p-Doping of Squaraine with F4-TCNQ by Solution Processing

Gueorgui O. Nikiforov [†], Luis K. Ono [†], Yabing Qi ^{†,††}

Abstract We report p-type doping of 2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQ) with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) by solution processing. We confirm the presence of F4-TCNQ in the doped films and observe the Fermi level shift towards the highest occupied molecular orbital (HOMO) as the dopant concentration increases. Furthermore we note that the doped film conductivities, as well as the threshold voltages and ON/OFF ratios of transistors incorporating those films, show trends as a function of F4-TCNQ concentration consistent with p-type doping. The number of charge carriers in the film increases with doping, but no dependence on the doping level is observed for the extracted field-effect mobility. The latter is likely due to a lack of control over the morphology formation during the film crystallization and not to fundamental factors governing charge transport. The present findings may serve as a basis for the development of higher performance organic solar cells using SQ as a donor material.

Key words: squaraine, F4-TCNQ, doping, conductivity, solution processing, solar cell.

1. Introduction

The rapid developments in the field of inorganic electronics during the second half of the twentieth century were made possible only after the discovery of a method to grow extremely pure and high quality single crystals whose conductivity could be tuned in a controllable way over several orders of magnitude by introducing a precise amount of dopants. Nowadays, although research on organic semiconductors (OSCs) is following suit, the overwhelming majority of the literature in the field is still on intrinsic semiconductors. On the other hand, there are also a few reports, which already show that doping can improve the performance of OSCs.¹⁾²⁾³⁾⁴⁾ Therefore, further efforts to incorporate doping in practical devices and applications on a larger scale are warranted in order to harness those benefits.

One example of an OSC with a good performance even in its intrinsic state is the dye molecule 2,4-bis[4-(N,N-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (SQ), which has recently been identified as a suitable candidate for solar cell applications due to its high absorbance and stability.⁵⁾⁶⁾⁷⁾ A film of SQ, as thin as

8–12 nm, is reported to absorb over 50 % of the incident light of energy above its bandgap, which allows the fabrication of solar cells with efficiencies exceeding 6 %.⁸⁾ However, the low conductivity of intrinsic SQ has been identified as a possible bottleneck for device performance.⁶⁾⁹⁾¹⁰⁾ Thus, thicker films, which could absorb even more of the incoming radiation, cannot be employed because the light-generated charges could not travel across larger distances. In that case increasing the SQ conductivity via doping could be potentially beneficial for device performance.

In this study we doped SQ via a solution process using 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ). F4-TCNQ has a very deep-lying lowest unoccupied molecular orbital (LUMO) level, which makes it a very strong p-type dopant.¹¹⁾ We investigated the doping effects using a combination of spectroscopy studies, I-V measurements, and surface imaging. On the basis of our results we conclude that F4-TCNQ does indeed p-dope SQ leading to an increase in conductivity by up to four orders of magnitude.

2. Experimental procedure

The films reported herein were solution processed and all preparation steps were carried out in a N₂ glovebox with both O₂ and H₂O levels below 0.1 ppm. In order to obtain samples with various molar doping ratios, a 1 mg/mL chloroform solution of F4-TCNQ ($\geq 97\%$,

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[†] Energy Materials and Surface Sciences Unit (EMSS), Okinawa Institute of Science and Technology Graduate University (OIST) (Okinawa, Japan)

^{††} Corresponding author: Yabing.Qi@oist.jp

Fig. 1 Molecular structures of (a) SQ and (b) F4-TCNQ.

Wako) was sequentially diluted before being added to a 2 mg/mL chloroform solution of SQ ($\geq 97\%$, Sigma Aldrich) (Fig. 1). In this work, the molar ratio is defined as the number of F4-TCNQ molecules with respect to the number of SQ molecules present in the mixtures and the solutions of various molar doping ratios were prepared by taking into consideration the molecular weight of each material provided by the suppliers. Both SQ and F4-TCNQ were used as received without further purification. Qualitative X-ray photoelectron spectroscopy analysis confirmed the absence of traceable amounts of impurities (Fig. 3a, cyan and black curves). Due to the low solubility of SQ, the SQ solutions were prepared by overnight stirring on a hotplate at 40–50 °C. It was verified that all mixtures were fully dissolved before further use. Both oxidation of SQ in the solution state as well as material decomposition are unlikely due to the controlled nitrogen environment where the procedure was carried out and the relatively low temperatures involved. The films were then deposited by spin-coating for 30 s at 1000 rpm and annealed on a hotplate for 5 min at 100 °C. The thickness of the resulting films varied slightly due to the different added amounts of F4-TCNQ and had an average value of ~ 20 nm.

The effects of doping SQ with F4-TCNQ were investigated by ultraviolet and X-ray photoelectron spectroscopy (UPS/XPS) using a surface analysis system (Kratos AXIS Ultra DLD). The films were prepared on top of bare Si substrates covered only by a native oxide. XPS allowed us to monitor the chemical composition of the samples, while UPS was used to study the Fermi level (E_F) and highest occupied molecular orbital (HOMO) of the films. Extra care was taken when transferring the spin-coated samples from the glovebox to the measurement system to minimize sample exposure to ambient air. In addition, UV-vis absorption spectra were taken in ambient air (Thermo Scientific Evolution 600 UV-Vis spectrometer) in order to estimate the op-

Fig. 2 Schematic diagram of the employed TFT architecture.

tical bandgap and thus determine the LUMO levels of the investigated films.

To complement the spectroscopy data, the doping effects were also studied by measuring the I-V characteristics of doped SQ films, incorporated as the active layer in top gate bottom contact thin film transistors (TFTs) (Fig. 2). For this experiment, the films were spin-coated using exactly the same recipe as before, but this time the TFTs were fabricated on a glass substrate. The transistor channel, with a length of $L = 20\ \mu\text{m}$ and a width of $W = 1\ \text{cm}$, was defined by lithographically prepatterned interdigitated source and drain electrodes, composed of $\sim 13\ \text{nm}$ thick evaporated Au. After depositing the SQ active layer, a 400 nm dielectric layer of CYTOP was spin-coated and annealed on a hotplate for 20 min at 80 °C. The devices were then completed by evaporating an Au gate electrode through a shadow mask. The resulting TFTs were measured in a N_2 glovebox using a semiconductor parameter analyzer (Keithley 4200 SPA).

Finally, to gain an insight into the morphology of the doped SQ films, as well as to explain some of the I-V measurement observations, the samples were imaged using a dark field optical microscope (Leica DM4000 B) and an atomic force microscope (Asylum MFP-3D AFM).

3. Measurement results

3.1 UPS/XPS

For the purpose of the spectroscopy study, we prepared films with a molar doping ratio of 1 %, 2 %, 10 %, and 50 %, as well as an undoped SQ film and a pure F4-TCNQ film. At first, we performed an XPS survey scan to confirm the presence of the chemical el-

Fig. 3 High resolution XPS scans of F4-TCNQ-doped SQ films spun on a bare Si substrate with a native oxide. (a) Survey scans identifying all the elements present in the films. (b) Detailed scans of the F 1s peak. Fluorine could not be detected for molar doping ratios below 10 %.

elements contained in the SQ molecule (C, N, and O) and those contained in the F4-TCNQ molecule (C, N, and F) (Fig. 1). We identified peaks in the spectrum from all those elements as well as from the Si substrate (Fig. 3a). A detailed scan of the F peak reveals that it grows as the proportion of F4-TCNQ present in the film increases (Fig. 3b). However the F 1s signal is below the detection limit of the instrument for molar doping ratios below 10 % making it difficult to reliably extract the dopant concentration from the XPS data.

We also performed UPS spectroscopy on the same set of samples in order to extract their E_F and HOMO levels with respect to the vacuum level E_{vacuum} (Fig. 4). The HOMO level value for an undoped SQ film extracted from our measurements (4.97 eV) is slightly lower than the value reported in the literature (5.1 eV).¹⁰⁾ This discrepancy could be caused by measurement uncertainty and/or difference in the sample preparation methods. The Fermi level is observed to shift towards the HOMO edge as a function of the molar doping ratio (Fig. 4a). Such a rigid shift of UPS spectra towards the Fermi level suggests that the top surface of the film is dominated by SQ. The difference between E_F and HOMO is 0.92 eV for undoped SQ film and it decreases progressively until it reaches 0.68 eV for a doping concentration of 50 %. The value of E_F of pristine SQ is 4.05 eV and it increases as more F4-TCNQ is added, reaching a value of 4.17 eV for a doping concentration of 50 %. A schematic summary of the energy levels of the various films is presented in Fig. 4b. The LUMO levels of the SQ films were calculated on the basis of the onset of absorption in the UV-vis spectra, which

was found to occur at $\lambda = 765$ nm, corresponding to a bandgap of 1.62 eV (inset in Fig. 4b). This value is in good agreement with the literature reported value of 1.60 eV.⁶⁾ The HOMO, LUMO and E_F levels for pure F4-TCNQ were taken from literature.¹¹⁾ The HOMO and LUMO levels of pristine SQ and doped SQ samples were roughly constant within experimental error through all the different dopant concentrations until a very high molar doping ratio of 50 % was reached, at which point the film starts turning into an alloy. In addition, the major HOMO features remain basically the same for different doping concentrations.

3.2 I-V characterization

Three batches of TFTs were fabricated for the purpose of I-V measurements. Batch 1 consisted of devices with an F4-TCNQ molar doping ratio of 0.01 %, 0.02 %, 0.1 %, 0.2 %, 1 %, 2 %, and 10 %; batch 2 – of 1 %, 2 %, 5 %, 10 %, and 20 %; and batch 3 – of 5 %, 10 %, 20 %, and 50 %. In addition, each batch included undoped SQ TFTs as a reference.

Transfer and output characteristics of two devices from batch 2, one without doping and another with 20 % doping, are shown in Fig. 5. The undoped TFT (Fig. 5a,c) exhibits a textbook-like behavior with no hysteresis, no noticeable contact resistance, low leakage current, well-defined linear and saturation regimes and large ON/OFF ratio. On the other hand, the characteristics of the 20 % doped film (Fig. 5b,d) are substantially different. While there is no apparent change in the amount of hysteresis and contact resistance, and the gate leakage is still much smaller than the source-drain signal, the overall current levels are significantly larger.

Fig. 4 High resolution UPS scans of F4-TCNQ-doped SQ films spun on a bare Si substrate with a native oxide. (a) He-I ($h\nu = 21.22$ eV) scans showing a trend in the HOMO and onset levels as a function of molar doping ratio. The difference between E_F and the leading edge of the HOMO consistently decreases as the F4-TCNQ concentration is increased, which is a footprint of p-type doping. (b) Energy level diagram showing the HOMO, LUMO and E_F levels as a function of molar doping ratio. The HOMO and E_F values for the doped SQ films were extracted from the curves shown in (a), while the LUMO values were calculated on the basis of the HOMO levels and an optical bandgap of $E_G = 1.62$ eV, estimated from the onset of the UV-vis absorption spectrum, shown as an inset in (b). The F4-TCNQ HOMO, LUMO and E_F values are literature values taken from Ref. 11.

The ON current increases by a factor of two, while the OFF current increases by as much as three orders of magnitude for large V_{ds} values (Fig. 5b). This substantially decreases the ON/OFF ratio and prevents the transistor from having a well-defined saturation regime. In fact, because the channel is conducting even in the absence of V_g , which means that it effectively acts as a resistor, the output characteristics of the 20% doped device resemble the behavior of a transistor in parallel with a resistor (Fig. 5d).

The linear and saturation mobilities μ_{lin} and μ_{sat} , the channel conductivity in the absence of gate voltage σ , the threshold voltage V_{th} , and the ON/OFF ratio were extracted for each one of the fabricated devices and the results are plotted as a function of molar doping ratio in Fig. 6. In each batch, for every doping level, at least two identical samples were prepared and each sample had three TFTs on it. Therefore, with the exception of the cases where some of the devices failed to work, each data point in Fig. 6 represents an average of the data gathered from six transistors and is thus statistically representative.

No clear trend is observed for the extracted μ_{lin} and μ_{sat} as a function of molar doping ratio (Fig. 6a). While it could be argued that in batch 1 there is a slight increase in the mobility as more F4-TCNQ is added to the film, in batch 2 exactly the reverse trend

is observed. Furthermore, in batch 3 the best mobility is obtained for undoped and 50% doped films with the doping levels in between resulting in inferior mobility values. Finally, although there is no clear trend within a single batch, there is a large spread in the extracted mobility values between devices with the same molar doping concentration from different batches. As an example, for the undoped case in batch 1, the average $\mu_{lin} = 4.53 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while for the same doping level in batch 3, the average $\mu_{lin} = 9.45 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is more than an order of magnitude larger. Therefore on the basis of the experimental results, the mobility of SQ does not change significantly upon doping with F4-TCNQ, and it can be substantially different from batch to batch.

In contrast to the mobility, the conductivity of SQ depends strongly on the amount of F4-TCNQ for concentrations above 1% (Fig. 6b). For example, in batch 2, the channel conductivity in the absence of applied gate voltage increases from $\sigma_{0\%} = 8.69 \times 10^{-7} \text{ S m}^{-1}$ to $\sigma_{20\%} = 4.65 \times 10^{-3} \text{ S m}^{-1}$, while in batch 3, it increases from $\sigma_{0\%} = 2.28 \times 10^{-7} \text{ S m}^{-1}$ to $\sigma_{50\%} = 4.17 \times 10^{-3} \text{ S m}^{-1}$. In both cases the increase is about four orders of magnitude. These data represent the lateral film conductivity, estimated under the assumptions that, in the absence of V_g , the current flows uniformly across the entire SQ film thickness¹²⁾ and that the SQ

Fig. 5 Transfer (a,b) and output (c,d) characteristics of an undoped (a,c) and F4-TCNQ doped with a 20 % molar doping ratio (b,d) SQ TFTs.

films in all samples are equally thick. It was not possible to measure the perpendicular film conductivity in a sandwich-like metal/semiconductor/metal structure as the SQ layer was only ~ 20 nm thin and shorts between the two metal electrodes were imminent.

The observed increase in the lateral SQ film conductivity as a function of F4-TCNQ concentration is accompanied by changes in the transistor threshold voltages and ON/OFF ratios. V_{th} increases substantially as the molar doping ratio increases (Fig. 6c), while at the same time the ON/OFF ratio decreases by several orders of magnitude (Fig. 6d).

3.3 Optical and AFM imaging

Upon examining the SQ thin films using a dark field optical microscope, it becomes apparent that the annealing step immediately after spin-coating has very important consequences (Fig. 7). A freshly-spun film appears to be smooth and amorphous (Fig. 7a), while after annealing it on a hot plate for 5 min at 100°C , the morphology changes dramatically. Large crystal

grains as well as what appears as fractal-like regions of much smaller crystals in between are observed (Fig. 7b). When a sample was placed and annealed on a hot stage under an optical microscope, the formation of these crystals could be monitored in real time.

This crystallization step as a result of annealing plays a vital role in the subsequent TFT performance. Unfortunately, it seems to be a rather random process. As an example, two devices, which were spin-coated immediately one after the other and annealed together at the same time, show very different crystal sizes and morphologies (Fig. 7c,d). The sample with the smaller crystal sizes had an extracted mobility of $3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while the one with the larger crystal sizes – $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This is an order of magnitude difference in transistor performance.

Further insight into the nature of the film crystallinity could be obtained via AFM images. A dark field optical image of a part of a transistor clearly shows crystalline and fractal-like areas (Fig. 8a). An AFM im-

Fig. 6 Device parameters, extracted from I-V measurements and plotted as a function of molar doping ratio: (a) μ_{lin} and μ_{sat} – linear and saturation field-effect mobilities, (b) σ – lateral film conductivity in the absence of a gate voltage, (c) V_{th} – transistor threshold voltage, and (d) ON/OFF ratio. The insets in (b-d) are identical to the respective large plots with the exception of the scale of the x axis.

age of a portion of the same region reveals even further details (Fig. 8b). The surfaces of the crystalline areas and fractal-like areas are very dissimilar (Fig. 8c). In particular, the root mean square (RMS) roughness of the crystalline areas was estimated to be 0.4 nm, while that of the fractal-like areas was 23 nm. In addition, since the total thickness of the SQ film was estimated to be ~ 20 nm, it could be concluded that the fractal-like regions might not even provide complete coverage.

4. Discussion and analysis

Doping of OSCs can be explained by transfer of charges between the host material and the dopant molecules.¹³⁾ In the case of p-type doping, the HOMO level of the host material should be above (or close to) the LUMO level of the dopant, so that an electron transfer from the host HOMO to the dopant LUMO is energetically favorable (Fig. 9). This process creates holes

in the HOMO of the host material, which causes its Fermi level to shift down closer to the HOMO.

In the case of SQ and F4-TCNQ, the HOMO of SQ is reported to be at 5.1 eV,⁶⁾ while the LUMO of F4-TCNQ is very deep-lying at 5.24 eV.¹¹⁾ It is therefore expected that efficient charge transfer can occur between the two molecules. Indeed, our UPS data are consistent with this interpretation as we observe the E_F level to move downwards in the electron energy potential (Fig. 4b). Thus, it can be concluded that SQ is p-doped in the presence of F4-TCNQ. What is slightly surprising is the fact that the F 1s peak is not detectable by XPS for dopant concentrations $< 10\%$ (Fig. 3b). This might indicate that a phase segregation of SQ and F4-TCNQ exists within the film with F4-TCNQ being depleted from the top surface of the doped film. Thus the X-ray induced photoelectrons generated from the small molecular density of F4-TCNQ are not readily

Fig. 7 Dark field microscope images of SQ thin films spun on a glass substrate. The morphology of an as-spun unannealed film (a) differs significantly from that of an identically prepared film annealed for 5 min at 100 °C (b). The annealing step induces the formation of clearly visible crystals; however, it is not a stable process. Two samples (c,d), processed in the same batch under identical conditions and annealed simultaneously, show very different crystal grain sizes and coverage. The corresponding mobility values are $3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (c) and $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (d) respectively.

Fig. 8 (a) Dark field microscope image of a SQ film spun on a glass substrate, prepatterned with Au electrodes. Both crystalline and fractal-like regions are observed. (b) High resolution AFM scan of a portion of the film shown in (a). (c) Height profile of the AFM scan along the red line shown in (b). A schematic diagram of the sample cross-section along the line of the height profile scan is shown as an inset in (c). The 13 nm step on the right side of the height profile is due to the thickness of the underlying Au electrode. The crystalline regions of the film are extremely flat (RMS roughness = 0.4 nm), while the fractal-like regions are much rougher (RMS roughness = 23 nm) and might not even provide continuous coverage.

detectable by XPS due to the relatively small probing depth of the technique ($< 3 \text{ nm}$).¹⁴⁾¹⁵⁾

In addition to the spectroscopy data, which indicates that F4-TCNQ dopes SQ, our I-V measurement also support the same interpretation. The conductivity σ of SQ increases by several orders of magnitude as more F4-TCNQ is added to the film (Fig. 6b), which is a clear footprint of doping.⁴⁾¹⁶⁾¹⁷⁾ In particular, it is inter-

esting to note that there is a significant improvement in conductivity for doping concentrations between 1 % and 5 %. This observation can be rationalized in several ways. First, even though no clear trend was observed in the extracted charge mobility as a function of doping (Fig. 6c), the increase in conductivity (σ) could be attributed to charge transport enhancement due to doping-induced trap filling.³⁾¹⁸⁾ Second, the enhance-

ment of σ can be interpreted as a footprint of improved charge injection from the metal electrodes due to doping.¹⁶⁾ Finally, even though σ depends linearly on the number of charges available for transport,¹⁹⁾

$$\sigma = n\mu q \quad (1)$$

where n is the number of charges, μ is the charge mobility and q is the elemental charge, the number of charge carriers itself depends exponentially on the position of the Fermi energy within the bandgap. For example, the ratio between the number of charges n_1 and n_2 , which correspond to Fermi levels E_F^1 and E_F^2 , is given by

$$\frac{n_1}{n_2} = \exp \frac{E_F^1 - E_F^2}{kT} \quad (2)$$

where k is the Boltzmann constant and T is temperature.¹⁷⁾ Hence, σ depends exponentially on the position of the Fermi energy. Therefore, the observed shift of E_F towards the HOMO level, as evident from the UPS data (Fig. 4), can also be used to explain the corresponding four orders of magnitude increase in σ .

The observed trends in V_{th} and ON/OFF ratio (Fig. 6c,d) can also be rationalized in terms of an increase in the number of charge carriers and can thus be interpreted as a signature of doping. In the case of the threshold voltage shift, the dopant provides charges, which otherwise should have been accumulated through application of V_g . Hence, the higher the dopant concentration, the smaller the gate bias that needs to be applied in order to induce a conducting path and turn the transistor on. This results in V_{th} shifting towards more positive values, exactly as observed. Furthermore, when doped, due to the larger number of available charges, the channel becomes conducting even in the absence of V_g , meaning that the OFF current is larger, which explains why the ON/OFF ratio decreases with increasing F4-TCNQ concentration.

The increase of the conductivity σ of OSCs upon doping is well documented in the literature. However, a large portion of the published papers only include measurements of σ on a two terminal⁴⁾¹⁶⁾ device. Yet, as evident from eq. 1, such measurements alone cannot reveal any direct information about μ , which is an important figure of merit for charge transport. There have also been studies focusing explicitly on the dependence of charge mobility on doping concentration, however interpreting all reported results in a consistent way is not a straightforward task.

Some authors report an increase in μ as more dopant

Fig. 9 Energetics of p-type doping in OSCs. It is more favorable for an electron to transfer from the host HOMO to the dopant LUMO. As a result, a hole becomes available in the host HOMO and the host E_F shifts closer to the HOMO.

is added to the film.²⁰⁾²¹⁾ This observation is rationalized in terms of trap filling. As the number of charges n increases due to doping, deep traps, which represent highly localized states, get filled up, while any excess charges are forced to occupy shallower traps, which are more delocalized.²²⁾ It is exactly the highest energy charges which take part in charge transport and as the doping concentration is increased, they are progressively driven towards more delocalized states. As a result, the average film mobility increases.

However, other studies indicate that μ decreases as a function of doping concentration.²³⁾²⁴⁾²⁵⁾ This result is explained by postulating that due to their finite size, dopant molecules create additional disorder in the host material lattice, which introduces new trap states. Furthermore, a dopant molecule becomes charged once it gives away or accepts a charge in the process of doping the host material. As a result, it starts acting as a Coulombic trap, thus impeding charge transport and decreasing the film mobility even further.

Yet other studies claim that at low molar doping ratio, the film mobility decreases as a function of doping concentration, while at high molar doping ratio, it increases as a function of doping concentration.²⁶⁾²⁷⁾²⁸⁾ The explanation given in this case is that the two mechanisms described above are dominant at different doping concentrations. At low doping concentrations, on average doping impedes charge transport, since the negative influence of the traps created by the dopant molecules outweigh the benefit of increasing the number of charges available for transport. At high doping concentrations the opposite is true. Furthermore, the

authors also recognize that the disorder in the intrinsic film, as well as the magnitude of the electric field also play an important role in determining the observed trend in mobility upon doping.²⁷⁾

It is clear that many factors come into play when determining the effect of doping on the mobility of OSCs. In our present study, the charge mobility was not observed to exhibit a trend as a function of doping (Fig. 6a). It is possible that in the case of F4-TCNQ-doped SQ the two competing effects proposed in the literature are of comparable magnitude, thus producing a zero net change in the mobility. However, given the very large spread in the extracted mobility values for devices with the same doping concentration but from different batches, as well as the strong indication that this spread is a result of random crystallization during the annealing process (Fig. 7c,d), it is likely that in our case it is the film morphology which plays the dominant role in determining charge mobility.

Since the random morphology formation might mask a trend in the film mobility as a function of doping concentration, persistent efforts were made towards gaining more control over the crystallization process. We tried substituting chloroform with the lower boiling point dichloromethane, filtering the solution through several different filter sizes to remove particles that might induce crystallization, varying the annealing temperature and duration, as well as annealing the sample only upon completing the entire device. However none of these attempts produced the desired outcome. We also tested TFTs with as-spun unannealed SQ films, as well as bottom gate top contact devices, but they did not exhibit any transistor behavior.

5. Conclusions

In this report we presented a comprehensive study of doping SQ with F4-TCNQ via a solution process using a combination of spectroscopy, I-V measurements and surface imaging techniques. We could confirm that p-type doping does take place. XPS could detect fluorine for large doping concentrations and the UPS spectra showed a rigid shift towards E_F with increasing F4-TCNQ concentrations, which is a clear evidence for p-type doping. Furthermore, the film conductivity as well as the transistor threshold voltages and ON/OFF ratios exhibited trends consistent with an increased number of charges due to p-doping of the SQ film. No clear evidence for a change in the extracted field-effect mobility values as a function of doping level was detected, but

this was attributed to an instability in the film crystallization process upon annealing leading to random morphology formation.

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Yabing Qi is Assistant Professor and Head of the Energy Materials and Surface Sciences Unit at the Okinawa Institute of Science and Technology Graduate University. Prior to his current appointment, Dr. Qi was a postdoctoral research fellow in Prof. Antoine Kahn's group in Princeton University. He received his B.S., M.Phil., and Ph.D. from Nanjing University, Hong Kong University of Science and Technology, and University of California Berkeley, respectively. His research interests include perovskite solar cells, energy materials and devices, organic electronics, surface sciences, and condensed matter physics.

Gueorgui O. Nikiforov received his B.S.E. in Electrical Engineering in 2005 from Princeton University (USA), MSc in Information Technology and Electrical Engineering in 2007 from ETH Zurich (Switzerland), and PhD in Physics in 2013 from the University of Cambridge (UK). He is presently a postdoctoral researcher at the Okinawa Institute of Science and Technology (Japan) and his current research focuses on charge transport and doping of organic semiconductors.

Luis K. Ono is a postdoctoral researcher at the Okinawa Institute of Science and Technology Graduate University in Japan. He obtained his B.S. in Physics/Microelectronics in 2000 from the University of Sao Paulo, Brazil. Later he joined the Department of Nuclear Engineering in Kyoto University, Japan, and the University of Central Florida, USA, where he obtained his M.S. in 2003 and Ph.D. in 2009, respectively. His current research focuses on perovskite solar cells.