Optical properties of a new p-phenylenevinylene oligomer containing quinolines and ferrocene for organic solar cells

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Abstract. In the present work, we studied a conjugated phenylenevinylene oligomer containing quinolines and ferrocene (2FcQF1C) as end groups. The optical properties were analyzed by UV-vis and fluorescence spectroscopy. The energies of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) were calculated by the oxidation/reduction potentials obtained by cyclic voltammetry in solution. A prototype of photovoltaic device was realized using a mixture 2:3 w/w of the oligomer (2FcQF1C) with the commercial [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) with a typical configuration of ITO/2FcQF1C:PCBM/Al. Current density-voltage (JV) curves were obtained in dark and using a laser at $\lambda = 405$ nm as illumination power source. Preliminary values of conversion efficiencies around of $10^{-4}$ % were obtained. These results are promising for optimization studies of the cells.

1. Introduction
Since the oil crisis in the early 1970's, there has been an increasing interest in the development of photovoltaic solar cells, in order to use the cleanest of all possible sources of renewable energy that is solar radiation. Nowadays, the technology of silicon devices still dominates the world market with a photon-to-current (PCE) conversion in the range of 24%, but its principal disadvantage is the high cost of production. As alternative materials, organic conjugated systems allow the fabrication of devices through less expensive techniques such as spin coating, doctor blade and ink jet printing. Despite that the PCE conversion of organic photovoltaic devices has passed from 0.001% in 1975 to 10.3 % in January 2012, it is still far from the values obtained with the inorganic counterparts. The origin of the lower PCE in organic photovoltaic cells is mainly due to the limited range of absorption of these materials. Several approaches have been proposed to overcome this problem such as combine different conjugated polymers in tandem solar cells [1], preparing composites or blends with quantum dots or metallic nanoparticles, and/or lowering the optical band gap by inserting electron donor groups in the conjugated chain. Ferrocene is a good electron donor and photoinduced electron transfer has been demonstrated for ferrocene bearing materials. Recently, charge transfer in ferrocene substituted poly(thiophene)s have been demonstrated in bilayer solar cells. Also, improved open circuit voltages have been obtained in heterojunction photovoltaic devices made of ferrocene as electron donor and fullerene as electron withdrawing material.
In this contribution we show that ferrocene strongly affects the optical and electrochemical properties of a novel phenylenevinylene oligomer with respect to its precursor that does not present in its structure ferrocene end groups. Particularly, the absorption spectrum becomes broad and unresolved, the fluorescence quantum yield decreases as well as the band gap. The free energy for intermolecular photoinduced energy transfer with PCBM as calculated by the Weller equation indicates that only the heptamer is a possible candidate for solar cells application. The intrinsic photovoltaic properties are studied in a heterojunction prototype.

2. Experimental
The chemical structure of the oligomer 2FcQF1C is reported in the figure 1b together with its precursor pentamer 2BrQF1C (figure 1a) that was studied as a term of comparison for optical and electrochemical characterization.

2.1 Optical characterization
The absorption and emission spectra were obtained in CHCl$_3$ and thin films using a Shimadzu 2401PC spectrophotometer and a Perkin Elmer LS50B spectrofluorimeter, respectively. For the fluorescence spectra, the samples were excited at 10 nm below the absorption maxima. Fluorescence quantum yield in solution was obtained according to the literature method [2]. The temperature was controlled to 25.0±0.3 °C with a water circulating bath. The optical band gap $E_{g,op}$ was obtained from the intersection between the X axis and the tangent at the normalized absorption curve drawn in correspondence of optical density of 0.1.

2.2. Electrochemical characterization
The electrochemical properties of oligomers were investigated at room temperature in 0.5 mM CH$_3$Cl$_2$ solutions by cyclic voltammetry in a C3 Stand cell from Basi coupled to a potentiostat/galvanostat ACM Gill AC. Bu$_4$NPF$_6$ (0.1M) was used as the supporting electrolyte, a glassy carbon as working electrode, Pt wire as counter electrode, Ag/AgCl as the reference electrode and ferrocene/ferrocenium as internal reference. The molecular orbital energies HOMO and LUMO were calculated from the oxidation ($E_{ox}$) and reduction ($E_{red}$) potentials with the equation 1:

$$E^{HOMO[LUMO]} = -e \left( E^{ox}_{1/2}(Ag/AgCl) - E^{onset}(Fc/Fc^- vs Ag/AgCl) \right) - 4.8 eV$$

The free energy ($\Delta G$) associated with the possibility to have intermolecular photoinduced electron transfer has been calculated with the electrochemical and fluorescence information modifying the Weller equation (equation 2) by considering that, for intermolecular process, the distance anion-cation trends to infinite [3]:

$$\Delta G = -e \left( E^D_{ox} - E^A_{red} \right) - E_{10} - \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r^-} + \frac{1}{r^+} \right) \left( \frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_s} \right)$$

The cation (electron donor material) radium, $r^+$ has been obtained by simulating the equilibrium geometry of the molecules at AM1 semiempirical level in Spartan 10. The anion (electron withdrawing material) is in our case PCBM and its radium has been reported to be 5.6 Å [3].
2.3 Solar Cells

Devices were prepared with the configuration ITO/PEDOT:PSS/active layer/Al. PEDOT:PSS (5:8) with a σ = 1S/cm and dispersed in water (1.3% weight) from Aldrich was deposited on the Indium Tin Oxide (ITO) by spin coating at 1000 rpm to give a 25 nm layer. Active layers with thickness around 160 nm were obtained from a 2:3 weight mixture of 2FcQF1C and commercial PCBM (Aldrich) dissolved in 1:1 toluene/CHCl3 mixture. The aluminum was vacuum evaporated at a rate of 3 Å/s at a typical pressure of 10⁻⁶ torr in an Intercovamex TE18P vacuum chamber; the thickness was controlled by the quartz balance monitor ~100 nm. The current density-voltage (J-V) curves were obtained using a Keithley 6517A electrometer by illuminating the devices from the ITO side with 405 nm Newport laser (40 mW power).

3. Results

3.1 Optical characterization in solution

2BrQF1C can be considered, in terms of its optical properties, as a sum of two chromophores: the quinoline-phenylenevinylene conjugated part and ferrocene. The first one is also a fluorophore while ferrocene does not emit. The UV-VIS spectrum of 2BrQF1C (figure 2, dashed line) shows an excitonic spectrum with a maximum at 430 nm, similarly to other phenylenevinylene pentamers. On the contrary, the absorption spectrum of 2FcQF1C presents a broad unresolved absorption, suggesting electronic interactions in the ground state between the two chromophores. The optical band gap $E_{g,op}$ decreases from 2.41 eV to 2.36 eV and the fluorescence maximum (inserted figure) red shifts from 507 nm to 517 nm, in agreement with the increase in the conjugation length. The incorporation of ferrocene affects the fluorescence quantum yield that decreases from 0.31 (2BrQF1C) to 0.03 (2FcQF1C). A similar behaviour was previously found in other conjugated systems and ascribed to photoinduced energy transfer [4].

3.2 Electrochemical characterization

The cyclic voltammetry studies allowed us to calculate the values of reduction and oxidation potential for the determination of the electrochemical band gap. Table 1 shows the electrochemical properties determined from the voltograms.

| Compound | $E_{ox}^{max}$ (V) | $E_{red}^{max}$ (V) | $E_{onset}^{ox}$ (V) | $E_{onset}^{red}$ (V) | $E_{1/2}^{ox}$ (V) | $E_{1/2}^{red}$ (V) | HOMO (eV) | LUMO (eV) |
|----------|------------------|------------------|------------------|------------------|-----------------|-----------------|-----------|-----------|
| 2BrQF1C  | 2.30             | -1.10            | 1.82             | -0.87            | 2.06            | -0.98           | -6.86     | -3.31     |
| 2FcQF1C  | 0.85             | -0.66            | 0.64             | -0.45            | 0.75            | -0.55           | -5.55     | -4.25     |

2BrQF1C presents one oxidation/reduction peak associated with the removal/addition of one electron to the conjugated chain giving a polaron excited state. 2FcQF1C shows two oxidations peaks (maxima at 0.85 and 1.25 V) that can be ascribed to polaron and bipolaron formation. The first oxidation peak is shifted with respect to the ferrocene as found for other ferrocene substituted molecules. The semiempirical molecular simulation gave a cation radius of 16.5 Å and 20.4 Å for 2BrQF1C and 2FcQF1C respectively. These values were introduced in equation 3 together with the oxidation and reduction potentials obtained by voltammetry and the value for the $E_{10}$ (2.57 eV for 2BrQF1C and 2.67 eV for 2FcQF1C) obtained from the optical study, to give the free energy $\Delta G= 0.36eV$ for 2BrQF1C and -1.21eV for 2FcQF1C. As photoinduced energy transfer is spontaneous when $\Delta G$ is negative, this result suggests that only 2FcQF1C is a good candidate for solar cells application.

3.3 Cells

On the basis of the previous discussions, solar cells were prepared only for 2FcQF1C in heterojunction with PCBM. It is to be noted that the prototypes were fabricated in laboratory conditions, without
optimization of the film preparation just in order to study the intrinsic optoelectronic properties of the new molecule. The active layer presents an increase in the absorption in the 450-800 nm with respect to the film of 2FcQF1C (figure 3), which permits an antenna effect in the solar maximum emission (that is around 500 nm).

The solar cell prototype shows the typical J-V curve (figure 4a) with a low $V_{OC}$ (0.67 V). However the saturated current density ($3.92 \times 10^{-3}$ mA/cm²) and the efficiency ($10^{-4}$ %) are lower than usually reported for OPVs. This can be due to microsegregation phenomenon with PCBM as found by Atomic Force Microscopy (AFM, figure 4b). This is to be pointed out that the present prototype was not optimized in terms of the film preparation conditions. Morphology has been demonstrated to be an important factor to reduce the exciton diffusion inside the bulk heterojunction. Changing the solvent, using additives or annealing can improve this aspect and therefore the efficiency [5]. For this reason, works in progress are addressed to investigate the better conditions for the film preparation (deposition technique, solvent, annealing, etc) for increasing the device efficiency.

3.3. Conclusions
The optical and electrochemical properties of a conjugated phenylenevinylene heptamer bearing ferrocene and quinoline were studied and compared with its precursor pentamer, which is not substituted with ferrocene. The free energy for intermolecular photoinduced energy transfer to PCBM was calculated for both molecules by inserting the oxidation/reduction potentials and the first excited state energy obtained by fluorescence in the Weller equation. According to this study, just the ferrocene heptamer is a good candidate for solar cells application. The efficiency of the prototype solar cell based on heterojunction with commercial PCBM was low (around $10^{-4}$ %), most likely due to microsegregation process between the oligomer and the fullerene derivative. Optimization of film preparation conditions is currently in progress.

4. References
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