

Giovanni Ridolfi · Nadia Camaioni
Giuseppe Casalbore-Miceli · Anna Maria Fichera
Michele Maggini · Giorgia Possamai

Structural characteristics of soluble fullerene films

Received: 19 May 2003 / Accepted: 4 August 2003 / Published online: 2 October 2003
© Springer-Verlag 2003

Abstract Films of two fullerenes, functionalized with different solubilizing moieties, in the pure form and blended with poly(3-hexylthiophene), have been investigated by cyclic voltammetry, X-ray diffraction and UV-Vis spectroscopy techniques. The conclusion drawn from this characterization is that the supramolecular order of the films affects the physicochemical characteristics of these materials, and depends on the nature of the solubilizing substituents linked to the fullerene moiety. Implications for the use of such films in fullerene-based solar cells are also presented and discussed.

Keywords Cyclic voltammetry · Fulleropyrrolidines · Poly(3-hexylthiophene) · Solar cells · X-ray diffraction

Introduction

A remarkable improvement in the power conversion efficiency of organic photovoltaic devices has been attained with donor/acceptor (D/A) blends. In particular, conjugated polymers [polythiophenes or poly(*p*-phenylenevinyls), D] and highly soluble, functionalized fullerene derivatives (A) have been employed for the preparation of high-performance plastic solar cells that, recently, have reached power conversion efficiencies up to 3.3% under AM1.5 solar irradiation [1]. In these systems an ultra-fast (in the femtosecond time regime) D to A electron transfer takes place upon irradiation,

with quantum efficiency close to unity [2, 3]. The back electron transfer is orders of magnitude longer. This has been ascribed to the peculiarly small reorganization energy of fullerene [4]. An alternative explanation takes into consideration different electronic couplings, estimated by theoretical calculations, for photoinduced charge separation and charge recombination, respectively [5]. A wide literature reports on the photoinduced electron transfer in conjugated polymer/fullerene composites. The electron transfer has been demonstrated by ultra-fast transient measurements, and theoretical approaches on the same phenomenon have been published [6].

The electrochemistry of pure fullerene films has been widely investigated [7]. It was ascertained that there is a dependence of the voltammetric pattern on the counterion used and, in the case of large cations, a potential shift between the fullerene reduction and its reoxidation. Recently, Kvarnström et al. [8] have reported an in situ FT-IR study of the electrochemical reduction of fullerene thin films. The authors stress the importance of the supporting electrolyte in determining the nature of the reduced species and the pattern of the voltammetry and also suggest the possibility of C₆₀ polymerization upon reduction. Investigations on films of fullerene-based D/A blends have been accomplished by voltammetry and spectrophotometry. Yoshino and co-workers [9] reported a ground state effective doping of poly(3-hexylthiophene) by fullerene, shown by the modification of the voltammetric peaks of the fullerene reduction and the polythiophene oxidation. By contrast, subsequently, only a partial charge transfer from fullerene to the polymer was observed in the ground state of poly(3-octylthiophene)/fullerene blends [10]. However, further work is necessary to shed light on the intimate nature of the D/A interactions in the blends, owing to the considerable number of soluble fullerenes and polyconjugated polymers nowadays available and the wide variety of methodologies to prepare polymer/fullerene blends, sometimes tending to handicrafts.

G. Ridolfi · N. Camaioni · G. Casalbore-Miceli (✉)
A. M. Fichera
Istituto ISOF-CNR, Via P. Gobetti 101,
40129 Bologna, Italy
E-mail: casalbore@frae.bo.cnr.it
Fax: +39-51-6399844

M. Maggini · G. Possamai
Dipartimento di Chimica Organica,
Istituto ITM-CNR Sezione di Padova,
Università di Padova, Via Marzolo 1, 35131 Padova, Italy

In this paper, we report a voltammetric, spectrophotometric and X-ray diffraction investigation on films of two fullerene derivatives in the pure form and blended with poly(3-hexylthiophene). The results highlight how the structure of the investigated fullerenes impacts the electrochemical and photophysical solid state characteristics of the resulting films. The D/A blends investigated in this paper have been previously used as active layers in organic solar cells [11].

Experimental

The synthesis and characterization of fullerene derivatives F-1 and F-2 (Fig. 1) has been reported earlier [11]. Poly(3-hexylthiophene-2,5-diyl) (PHT, Fig. 1) was prepared as described in the literature [12]. Its molecular weight, determined by gel permeation analysis (GPC) relative to polystyrene standards, was $M_n=18,000$, $M_w=29,500$; the polydispersity index was 1.64.

An AMEL 5000 multifunction apparatus was used for the electrochemical characterization. A Pt wire was used as counter electrode and a saturated calomel electrode (SCE, to which all the potentials are referred in this work) as reference. Both electrodes were separated from the solution by a glassy septum. The cyclic voltammeteries of F-1 and F-2 solutions, 1.5 mM and 0.6 mM, respectively, were measured in chlorobenzene (CB, Aldrich, 99.5%)+0.1 M tetrabutylammonium perchlorate (TBAP). Cyclic voltammeteries of films were carried out in pure acetonitrile (AN)+0.1 M TBAP or +0.1 M LiClO₄. AN (UVASOL, Merck) was stored and manipulated under argon pressure. TBAP (Fluka, purum) was crystallized from methanol. Lithium perchlorate (Fluka, pro analysis) was used as received.

The films were spin-coated (2000–3000 rpm) from chloroform (Merck, pro analysis) solutions (10 mg/mL) onto ITO/glass substrates (Balzers, 23 Ω/sq). Film thickness, measured with a Tencor Alphastep 200 profilometer, was between 30 and 60 nm.

Absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer.

The X-ray diffraction patterns were collected by a Philips X'Pert PRO system, equipped with a parallel beam optic for thin film analysis (incident glancing angle 2°) and a graphite monochromator in the diffracted beam. Cu-Kα X-radiation was employed and the recording was performed in continuous mode, with 0.02° 2θ steps, each for 2.5 s counting time. The samples were deposited by spin-coating onto a low-background quartz plate.

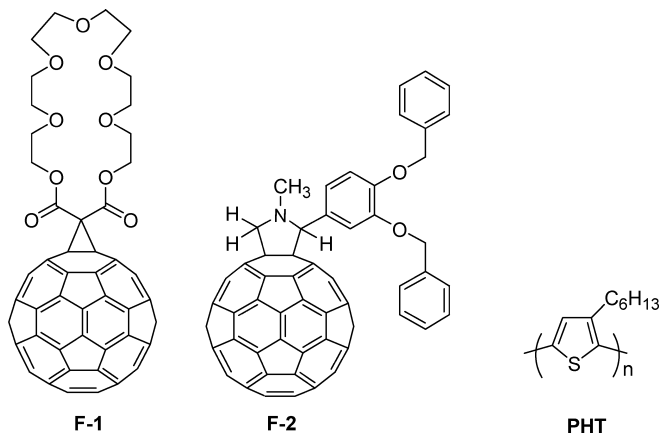


Fig. 1 Molecular structures: F-1, methano-fullerene; F-2, fulleropyrrolidine; PHT, poly(3-hexylthiophene-2,5-diyl)

Results and discussion

Pure fullerene films

Compounds F-1 and F-2 showed partially reversible reduction processes in CB solution. Reduction peaks were centred at $-0.6/-0.7$ V (Fig. 2). F-1 films showed an irreversible peak at -0.66 V at 20 °C (or $-1.05/-1.25$ V at -10 °C, depending on the scan rate, Fig. 3A,

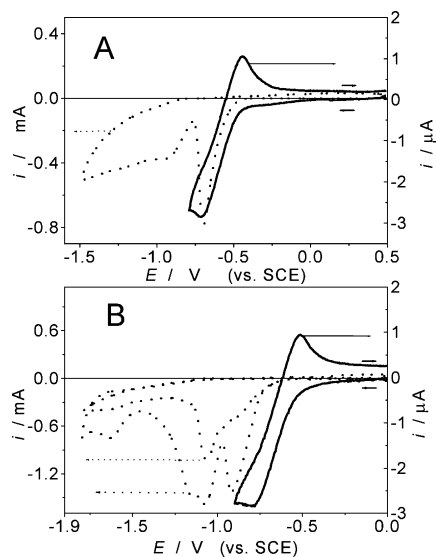


Fig. 2 A Voltammetry of 1.5 mM F-1 in CB+0.1 M TBAP, 50 mV s^{-1} , $T=+20$ °C (solid line); F-1 film on ITO glass in AN+0.1 M TBAP (dashed line). B Voltammetry of 0.6 mM F-2 in CB+0.1 M TBAP, 50 mV s^{-1} , $T=+20$ °C (solid line); F-2 film on ITO glass in AN+0.1 M TBAP (dashed line), F-2 film on ITO glass in AN+0.1 M LiClO₄ (dotted line)

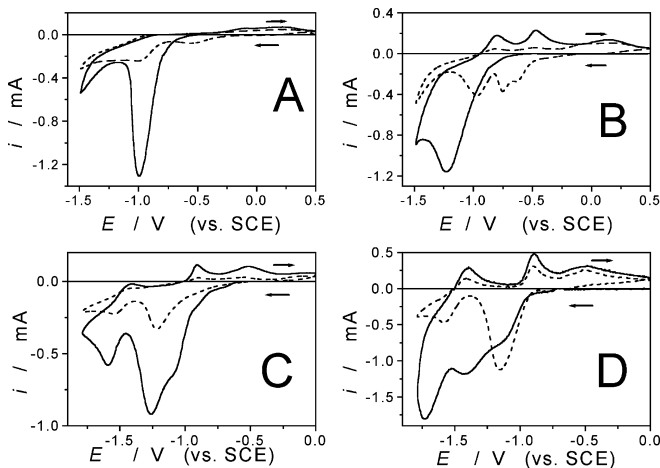


Fig. 3 Voltammetry of F-1 film on ITO glass in AN+0.1 M TBAP, $T=-10$ °C: A 50 mV s^{-1} , 1st cycle, solid line, 2nd cycle, dashed line; B 150 mV s^{-1} , 1st cycle, solid line, 2nd cycle, dashed line. Voltammetry of F-2 film on ITO glass in AN+0.1 M TBAP, $T=-10$ °C: C 50 mV s^{-1} , 1st cycle, solid line, 2nd cycle, dashed line; D 150 mV s^{-1} , 1st cycle, solid line, 2nd cycle, dashed line

B) that is associated with the formation of the fullerene radical anion. At ambient temperature and 50 mV s^{-1} , the charge amount connected to the first reduction peak of F-1, the width of which was $\sim 90 \text{ mV}$ at the half-height, was roughly proportional to the film thickness in the range 30–60 nm. A reliable calculation of the number of electrons exchanged in the first reduction process was impossible as the density of the film was unknown. However, by assuming that the film density was equal to 1, the exchange of 2 electrons per F-1 molecule could be estimated. In the range $\nu = 50\text{--}150 \text{ mV s}^{-1}$ the peak current (i_p) was proportional to $\nu^{1/2}$, and this is an indication that the reduction process was controlled by the counterion diffusion. The lack of the reverse peak could be due to a fast reaction of the fullerene radical anion with the solvent, with other F-1 molecules or, more likely, to the solubilization of the reduced species. F-2, at 20°C , showed the first peak at -0.89 V , visible as a shoulder of a subsequent successive peak centred at -1.07 V (Fig. 2B). The i_p of the first reduction process of F-2 (the peak potential for this process was taken at the flex point of the shoulder) was roughly equal to the i_p of the equivalent peak of F-1 and also dependent on $\nu^{1/2}$ in the range $50\text{--}250 \text{ mV s}^{-1}$. Nevertheless, the first reduction peak of F-2 film was displaced at more negative potential with respect to that of F-1 ($\sim 240 \text{ mV}$ for 30 nm thick films, at ambient temperature and 50 mV s^{-1}). This shift cannot be completely ascribed to the interaction between the counterion (TBA^+) and fulleride anions, as the change of the supporting electrolyte (LiClO_4 instead of TBAClO_4 , Fig. 2B) modifies the shape of the peak but not its potential. Otherwise, this shift could be related to a different structural organization of F-1 and F-2 films.

In order to shed light on the structural characteristics of F-1 and F-2 films, X-ray reflection measurements on quartz were carried out (Fig. 4). The X-ray pattern of F-2 shows a very sharp and intense peak at 23.2 \AA ($2\Theta = 3.8$) and two other reflections at 11.7 \AA ($2\Theta = 7.6$) and 7.8 \AA ($2\Theta = 11.3$), respectively, that apparently correspond to higher order reflections of the first peak. In the same pattern the amorphous phase is not evident. These observations indicate that the structure is very ordered along one direction and that many atoms are disposed on planes whose distance is about 23.2 \AA . On the other hand, the X-ray pattern of F-1 shows a much

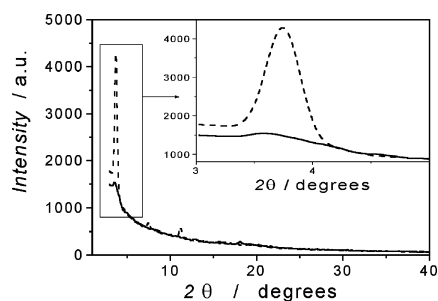


Fig. 4 X-ray diffraction pattern of fullerene film on quartz F-1 (solid line) and F-2 (dashed line). Inset: enlarged peak

smaller main peak (at about 24.5 \AA , $2\Theta = 3.6$), without any higher order peak. The F-1 molecules are disorderly repeated in almost all directions and just a few of them are distributed by crystallographic planes, indicating a lower supramolecular order with respect to F-2. The nature of the substituents plays a fundamental role for the structure organization and, consequently, affects the voltammetric behaviour of the films. An activation energy is required in order to modify the structure of the fullerene films, necessary for the settling of counterions into the solid and to reach the new order of the final reduced state. This activation energy is likely higher for the more ordered material. Therefore, the reduction of F-2 could reasonably require a more cathodic potential than F-1 reduction.

Fullerene/PHT blends

At 20°C , the voltammetric pattern of the F-1/PHT blend shows the first reduction peak at $\sim -0.85 \text{ V}$ (Fig. 5A). At -10°C , it was observed at -1.3 V (20 mV s^{-1}).

An interesting phenomenon was detected, both at 20°C and at -10°C , whenever a complete scan $0 \text{ V} \rightarrow -1.7 \text{ V} \rightarrow 1.2 \text{ V} \rightarrow 0 \text{ V}$ was carried out (Fig. 5).

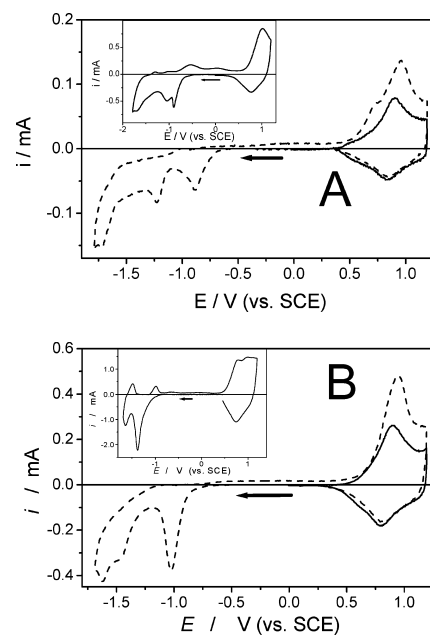


Fig. 5 Voltammetry in AN+0.1 M TBAP of blends films on ITO glass, 20 mV s^{-1} , $T = +20^\circ \text{C}$: **A** F-1/PHT (1:1, w/w) blend; *solid line*: first anodic cycle (scan range: $0 \text{ V} \rightarrow +1.2 \rightarrow 0 \text{ V}$); *dashed line*: subsequent cathodic-anodic cycle (scan range: $0 \text{ V} \rightarrow -1.8 \text{ V} \rightarrow +1.2 \text{ V} \rightarrow 0 \text{ V}$). *Inset*: cathodic-anodic cycle (scan range: $0 \text{ V} \rightarrow -1.8 \text{ V} \rightarrow +1.2 \text{ V} \rightarrow 0 \text{ V}$), scan rate 150 mV s^{-1} . **B** F-2/PHT (1:1, w/w) blend; *solid line*: first anodic cycle (scan range: $0 \text{ V} \rightarrow +1.2 \rightarrow 0 \text{ V}$); *dashed line*: subsequent cathodic-anodic cycle (scan range: $0 \text{ V} \rightarrow -1.8 \text{ V} \rightarrow +1.2 \text{ V} \rightarrow 0 \text{ V}$). *Inset*: cathodic-anodic cycle (scan range: $0 \text{ V} \rightarrow -1.8 \text{ V} \rightarrow +1.2 \text{ V} \rightarrow 0 \text{ V}$), scan rate 150 mV s^{-1}

During this voltammetric cycle, the oxidation of the polythiophene conjugated system, occurring at positive potentials ($\sim +0.4 \rightarrow +1.2$ V), supplied more charge than the corresponding reverse reduction process ($+1.2$ V $\rightarrow \sim +0.4$ V). This was only observed when the scan was continued towards positive potentials after a scan run up to cathodic potentials, where the reduction of the fullerene moiety occurs. A similar behaviour has been observed in the case of polythiophenes films bearing a reducible substituent [13] connected to the main polythiophene chain by a conjugated bridge. This was interpreted in terms of the negative charge delocalization over a wide molecular region after reduction. In the present case, the high anodic shift of the re-oxidation peak could suggest a stabilization of the negative charge through its delocalization over an extended "super-structure" which includes the polythiophene chain. We infer that after reduction of the fullerene moiety, a compact and probably ordered structure including F-1⁻, TBA⁺ and PHT species is formed, which hinders the counterion diffusion. The oxidation of this structure should only be possible at potentials at which this array is modified by the oxidation centred on polythiophene conjugated double bonds. The same behaviour was also observed with F-2/PHT blends during the scan in the potential range 0 V $\rightarrow -1.7$ V $\rightarrow 1.2$ V $\rightarrow 0$ V. An anodic-shifted re-oxidation of C₆₀ anion has been often observed, in the solid state, in the presence of large cations and Li⁺ [7]. This phenomenon was ascribed to the reorganization of the structure of C₆₀⁻/counterion occurring just after the fullerene reduction [14] and is typical of systems characterized by a so-called N-shaped free energy function [15]. In our case, pure F-1 did not show any re-oxidation peak up to 1.2 V. The tentative hypothesis that the polymer has simply the role of avoiding diffusion and, therefore, the solubilization of fulleride species is not convincing. In this case the fullerides would be solvated and ready to be reduced at $\sim -0.5/-0.6$ V (see, for example, in Fig. 3B–D relative to pure fullerenes, the peaks detectable in that region, due to the re-oxidation of solvated fulleride molecules included into the films). On the other hand, the presence of trapped electrolyte solution in the voltammeteries of fullerene films is not unprecedented [16].

In the case of the F-2/PHT blend, the first reduction peak (Fig. 5B) was shifted to a more negative potential than that of pure F-2 film (-1.21 V for pure F-2, -1.36 V for F-2/PHT in 3:2 weight ratio, -1.41 V for F-2/PHT in 1:1 weight ratio). This could suggest that the supramolecular order of F-2 is gradually destroyed because of the increasing interaction of this molecule with PHT. The use of a different counterion (LiClO₄ instead of TBAP) changed only the shape of the cathodic peak but not its potential (Fig. 6).

The X-ray diffraction patterns of F-2/PHT films (Fig. 7) show a strong dependence on the relative concentration of the two components. Fullerene domains with a high-order degree are clearly visible in X-ray diffraction patterns of blends with F-2 concentrations

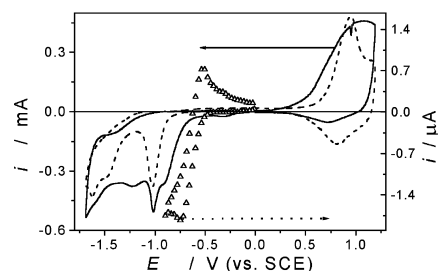


Fig. 6 Voltammetry of F-2/PHT (1:1, w/w) blend film on ITO glass, 20 mV s⁻¹, $T = +20$ °C; supporting electrolyte: 0.1 M TBAP (solid line), 0.1 M LiClO₄ (dashed line); up triangles: voltammetry of 0.6 mM F-2 solution in CB + 0.1 M TBAP, 20 mV s⁻¹

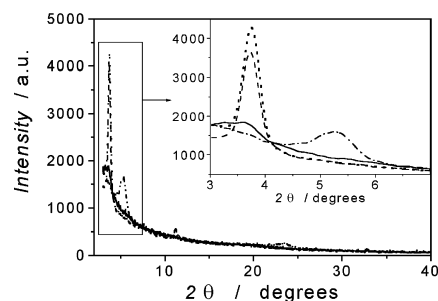


Fig. 7 X-ray diffraction pattern of F-2/PHT blend films on quartz: dotted line, 100% F-2; dashed line, F-2/PHT (3:1, w/w); solid line, F-2/PHT (1:1, w/w); dash-dotted line, 100% PHT. Inset: enlarged peak

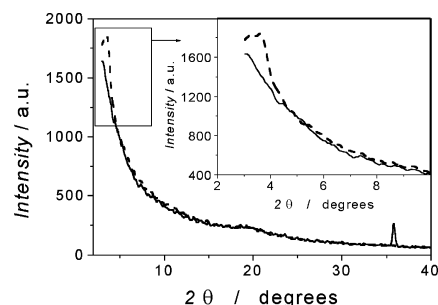


Fig. 8 X-ray diffraction pattern of 1:1 (w/w) blend films on quartz: solid line, F-1/PHT; dashed line, F-2/PHT. Inset: enlarged peak

greater than 50% by weight, while they are hardly detectable at lower fullerene concentrations as their size gradually decreases. In Fig. 7 the X-ray diffraction pattern of pure PHT is also reported, showing an interchain distance of about 16.8 Å ($2\theta = 11.3$), in agreement with previous results [17] on regioregular polythiophenes. For F-1/PHT blends, in the whole range of their respective relative concentration, the X-ray diffraction measurements showed a much lower order degree. This could be ascribed to a more amorphous structure of F-1 (Fig. 8).

Photovoltaic devices, performed at ambient conditions, were compared at the same fullerene/polymer weight ratio (1:1) and active layer thickness (ca.

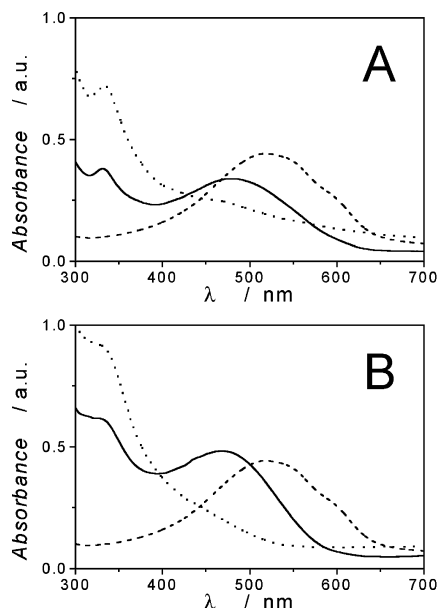


Fig. 9 Spectra of film on ITO glass: **A** dotted line: pure F-1 film; dashed line: pure PHT film; solid line: F-1/PHT (1:1, w/w) blend; **B** dotted line: pure F-2 film; dashed line: pure PHT film; solid line: F-2/PHT (1:1, w/w) blend

100 nm). Under a white-light irradiation power of about 20 mW cm^{-2} , higher values for the power conversion efficiency (η) and fill factor (FF) were obtained when the acceptor F-2 was used (F-2/PHT based-cells: 0.56% and 0.27 for η and FF respectively; F-1/PHT based-cells: 0.37% and 0.20). The higher order degree shown by F-2/PHT probably translates into a better charge transport properties of the active layer and a superior photovoltaic performance of the device. A study of the dependence of the device power conversion efficiency on the fullerene/polymer relative concentration was carried out for the F-2/PHT couple [11]. A maximum of the device performance was observed for relatively low values of the fullerene concentration (between 30% and 40% in weight), in spite of the improvement of the order degree exhibited by the blends by increasing the F-2 concentration. A growing tendency to phase segregation of the blend components could account for loss of efficiency by increasing the acceptor concentration. The fact that F-2, both pure and blended with PHT, tends to form more ordered domains compared to F-1 could be due to the minor stiffness of the solubilizing substituent in F-1.

As expected, the UV-Vis spectra of the blends, both F-1/PHT and F-2/PHT (Fig. 9), are different from the sum of the spectra of the two separated components, and reveal interactions between the two species depending on the used functionalized fullerene. The spectrum of PHT showed a band with a maximum absorbance at 520 nm, which marks the vibronic components. The fullerene/PHT blends (Fig. 10) did not show the vibronic structure of the polymer, while the PHT band shifted towards shorter wavelengths and decreased in absorbance. This phenomenon is very similar

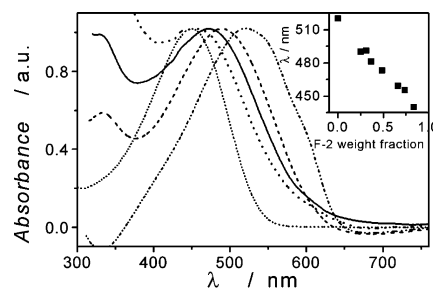


Fig. 10 Spectra of F-2/PHT blend films on ITO glass: 100% PHT (dash-dotted line), 1:2 (w/w) (dashed line), 1:1 (w/w) (solid line), 2:1 (w/w) (dotted line, large dots). PHT solution in chloroform (dotted line, small dots). Peaks normalized to absorbance 1. Inset: λ_{max} vs. F-2 weight fraction

to the solvatochromism of polyalkylthiophenes [18] dissolved in solvents with different dielectric constants, basicity and hydrogen donating power [19]. Therefore, by mixing F-2 with polythiophene, the structural order of the pure polymer gradually vanishes. The nature of the F-2/polythiophene interaction cannot be identified at the present state of the research. If a charge transfer complex was formed, its absorption band should have appeared at longer wavelengths than those of both free fullerene and polythiophene (polythiophene without any supramolecular organization, close to the polythiophene dissolved in CH_3Cl , i.e. 430 nm). In the present case, an absorption band would have been observed at wavelengths $>430 \text{ nm}$ at the expense of the band of polythiophene with supramolecular order. Unfortunately, the increase of an eventual charge-transfer band at wavelengths between 430 and 520 nm could not be detected because of the presence of other bands in that wavelength range. Therefore charge-transfer complex formation cannot be ruled out.

Conclusions

The supramolecular order strongly affects the electrochemical properties of the investigated fullerenes. The order depends on the substituent, as the X-ray diffraction measurements performed on the films clearly indicate a more organized structure for F-2 than that for F-1, probably due to a minor stiffness of the substituent in the former compound. The voltammetric measurements showed a cathodic shift of the first reduction peak for the more ordered F-2 film with respect to the F-1 film. This shift can be due to a more intimate intermolecular interaction binding the F-2 molecules. In the case of the F-2/PHT blend, by increasing the PHT/F-2 ratio, the size of the ordered domains of pure fullerene gradually decreased. The more organized fullerene domain, liable for better charge-transport properties through the acceptor network, was probably the reason of the better photovoltaic performances of F-2/PHT blends with respect to the F-1/PHT ones [11]. Moreover, the investigated fullerenes interact with PHT. The voltammetries

of the relative blends gave a clear indication of this interaction. In fact, while the pure fullerenes did not show any re-oxidation of the anion produced in the first reduction peak, probably because of material dissolution, the blend with PHT re-oxidized, though at anodic-shifted potentials. The shift was reasonably due to the stabilization of the fullerene anion as a consequence of an interaction with the polythiophene conjugated chain.

Acknowledgements Thanks are due to Dr. L. Garlaschelli (Dipartimento di Chimica Organica, Università di Pavia) for a generous gift of the F-1 compound. We are grateful to Mr. A. Geri (ISOF-CNR, Bologna) for his help in performing the CV measurements and Dr. R. Mendichi (ICM-CNR, Milano) for the molecular weight determination of PHT. This work was supported by CNR within the framework of the Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate II" and Agenzia 2000, and MIUR (contract nos. MM31198284 and 2002032171).

References

1. Brabec CJ, Shaheen SE, Winder C, Sariciftci NS, Denk P (2002) *Appl Phys Lett* 80:1288
2. Sariciftci NS, Smilowitz L, Heeger AJ, Wudl F (1992) *Science* 258:1474
3. Zerza G, Brabec CJ, Cerullo G, De Silvestris S, Sariciftci NS (2001) *Synth Met* 119:637
4. Imhaori H, Sakata Y (1999) *Eur J Org Chem* 10:2445
5. Lowson JM, Oliver AM, Rothenfluh DF, Han Y-Z, Ellis GA, Ranasinghe MG, Kan SI, Franz AG, Ganapathi PS, Shepard MJ, Paddon-Row MN, Rubin Y (1996) *J Org Chem* 61:5032
6. See, e.g.: Sariciftci NS, Heeger AJ (1997) Photophysics, charge separation, and device applications of conjugated polymer/fullerene composite. In: Nalwa HS (ed) *Handbook of organic conductive molecules and polymers*, vol 1. Wiley, New York, pp 413-455
7. See, e.g.: Chlistunoff J, Cliffl D, Bard AJ (1997) Electrochemistry of fullerenes. In: Nalwa HS (ed) *Handbook of organic conductive molecules and polymers*, vol 1. Wiley, New York, pp 333-412
8. Kvarnström C, Neugebauer H, Kuzmany H, Sitter H, Sariciftci NS (2001) *J Electroanal Chem* 511:13
9. Morita S, Zarkhidov AA, Yoshino K (1992) *Solid State Commun* 82:249
10. Smilowitz L, Sariciftci NS, Wu R, Gettinger C, Heeger AJ, Wudl F (1993) *Phys Rev B* 47:13835
11. Camaioni N, Garlaschelli L, Geri A, Maggini M, Possamai G, Ridolfi G (2002) *J Mater Chem* 12:2065
12. Loewe RS, Khersonsky SM, McCullough RD (1999) *Adv Mater* 11:250
13. Casalbore-Miceli G, Gallazzi MC, Zecchin S, Camaioni N, Geri A, Bertarelli C (2003) *Adv Funct Mater* 13:307
14. Jehoulet C, Obeng YS, Kim YT, Zhou F, Bard AJ (1992) *J Am Chem Soc* 114:4237
15. Strasser P (2000) *Interface* 9:46
16. Koh D, Dubois W, Kutner W, Jones TM, Kadish KM (1993) *J Phys Chem* 96:6871
17. Winokur MJ, Spiegel D, Kim Y, Hotta S, Heeger AJ (1989) *Synth Met* 28:C419
18. See, e.g.: O. Inganäs (1997) Thermochromism and solvatochromism in substituted polythiophenes. In: Nalwa HS (ed) *Handbook of organic conductive molecules and polymers*, vol 3. Wiley, New York, p 788
19. Kamlet MJ, Abboud JL, Abraham MH, Taft RW (1983) *J Org Chem* 48:2877