



High resolution electron energy loss spectroscopy study of Zinc phthalocyanine and tetrafluoro tetracyanoquinodimethane on Au (1 1 1)

Jiong Lu, Kian Ping Loh *

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

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ABSTRACT

Using high resolution electron energy loss spectroscopy, we have examined the vibrational and electronic information of Zinc phthalocyanine (ZnPc) and tetrafluoro tetracyanoquinodimethane (F4-TCNQ) on Au (1 1 1). The changes in the vibrational loss features reveal distinct changes in growth modes at different film thickness as well as occurrence of charge transfer between adsorbate and substrate. Up to a thickness of 10 monolayers, ZnPc film grows with its molecular plane parallel to the substrate. After the introduction of small quantities of F4-TCNQ on ZnPc film, evidence of p-doping can be seen from the red shift of C≡N stretching in F4-TCNQ.

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1. Introduction

Organic semiconductor with conjugated π -electron systems are widely investigated in connection with their technological applications in optoelectronic devices such as organic light emitting diodes, field-effect transistors and solar cell [1–6]. The molecular structure and orientation of these organic molecules on the electrode are important parameters that determine the efficiency of charge transport. The introduction of an organic layer may introduce interface dipole which changes the injection barriers of holes or electrons at the electrode. Doping of the organic semiconductor based on donor–acceptor interaction is one way of increasing the device efficiency by improving the film conduction and enhancing the carrier injection [7–10].

Due to their macrocyclic nature and extended π -systems, phthalocyanines are p-type organic conductors where the charge transport is enabled by specific orientation such as planar, stacked and axially bridging (structure of ZnPc is shown in the inset of Fig. 1), and enhanced by doping [11]. Tetrafluoro tetracyanoquinodimethane [(F4-TCNQ), the structure shown in the inset of Fig. 2], a strong molecular electron acceptor with high electron affinity, has been widely used in organic light-emitting diodes to reduce the hole injection barrier by forming a narrow space-charge region near the metal contact [12–14]. p-Type doping of ZnPc by the incorporation of small amount of F4-TCNQ molecules in order to enhance the conductivity of organic layer and improve charge carrier injection has been demonstrated previously [14–16].

High resolution electron energy loss spectroscopy (HREELS) is ideally suited for studying organic thin films because both vibrational and electronic properties of the organic film can be studied

simultaneously [17,18]. In particular, HREELS allow us to investigate the presence of electron–phonon coupling and interfacial charge transfer both at the intra- and inter-molecular level. The adsorption geometry and interfacial interactions of several large conjugated organic molecules on metal or semiconductor surfaces had been investigated by several groups. Previous studies found that copper phthalocyanine (CuPc) molecules lie flat on the Au (100) and HOPG surfaces [19,20]. The interfacial interaction in CuPc/Au (100) is relatively weak, whereas the molecule–substrate interaction is stronger for metal-free phthalocyanine on InAs substrate due to chemisorption [21]. Using HREELS, Tautz et al. [22,23] reported charge transfer type interaction between Ag and 3,4,9,10-perylene-tetracarboxylic acid-dianhydride (PTCDA). The present work is motivated by the fact that to date, no detailed vibrational and electronic information of F4-TCNQ and ZnPc molecule has been reported. In order to understand the influence of the interface to the intramolecular vibration, as well as to decipher charge transfer interactions between the acceptor F4-TCNQ and donor ZnPc, we performed HREELS measurements during the adsorption of F4-TCNQ and ZnPc on Au (1 1 1).

2. Experiment

The measurements were performed in a HREELS analysis chamber (3×10^{-10} torr) which is adjoined to a sample preparation chamber and a sample transfer system. The gold substrate used in this study was a polished Au (1 1 1) (Mateck). The sample surface was cleaned by repeated cycles of 800 eV argon ion sputtering and annealing. The surface cleanliness was checked by low electron energy diffraction and HREELS. F4-TCNQ and ZnPc were evaporated onto the gold surface at room temperature using two Knudsen cells (MBE Komponenten, Germany) mounted in the preparation chamber. The film thickness was monitored using a quartz microbalance.

* Corresponding author. Fax: +65 67791691.

E-mail address: chmlhokp@nus.edu.sg (K.P. Loh).

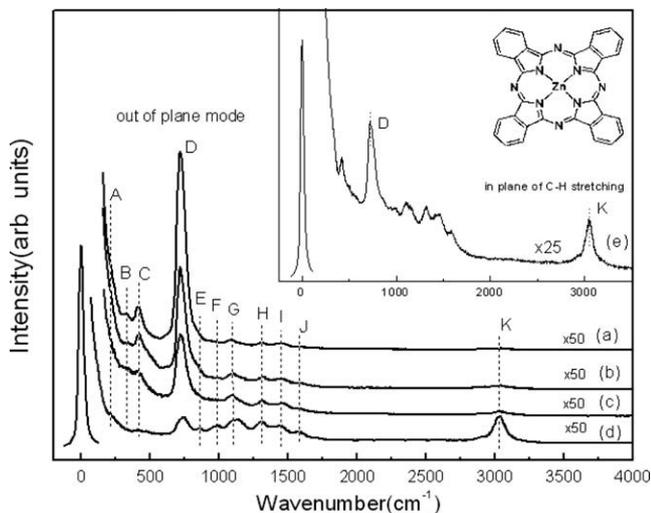


Fig. 1. HREELS spectra of ZnPC deposited on Au (111) surface at different thickness: (a) 1 ML; (b) 4 ML; (c) 10 ML; (d) 20 ML; and (e) off-specular (10°) HREELS spectrum for 1 ML ZnPC/Au (111).

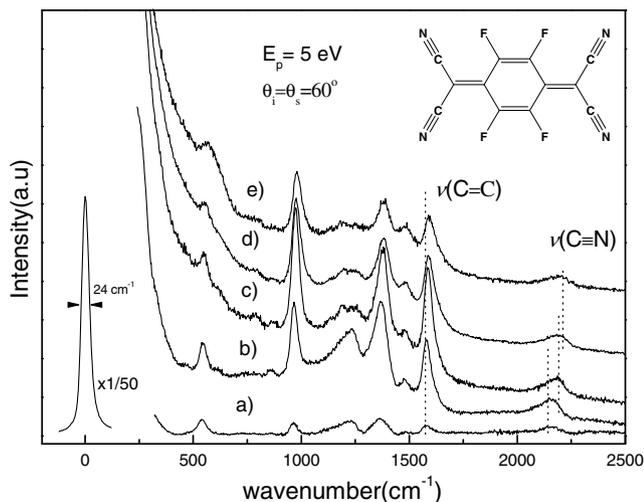


Fig. 2. HREELS spectra of F4-TCNQ deposited on Au (111) surface of various thickness (a) 0.4 ML; (b) 1 ML; (c) 3 ML; (d) 6 ML; and (e) 10 ML.

The accuracy of the film thickness was estimated to be ± 0.2 ML. The evaporation rate was $1 \text{ \AA}/\text{min}$ at the pressure at 2×10^{-9} torr. After dosing, the sample was transferred into the HREELS chamber (SPECS GmbH Delta 0.5). The primary electron energy of 5 eV was used to obtain the HREELS spectra. The full-width-at-half-maximum (FWHM) of the elastic peak was typically 3 meV on clean Au (111) and slightly increased to 6 meV after deposition organic film. For electronic EELS, incident electron energy was set at 25 eV and the FWHM of the peak was 8 meV.

3. Results and discussion

3.1. ZnPC on Au (111)

Fig. 1 shows the specular HREELS spectra ($\theta_i = \theta_s = 60^\circ$) of ZnPC thin films on Au (111) as a function of film thickness. The HREELS spectra present many well-resolved vibrational modes. The prominent loss peaks are labeled 'A' to 'K'. Table 1 shows the peak assignments of the ZnPC stretching, bending and deformation modes [20,21,24,25]. At monolayer coverage of the ZnPC, the

Table 1
Assignment of ZnPC vibrational modes.

Peak	HREELS loss (meV/cm ⁻¹) observed	Assignment from IR and HREELS data [20,21,24,25]
A	27/217	Zn–N stretching
B	41/330	Zn–N bond deformation
C	53/426	Macrocycle angular deformation (C–H)
D	90/724	Out of plane C–H bending
E	108/865	Isoindole deformation
F	124/997	Benzene breathing in-plane C–H bending deformation
G	136/1094	C–C and C–N bond stretching
H	164/1319	Isoindole stretching
I	180/1448	C=N and C=C bond stretching
J	198/1598	C=C stretching and isoindole deformation
K	378/3040	C–H stretching

HREELS spectrum in Fig. 1a is dominated by the peak 'D' at 726 cm^{-1} which can be assigned to out-of-plane C–H bending mode. The in-plane modes are weak at the monolayer stage, peaks labeled as 'F', 'G', 'I', 'K' are due to in-plane C–H bending deformation, C–C and C–N stretching, C=N and C=C stretching and C–H stretching, respectively.

An isolated ZnPC molecule has almost planar geometry (D_{4h} symmetry group) and stacks readily to form molecular columns [26]. The specular HREELS spectra as shown in Fig. 1a–d is governed by the dipole selection rule – dipoles oriented perpendicular to a metal surface are strongly excited by dipole scattering, whereas vibrational modes parallel to the surface are screened by their image charges and thus are significantly suppressed [27]. For film thickness below 10 MLs, the out-of-plane C–H bending mode at 724 cm^{-1} (peak 'D') is the prominent feature, while in-plane modes above 800 cm^{-1} have very weak intensities. The inset spectra (curve 'e' in Fig. 1) shows the HREELS measurements for monolayer ZnPC sample collected in the off-specular direction, where the scattering mechanism is dominated by impact scattering. Modes that are forbidden in the dipole regime can be found in the impact scattering. In Fig. 1e, the intensity of the out-of-plane mode (peak 'D') decreases while that of the in-plane modes such as C–H stretching (peak 'K') increases. The changes in relative intensities of the HREELS peak in the in-plane and out-of-plane modes in the dipole and impact scattering regime indicate very clearly that ZnPC molecules are oriented flat on the surface initially and start to orient randomly for layers that exceeded 20 monolayers (ML) coverage. As shown in Fig 1d, when the thickness of the ZnPC film is increased to 20 ML, the intensity of the out-of-plane modes is comparable with that of the in-plane stretching modes, suggesting that molecule starts to adopt a stand-up configuration. Aside from the changes in the relative intensities of the loss peaks, there are no observable shifts in the vibration peaks when the thickness increases from sub-monolayer to multilayers, such a shift is expected if there is charge transfer at the Au–organic interface. The absence of these vibrational shifts suggests that in the deposited films, ZnPC maintains similar property throughout its depth, and there is little charge transfer between Au and ZnPC at the interface.

3.2. F4-TCNQ on Au (111)

3.2.1. HREELS vibrational spectra of F4-TCNQ

Specular HREELS spectra recorded after dosing F4-TCNQ of different thickness on Au (111) is shown in Fig. 2. The principle loss frequencies in the 0.4 ML F4-TCNQ (the bottom spectrum) and 10 ML F4-TCNQ (the top spectrum) adsorption cases are listed in the Table 2. The assignment of energy loss features is made by comparison with the group frequencies assigned in IR and Raman studies of F4-TCNQ crystal previously [28,29]. For sub-monolayer

Table 2
Assignment of F4-TCNQ on Au (111).

0.3 ML F4-TCNQ/Au (111)/(cm ⁻¹)	10 ML F4-TCNQ/Au (111)/(cm ⁻¹)	Modes assignment from IR [28,29]
539	550	b_{3u}
855	857	$b_{1u}v_{22}$
965	965	$b_{2u}v_{36}$
1175	1191	$b_{2u}v_{35}$
1236	1250	a_gv_4
1361	1371	$b_{2u}v_{34}$
1475	1477	$b_{1u}v_{19}$
1574	1589	$b_{2u}v_{33}$
2147	2198	$b_{2u}v_{32}$

F4-TCNQ film, the out-of-plane mode (b_{3u} 539 cm⁻¹) and in-plane modes ($b_{2u}v_{36}$ 965 cm⁻¹, $b_{2u}v_{34}$ 1361 cm⁻¹, $b_{1u}v_{19}$ 1475 cm⁻¹, $b_{2u}v_{33}$ 1574 cm⁻¹ and $b_{2u}v_{32}$ 2140 cm⁻¹) are well-resolved in the spectrum. It appears that the intensity of the in-plane modes is comparable with that of out-of-plane mode at sub-monolayer film coverage, suggesting that F4-TCNQ is oriented at an angle to the Au (111) surface at low coverage, i.e. not lying flat. Fig. 2 shows the evolution of the vibrational features as a function of film thickness from 0.4 ML to 10 ML. Clear changes can be seen in the intensity of some bands, along with significant shifts in the vibrational frequencies (1400–2200 cm⁻¹). One significant observation is the presence of red shifts for the $b_{2u}v_{33}$, $b_{2u}v_{32}$ modes at sub-monolayer coverage relative to the multilayer films. The $b_{2u}v_{33}$ vibrational mode, which is dominated by C=C stretching, is situated at 1574 cm⁻¹ in the sub-monolayer regime. It increases in intensity after 1 ML deposition and its frequency shifts gradually to 1598 cm⁻¹ at 10 ML thickness. The red-shift in the vibrational frequencies of the sub-monolayer film relative to the multilayer film is also apparent in the C≡N stretching vibrational frequency, it is situated at 2147 cm⁻¹ for sub-monolayer film and it shifts monotonically to 2198 cm⁻¹ after 10 ML deposition. The high electron affinity (5.24 eV) of F4-TCNQ compared to pristine Au (111) (work function ~ 5.2 eV) facilitates electron transfers from gold, producing negatively charged F4-TCNQ⁻¹ anion at the gold–F4-TCNQ interface. The charge transfer in the interface is due to the formation of hybrid orbitals between F4-TCNQ π -electron systems and metal states [22,23]. The presence of these ‘softened’ bonds corresponding to the acceptor functional groups (e.g. C≡N) at the interface is consistent with charge transfer from the Au to F4-TCNQ, and more specifically to the anti-bonding MOs associated with the C≡N groups due to their electron withdrawal property. This will cause a reduction in bond order and leads to appearance of the red-shifted modes. Such charge transfer also contributes to the increase in the bond length of the C=C groups in F4-TCNQ which accompanies the deformation from a quinonoid [30] towards a benzenoid structure in the formation of the F4-TCNQ anion [31]. The charge transfer resulted in the observed red shift of the C=C stretching at the Au–F4-TCNQ interface.

3.2.2. Electronic transition

EELS measurements of the F4-TCNQ films on Au (111) at different film thickness are shown in Fig. 3. The gold surface plasmon at 2.51 eV is detected on clean Au (111) surface [32]. After the deposition of 0.2 ML F4-TCNQ, the plasmon peak is attenuated and shifted downward to 2.43 eV. Similar shift had been observed by Shklover for the adsorption of PTCDA on Ag (111) [23]. Charge transfer from metal surface to organic molecule, together with the increase in dielectric constant at the sample–vacuum interface after the adsorption of F4-TCNQ, contributes to the red shift of the plasmon peak. The Q band corresponding to electronic excitation from HOMO to LUMO of F4-TCNQ can be seen around 3 eV. The Q band first appears at 3.05 eV, and it shifts to 3.15 eV at multilayer coverage. After charge

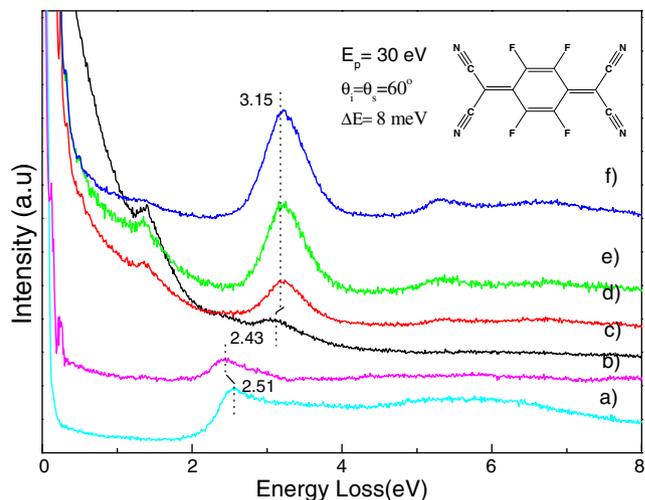


Fig. 3. EELS spectra of F4-TCNQ of various film thickness (a) clean Au (111); (b) 0.2 ML F4-TCNQ; (c) 1 ML; (d) 3 ML; (e) 6 ML; and (f) 10 ML.

transfer from Au to the LUMO of F4-TCNQ, the partially occupied LUMO level relaxes into the gap, forming interface gap states. Electronic excitation involving the interface gap states contributes to the slight red shift of the Q band in the thin F4-TCNQ film. Previous UPS studies have also shown the emergence of interface gap states upon the adsorption of 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCDI) on Ag surface [33].

4. Doping of ZnPc film with F4-TCNQ

4.1. Vibrational spectra of F4-TCNQ/ZnPc film

Fig. 4 shows the HREELS spectra after the evaporation of sub-monolayer of F4-TCNQ on Au (111) that was pre-deposited with 1 ML of ZnPc. Upon the evaporation of 0.4 ML F4-TCNQ on ZnPc film, loss peaks at 542 cm⁻¹, 955 cm⁻¹, 1360 cm⁻¹, and 2136 cm⁻¹ attributable to the functional groups in F4-TCNQ emerge. There are two noteworthy features in the HREELS spectra shown in Fig. 4. First, there is a considerable broadening of the vibrational peak at 3040 cm⁻¹ which corresponds to the ν (C–H) stretching. This may be a result of hydrogen bond formation between F4-TCNQ and ZnPc. Second, the frequency of C≡N stretching was red shifted to 2136 cm⁻¹, which indicate that F4-TCNQ anion is formed due to charge transfer. In order to prevent the influence of the Au (111) substrate on the spectra, thick layers of ZnPc films were pre-depos-

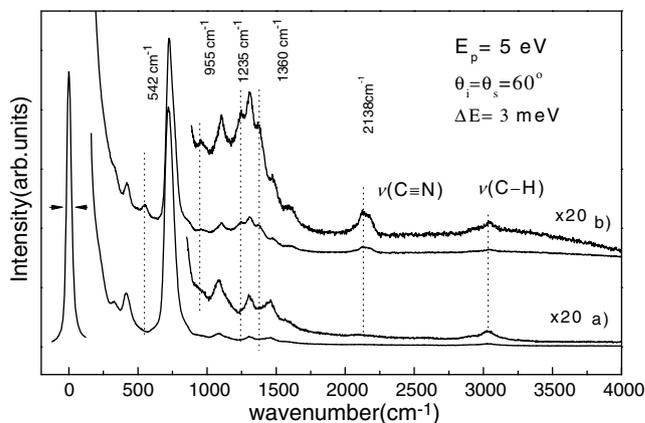


Fig. 4. HREELS spectra of F4-TCNQ dosed on 1 ML ZnPc film (a) 1 ML ZnPc/Au (111); and (b) 0.4 ML F4-TCNQ/1 ML ZnPc/Au (111).

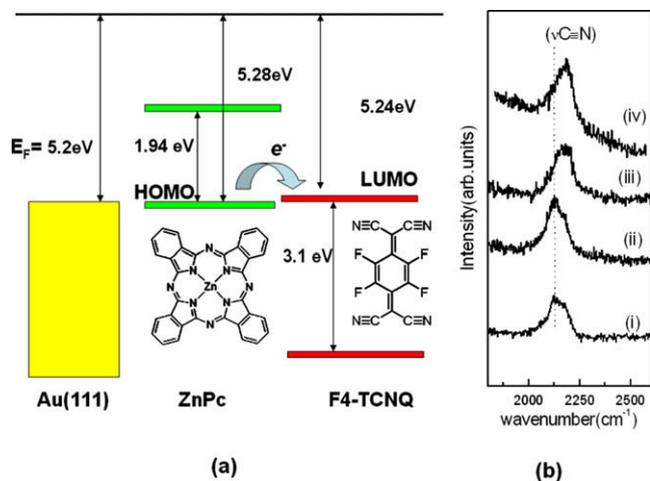


Fig. 5. (a) Interfacial energy line-up of ZnPc and F4-TCNQ obtained from previous UPS and IPES study [13,34] and (b) HREELS spectrum highlighting the shift in $\nu(\text{C}\equiv\text{N})$ stretch (i) 0.4 ML F4-TCNQ/4 ML ZnPc; (ii) 1 ML F4-TCNQ/4 ML ZnPc; (iii) 2 ML/4 ML ZnPc and (iv) bulk F4-TCNQ.

ited on gold surface. Fig. 5b shows the magnified spectrum of the $\text{C}\equiv\text{N}$ stretching vibration for different coverages of F4-TCNQ on 4 ML ZnPc film where the peak shifts are highlighted. It can be seen that the $\text{C}\equiv\text{N}$ stretching vibration appears at 2137 cm^{-1} for F4-TCNQ with thickness <1 ML, and it shifts to 2180 cm^{-1} after the dosing of thicker F4-TCNQ films. This indicates that the F4-TCNQ^{-1} anion is dominant at the interface due to charge transfer from ZnPc to F4-TCNQ, whereas for thicker films, the F4-TCNQ molecules exhibit the properties of the bulk film.

The charge transfer observed here is consistent with the ionization energy of ZnPc (HOMO 5.28) and the high electron affinity of F4-TCNQ (LUMO 5.24 eV), as illustrated in Fig. 5a [13,34]. The band gap of ZnPc and F4-TCNQ can be inferred from EELS spectra. The HOMO level of ZnPc is found to be approximately equal to the LUMO level of F4-TCNQ, which facilitates the charge transfer from ZnPc to F4-TCNQ.

5. Conclusion

HREELS was applied to study the F4-TCNQ/Au (111), ZnPc/Au (111) and F4-TCNQ/ZnPc interfaces. In the case of ZnPc, ZnPc adopts a nearly flat-lying structure on Au (111) for thickness less than 10 MLs. The interaction between ZnPc and Au (111) is relatively weak. However, in the case of F4-TCNQ, molecule–substrate interaction leads to significant changes not only in the vibrational but also electronic excitation spectra for the first monolayer of F4-

TCNQ on Au substrates. The vibrational ($\text{C}\equiv\text{N}$ stretching and $\text{C}=\text{C}$ stretching) and electronic excitations (HOMO–LUMO transition) of the F4-TCNQ at the metal–organic interface shift to lower energies relative to the bulk films, which is evident of charge transfer from Au (111) to molecule. When F4-TCNQ is dosed onto ZnPc, charge transfer from ZnPc to F4-TCNQ can also be detected from the red-shift of the $\text{C}\equiv\text{N}$ stretching at the interface.

References

- [1] R.H. Friend et al., *Nature* 397 (1999) 121.
- [2] G. Horowitz, *Adv. Mater.* 10 (1998) 365.
- [3] C.D. Dimitrakopoulos, P.R.L. Malenfant, *Adv. Mater.* 14 (2002) 99.
- [4] C.W. Tang, S.A. Van Slyke, *Appl. Phys. Lett.* 51 (1987) 913.
- [5] B. Crone et al., *Nature* 403 (2000) 521.
- [6] P.W.M. Blom, V.D. Mihailetchi, L.J.A. Koster, D.E. Markov, *Adv. Mater.* 19 (2007) 1551.
- [7] J. Blochwitz, M. Pfeiffer, T. Fritz, K. Leo, *Appl. Phys. Lett.* 73 (1998) 729.
- [8] M. Pfeiffer, A. Beyer, T. Fritz, K. Leo, *Appl. Phys. Lett.* 73 (1998) 3202.
- [9] A. Nollau, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, K. Leo, *Appl. Phys. Lett.* 78 (2001) 410.
- [10] J. Blochwitz, M. Pfeiffer, T. Fritz, K. Leo, D.M. Alloway, P.A. Lee, N.R. Armstrong, *Organ. Electron.* 2 (2001) 97.
- [11] C.C. Leznoff, A.B.P. Lever, *Phthalocyanines – Properties and Applications*, vol. 1, VCH Weinheim, New York, 1989; vol. 2, 1992; vol. 3, 1993; vol. 4, 1996.
- [12] X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, K. Leo, *Appl. Phys. Lett.* 78 (2001) 410.
- [13] W.Y. Gao, A. Kahn, *Appl. Phys. Lett.* 79 (2001) 4040.
- [14] W.Y. Gao, A.J. Kahn, *Appl. Phys.* 94 (2003) 359.
- [15] K. Harada, A.G. Werner, M. Pfeiffer, C.J. Bloom, C.M. Elliott, K. Leo, *Phys. Rev. Lett.* 94 (2005) 036601.
- [16] B. Maennig, M. Pfeiffer, A. Nollau, X. Zhou, K. Leo, P. Simon, *Phys. Rev. B* 64 (2001) 195208.
- [17] O. Pellegrino, M. Rei Vilar, G. Horowitz, F. Kouki, F. Garnier, J.D. Lopes da Silva, A.M. Botelho do Rego, *Thin Solid Films* 327–329 (1998) 252.
- [18] Y. Azuma, T. Yokota, S. Kera, M. Aoki, K.K. Okudaira, Y. Harada, N. Ueno, *Thin Solid Films* 327–329 (1998) 303.
- [19] S.D. Wang, X. Dong, C.S. Lee, S.T. Lee, *J. Phys. Chem. B* 108 (2004) 1529.
- [20] J.M. Auerhammer, M. Knupfer, H. Peisert, J. Fink, *Surf. Sci.* 506 (2002) 333.
- [21] E. Salomon, T. Angot, N. Papageorgiou, J.M. Layet, *J. Phys. Chem. C* 111 (2007) 5721.
- [22] F.S. Tautz, S. Sloboshanin, J.A. Schaefer, *Phys. Rev. B* 61 (2000) 16933.
- [23] V. Shklover, F.S. Tautz, R. Scholz, S. Sloboshanin, M. Sokolowski, J.A. Schaefer, E. Umbach, *Surf. Sci.* 454–456 (2000) 60.
- [24] E. Salomon, T. Angot, N. Papageorgiou, J.-M. Layet, *Surf. Sci.* 596 (2005) 74.
- [25] Meng Bao, Yongzhong Biana, Jianzhuang Jiang, *Vib. Spectrosc.* 34 (2004) 283.
- [26] P.N. Day, Z. Wang, R. Pachter, *J. Mol. Struct.: Theochem.* 455 (1998) 33.
- [27] H. Ibach, D.L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, London, 1982.
- [28] Moreno Meneghetti, Cesare Pecile, *J. Chem. Phys.* 84 (1986) 4149.
- [29] H. Okamoto, Y. Tokura, T. Koda, *Synth. Met.* 19 (1987) 527.
- [30] Thomas J. Emge, Macrae Maxfield, Dwaine O. Cowan, Thomas J. Kistenmacher, *Mol. Cryst. Liq. Cryst.* 65 (1981) 161.
- [31] T.J. Emge, W.A. Bryden, F.M. Wiygul, D.O. Cowan, T.J. Kistenmacher, *J. Chem. Phys.* 77 (1982) 3188.
- [32] Michel Bosman, Vicki J. Keast, Masashi Watanabe, Abbas I. Maarroof, Michael B. Cortie, *Nanotechnology* 18 (2007) 165505.
- [33] I.G. Hill, J. Schwartz, A. Kahn, *Org. Electron.* 1 (2000) 5.
- [34] M. Pfeiffer, K. Leo, X. Zhou, J.S. Huang, M. Hofmann, A. Werner, J. Blochwitz-Nimoth, *Org. Electron.* 4 (2003) 89.