The Effect of Cesium Carbonate on PCBM Aggregation in Films

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Surface-pressure isotherms, X-ray reflectivity and X-ray near-total-reflection fluorescence were used to study the properties of 1-(3-methoxy carbonyl)propyl-1-phenyl[6,6]C_{61} (PCBM) that was pre-mixed with cesium carbonate and spread as a film at the air-water interface. The pre-mixed PCBM with cesium carbonate demonstrated a strikingly strong effect on the organization of the film. Whereas films formed from pure PCBM solution were rough due to strong inter-molecular interactions, the films formed from the mixture were much smoother. This indicates that the cesium carbonate moderates the inter-molecular interactions among PCBM molecules, hinting that the cesium diffusion observed in inverted organic photovoltaics and the likely ensuing ionic Cs-PCBM interaction decreases aggregation tendency of PCBM. This implies that the use of cesium salts affects the morphology of the organic layer and consequently improves the efficiency of these devices.

In recent years, organic photovoltaics (OPVs) have been the subject of numerous studies due to their potential as an inexpensive and efficient energy source. Power conversion efficiencies of these devices have improved dramatically, now exceeding 10%. Although numerous structures have been studied, devices based on semiconducting fullerene derivatives as acceptors dominate the research. In particular, PCBM (formally: 1-(3-methoxy carbonyl)propyl-1-phenyl[6,6]C_{61}) is frequently used in the production of OPVs. Since the discovery that cesium carbonate (Cs_{2}CO_{3}) interlayers could improve the efficiency of inverted OPV interlayers of cesium salts such as cesium carbonate, cesium iodide, cesium fluoride, cesium acetate and cesium stearate have become common architectural features of fullerene-based devices. Recent X-ray near-total-reflection fluorescence (XNTRF) studies of devices containing CsI, P3HT (formally: poly(3-hexylthiophene-25-diyl)) and PCBM in a CsI/P3HT:PCBM structure have demonstrated the diffusion of cesium ions into the P3HT:PCBM layer. Secondary ion mass spectroscopy (SIMS) profiles of CsF-containing devices also demonstrated the diffusion of cesium into the P3HT:PCBM layer, and the concentration profile of Cs in this layer qualitatively matches the concentration profile of PCBM in a similar layer, as determined by a different, neutron-reflection study.

These studies suggest a strong interaction between PCBM and cesium ions. This may be due to the fact that PCBM is an acceptor and is very electronegative, whereas cesium is an electropositive ion. Indeed, intercalation studies have previously demonstrated the interaction of cesium with carbon compounds. Although the interaction of cesium and fullerenes may have a significant effect on the efficiency of cesium containing OPVs, no study has demonstrated the nature of the effect cesium ions have on PCBM. Here, we examine the effect of cesium carbonate on PCBM in the form of films at the vapor/water interface. Fullerene compounds - including PCBM - are highly hydrophobic. It is therefore possible to study their behavior by spreading them on the surface of water. Once they are spread, it is possible to manipulate the surface density by compression in a Langmuir trough. Whereas pure C_{60} does not form a single layer at the air water interface due to strong aggregation forces, fullerene derivatives can form monomolecular layers and even exhibit short range in-plane order at the vapor/water interface. In the present study, we examine by X-ray reflectivity and XNTRF techniques the structure of films of PCBM that are spread from chloroform:methanol solutions and compare them with films of a similar solution containing PCBM and Cs_{2}CO_{3} (known to be highly soluble in both water and alcohols). PCBM was purchased from Nano-C and was used as obtained. Chloroform and methanol were purchased from Fisher Scientific. Cs_{2}CO_{3} (99% purity) was purchased from Sigma Aldrich and was used as obtained. To prepare each solution, a stock solution of 10 g/L PCBM in chloroform was produced. 250 µL of PCBM stock solution was then diluted in 10 mL of ~1:1 chloroform:methanol. Finally, 80 mg of Cs_{2}CO_{3} was added to one of the dilute PCBM solutions. The result was a solution of 0.25 g/L PCBM and 8.0 g/L Cs_{2}CO_{3} (along with a control solution of 0.25 g/L PCBM) in 1:1 chloroform:methanol. To perform reflectivity measurements, these solutions were spread on ultrapure water (Millipore, Milli-Q, 18.2 MΩ-cm) using a 100 µL pipette. Here the majority of the Cs_{2}CO_{3} dissolved into the water, whereas the hydrophobic PCBM remained at the surface. To compress and characterize PCBM films, a water subphase was maintained at a constant 20°C in a thermostatic, Teflon Langmuir trough PCBM solutions were spread on the water surface, and the surface pressure (II) was measured using a filter-paper Wilhelmy plate. Since

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the surface concentration of PCBM solution was so dilute before compression, it was expected that Cs$_2$CO$_3$ would rapidly dissolve into the aqueous subphase. According to this hypothesis, without a strong interaction between Cs$_2$CO$_3$ and PCBM, only PCBM would remain at the surface by the time measurements were taken. Prior to compression, 700 µL of pure PCBM solution and 500 µL of PCBM/Cs$_2$CO$_3$ solution were spread. Each solution was allowed to equilibrate for 30 minutes, and was then compressed until a pressure of Π ≈ 9 mN/m was reached. The trough for X-ray measurements was sealed in an air-tight container and water-saturated helium was flushed through the trough. This protected the sample radiation damage, decreased diffuse-scattering, and ensured that the sample did not evaporate over time. Reflectivity measurements were performed on the Ames Laboratory liquid surface spectrometer using an UltraX-18 Rigaku X-ray source (rotating copper anode) operating at 50 kV and 250 mA. A Ge(111) crystal selected the Cu Kα wavelength (λ = 1.54 Å), steering the downstream beam towards the liquid surface at a desired angle of incidence α.

Using a discrete multi-layer model (sometimes known as a multi-box model), electron density (ρ$_e$) profiles of the liquid surface are used to calculate the expected reflectivities from the films. The calculated reflectivity (R) at a given momentum transfer ($Q_z = 4\pi \sin(\alpha_i)/\lambda$) is given by

$$R(Q_z) = R_0(Q_z) e^{-Q_z^2 \sigma^2} \quad (1)$$

where $Q_z$ is along the surface normal (z-axis), $\sigma$ is the surface roughness and $R_0(Q_z)$ is the intrinsic reflectivity of the electron density profile. $R_0(Q_z)$ is calculated using the Paratt’s exact recursive method, assuming a 2-box model for the electron density.$^{21,22}$ Electron density and roughness parameters are calculated using non-linear least-squares curve-fitting methods. For X-ray fluorescence measurements, a Vortex-EX multicathode X-ray energy dispersive detector (EDD) is suspended approximately 2 cm above the liquid surface. Fluorescence intensity is recorded as a function of the incident angle. Estimates of the ion surface densities at the surface have been detailed elsewhere.$^{23}$ Fluorescence below the critical angle of water ($\alpha_c = 0.152^\circ$, the angle where $Q_c ≈ 0.022$ Å$^{-1}$) is almost entirely from ions at the surface (up to a depth of ~ 80 Å near the critical angle), whereas the fluorescence above the critical angle includes contributions from both the surface and the subphase.

Figure 1 shows surface pressure versus PCBM-molecular area isotherms for pure PCBM (black) and PCBM/Cs$_2$CO$_3$ (red) solutions. Both isotherms show that the molecular area is much smaller than expected from a cross section of PCBM estimated at ≈ 100 Å$^2$. This is strong evidence that the films formed on the surface of water consist of multi-layered PCBM molecules. Based on the cross section of a PCBM molecule ($\sim 100$ Å$^2$) we estimate that the average thickness of the film is 10 or 4 layers of PCBM, depending on whether PCBM was spread from pure solvent or was mixed with Cs$_2$CO$_3$, respectively. These isotherms - reproduced on two different Langmuir troughs - suggest that the addition of cesium carbonate has a significant effect on the organization of PCBM films on water surfaces. XR and XNTRF measurements were made at the highest observed pressure for each isotherm.

Normalized X-ray reflectivities ($R/R_F$, where $R_F$ is the Fresnel reflectivity of ideally flat water surface) of PCBM films spread from pure and cesium carbonate solutions are displayed in Figure 2. The measurements were conducted at the highest stable surface pressures achievable for both films, as shown in Figure 1. Qualitative examination of Figure 2A of the pure PCBM shows dramatic fall of $R/R_F$ above $Q_c$, indicating an extremely rough surface. This profile is similar to reflectivities from pure C$_{60}$ molecule at the vapor/water interface.$^{24}$ In contrast, above $Q_c$ the $R/R_F$ from PCBM mixed cesium carbonate is more than an order of magnitude stronger (Figure 2C), indicating a much smoother and more uniform film. Measurements were recorded for the cesium carbonate solution immediately following spreading and compressing and also approximately 2 days later. The solid lines through the measured reflectivity data in Figure 2 are best fit calculations using the model electron densities beside the reflectivity profiles. Best fit parameters and their uncertainties are listed in Table I.

![Figure 1](image.png)

**FIG. 1.** (Color online) Area-pressure isotherms for films of pure PCBM and PCBM/Cs$_2$CO$_3$ at the vapor/water interface as indicated. Molecular area is calculated per PCBM molecule for both curves. XR and XNTRF analysis was performed at the highest surface pressure (Π) of each isotherm. Uncertainty in Π is approximately ±1 mN/m.
observed in the PCBM/Cs$_2$CO$_3$ film. Measurements were performed both on the PCBM/Cs$_2$CO$_3$ solution and on a bulk, 9×10$^{-5}$M Cs$_2$CO$_3$ subphase. Although cesium fluorescence barely exceeds the detection limit of the EDD, the difference between the integrated surface signal (Figure 3 of the subphase and the solution is still pronounced. Note here that the fluorescence intensity of the subphase is divided by two, since the expected bulk concentration of Cs$_2$CO$_3$ from the PCBM solution is only 4×10$^{-5}$M (assuming all the Cs$_2$CO$_3$ of the spread mixture is dissolved in water). This result supports the finding of cesium in the PCBM layer although in a very small amount, namely much lower than Cs per PCBM, consistent with the X-ray reflectivity analysis.

X-ray reflectivity results indicate that the introduction of Cs$_2$CO$_3$ into a solution of PCBM in 1:1 chloroform:methanol drastically alters the morphology of PCBM films that are subsequently formed at the vapor/water interface. In particular, the films that are formed with the Cs$_2$CO$_3$ are smoother, with significantly lower roughness than films of pure PCBM. This indicates that the cesium carbonate lowers the aggregation forces between PCBM molecules, since these forces would tend to make the film highly nonuniform. This result supports the hypothesis that cesium migration in organic photovoltaics is caused by cesium-PCBM interactions. Based on the relatively low fluorescence intensity of cesium, we estimate that the concentration of cesium within the PCBM film was relatively low - far lower than 1 cesium ion per PCBM molecule - and therefore believe that this system is a reasonable proxy for the behavior of PCBM in OPVs. The addition of cesium salts may therefore

![Figure 2](image)

**FIG. 2.** (Color online) Reflectivity (left) and electron density (right) profiles for (A and B) pure PCBM on water, (C and D) PCBM/Cs$_2$CO$_3$ on water immediately after spreading, and (E and F) PCBM/Cs$_2$CO$_3$ on water 2 days after spreading. The electron densities were fitted using 2-box models. Though not an ideal model, the fitting for A) demonstrates the roughness of the PCBM film. The high electron density for D) demonstrates the presence of cesium at the surface.

| Parameters | $\chi^2$ | $\rho_e$ | $\rho_c$ | $\Delta^1$ | $\Delta^2$ | $\sigma$ |
|------------|---------|---------|---------|----------|----------|--------|
| Pure       | 9.82    | 0.23±0.03 | 0.29±0.03 | 41±5     | 25±6     | 4.6±2  |
| Cs$_2$CO$_3$ | 4.82    | 0.48±0.02 | 0.39±0.01 | 38±4     | 20±4     | 4.4±2  |
| Cs$_2$CO$_3$ (Aged) | 2.67    | 0.33±0.01 | 0.37±0.01 | 44±5     | 25±5     | 5.4±2  |

### Table I. Best fit parameters (and uncertainties) for reflectivity data from solutions of PCBM. $\rho_e$ is the electron density ($\text{Å}^{-3}$) of a layer, $\Delta$ is the thickness ($\text{Å}$) of a layer, $\sigma$ (in $\text{Å}$) is the roughness (assumed to be constant for each interface) and $\chi^2$ is a measure of the quality of fit, as described in the Materials and Methods section. Superscripts 1 and 2 denote (for $\rho_e$ and $\Delta$ values) the box which each parameter represents. Box 1 is the layer closest to air, and box 2 is the layer closest to water.

The electron density of the PCBM/Cs$_2$CO$_3$ solution prior to aging ($\rho_e = 0.48\text{Å}^{-3}$) exceeds both the observed and the theoretical electron density of closely packed PCBM, suggesting the presence of relatively small amount of cesium in the multilayer. Over time, the electron density of the film decreases slightly accompanied by increased roughness, indicating instability of the film with time.

Although cesium fluorescence was too low to make definitive conclusions, enhancement of cesium peaks was
have a significant effect on the aggregation and electronic structure of PCBM within OPVs, which may in turn affect device performance. Similar experiments were attempted on other cesium salt solutions, but most cesium salts could not dissolve in the organic solvents used to dissolve PCBM. Salts containing carbonate ions were also tested, but no suitably soluble carbonate was found. The salts could not dissolve in the organic solvents used to disperse PCBM. Salts containing carbonate ions were also attempted on other cesium or carbonate containing salts that dissolved in PCBM solutions. A qualitative representation of the difference between A) Pure PCBM on water and B) PCBM/Cs$_2$CO$_3$ solution on water. The films are much smoother when spread from the mixed solution.

We hypothesize that the addition of Cs$_2$CO$_3$ to OPVs is related to the miscibility of P3HT and PCBM thereby affecting device morphology. Regions of each phase must be large enough so they can percolate to allow holes and electrons to reach the electrodes before recombining and yet small enough domains are necessary to allow a large interfacial area between the two phases, maximizing the dissociation of excitons. Maximizing efficiency means finding an appropriately optimized middle-ground. Thus, the inclusion of Cs in the vicinity of PCBM may create an optimized network of P3HT/PCBM by lowering the strong aggregation forces between PCBM molecules.

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