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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · APRIL 2014

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# EDOT-based Copolymers with Pendant Anthraquinone Units: Analysis of their Optoelectronic Properties within the “Double-Cable” Context.

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## Abstract

Here we present the synthesis, optical and structural characterization of a new series of alternating donor-acceptor copolymers based on 3,4-ethylenedioxythiophene (EDOT). The donor consists of phenylene, alkylated fluorene or diethynyl-1,4-phenylene as the aryl units copolymerized with the EDOT group with and without a 9,10-anthraquinone (AQ) side chain as the acceptor group. The changes in the electronic absorption/emission spectra and redox properties are analysed in detail as a function of (i) the composition of the copolymers and (ii) the inclusion of the pendant 9,10-anthraquinone. Density functional theory calculations are used to interpret the experimental results. Special emphasis is put into the flexibility of the phenylene-based copolymer spine which together  $\pi$ - $\pi$  stacking confers interesting solvathocromic and thermochromic properties when external conditions are varied. This is explained by means of an order-disorder conformational transformation in solution upon ultrasonication, temperature changes and nature of solvents. A comparison of the transient triplet-triplet absorption spectra of **PEB** and **PEB-AQ** show that the intramolecular triplet states of the copolymer backbone become inactive upon insertion of the AQ unit as a result of the tendency towards aggregation. These studies highlight the relevance of the precise control of the polymer architecture to achieve a suitable tunability of the optical and electronic properties of highly processable polymers with potential applications in organic electronics.

## 1. Introduction.

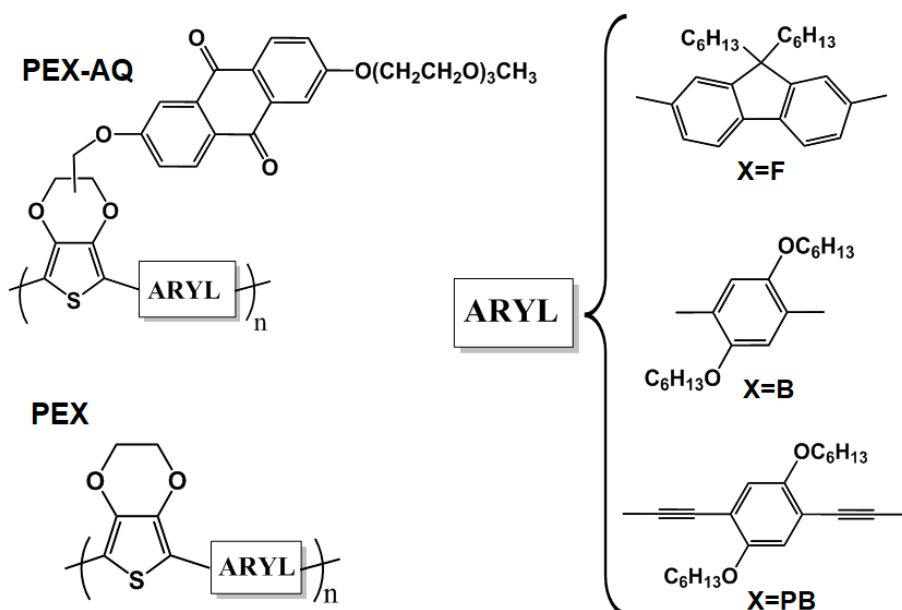
Conjugated polymers have attracted great interest in the recent years as they offer an innovative and versatile route towards the development of cost-effective, lightweight and flexible substrates for organic photovoltaic (OPV) solar cells<sup>1,2,3,4,5,6,7,8</sup>. For photovoltaic applications, the main improvement of the conversion efficiency was obtained with the preparation of bulk heterojunction architectures, where the photoactive layer consists of an interpenetrating network (blend) of a  $\pi$ -conjugated polymer (electron donor) and a soluble fullerene derivative (electron-acceptor)<sup>7,9,10,11,12,13,14</sup>. However, one of the main problems of this cell is the control of the phase separation between the conjugated polymer and the fullerene derivatives<sup>15,16,17,18</sup>. Generally, the electron donor and electron acceptor species are of different chemically nature and tend to undergo uncontrolled microphase segregation, which negatively influences the photoinduced electron transfer and the charge transport in the blend<sup>19,20</sup>. A large number of studies have been conducted to achieve optimal donor/acceptor blend morphology for device operations; for instance, by changing the thin film processing conditions, including solvent and annealing treatments<sup>12</sup>.

One approach to attain an intimate microphase mixing of the donor-acceptor components and to control the film morphology is given by the concept of the covalent union of the donor and acceptor subunits in *double-cable* polymeric architectures<sup>21,22</sup>. These materials are composed of electron-accepting moieties covalently linked to a hole-transporting conjugated polymer backbone and therefore exhibiting two different pathways (“cables”) for different signs of charges. Among the advantages over the bulk heterojunction cells, the chemical tuning by ad hoc synthesis of the donor-acceptor interface is to be highlighted, a factor known to improve exciton and charge transport which contrasts with the somehow random control by phase mixing. This is significant since processing conditions are simplified given the creation in a one step of the active layer without relying upon post-processing techniques<sup>23,24,25</sup>. Most studies have so far targeted conjugated polymer donors that are functionalised with pendant acceptors such as fullerene units<sup>26</sup>, perylenediimides<sup>27</sup>, phthalocyanines<sup>28</sup>, tetracyanoquinodimethane<sup>29</sup> or 9,10-anthraquinone derivatives<sup>22</sup>.

A good matching between the electron donor-ability and optical band gap of the polymer backbone with the electron acceptor character of the pendant acceptor groups is

essential for the realization of compatible ‘double cable’ polymers. Therefore, tailoring of the electronic properties by systematic variation of the nature of the polymer backbone acquires special relevance in this context. Recently, poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have received a great deal of attention because of their relatively low ionization potential, chemical stability, low band gap and good film forming ability<sup>30,31</sup>. Nevertheless, the PEDOT is rather insoluble in common solvents. In order to increase the solubility and also decrease the band gap, donor-acceptor conjugated polymers based on 3,4-ethylenedioxythiophene (EDOT) have been recently reported<sup>32,33,34,35,36,37,38,39</sup>.

With the aim to prepare processable photoactive materials with tunable electronic properties within the double-cable context, we have prepared three EDOT-based **PEX-AQ** copolymers containing, in the backbone, phenylene, alkylated fluorene or diethynyl-1,4-phenylene units with the EDOT group bearing a 9,10-anthraquinone (AQ) as a pendant acceptor group (see Chart 1). Their structural, optical and electronic properties are investigated by using electrochemistry, electronic absorption/emission, transient triplet-triplet absorption and DFT calculations. To gain a better understanding of the effect of the pendant AQ side chain, the results for **PEX-AQ** are compared to those for their reference **PEX** copolymers (see Chart 1). The phenylene-based **PEB** and **PEB-AQ** polymers exhibit interesting solvathochromic and thermochromic properties; a behavior explained by the promotion of an order-disorder conformational transformation in solution as a function of the solvent, temperature changes and ultrasonication.



**Chart 1.** Chemical structures of the three EDOT-based reference **PEX** copolymers and the three **PEX-AQ** copolymers with the EDOT unit bearing a pendant 9,10-anthraquinone (AQ) moiety.

## 2. Methodology: Experimental and Theoretical Details

### 2.1 Experimental techniques

#### Synthesis.

NMR spectra were recorded on a Bruker Avance 300 or AMX 400 spectrometer at 25 °C, and the chemical shifts are reported in parts per million using the solvent as reference. The splitting patterns are designated as follows: s= singlet, br s = broad singlet, d= doublet, t= triplet, m= multiplet, dd= doublet of doublets, and the assignments are *Ant* (anthraquinone) and *Th* (thiophene). Mass spectra were recorded with a Varian Saturn 2000 and with a MALDI-TOF MS Bruker Reflex 2. GPC measurements were carried out at 145 °C in a Waters GPCV2000 (D04180221P) apparatus using 1,2,4-trichlorobenzene as the solvent with a flux of 1ml/min and using polystyrene as standard. Melting points were measured with an electrothermal melting points apparatus and are uncorrected. FTIR spectra were recorded as KBr pellets in a Shimadzu FTIR 8300 spectrometer. Elemental analyses were performed on a Perkin-Elmer EA 2400.

2-(2-(2-Methoxyethoxy)ethoxy)ethyl *p*-Toluenesulfonate<sup>40</sup> (**2**) and 2-Chloromethyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine<sup>41</sup> (**5**) 1,4-diethynyl-2,5-dihexyloxybenzene<sup>42</sup> (**8**), 2,5-

dihexyloxy-1,4-phenyldiboronic acid<sup>43</sup> (**10**) and 2,5-dibromoethylenedioxythiophene<sup>44</sup> (**11**) were prepared according to the literature. All other chemicals were purchased from Aldrich and used as received without further purification.

The details of general procedure for the synthesis of **PEX** and **PEX-AQ** copolymers are given in the Supporting Information.

**Spectroscopic measurements.** UV/Vis absorption spectra were recorded in N,N-dimethylformamide, dichloromethane and 2-methyl tetrahydrofuran solutions by using an Agilent 8453 instrument equipped with a diode-array detection system. Emission spectra were recorded in N,N-dimethylformamide and 2-methyl tetrahydrofuran using a spectrofluorometer from Edinburgh Analytical (FLS920P) equipped with a Xenon lamp. No fluorescent contaminants were detected upon excitation in the wavelength region of experimental interest. For the measurements of the microsecond time resolved transient absorption spectra (triplet-triplet absorption spectra) in the visible region, a laser flash photolysis system Luzchem LFP-111 was used, with Xe ceramic lamps of 300 W UV-Vis, a 125 mm monochromator, Tektronix TDS 2001C oscilloscope with a bandwidth of 50 MHz and a compact photomultiplier. Samples were excited with the third harmonic frequency (355 nm) of a Nd:YAG laser (Lotis TII LS-2132 UTF) controlled by a pulse generator Quantum Composers 9520 with tunable frequencies.

**Electrochemical measurements.** Cyclic voltammetry experiments were performed with a computer controlled Autolab PGSTAT 302 potentiostat in a three electrode single-compartment cell (5 ml). The platinum working electrode consisted of a platinum wire with a surface of  $A = 0.785 \text{ mm}^2$ , which was polished down to 0.5  $\mu\text{m}$  with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgCl electrode. The measurements were carried out in freshly deaerated dichloromethane (HPLC, Aldrich) and 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka) which was twice recrystallized from ethanol and dried under vacuum prior to use.

## 2.2 Computational Methods

Theoretical results presented here were calculated at the Density functional theory (DFT) level, using the B3LYP hybrid exchange functional<sup>45,46</sup>. All polymer (via

Periodic Boundary Conditions, PBC) and oligomer calculations were performed with Gaussian09 package<sup>47</sup>, and the 6-31G\*\* basis set<sup>48,49,50</sup> was chosen. It has been showed that band gaps predicted for conducting polymers using the hybrid B3LYP functional coupled with PBC are in excellent agreement with experimental values<sup>51,52,53</sup>. In all cases, long alkyl and alkyloxy chains were substituted with methyl and methoxy groups in order to minimize computational cost.

Calculations of the electronic band structures and densities of states were carried out using CRYSTAL09 package<sup>54</sup> (see theoretical section in the Supporting information for more details).

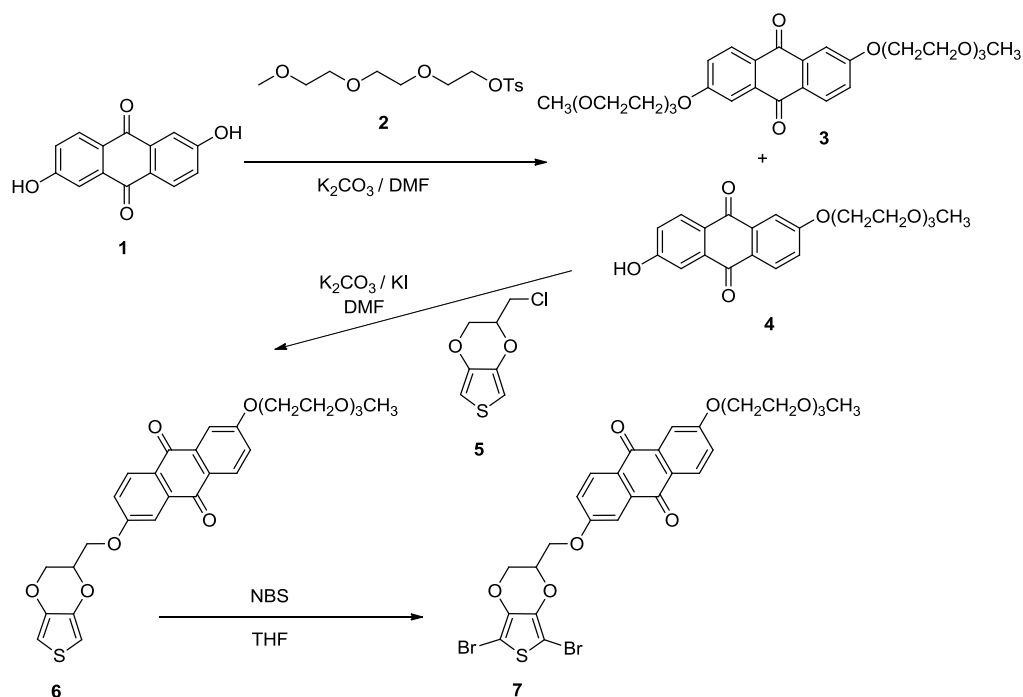
### **3. Results ad Discussion**

#### **3.1 Synthesis of the Polymers.**

##### **a) Synthesis of EDOT-based comonomer**

In order to synthesize the desired EDOT-based copolymers endowed with electron acceptor moieties it has been necessary the synthesis of a new EDOT comonomer which has been designed to bear suitable functionalities to allow, on the one hand, its covalent linkage with a suitable electron acceptor (anthraquinone) unit and, on the other hand, to be used in subsequent polymerization reactions.

Among the differently functionalized EDOT derivatives,<sup>55</sup> chloromethyl-EDOT (**5**, Scheme 1) has revealed in our hands as a versatile building block that has allowed for the synthesis of a variety of EDOT derivatives by reaction with moieties bearing complementary functional groups (as for example phenolic groups).<sup>56-...,61</sup> With this aim, we have synthesized a 9,10-anthraquinone (AQ) derivative endowed with a phenolic functionality (**4**) thus allowing its covalent linkage to chloromethyl-EDOT through a Williamson's etherification reaction as shown in Scheme 1.



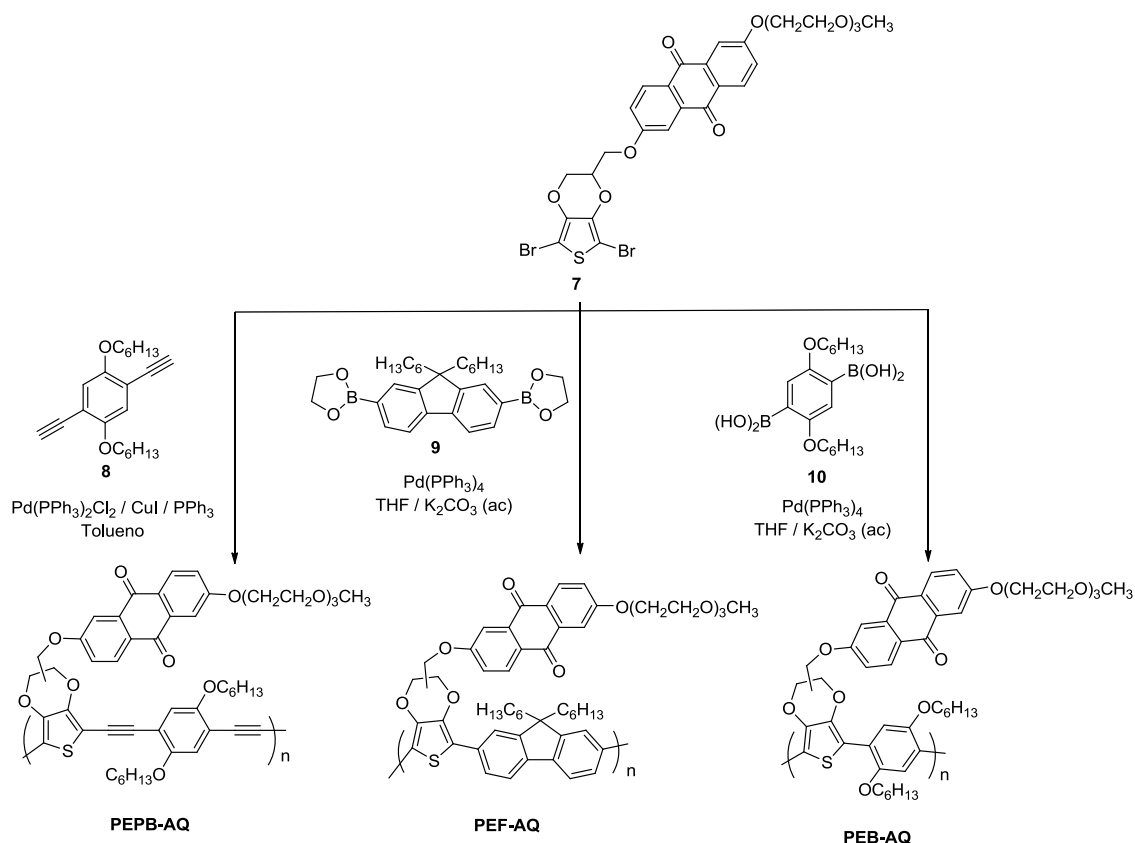
**Scheme 1**

The anthraquinone functionalized derivative was synthesized through transesterification reaction of the anthraflavic acid with the activated ethylene glycol derivative **2** under stoichiometric control conditions. Column chromatography was used to separate the target compound **4** (54 % yield) from the disubstituted derivative **3** (18 % yield) which is also formed in the reaction. Williamson's etherification reaction between functionalized anthraquinone **4** and chloromethyl-EDOT **5** affords the EDOT-anthraquinone derivative **6** which was further brominated at the  $\alpha$ -positions of the thiophene moiety by treatment with NBS to afford the suitably functionalized EDOT comonomer **7** (Scheme 1).

#### **b) Synthesis of donor-acceptor EDOT-based copolymers by Pd-catalyzed cross-coupling reactions**

The synthesis of the novel donor-acceptor EDOT-based copolymers (**PEPB-AQ**, **PEF-AQ** and **PEB-AQ**) endowed with anthraquinone functionalities has been carried out by means of Sonogashira and Suzuki cross coupling reactions as depicted in Scheme 2.





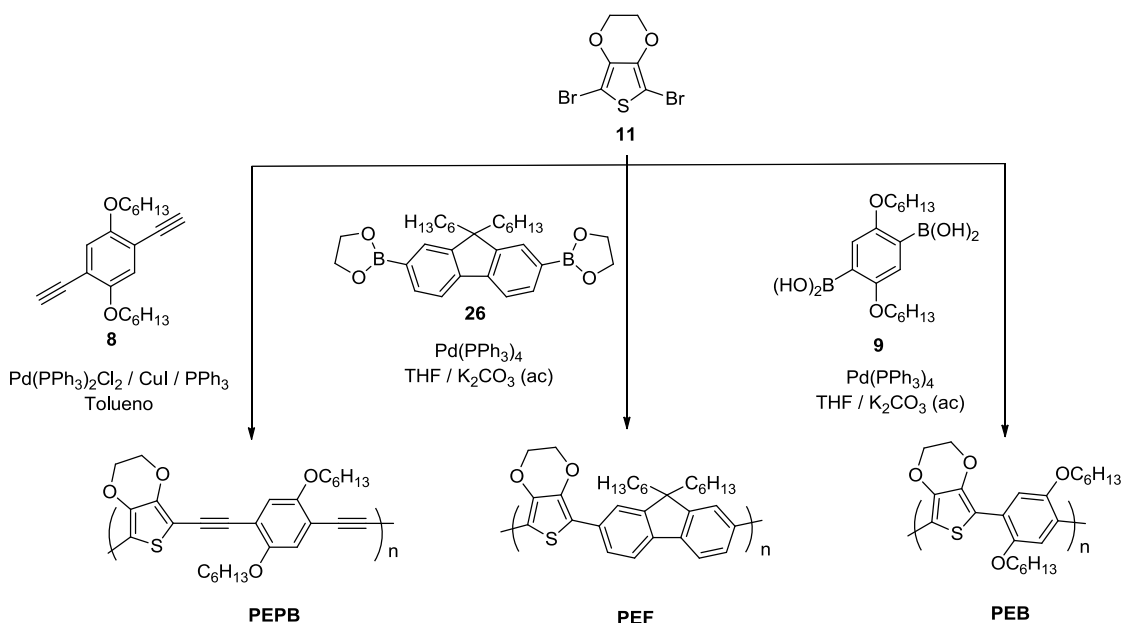
**PEPB-AQ** was synthesized through Sonogashira polycondensation reaction between the EDOT comonomer (**7**) and 1,4-diethynyl-2,5-dihexyloxybenzene (**8**) in the presence of  $\text{Pd(PPh}_3)_2\text{Cl}_2$ , copper iodide and triphenylphosphine, using toluene as the solvent (Scheme 2).

On the other hand, polymers **PEF-AQ** and **PEB-AQ** were synthesized through Suzuki cross-coupling reactions. Thus, they were obtained by reaction of equimolecular mixtures of EDOT comonomer **7** with 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborolane) (**9**) and 2,5-dihexyloxy-1,4-phenyldiboronic acid (**10**) respectively in the presence of  $\text{Pd(PPh}_3)_4$  as the catalyst (Scheme 2).

After the conclusion of the reaction, the resulting copolymers were precipitated from the crude reaction by addition of methanol and then purified by dissolving them in dichloromethane and filtering the solutions through a Teflon micro filter to remove the rests of catalyst. The polymers were subsequently precipitated by addition of methanol and thoroughly washed with methanol and diethyl ether to remove the ionic residues and the rest of unreacted reagents.

Thus, **PEPB-AQ**, **PEF-AQ** and **PEB-AQ** were obtained respectively with 79 %, 87% and 80 % yields and molecular weights of 7590 (PDI=1.46), 6418 (PDI=1.95) and 5183 (1.29) as determined by GPC measurements. All the polymers are thermally stable with decomposition temperatures above 350 °C as revealed by TGA measurements.

On the other hand, analogous polymers without anthraquinone moieties (**PEPB**, **PEF** and **PEB**) to be used as reference materials were obtained by reactions between 1,4-dihexyloxy-2,5-diiodobenzene (**11**) and suitable comonomers **8**, **9** and **10** as depicted in Scheme 3.

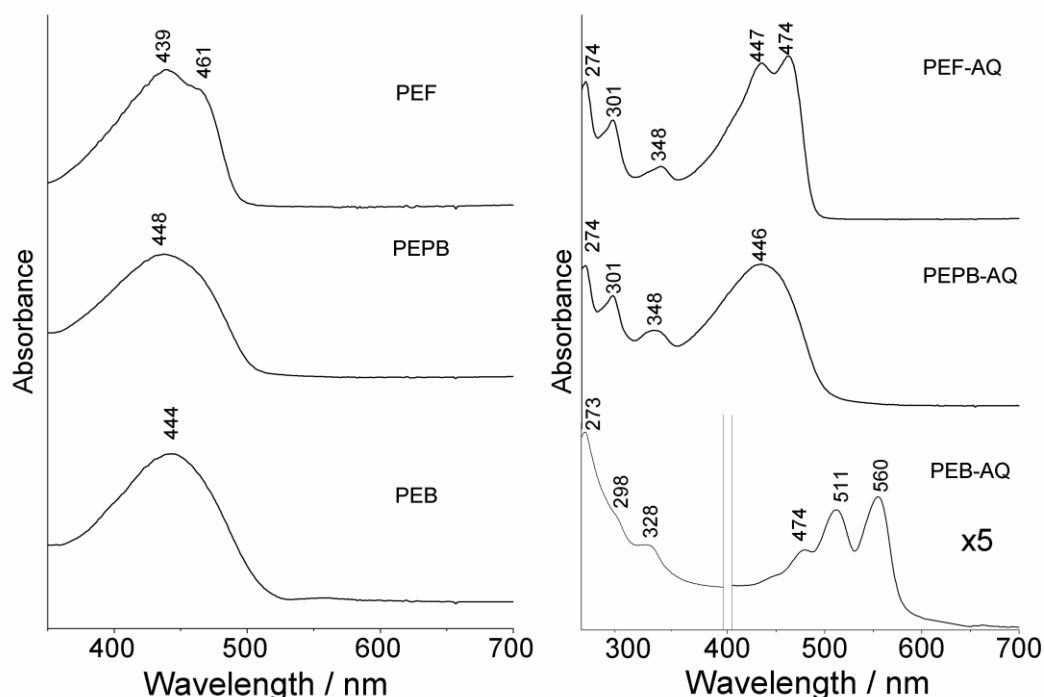


**Scheme 3**

### 3.2 Electronic Absorption Properties.

**a) PEX-AQ vs. PEX copolymers.** Figure 1 shows the UV/Vis absorption spectra of the donor-acceptor **PEX-AQ** copolymers and those of reference **PEX** copolymers in N,N-dimethylformamide solution at room temperature. The spectra of the reference **PEX** compounds display intense absorption bands at ca. 450 nm that corresponds to  $\pi$ - $\pi^*$  transitions of the conjugated polymer backbone. On the other hand, the insertion of the anthraquinone group in **PEF-AQ** and **PEPB-AQ** copolymers basically consists in the superposition of the absorption spectra of the two individual electroactive groups

suggesting a negligible ground-state intramolecular communication between the two chromophores, the copolymer and the AQ unit.

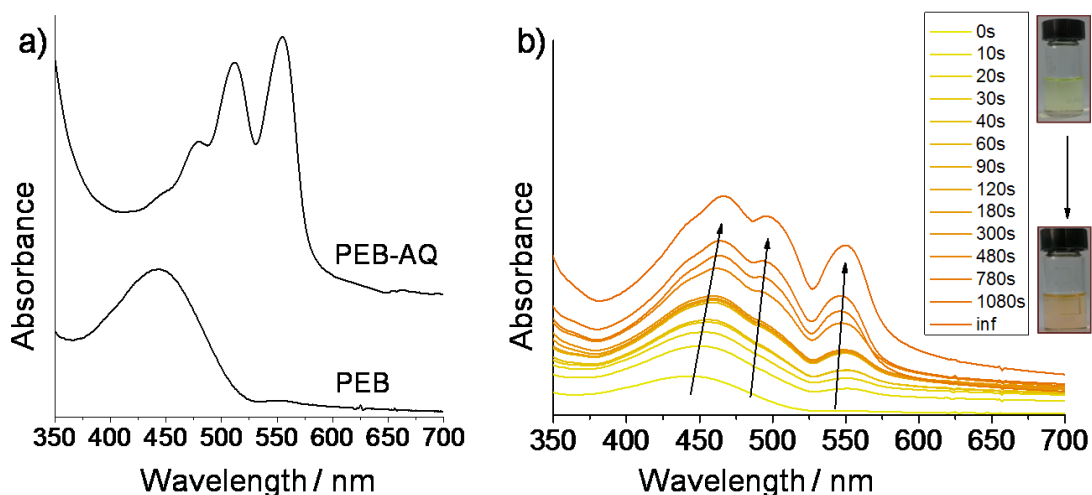


**Figure 1.** Absorption spectra of **PEX** (left) and their anthraquinone substituted **PEX-AQ** homologues (right) in N,N-dimethylformamide at room temperature.

In contrast, a different spectral pattern is observed for the phenylene-based **PEB-AQ** copolymer, with the appearance of: (i) a vibronically structured band with maxima at 474, 511 and 560 nm which often results in conjugated polymers from the stiffening of the polymer backbone, in this case promoted by the insertion of the AQ unit. Given the length of the alkyl spacer, the electronic interaction might probably acts through a cofacial interaction of an AQ unit of one chain with the copolymer backbone of an adjacent chain allowing to a rigidified sandwich-type  $\pi$ -structure. It is also interesting to note that the presence of planar AQ units are known to stabilize the  $\pi$ - $\pi$  stacking interactions resulting in more favourable supramolecular interactions<sup>63-68</sup>. A collateral effect of this interaction is the shifting of the three absorption features associated to the AQ unit (*i.e.*, observed at 273, 298, 328 nm in **PEB-AQ** and 274, 301, 348 nm in isolated anthraquinone **3**, see Figure S1). These results are in consonance with the flexible molecular structure of the phenylene-EDOT-based backbones (see discussion

below). A similar spectral pattern evolution along the series of copolymers is also found when using 2-methyl tetrahydrofuran as a solvent (see Figure S2).

**b) Promotion of Order-Disorder Transformation in the phenylene-based PEB and PEB-AQ copolymers by ultrasonic treatment, temperature changes and solvent effects.** Aimed with the above findings on the phenylene-based polymers, we now focus on the investigation of the thermochromic and solvathochromic properties of **PEB** and **PEB-AQ**. To help the dissolution of **PEB-AQ**, ultrasonic treatment was applied (Figure 2a). Interestingly, we realized that the application of the same ultrasonic protocol to an anthraquinone free **PEB** solution (Figure 2b) the spectrum results in a red-shift of the low-lying absorption together with the emergence of new sub-bands of vibronic nature (as in the case of **PEB-AQ**). These spectral changes are easily followed by the eye with color changes from yellow (before) to orange (after). This suggests that the energy provided by the ultrasonic excitation accelerates the co-facial coupling between the conjugated backbones and, such as in the case of the covalent union with AQ, the intermolecular coupling rigidifies the cores resulting in a stacked  $\pi$ -structure promoting the vibronic structure of the  $\pi$ - $\pi^*$  electronic absorption. Note that recent works have shown that ultrasonic irradiation favours the formation of ordered assemblies in conjugated polymeric materials<sup>69-71</sup>.

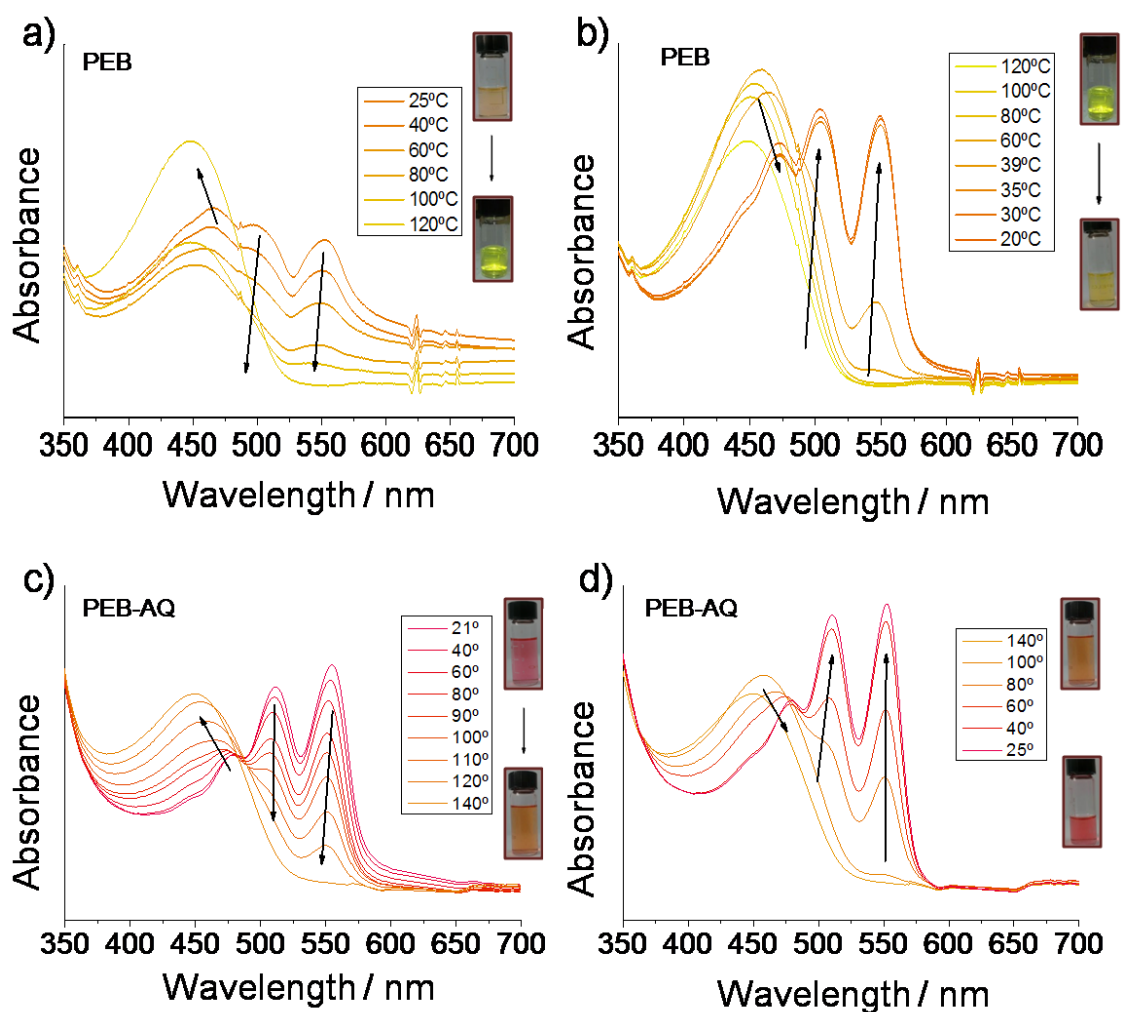


**Figure 2.** Absorption spectra of **PEB** and **PEB-AQ** in N,N-dimethylformamide (a) and evolution of the absorption spectra of **PEB** as a function of time upon ultrasound treatment (b).

In line with the previous findings, **PEB** also exhibits interesting thermochromic behaviour in solution, a phenomenon exhibited by many  $\pi$ -conjugated polymers, and that it is also intimately related with the aggregation ( $\pi$ -stacking) phenomena<sup>72-74</sup>. As

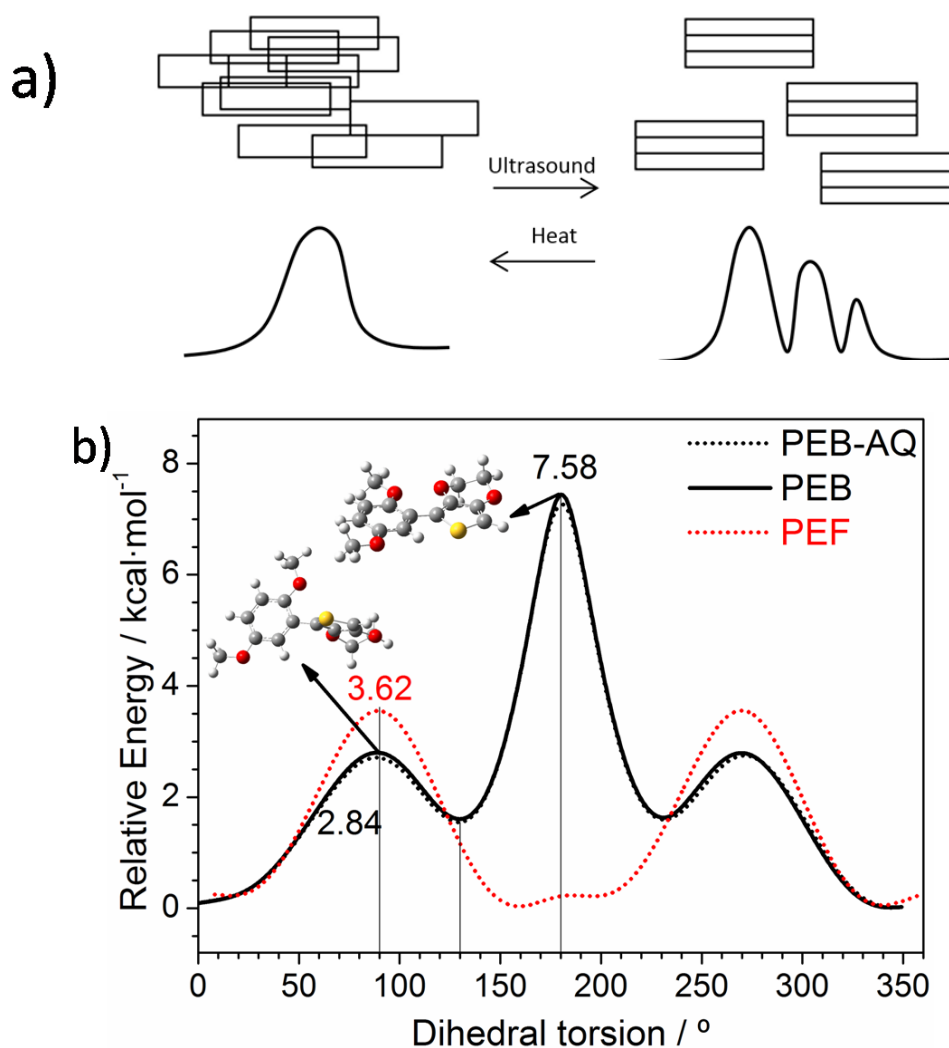
seen in Figure 3, once the ultrasound treatment is applied the spectral effect can be thermally reversed. Thus, heating the ultrasonicated **PEB** solution results in a blue-shift of the absorption accompanied by the lack of the vibronic structure with a total recovery of the broad band at 444 nm at the highest temperature 120 °C (*i.e.*, the solution becomes yellow, see Figure 3a). On the other hand, cooling the sample back to room temperature causes the regeneration of the structured band at longer wavelengths (*i.e.*, solution recovers the orange color, see Figure 3b).

The degree of aggregation of **PEB** is also examined in a much less polar media such as dichloromethane. This is a good organic solvent for these copolymers and will favor the molecularly dissolved sample and preventing them from aggregation. In dichloromethane, we observe that the strongest broad absorption characterizing the yellow solutions of **PEB** is unaltered upon ultrasonic treatment (see Figure S3) in accordance with the aggregation origin of the vibronically resolved band in N,N-dimethylformamide.



**Figure 3.** Temperature dependence of the absorption spectra of **PEB** (a,b) and **PEB-AQ** (c,d) in N,N-dimethylformamide upon heating (a,c) and cooling down (b,d).

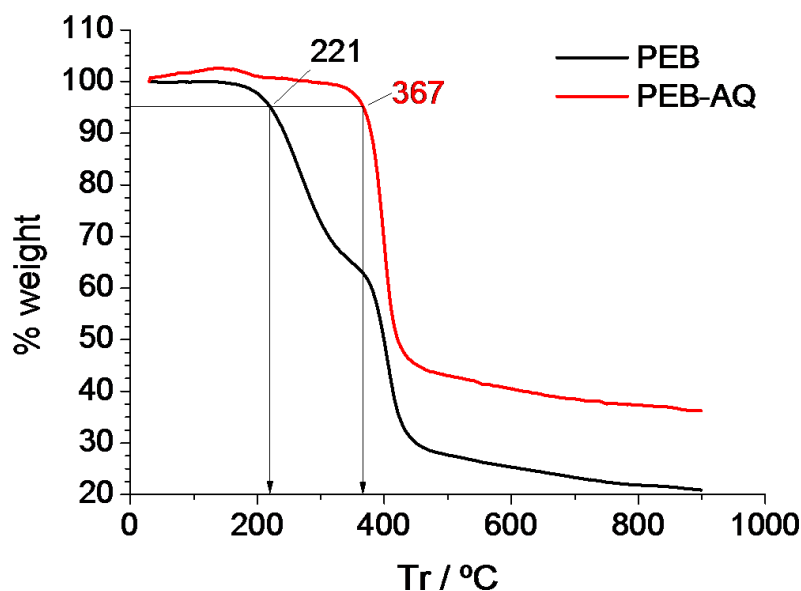
As in the case of **PEB**, the aggregated **PEB-AQ** solution also shows thermally reversible color cycle. By heating the ultrasonicated solution, the vibronic structure of the absorption band progressively disappears and its maximum blue-shifts again, see Figure 3c. After cooling to room temperature, the vibronic structured band is recovered, see figure 3d. Again the whole process is easily followed by the eye, upon heating, the color of the solution changes from intense pink to orange, while cooling makes the sample to recover its original pink color.



**Figure 4.** Schematic picture of the reversible transition between disordered and ordered polymer chains upon temperature changes and ultrasonication (a). DFT rotational barrier for **PEB**, **PEF** and **PEB-AQ** as a function of the inter-ring dihedral angle between the EDOT and the phenylene unit. The structure of the less accessible conformers are also shown (b).

Figure 4a shows a scheme where an order-disorder (*i.e.*, stacked-unstacked) transformation is proposed to exist in order to account for the thermochromic behavior. Although we propose a co-facial interaction between the copolymer spine and the AQ unit and/or between two copolymer chains as the source of the spectral changes, this can be only induced owing to the flexibility of the copolymer segment which gets further rigidified with the interaction. In consequence, we have examined the DFT rotational energy profile of **PEB** monomer along the inter-ring dihedral angle coordinate between the EDOT and phenylene unit (see Figure 4b). It is shown that for the fluorene-based **PEF** copolymers the energy barriers for the full rotation are significantly smaller than for the **PEB** and **PEB-AQ** copolymers, thus these latter can be viewed as much more

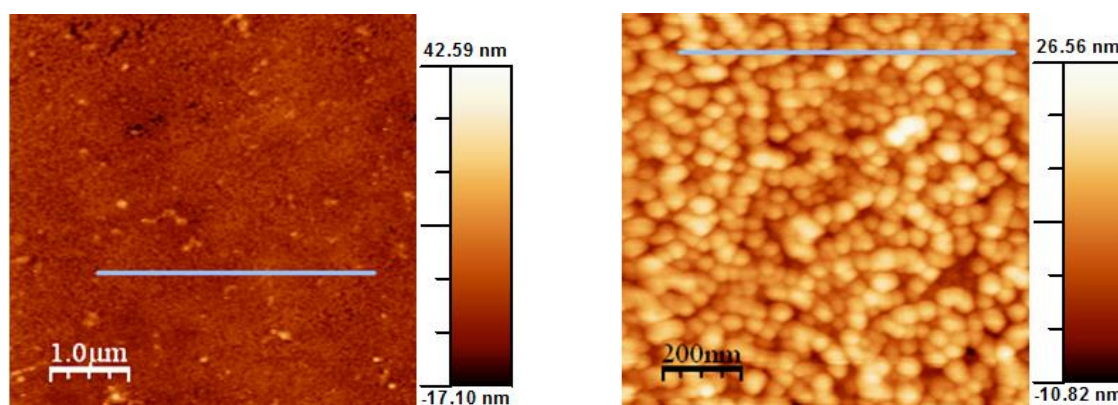
rigid. This might suggest that **PEF** needs stronger intermolecular forces to rigidify the  $\pi$ -electron structure while in phenylene-based derivatives with smaller stimuli we might get stiffened structures. This reveals that in all copolymers studied we might have the same intermolecular copolymer/AQ couplings but only in the **PEB/PEB-AQ** pair their intrinsic smaller flexibility and the intermolecular donor-acceptor interaction with the AQ acting together are sufficient to promote the spectral changes observed. Although further details about the conformational description are beyond the objective of this paper we notice that the intrinsic rigidity of the **PEB** copolymer might be due to a larger steric crowding absent in the other polymers. In line with the intermolecular effect and the more effective formation of sandwiched forms in the **PEB-AQ** copolymer, we compared in Figure 5 the TGA plots for **PEB** and **PEB-AQ** observing a much higher decomposition temperature for the latter.



**Figure 5.** TGA plots of the **PEB** and **PEB-AQ** polymers with a heating rate of 10 °C/min in the air.



Thanks to the presence in equilibrium of the absorption bands of the molecularly dissolved copolymer and of the aggregated sandwiched form we can derive the equilibrium constant at a given temperature. From the temperature dependence of the equilibrium constant using, a van't Hoff plot, the standard enthalpies ( $\Delta H^\circ$ ) for the stacking process were obtained.  $\Delta H^\circ$  for **PEB** and **PEB-AQ** are 5-10 kcal/mol which are of the same order of magnitude than those energy barriers in Figure 4. Given the similar values of the  $\pi$ - $\pi$  interaction energy and conformational effect, it is reasonable to assume that together could impart a significant rigidification of the conjugated core such as deduced in the vibronically resolved absorption spectra. This subtle balance between the conformational effect and the stacking forces can justify the existence of a spherulite or grain structure for the film substrate obtained by dip-coating of **PEB-AQ** such as observed in the AFM images shown in Figure 6 (see Supporting Information for more details). In this case a more flexible backbone structure (molecularly dissolved copolymer in dichloromethane) would promote more spherical microphases.



**Figure 6:** AFM height images of **PEB-AQ** dip-coated at 800  $\mu\text{m/s}$  on dichloromethane solutions (0.025 mg/mL) solutions on Si/SiO<sub>2</sub> wafer and kept for 5 min. in the polymer solution. a) Left: 5  $\mu\text{m}$  x 5  $\mu\text{m}$  image; b) right: 1  $\mu\text{m}$  x 1  $\mu\text{m}$  image.

### 3.3 Electrochemical characterization.

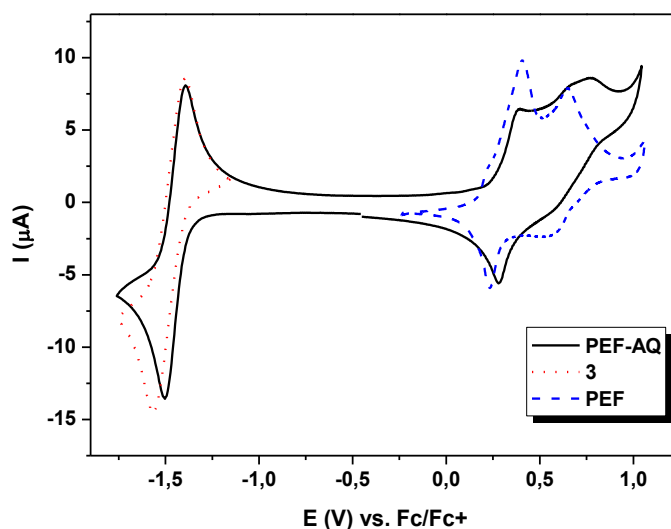
**a) Cyclic voltammetry.** The electrochemical behaviour of the **PEX** and **PEX-AQ** copolymers was investigated by cyclic voltammetry (CV). The corresponding data are summarized in Table 1. The **PEX** copolymers show one electron quasi-reversible oxidation between 0.39 and 0.69 V associated with the oxidation of the EDOT unit somehow slightly coupled with the vicinal conjugated unit: **PEB** (0.39 V) and **PEF**

(0.41 V) because of their similar aromatic nature. In the case of **PEPB** this is displaced to more anodic values, 0.66 V, due to the electron-withdrawing effect of the acetylene bridge over the EDOT group. Upon insertion of pendant AQ groups, the **PEX-AQ** polymers exhibit amphoteric behaviour. As illustrated in Figure 7 for the molecularly dissolved **PEF-AQ** at room temperature, it is observed a distinct one-electron reversible reduction wave corresponding to AQ unit (in the independent 2,6-dialkoxy-9,10-anthraquinone -compound **3** in Scheme 1- this cathodic wave appears at ca -1.45 V) displaced by 0.04 V at more negative potentials highlighting that the AQ unit act independently of the copolymer in the molecularly dissolved case. As a result, little variation is found for the oxidation potential of **PEF-AQ** with respect to that of **PEF**, 0.39 to 0.41 V. A similar behaviour is also found for **PEPB-AQ** that exhibits almost identical oxidation and reduction potentials to that of **PEPB** and **3**, respectively (see Table 1). However, the **PEB-AQ** copolymer deviates again from this trend and its redox potentials are more affected related to that of **PEB** and **3** (see Table 1 and Figure S4); this suggests the existence of ground-state intermolecular interactions between the two **PEB** and **AQ** moieties in the electrochemical medium used.

**Table 1.** Electrochemical Properties of **PEX** and **PEX-AQ** copolymers and the isolated anthraquinone unit, **3**.

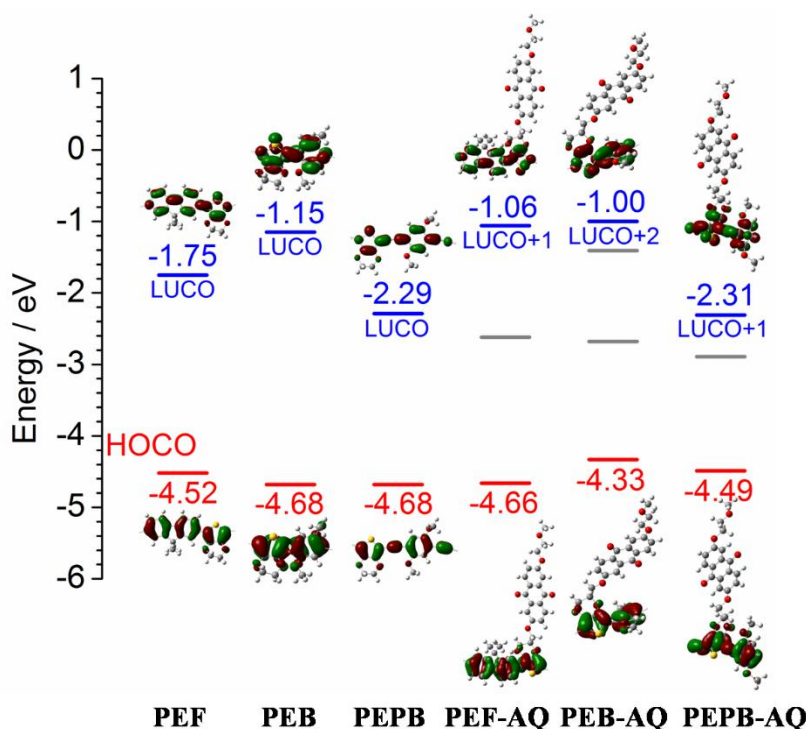
compound	Cyclic voltammetry <sup>a</sup>		
	E <sub>ox,o</sub> (V)	E <sub>red,o</sub> (V)	E <sub>ox</sub> - E <sub>red</sub> (V)
<b>PEF</b>	+0.41		
<b>PEB</b>	+0.39		
<b>PEPB</b>	+0.66		
<b>PEF-AQ</b>	+0.39	-1.45	1.84
<b>PEB-AQ</b>	+0.26	-1.40	1.66
<b>PEPB-AQ</b>	+0.69	-1.43	2.12
<b>3<sup>b</sup></b>		-1.49	

<sup>a</sup>In dichloromethane/TBAPF<sub>6</sub> (0.1 M) at a scan rate of 100 mV/s using Pt as working electrode and counter electrode, and Ag/AgCl as reference. <sup>b</sup>**3** refers to the anthraquinone unit displayed in Scheme 1.



**Figure 7.** Cyclic voltammograms of **PEF-AQ** (black solid line) along with references **PEF** (blue dashed) and isolated antraquinone unit **3** (red dotted line) recorded in dichloromethane.

**b) DFT Electronic Structure. Frontier Orbitals.** Figure 8 depicts the electronic energies and topologies of the highest occupied crystal orbital (HOCO) and lowest unoccupied crystal orbital (LUCO) of **PEX** and donor-acceptor **PEX-AQ** copolymers as obtained from DFT calculations using periodic boundary conditions (PBC). In the reference **PEX** copolymers, both HOCO and LUCO orbitals are of  $\pi$ -nature and are delocalized over the whole  $\pi$ -conjugated backbone, that is, on both EDOT and X (X= phenylene, fluorene or alkynyl-phenylene) comonomers. As expected, larger changes are found for the LUCO values in comparison to the HOCO values given the variable dimension of the orbital  $\pi$ -space, thus the highest LUCO value is found for the compound with less number of  $\pi$ -electrons per comonomer, **PEB** (in general: alkynyl-phenylene > fluorene > phenylene). Given the more aromatic-like and localized character of the HOCO, their values keep more or less constant within the series with a predominant role of the EDOT unit.



**Figure 8.** HOCO and LUCO topologies and electronic energies (in eV) for the **PEX** calculated at the PBC/B3LYP/6-31G\*\* level. HOCO, LUCO +1 or LUCO+2 topologies and electronic energies (in eV) for **PEX-AQ** copolymers calculated at the PBC/B3LYP/6-31G\*\* level. The LUCO topologies and electronic energies of **PEX-AQ** copolymers are shown in the Supporting Information (Figure S5).

In the donor-acceptor **PEX-AQ** copolymers, HOCO is delocalized over the whole  $\pi$ -conjugated backbone as for the reference **PEX** copolymers; however LUCO is totally localized over the strong electron-accepting AQ unit (see Figure S5). Therefore, in comparison to the **PEX** copolymers, the energy of the HOCO levels are relatively fixed (only slightly destabilized by about 0.15 eV) whereas the LUCO levels are strongly stabilized (*i.e.*, by 0.9 eV in **PEF-AQ**, 1.53 eV in **PEB-AQ** and 0.6 eV in **PEPB-AQ**). Unfortunately for charge and exciton mobility the LUCO of the **PEX-AQ** copolymers is decoupled of the main  $\pi$ -conjugated spine.

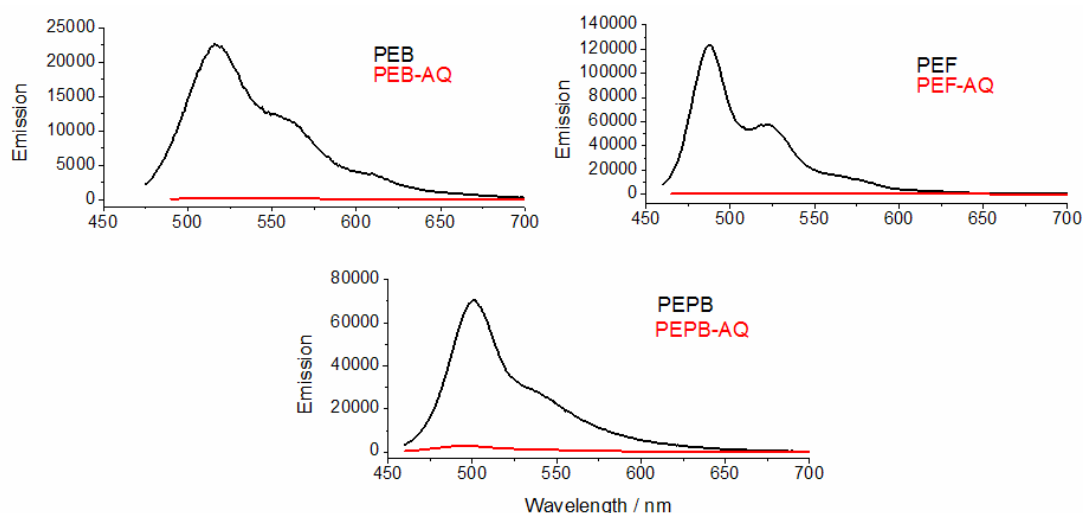
The electronic band structure calculations are in very well accordance with the PBC calculations: (i) within the **PEX** series the shapes of the conduction and valence bands are very similar with significant band dispersions ( $\approx 1$  eV) along the polymer molecular axis, while the insertion of an AQ moiety results in a flat conduction band (practically zero dispersion), greatly stabilized energetically in comparison to the reference **PEX** copolymer (see Figure S6). This is in agreement with the orbital

topologies presented in Figure 8 and could originate charge and exciton trapping more than mobile particles.

These DFT-calculated frontier molecular orbital energies and topologies are in good accordance with the electrochemical data that show (i) very similar oxidation potentials for the **PEX** and **PEX-AQ** copolymers and (ii) almost identical reduction potential value for the **PEX-AQ** polymers as that found for the AQ unit **3**. The only exception to this trend is found for **PEB-AQ** which exhibits oxidation and reduction potentials moderately shifted in comparison to those obtained for **PEF-AQ** and **PEPB-AQ** analogues (see Table 1). This can be ascribed to the intermolecular interactions between the two **PEB** and **AQ** moieties; note that our DFT-calculations have been performed for the isolated chains.

### 3.4 Photophysical properties.

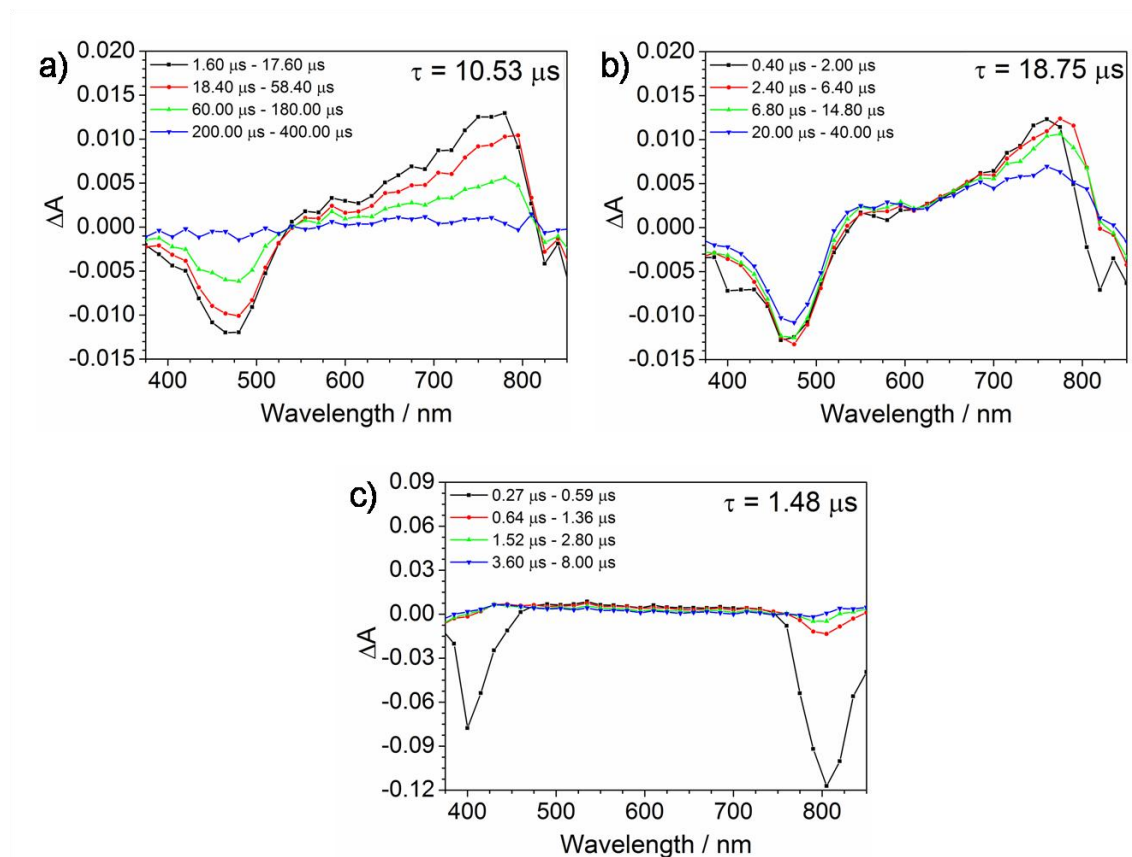
**a) Photoluminescence spectra.** The photoluminescence (PL) spectra of the **PEX** and **PEX-AQ** polymers in N,N-dimethylformamide solution are shown in Figure 9. The photoluminescence signal of the **PEX-AQ** polymers in solutions is strongly quenched compared to the **PEX** copolymers. The same observation was already reported in the literature for other similar double-cable polymers<sup>75-76</sup>. Given that the relevant optical excitations in the AQ copolymers always concern the  $\pi$ - $\pi$  structure of the backbone, the PL quenching can be attributed to a relaxation of the excitation to a AQ excited state from which deactivates non-radiatively. A photoinduced electron transfer can not be argued since relevant optical excitations do not involve any charge-transfer state.



**Figure 9.** Photoluminescence spectra of **PEX** (black) and **PEX-AQ** (red) in N,N-dimethylformamide solution.

**b) Transient triplet-triplet absorption spectra.** The triplet-triplet absorption spectra of **PEB** were conducted in several conditions, such as 2-methyl tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) at room temperature and in DMF at high temperature (340 K). As seen in Figures 10a,b for the experiments in THF solution (see the ESI for those in DMF), we observe the same spectral pattern consisting of the depletion or photo-bleaching of the ground state absorption and the appearance of a triplet-triplet absorption at 780 nm independently of the conditions; this band is associated with the formation of microsecond long-lived transient triplet species. However, the triplet lifetime decreases with the heating and also in passing from DMF to THF. The existence of an accessible triplet excited state manifold is in consonance with the molecular flexibility which promotes intersystem crossing from the initially populated low energy lying  $\pi$ - $\pi^*$  singlet excited state from which triplet population takes place. The transient experiment of **PEB** has been also carried out in THF after ultrasound treatment (inducing aggregation). Interestingly we observe the emergence of the transient signal at 780 nm in much smaller amount than in the untreated case. It is well known that  $\pi$ - $\pi$  stacking promotes intermolecular charge transfer states or intermolecular exciton states which always acts against intramolecular triplet states. The inactivity of these in the aggregate state gives good account of the persistence of the ground state absorption and of the much less triplet population. In line with this discussion, the AQ-based copolymers displays full disappearance of the transient

spectra highlighting the conversion of the excitation into the AQ exciton trapped state from which intersystem crossing is unviable.



**Figure 10.** Transient triplet-triplet absorption spectra of **PEB** before (a) and after (b) ultrasonic oscillating and of **PEB-AQ** (c) in 2-methyl tetrahydrofuran at different delay times after the pulse. The inset shows the lifetimes ( $\tau$ ) measured for the compounds.

#### 4. Conclusions

We have prepared a new series of well-defined EDOT-based copolymers containing in the backbone phenylene (**PEB**), alkylated fluorine (**PEF**) or diethynyl-1,4-phenylene (**PEPB**) and bearing pendant an electron-acceptor 9,10-anthraquinone (AQ). The optical and electronic properties of these **PEX-AQ** compounds are compared with those of their reference anthraquinone-free **PEX** copolymers. The phenylene-based **PEB** and **PEB-AQ** copolymers have shown interesting solvathochromic and thermochromic properties, which is ascribed to their flexible conjugated backbones that tend to get stiffened structures upon external stimuli (*i.e.*, ultrasound irradiation) promoting more ordered  $\pi$ -structures. However, the electronic absorption and redox properties of **PEF-AQ** and **PEPB-AQ** copolymers show negligible ground-state intramolecular communication

between the EDOT-based backbone and pendant AQ unit. The photoluminescence quenching found in the AQ-copolymers is attributed to a relaxation of the excitation to an AQ excited state that favours the non-radiative path. A loss of the accessible triplet excited state is observed in **PEB-AQ** when compared to AQ-free **PEB** homologue which might be ascribed to the presence of an AQ excitation trapped state. This work might contribute to the development of a more thorough understanding of structure-property correlations of processable polymers with potential applications in organic electronics.

## **.5. Acknowledgement**

The work at the University of Málaga was supported by MINECO (project reference CTQ2012-33733) and Junta de Andalucía (P09-FQM-4708) and at the Complutense University of Madrid by the Comunidad Autónoma de Madrid (project S2009/MAT-1467) and MINECO (CTQ2010-14982). We wish to thank F. Zamora for his assistance in the performance of the AFM measurements. R.C.G.C acknowledges the Junta de Andalucía for a personal doctoral grant. M.C.R.D. thanks the MICINN for a “Ramón y Cajal” Research contract.



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