

# Synthesis of Soluble Donor–Acceptor Double-Cable Polymers Based on Polythiophene and Tetracyanoanthraquinodimethane (TCAQ)

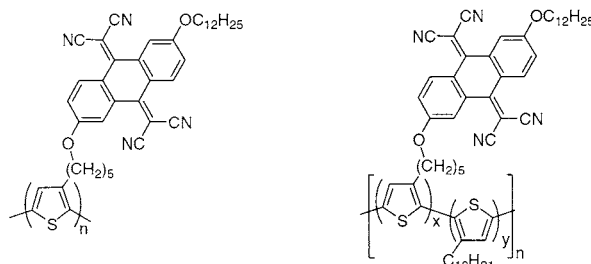
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## ABSTRACT



Novel suitably functionalized tetracyanoanthraquinodimethane (TCAQ) derivatives covalently linked to thiophene moieties have been synthesized. The thiophene-based monomers have been chemically polymerized and copolymerized to yield new and soluble donor–acceptor double-cable polymers. The absorption and emission data reveal that the optical properties can be finely tuned by modifying the ratio of monomers in the copolymerization process.

The most recent and efficient polymer solar cells fabricated today are based on the concept of bulk heterojunction.<sup>1,2</sup> They consist of a p-type conjugated polymer with an acceptor moiety mixed into it as an n-type material. The different solubilities of the two components in the organic solvents used for the film preparation and their limited miscibility cause phase segregation. This tendency to phase segregation has to be tailored to optimize both charge photogeneration and transport. Since the charges are preferentially formed at the donor–acceptor interface, an intimate mixing of the donor

and acceptor is beneficial for charge generation. It is also necessary to attain an efficient transport to the electrodes of holes through the donor and of electrons through the acceptor phase. For these reasons the donor and acceptor components have to be organized toward a nanoscopic phase-segregated bicontinuous network. Indeed the most significant improvements of the device efficiencies have been attributed to more favorable morphologies.<sup>3</sup> One approach to attain an intimate mixing of the donor–acceptor components and to control the film morphology is given by the concept of “double cables”.<sup>4</sup> This kind of material consists of a hole-conducting conjugated polymer chain carrying pendant electron-conducting moieties. In this way, electron-acceptor and donor moi-

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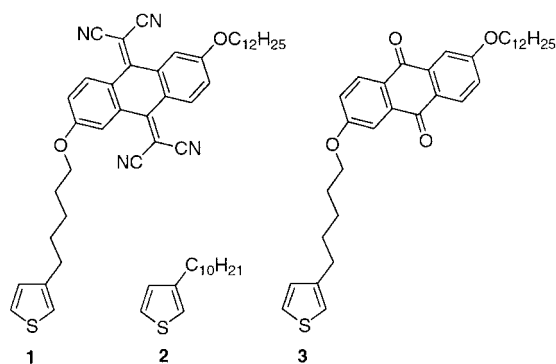
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**Figure 1.**

eties are forced to form a p- and n-conducting network with well-defined links. Different groups have recently reported similar structures consisting of a conducting polymer and pendant fullerenes as electron-accepting units.<sup>4,5</sup>

Although a great deal of work has been devoted to the use of fullerene derivatives as acceptor materials in plastic solar cells,<sup>6</sup> not so much effort has been dedicated to other acceptor moieties. However, different TCNQ-based acceptors were tested with respect to their charge-transfer efficiency to conjugated polymers showing that TCAQ is a more efficient electron acceptor than TCNQ despite its lower electron affinity.<sup>7</sup> Thus, we have recently investigated the efficiency of photovoltaic devices based on conjugated polymers sensitized with TCAQ-type acceptors endowed with long alkyl chains. Despite the high solubility of these TCAQ derivatives, the efficiency of the devices was limited by (severe or strong) phase segregation between the polymer and the TCAQ systems.<sup>8</sup>

We are currently investigating the possibility of covalently attaching this efficient acceptor system to conjugated polymer backbones<sup>9</sup> in order to prevent the phase separation to explore its potential in photovoltaic devices. Here we report preliminary results on a novel polythiophene bearing pendant TCAQ substituents obtained by chemical polymerization of suitable thiophene derivatives **1** and **2** (Figure 1). In contrast to the previously reported polythiophene/TCAQ systems<sup>8</sup> obtained by electropolymerization, this communication specifically refers to the facile synthesis of copolymers by reaction chemistry, which is all the better from the point of processability.

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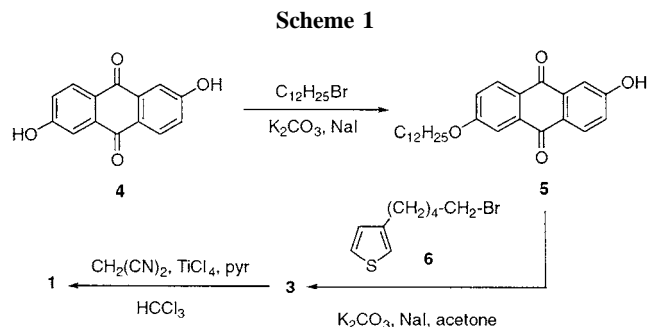
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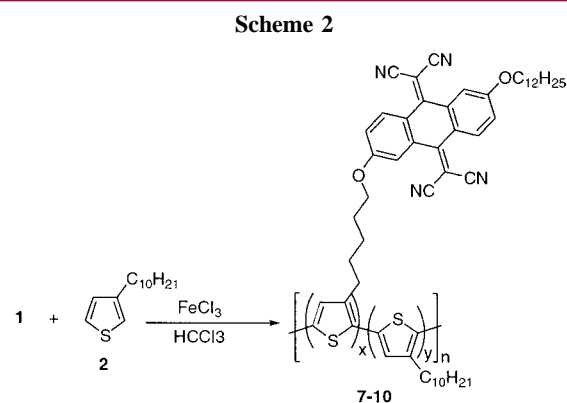
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3-Decylthiophene (**2**) was synthesized following the method reported in the literature,<sup>10</sup> and TCAQ derivative **1**<sup>11</sup> (Figure 1) was obtained in a 84% yield from the corresponding quinone **3** (Figure 1) by reaction with  $\text{CH}_2(\text{CN})_2$  in the presence of Lehnert's reagent ( $\text{TiCl}_4$  and pyridine in chloroform solution, Scheme 1).<sup>12</sup>



The starting quinone **3** was in turn prepared in two steps from commercially available anthraflavic acid **4**. Williamson etherification reaction with dodecylbromide under stoichiometric control yielded **5**. Further reaction with thiophene derivative **6**<sup>13</sup> in acetone by using potassium carbonate as base and sodium iodide as catalyst (Scheme 1) led to **3** in 75% yield.

A series of copolymers has been prepared via chemical oxidation with  $\text{FeCl}_3$  in chloroform<sup>14</sup> starting from mixtures of monomers **1** and **2** in a well-defined molar ratio (Scheme 2).



Thus, copolymers were prepared by using 100 mol % (**7**), 75 mol % (**8**), 50 mol % (**9**), and 25 mol % (**10**) of the TCAQ-monomer **1** in the feed (Table 1). The copolymers were obtained with yields between 80% and 90% by weight with respect to the monomers after washing several times with methanol in order to remove the oxidant. As a result of the presence of long alkyl chains on the monomeric units,

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**Table 1.** SEC Measurements of Copolymers

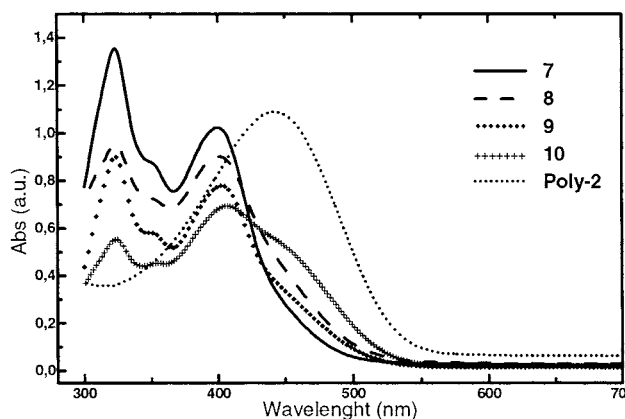
polymer	% of <b>1</b> in the feed	$M_w$	D
<b>7</b>	100	4 700	1.85
<b>8</b>	75	56 800	4.2
<b>9</b>	50	21 400	1.42
<b>10</b>	25	5 900	1.62

the purified copolymers show good solubility in tetrahydrofuran, chloroform, and carbon disulfide.

In Table 1 are reported the weight-average molar mass  $M_w$  and the dispersity index  $D$  of the polymers obtained by size exclusion chromatography (SEC) using chloroform solvent, UV-vis detector, and polystyrene as standard.

The  $^1\text{H}$  NMR spectrum of the polymers in tetrachloroethane shows, together with the characteristic signals corresponding to the TCAQ moiety (8.1, 7.7, and 7.1 ppm)<sup>15</sup> and the alkyl chains, a singlet centered at 6.9 ppm corresponding to the thiophene proton at C-4 of polyalkylthiophenes.<sup>16</sup>

The electronic properties of these polymers can be modulated by tuning the amount of monomer **1** in the feed. Figure 2 shows the optical absorption spectra of chloroform solu-

**Figure 2.** UV-vis absorption spectra of chloroform solutions of polymers **7**, **8**, **9**, **10**, and poly-**2**.

tions of polymers **7–10** together with that of polydecylthiophene, which is the homopolymer prepared by using only monomer **2**.

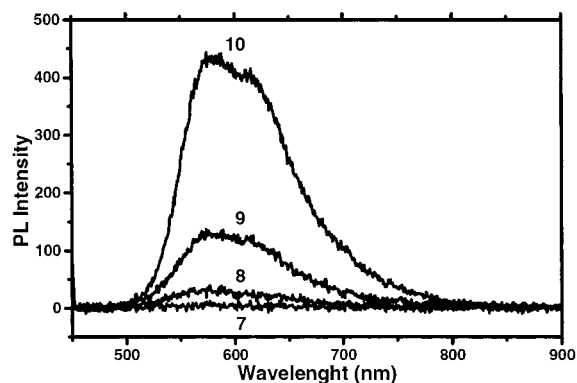
The maxima at 320 and 400 nm are characteristic of alkoxy-substituted TCAQ derivatives, whereas the band with

(11) Data for **1**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  8.16 (d, 2H,  $J = 8.8$  Hz), 7.70 (d, 1H,  $J = 2.2$  Hz), 7.69 (d, 1H,  $J = 2.2$  Hz), 7.27–7.23 (m, 1H), 7.17 (deceptively simple triplet, 1H,  $J = 2.3$  Hz), 7.13 (deceptively simple triplet, 1H,  $J = 2.3$  Hz), 6.94 (m, 2H), 4.11 (t, 4H,  $J = 6.4$  Hz,  $-\text{CH}_2-\text{OC}_6\text{H}_4$ ), 2.68 (t, 2H,  $J = 6.8$  Hz), 1.91–1.43 (m, 8H,  $-\text{CH}_2-$ ), 1.40–1.25 (m, 18H), 0.88 (t, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CHCl}_3$ , 50 MHz)  $\delta$  162.2, 162.1, 142.5, 132.7, 129.6, 128.1, 125.2, 121.8, 121.7, 120.0, 118.4, 113.6, 113.1, 80.8, 80.7, 69.2, 69.0, 31.9, 30.1, 30.0, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.7, 25.9, 25.5, 22.7, 14.1; FTIR (KBr)  $\nu$  2926, 2854, 2226, 1606, 1558, 1466, 1333, 1304, 1244, 1120, 758  $\text{cm}^{-1}$ ; MS  $m/z$  (EI) (%I) 656 ( $\text{M}^+$ , 32), 594 (15), 488 (4), 338 (8), 285 (4), 153 (28), 97 (100).

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maximum at 450 nm corresponds to the  $\pi-\pi^*$  polythiophene transition (UV-vis absorption of poly-**2** is included for comparison purposes). The band intensity of the conjugated backbone is low for the homopolymer **7** and increases with the decreasing of the TCAQ content in the copolymers. In the solid state the electronic absorption spectra of poly-**2** displays a  $\pi-\pi^*$  band red shift of 50 nm, which is indicative of a backbone planarization.<sup>17</sup> The spectra of spin-coated polymers **7–10** show a smaller red shift (10 nm) passing from solution to the solid state. This fact strongly suggests that, because of the steric hindrance produced by the bulky TCAQ system, the conjugated chain is distorted from planarity as the amount of TCAQ-containing monomer increases.

It is also worth mentioning how, after photoexcitation at 450 nm, the photoluminescence of the TCAQ-containing polymer solutions is quenched by 1–2 orders of magnitude with respect to poly-**2** and the quenching increases with the TCAQ content (Figure 3). This suggests that electron transfer

**Figure 3.** Photoluminescence spectra normalized to the number of absorbed photons of chloroform solutions of polymers **7**, **8**, **9**, and **10** after excitation at 450 nm.

from the photoexcited polythiophene backbone to TCAQ is occurring and that the charge transfer is fast enough to compete with the radiative recombination of the excitons. This is in agreement with previous observations of photo-induced electron transfer in blends containing conjugated polymers and TCAQ derivatives, which can be accounted for by the strong acceptor ability of the TCAQ moiety.<sup>18</sup>

An interesting feature of the PL quenching is that a less efficient quenching takes place when mixtures of poly-**2** and

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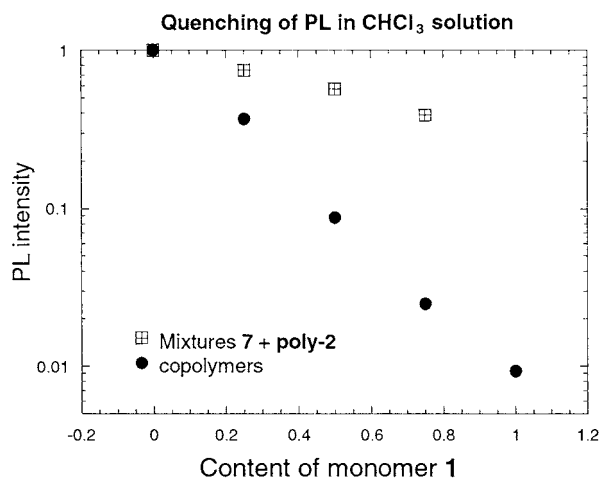
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(18) A reduction potential value ( $E_{\text{red}}$ ) of  $-0.26$  (V vs SCE) for monomer **1** has been determined by cyclic voltammetry in dichloromethane solution at room temperature (0.1 M in  $\text{Bu}_4\text{NClO}_4$ ; working electrode, GC; counter electrode, Pt; scan rate, 200  $\text{mV}\cdot\text{s}^{-1}$ ).



**Figure 4.** Comparison between the PL intensity in the copolymers and in mixtures of polydecylthiophene (poly-2) and polymer **7** in chloroform solution. PL intensity is normalized to the number of absorbed photons.

polymer **7** are used (Figure 4). This is evidence that in our materials the hole-conducting backbone and the acceptor TCAQ moiety are covalently attached. The photoinduced electron transfer in solutions of polymers **7–10** is an intramolecular process, whereas in the mixtures we observed a less efficient intramolecular process. This fact indicates that in the copolymers the hole-conducting backbone and the acceptor molecules are closer and can interact better than in a mechanical mixture of poly-2 and polymer **7**. For this

reason the photoinduced electron transfer process is more efficient when the TCAQ moiety is covalently attached to the conjugated chain.

In conclusion, we have prepared a new family of copolymers endowed with different amounts of TCAQ moieties covalently attached to the main polymeric chain. The tuning of the absorption and emission properties of these copolymers can be achieved by modifying the amount of TCAQ-containing monomer in the feed. An efficient quenching of the characteristic fluorescence of the polythiophene system is observed in the copolymers, the quenching being more efficient as the amount of TCAQ monomer in the feed increases. Comparison of the PL quenching in the copolymers with that of mixtures of homopolymer **7** and polydecylthiophene shows that a more efficient quenching occurs when the TCAQ moiety is covalently attached to the conjugated polymer system. This finding suggests that the double cable strategy can be an efficient way to prepare materials for photovoltaic devices.

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**Supporting Information Available:** General experimental procedures and spectroscopic characterization, NMR spectra, cyclic voltammograms of **1** and **3**, and solid film UV-vis and PL spectra of **7–10** and poly-2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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