal profile of the voltage generated upon 355 nm laser flash excitation (7 ns duration, 5 mJ pulse^{-1}) of: 1) a pristine Al_2O_3 membrane; 2) a membrane containing $[Ru(bpy)_3]^{2+}$; 3) a $[Ru(bpy)_3]^{2+}$/PEDOT diad; and 4) a membrane containing the $[Ru(bpy)_3]^{2+}$/PEDOT/MV^{2+} triad.

It can be seen there that upon laser excitation of the pristine Al_2O_3 membrane or excitation of a membrane containing $[Ru(bpy)_3]^{2+}$ the responses are negligible. In contrast a voltage buildup is already recorded for the $[Ru(bpy)_3]^{2+}$/PEDOT membrane (same absorption intensity as in the control experiment) as consequence of the electron transfer between $[Ru(bpy)_3]^{2+}$ to the conducting PEDOT polymer. This agrees with the $[Ru(bpy)_3]^{2+}$ phosphorescence quenching observations and with PEDOT connecting both sides of the membrane. Remarkably, this voltage buildup as consequence of photochemical excitation is significantly enhanced (2.7 times with respect to the membrane lacking the acceptor) for the DCA membrane (same absorption intensity at 355 nm as in the control experiment), that is, a membrane containing all the required components. The temporal profile of the voltage signal is interesting, since after a short laser pulse (7 ns) the flow of electrons is extended over hundreds of microseconds indicating that triplet excited states of $[Ru(bpy)_3]^{2+}$, generated instantaneously during the laser pulse but decaying in the microsecond timescale, are responsible for this electron flow. This is compatible with the known photochemistry of $[Ru(bpy)_3]^{2+}$ for which, upon light absorption, long-lived triplet excited states extending in microsecond timescale are formed and are quenched by electron acceptors.[9]

The DCA membrane was also exposed to the irradiation of a solar simulator (900 W) through a AM1.5 filter. Upon illumination a photovoltage was observed. Figure 6 illus-

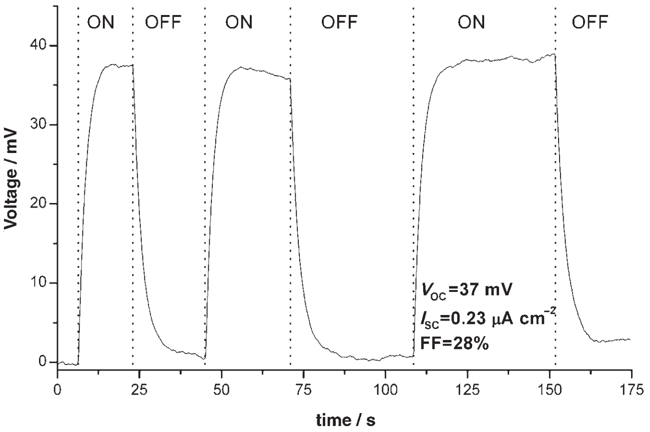

Figure 6. Temporal profile of the photogenerated electric voltage throughout the DCA solar cell containing the RuBD/PEDOT/MV^{2+} triad. "ON" and "OFF" stand for illuminated and dark phases, respectively. The main characteristics of the cell are presented in the textbox, in which V_{OC}, I_{SC} and FF stand for open circuit voltage, short circuit current and fill factor (in %), respectively.

trates the response measured and the photovoltaic behaviour of our membrane containing RuBD as the electron donor. As it can be seen there, upon illumination, there is a voltage buildup that takes over 15 s before the maximum voltage is obtained. Also, after switching off the light, the voltage decays in about 20 s. This voltage growth and decay is a manifestation of the way in which the membrane operates. Upon excitation and charge separation at the molecular level, electrons flow toward the acceptor molecule and, therefore, charge separation occurs at the submillimetric-length scale with development of a capacitance with one face being positive and other being negative. When a stationary regime is achieved, the maximum voltage is reached. Upon shut down, the membrane acts as capacitor self-discharging through the circuit. The cycle can be repeated reproducing the same behaviour without fatigue or decrease in the response. This photovoltaic behaviour of DCA membranes is quite general, since other series of D and A (benzoquinone, xanthone, diquat, etc) behave similarly, but with varied efficiency.

With respect to the efficiency and fill factor of our solar cell device, the inset of Figure 5 lists the relevant parameters. Although these values are far from being the maximum ever reported, they are not uncommon for organic solar cells, particularly considering the large dimensions of our cell (2.5 cm diameter). Although, it is evident that our device still needs optimization particularly in terms of less resistive connections at the molecular and submillimetric scale (the internal resistance of many optoelectronic devices are in the range of a few tens of Ω, as compared to our kΩ value), our cell opens the way for easily manufacturable, electrolyte-less organic solar cells.

Experimental Section

Ternary Ru/PEDOT/MV systems assembled in macroporous membranes were prepared following a three-step process. First, poly(3,4-ethylenedioxythiophene) (PEDOT) was synthesised inside the pores of anodised alumina membranes (Whatman ANODISC 25), according to the procedure recently reported by Han and Foulger.[8] Briefly, the membrane (2.5 cm diameter) was placed in a conventional polycarbonate filter holder (Albet PF-25-P-02) , and the liquid monomer 3,4-ethylenedioxythiophene (200 μL) was repeatedly passed through it backward and forward with a syringe in order to soak completely the pores. The volume of 200 μL is enough to ensure that the membrane pores are completely filled by the liquid monomer. The excess monomer was eliminated by simply drying the membrane between two pieces of clean filter paper. The membrane was then immersed in an aqueous solution containing $FeCl_3$ as the polymerization catalyst. The excess iron solution was quickly eliminated by drying the membrane with a clean filter paper, as it was always observed that the membrane immediately turned dark blue, thus indicating that under the experimental conditions used polymerization starts without appreciable induction time. Nevertheless, in order to ensure that the polymerization was complete, the membrane was kept into an oven at 80 °C for 1 h. Different $FeCl_3$ concentrations (ranging from 3 to 9 M) were tested, so as to check for any possible effects of the catalyst concentration of the conductivity of the final polymer.

The next two steps consisted of the sequential adsorption on one side of the PEDOT-containing membrane of either tris(bipyridyl) ruthenium chloride, $[Ru(bpy)_3]Cl_2$, or the Solaronix ruthenium complex "Black-Dye" (RuBD), and methylviologen, $[MV]^{2+}$, on the other side. The procedure was as follows: the ruthenium complex (20 mg) was dissolved in ethanol (200 μL) and spin-coated (1500 rpm, 80 s, slope 1000 rpm s^{-1}) on one side of the membrane. Next, methylviologen chloride (10 mg) in distilled water (200 μL) was also spin-coated (same conditions as above) on the other side of the membrane. Spin-coating was chosen as the adsorption technique because it gives superior results concerning homogeneity of the adsorbed layers, and at the same time ensures the lack of contamination of the unexposed face. Simple control experiments monitoring phosphorescence showed that when $[Ru(bpy)_3]Cl_2$ is cast on one face, its emission was negligible in the other face.

After each step of the preparation, the samples were thoroughly characterised by means of conductivity measurements (*I-V* curves), scanning electron microscopy, and Raman spectroscopy. Blank membranes as well as samples containing only one or two of the components (ruthenium complex, $[MV]^{2+}$ and PEDOT) were also prepared and characterised for comparison. Some of the PEDOT-containing membranes were treated with an aqueous HF (20 vol %) solution to dissolve the alumina membrane in order to isolate the PEDOT nanorods for their further characterization.

For both conductivity measurements and transient laser experiments, the membranes were sandwiched within a transparent indium tin oxide (ITO) and a platinum electrode (with the face containing the ruthenium dye placed in contact with the ITO electrode) and pressed with the aid of tight clamps, without the use of liquid electrolytes. Conductivity measurements were carried out in air and at room temperature by using a Keithley 6200 apparatus controlled from a PC.

For transient laser experiments, the membranes were irradiated with 355 nm laser pulses (third harmonic of a Nd/YAG laser, 5 mJ pulse^{-1}, 7 ns fwhm) exposing the side of the membrane corresponding to the ruthenium complex. As a consequence of this laser excitation, an electric voltage pulse was generated between the two electrodes. The time decay of this signal was captured by a Tektronik 2420 oscilloscope synchronised with the laser pulse. Emission quenching experiments were performed in N_2-purged acetonitrile solutions contained in suprasil quartz cuvettes capped with septa, using an Edinburgh FL4000 spectrofluorimeter.

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