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Full Paper

Unexpected Equilibrium Ionic Distribution in Cyanine / C₆₀ Heterojunctions

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The equilibrium ionic distribution in cyanine donor – fullerene acceptor bilayer systems was investigated using Rutherford backscattering spectroscopy (RBS), elastic recoil detection analysis (ERDA) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Simultaneously, the potential profile inside the C₆₀ layer was followed by Kelvin probe force microscopy (KPFM). Experimental verifications were obtained by using different device architectures, different mobile counter ions and alternative acceptor layers. The unexpected constant iodide profile inside C₆₀ and the potential shift close to the donor – acceptor interface could be explained by an exchange of electrons and ions from acceptor to donor and vice versa. The proposed model explaining all of the observed experimental findings is supported by a thermodynamic model.

1. Introduction

Solid state semiconductor devices gain most of their functionality from the electronic properties at the interface between different materials. A semiconductor diode is made from a single p-n junction, where a p-doped material is joined with an n-doped material. Electronic characteristics of the entire device depend on the energetics at the interface.

In the p-n junction, charge transfer across the interface and the resulting depletion zones lead to large vacuum level shifts (band bending). Vacuum level shifts can also be the result of dipoles, orientation of organic molecules at interfaces^[1] or the diffusion of organic and inorganic compounds across interfaces.^[2,3] Moreover, p-n junctions can also be obtained by in-situ electrochemical doping. In mixed ionic and electronic semiconductors, redistribution of ions under applied bias and injection of charges eventually leads to p- and n-doped regions. This principle is applied in light-emitting electrochemical cells (LECs) where ionic charges are a fundamental requirement for device operation. Their distribution during operation has been analyzed by ToF-SIMS as it is crucial to fully understand the LEC operation

principle.^[4,5] Ionic charge carriers are not only important in LECs but can also alter the device performance in organic solar cells (OSCs).^[6-8]

In these cases, the effect of ion diffusion on the electronic landscape is undisputed. A direct correlation between ion diffusion and electronic properties at interfaces has however mostly been the subject of theoretical investigations while experimental data directly connecting both are scarce. Mapping the ions inside the device is important because electronic and ionic charge carriers may not be distinguishable by methods probing the electronic band structure.

Diffusion of ions across an interface is difficult to detect as the changes in ion distribution are marginal, especially in unbiased samples. ToF-SIMS and XPS depth profiling are elemental and molecular depth profiling techniques that are widely applied in organic electronics.^[9-11]

Despite the comprehensive information that could be obtained, it has to be noted that these methods are not always straightforward to apply and that results have to be interpreted carefully. Film roughness due to a specific fabrication technique or induced by sputtering to obtain depth resolution can lead to misleading artefacts of material that apparently diffused through the whole sample.^[10] Movements of small ions or atoms that are induced by the sputtering beam or because of sample charging are other causes of measurement artefacts that have occasionally been observed in literature.^[4] Ion beam techniques, such as RBS and ERDA, have rarely been applied in semiconducting organic materials. They have been used for specific experimental configurations with distinct advantages over the former techniques as they bypass problems inherently connected to depth profiling based on sputtering techniques. However, artefacts, such as chemical modifications, have been reported for ion beam techniques.^[12,13]

The experimental determination of energy band diagrams in electronic device structures can be achieved with a number of techniques and this has resulted in a fundamental understanding of electronic processes at interfaces.^[14] One method that has been applied successfully to determining Fermi levels and band bending at interfaces is the Kelvin probe technique.^[15,16]

A possible model to describe the observed effects theoretically is the Smoluchowski diffusion equation and the connected Poisson-Boltzmann equation, describing ion diffusion under the influence of the field of a charged interface.^[17] The same formalism can be applied to a bilayer system in which a mobile counter ion can diffuse to the adjacent layer. Diffusion forces the ion to enter the neighboring layer, whereas the Coulomb binding between cation and anion acts as the retention mechanism. The expected diffusion profile drops close to the interface. The parameter that describes the extension of the ions into the neighboring layer is the Debye length which is typically in the range of 10 nm.

In an ionic system with electronic charge carriers (semiconductors), the situation is much more complex but may be described using a standard semiconductor model for both electronic charges and ions. The carrier density is then expressed in terms of the chemical potential for electrons and ions^[18] and is subject to different driving forces, namely chemical and charge concentration gradients. The concentration of dopants and defects is of utmost importance as this determines the number of majority and minority carriers.

In the present paper, the ion diffusion profile and the electronic band structure in a thin fullerene C₆₀ layer evaporated on top of a thin layer of a cyanine salt, Cy3⁺-X⁻ has been scrutinized. I was chosen as the charge compensating counter anion (X⁻) in the cyanine layer to take advantage of the strong dependence of the kinematic factor and scattering cross section with mass in ion beam depth profiling techniques. Band bending was followed with Scanning-Kelvin probe force microscopy. We observed an unexpected ion diffusion profile and unexpected band bending which can be understood from a thermodynamic model connecting electrochemical potentials of electrons and ions and including defects and impurities acting as donors in the C₆₀ layer.

2. Results and Discussions

The equilibrium iodine distribution in bilayers of 20 - 40 nm thick layers of Cy3-I and 100 nm thick layers of C₆₀ was determined using RBS (see **Figure 1**). As the beam-sample interaction used in this technique relies on nuclear elastic scattering cross sections, the charge configuration of the element cannot be determined. Therefore, I is used instead of I⁻ when discussing RBS results. Figure 1 shows the I profiles for normal (b) and inverted (c) structures. For both architectures, the I profile was constant over the 100 nm thick C₆₀ layer and extends to the sample surface and the substrate interface in normal and inverted structures, respectively. The concentration was approximately 0.1-0.2 at% inside the C₆₀ layer. The obtained profile is in contradiction to the expected result based on the Poisson-Boltzmann distribution.

The potential trend over the C₆₀ film was followed by performing KPFM measurements on ITO / Cy3-I / C₆₀ samples with varying C₆₀ layer thickness (see **Figure 2**). The surface potential as a function of C₆₀ layer thickness exhibited a significant change from -5 eV to -4.6 eV for films thinner than 10 nm. For thicker films, this value was constant at *circa* -4.6 eV which is in agreement with the Fermi level of pure C₆₀.^[19] The bending behavior close to the cyanine / C₆₀ interface can be interpreted as a surface potential modification due to ion rearrangement, an electronic energy band bending, or a combination thereof. These hypotheses were tested by investigating the surface potential trend of C₆₀ directly evaporated onto ITO. Similar to the bilayer system, bending was observed for thin C₆₀ films, whereas for thicknesses above 20 nm the value approached the Fermi level energy reported in the literature (see SI). This Fermi level pinning observed for C₆₀ on ITO demonstrated its ability to adapt to different adjacent materials by electronic rearrangement. It should be noted that Cy3-I did not exhibit a surface potential change with increasing thickness if coated on ITO. The measured value immediately reached the bulk value of -5 eV (see SI). Thus we conclude that the KPFM measurement on the bilayer system reflected the electronic energy band

situation inside the device or more precisely, the band bending of C_{60} close to the interface with Cy3-I. In addition, the direction of the potential shift observed in KPFM experiments supported a mechanism that is different from plain ion diffusion. The shift at the interface is such that the dye is charged negatively with respect to the C_{60} layer, thus a charging effect opposite to anion diffusion into C_{60} is observed. This can be explained with a standard semiconductor model without taking the effect of ions into account. The Fermi level in C_{60} and Cy3-I were measured using KPFM to be -4.6 and -5 eV, respectively. If these materials are brought together in a bilayer device, the energy bands in the C_{60} will bend to maintain a constant Fermi level throughout the system.

Experimental evidence that the observed profile was not the result of a fabrication or a measurement artifact was evident. For example, if the C_{60} layer were not continuous or had a high roughness, the resulting profile could have been a misleading artefact of beam ions hitting the cyanine surface directly. The same would have been true if the RBS measurement itself induced cracks in C_{60} . However, both explanations for the possible observation of a non-continuous, inhomogeneous C_{60} layer could be ruled out. Firstly, both normal and inverted structures showed the same profile and the substrate edge was well defined for both samples. A considerable roughness would have been seen as a smearing out of the Si signal originating from the substrate. Secondly, the normal structure was mimicked by replacing Cy3-I by NaI salt mixed into a polymer matrix (see **Figure 3**).

As a beam induced C_{60} damage would have happened independently of the underlying layer, the profiles in Figure 1b and Figure 3 would have been similar. However, for the NaI in polymer / C_{60} sample the I signal originated only from the polymer layer and no diffusion into C_{60} was observed. Thirdly, elemental profiles for the Cy3-I / C_{60} bilayer structure were additionally obtained by ERDA. This method allows the distribution of light elements to be determined. The N signal can be directly linked to the occurrence of $Cy3^+$. Although it

partially overlapped with the ^{13}C band, there was clearly no N detectable at the C_{60} surface (Figure 4).

Furthermore, a quantitative mass spectrum was extracted from ERDA data for the top half of the C_{60} layer, which indicated that the N concentration at the surface was below 0.04 at%. Thus it can be concluded from these observations that an increased roughness and/or porous C_{60} layer induced by the fabrication procedure or during measurement did not lead to the observed I profile in the Cy3-I / C_{60} bilayer systems observed by RBS.

Other experimental anomalies that may lead to the observed profile were a charging effect at the sample surface or a displacement of I due to the probing ion beam. In both cases, the I movement would have occurred during the measurement and only arise because of the chosen RBS technique. However, both can be excluded as the origin of the observed I profile. The same profile was observed for both normal and inverted device architectures. If, the measurement had induced a positive charging of the surface, the I would have been attracted to C_{60} in the normal configuration but rejected in the inverted structure. Similarly, the I atoms would have been pushed towards the substrate in both architectures. Consequently they would not have been found close to the sample surface, as seen in the normal device architecture, if ion beam induced movement had taken place. Charging, as well as ion beam induced migration, would also have occurred for the alternative sample NaI salt in polymer matrix / C_{60} . However, no I signal was detected in the C_{60} layer of this sample. Therefore, experimental defects related to the chosen RBS technique can be excluded as the origin of the observed I diffusion profile.

An alternative explanation for the Γ profile failing to following the predictions of Poisson-Boltzmann theory could be that the positive chromophore Cy3^+ is moving together with the Γ^- . Such a scenario would explain the observed profile because the distribution of the neutral Cy3-I pair is only governed by diffusion but not by Coulombic retention. Although this hypothesis is very unlikely because of the large size of the Cy3^+ ion it could also be excluded

experimentally by following the N signal in 2D-ERDA (Figure 4). There was no significant quantity of N detected throughout the C₆₀ (below 0.04 at% at the surface). As the N signal is a selective marker for the positive chromophore Cy3⁺, a co-diffusion of cation and anion can be excluded. A further explanation could be that the I signal is not coming from the I⁻ ion but from neutral I₂. If this molecule was formed inside the C₆₀, it could also move freely to the sample surface because it is no longer charged and therefore not governed by Coulomb forces. In order to investigate this possibility and separate I⁻ from I₂ signal, ToF-SIMS measurements were performed. The analysis of the sample surface revealed that the signals related to I for samples with C₆₀ thickness of more than 10 nm were mainly composed of I⁻, whereas the I₂⁺ counts were close to the background obtained when measuring a pure C₆₀ film (data not shown). However, as the ToF-SIMS measurements lack quantitative certainty due to surface roughness, unknown secondary ion yields and statistical scatter of results for different points on the same sample more evidence was needed to exclude I₂ formation as the main reason for the diffusion profile. I₂ formation could not be excluded as the ability of I⁻ to reduce photoexcited cyanines has been shown.^[20] Therefore, the redox-inert charge compensating anions ClO₄⁻ or PF₆⁻ were included into this study. Samples with the structure Cy3-PF₆ / C₆₀ and Cy3-ClO₄ / C₆₀ were prepared and the counter ion profile was monitored by following the F and the Cl profiles, respectively. Analyzing these samples using RBS was difficult as the masses of F and Cl are close to the other elements present and/or there are different isotopes that overlap. Using ERDA allowed these difficulties to be circumvented with the drawback that the elemental profiles are less quantitative. The results for both samples showed a profile over the whole range of C₆₀ with a non-zero value at the surface (see SI). The similarity of the I⁻, ClO₄⁻ and PF₆⁻ profiles all extending over the whole 100 nm thick C₆₀ layer demonstrated the wide validity of the profiles obtained for the cyanine / C₆₀ bilayer systems, and indicates that the counter ions are not oxidized by the excited dye.

To summarize, fabrication and experimental anomalies, anion-cation co-diffusion, and redox reactivity of the counter ion towards the dye can be excluded as explanations for the I profiles shown in Figure 1. Nevertheless, the dramatic deviation from the expected Poisson-Boltzmann distribution for charged particles indicated that the ionic charge of Γ^- is locally compensated in some way. An indication that electronic charge played a major role in the observed ion diffusion was given by the control experiment performed with the NaI in polymer / C_{60} system.

We propose a mechanism that is in agreement with all the measurements presented so far and describes the fundamental requirements for the observed ion diffusion. **Figure 5** schematically summarizes HOMO, LUMO and Fermi level at the dye/ C_{60} interface. Additionally, a simple thermodynamic model has been described to support the proposed mechanism.

The Fermi level alignment at the interface resulted in a strong potential shift caused by electrons transferred to the Cy3-I layer. It is assumed that the binding energy between $Cy3^+$ and Γ^- is low enough to allow some degree of dissociation. The associated electric field close to the Cy3-I / C_{60} interface may have facilitated the dissociation, but it was not necessarily a condition for the ionic dissociation. Consequently, the free Γ^- ions entered the adjacent C_{60} layer. Diffusion caused the Γ^- ions to move away from the interface into the C_{60} layer. Unexpectedly, continuing ion diffusion did not appear to be inhibited by the build-up of an internal electrical field. The almost constant counter ion concentration throughout the entire C_{60} layer and the final potential distribution reflected in the KPFM data shown in Figure 2, indicated that negatively charged Γ^- was locally compensated or oxidizes / reacts to form a neutral species. To a limited amount, free electrons were present through the n-type semiconductor character of C_{60} . These electrons would have drifted out of the C_{60} layer and have been replaced by Γ^- . For intrinsic C_{60} , a work function of 4.83 eV has been reported, with a difference of 0.89 eV to the LUMO level.^[21] The low activation energy of 0.1-0.3 eV is

attributed to intrinsic and oxygen related defects.^[22] However, even in highly doped C₆₀, doping densities are in the range of 10¹⁹ cm⁻³.^[21] The doping density of the C₆₀ layer described here can be estimated from the observed energy level shifts of C₆₀ on ITO. For a Schottky junction the number of charge carriers N_D in the depletion zone w can be calculated using:

$$N_D = \frac{2\varepsilon\varepsilon_0\Delta\varphi}{ew^2} \quad (1)$$

where ε is the relative permittivity of C₆₀ (assumed to be 4^[23]), $\Delta\varphi$ is the potential difference inside C₆₀ and e is the elementary charge. Using the numbers from Figure S1, this amounts to approximately $2 \cdot 10^{17}$ cm⁻³, which is much lower than the number of counter ions in the C₆₀ (10²⁰ cm⁻³, from Figure 1). In addition, transferring electrons from C₆₀ to the dye decreases the Fermi level in C₆₀ and increases it in the dye. This decreases the potential difference between the two layers which initiates ion diffusion. This apparent discrepancy could be resolved when one assumes that there is n-type doping of C₆₀ by I⁻. Efficient n-type doping of C₆₀ with tetrabutylammonium salts with the counter ions F⁻, OH⁻, AcO⁻, Br⁻ and I⁻ in solution and the solid state has been reported in the literature.^[24,25] If this mechanism can be applied here, electron transfer from I⁻ ions into the C₆₀ layer would generate a C₆₀ anion radical and a neutral iodide radical. Compared to that found by Li *et al.*,^[24,25] doping is more efficient as the counter ion is already dissociated. The electron from the doped C₆₀ can in turn drift towards the dye layer and local charge neutrality is re-established.

To verify the proposed model, the Fermi levels at the heterojunction were experimentally matched more closely. Thus an alternative adjacent layer to Cy3-I with a considerably lower Fermi energy compared to C₆₀ was required. Fluorination is a common procedure to lower the LUMO level of fullerenes. Therefore, C₆₀F₄₈ with LUMO energy of -5.2 eV was used as the new acceptor layer.^[26] If the band bending did not occur because of the new energy level situation the I⁻ movement into the adjacent layer would not be allowed anymore. Besides a low LUMO level, C₆₀F₄₈ has less electron-providing defects than C₆₀ that could compensate

ion diffusion. Consequently, the Γ profile in the Cy3-I / C₆₀F₄₈ device should be restricted to the cyanine layer. The measured RBS profile did indeed show no diffusion of I inside the new acceptor (**Figure 6**). This provides more experimental evidence that the proposed model explains the underlying mechanism of ionic diffusion in the bilayer system.

For a further understanding of the observed effect, a thermodynamic model was considered, which was solved for mass and charge balance equations. The following assumptions were made: positive ions (dye chromophore) were confined to the dye layer, electrons could transfer to the dye phase from C₆₀ (Fermi level alignment), and concentrations are relatively low such that ideal mixing entropy applies. In the first step we did not consider the chemical potential of electrons in C₆₀ and dye but only used the experimentally accessible quantities φ^{dye} , φ^{C60} (Fermi levels inside the two layers). An extension to the model also including electrons is presented in the supporting information.

The chemical potential, including electrostatic contributions, was used to calculate the partitioning of the ions between the two phases. The chemical potential μ_I^{dye} for the negative ions from the dye phase is composed of an electrostatic contribution and a translational (or mixing) entropy term,

$$\mu_I^{dye} = k_B T \ln \left(\frac{n_I^{dye}}{n_I^{(0)}} \right) - e\varphi^{dye} \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature, n_I^{dye} is the ion concentration inside the dye layer in contact with C₆₀, $n_I^{(0)}$ is the initial ion concentration, e is the electronic charge and φ^{dye} is the Fermi level inside the dye film. Likewise, the chemical potential of the ions in the C₆₀ phase μ_I^{C60} is composed of the same translational entropy and electrostatic term, but also comprises a transfer (free) energy ΔE to bring an ion from the dye to the C₆₀ including the free energy cost of ionic dissociation.

$$\mu_I^{C60} = k_B T \ln \left(\frac{n_I^{C60}}{n_I^{(0)}} \right) - e\varphi^{C60} + \Delta E. \quad (3)$$

In case of thermodynamic equilibrium, the chemical potential of an ion in the dye phase should equal the chemical potential of an ion in the C₆₀ phase.

$$\mu_I^{C60} = \mu_I^{dye} \quad (4)$$

The ions satisfy conservation of mass, i.e.

$$L^{C60} n_I^{C60} + L^{dye} n_I^{dye} = L^{dye} n_I^{(0)}, \quad (5)$$

with L^{C60} and L^{dye} being the thickness of the C₆₀ and the dye layer, respectively. Inserting (2) and (3) into (4) and using (5) results in:

$$\frac{n_I^{C60}}{n_I^{(0)}} = \frac{1}{L^{C60}/L^{dye} + e^{-(e\Delta\phi - \Delta E)/kT}} \quad (6)$$

where $\Delta\phi = \phi^{C60} - \phi^{dye}$ represents the electrostatic potential difference between C₆₀ and dye.

Equation (6) gives the conditions that are necessary to make ion diffusion into C₆₀ possible.

When the potential difference $\Delta\phi$ between C₆₀ and dye becomes comparable to the transfer free-energy ΔE , ion diffusion is favorable. In the case of Cy3-I / C₆₀ bilayers, Fermi level alignment at the dye / C₆₀ interface creates this potential difference. If ΔE remains large compared to the potential difference between C₆₀ and dye $\Delta\phi$, ion diffusion is not feasible. This was the case in the control samples where no additional electrical potential could build up.

From the experimental data, we can extract values for $n_I^{C60} / n_I^{(0)}$ and $\Delta\phi$. This allows an estimate of the value for ΔE , which was high enough to prevent ion diffusion under “normal” conditions i.e. no positive $\Delta\phi$ (see Table 1). The similarity of the numbers for ΔE for the two configurations can be understood as a validation of the model. The model connects the ratio of ions in C₆₀ to total ion concentration $n_I^{C60} / n_I^{(0)}$ to the ratio of C₆₀ to dye layer thickness L^{C60} / L^{dye} . The interpretation of equation (6) becomes straightforward when looking at some extreme cases. Let us set $L^{C60} = L^{dye}$. At $e\Delta\phi = \Delta E$ electrostatic interactions do not play a role and equation (6) becomes $n_I^{C60} = 0.5 n_I^{(0)}$, which means the ions are distributed evenly

throughout the bilayer. Under a strictly entropic driving force, ions would diffuse towards the region of lower ion concentration until the concentration gradient has vanished.

In the case that the energy cost ΔE to bring an ion into C_{60} is much larger than the potential difference, $e\Delta\phi \ll \Delta E$, the exponential term in the denominator becomes large and n_I^{C60} goes towards 0. For the opposite case, $e\Delta\phi \gg \Delta E$, equation (6) becomes $n_I^{C60} = n_I^{(0)}$, which means all ions diffuse into the C_{60} layer. At very large energy differences between $e\Delta\phi$ and ΔE , the entropy term is overruled and the energy term determines if the ions remain in the dye layer or fully move into C_{60} .

In a realistic experimental situation, the ion concentration will be determined by both, entropy and energy terms. In the case of Cy3-I / C_{60} bilayers, Fermi level alignment at the dye / C_{60} interface creates the potential difference $\Delta\phi$, which we determined experimentally. Similarly, the ratio of $n_I^{C60} / n_I^{(0)}$ can be extracted from our data. ΔE is an unknown quantity, but can now be calculated with the help of equation (6) (Table 1). We find a value of $\Delta E = 0.42$ eV for the normal device structure and $\Delta E = 0.44$ eV for the inverted device geometry. The similarity of the numbers for ΔE for the two configurations with different thickness ratios can be understood as a first validation for the model. In the control samples (Figure 3 and 6) no electrical potential $\Delta\phi$ was building up and ion diffusion remains negligible. The course of $n_I^{C60} / n_I^{(0)}$ as a function of $(e\Delta\phi - \Delta E)$ (equation 6) is also shown in the Supplementary Figure S3, visualizing the discussion from above.

3. Conclusion

Ion beam techniques have been shown to be suitable methods to probe the ionic distribution in organic thin film heterostructures when heavy “model counter ions” are used.

Unbiased ion diffusion into a C_{60} film that was evaporated on top of a cyanine salt shows diffusion of the counter ion into C_{60} up to the saturation level throughout the entire film. The

intuitive picture that ions redistribute to reach thermodynamic equilibrium and that electronic charges adapt to this new environment is erroneous. Instead, chemical gradients and charge concentration gradients of both electrons and ions have to be taken into account simultaneously. Electrons transferred to the dye induce a potential shift at the interface that makes ion diffusion into C₆₀ possible. To establish a constant I⁻ profile within C₆₀, a charge compensation mechanism is necessary. It is proposed that a combination of electronic charges due to impurities and electronic doping are responsible for the underlying mechanism. We also suggest that a novel method for controlled doping of organic semiconductors could be based on this mechanism. To the best of our knowledge, this mechanism has not been previously considered when describing ionic junctions.

4. Experimental Section

Sample preparation: All materials and solvents were purchased from commercial suppliers and were used without further purification. For RBS experiments, samples were prepared on glassy carbon substrates (GC, HTW Hochtemperatur-Werkstoffe GmbH, Germany) or Si-wafers (Si-Mat Silicon Materials, Landsberg, Germany). For ToF-SIMS and KPFM experiments ITO coated glass substrates (Geomatec, 20 Ohms square⁻¹) were used. The different substrates were cleaned in acetone, isopropanol, detergent (only for ITO substrates) and water in an ultrasonic bath. Then they were transferred to a nitrogen-filled glovebox for further processing. The cyanine dye 1-Ethyl-2-[3-(1-ethyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-propenyl]-3,3-dimethyl-3H-indolium iodide (Cy3-I, FEW Chemicals, product S0128) was spin-coated from a 0.5 wt% 2,2,3,3-tetrafluoro-1-propanol (Sigma-Aldrich, 98%) solution at 4000 rpm. Layers of C₆₀ (SES Research, 99.5%) were vapor-deposited at a base pressure of $< 5 \cdot 10^{-6}$ mbar using a rate of 0.5 Å s⁻¹. All samples were stored for at least 3 weeks in the dark under nitrogen atmosphere to ensure full establishment of the equilibrium situation.

Rutherford backscattering spectroscopy (RBS): Samples were analyzed by Rutherford Backscattering Spectrometry (RBS)^[27] at the ETH Laboratory for Ion Beam Physics. Measurements were performed using a 2 MeV ^4He beam and a silicon PIN diode detector under 168° backscattering angle. The He beam spot diameter was 1 mm. In order to enhance the depth resolution of elemental profiles, samples were tilted against the incident beam direction by an angle between 45° and 65° (exact values are indicated in figures). The collected data were evaluated using the RUMP program.^[28] The at% scale of the iodine depth profiles was obtained by simulating a uniform 1 at% concentration of iodine in C60 and renormalizing the ordinate scale to this level. No deconvolution of the spectrum has been performed. Such a procedure is known to be accurate to better than 5% for thin layers close to the surface. The width of the left and right edges of the box-like depth distribution of the dye in Figure 3 gives a good indication of the depth resolution of the technique. In Figure 1 and 6 the Cy3-I layers are too thin to be resolved as a flat top depth profile by RBS.

Elastic recoil detection analysis (ERDA): Depth profiles of light elements were measured by Heavy Ion ERDA^[27] using a 13 MeV ^{127}I projectile beam. The ERDA spectrometer is a combination of a time-of-flight detector for velocity measurement with a gas ionization chamber for energy determination of recoiling sample species.^[29] The scattering angle was 36° . The data was analyzed by custom software and the DataFurnace computer code.^[30]

Time-of-flight secondary ion mass spectrometry (ToF-SIMS): A ToF-SIMS 5 (ION-TOF GmbH) was used to analyze the surface. Primary ions of Bismuth (Bi_3^{2+}) with energies of 25 keV were fired in packets at the sample surface. 100 scans were measured on an area of $300 \times 300 \mu\text{m}$. Upon impinging the solid surface, the primary ions transfer their charge and momentum in binary collisions to the atoms of the target. These target atoms are displaced from their original sites and collide in turn with other target atoms until the energy transferred is insufficient to cause atom displacement. Most of these sputtered particles (90 %) are neutral and cannot be detected. The remaining 10% consist of secondary ions of both polarities and

secondary electrons. These are emitted in an angular distribution from the sample surface with a range of energies. Time-of-flight (ToF) is used to detect the secondary ions up to a mass of m/z 430. To avoid errors from sputtering through the films by an ion beam, only top-most surface of the sample was analyzed. Depth resolution was obtained by fabricating a series of devices with varied thickness of C_{60} between 0 – 100 nm.

Scanning Kelvin probe force microscopy (KPFM): Scanning Kelvin probe force microscopy was performed with a commercial AFM (Nanoscope Ila, Digital Instruments). The cantilevers (resonance frequency $f = 75$ kHz, force constant $k = 2.8$ N/m, conductive PtIr coating) were obtained from Bruker (SCM-PIT). The topographic profile was first determined along a line using the tapping mode of operation. The tip was then lifted off the surface by 43 nm, and the line is rescanned with the tip maintained at that exact distance. The potential measurements were calibrated with a freshly polished pure Ni surface. All samples were measured in an environmental chamber flushed with nitrogen. Similar to ToF-SIMS, a depth profile was approximated by fabricating a series of devices with varied C_{60} layer thickness between 0 – 100 nm. Potential values were taken in film regions that were uniform and smooth as confirmed by the morphology scans in the scanning Kelvin probe force microscope.

UV-Vis spectroscopy: Dye film thicknesses were confirmed by absorbance measurements on a Cary 50 UV-Vis spectrometer. The absorbance signal was normalized with reference samples for which the thickness has been determined by ellipsometry.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) Chemical structure of Cy3-I. Iodine profile in the normal (b) and inverted (c) structure measured by RBS. The sample tilt was 65° in (b) and 55° in (c). The at% scale applies for iodine in the C_{60} layer.

Figure 2. KPFM data on the surface of Cy3-I / C_{60} bilayer stacks with varied thickness of C_{60} . Error bars indicate the highest number out of uncertainty because of scan drift, change in Ni calibration or route mean square over a $4 \mu m^2$ sample surface area. As guidelines the HOMO and LUMO values of Cy3-I and C_{60} are indicated as well. The Fermi level of pure C_{60} is shown as dashed line.^[18]

Figure 3. Iodine profile obtained by RBS in the reference sample with the structure indicated in the inset. The sample tilt was 45° . No diffusion of iodine into C_{60} is observed. The at% scale applies for iodine in the C_{60} layer.

Figure 4. 2D-ERDA spectra of Cy3-I / C_{60} bilayer system. Interfaces and relevant elements are indicated. The trace of N (red circled) ends at the organic interface and does not appear at the sample surface.

Figure 5. Schematic representation of HOMO, LUMO and Fermi level at the dye/C₆₀ interface. Fermi level alignment leads to a potential shift caused by electron transfer from C₆₀ to the dye. Diffusion of iodide into C₆₀ eventually leads to reduction of C₆₀ to the C₆₀ anion radical.

Figure 6. Iodine profile obtained by RBS in the control sample using C₆₀F₄₈ as acceptor material. The structure is indicated in the inset. The sample tilt was 65°. No diffusion of I into C₆₀F₄₈ is observed. The at% scale applies for iodine in the C₆₀F₄₈ layer.

Table 1. Variables used in the thermodynamic model.

Variable	Description	Value / extracted from
$n_I^{C60} / n_I^{(0)}$	Ratio of ions in C_{60} to total ion concentration	0.2 / RBS experiment (Figure 1b) 0.1 / RBS experiment (Figure 1c)
L^{C60} / L^{dye}	Ratio of C_{60} to dye layer thickness	3 / RBS experiment (Figure 1b) 6 / RBS experiment (Figure 1c)
ϕ^{dye}	Fermi level in the dye	-5 eV / Scanning Kelvin probe force microscopy of pure films (Figure S1b)
ϕ^{C60}	Fermi level in C_{60}	-4.6 eV / Scanning Kelvin probe force microscopy of pure films (Figure S1a) and reference [18]
ΔE	Energy cost (if >0) or gain (if <0) to bring an ion from the dye to the C_{60} (not including electrostatic potential energy difference)	0.42 eV (for normal structure) 0.44 eV (for inverted structure)

TOC entry

Unexpected Equilibrium Ionic Distribution in Cyanine / C_{60} Heterojunctions

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The equilibrium ion distribution and electronic potential shift at the heterojunction of a cationic cyanine dye and the electron acceptor C_{60} is investigated. Massive ion diffusion into C_{60} is observed that is in contradiction to current models. A picture that includes doping of C_{60} by the counter ions accounts for all observations.