Modulating Electrical Conductivity by Activating Open-Metal Sites in Interfacially Grown Coordination Polymer Thin Film

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Dedicated to

Amma, Babuji, Didi and Babu.

Certificate

This is to certify that this dissertation entitled ***"Modulating Electrical Conductivity by Activating Open-Metal Sites in Interfacially Grown Coordination Polymer Thin Film"*** towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by **Anupam Prasoon** at Indian **Institute of Science Education and Research, Pune** under the supervision of **Dr. Nirmalya Ballav, Department of Chemistry, Indian Institute of Science Education and Research, Pune** during the academic year 2018-2019.

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Declaration

I hereby declare that the matter embodied in the report entitled ***"Modulating Electrical Conductivity by Activating Open-Metal Sites in Interfacially Grown Coordination Polymer Thin Film"*** are the results of the work carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research, Pune, under the supervision of Dr. Nirmalya Ballav and the same has not been submitted elsewhere for any other degree.

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Of the various friends who have been a part of my life, a special thank you goes out to a special someone who have partnered through the various ups and down and stayed by consistently with unwavering support from afar. Sravan, my friend, my partner in crime, my brother who has been by me throughout my metamorphosis in IISER, I do not know where I would have been without you.

Last but not the least, wherever I am it is entirely due to the blessings and well wishes of my family- Amma, Babuji, Didi and Babu. I am nothing without them and it is with their support that I could come this far overcoming the obstacles. I derive my strength from them and I bow my head in respect and gratitude for inculcating different values in me and standing by decisions but scolding and correcting me whenever necessary.

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Abstract

Downsizing metal-organic frameworks (MOFs) to thin films and bringing conductivity in such systems is not only beneficial for scientific pursuits but also holds great potential in electronic device applications. Here, we demonstrate, for the first time thin film fabrication of Cu-BTEC using layer-by-layer (LbL) approach resulting in the generation of intrinsic open-metal sites. The as-synthesized film was further doped with a well-known redox-active molecule, TCNQ which is giving rise to a huge conductivity enhancement along with an unheralded rectification ratio (RR) value exceeding five orders of magnitude which remained unchanged at temperatures as high as 450 K. The formation of an electronic heterostructure and not a lattice heterostructure was accounted for this remarkable observation. Additionally, the doping transformed the thin film character from being hydrophilic to highly hydrophobic. Our solution-processable thin film thus appears to be a promising candidate for electronic devices such as diodes and transistors by sustaining high temperatures and being moisture tolerant.

Introduction

Metal-organic frameworks (MOFs) form a unique class of nano-porous materials which have been extensively explored in various applications such as gas adsorption, separation, sensors, catalysis and many others.[1, 2] Their porosity can be engineered to accessible volume with dopant molecules to give rise to numerous applications. Recently, Thomas Pichler and co-workers demonstrated that Co-MOF-74, advances its physical properties by accommodating TCNQ, which allows the MOF to be utilized for resistive gas phase and photo-sensing.[3] Two dimensional (2D) $[Cu(TPyP)Cu_2(O_2CCH_3)_4]$ MOF thin film doped with TCNQ showed stronger paramagnetic properties as well as enhanced electrical conductivity.[4] However, it was only recently that MOFs could foray into the domain of electrical conductivity. The limitation primarily being the insulating nature of the organic linker and the poor overlap between the s or p orbitals of ligand and the d orbitals of the metal ions.[5] Combining the crystalline order of MOFs with the ability to conduct electrical charge has the potential to create a new class of materials that would open the door to various applications ranging from chemiresistive sensing, FETs, fuel cells, supercapacitors, artificial light harvesting, thermoelectrics to photovoltaics.[4] Therefore, there is increased demand now, than ever before, for the integration of MOFs into thin films for the actualization of real-time electronic devices.

Various approaches to confer conductivity to MOFs include linking metal sites with redox-active linkers, hybridizing them with other conductive media, composite formation and incorporation of redox-active guest molecules.[3] Of the aforementioned strategies, the introduction of guest molecules remain one of the most popular choice for imparting conductivity to an otherwise non-conducting MOF as the pores themselves act as a venue for modulating the electrical transport properties. Although several molecules have been used as a dopant to render conductivity to MOFs, TCNQ molecule has shown the way to rationally design and enhance the conductivity of such systems by several orders of magnitude. In thin films, this was first demonstrated by Talin *et al.* where a continuous conductivity path between TCNQ and the open metal sites of binuclear Cu^{2+} paddlewheel units was attributed to the conductivity enhancement by six orders of magnitude.[6, 7] Thus, thin films of MOF with controlled assembly and orientation doped with redox-active guest molecule may pave the path for future applications in this domain. Such thin films may be fabricated by numerous techniques, but the layer-by-layer (LbL) approach is considered to be the most suitable option as it not only results in highly oriented thin films of numerous MOF topologies but is also known for being economical and easily processable.[5]

Herein, we describe the first time synthesis of Cu-BTEC thin film on self-assembled monolayer (SAM) template realized through LbL technique followed by doping with the redox-active TCNQ molecule. Interestingly, the TCNQ molecule could be doped into the Cu-BTEC thin film without the need for activation of the open coordination sites of the metal.[8-10] Inspired from the anisotropic nature of thermal conductivity, where the heat conducting capability in the direction perpendicular to the film plane (cross-plane) differs from that parallel to the film plane (in-plane), *I-V* measurements for our thin film was carried out both in-plane as well as cross-plane. Exceptional increment of electrical conductivity of six orders of magnitude was noted when the *I-V* measurements were done in-plane coupled with a record value of rectification ratio $\sim 10^5$ when measurements were performed across the film. This, to the best of our knowledge, is the highest value of RR reported till date in organic- inorganic hybrid materials like MOFs. Such remarkable enhancement of conductivity is attributed to electronic heterostructure formation via molecular doping and not the formation of lattice heterostructure as observed earlier. TCNQ doping of the Cu-BTEC thin film not only contributed to the conductivity increase but also lead to the dramatic change from hydrophilic to highly hydrophobic character of the thin film.

Materials and Methods

Chemicals

Copper acetate [$Cu(OAc)_2.H_2O$], 1,2,4,5-Benzenetetracarboxylic acid (BTEC), Au(100nm) coated silicon wafer, 11-Mercaptoundecanoic acid (MUDA), hydrogen peroxide solution (H_2O_2), sulfuric acid (H_2SO_4) were purchased from Sigma-Aldrich. All chemicals were used as such without any further purification. Ethanol was used as the solvent.

Substrate Cleaning

Au coated silicon substrate cleaned by dipping in Piranha solution (H_2SO_4 (95%-98%)/H_2O_2 (30%)-v/v 3:1) for 30 minutes followed by washing with milli-Q water, Ethanol and then drying in stream of N_2 gas.

Preparation of SAM (self-assembled monolayer)

Carboxy-terminated (-COOH) SAM was prepared by dipping Au coated silicon substrate into 1 mM solution of MUDA in ethanol/acetic acid (vol:vol=9:1) for ~48 hours followed by washing with ethanol and drying under the stream of N_2 gas.

Fabrication of Cu-BTEC Thin Film

Thin-Film was fabricated by using Layer-by-Layer approach. Firstly, carboxy-terminated SAM was immersed into 1 mM ethanolic solution of $Cu(OAc)_2.H_2O$ followed by rinsing with ethanol and drying under the stream of N_2 gas. Then it was dipped into 1 mM ethanolic solution of BTEC for 30 min to complete 1 cycle of LbL growth and was repeated upto 10 cycles. Both the metal ion and ligand solutions were maintained at 330 K during the cycling experiment.

Doping in Cu-BTEC thin film

Cu-BTEC thin film was soaked in a saturated ethanolic solution of TCNQ for different set of time ~12, ~24, ~36 and ~48 hours and subsequently washed with ethanol to remove surface adsorbed TCNQ. Doped thin film was further characterized by complimentary techniques.

Fabrication of Cu-TCNQ Thin Film

Cu-TCNQ thin film was prepared by using previously reported layer-by-layer approach. Firstly, carboxy-terminated SAM was immersed into 1 mM ethanolic solution of $Cu(OAc)_2.H_2O$ followed by rinsing with ethanol and drying under the stream of N_2 gas. Then it was dipped into 1 mM ethanolic solution of TCNQ for 30 min to complete 1 cycle of LbL growth and was repeated upto 10 cycles. Both the metal ion and ligand solutions were maintained at 330 K during the cycling experiment for accelerated growth of the thin film.

Synthesis of Cu-BTEC Bulk (Powder)

Bulk Cu-BTEC (powder) was synthesized by a simple solution precipitation method at room temperature. Firstly, 20 mL ethanolic solution of BTEC (0.254 g, 1.0 mmol) was added to a 20 mL ethanolic solution of 0.498 g, 2.5 mmol, $Cu(OAc)_2 \cdot H_2O$ under stirring. The mixture was stirred for 24 hours at 330 K at 1200 RPM. The resulting blue precipitate was separated by centrifugation, washed with Ethanol, subsequently dried under vacuum at 350 K for 12 hrs.

Doping in Cu-BTEC Bulk (Powder)

After synthesizing Cu-BTEC, powder was activated at 420 K for 120 minutes to remove coordinated water molecules. The doping of the Cu-BTEC powder with TCNQ was achieved by soaking the activated powder in a saturated ethanolic solution of TCNQ for upto 72 hrs. Cu-BTEC@TCNQ was then dried under vacuum followed by characterization by complimentary techniques.

Characterization

The uniformity, elemental compositions and thickness of Cu-BTEC and doped Cu-BTEC@TCNQ thin films were analyzed with Zeiss Ultra Plus FESEM with EDXS attachment. Contact angle measurements were carried out by Holmarc's Contact Angle meter. Out of plane XRD data were recorded at room temperature from a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5406 A). Raman spectra (λ_{exc} = 632 nm) were recorded at Raman microscope (LabRAM HR, HorbiaJobinYvon) with a 60X objective lens. High-resolution XPS spectra were recorded using a Scienta R4000 analyser and a monochromatic Al Kα source. The instrumental energy resolution is ~0.3 eV. The transmission lens mode used and the pass energy is set to 100 eV. FTIR spectra were recorded on a Cary 600 Series FTIR (Agilent Technologies) spectrometer attached with microscope. Solid state UV-vis absorption spectra were recorded on Shimadzu UV- 3600 UVVIS-NIR spectrophotometer. Electrical measurements (*I-V*) on various thin film samples were carried out by Keithley 4200 SCS Parameter Analyzer system attached to Everbeing probe station (equipped with thermal chuck) with EGaIn as a top electrode.

Results and Discussion

To check the formation of SAM on polycrystalline Au substrate, we have done water contact angle (CA) measurement. SAM/Au system CA value was observed to be ~ 23° appreciably lower than pristine Au substrate ~65° (Figure 1).[11]

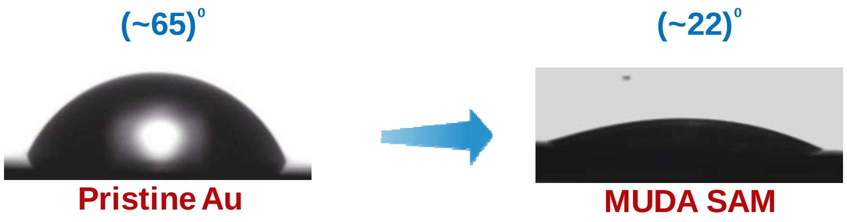


Figure 1. *Water contact angles on pristine Au and MUDA SAMs on Au substrate.*

We have implemented solid-liquid interfacial chemical reaction for fabricating Cu-BTEC thin film through LbL process by immersing SAM/Au templates into Cu ion and BTEC ligand solutions, with EtOH washing steps in between every step. Visual inspection of the bare SAM/Au, after growing the thin film and after doping with TCNQ revealed the stark change in colour from golden to yellowish green to dark green. This phenomenal colour change from the initial yellowish green of Cu-BTEC to dark green of the doped film was a primary indication of pore filling with TCNQ molecules (Figure 2).

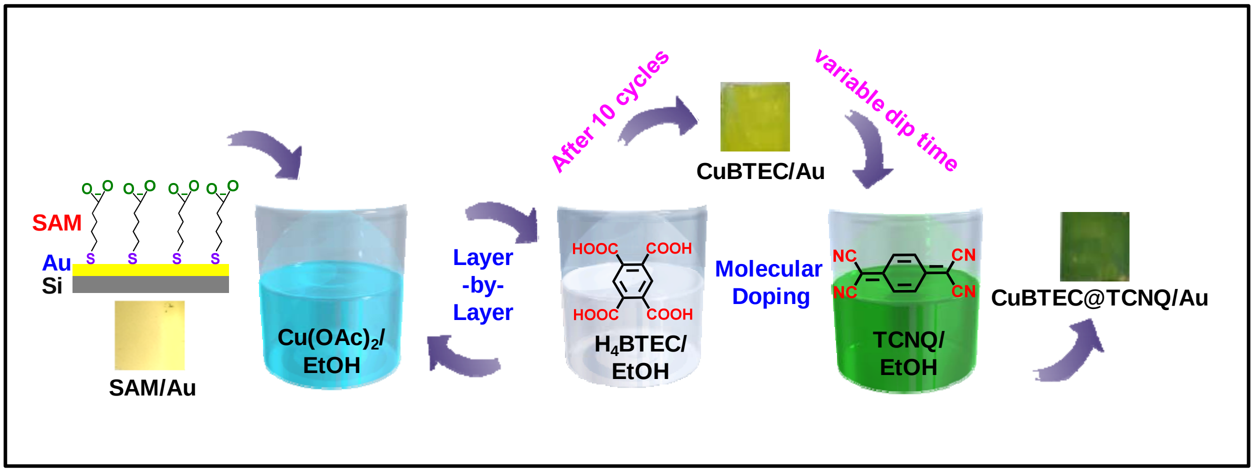


Figure 2. *Schematic representation of LbL growth of Cu-BTEC thin film on SAM/Au substrate. Sequential dipping into Cu(II) and BTEC solutions constitute one cycle of the layer-by-layer (LbL) growth. After 10 cycles of LbL growth, molecular doping was performed by soaking Cu-BTEC thin film into a saturated ethanolic solution of TCNQ for 48 hr.*

The surface morphology of the Cu-BTEC thin films with and without TCNQ loading grown on SAM/Au substrate is shown in the FE-SEM images in figure 3a.

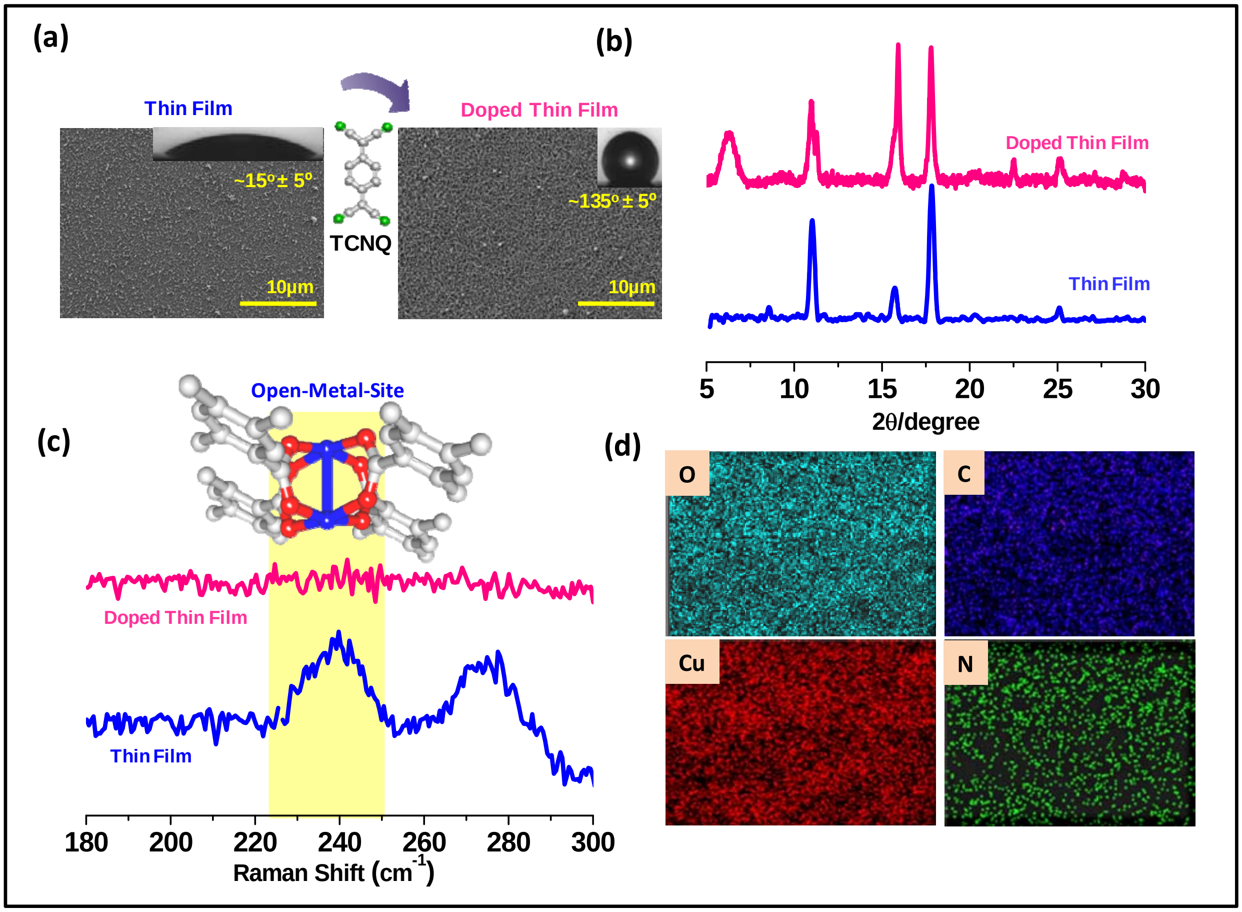


Figure 3. *(a) FE-SEM images of pristine and doped Cu-BTEC thin films (inset: optical image of water droplets on the respective surfaces). (b) Out-of-plane XRD patterns of pristine (blue) and doped (pink) Cu-BTEC thin films. Characteristic diffraction peak of pore-filling phenomenon is highlighted in yellow. (c) Raman spectra of pristine (blue) and doped (pink) Cu-BTEC thin films revealing the activation of open-metal site (characteristic band at ~240 cm*$^{-1}$ *highlighted in yellow) upon doping with TCNQ. (d) EDXS mapping of doped thin film (elements are mentioned).*

The images display a dense continuous film with uniform coverage of the entire substrate. The water contact angle measurements revealed the conversion from a hydrophilic surface in the undoped thin film (CA ~ 15±5°) to a highly hydrophobic surface in the doped Cu-BTEC thin film (CA ~ 135±5°) (Figure 3a).

PXRD patterns of the thin film showed that the crystalline structure of Cu-BTEC was retained even after doping with TCNQ molecule.[12] The most noticeable change was in the appearance of a new peak at 2θ ~ 5.8° which can be attributed to the incorporation of TCNQ into Cu-BTEC thin film likewise previous reports[13] on guest molecule incorporation (Figure 3b).[6, 7, 14, 15] Additionally it also hints at the possibility of long-range order.[15] The infiltration of TCNQ into the pores of Cu-BTEC was further supported by Raman measurements, where a peak at ~240 cm^{-1} corresponding to the presence of open metal site vanished after filling the pores with TCNQ molecule (Figure 3c).[8-10] Energy dispersive X-ray spectroscopy (EDXS) analysis showed that in doped thin film system, Copper (Cu), carbon (C), Oxygen (O) and Nitrogen (N) elements were present homogeneously throughout the doped thin film (Figure 3d).

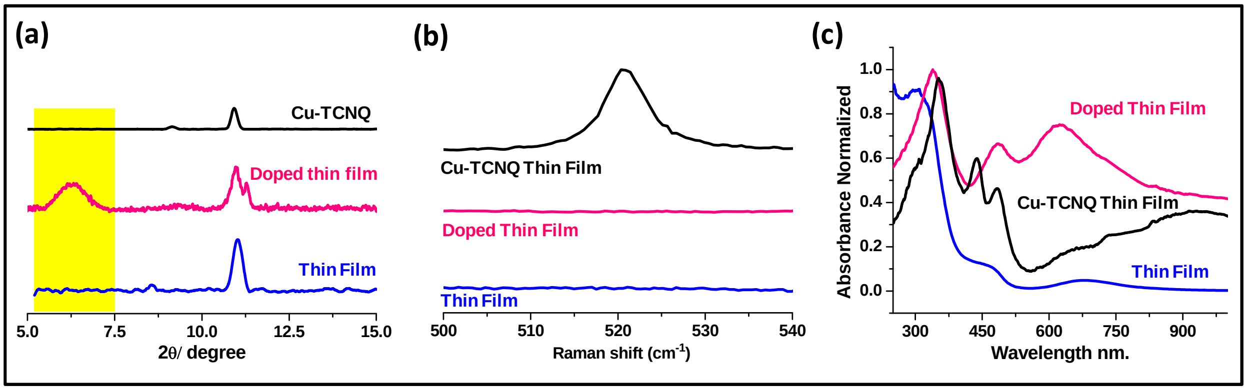


Figure 4. *(a) Out-of-plane XRD pattern of pristine (blue) and doped (pink) Cu-BTEC thin films and (black) of pristine Cu-TCNQ thin film. The peak at 2θ ~ 5.8º characteristic of pore-filling phenomenon in Cu-BTEC system is not a characteristic of pristine Cu-TCNQ thin film (highlighted in yellow). (b) Raman spectra of pristine (blue) and doped (pink) Cu-BTEC thin films and of pristine Cu-TCNQ thin film (black). Raman band at ~520 cm^{-1} is due to Cu---Cu interaction mode appeared in pristine Cu-TCNQ thin film was consistently absent in both pristine and doped Cu-BTEC thin films. (c) Distinctive solid-state UV-vis spectra of pristine (blue) and doped (pink) Cu-BTEC thin films and of pristine Cu-TCNQ thin film (black).*

At this point, we would like to point out that the ordering of TCNQ molecules does not take place at the cost of growing Cu-TCNQ on Cu-BTEC thin film. Although a recent report shows the conversion of Cu_3BTC_2 to Cu-TCNQ on exposing to methanolic solution of TCNQ, no such transformation was observed in the present work.[16] This was evidenced from our various complementary measurements ruling out the possibility of formation of Cu-TCNQ/Cu-BTEC lattice heterostructure: (1) PXRD measurements showed that the crystalline structure of Cu-BTEC was well-preserved in the doped thin film;[12] specifically, characteristic diffraction peak at $2\theta \sim 5.8^{o}$ was absent in pristine Cu-TCNQ thin film (Figure 4a);[16] (2) one characteristic Raman signal of pristine Cu-TCNQ at ~520 cm^{-1} (perhaps due to Cu---Cu interaction mode) was absent in our doped thin film (Figure 4b); (3) a uniform presence of oxygen (O) in our EDXS analysis on the surface as well as the cross-section, in both pristine and doped thin film was noticed (Figure 5); (4) in case of pristine Cu-TCNQ, one main peak in the N1s XPS signal is expected; however, N1s XPS spectrum of our doped thin film clearly exhibited two distinctive peaks (Figure 6b);[17] (5) solid-state UV-vis spectra of pristine Cu-TCNQ thin film and our doped thin film were markedly different (Figure 4c).

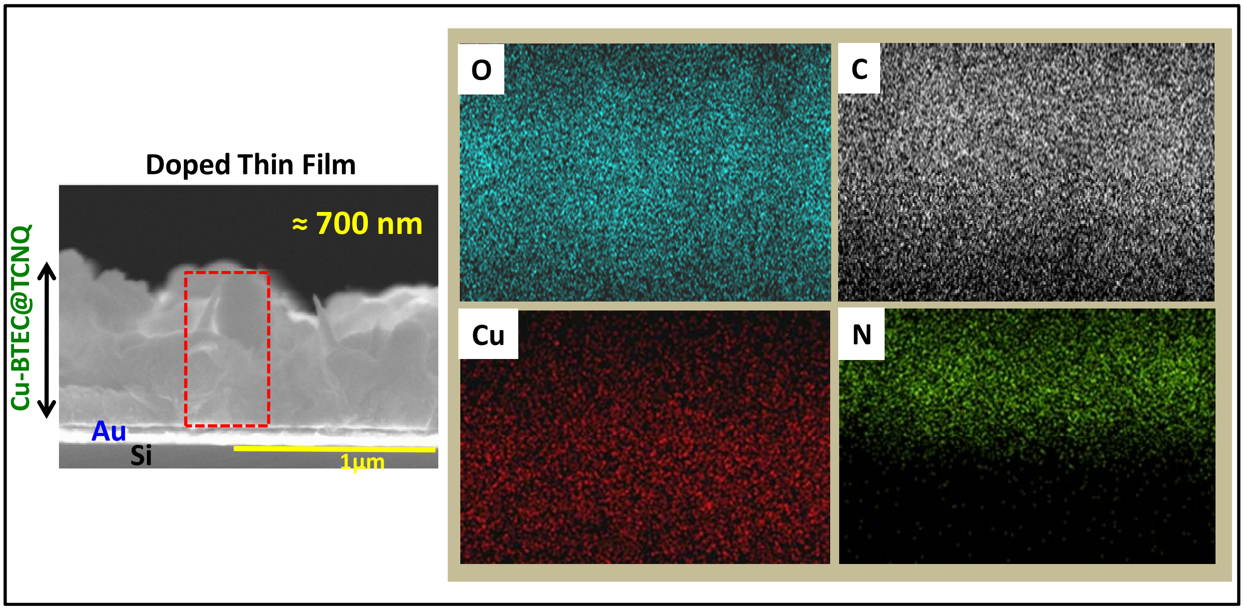


Figure 5. *Cross-sectional elemental mapping of O, C, Cu and N on the doped Cu-BTEC thin film by EDXS analysis showing the absence of TCNQ in lower region near the Au substrate.*

From aforementioned study, we ruled out the possibility of formation of Cu-TCNQ/Cu-BTEC lattice heterostructure and reinforced the idea of TCNQ ordering in Cu-BTEC framework.

The presence of inherent open-metal sites in Cu-BTEC thin film not only helped in coordinating the TCNQ molecules to such sites but also ordering the redox-active guest molecules into the pores of Cu-BTEC. The prospect of having innate open metal sites/ open coordination site (OCS) in the Cu-BTEC thin film framework is exciting not only in terms of coordinating the incoming guest molecule to the metal centre but also because it bypasses the need of any activation process which is invariably associated with some potential structural damage.[18, 19]

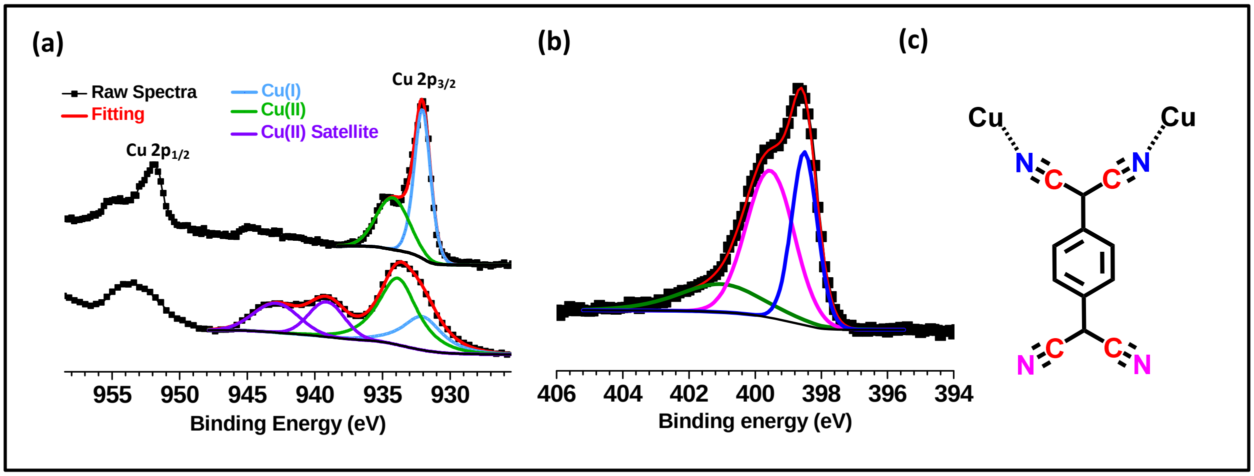


Figure 6. *(a) High-resolution Cu 2p XPS spectra of pristine (bottom) and doped (top) Cu-BTEC thin films. Satellite spectral zones characteristics of Cu(II) species is almost vanished after doping. (b) N 1s XPS data showing two peaks which can be attributed to the distinctive chemical environments, bonded (blue) and free (pink) Ns of TCNQ, in the doped Cu-BTEC thin film. The green fitted line is assigned to satellite feature. (c) Schematic representing bonding motif of TCNQ to Cu-BTEC framework.*

The oxidation state of Cu before and after doping with TCNQ was probed with the help of X-ray photoelectron spectroscopy (XPS). The thin film of Cu-BTEC exhibited the Cu $2p_{3/2}$ signal at ~934.1 eV and ~932.1 eV with strong satellite features indicating that Cu(II) was majorly present.[19] However, the TCNQ doped thin film showed the Cu $2p_{3/2}$

signal at ~932.0 eV and the satellite features was almost disappeared which confirms that Cu(I) was now the dominant species (Figure 6a).[15, 20]

The bonding motif of Cu-BTEC@TCNQ was extensively studied by various spectroscopic techniques, namely XPS, Raman and Vibrational spectroscopy. The XPS of Cu-BTEC@TCNQ thin film revealed the presence of two N 1s peaks, hinting at a non-equivalent bonding environment of nitrogen in Cu-BTEC@TCNQ.[21] It is well documented in literature that all the four nitrogens in Cu-TCNQ exhibit a single equivalent peak ~398.0 eV which is due to their similar bonding environment. However, the splitting of the N 1s peak into two in our system at ~398.5 eV and ~399.5 eV is a strong indication that not only is the bonding environment of the four nitrogens is different but also two of them exist in a neutral state (~398.5 eV) while the other two are bonded strongly to the Cu metal centre and exist in a uninegative state (~399.5 eV) (Figure 6b).

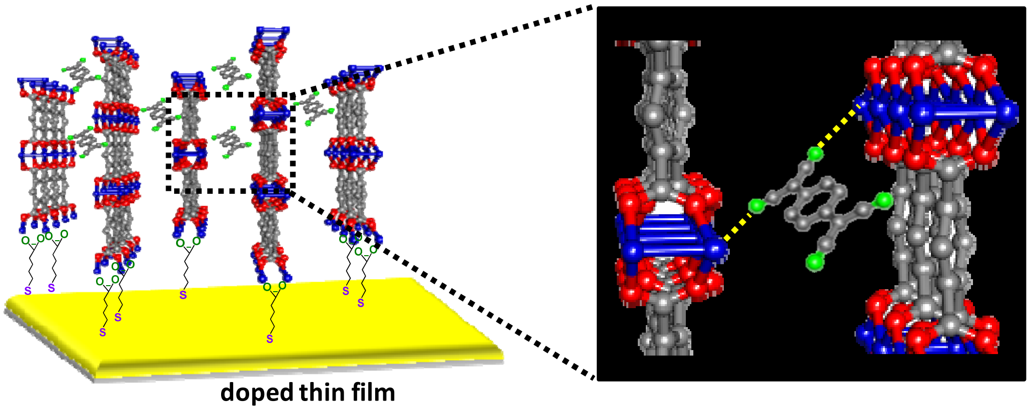


Figure 7. *Schematic representing the bonding motif of TCNQ to the Cu-BTEC framework.*

Raman spectra of Cu-BTEC@TCNQ indicates that the C=C stretching frequency of TCNQ was shifted from ~1455 cm^{-1} to ~1374 cm^{-1}. A shift of ~80 cm^{-1} for C=C wing stretching mode suggest a partial charge transfer of between Cu-BTEC framework and TCNQ (Figure 8c).[22] The nitrile $C\equiv N$ stretching frequency at ~2208 cm^{-1} was observed to split into two peaks at ~2202 cm^{-1} and ~2217 cm^{-1} which is an indication that the bonding environment of TCNQ is non-equivalent.[6] This arises as two of the CNs are bound to the active metal centre while the remaining two CNs remain unbound which can be visualized from the proposed structure (Figure 8a), in good agreement with an earlier similar observation.[6]

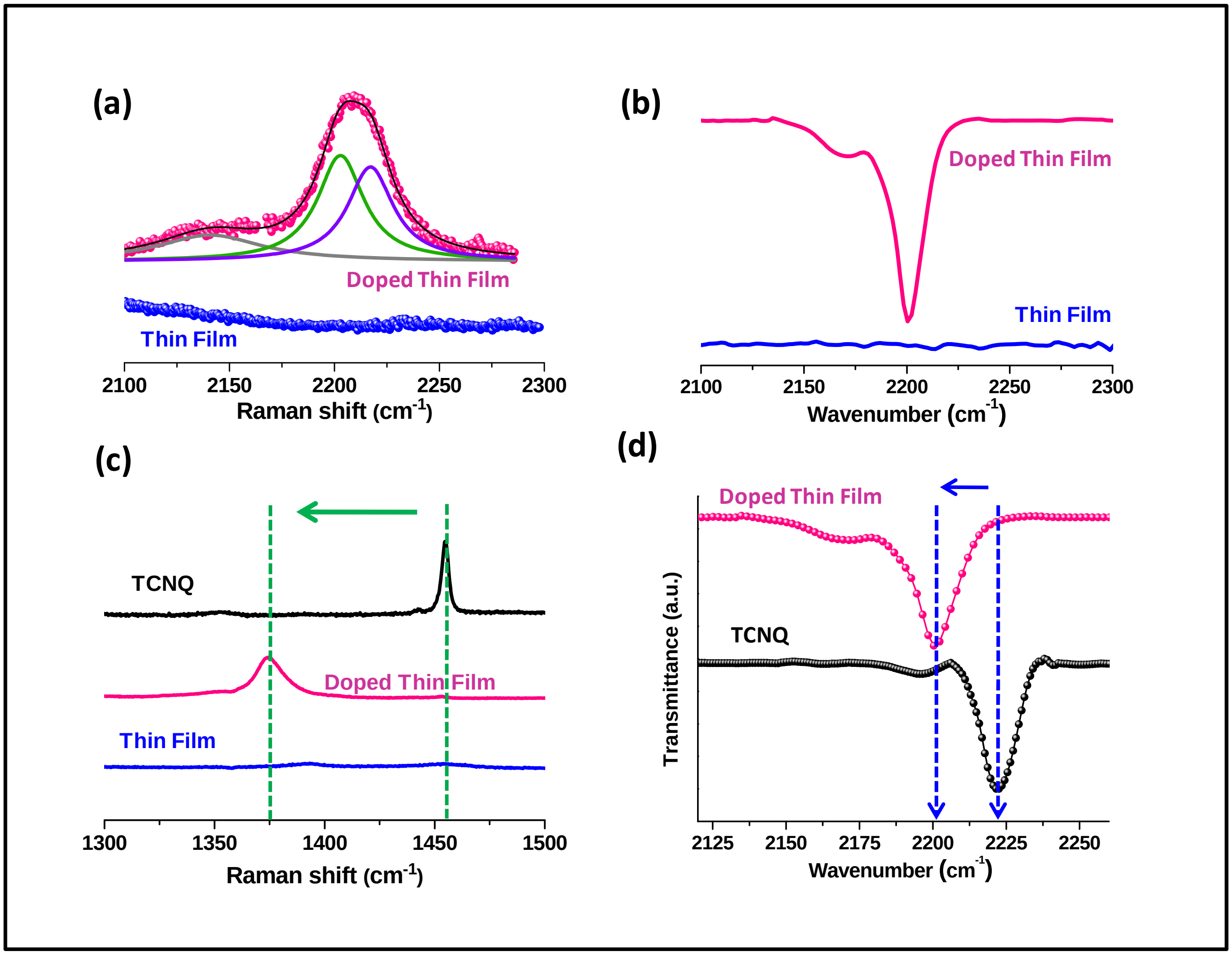


Figure 8. *(a) Raman spectra of pristine (blue) and doped (pink) Cu-BTEC thin films. Splitting of nitrile C≡N stretching frequency, a feature absent in pristine thin film is represented by fitted lines. (b) Infrared reflection-absorption spectroscopy (IRRAS) data revealing the presence of C≡N stretching frequency in the doped Cu-BTEC thin film (pink) when compared with the pristine Cu-BTEC thin film (blue). (c) Raman spectra of pristine (blue) and doped Cu-BTEC (pink) thin films with pure TCNQ (black). Band characteristics of C=C wing stretching mode of TCNQ, a significant red-shift from ~1455*

cm^{-1} to ~1374 cm^{-1} was observed in doped thin film (pink). FTIR spectrum of pure TCNQ (black) and IRRAS spectrum of doped Cu-BTEC thin film.

Furthermore, the peak at ~2142 cm^{-1} suggests the formation of some quantity of neutral TCNQ at the surface of the doped Cu-BTEC@TCNQ thin film. These findings were further assisted by the infrared spectra which showed that the C≡N stretching frequency of the doped thin film was shifted from ~2223 cm^{-1} to ~2202 cm^{-1} with respect to the TCNQ moiety. This shift of ~20 cm^{-1} can be attributed to partial charge transfer between TCNQ and Cu-BTEC framework (Figure 8d).[23] The emergence of this peak in the doped sample is a strong indication that TCNQ interacts with the open metal sites available on the Cu^{2+} ions in the framework (Figure 8b).[24]

For estimating the optical band gap values for thin films, the Tauc plots were recorded from the solid state UV-vis absorption spectra. Surprisingly, there was a lowering of band gap in the doped Cu-BTEC@TCNQ thin film to ~3.0 eV from the ~3.48 eV for the undoped Cu-BTEC thin film.[25] Additionally there was the emergence of two new bands at ~1.5 eV and ~2.2 eV in the Cu-BTEC@TCNQ thin film, evincing the formation of excitonic band between conduction and valence band which might be responsible for reducing the band gap. There is, thus, a semiconductor feature which could facilitate electrical transport.[14, 26] (Figure 9a)

Such gap-states might reduce the electronic band gap and facilitate electron transport in the thin film. To investigate the effect of molecular doping on the electrical conductivity, *I-V* measurements on our thin films were carried out in-plane mode. An impressive enhancement (7.8×10^6 times) was observed for the in-plane electrical conductance value of the doped thin film in comparison to that of the pristine thin film (Figure 9b) – pretty much in consistent with an earlier report highlighting electronic coupling between HKUST-1 MOF (comprised of Cu(II) ion and 1,3,5-Benzenetricarboxylic acid (BTC) also known as Cu-BTC) and dopant TCNQ generating conducting path via Cu---TCNQ links.[6, 7]

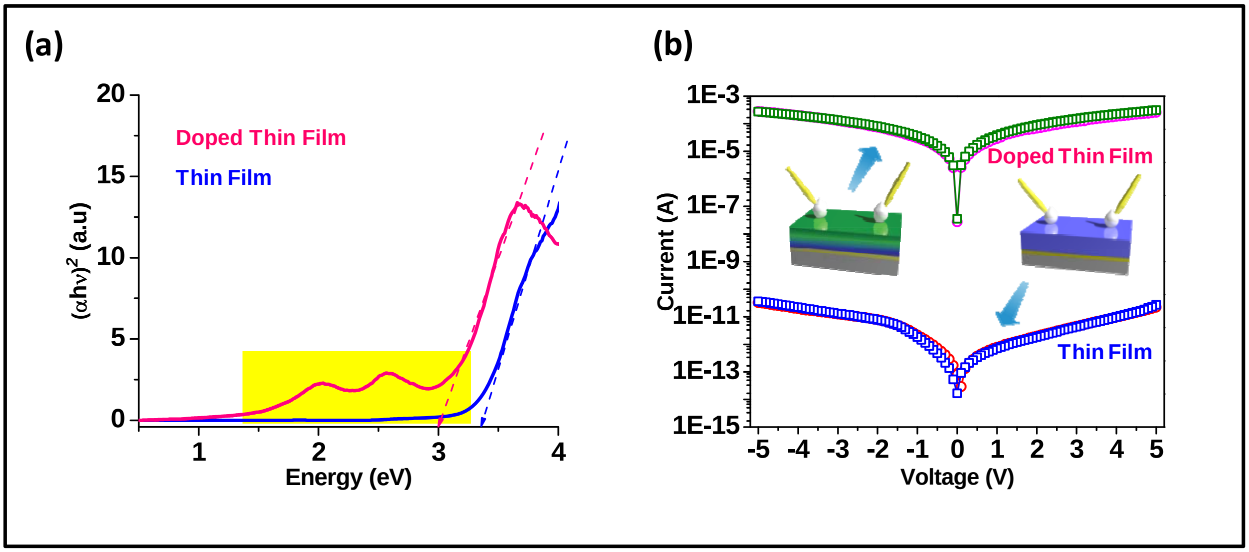


Figure 9. (a) *Tauc plot of doped thin film suggest the existence of gap-states in the doped thin film which were absent in the pristine thin film. (b) In-plane current−voltage (I−V) characteristics of pristine (blue and red) and doped (green and magenta) Cu-BTEC thin films, carried out for two different batches of samples, showing a significant enhancement in the conductivity in the latter.*

Motivated by the anisotropic nature of thermal conductivity, *I-V* measurements for our thin film were carried out both in-plane as well as cross-plane. A million-fold enhancement was observed in the electrical conductivity of the TCNQ infiltrated Cu-BTC[6, 7] thin film but surprisingly no rectification feature was noticed. Remarkable rectification feature was observed in Cu-BTEC@TCNQ thin film when the *I-V* measurements were carried out in cross-plane. The current rectification ratio (RR), define as the absolute value of the quotient between the current recorded for one voltage polarity and the current recorded for the same voltage at opposite polarity, estimated in the order of ~3.1×10^5 is a record value in the realm of organic-inorganic hybrid materials (Figure 10b). This is a huge achievement considering the fact that MOFs (either in bulk form or in thin films) have not been able to reach the 10^2 mark in RR values.[25, 27-30]

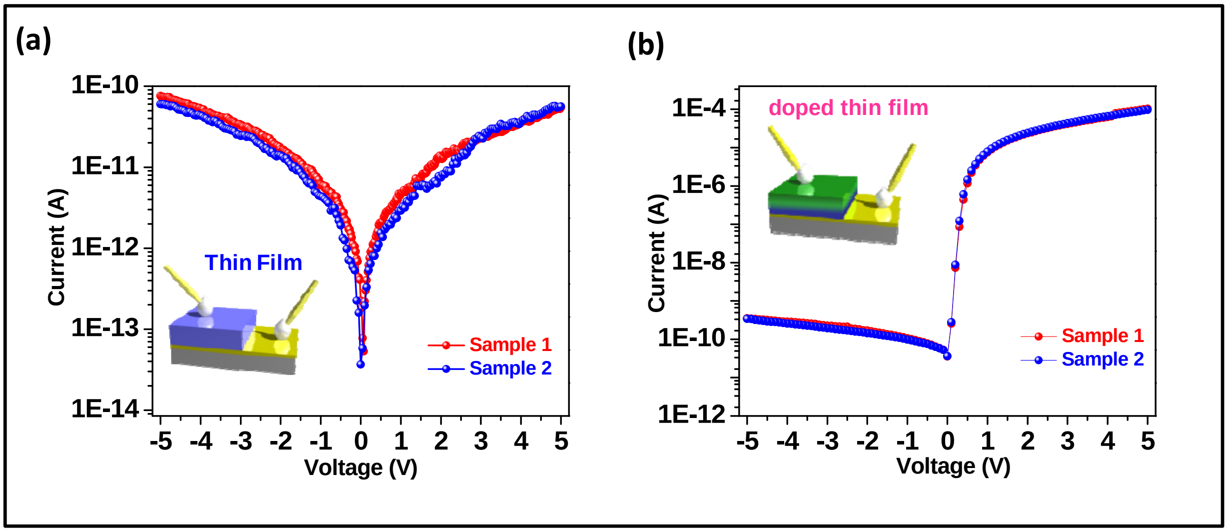


Figure 10. *(a) Cross-plane current−voltage (I−V) characteristics of pristine (red and blue) Cu-BTEC thin film, carried out for two different batches of samples, showing no current rectification. (b) Cross-plane current−voltage (I−V) characteristics of doped (blue and red) Cu-BTEC thin film, carried out for two different batches of samples, showing a clear current rectification with RR value ≥10^5*

When *I-V* measurements were carried out in cross-plane mode, electrical conductance value of the pristine thin film was observed to be similar to that of in-plane conductance value ~3.6 x 10^{-11} and ~6.8 x 10^{-11} S, respectively (Figure 10a).

At this point, we would like to highlight that in-plane *I-V* characteristics of our doped thin film, both at room-temperature and high-temperature, were observed to be distinctive from that of the pristine Cu-TCNQ thin film (Figure 11).[11, 31] Also *I-V* measurement analysis ruled out the possibility of formation of Cu-TCNQ-Cu-BTEC lattice heterostructure.

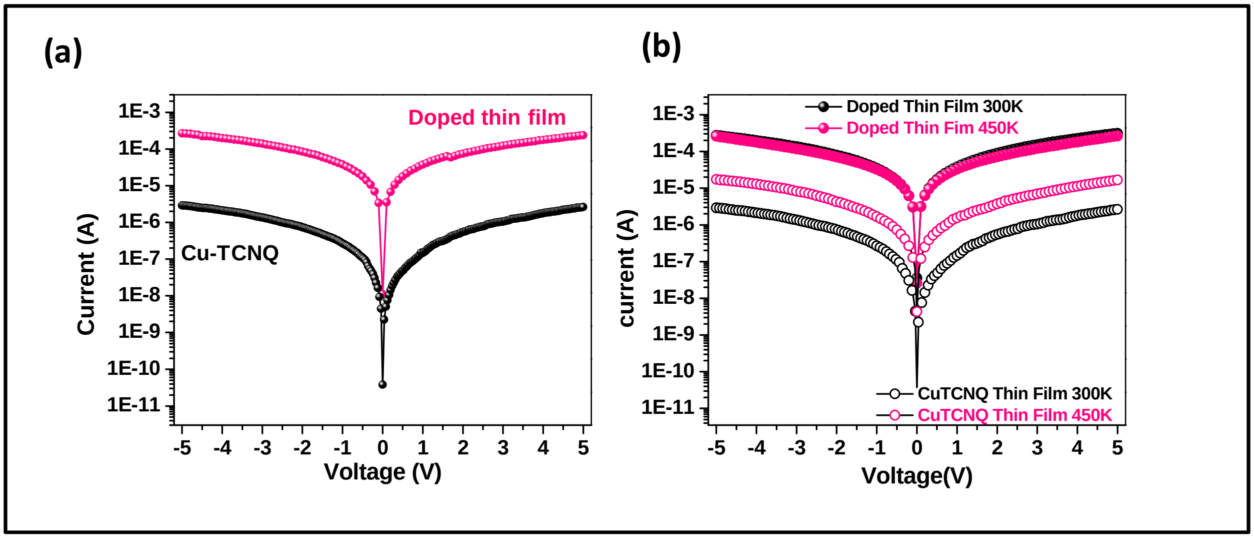


Figure 11. *(a) Current−voltage (I−V) characteristics of doped (pink) Cu-BTEC and pristine Cu-TCNQ (black) thin films. (b) Variable-temperature I-V characteristics of doped Cu-BTEC thin film recorded at 300K (black filled circle) and at 450 K (pink filled circle); and of pristine Cu-TCNQ thin film recorded at 300K (black open circle) and at 450 K (pink open circle).*

Further, moving one step ahead, we want to check our doped thin film is thermally stable or not, for that we did temperature-dependent PXRD measurements and found to be very much stable and can sustain temperatures as high as 450 K (Figure 12a). The RR values were constant at ~10^5 when the temperature was increased to 450 K and again cooled down to room temperature (Figure 12b). This implies that our device is stable and can sustain temperatures as high as 450 K, a rarity in MOFs.

Now the question is, why the unusual rectification and the giant enhancement of electrical conductivity. It can be reasoned that there is a gradient of TCNQ molecule in the framework, i.e. for a film thickness of ~700 nm, (Figure 13) only 300-350 nm was doped with the guest molecule while the remaining layers closer to the SAM/Au substrate remained undoped.[32]

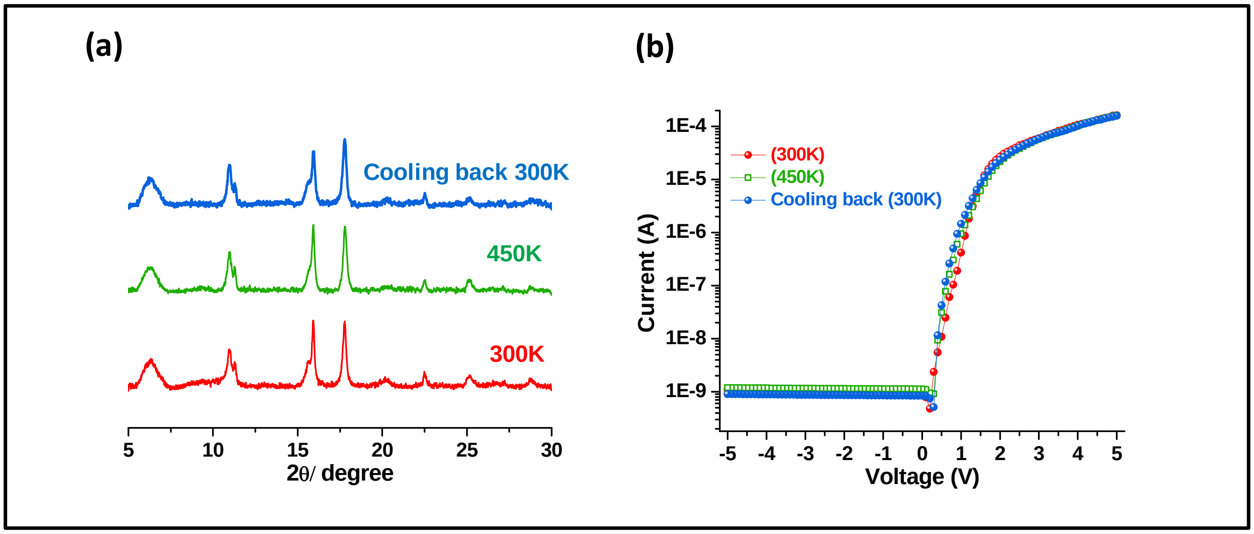


Figure 12. *(a) Variable-temperature out-of-plane XRD patterns of the doped Cu-BTEC thin film recorded at 300 K (red), at 450K (green) and cooling back to 300 K (blue). (b) Variable-temperature I-V characteristics of the doped Cu-BTEC thin films recorded at 300 K (red), at 450 K (green) and cooling back to 300 K (blue).*

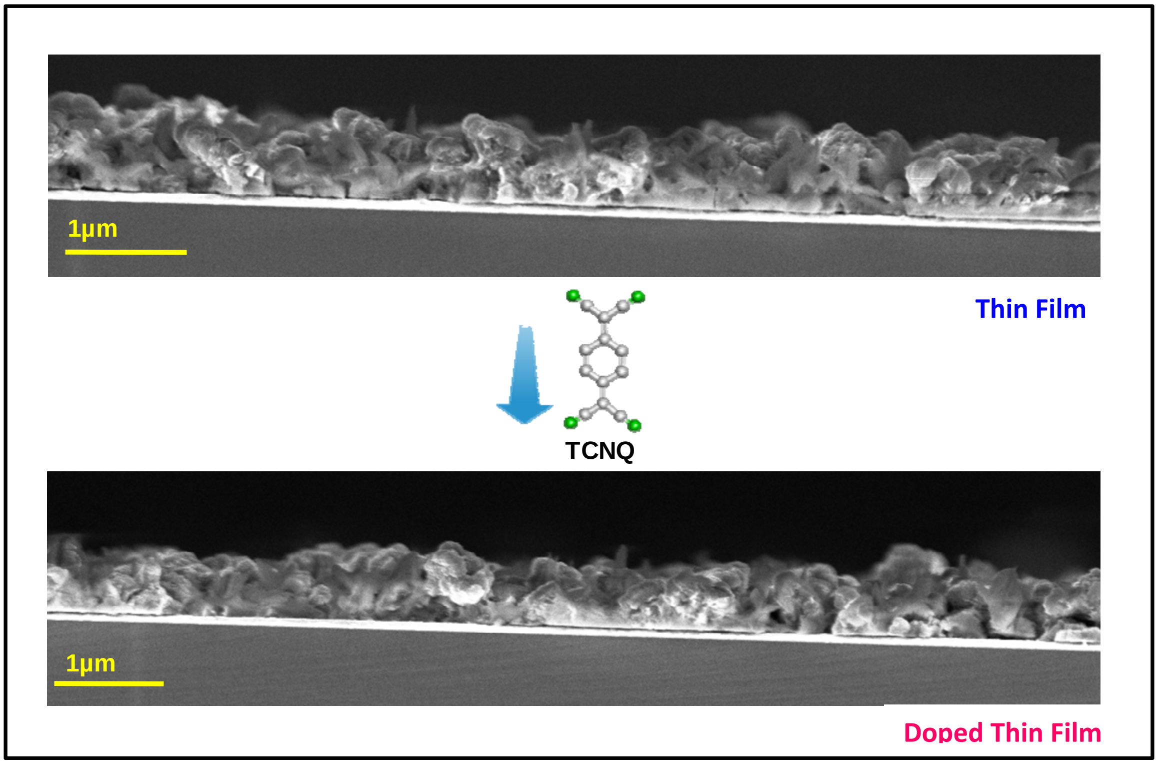
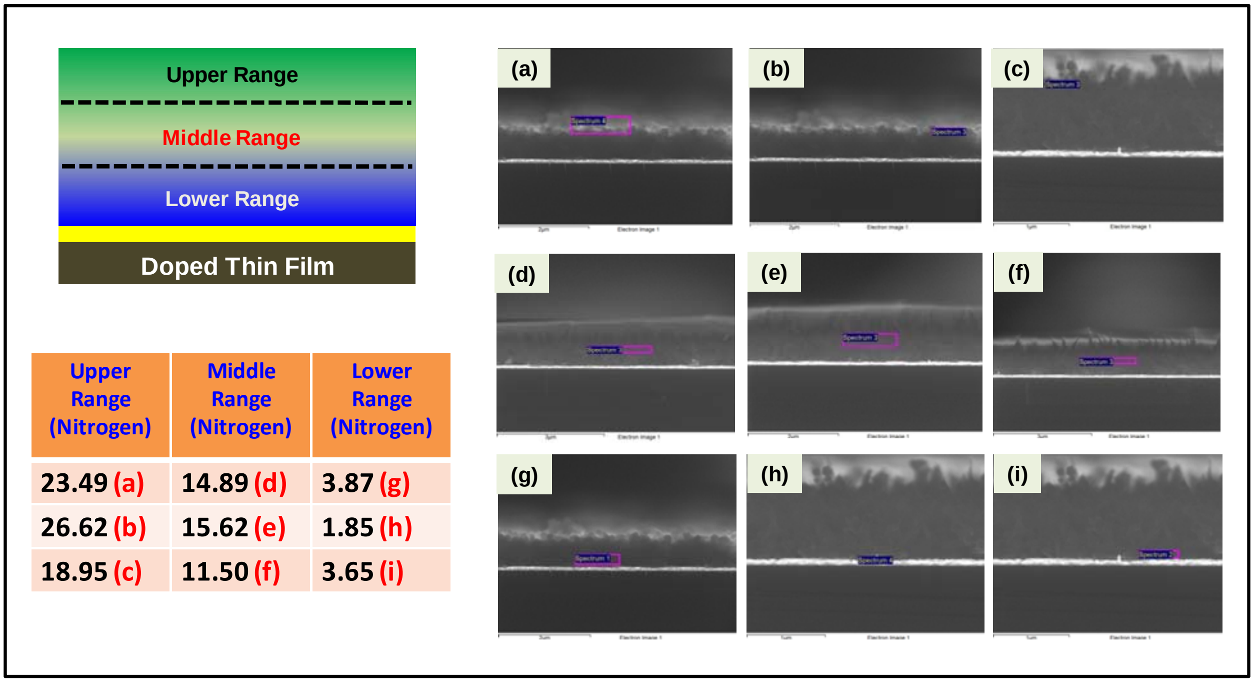


Figure 13. *Cross-sectional FE-SEM image of the Cu-BTEC thin film and doped Cu-BTEC thin film.*

This was clearly seen in the cross-sectional EDXS where nitrogen, acting as a marker for TCNQ was heavily present on the top surface of the film but was conspicuous by its absence in the bottom layers (Figure 5). Thus while carrying out *I-V* measurements in-plane, only enhancement of electrical conductivity was observed, however for *I-V* measurements performed in cross-plane, rectification was noticed because the flow of current was restricted in the cross-plane. So, half of the thin film was conducting while the other half was insulating in nature, giving rise to rectification having resistance value in order of $10^{11}\Omega$. If one looks closely at the resistance values for *I-V* measurements carried out in cross-plane, one can see that the values in negative potential correspond very closely to that observed for the as-synthesized undoped thin film (in the order of 10^{11}-10^{10}) while the values pertaining to the positive potential resemble that of the doped thin film (~10^4) (Figure 10). This finding also corroborates the earlier claim of gradual diminishment of TCNQ along the layers from the surface.



Upper Range (Nitrogen)	Middle Range (Nitrogen)	Lower Range (Nitrogen)
23.49 (a)	14.89 (d)	3.87 (g)
26.62 (b)	15.62 (e)	1.85 (h)
18.95 (c)	11.50 (f)	3.65 (i)

Figure 14. *Cross-sectional EDXS analysis of the doped Cu-BTEC thin film in three different ranges (upper, middle and lower) with corresponding FE-SEM images.*

Now the question is “Is 48 hours a magic number?” for enhanced million fold conductivity “In-plane” and with a record value of RR in “Cross-plane”. To address this question, we carried time dependent doping studies. Interestingly we find that with increasing in doping time, conductivity increases (in-plane) measurement and also RR in cross-plan *I-V* measurement.(Figure 15)

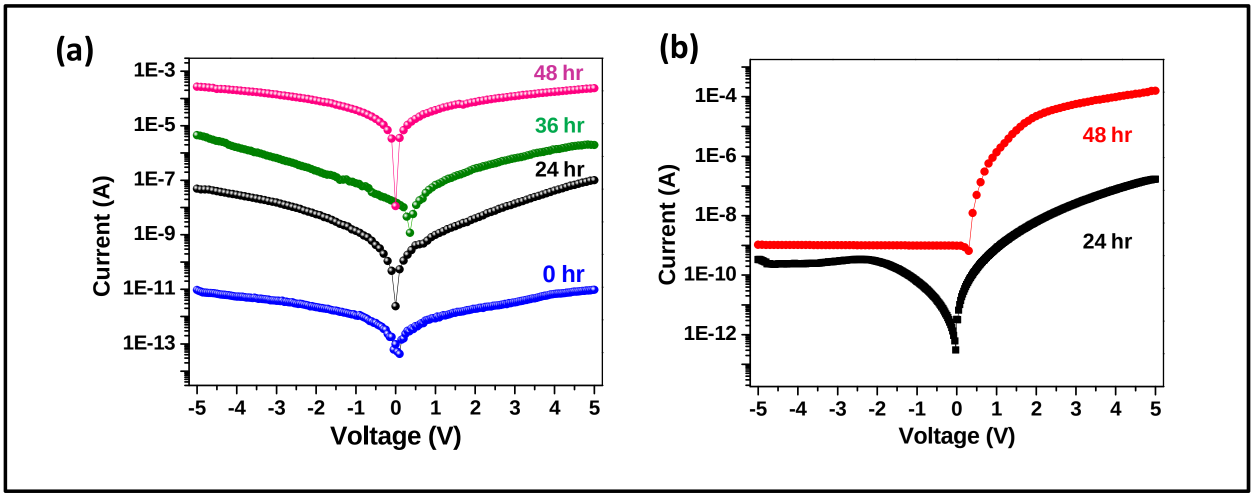


Figure 15.*(a) In-plane current−voltage (I−V) characteristics of doped Cu-BTEC thin films, carried out for 4 different doping time i.e. 0 hr (undoped) (blue),24 hr (black),36 hr (green) and 48 hr (pink) showing a significant enhancement in the conductivity when increasing doping time (b) Cross-plane current−voltage (I−V) characteristics of doped Cu-BTEC thin films, carried out for 2 different doping time i.e. 24 hr (black) and 48 hr (red) showing a significant enhancement in the RR when increasing doping time.*

To cross verify that the rectification behavior was arising due to our material and not instrument, the directionality of current flow was reversed to SMU2 (source measure unit) from SMU1, and indeed a reverse pattern was observed indicating that the effects were due our material and not any external art effect (Figure 16).

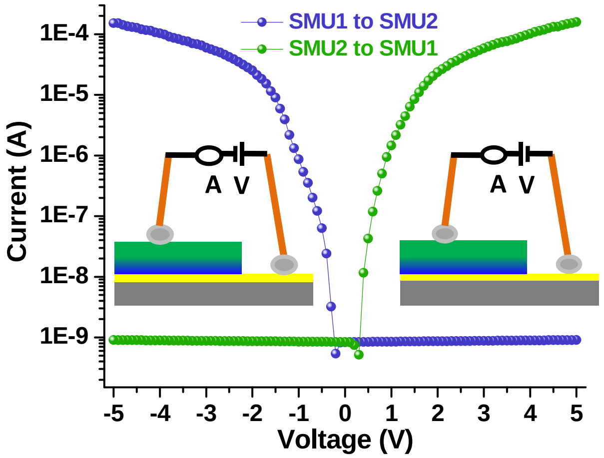


Figure 16. *I-V characteristics of the doped Cu-BTEC thin film with changing the direction of current flow by reversing to source measure unit (SMU)-2 (green) from source measure unit (SMU)-1 (blue) and vice versa.*

Motivated by such an unusual observation, we wanted to directly compare the *I-V* characteristics of our system with those of commercial Si rectifier diodes (1N4007 and 1N4733A) and RR values were estimated to be at par (Figure 17)!

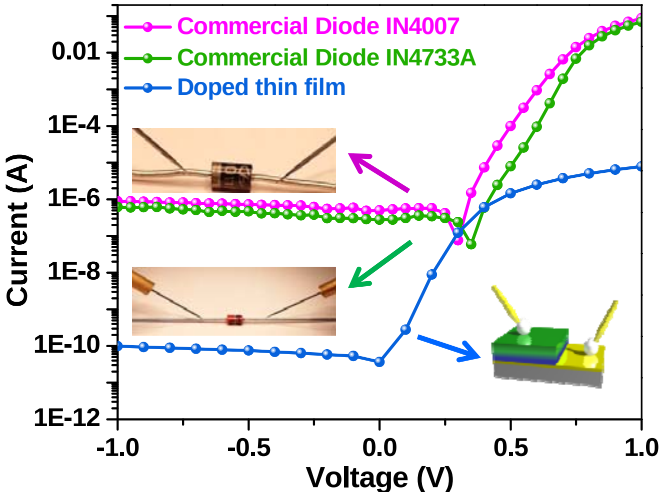


Figure 17. *Direct comparison of I-V characteristics of the doped Cu-BTEC thin film (blue) with commercial Si rectifier diodes (1N4007, magenta and 1N4733A, green).*

Conclusion

We have been successful in fabricating a Cu-BTEC thin film for the first time using the LbL method. The as-synthesized film was found to be abounding with inherent open-metal sites which helped in ordering of the incoming redox-active guest molecule, TCNQ. The ordered TCNQ molecules into the pores of Cu-BTEC system helped in creating a conductive path leading to the giant enhancement of conductivity. The improved conductivity values were stemming from the molecular doping giving rise to electronic heterostructure and not the formation of lattice heterostructure as was confirmed from both PXRD and EDXS measurements. Along with the improved conductivity value, a never observed before, rectification ratio (RR) value was observed in our system when the *I-V* measurements were performed in cross-plane which was constant at high temperatures (450 K). The reason for this high value was investigated and found to be the gradual diminuendo of TCNQ along the layers from the surface. Additionally, the doping was found to modulate the thin film character by making it highly hydrophobic from its initial hydrophilic state. Thus, such thin films which can sustain not only high temperatures but are also resistant to moisture are interesting in terms of scientific pursuit as well as for realizing them in real world applications for various electronic devices. We hope that our findings may open a new direction in the realm of conductivity in thin films.

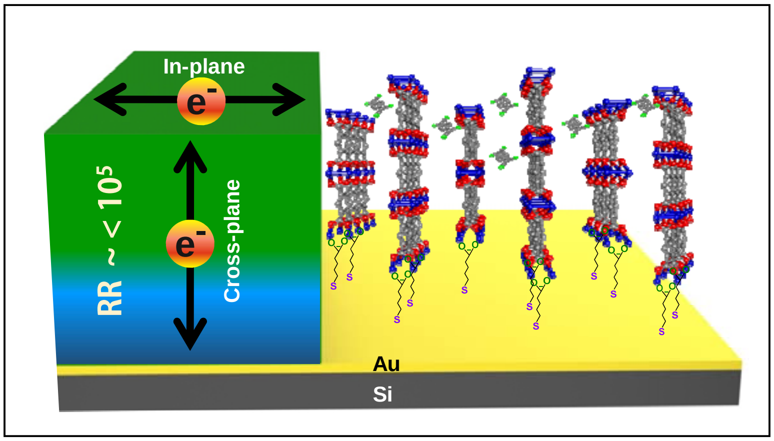


Figure 18. *A schematic representation of doped thin film of Cu-BTEC on SAM template and the bonding motif of TCNQ in the Cu-BTEC framework.*

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