

Tuning of the Photoinduced Charge Transfer Process in Donor-Acceptor “Double Cable” Copolymers

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ABSTRACT

The covalent linking of acceptor molecules to electron donating conjugated polymer is an approach for the development of new photoactive materials for the fabrication of organic photoelectric conversion devices. With this strategy we have designed a polyalkylthiophene copolymer series containing in the side chain anthraquinone molecules as electron acceptor. The peculiar features of the copolymers are the good processability and the ease in tailoring the content of acceptor moieties. Their potential use as photoactive materials is investigated in terms of the photoinduced charge transfer properties, studied by FTIR photoinduced absorption and Light Induced Electron Spin Resonance spectroscopies. The results indicate the photoinduced electron transfer from the polythiophene backbone to the anthraquinone substituents and its tunability by changing the content of acceptor molecules. The photovoltaic response of these polymers is also discussed.

Keywords: photoinduced charge transfer, polyalkylthiophene copolymers, anthraquinone, photovoltaic devices, spectroscopy

1. INTRODUCTION

The preparation of polymeric photovoltaic cells processable as easily as plastics can provide a new hint both in the exploitation of solar energy and in the demands for more advanced photodetectors. For these reasons the possibility to use conjugated polymers to fabricate inexpensive and flexible large area solar cells and photodetectors is intensively investigated^{1,2}. The photovoltaic effect in conjugated polymers consists in photogeneration of excitons on the chain and their dissociation in presence of electron-acceptor species like fullerene. The most promising active layer is the so called bulk-heterojunction where the electron donor polymer (D) and the acceptor molecules (A) are blended together^{3,4}. The blend morphology is affecting both charge photogeneration and transport, having thus a crucial role for the device performance. The tendency to phase segregation of the two components has to be tailored having in mind that: i) an intimate mixing of the donor and acceptor is beneficial for charge photogeneration; ii) a bicontinuous network of the donor and acceptor phases favours a balanced transport of the photogenerated charges to the electrodes.

A proposed approach to attain an intimate mixing of the D/A components is the covalent linking of electron accepting moieties to a hole transporting conjugated polymer backbone. This kind of material is called “double cable” because has, in principle, two different pathways (cables) for the transport of electrons and holes to the electrodes⁵. Different types of conjugated polymers, bearing as acceptor substituents fullerene⁶⁻⁸ or tetracyanoanthraquinodimethane⁹ moieties have been synthesised, and their use for photovoltaics has been studied. One of the major issues in the design of “double cable” polymers is to improve the processability in order to obtain soluble materials with a high content of acceptor moieties. For example, soluble conjugated polymers containing fullerene exhibit a content of acceptors not exceeding 20 % by weight⁵.

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To obtain donor-acceptor “double cable” polymers with good processability, we have prepared a series of polythiophene copolymers containing, in the backbone, alkylthiophene units and thiophene rings with anthraquinone acceptor moieties in the substituent chain (see fig. 1). The peculiar feature of these materials is that the content of acceptor can be easily tuned and even a 100 % anthraquinone substitution is leading to a soluble polymer. Moreover the flat geometry of the anthraquinone acceptor is helping a 3-D assembling which may favour the formation of a pathway for the transport of electrons through the photoactive layer¹⁰.

The photophysical study of the photoinduced charge transfer process is of fundamental interest for both material characterisation and device fabrication. In particular the formation of long-lived metastable charged states, arising from a fast electron transfer from the electron donating conjugated backbone to the acceptors, are a prerequisite for the photogeneration of free carriers in polymeric bulk heterojunction. In this paper the potential use of these copolymers as photoactive materials is investigated by FTIR photoinduced absorption and with Light Induced Electron Spin Resonance spectroscopies. Preliminary results on the photovoltaic response of these materials are also presented.

2. EXPERIMENTAL

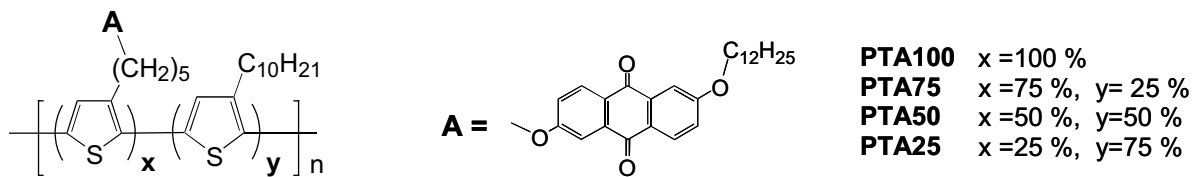


Fig. 1: chemical structure of donor-acceptor copolymer series containing anthraquinone (PTAs)

The copolymers, containing 3-decylthiophenes and anthraquinone-substituted thiophenes monomers, have been prepared by chemical oxidative coupling with FeCl_3 . We synthesized a polymer with all the thiophene rings substituted with anthraquinone and three copolymers containing 25, 50 and 75 % of units with the acceptor molecules (**PTA25**, **PTA50**, **PTA75**) (see fig. 1). The macromolecular characterisation indicates¹⁰ that the resulting random copolymers have the same composition of the monomer feed. Their photophysical behaviour has been compared to a polydecylthiophene (**PDT**) obtained with the same synthetic route and thus with the same degree of regioregularity. The fluorescence spectra have been measured with a flat field spectrograph coupled with a N_2 cooled detector, with a Xe lamp excitation, passing through a monochromator. The PA spectra have been measured with a FTIR spectrometer covering a spectral range from 0.05 to 1 eV. The fractional changes in transmission have been measured in response to an Argon laser line incident on the sample, by the subsequent accumulation of scans with laser on and laser off. The PA measurements in solution have been performed in chloroform at room temperature. To avoid oxygen quenching, the solutions have been prepared in N_2 atmosphere, with freshly distilled solvent and poured in anaerobic spectroscopical cuvettes. For the PA measurements in the solid state, solution drop cast films have been prepared on KBr windows and the film thickness of the different copolymers has been adjusted in order to obtain similar absorbance at the laser excitation wavelength (O.D of 1.7 at 514 nm). The temperature has been kept at 80 K. LESR has been measured with a Bruker EMX spectrometer (X band), with a 459 nm laser line excitation at a temperature of 20 K. A microwave power of 20 μW was used for all measurements. g-values were determined using a Bruker weak pitch samples to calibrate the spectrometer. The detailed measurement procedure is described elsewhere¹¹. Photovoltaic (PV) devices consist of a layered structure made with indium tin oxide/ PEDOT [poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)/ PTAs/ LiF/Al or Ca, following the procedure described elsewhere¹². The active layers (thickness of app. 50 nm) have been deposited by spin coating from chloroform solution. The PV devices has been prepared and characterized in a glove box, under Ar atmosphere. The current-voltage characteristics has been recorded with a Keithley SMU 2400 unit. The devices have been illuminated from the transparent ITO side with a 800 Wm^{-2} white light of a Steuernagel solar simulator, simulating AM 1.5 sun spectrum, with a mismatch factor of 0.95. The external quantum efficiency (defined as $\text{IPCE} [\%] = 1240 \times I_{\text{sc}} / (\lambda \times I_p)$, where $I_{\text{sc}} [\mu\text{A cm}^{-2}]$ is the short circuit current density measured at the wavelength λ [nm] and $I_p [\text{Wm}^{-2}]$ is the light intensity) is recorded with a lock-in detector after illumination with a tungsten lamp passing through a monochromator.

3. RESULTS AND DISCUSSION

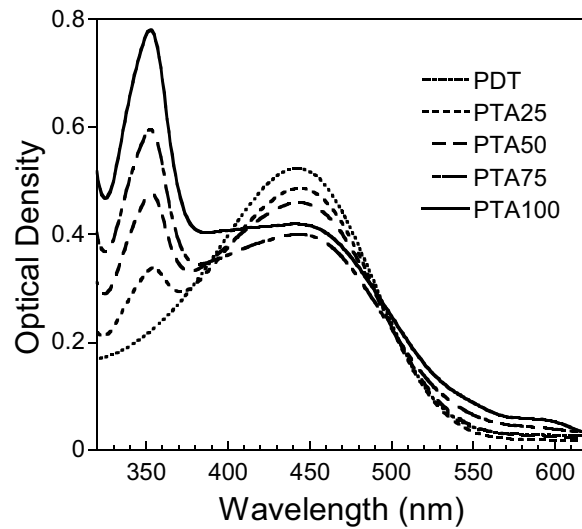


Fig.2: UV-Vis absorption spectra of PTAs copolymer series and of PDT in chloroform solution; $3.3 \cdot 10^{-4}$ M, 2 mm optical path.

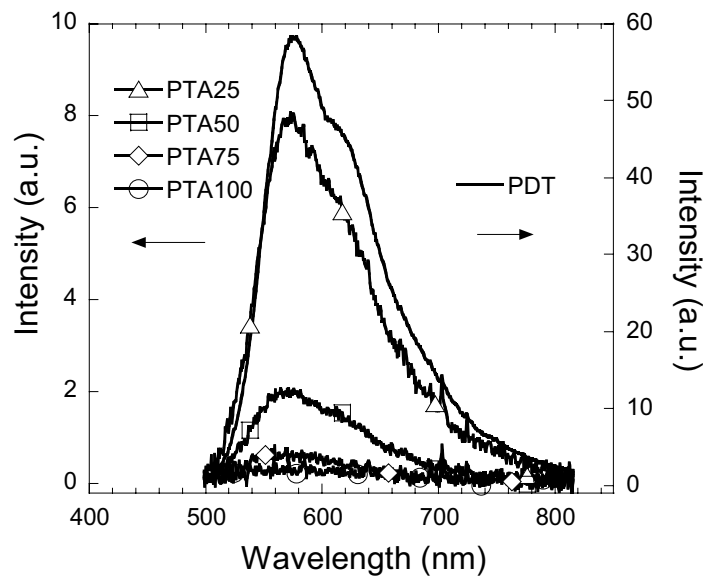


Fig. 3: photoluminescence spectra of the PTAs copolymer series and of PDT in chloroform solution; exc. wavelength: 450 nm.

The UV-Visible absorption of the PTA series in chloroform solution are reported and compared to those of a polydecylthiophene (PDT) in figure 2. The electronic absorption spectra display an absorption band in the visible region which is due to the $\pi-\pi^*$ transition of the polythiophene backbone, and a series of bands in the UV region, originating from the anthraquinone moieties¹³. The intensities of both polythiophene and anthraquinone bands depend from the donor/acceptor ratio. It can be seen that PTA100 and PTA75 show an absorption maximum at 450 nm, that is 10-20 nm

higher than the usual value of regiorandom polyalkylthiophene in good solvent, and for the copolymers **PTA50** and **PTA25** λ_{\max} is close to 440 nm. This feature can be due to a more planar conformation of the conjugated backbone in solution respect to random polyalkylthiophene or can be due to some aggregation.

The photoluminescence (PL) of **PTA** materials, obtained with an excitation wavelength of 450 nm in chloroform solution are reported in figure 3; the solutions have a dilution adjusted to have the same number of absorbed photons at 450 nm. The PL of the D/A polymers is quenched by 1-2 orders of magnitude with respect to **PDT** and the quenching increases with the acceptor content. This suggests that electron transfer from the photoexcited polythiophene backbone to anthraquinone is occurring and that the charge transfer is fast enough to compete with the radiative recombination of the excitons. It is interesting to note that, in this case, an energy transfer from the polymer to the acceptor cannot explain the PL quenching because the electronic transitions of the anthraquinone are at higher energies with respect to the $\pi-\pi^*$ transition of the conjugated backbone. This is a relevant difference respect to solutions of conjugated polymers and fullerene, where the energy transfer from the chain to the acceptor has been identified as an important step of the photoexcitation mechanism of these D/A systems¹⁴.

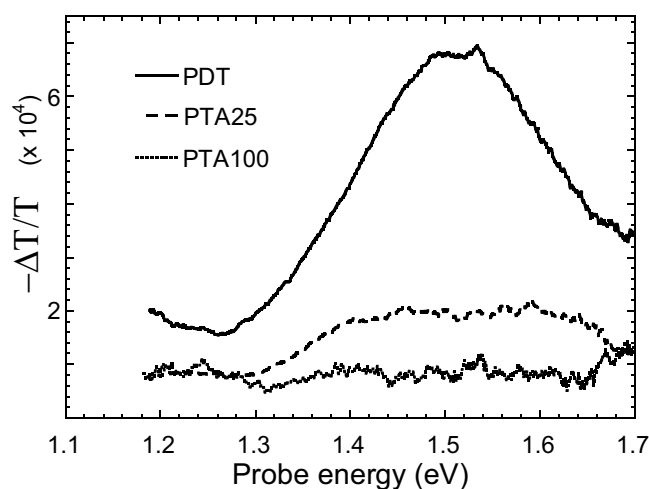


Fig. 4: FTIR PA spectra in chloroform solutions; 25 °C; exc. wavelength: 457 nm, 10 mW/cm².

The FTIR PA spectra obtained in chloroform solution are reported in fig. 4. The **PDT** spectrum is dominated by a broad peak at 1.5 eV which is ascribed to a triplet transition¹⁵. This band disappears completely when the solution is in contact with air because of strong oxygen quenching which is a typical feature for the triplet states. **PTA25** displays the same band of **PDT**, but quite reduced in intensity, while the triplet transition is not detectable anymore for higher contents of anthraquinone. Therefore, like for PL quenching, the quenching of the polythiophene triplet excitations by the presence of the anthraquinone moieties, is an indication of the electron transfer from the photoexcited polythiophene backbone to anthraquinone. The charge transfer can occur either from the singlet, prior to triplet formation, or from the triplet state. The steady state PA measurements here reported cannot help in discerning between these two possible mechanisms, fast spectroscopies may help in clarifying these features.

The UV-Vis absorption spectra of the copolymers films are reported in fig. 5. The copolymer composition is affecting the absorption features of the thiophene backbone. A red shift is observed upon increasing the anthraquinone content, suggesting that the acceptor substituents are inducing a better conjugation and/or a better three-dimensional organization of the chains. The spectrum of the homopolymer **PTA100** displays the spectrum mostly red shifted, with a λ_{\max} at 540 nm. This can be reasonably ascribed to a better order due to the homogeneity of the side chains. However, considering that the λ_{\max} of **PDT** films is at 510 nm and this homopolymer has the same degree of regioregularity of **PTA100**, the anthraquinone molecules may play a specific role in driving the chain organization. This is supported by the X-ray characterization¹⁰ which indicates that **PTA100** has a long distance periodicity consistent with the lamellar organization of polyalkylthiophenes¹⁶. **PTA100** films are completely amorphous and thus it is impossible to obtain a precise structural picture but it is quite probable that the lamellar organization leads to the formation of domains of

anthraquinone units of neighboring side chains, organized to some degree into columnar or layered structures. We suggest that the domains of anthraquinone substituents may induce some planarisation of the thiophene backbone with a subsequent red shift of the optical absorption spectrum.

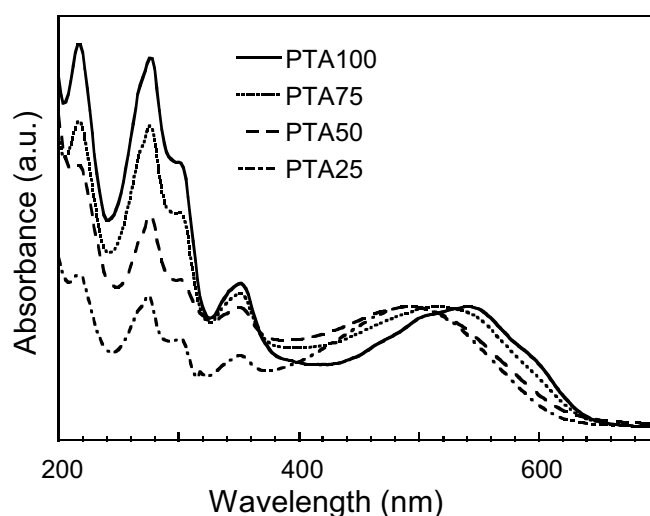


Fig. 5: UV-Vis absorption spectra of PTAs films

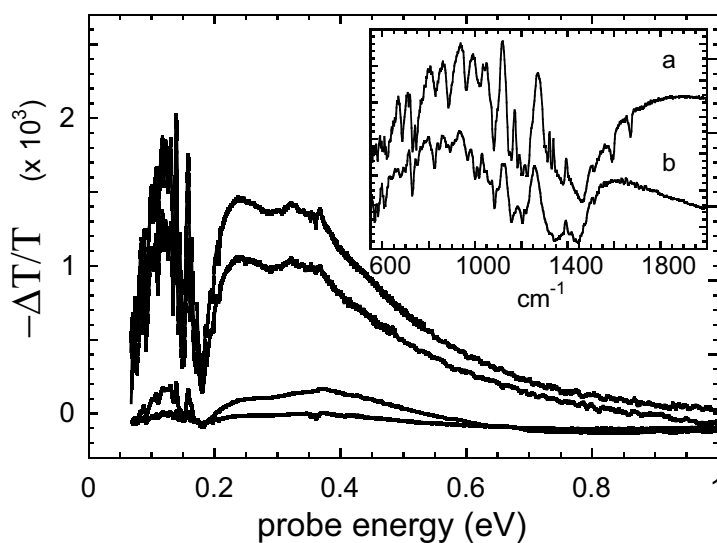


Fig. 6: FTIR PA spectra of PTAs. From the bottom to the top : PTA25, PTA50, PTA75 and PTA100. The inset: IRAVs bands of PTA100 (a) and of PDT (b). Temperature: 80 K; exc. wavelength: 514 nm, 1.75 mW/cm^2

The PA spectra of PTAs films are reported in fig. 6. The electronic broad band as well as part of the infrared active vibrations (IRAV) has the same spectral pattern of polyalkylthiophenes (see the inset), probing thus the formation of polaron charged excitations into the polythiophene backbone. The bleaching of two anthraquinone IR bands at 1589 and

1668 cm^{-1} are indicative for the formation of anthraquinone radical anions¹³. Therefore the PA spectra provide a spectroscopical indication that the electron transfer from the photoexcited polythiophene to the anthraquinone is occurring, forming long living metastable polaron cations into the polythiophene backbone and radical anions into the anthraquinone moieties. It is interesting to note that a high energy and a low energy contribution to the polaron electronic band coexists in the PA spectra. These features can be ascribed to different organizations of the polyalkylthiophenes. Previous assignments^{17,18} suggest that the high energy contribution is due to disordered chains while the low energy contribution probes a more ordered phase, with the chains in a lamellar structure. Therefore like the UV-Vis spectra, the PA spectra suggest that a high content of anthraquinone molecules is beneficial to the copolymer chain organization.

The PA signal is increasing with the anthraquinone content because of the increased number of metastable charged states arising from the photoinduced charge transfer process. Longer lifetimes may also account for this feature. By varying the laser on/off exposure time, we have found that the copolymer composition is indeed affecting the lifetimes of the photo-generated charged states. We have observed that the steady state condition is fulfilled for **PTA25** and **PTA50**: the variation of the shutter modulation frequency is not changing the PA signal. Considering our experimental conditions, this indicates that the recombination of the photogenerated charged states occurs within 1 sec. For **PTA75** and **PTA100** the PA signal is reduced by increasing the shutter frequency. Thus the lifetimes of the metastable charged states can be longer than 10 sec when more than 50% of the thiophenes are carrying an acceptor molecule. In analogy to polymer/fullerene bulk heterojunctions^{11,19}, very long-lived charges observed in double cables are suggesting that this effect is intrinsic to the photoexcitation mechanisms of the donor/acceptor composite systems.

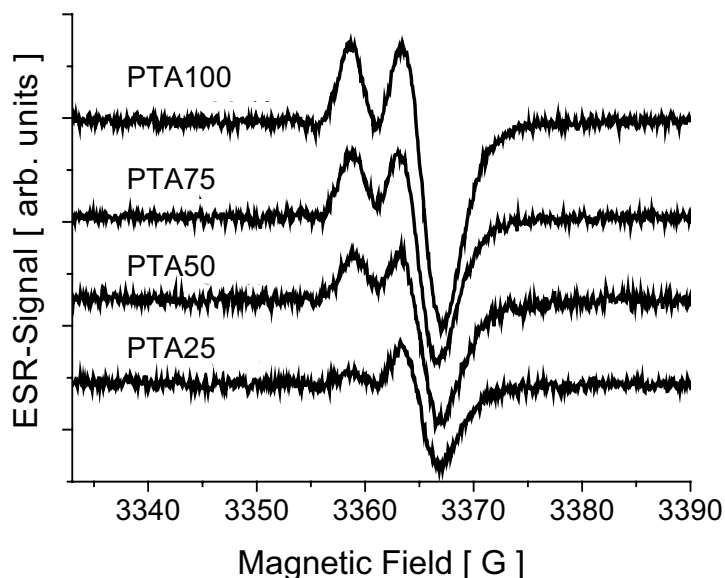


Fig. 7: LESR spectra of **PTAs**. Measurements were performed at 20 K, microwave power 20 μW . The shown spectra are corrected for the weak dark signal and shifted on the y-axis.

The LESR measurements of the copolymers are reported in fig. 7. The spectra display two overlapping lines at magnetic field of ~ 3361 G and ~ 3365 G corresponding respectively to $g=2.0042$ and $g=2.0024$. The high g -value signal is assigned to radical anions on the anthraquinone molecule²⁰ and the low g -value signal to positive polarons on the polythiophene chain²¹. Microwave saturation studies show different relaxation times for these spins, giving a clear evidence of independent photoinduced spins. The number of photogenerated spins is increasing with the content of anthraquinone acceptors in the copolymers.

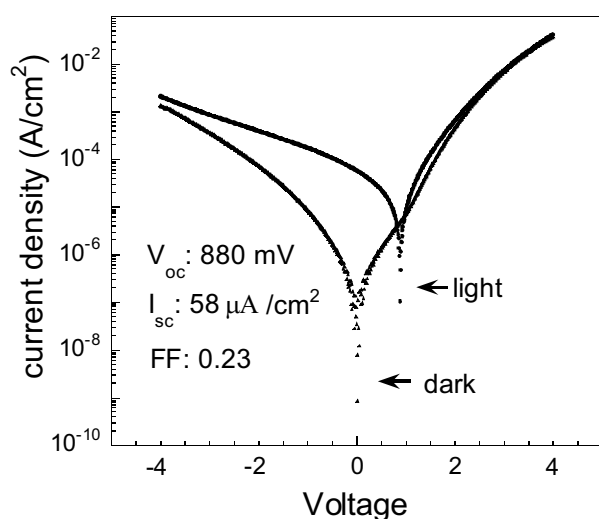


Fig.8: current-voltage characteristics of a PV device with **PTA75** as active layer and Ca electrode. Solar simulator at 80 mW/cm²

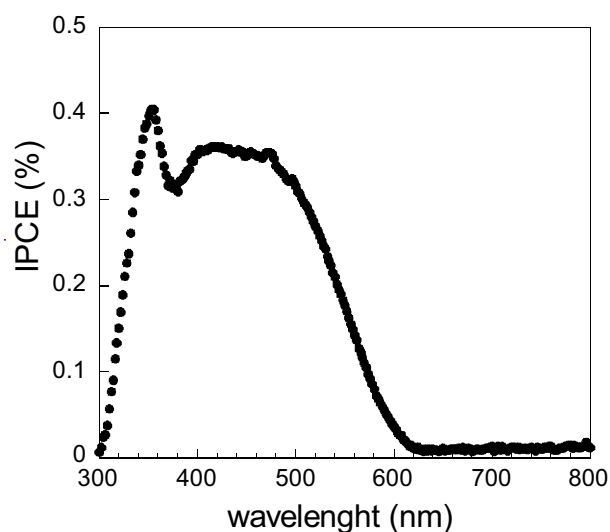


Fig. 9: external quantum efficiency of a PV device with **PTA75** as active layer, Ca electrode

The first diode characterizations have been carried on **PTA50** and **PTA75**, using Al as electrode. Even though these initial results showed an inverted rectification due to the bad selectivity of the interfaces, we have found some photovoltaic response and the short circuit current is increasing with the acceptor content. Work is now in progress to optimize the device geometry; the diode characteristic is slightly improved using a Ca electrode (see fig. 8) probably because the lower work function of Ca facilitates the electron injection from the anode. The photocurrent action spectrum, reported in fig. 9 follows the UV-Vis absorption spectrum shown in fig. 5. The band at 360 nm is a transition of the anthraquinone moiety, thus charge photogeneration is occurring either by the photoexcitation of the conjugated polythiophene backbone either by the photoexcitation of the anthraquinone substituent.

4. CONCLUSIONS

In this paper we have discussed the potential use as photoactive materials of a new series of polythiophene copolymers bearing anthraquinone substituents. The peculiar feature of these materials is that the content of acceptor can be easily tuned and even a 100 % anthraquinone substitution is leading to a soluble polymer. Moreover the flat geometry of the anthraquinone acceptor is helping a 3-D assembling which can be beneficial for the formation of a pathway for the transport of electrons through the photoactive layer. The photo-physical study here reported shows that in these conjugated polymers, the photoinduced electron transfer from the polythiophene backbone to the anthraquinone acceptor moieties is occurring and that this process is easily tuned by tailoring the content of acceptor substituents in the polymer. Preliminary photodiodes are fabricated and characterized indicating that these materials exhibit a photovoltaic response. These features make these copolymer series a good model system towards the donor/acceptor “double cable” polymer approach.

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