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New polythiophenes bearing electron-acceptor phthalocyanine chromophores

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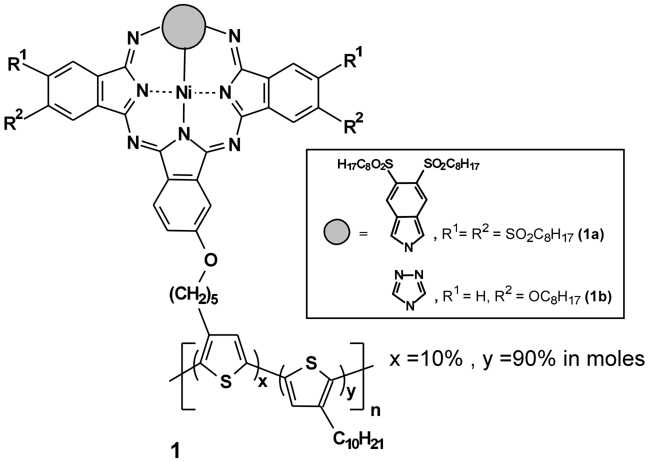
Abstract—Two new donor–acceptor copolymers comprising a polythiophene backbone, and bearing phthalocyanine chromophores on the side chains have been prepared. Preliminary photophysical characterization of these materials by FTIR photoinduced absorption indicates that electron transfer from the polythiophene to the phthalocyanine units takes place.

Electron-donor conjugated polymers are increasingly used in blends with electron-acceptor molecules such as fullerenes for the fabrication of photovoltaic (PV) devices.[1] The morphological problems of these bulk heterojunctions have suggested the preparation of intrinsically bipolar polymeric materials[2] in which the acceptor molecules are covalently grafted to the conjugated backbones. In comparison to bulk heterojunctions, the effective interfacial area between donor and acceptor in these materials is maximized as the phase segregation is prevented. Poly(3-alkylthiophenes) (PATs), together with poly(*p*-phenylene vinylenes) (PPVs), are by far the most widely used donor conjugated polymers as hole conducting materials for solar cell applications.[1,3] PATs are easily prepared whether electrochemically or chemically[4] and display low oxidation potentials allowing photo-induced electron transfer from the polymeric backbone onto an electron-acceptor moiety such as fullerene.[5]

Phthalocyanines[6] (Pcs) are organic aromatic molecules widely used in the field of molecular materials. This is mainly due to their outstanding stability and interesting optical properties, i.e. intense absorption in almost all the visible region and high polarizability, derived from their delocalized electronic system. Like their porphyrin equivalents, they are frequently used as donor units in donor–acceptor assemblies.[7] Moreover, the chemical versatility of Pcs allows different transformations such as replacement of the metal center, peripheral functionalization with electron-withdrawing groups and the formal substitution of one of the isoindoles by a different acceptor heterocyclic unit such as 1,2,4-triazole.[8] These transformations give access to a wide variety of materials having different electrochemical properties.[9]

Herein we describe the preparation of new donor–acceptor polythiophene-based materials **1** by copolymerization of 3-decylthiophene and thiophene monomers bearing electron-acceptor phthalocyanine chromophores. Two types of copolymers have been synthesized, one functionalized with Ni(II) phthalocyanines bearing electron withdrawing alkylsulfonyl groups (**1a**) and the other with Ni(II) triazolephthalocyanines (**1b**).



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Keywords: polythiohene; phthalocyanine; electron-transfer; photovoltaic applications.

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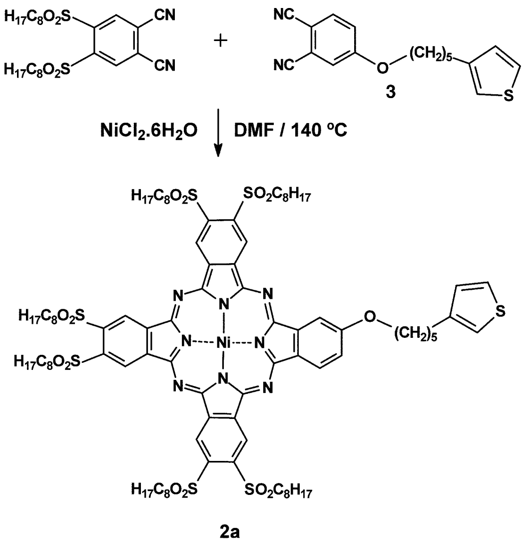
The phthalocyanine–thiophene monomer **2a** has been prepared with a 10% yield by a standard crossover condensation of 4,5-di(octylsulfonyl)phthalonitrile[10] and 4-(5′-(3″-thienyl)-pentoxyphthalonitrile **3**[11] in the presence of $NiCl_2 \cdot 6H_2O$ (Scheme 1).

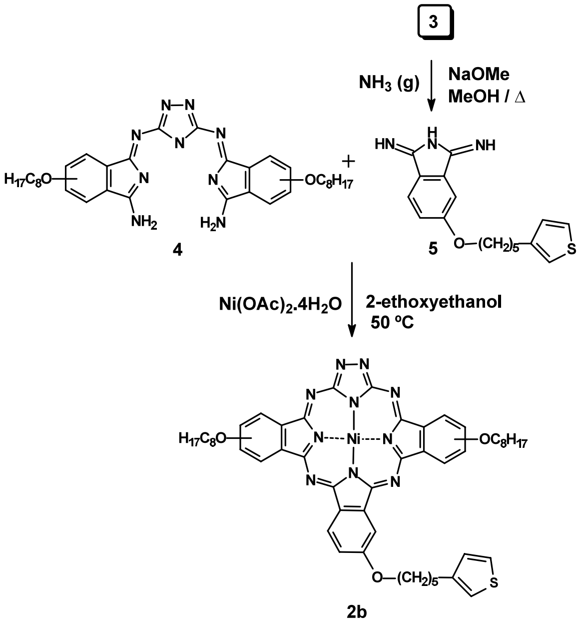


Scheme 1. Synthesis of phthalocyanine-thiophene monomer **2a**.

Compound **2a** was purified by column chromatography on silica gel using $CHCl_3$ as eluent, and characterized by ^1H NMR, UV-vis and MALDI-TOF mass spectrometry.[12] Phthalonitrile **3** was synthesized by *ipso* substitution of the nitro group of 4-nitrophthalonitrile[13] with 5-(3′-thienyl)pentanol, which was prepared in two steps from commercially available 3-bromothiophene and 5-bromopentene following a synthetic procedure reported for 3-(11′-hydroxyundecyl)thiophene.[14]

Nickel(II) triazolephthalocyanine **2b** was prepared in 46% yield by reacting the corresponding three-unit-compound **4**,[15] 1,3-diiminoisoindoline **5**[16] and $Ni(OAc)_2 \cdot H_2O$ in 2-ethoxyethanol at 50°C (Scheme 2). The macrocycle was purified by column chromatography on silica gel using a mixture of CH_2Cl_2/MeOH (20:1) as eluent, and fully characterized by NMR, FABMS, IR and UV-vis techniques.[17]

The copolymerization of a 1/9 molar ratio mixture of **2** and 3-decylthiophene via oxidative coupling with $FeCl_3$ produced random copolymers **1** in 80% yield.[18] The preparation of copolymers having a low phthalocyanine content was necessary to maintain a sufficient solubility of the material in $CHCl_3$. Copolymers **1** were washed with a hydrazine solution in methanol (1% in volume) in order to eliminate traces of catalyst, and then extracted with methanol in a Soxhlet apparatus in order to remove eventual oligomers.



Scheme 2. Synthesis of triazolephthalocyanine-thiophene monomer **2b**.

Copolymers **1a** and **1b** were characterized by ^1H NMR,[19] absorption spectroscopy and size exclusion chromatography (SEC). The molecular weight distribution (MW) of copolymer **1a** obtained by SEC in THF using polystyrene as standard and a UV-vis diode array detector was 52200 g/mol, and the dispersity index D was 3.97. The SEC analysis for copolymer **1b** indicated a mean molecular weight of 29800 g/mol and a dispersity index of 2.29.

Figure 1 shows the UV-vis spectra of monomer **2a** and copolymer **1a** in $CHCl_3$. The spectrum of compound **2a** shows the typical Q-band split around 650 nm characteristic of non-symmetrical Pcs (Fig. 1). The same band is observed for the copolymer spectrum, which also includes a band located at 437 nm arising from the π–π^* transition of the conjugated backbone. An important broadening and a slight blue shift of the Q-band can clearly be observed for the copolymer, indicating that the phthalocyanine moiety is close to the polymeric backbone.

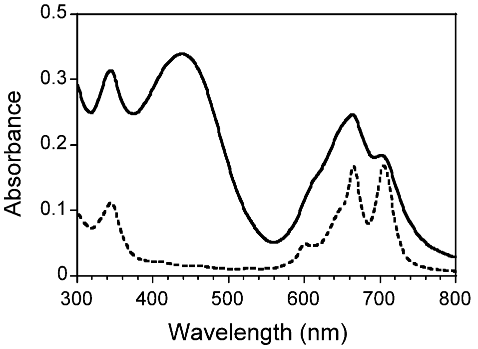


Figure 1. Electronic absorption spectra of copolymer **1a** (full line) and of monomer **2a** (dashed line) in chloroform solution.

The UV-vis absorption spectrum of **1b** in chloroform is reported in Figure 2 and compared to that of its corresponding monomer **2b**. The copolymer displays an absorption band at 640 nm due to the macrocycle and another more intense one at 430 nm due to the π–π* transition of the backbone.

The steady-state fluorescence spectra of **1a**, **1b** and polydecylthiophene (**PDT**) are shown in Figure 3. The photoluminescence (PL) intensity of both copolymers is lower than that of **PDT** upon excitation at 438 nm. This quenching of the PL suggests that some electron transfer occurs from the excited polymer backbone to the phthalocyanine, fast enough to compete with radiative deactivation.

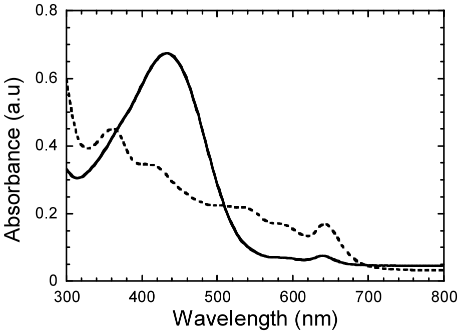


Figure 2. Electronic absorption spectra of copolymer **1b** (full line) and of monomer **2b** (dashed line) in chloroform solution.

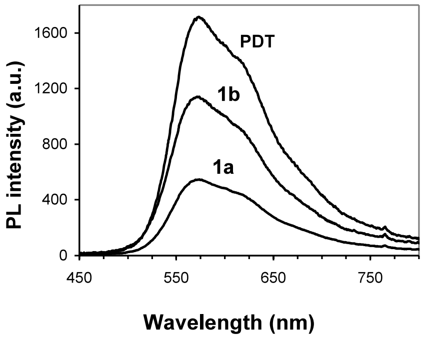


Figure 3. Steady-state fluorescence spectra of copolymer **1a**, **1b** and polydecylthiophene **PDT** in chloroform solution (excitation at 438 nm).

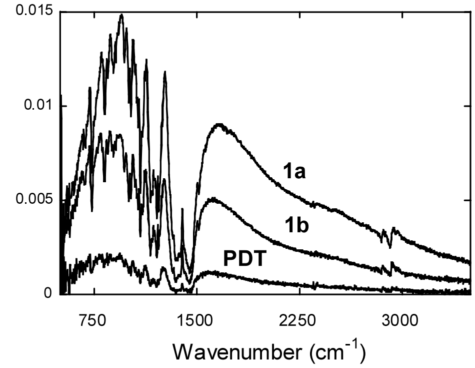


Figure 4. FTIR photo-induced absorption of copolymer **1a**, **1b** and of polydecylthiophene **PDT** (excitation at 457 nm, $T=78$ K, $P=10$ mW/cm^2).

Preliminary studies on the photo-induced charge transfer properties of these copolymers processed in drop cast films were carried out by FTIR photo-induced absorption spectroscopy (PA). The PA spectra of copolymers **1a** and **1b** are compared with the one of polydecylthiophene **PDT** in Figure 4. The samples have the same absorbance at the excitation wavelength of 457 nm. It can be seen that the spectral pattern of the copolymers are similar to the one detected for a polythiophene. Therefore, the vibrational bands (IRAV bands) observed are the spectral signature of the formation of charges on the polyalkylthiophene backbone. A relevant enhancement of the PA signal (from five to ten times) is observed in the copolymers. As in the case of polyalkylthiophene/fullerene blends, this large enhancement of the PA signal can be ascribed to an increased number of long-lived cations, arising from the photo-induced electron transfer from the polythiophene backbone to the Pc units.[20] The infrared bands of the Pc anions cannot be detected probably because, like fullerene anions,[20] their oscillator strength is much weaker than the one of the PAT cations. These results strengthen the electron acceptor role of the phthalocyanine unit foreseen from the redox potentials of these derivatives.[9]

Shifting the excitation wavelength to 633 nm, where the incident photons are mainly absorbed by the Pc units, leads to spectral features similar to those reported in Figure 4. However, in this case the PA signals measured for copolymers **1b** and **1a** are respectively fifteen to fifty times bigger in magnitude than the one of **PDT**. This indicates that photo-induced charge generation is more efficient at lower excitation energies, where a significant fraction of the absorbed photons is exciting the phthalocyanine units. A hole transfer from the phthalocyanine to the polythiophene chain may account for this feature.

The photophysical characterization reported here, provides an indication for a good charge photogeneration arising from the photoinduced electron transfer from the polythiophene backbone to the phthalocyanine moieties. The charge photogeneration is more efficient at lower excitation energies, where a significant fraction of the absorbed photons is exciting the phthalocyanine units. The phthalocyanine units thus have a dual function: they sensitize polythiophene-based materials to charge generation and harvest light in the lower energy region of the visible spectrum, leading to a better match with the solar spectrum of the these copolymers with respect to polyalkylthiophenes. These features open up interesting perspectives for the use of these copolymers in the field of photovoltaic devices.

Acknowledgements

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12. Selected data for **2a**: ^{1}H NMR (CDCl$_3$, 200 MHz, 25°C, TMS): $\delta = 10.3$, 10.2, 10.1, 10.0 (4×br s, 6H, Pc ring), 9.1–8.9, 8.7–8.4, 7.8–7.6 (3×m, 3H, Pc ring) 7.3–7.2, (m, 1H, thiophene), 7.1–7.0 (m, 2H, thiophene), 4.7–4.5 (m, 2H, OCH$_2$), 4.2–3.9 (m, 12H, SO$_2$CH$_2$), 2.84 (t, $J = 6$ Hz, 2H, thiophene CH$_2$), 2.3–1.5 ppm (several m, 96H, CH$_2$, CH$_3$); UV/vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 345 (4.99), 665 (4.92), 706 (4.98) nm; MS MALDI-TOF: $m/z = 1795$ [M$^+$].
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17. Selected data for **2b**: ^{1}H NMR (d-TFA, 300 MHz, 25°C, TMS): $\delta = 8.0$–6.9 (broad m, 12H); 4.5–3.8 (broad m, 6H), 2.9–2.7 (m, 2H), 2.7–2.6 (m, 2H), 2.1–1.9, 1.6–1.3 (2×m, 28H), 1.0–0.8 ppm (m, 6H); UV/vis (CHCl$_3$): $\lambda_{\max}$ (log ε) = 274 (4.39), 365 (3.79), 423 sh (3.15), 638 (3.05) nm; MS FAB (NBA): $m/z = 947$ [M+H$^+$].
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