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SYNTHESIS AND PROPERTIES OF [60]FULLERENE-POLYVINYLPYRIDINE CONJUGATES FOR PHOTOVOLTAIC DEVICES

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SYNTHESIS AND PROPERTIES OF [60]FULLERENE-POLYVINYLPYRIDINE CONJUGATES FOR PHOTOVOLTAIC DEVICES

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

A two-phase radical polymerization was applied for the synthesis of fullerene-containing poly(4-vinylpyridine), which were used as polyelectrolytes in the fabrication of photovoltaic devices. Two-phase radical polymerization resulted in the products of poly(4-vinyl pyridinated) fullerenes (PVPyF) containing a high fullerene content and poly(4-vinylpyridine) arms of short length. These polyelectrolytes with a C_{60} content of up to 35% by weight are soluble in organic solvents and water at a low *pH*. High efficient photoinduced charge transfer in samples of PVPyF and polyanionic polythiophene derivatives fabricated by the electrostatic layer-by-layer deposition technique in producing self-assembled multilayers (SAMs) was demonstrated. As a result, high response to the increase of photoinduced conductivity was observed on the 75 bilayer device of PVPyF-3^{+}/H-PURET^{-} upon irradiation. Photoconductivity was found to increase in more than one order of magnitude from 0.024 to 0.31 S/cm at an applied voltage of 1.0 volt. The sign of short-circuit photocurrent

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was consistent with electrons flowing from Al electrode towards the ITO modified substrate.

Key Words: Poly(4-vinyl pyridinated)fullerenes; Polyelectrolytes; Photovoltaic devices

INTRODUCTION

High electrophilicity of C_{60} makes multiple additions of the electron-deficient organo-radicals, such as benzyl and *tert*-butyl radicals, possible to the fullerenic double bonds [1, 3] Rate constants for the addition reaction of the alkyl radicals onto C_{60} were reported to be $10^7 10^9$ $m^{-1}s^{-1}$, [4, 6] much higher (10^5 times) than those for the propagation of polymer or oligomer chain-end radicals with monomers during the free-radical polymerization of styrene and methylmethacrylates. Therefore, it was proposed that the radical initiators were consumed in the early stage of polymerization by multiple additions onto C_{60}, leading to formation of highly substituted C_{60} derivatives. Polymerization of styrene and methylmethacrylates began to proceed when the rate of addition of radical initiators to highly substituted C_{60} derivatives became relatively slow as compared with that of the polymer radical propagation with monomers [7].

Preparation of highly charged C_{60}-containing vinyl polymers attracts interest in their potential uses as polyelectrolytes in aqueous medium [8, 9]. Fullerene-grafting reaction during the polymerization of the polar vinyl monomer was found to be rather complex. To facilitate better understanding of the radical reaction pathway in the presence of fullerene molecules and insight of the polymer product structure, a two-phase radical polymerization method was investigated for the preparation of poly(4-vinylpyridinated) [60]fullerene (PVPyF). By introducing hydrophilic oligopyridinyl groups onto the fullerene cage, the resulting C_{60}-containing macromolecules should exhibit an appreciable water-solubility after protonation and can e used as polycations in the fabrication of photovoltaic cells in the presence of polyanionic polythiophene derivatives using a static self-assembly technique, as demonstrated by Rubner [10, 11].

EXPERIMENTAL

General

4-vinylpyridine (4VP) was purified by distillation under a reduced pressure. Fullerene containing 99.5% C_{60} was purchased from Southern Chemical Group. 2,2’-azobisisobutyronitrile (AIBN), *o*-dichlorobenzene (*o*-DCB) and ethylene glycol (EG) were used as received. Infrared spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer. Differential scanning calorimetric (DSC) and thermogravimetric (TGA) analyses data were collected using TA instruments equipped with a DSC 2910 calorimeter, and a TGA 2950 analyzer, respectively. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda spectrophotometer and a GBC UV/vis 916 spectrometer.

Elemental analyses were carried out at Atlantic Microlab, Inc. Deionized water was purified via Millipore SA67120. Electrostatically-assembled multilayers were fabricated using a HMS Series Programmable Slide Stainer. Ellipsometric measurements for the multilayer devices were carried out by a Rudolph Research, Auto EL III ellipsometer. An air-cooled argon laser was used as a light source at 488 nm.

Synthesis of Poly(4-Vinylpyridine) (PVPy-1) and Poly(4-Vinylpyridinated) [60]fullerene (PVPyF-1) by Homogeneous Free-Radical Polymerization

One poly(4-vinylpyridinated) [60]fullerene sample of PVPyF-1 was prepared by using AIBN as a radical initiator under conditions shown in Table 1. *O*-dichlorobenzene (*o*-DCB) was selected as the reaction solvent due to its good solubility to C_{60}. Prior to the polymerization, a C_{60} solution in *o*-DCB was prepared and stirred at room temperature until thee was complete dissolution of fullerene particles. A three-necked flask equipped with a condenser, an inert gas bubbler and a mechanical stirrer, was charged with AIBN (75 mg), 4-vinylpyridine (1.4 ml), and the C_{60} solution in *o*-DCB solution (73 mg in 4.0 ml, 5.0% by wt), followed by deoxygenation by bubbling with a stream of dry nitrogen gas for 30 minutes. The initiation of polymerization became effective at 70°C in an oil-bath under N_2 and continued for a period of 20 hours. At the end of polymerization,

Table 1. Conditions and the Polymerization Product Yield of 4-Vinylpyridine in the Presence of C_{60} and AIBN

	Quantity of Reactants				Product	
Sample	4VP (ml)	AIBN (mg)	C_{60} (mg)	Solvent (ml)	Solubles (g)	ISF (mg)
Homogeneous radical polymerization						
PVPy-1	0.5	35	—	1.5 (*o*-DCB)	0.42 (86%)[a]	—
PVPyF-1	1.4	75	73 (5 wt%)	4 (*o*-DCB)	1.21 (84%)	9.8
Two-phase radical polymerization						
PVPy-2	4	160	—	12 / 6 (*o*-DCB/EG)	3.71 (95%)	—
PVPyF-2	4	160	200 (5 wt%)	12 / 6 (*o*-DCB/EG)	1.58 (36%)	64.0
PVPyF-3	2	80	200 (10 wt%)	6 / 3 (*o*-DCB/EG)	0.43 (15%)	76.4

[a] The yield was estimated based on the conversion of 4-vinylpyridine monomer without considering the initiator fragments.

methanol (20 ml) was added for dissolving the reaction mixtures. Insoluble dark solids were separated by centrifuge and washed twice with methanol. All methanol fractions were combined, partially concentrated, and added with toluene (40 ml) to cause precipitation of the polymer products, PVPyF-1. The mother liquor containing unreacted monomers, initiator, and the parent C_{60} residues was discarded. Low coloration of the mother liquor allowed us to assume a nearly complete consumption of C_{60} in the copolymerization. The insoluble dark solids (ISF, 9.8 mg) exhibited low solubility in common organic solvents, differing largely to the good solubility of PVPyF-1 in methanol, chloroform, and DMF.

Further purification of PVPyF-1 was carried out by dissolving it in dil. HCl at *pH* 3.0 followed by filtration through Celite 521 for removal of any insoluble impurities in acid water. The products were recovered by precipitation from the solution upon titration with dil. NaOH (1.0 N) and washed with water until neutral. The resulting dark solids were dried *in vacuo* at 60°C overnight to provide poly(4-vinylpyridinated) [60]fullerene of PVPyF-1 in 84% yield (1.2 g). Similar reaction conditions were applied for the preparation of poly(4-vinylpyridine), PVPy-1, in 86% yield.

Synthesis of Poly(4-Vinylpyridine) (PVPy-2) and Poly(4-Vinylpyridinated) [60]Fullerenes (PVPyF-2 and PVPyF-3) by Two-Phase Free-Radical Polymerization

A three-necked flask equipped with a condenser, an inert gas bubbler, a mechanical stirrer, and a solid-addition funnel, was charged with C_{60} (200 mg) and *o*-dichlorobenzene (12 ml) at ambient temperature. It was added slowly to 4-vinylpyridine (4.0 ml) in ethylene glycol (6 ml) as the second phase (top layer) of the reaction mixture without giving much disturbance to the other phase of the solution. A solid of 2,2'-azobisisobutyronitrile (160 mg) was placed in the solid-addition funnel which was attached on the three-necked flask. The solution was then gently deoxygenated by bubbling with a stream of dry nitrogen gas for 30 minutes. An addition of AIBN to the solution via the solid-addition funnel was done by tapping. Only the bottom *o*-dichlorobenzene layer was heated at 70°C under N_2 in an oil-bath with a gentle stirring while maintaining the solution mixture in a two-phase state. The initiation of polymerization became effective within few minutes and continued for a period of 20 hours. As the reaction proceeded, the dark *o*-DCB layer became light in color progressively with the layer of ethylene glycol turning into dark reddish brown, showing a dramatic color switch. At the end of polymerization, the reaction mixture was cooled to room temperature and added to diethyl ether (40 ml), causing effective precipitation of polymers from the ethylene glycol layer. Solids were separated by centrifugation, and washed twice with diethyl ether. It was then dissolved in methanol (10 ml). Insoluble dark solids (ISF, 64 mg) were separated by centrifugation, and washed twice with methanol. The polymer products were reprecipitated from methanol upon addition of toluene (40 ml). Further purification was carried out by dissolving the solids in dil. HCl at *pH* 3.0 followed by filtration through Celite 521 for removal of any insoluble impurities in acid water. The products were recovered by precipitation from the solution upon titration with dil. NaOH (1.0 N) and washed with water until neutral. The resulting dark solid products were dried *in vacuo* at 60°C overnight to afford poly(4-vinylpyridinated) [60]fullerene of PVPyF-2 in 36% yield (1.58 g).

Similar reaction procedures were utilized for the preparation of PVPyF-3, except a different quantity of reagents applied as C_{60} (200 mg), AIBN (80 mg), *o*-dichlorobenzene (6.0 ml), 4-vinylpyridine (2.0 ml), and ethylene glycol (3.0 ml). The product yield of PVPyF-3 was found to be 15% (0.43 g).

In the case of poly(4-vinylpyridine), PVPy-2, the quantity of reagents applied was AIBN (160 mg), *o*-dichlorobenzene (12 ml), 4-vinylpyridine (4.0 ml), and ethylene glycol (6.0 ml). During the early stage of polymerization, the *o*-dichlorobenzene layer of the reaction solution turned into white and cloudy from, originally, clear and colorless. After an additional stirring for a period of 4 hours, the *o*-DCB layer returned back to clear and colorless with the layer of ethylene glycol turning into amber in color, indicating the formation of poly(4-vinylpyridine). A similar workup procedure was followed. The product yield of PVPy-2 was found to be 95% (3.71 g).

Preparation of Water-Soluble Poly(Thiophene-3-acetic acid) (PTAA) and Poly[2-(3-Thienyl)ethanol Hydroxycarbonyl-methyl Urethane] (H-PURET)

Two water-soluble polythiophene derivatives, PTAA and H-PURET, were prepared using the procedure reported previously [12]. PTAA contains a short alkyl side-chain of acetic acid on each thiophene unit. It was synthesized by polymerization of ethyl thiophene-3-acetate in the presence of ferric chloride, followed by hydrolysis of the ester group. Poly[2-(3-thienyl)ethanol hydroxycarbonyl-methyl urethane] (H-PURET) with a long urethane-linked side-chain on each thiophene unit was synthesized according to the literature procedure [13].

RESULTS AND DISCUSSION

Free radical copolymerization of vinyl monomers and C_{60} was demonstrated previously using 2,2'-azobisisobutyronitrile (AIBN) as an initiator at 65°C in either benzene or *o*-dichlorobenzene [14-17]. A similar polymerization of 4-vinylpyridine in the absence or in the presence of C_{60} was carried out in *o*-dichlorobenzene at 70°C yielding poly(4-vinylpyridine), PVPy-1, or C_{60}-containing poly(4-vinylpyridine), PVPyF-1, in 86 or 84%, respectively. In our two-phase radical copolymerization reaction, *o*-dichlorobenzene (*o*-DCB) was the primary solvent for the fullerene molecules with ethylene glycol (EG) as the second phase in the reaction system. The high boiling point of EG (196°C) matches well with that of *o*-DCB (180°C). Hydrophilic ethylene glycol is a good solvent to both 4-vinylpyridine and poly(4-vinylpyridine) with a low solubility for C_{60}. It was applied for full separation of fullerene molecules and 4-vinylpyridine monomers into two different phases. Meanwhile, the solubility of AIBN in *o*-DCB is higher than in ethylene glycol, it was assumed that, by a careful control of the heating region of the *o*-DCB phase, most of free radical initiators generated in *o*-DCB may have an appreciable retention time in the phase and accessible in the reaction with C_{60}.

Without C_{60}, free radical initiators generated in the *o*-DCB phase is able to initiate polymerization of 4-vinylpyridine at the interface, showing increasing cloudiness in the *o*-dichlorobenzene layer during the early stage of reaction. As the molecular weight of poly(4-vinylpyridine) increases with the polarity at a polymerization period of more than 4 hours, progressive transfer of PVPy-2 from the *o*-DCB layer into the EG layer was evident as the former layer returning back to clear and colorless with the layer of ethylene glycol becoming amber in color. The yield of PVPy-2 in the two-phase reaction was found to be 95%.

In the presence of C_{60}, the dark color of the *o*-DCB layer prohibited attempts in monitoring the proceeding of polymerization at the interface. Interestingly, a dramatic reddish brown color switch from the *o*-DCB phase to the EG phase was observed as the reaction advanced, indicating great enhancement of the solubility of C_{60} moieties in polar solvent by incorporation with segments of PVPy. Complete consumption of C_{60} was evident as the *o*-DCB layer becoming colorless. Two concentrations of C_{60} in 5.0 and 10% by weight were applied in the investigation resulting in a yield of poly(4-vinylpyridinated) [60]fullerenes PVPyF-2 and PVPyF-3 as 36 and 15%, respectively, as shown in Table 1. The insoluble dark byproducts (ISF) were found to increase as the concentration of C_{60} increased in the polymerization.

The average content of C_{60} incorporated on poly(4-vinylpyridine) products was estimated by the assumption of the full retention of fullerene in quantity during the AIBN-initiated polymerization of 4-vinylpyridine. Accordingly, the absence of the starting C_{60} molecules or the functionalized fullerene derivatives in the *o*-dichlorobenzene phase, as shown by the lack of color, allowed us to conclude that all C_{60} molecules should exist in either soluble fullerenic poly(4-vinylpyridine) or the insoluble black ISF byproducts. Optical absorption bands of the infrared spectrum (Figure 1e) of these insoluble products correlated well with a composition of mostly fullerenic condensates with only a trace amount of characteristic PVPy moieties, as shown in Figure 1a. Therefore, the weight of C_{60} in copolymers was estimated approximately by subtracting the weight of black byproducts from the total amount of C_{60} used as 5.8, 8.7, and 29.3% by wt. for PVPyF-1, PVPyF-2, and PVPyF-3, respectively. These values may be lower than the actual content of C_{60} in the polymer products due to unaccounted 2-cyanopropyl groups in the composition of ISF.

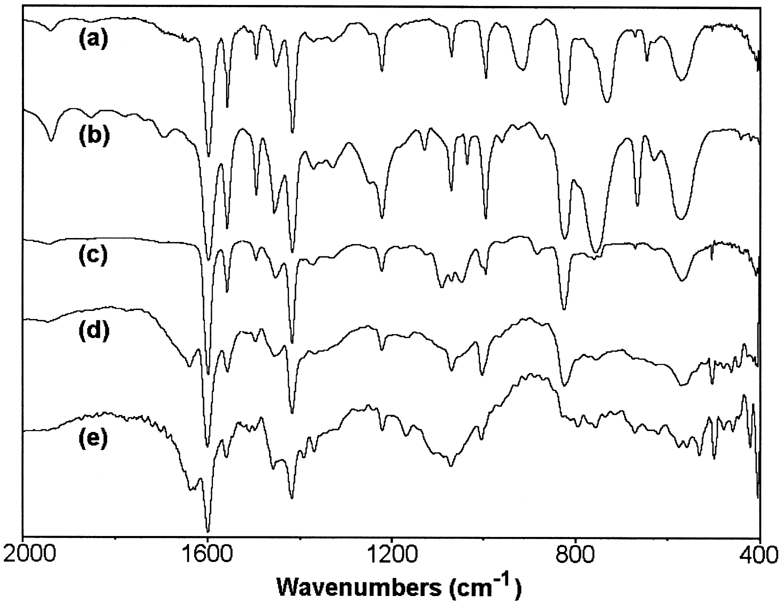

Figure 1. Infrared spectra of: (a) poly(4-vinylpyridine) of PVPy-1; (b) poly(4-vinylpyridinate [60]fullerenes of PVPyF-1; (c) PVPyF-2; (d) PVPyF-; and (e) insoluble byproducts (ISF).

According to the thermogravimetric analysis (TGA) data, a substantial weight loss of poly(4-vinylpyridine) took place at temperatures near 400°C, which is far below the decomposition temperature of C_{60}. An isothermal gravimetric experiment carried out on poly(4-vinylpyridinated) [60]fullerene samples at 400°C under N_2 for a period of 30minutes indicated a sharp weight loss of the material after 15 minutes of thermal treatment, as shown in Figure 2. Elimination of poly(4-vinylpyridine) moieties was confirmed by the infrared spectrum of the thermal residuals at 30 minutes treatment (the insert of Figure 2). The residual mass was utilized for estimation of the C_{60} content in the parent polymers. Since the residuals were believed to be more than the actual quantity of the fullerene component, the calculated content of C_{60} based on the isothermal TGA data should be slightly higher than the real value. Accordingly, the estimated C_{60} content of samples PVPyF-1, PVPyF-2, and PVPyF-3 was found to be 5.3, 11.8, and 38.9% by wt., respectively. These values were deviated from those as 7.3, 7.9, and 17.5% by wt., respectively, obtained by elemental analyses (EA) of the C, H, and N contents for the composition of PVPyF samples. The EA results are generally unreliable due to a high decomposition temperature of the fullerene cage above 700°C. Therefore, the deviation is larger for the polymer sample with high fullerene content. By taking an average value obtained from the isothermal TGA data and the calculated yield of PVPyF polymers vs ISF, we derived the molar ratios of C_{60} to 4-vinylpyridine repeating unit as 1:118, 1:60, and 1:13 for samples of PVPyF-1, PVPyF-2, and PVPyF-3, respectively.

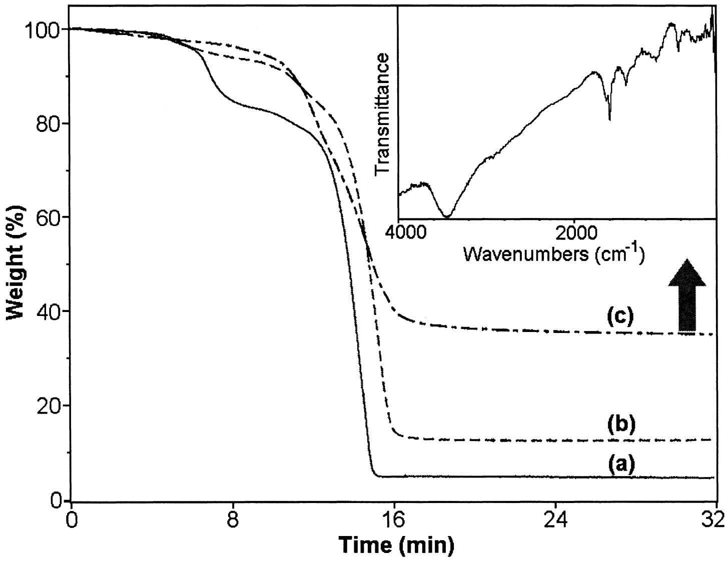

Figure 2. Isothermal gravimetric experiments of: (a) PVPyF-1; (b) PVPyF-2, and; (c) PVPyF-3. The insert displays the infrared spectrum of thermal residuals at 30 minutes treatment.

A star structure of poly(4-vinylpyridino)fullerenes is suggested for PVPyF copolymers of C_{60} and 4-vinylpyridine. Multiple addition of oligo(4-vinylpyridine) chains on the fullerene cluster is plausible owing to the faster reaction rate between intermediate radicals and C_{60} than the propagation rate of oligomer chain-end radicals with monomers. That leads to a much shorter length of each oligo(4-vinylpyridine) arm than that of PVPy-1 and PVPy-2. As an example, the average number of 4-vinylpyridine repeating unit on each oligomer arm of PVPyF-1 should be only a fraction of 118. Evidently, a single glass transition temperature (T_g) of PVPy-1 at 134°C, as detected in its second heating differential scanning calorimetric (DSC) thermogram, was not fully reproducible in all cases of C_{60}-linked macromolecules, PVPyF-n. Change of the DSC thermal profile may be interpreted as due to either the variation in chain length of PVPy arms or the restriction of segmental motions of 4-vinylpyridine sequences nearby the C_{60} cluster. Formation of fullerene clusters is more likely in the two-phase polymerization system than in the homogeneous radical reaction, leading to a higher yield of ISF solids. It was also accompanied with oligo(4-vinylpyridine) addends on the fullerene moiety of PVPyF-2 or PVPyF-3 in a shorter chain length than that of PVPyF-1.

The UV-vis spectra of PVPy-1 and three PVPyF compounds in methanol, after filtration through a 0.2 μm filter, were shown in Figure 3. The tail-up baseline caused by the scattering effect and the absorption of pyridine moieties has dominated the whole spectra at the UV and visible region. In comparison with the spectrum of PVPy-1 (Figure 3a), the presence of C_{60} in the polymer resulted in absorptions as three extra shoulders centered at 230, 278, and 287 nm, which were more identifiable in the first derivative of the spectrum (the insert of Figures 3c

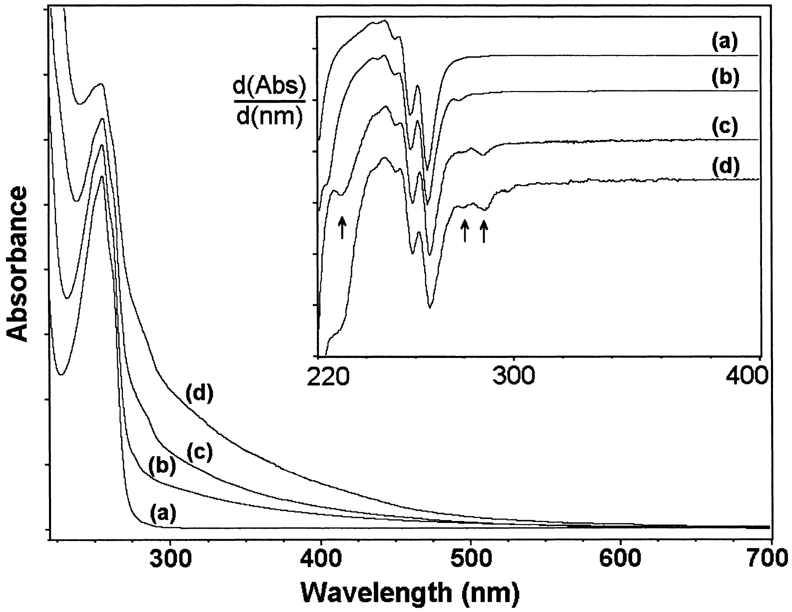

Figure 3. UV-vis spectra of: (a) PVPy-1; (b) PVPyF-1; (c) PVPyF-2 and; (d) PVPyF-3. The insert shows the first derivative of the related spectrum.

and 3d). The scattering baseline contributed from the formation of stable micelles in the polar solvent was reported [8]. In many cases, it is the reason for low detectability of fullerene moieties in many C_{60}-containing polymers by UV-vis optical absorption, even though these polymers are dark in color in either solution or solid state. Meanwhile, in PVPyF analogous copolymers, the interaction between C_{60} and the pyridine group, which contains a lone pair of electrons on heteroatom, was found to be visible. Figure 4 presents the infrared spectra of PVPy-1, PVPyF-n, and the insoluble ISF byproducts at the region corresponding to the optical absorption of pyridine rings. It correlates to characteristic free and polarized pyridine bands at 993 and 1003 cm^{-1}, respectively [18]. In the spectra of PVPy-1 (Figure 4a) and PVPyF-1 (Figure 4b), only the free pyridine absorption band at 993 cm^{-1} was observed. As the C_{60} content increases in samples of PVPyF-2 and PVPyF-3, intensity of the polarized pyridine band centered at 1003 cm^{-1} increases correspondingly, indicating the existence of interaction between the electron-acceptive C_{60} and pyridine moieties in the copolymer.

Fabrication of Multilayer Thin Films by the Electrostatic Layer-by-Layer Deposition Technique

Solubility curves (Figure 5) of PVPy-1, PVPyF-3, poly(thiophene-3-acetic acid) (PTAA), and poly[2-(3-thienyl)ethanol hydroxycarbonyl-methyl urethane]

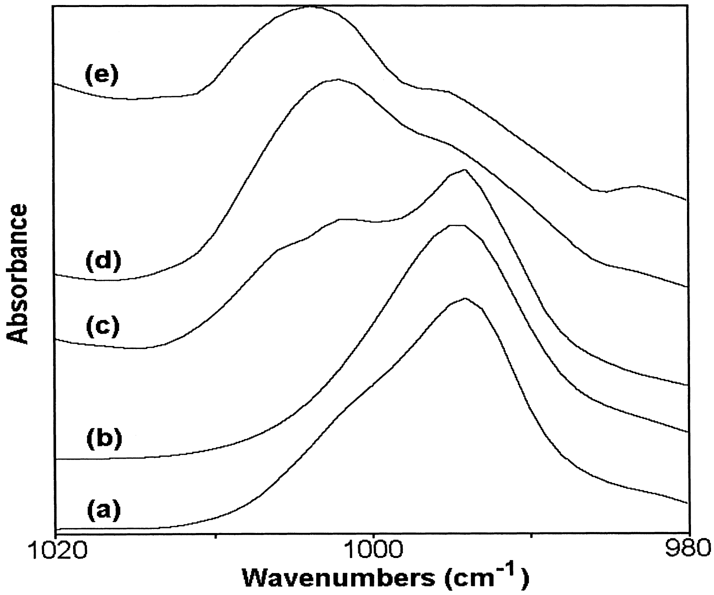

Figure 4. The characteristic infrared absorption bands of pyridine moieties, centered at roughly 993 and 1003 cm^{-1}, of: (a) PVPy-1; (b) PVPyF-1; (c) PVPyF-2; (d) PVPyF-3, and; (e) insoluble fullerenic byproducts (ISF).

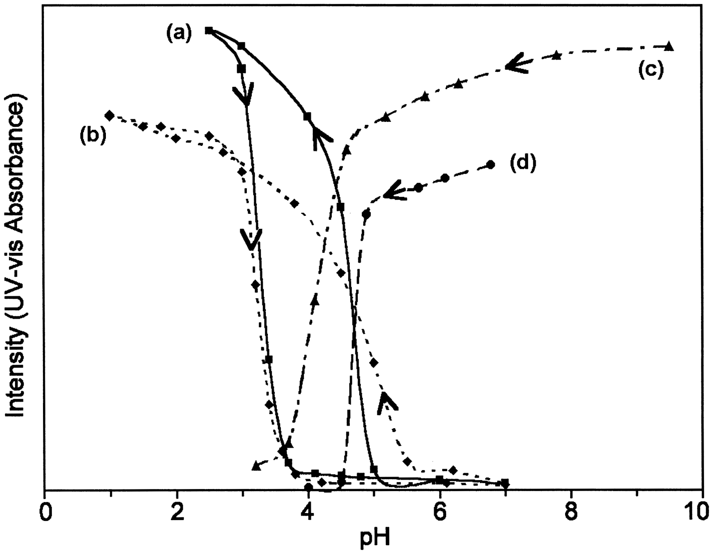

Figure 5. Solubility curves of: (a) PVPy-1; (b) PVPyF-3; (c) poly(thiophene-3-acetic acid) (PTAA), and; (d) poly[2-(3-thienyl)ethanol hydroxycarbonyl-methyl urethane] (H-PURET).

(H-PURET) as polyelectrolytes were measured for their pK_a values and solubility in aqueous solution at various *pH* prior to the electrostatic layer-by-layer deposition of these polyelectrolytes for producing multilayer ultra-thin films. Experimentally, PTAA or H-PURET (10 mg) was dissolved in dil. NaOH (20 ml, *pH* 10). Intensity of the UV-vis absorption of the solution at λ_{max} (410 nm) was monitored while the *pH* of the solution was titrated by slow addition of dil. HCl at *pH* 3.0. At the critical *pH* value, precipitation of the compound occurs. With the removal of precipitated solids via filtration, intensity of the optical absorption of the remaining solution decreases significantly. The result can be correlated to its solubility in aqueous solution at a different *pH* value. We found that the polythiophene derivative of H-PURET with longer urethane side-chains showed good water-solubility at a higher *pH* of 4.7 as compared with that of PTAA at 4.2.

In the cases of PVPy and PVPyF, solubility curves in water were measured in their protonation and deprotonation states. As an example, PVPy-1 or PVPyF-3 (10 mg) was dissolved in chloroform (2.0 ml), followed by the addition of water (20 ml) as the top phase. UV-vis spectrum of the water phase was periodically recorded while its *pH* was reduced by slow addition of dil. HCl at *pH* 3.0. The progressive increase in intensity of the absorption band at λ_{max} 253 nm indicated the corresponding increase in quantity of protonated PVPy-1 or PVPyF-3 diffusing from the chloroform layer into the aqueous solution. The deprotonation spectra were monitored by the increase of *pH* upon addition of dil. NaOH (*pH* 10) to the solution. Note that an additional filtration was employed to remove any solid precipitation from the aqueous solution. Curves of Figure 7a and 7b showed the similar solubility profile of PVPy-1 and PVPyF-3, respectively. That revealed corresponding protonation and deprotonation *pH* value at roughly 3.4 and 4.7, respectively. Therefore, these *pH* values were applied in the subsequent experiments of self-assembly fabrication of multilayers

Three types of substrates were used for the self-assembly fabrication of multilayers. Hydrophilic surface on glass and quartz slides was made by treating the slides with alkaline aqueous alcohol (Chem-Solv, 1.0% by wt) in ultrasonic cleaner for 180 minutes, followed by ultrasonic treatment with water for 30 minutes three times to remove any residual Chem-Solv [19]. The indium-tin-oxide (ITO) coated glass slides were treated with Lysol solution (general household cleaner, 25% by wt.) in ultrasonic cleaner for 30 minutes. After rinsing with water thoroughly, the hydrophilic ITO glass slides were cleaned by ultrasonic treatment in acetone for 30 minutes, followed by washing with isopropyl alcohol in ultrasonic cleaner for 30 minutes. PVPy and PVPyF-n solutions were prepared by dissolving polymers in dil. HCl solution (0.01 N), followed by addition of dil. NaOH solution to *pH* of 3.0. The concentration of 4-vinylpyridine repeating units was adjusted to 2.0 mM. Aqueous solutions containing PTAA or H-PURET were prepared in dil. NaOH at *pH* 10 and then adjusted to *pH* 5.0 or 5.5, respectively, in a concentration of 2.0 mM (based on repeating units).

Self-assembled multilayers (SAMs) were fabricated by alternately dipping the substrates in solution containing polycations and polyanions at room temperature. The dipping time was fixed in 10 minutes for each layer. Between each deposition, rinsing with water was applied to remove unbounded polymers. Each bilayer was found to be in a thickness of 40 Å as measured by ellipsometer.

In Figure 6, a linear superposition of spectra was obtained in the fabrication of five bilayers of polycationic PVPyF-1 and polyanionic PTAA onto the quartz slide. Both deposition layer structures of PVPyF-1^+ and PTAA$^-$ became steady after the second bilayer was deposited. Up to 100 bilayers of alternate PVPyF-1^+ and PTAA$^-$ were also demonstrated as shown in Figure 7. A linear deposition pattern was obtained by monitoring the absorbance at 376 nm associated with the π-π* electronic transitions of the conjugated polythiophene (see the insert). Similar optical absorption properties were obtained by using PTAA$^-$ and other polycationic PVPy-n polymers. These results indicated good stability and reproducibility of the self-assembly multiplayer depositions by this technique and the material system.

In the case of the ITO-coated glass substrate, optical absorption spectra of PVPyF-1^+/PTAA$^-$ SAMs revealed a layer-dependence behavior, as shown in Figure 8. The characteristic optical absorption band centered at 410 nm corresponding to conjugated thiophene moieties of PTAA was absent on films composed of the first 25 bilayers. Instead, the appearance of a new broad absorption band centered at 460-480 nm revealed a *p*-type doping effect of PTAA at the

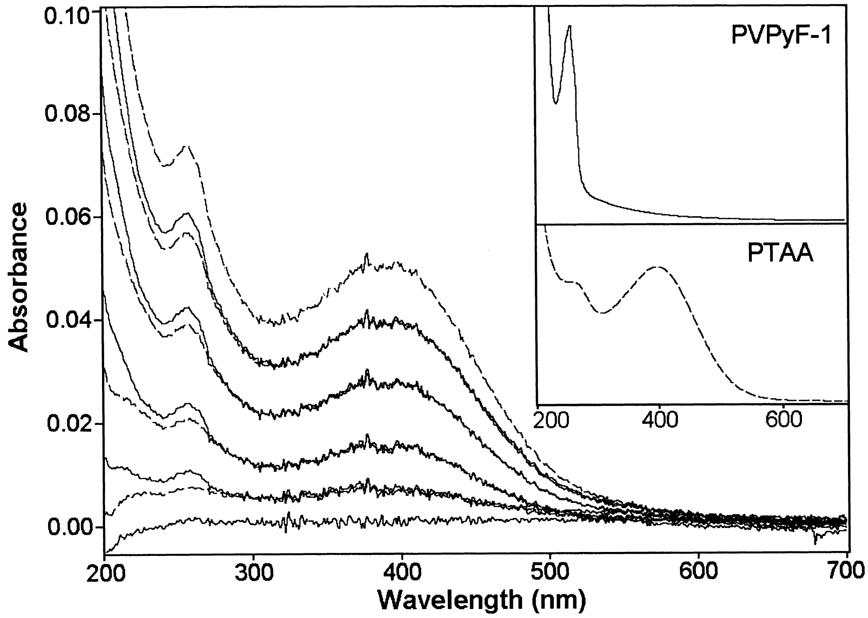

Figure 6. UV-vis spectra of 1 to 5 bilayers of polycationic PVPyF-1 and polyanionic PTAA on quartz slides. Inserts were the parent spectrum of PVPyF-1 and PTAA in aqueous solution at *pH* 3 and 5, respectively.

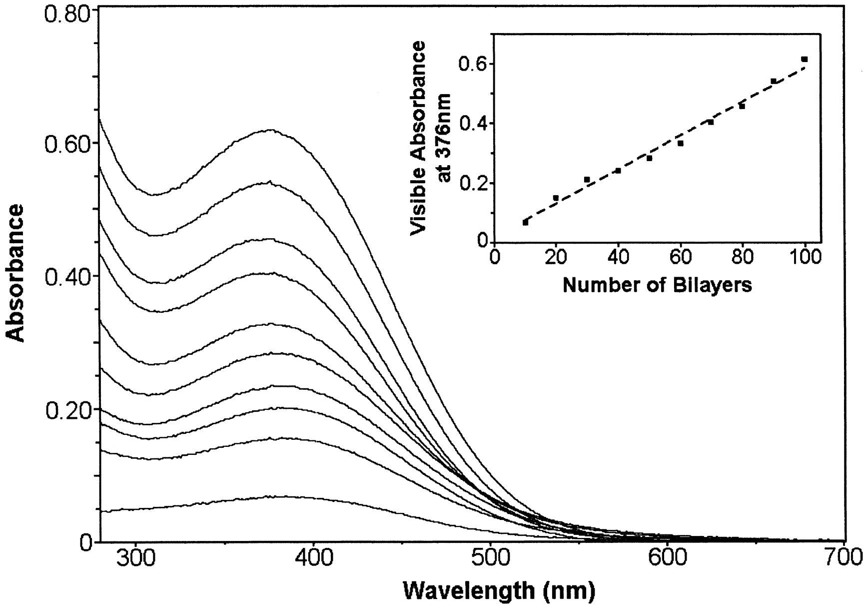

Figure 7. UV-vis spectra of polycationic PVPyF-1 and polyanionic PTAA multilayers (up to 100 bilayers) on quartz slides.

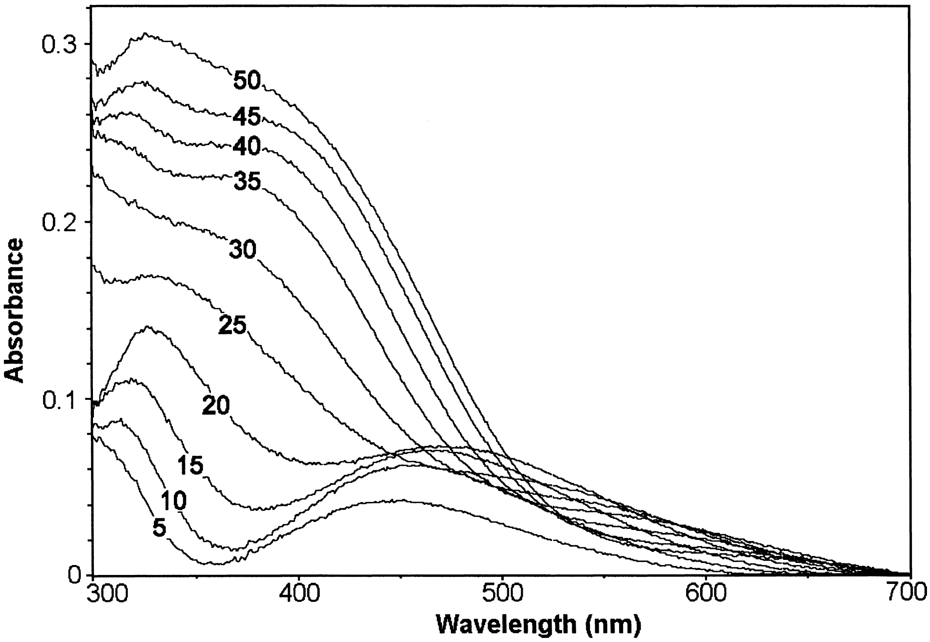

Figure 8. Layer-dependent absorption spectra of PVPyF-1$^+$/PTAA$^-$ multilayers on ITO coated glass slides (from bottom: 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 bilayers).

vicinity of the hole injecting ITO surface in the presence of C_{60}-grafted poly(4-vinylpyridinium) polycation, forming an extended charge delocalization along the polythiophene chain. With the increase of the film thickness above 25 bilayers, the effect of ITO surface activation became less efficient, and shifted the optical absorption band back to a broad peak centered at 400 nm. Similar phenomena were observed in multilayers of polycationic PVPyF-1 and polyanionic H-PURET, but not in devices processed by spin coating or solution casting. This surface interaction effect extends over a range of roughly 320 Å, which is the thickness of 25 bilayers as measured by ellipsometry.

The photovoltaic device was fabricated in a structure of Al/multilayers/ITO. Multilayers used in the device consisted of 50 bilayers of PVPy-2^+/H-PURET$^-$ or PVPyF-3^+/H-PURET$^-$ or 75 bilayers of PVPyF-3^+/H-PURET$^-$. Typical current density-voltage characteristics of devices, either under dark condition or under light irradiation at 488 nm with intensity of 4.1 mW/cm^2, are shown in Figure 9. The forward current was observed when a positive voltage was applied to the ITO electrode with respect to the aluminum electrode. As evident in this figure, these devices have current-rectifying behavior as a diode. The open circuit voltage (V_{OC}) of devices with 50 PVPy-2^+/H-PURET$^-$ or PVPyF-3^+/H-PURET$^-$, and 75 PVPyF-3^+/H-PURET$^-$ bilayers was found to be –0.90, –0.56, and –0.65 volts, respectively. The short circuit current (I_{SC}) of the same devices upon irradiation was found to be 130, 170, and 440 nA/cm^2, respectively.

Figure 10 presents the voltage-dependent photoconductivity (S/cm) of PVPy-2^+/H-PURET$^-$ and PVPyF-3^+/H-PURET$^-$ SAMs samples converted from

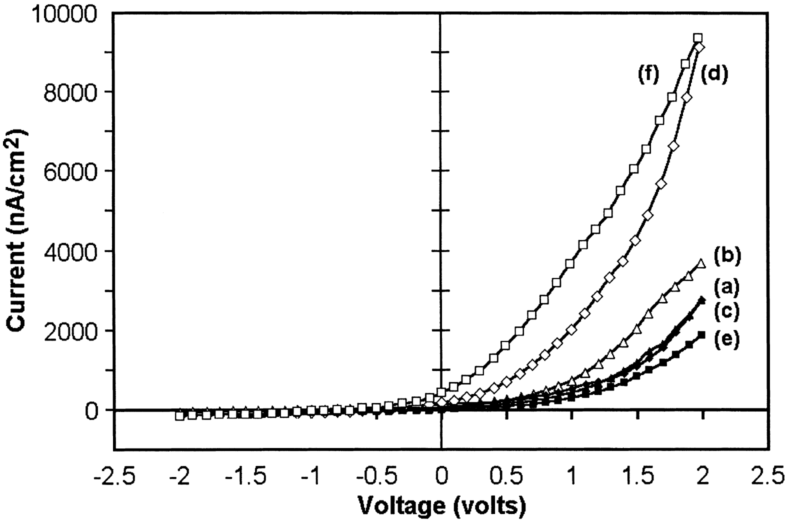

Figure 9. Current-voltage characteristics of PVPy-2^+/H-PURET$^-$ and PVPyF-3^+/H-PURET$^-$ samples either in the dark or under light irradiation at 488 nm with intensity of 4.1 mW/cm^2: (a) dark and (b) light of PVPy-2^+/H-PURET$^-$ with 50 bilayers; (c) dark and (d) light of PVPyF-3^+/H-PURET$^-$ with 50 bilayers; and (e) dark and (f) light of PVPyF-3^+/H-PURET$^-$ with 75 bilayers.

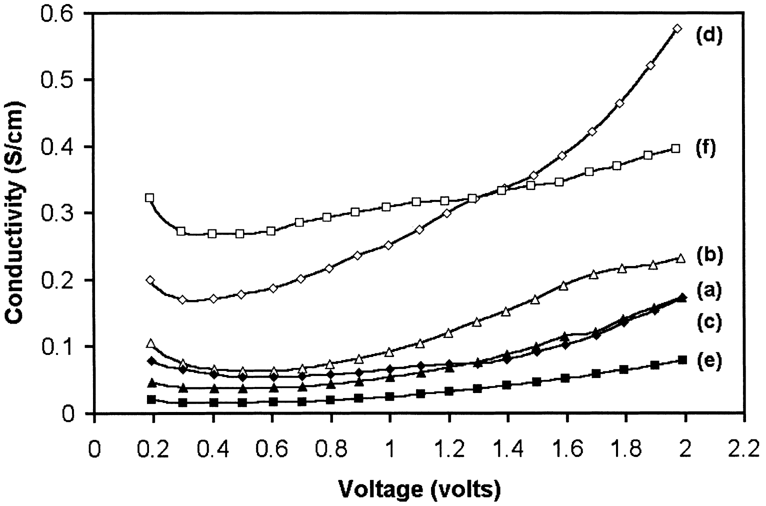

Figure 10. Voltage-dependent photoconductivity (S/cm) of PVPy-2^+/H-PURET$^-$ and PVPyF-3^+/H-PURET$^-$ samples either in the dark or under light irradiation at 488 nm with a laser of 4.1 mW/cm^2: (a) dark and (b) light of PVPy-2^+/H-PURET$^-$ with 50 bilayers; (c) dark and (d) light of PVPyF-3^+/H-PURET$^-$ with 50 bilayers; and (e) dark and (f) light of PVPyF-3^+/H-PURET$^-$ with 75 bilayers.

the I-V characteristics as shown in Figure 9. Under dark conditions, the I-V curves of Figures 10a, 10c, and 10e showed a slightly exponential dependence in the forward bias for all three devices with low measured conductivity along the direction perpendicular to the layer matrix, especially at a low applied voltage. Slightly higher dark conductivity of 50 bilayers samples than the 75 bilayers SAMs sample may have been contributed from the ITO electrode surface activated partial oxidation of polythiophene as discussed earlier. Increase of the layer thickness reduces this effect significantly at the top layers that provide an insulating layer at the top, where leads to an overall higher intrinsic resistance of the sample.

Upon irradiation at 488 nm, the conductivity of all three devices increases by a different degree. Slightly increased conductivity of PVPy-2^+/H-PURET$^-$ SAMs samples in the absence of C_{60} derivatives at an applied high voltage was detected (Figure 10b). An enhanced photoconductive response was observed for the PVPyF-3^+/H-PURET$^-$ samples containing oligo(4-vinylpyridinated) C_{60}-derivatives. For example, the conductivity of 50 bilayer device of PVPyF-3^+/H-PURET$^-$ under irradiation was enhanced more than4–5 times compared to the dark conditions. In the case of 75 bilayer device of PVPyF-3^+/H-PURET$^-$, the conductivity was found to increase from 0.024 to 0.31 S/cm at an applied voltage of 1.0 volt. The increase of photoconductivity was more than one order of magnitude. These results confirmed the generation of steady-state photocurrent and photoconductivity of PVPyF-3^+/PTAA$^-$ and PVPyF-3^+/H-PURET$^-$ under light irradiation. The sign of short-circuit photocurrent was consistent with electrons flowing from Al electrode towards the ITO modified substrate. Intensity of the photocurrent was

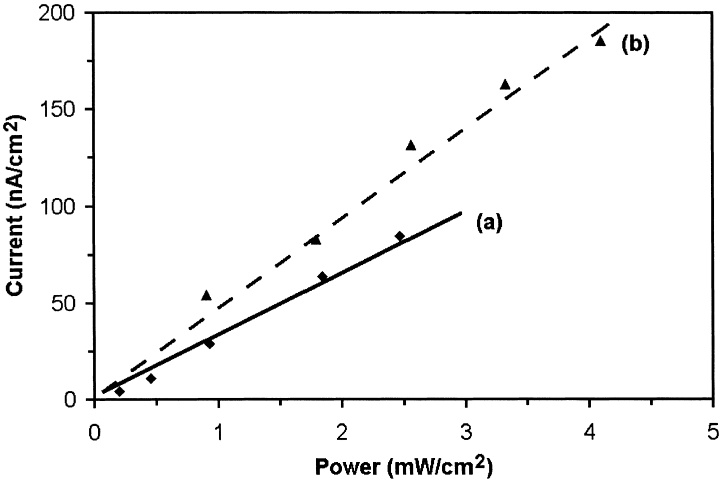

Figure 11. Light intensity-dependent photocurrent of (a) PVPyF-3^+/PTAA$^-$ with 50 bilayers and (b) PVPyF-3^+/H-PURET$^-$ with 50 bilayers.

found to be linearly proportional to the power of the light source in both samples of PVPyF-3^+/PTAA$^-$ and PVPyF-3^+/H-PURET$^-$ SAMs, as shown in Figure 11.

CONCLUSION

A two-phase radical polymerization was applied for the synthesis of fullerene-containing poly(4-vinylpyridine) which were applied as polyelectrolytes in the fabrication of photovoltaic devices. Two-phase radical polymerization allowed efficient exposure of oligo(4-vinylpyridine) radical intermediates to an excess of C_{60} molecules in the *o*-dichlorobenzene phase. Rapid addition rate of these radical intermediates with C_{60} may interrupt the chain propagation of oligo (4-vinylpyridine) radicals in the *o*-DCB phase. That resulted in the products of poly(4-vinylpyridinated) fullerenes (PVPyF) containing poly(4-vinylpyridine) arms in a short arm length and thus a high fullerene content. These electron-withdrawing polyelectrolytes with a high C_{60} content of up to 35% by weight are soluble in organic solvents and water at a low *pH*.

One of the most important characteristics of poly(4-vinylpyridinated) fullerenes is the photoinduced charge separation effect upon irradiation. High efficiency of photoinduced charge transfer between PVPyF samples and polyanionic polythiophene derivatives was demonstrated using the electrostatic layer-by-layer deposition technique with molecular level control in producing self-assembled multilayers. As a result, high response to the increase of photoinduced conductivity was observed on the 75 bilayer device of PVPyF-3^+/H-PURET$^-$ upon irradiation with a 488 nm laser. The photoconductivity was found to increase in more than one order of magnitude from 0.024 to 0.31 S/cm at an applied voltage of 1.0 volt. These results substantiated the generation of steady-state photocurrent and photoconductivity of PVPyF-3^+/PTAA$^-$ and PVPyF-3^+/H-PURET$^-$ SAMs under light irradiation. The sign of short-circuit photocurrent was consistent with electrons flowing from Al electrode towards the ITO modified substrate.

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