

# Synthesis of an optically active electron-acceptor tetracyanoanthraquinodimethane (TCAQ) main-chain polyester

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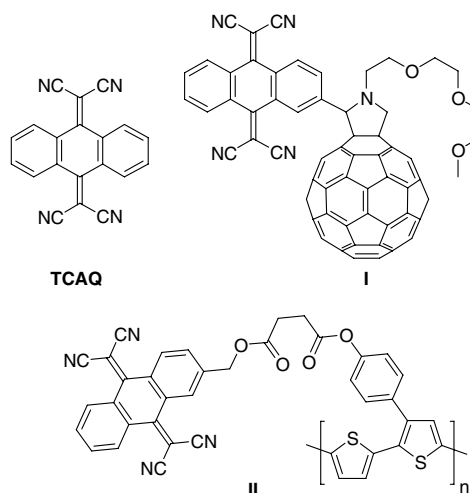
**Abstract**—The first main-chain copolymer containing TCAQ and enantiomerically pure binaphthyl moieties connected at 2,6 positions of the TCAQ ring was successfully synthesized by means of a polycondensation reaction. Cyclic voltammetry investigations show that TCAQ preserves its acceptor ability in the polymer system and preliminary photophysical investigations show fluorescence quenching in mixtures containing the acceptor polymer and fluorescent conjugated polymers.  
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Although a great deal of work has been devoted to the use of [60]fullerene derivatives as acceptor materials in plastic solar cells,<sup>1</sup> not much effort has been dedicated to other acceptor moieties. In this regard, the photophysical properties of different 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) based acceptors have been investigated with respect to their charge-transfer efficiency to conjugated polymers, showing that TCAQ is a more efficient electron acceptor than tetracyano-*p*-quinodimethane (TCNQ) despite its lower electron affinity.<sup>2</sup>

Thus, we have recently investigated the efficiency of photovoltaic devices based on electron donor conjugated polymers sensitized with TCAQ type acceptors (**I**) endowed with long alkyl chains.<sup>3</sup> Despite the high solubility of these TCAQ derivatives, the efficiency of the devices was limited by severe phase segregation between the polymer and the TCAQ systems.<sup>4</sup>

We have also investigated the possibility of covalently attaching this efficient acceptor system to donor conjugated polymer backbones (**II**) in order to prevent the phase separation and explore its potential in photovoltaic devices (see Fig. 1).

As a further step in the search for materials with enhanced miscibility in donor–acceptor blends to be

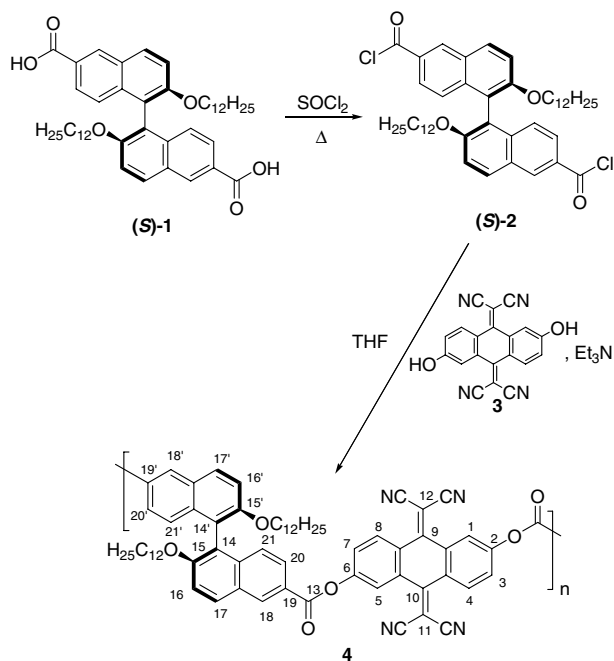


**Figure 1.** Selected examples of TCAQ-containing molecular (**I**) and polymeric (**II**) materials used in organic photovoltaic devices.

incorporated as active layer in solar cells, we present in this letter the synthesis of polyester **4**, which combines the good acceptor properties of the TCAQ moieties with the excellent thermal stability and mechanical properties typical of polyesters<sup>6</sup> and should be more compatible with binaphthyl-based conjugated–non conjugated block copolymers that have been previously synthesized in our group,<sup>7</sup> thus preventing phase segregation.

Among the methods stated in the literature to prepare polyesters, we have chosen the polycondensation reaction between bis acid chlorides and diols, as shown in

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Scheme 1.

Scheme 1. Thus, treatment of the (*S*)-2,2'-bis(dodecyloxy)-1,1'-binaphthyl-6,6'-dicarboxylic acid ((*S*)-1)<sup>8</sup> with thionyl chloride yields the corresponding bis acid chloride (*S*)-2, which is used without further purification. Polycondensation reaction of 2 with 2,6-dihydroxy-11,11,12,12-tetracyano-9,10-anthraquinodimethane (3)<sup>9</sup> affords the corresponding polymer in quantitative yield. The reaction is carried out at moderate temperature in an aprotic solvent and in the presence of triethylamine to eliminate the hydrogen chloride formed during the esterification process. Once diol 3 is consumed (TLC), the polymer is precipitated out of methanol, filtered and washed thoroughly with methanol.

The presence of alkyl chains in the 1,1'-binaphthyl moieties provides the polyester good solubility in common organic solvents, thus allowing its complete characterization despite its high molecular weight.<sup>10</sup> The FTIR spectrum shows a sharp band at around 2235 cm<sup>-1</sup> corresponding to the vibrational tension of the nitrile groups. The relatively high value of this band can be explained taking into account the non-planarity of the TCAQ fragment.<sup>11</sup> The presence of ester linkages is evidenced by the strong bands at 1740 and 1174 cm<sup>-1</sup> attributed to the stretching vibration of C=O and the asymmetric stretching of C–O bonds, respectively. Besides, the bands above 3000 cm<sup>-1</sup> appearing in the monomers ((*S*)-1 and 3, COOH and OH groups) disappear in the corresponding polymer.

The <sup>1</sup>H NMR spectrum shows the singlets corresponding to the hydrogen atoms in positions 1,5 of the dioxy-TCAQ ring at 8.14 ppm together with the protons in the 18,18' (see Scheme 1 for the arbitrary numbering) position of the binaphthyl moiety at 8.78 ppm. These signals appear as the most deshielded due to the vicinity of these positions to the ester carbonyl group. The

region of the aromatic protons is completed with 6 doublets, with a typical *ortho* coupling constant (<sup>3</sup>*J* ca. 8.8 Hz) although its complexity prompts a difficult assignment of those corresponding to the binaphthyl or TCAQ moiety. The methylene groups directly attached to the oxygen atom appear as a broad triplet. The <sup>13</sup>C NMR spectrum shows a relatively shielded signal for the carbonyl ester groups at 164.4 ppm and the signals corresponding to the carbon bearing the dodecyloxy and dicyanomethylene groups between 158 and 154 ppm. In the region between 137 and 115 ppm, the signal corresponding to the sp<sup>2</sup> carbons appears. Besides, two signals for the nitrile groups appear at around 113 ppm and the signal corresponding to the methylene moiety of the dicyanomethylene (C(CN)<sub>2</sub>) groups appears at around 83.5 ppm. Finally, the signals corresponding to the alkyl chains are displayed at higher fields. Evidence concerning the purity of the compounds is obtained from the satisfactory values obtained for elemental analyses in all cases.

As polymer 4 has been synthesized using an enantiomerically pure (*S*)-1,1'-binaphthyl derivative ((*S*)-1), a main-chain chiral polymer has been obtained with an optical rotation ([α]<sub>D</sub>) of +60 (*c* = 5 × 10<sup>-4</sup> g ml<sup>-1</sup>) in chloroform. The introduction of optically pure units provides a well defined stereoregularity, which is expected to increase miscibility. As it has been noted in other 1,1'-binaphthyl based polymers,<sup>7</sup> 4 rotates the plane of polarized light in the opposite direction of the binaphthyl precursor (*S*)-1. The relatively low optical rotation can be accounted for by the conformational flexibility that ester linkages provide to this polymer. Under the afore-mentioned conditions, 4 has been obtained with a narrow weight distribution. Size exclusion chromatography (SEC) versus polystyrene standards in chloroform shows *M*<sub>n</sub> and *M*<sub>w</sub> values of 12,000 and 21,000, respectively, and a polydispersity of 1.75. It is accepted that the numerical value of polydispersity is determined by the reaction mechanism of polymerization and by the conditions (e.g., temperature) under which it was carried out. Thus, a typical average value for the polydispersity of around 2 is stated for condensation polymers prepared by step reaction of bifunctional monomers, which is in agreement with the value shown by 4. On the other hand, the thermal stability of 4 has been studied by differential scanning calorimetry (DSC) under nitrogen atmosphere (Fig. 2). No noticeable decomposition occurs below 326 °C and, up to 530 °C, only 45% of the initial mass is consumed. This fact is in agreement with the high percentage of carbon in the polymer (ca. 80%), which, under an inert atmosphere, cannot be easily consumed.

In order to rationalize the structural, electronic and electrochemical features of polymer 4, we have prepared the model compound 6, in which a 2,6-dioxy-TCAQ moiety is linked to two naphthoic rings, in a similar way to the parent polymer. Thus, esterification reaction between a twofold excess of 6-dodecyloxy-2-naphthoic<sup>12</sup> 5 and 3 with 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) yields the corresponding model compound in 78% yield (Scheme 2).

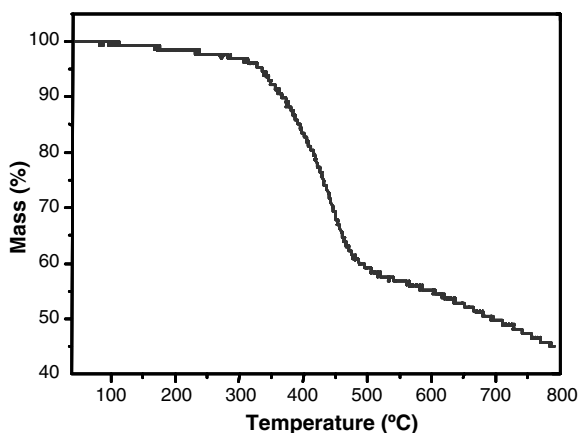
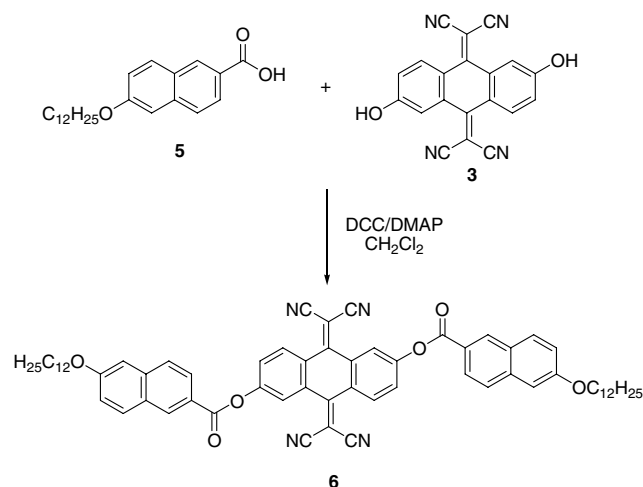


Figure 2. Differential scanning calorimetry (DSC) of polymer **4** from room temperature to 800 °C.

The structural characterization of **6** was also carried out by means of the usual techniques. The FTIR shows the characteristic bands at 2228, 1728 and 1190  $\text{cm}^{-1}$  corresponding to the nitrile and ester groups, respectively. Due to the high structural resemblance between the parent polymer **4** and the model compound **6**, their NMR spectral features are very similar, showing analogous signals. It is worth mentioning that the only difference in the  $^1\text{H}$  NMR spectrum arises from the fact that the doublet centered at 7.15 ppm in **4** turns into a multiplet in **6**. This can be explained considering the existence of a novel proton in  $\alpha$ -position to the alkoxy group in **6**, which is further coupled with other protons.

As it could be expected from their resemblance, the UV–vis spectra of copolymer **4** and its model compound **6** (Fig. 3), recorded in dilute dichloromethane solutions, are pretty similar showing maxima at around 330 nm for **4** and 347 nm for **6**.

The slight bathochromic shift of **4** can be accounted for by the aggregation of the polymeric chains and to the higher stiffness demanded by the polymeric chain as well.



Scheme 2.

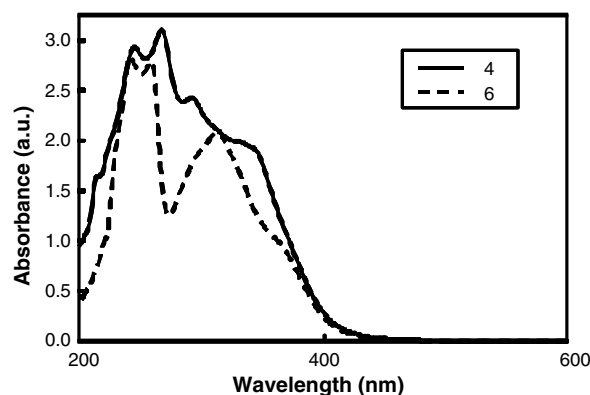


Figure 3. UV–vis absorbance spectra of **4** and **6** in dichloromethane.

The redox properties of polymer **4** and its model compound **6** were studied by cyclic voltammetry at room temperature in a three-electrode cell in dichloromethane solution and using  $\text{Bu}_4\text{NClO}_4$  as the supporting electrolyte ( $0.3 \text{ mg ml}^{-1}$ ) and glassy carbon, calomel and platinum wire as working, reference and counter electrode, respectively. Similarly to the parent TCAQ,<sup>13</sup> **4** and **6** show a single-wave, two-electron reduction to the dianion species at around  $-0.37$  and  $-0.39$  V, respectively. It has been previously demonstrated that the negative charges in the radical anion and dianion are mainly located at the two cyanomethylene groups. The cathodic shift of the reduction values with respect to the parent TCAQ ( $-0.35$  V under the same conditions) can be explained by the presence of the electron donor oxygen atom directly linked to the TCAQ ring, which increases its electron density thus slightly lowering its acceptor ability. No oxidation waves could be detected neither for **4** nor for **6** up to  $+2$  V. This fact could suggest that the electron withdrawing ester group reduces the density of the alkoxy-naphthalene ring and, therefore, the oxidation wave is so anodically shifted that it cannot be observed within the window of the solvent under the experimental conditions.

Films of the electron donor polymer MDMO-PPV and polyester **4** were prepared by spin casting 1:1 wt. toluene solutions and were investigated by fluorescence spectroscopy (Fig. 4). Whereas the pristine MDMO-PPV films showed their characteristic intense emission with maxima at 587 and 633 nm and a shoulder around 700 nm, in the composite films the MDMO-PPV photoluminescence is clearly quenched.

On the other hand, preliminary photoinduced absorption spectroscopy (PIA) studies on composite films of MDMO-PPV with the electron-acceptor polymer **4** show the appearance of PIA features in the composite with respect to films of pristine MDMO-PPV. These features may be assigned to radical anions of the TCAQ formed by photoinduced electron transfer from the electron donor MDMO-PPV to the electron-acceptor polymer **4**. This fact, together with the already mentioned photoluminescence quenching, suggests the existence of an electron transfer process in the composite films, thus enabling this material as a potential candidate for

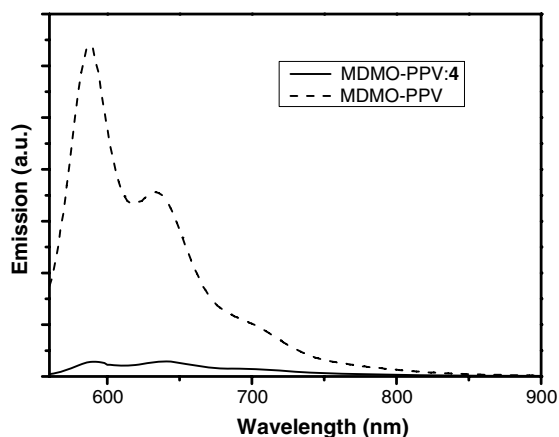


Figure 4. Solid state emission spectra of spin-casted films of pristine MDMO-PPV (dashed line) and MDMO-PPV:4 1:1 wt. (solid line).

the preparation of photovoltaic devices. Work is in progress to complete the photophysical study and to investigate the behaviour of **4** in composite organic solar cells.

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- Selected spectroscopic data for **4**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz).  $\delta$  (ppm) 8.78 (s, 2H), 8.26 (d, 2H,  $J = 8.7$  Hz), 8.14 (s, 2H), 8.09 (d, 2H,  $J = 9.3$  Hz), 7.83 (d, 2H,  $J = 9.3$  Hz), 7.58 (m, 2H), 7.47 (d, 2H,  $J = 9.3$  Hz), 7.15 (d, 2H,  $J = 8.7$  Hz), 3.97 (bt, 4H,  $-\text{CH}_2-\text{OC}_{\text{Ar}}$ ), 1.39 (s, 4H,  $-\text{CH}_2-$ ), 1.16 (s, 8H,  $-\text{CH}_2-$ ), 0.81 (s, 28H,  $-\text{CH}_2-$ ), 0.79 (t, 6H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz).  $\delta$  (ppm) 164.4 (C=O), 158.8, 157.2, 154.0, 137.1, 133.1, 131.9, 131.6, 129.3, 127.8, 127.1, 125.9, 125.7, 124.8, 122.6, 121.4, 119.3, 115.8, 112.8 (CN), 112.6 (CN), 83.5 (C(CN) $_2$ ), 69.2 ( $-\text{CH}_2-\text{OC}_{\text{Ar}}$ ), 31.9, 29.5, 29.3, 29.1, 25.6, 22.7, 14.1. FTIR (KBr).  $\nu = 2924, 2852, 2235, 1740, 1618, 1560, 1466, 1273, 1236, 1211, 1174, 1061, 806$   $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ).  $\lambda$  (nm) = 245, 267, 292, 330.  $[\alpha]_{\text{D}}^{+60}$  ( $c = 5 \times 10^{-4}$  g  $\text{ml}^{-1}$ ,  $\text{CHCl}_3$ ). Elemental analysis: calculated for  $[\text{C}_{52}\text{H}_{58}\text{N}_4\text{O}_3]_n$ : C: 79.38%, H: 6.76%, N: 5.72%. Found: C: 78.96%, H: 6.41%, N: 5.74%.
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