

Doping-Induced Electron Transfer at Organic/Oxide Interfaces: Direct Evidence from Infrared Spectroscopy

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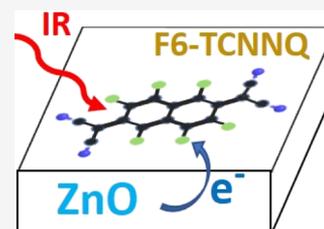
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ABSTRACT: Charge transfer at organic/inorganic interfaces critically influences the properties of molecular adlayers. Although for metals such charge transfers are well documented by experimental and theoretical results, in the case of semiconductors, clear and direct evidence for a transfer of electrons or holes from oxides with their typically high ionization energy is missing. Here, we present data from infrared reflection–absorption spectroscopy demonstrating that despite a high ionization energy, electrons are transferred from ZnO into a prototype strong molecular electron acceptor, hexafluoro-tetracyano-naphthoquinodimethane (F₆-TCNNQ). Because there are no previous studies of this type, the interpretation of the pronounced vibrational red shifts observed in the experiment was aided by a thorough theoretical analysis using density functional theory. The calculations reveal that two mechanisms govern the pronounced vibrational band shifts of the adsorbed molecules: electron transfer into unoccupied molecular levels of the organic acceptor and also the bonding between the surface Zn atoms and the peripheral cyano groups. These combined experimental data and the theoretical analysis provide the so-far missing evidence of interfacial electron transfer from high ionization energy inorganic semiconductors to molecular acceptors and indicates that n-doping of ZnO plays a crucial role.



INTRODUCTION

Organic/inorganic interfaces attract substantial interest because of the prospect to exploit electronic and optical effects occurring at such heterojunctions for applications in optics, electronics, energy storage and conversion, catalysis, and sensing.¹ The often unusual behavior at such interfaces results from combining two materials with rather different properties, for example, electronic structure, dielectric constants, and polarizabilities. In general, depending on the relative energies of the rather localized molecular orbital levels and the more dispersive electronic bands in the inorganic semiconductor, interfacial charge transfer can take place, leading to the formation of electric fields at these hybrid interfaces.² A unique prospect for engineering the properties of devices exploiting these effects arises from the possibility to tune these charge density rearrangements by doping, in particular, that of the inorganic part.

However, even for an easy-to-realize class of organic/inorganic interfaces—organic adlayers on inorganic substrates—the nature of the charge transfer remains elusive. An interesting wide band gap semiconductor for such hetero-interfaces is the metal oxide ZnO, and a number of studies have been reported recently in this context.^{3–6} Here, a large work function increase was observed for the adsorption of strong electron acceptors, such as tetrafluoro-tetracyano-quinodimethane (F₄-TCNQ).³ A straightforward explanation for this observation would be a substantial charge transfer from the ZnO substrate to the adsorbed electron acceptor, similar to the situation on coinage metals. However, evidence for such a large transfer, for example, in the form of a filled lowest unoccupied molecular orbital (LUMO) appearing in the ZnO band gap (as

indicated in Figure 1), is missing from ultraviolet photoelectron spectroscopy (UPS) experiments.³ In theory, for a moderately doped semiconductor, band-bending effects could reduce the amount of transferred charge up to the point where the molecules would be essentially uncharged.^{3,7}

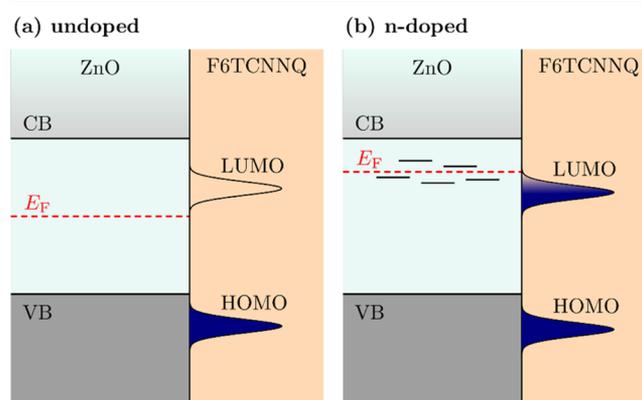


Figure 1. Schematic energy level diagrams of electron acceptor molecules on (a) an undoped semiconductor and (b) an n-doped semiconductor.

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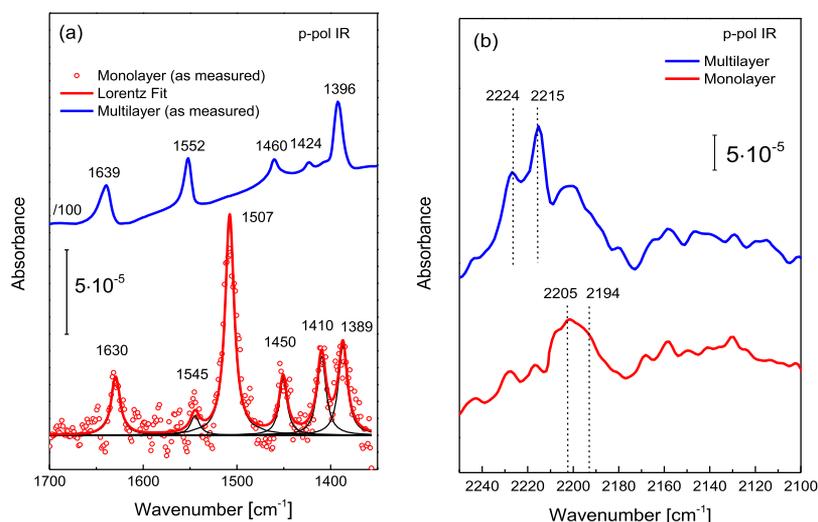


Figure 2. Experimental IRRAS spectra of F_6 -TCNNQ on the nominally undoped $ZnO(10\bar{1}0)$ measured with p-polarized light: (a) $C=C/C-C$ region, the intensity of the multilayer data are scaled by a factor of 100 and (b) $C\equiv N$ region.

In this contribution, we challenge the interpretation of basically neutral molecular adsorbates. Our data from infrared reflection–absorption spectroscopy (IRRAS) directly reveal that hexafluoro-tetracyano-naphthoquinodimethane (F_6 -TCNNQ), a common p-dopant for organic semiconductors,^{8–10} becomes strongly negatively charged upon adsorption.

For this purpose, F_6 -TCNNQ was deposited on a structurally well-defined $ZnO(10\bar{1}0)$ surface. IRRAS allows detecting charge transfer across the interface by measuring adsorption-induced changes of molecular vibrational frequencies. For metal substrates, IRRAS has already been applied successfully to evidence interfacial charge transfer by detecting frequency shifts of vibrations in molecular adsorbates.^{11–14} For PTCDA, another common, planar aromatic compound, adsorbed on $Ag(111)$, the changes in frequency were found to amount to $10\text{--}30\text{ cm}^{-1}$.¹¹ However, similar studies for molecular adsorbates on wide band gap inorganic semiconductors have not yet been reported. This is mainly due to severe challenges in measuring infrared (IR) spectra in reflection for nonmetallic substrates. Only more recently, these problems have been overcome by a number of groups (for a review, see ref 15).

EXPERIMENTAL SECTION

The experiments were conducted in a state-of-the-art ultrahigh vacuum (UHV) multichamber system (Prevac).¹⁵ The apparatus allows performing IR spectroscopy in combination with other surface sensitive techniques such as X-ray-photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED). The IR spectra were obtained in the reflection–absorption mode (IRRAS) using a Fourier-transform (FT)-IR spectrometer (Bruker VERTEX 80v) directly coupled to the UHV chamber via differentially pumped KBr-windows. The base pressure of the entire chamber is in the 10^{-10} mbar range.

As substrates, one nominally undoped $ZnO(10\bar{1}0)$ single crystal (CrysTec) and two Ga-doped $ZnO(10\bar{1}0)$ thin films grown on the bulk $ZnO(10\bar{1}0)$ single crystal by molecular beam epitaxy were used. In the latter case, the charge carrier density was determined by analyzing far-IR transmission spectra in the context of the Drude model,¹⁶ yielding n-doping levels of 7.8×10^{19} and $2.9 \times 10^{20}\text{ cm}^{-3}$, respectively.

The substrates were cleaned by repeated cycles of Ar^+ sputtering (1×10^{-6} mbar, 10 min) and annealing for 10 min at 800 K in a case of the undoped sample and at 700 K for Ga-doped ZnO . As a final step, the samples were annealed in an oxygen atmosphere (1×10^{-6} mbar) at 840 and 700 K for undoped and Ga-doped samples, respectively. The lower annealing temperature was applied for Ga-doped ZnO to keep the doping level unchanged. The cleanliness and structural quality of the substrate surface were monitored by XPS and LEED.

Deposition of F_6 -TCNNQ (Novaled) on $ZnO(10\bar{1}0)$ was carried out by directing the flux of an effusion cell toward the substrate. Deposition rates were determined using a quartz crystal microbalance. Based on the determined deposition rate, we estimate that the coverage of the monolayers used to record the data shown in Figure 2 amounted to 0.7 ± 0.3 monolayer, that is slightly less than a full monolayer (one monolayer corresponds to a surface fully covered by flat-lying molecules). For larger coverage (i.e., longer deposition times), bilayer formation was observed in the IR data. According to the calculated adsorption geometry (see Figure S11, Supporting Information), monolayer coverage corresponds to $\sim 4 \times 10^{13}$ molecule per cm^2 . This value is in good agreement with the estimates made by Katayama¹⁷ for F_4 -TCNNQ considering the larger size of the F_6 -TCNNQ molecule. For the F_6 -TCNNQ multilayer, the deposition time was 10 times longer; therefore, we estimate a film thickness of $\sim 70\text{ \AA}$.

All IRRAS experiments were carried out at room temperature. An internal polarizer module allowed to record IR spectra with s- and p-polarized light. All IR spectra shown here are difference spectra obtained by subtracting a spectrum recorded for the clean ZnO substrate before F_6 -TCNNQ deposition from that measured after molecule deposition. Note that in contrast to metal substrates, the bands in the IRRAS spectra can have different signs, positive or negative. For a detailed discussion, see the previous literature.^{15,18} The angle of incidence of the IR light was set to 80° with respect to the surface normal because according to previous spectrum simulations for adsorbates on ZnO ,¹⁸ the p-polarized signal adopts a maximum at $80\text{--}85^\circ$, while for s-polarized light, the dependence on Θ is only weak.

Table 1. Experimental and Theoretical Results for F₆-TCNNQ

symmetry/vibration	experiment, multilayer, cm ⁻¹	experiment, monolayer, cm ⁻¹	theory ^a , gas phase, neutral, cm ⁻¹	theory ^a , gas phase, charged, cm ⁻¹	theory ^a , surface, neutral, cm ⁻¹	theory ^a , surface, charged, cm ⁻¹
C–N Vibrations						
b _u ′ ₄₉	2224	2205	2248	2222	2229	2202
a _g ′ ₁	2224	2205	2246	2223	2219	2196
b _u ′ ₅₀	2215	2194	2221	2189	2197	2165
a _g ′ ₂	2215	2194	2221	2189	2191	2158
C–C Vibrations						
b _u ′ ₅₁	1639	1630	1638	1629	1632	1622
a _g ′ ₄	1552	1545	1552	1551	1551	1550
b _u ′ ₅₂	1552	1507	1552	1508	1567	1522
b _u ′ ₅₃	1460	1450	1470	1445	1490	1465
b _u ′ ₅₄	1424	1410	1431	1412	1434	1415
b _u ′ ₅₅	1396	1389	1402	1379	1420	1397

^aScale factors of 1.0095 for the C≡N and of 1.0198 for the C=C/C–C have been used.

COMPUTATIONAL DETAILS

As mentioned in the introduction, obtaining a reliable prediction of the charge state of the adsorbed molecule via semi-local density functional theory (DFT) is challenging. This is because the LUMO is spuriously below the valence band of ZnO, which yields superficial charge transfer, independent of the substrate's actual Fermi level. In principle, this problem can be solved using more sophisticated methods, such as DFT + *U*¹⁹ or hybrid DFT.²⁰ However, in either case, the amount of charge transfer depends sensitively on the parameter used to account for the Coulomb on-site energy (the Hubbard *U* or the amount of exact exchange) and on the precise doping concentration (and its nature),^{19,20} which still prevents a stand-alone computational prediction. Therefore, we pursue a different approach here: rather than calculating the charge state directly, the aim of the calculations is to predict the shift of vibrational frequencies as a consequence of (a) charging of the F₆-TCNNQ molecule and (b) binding of the molecule to the surface. We do this separately by calculating the shift due to charging for a free molecule in the gas phase and by calculating the vibrational frequencies for the molecule on the surface (where, in our calculations, we assume a charge transfer of approximately one electron). Assuming that these two effects are independent and additive, we can combine them to estimate the vibrational shift for arbitrarily charged molecules on the surface, as explained in more detail in the Supporting Information. Comparing the frequencies observed in the IRRAS experiment to the computed values then allows us to extract the factual charge state of the molecule on the surface.

All computed vibrational modes presented here were obtained by DFT calculations using the FHI-aims program package.²¹ The Perdew–Burke–Ernzerhof (PBE)²² density functional was used and van der Waals forces were included with the vdW-TS scheme,²³ using the appropriate parameters for the ZnO substrate.²⁴ The vibrational modes were computed numerically via the finite displacement method using a displacement amplitude of 0.005 Å. Initial geometries were optimized until residual forces were smaller than 10⁻⁴ eV/Å with “tight” basis sets and numerical settings.

Calculations for the free molecule were performed with open boundary conditions. The electronic structure of the F₆-TCNNQ/ZnO interface was determined using a periodic slab approach. The ZnO substrate was modeled using a five double-layer slab cell. For geometry optimization, the bottom three double-layers were fixed at their bulk positions and the top two layers were allowed to relax. For the vibrational analysis, we

restrict the discussion to vibrations of the molecule within the harmonic approximation. By keeping the substrate fixed, we omit changes in pure surface and pure bulk modes. To avoid artifacts arising from artificial surface states located at the bottom side of the slab, the bottom layer was passivated with hydrogen atoms. Calculations for the primitive surface unit cell are performed with a 16 × 24 × 1 *k*-grid and scaled accordingly for larger cells. The 4 × 4 supercell including the molecule was chosen such that there is no significant intermolecular interaction between the adjacent molecular adsorbates when employing periodic boundary conditions.

The adsorption of the F₆-TCNNQ molecules on the ZnO(10 $\bar{1}$ 0) surface is governed by weak binding of the protruding cyano groups to the surface Zn atoms, which act as docking sites, leading to a planar molecular adsorption geometry. Two different azimuthal orientations were considered: oriented along the rills of the mixed-terminated ZnO surface (i.e., along the ZnO[1 $\bar{2}$ 10] direction) and oriented perpendicular to the rills (the ZnO[0001] direction). The orientation perpendicular to the rills is energetically more favorable by 33 meV and was therefore used for the vibrational analysis in this work.

Vibrational frequencies usually strongly depend not only on the physics of the system but also on the density functional and the basis set used in the DFT calculations. Because of the systematic nature of the deviations, it is customary to apply uniform multiplicative scale factors to correct the computed vibrational frequencies.^{25–27} The scale factor used here was determined from experimental and theoretical data for F₄-TCNNQ.^{28–30} This procedure yields scale factors of 1.0095 for the C≡N and of 1.0198 for the C=C/C–C vibrational frequencies. (More details on the computational methods including how we obtained the scale factors can be found in the Supporting Information, Chapter 4.)

RESULTS AND DISCUSSION

To determine the charge state of the molecules in direct contact with the substrate, it is useful to first characterize a molecular multilayer, where the molecules are clearly charge neutral. This provides a baseline for comparing the vibrational signatures of the experiment and theory, allowing us to analyze shifts due to charging and binding to the surface afterward. In the following, we focus on the results for nominally undoped ZnO(10 $\bar{1}$ 0), which is actually unintentionally n-type doped;^{31,32} and the results are qualitatively equivalent to those obtained for highly

doped samples. It is necessary to mention that the IRRAS data recorded for F_6 -TCNNQ multilayers adsorbed on the Ga-doped ZnO samples look the same as for those adsorbed on the nominally undoped ZnO sample. Moreover, we measured thick (1000 Å) multilayers of F_6 -TCNNQ deposited on the oxidized Si wafer. The multilayer spectra recorded for these different substrates are virtually identical. Moreover, during coverage-dependent experiments, it was found that after completion of the monolayer, we immediately start to observe the features typical for the multilayer. This observation allows us to conclude that the charge transfer is limited strictly to the first adsorbed layer and that molecules further away are only affected very weakly by the presence of the ZnO substrate.

The inspection of the IRRAS data from multilayer F_6 -TCNNQ (Figure 2, top curves) reveals several well-defined, sharp vibrational bands. In the frequency regime below 1700 cm^{-1} (C=C/C-C region), four strong bands are seen in the experimental multilayer data, centered at 1639, 1552, 1460, and 1396 cm^{-1} . In addition, a small peak is seen at 1424 cm^{-1} . For their assignment, we rely on the comparison to the corresponding data for a structurally related molecule, F_4 -TCNQ,^{28–30} and to the results of DFT calculations for F_6 -TCNNQ in the gas phase (see Table 1).

Overall, the agreement between the positions of the bands in the experimental multilayer IR spectra and the DFT results for the free molecule is very good. Note that the small deviation between the experiment and theory is similar to that reported in previous work for F_4 -TCNQ multilayers.²⁹ On the basis of this comparison, in Table 1 (column “theory, gas phase, neutral”), we assign the four strong bands to the C–C vibrations $b_u\nu_{51}$, $b_u\nu_{52}$, $b_u\nu_{53}$, and $b_u\nu_{55}$ and the weak feature to $b_u\nu_{54}$. In the C≡N stretch regime, we observe four features at 2224, 2215, 2205, and 2194 cm^{-1} (Figure 2b, top curve). We assign the band at 2224 cm^{-1} to the degenerate $b_u\nu_{49}/a_g\nu_1$ vibrations and the band at 2215 cm^{-1} to the degenerate $b_u\nu_{50}/a_g\nu_2$ vibrations (see Table 1). This assignment is in analogy with that reported for F_4 -TCNQ multilayers.²⁹ Two features at lower wavenumbers are ascribed to signals still originating from the monolayer, see below. We would like to note that for F_4 -TCNQ/(co)polymer blends, an additional strong band at 2169 cm^{-1} has been found.²⁹ We were unable to observe such vibration band in our data, and all features seen in Figure 2b in the range 2180–2100 cm^{-1} are below the noise level.

Unfortunately, the bulk crystal structure of F_6 -TCNNQ is unknown. Also, in the case of thin films, Duva et al.³³ were unable to deduce structural parameters because out-of-plane diffraction peaks for F_6 -TCNNQ films could not be detected. However, we note that all vibrational modes discussed above have their transition dipole moments oriented within the molecular plane of F_6 -TCNNQ. Note that the experimental p-polarized multilayer data (Figure 2) do not reveal any vibrational bands with a negative signal (for a discussion of the interplay between orientation of transition dipole moments, the polarization of the incident IR-light, and the sign of vibrational bands in IRRAS at dielectric surfaces, see the Supporting Information). This observation implies that all F_6 -TCNNQ molecules must be orientated with their molecular plane parallel to the ZnO substrate, see Figure 3. IRRAS data recorded with s-polarization (see Figure SI11 in the Supporting Information) are fully consistent with parallel stacking in multilayers of this aromatic compound.

For the F_6 -TCNNQ monolayer on ZnO(10 $\bar{1}$ 0), the IRRAS data reveal pronounced differences compared to the multilayer

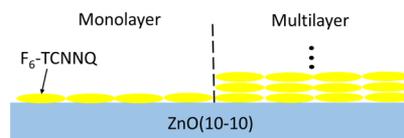


Figure 3. Orientation of F_6 -TCNNQ in the monolayer (left) and multilayer (right) regimes. The polarization dependence of the IR-data indicates an orientation of the molecular plane parallel to the substrate.

spectra (see Figure 2a, bottom curve). For the monolayer, the most pronounced peak is that at 1507 cm^{-1} . Lower intensity bands are observed at 1630, 1450, 1410, and 1389 cm^{-1} , and a small feature is observed at 1545 cm^{-1} .

In case of a neutral F_6 -TCNNQ adsorbate, the DFT results predict a small blue shift (15 cm^{-1}) of the strong $b_u\nu_{52}$ band at 1552 cm^{-1} relative to the molecule in the gas phase because of the bonding of the molecule to the surface.³⁴ Because experimentally, the peak actually shifts in the opposite direction, we conclude that the presence of neutral F_6 -TCNNQ molecules at the interface is unlikely. Conversely, for a negatively charged molecular species, the calculations predict a red shift of 30 cm^{-1} for the $b_u\nu_{52}$ band (see Figure SI5 in the Supporting Information), in agreement with the experimentally observed shift of 45 cm^{-1} . Such a substantial lowering of frequencies is typical for electron transfer to this organic acceptor.³⁰ In line with this hypothesis, the second sharp band for the monolayer observed at 1450 cm^{-1} can be assigned to the $b_u\nu_{53}$ band (1460 cm^{-1} in the multilayer), that is, a red shift of 10 cm^{-1} is observed for the monolayer. Also, in this case, the DFT results for the neutral species predict a small blue shift, whereas for the charged species, a small red shift is expected (5 cm^{-1}). Inspection of Table 1 confirms that the other vibrations also agree well with the theoretical results for a F_6 -TCNNQ anion at the interface with ZnO.

Assuming a charge transfer of 1 electron/molecule for the full monolayer, $\sim 10^{14}$ electrons for the transfer from the substrate to F_6 -TCNNQ are needed. This value is absolutely reasonable for the n-doping levels present in the substrate.

In the C≡N-stretch region, the experimental monolayer data reveal only one rather broad feature (2212–2188 cm^{-1}) centered at 2205 cm^{-1} (Figure 2b, bottom curve). The center of this band is red-shifted by 10–20 cm^{-1} with respect to the strongest multilayer peaks at 2215 cm^{-1} and 2224 cm^{-1} . Although the lower intensity of the C≡N bands in the experimental data prohibits a more detailed analysis, the red shift in the measured monolayer data is consistent with the theoretical results for the negatively charged species, where for all C≡N stretch vibrations, red-shifts between 40 and 60 cm^{-1} are found.

Analysis of the experimental data confirms the plane of the F_6 -TCNNQ monolayer to be orientated parallel to the substrate, as also indicated by the theoretical results.

Overall, our findings for the nominally undoped ZnO substrate clearly show that the adsorbate is negatively charged, in variance to the naive expectation depicted in Figure 1b. Importantly, this is in agreement with the observation that the measured band bending for semiconductor/organic interfaces is significantly smaller than that required to obtain charge-neutral adsorbates.^{3,35} Notably, although theory suggests that the amount of charge transfer should be dependent on the doping concentration,^{3,20} experiments for more strongly doped samples showed no difference to the nominally undoped sample.

As a final remark, we note that our experimental and theoretical findings cannot reconcile the apparent absence of filled molecular states in previous ultraviolet photoelectron spectroscopy experiments. Possible origins include strong charge localization in the molecular layer, which could shift the filled states far below E_F ,^{36,37} or a pronounced hybridization of the surface states with the molecular orbitals, which could also lead to masking of ebbing molecular states by the ZnO valence band. However, a conclusive answer would require significant improvements over state-of-the-art theory, which is outside the scope of the present contribution.

CONCLUSIONS

The experimental IRRAS data obtained for F_6 -TCNNQ molecules deposited on a ZnO(10 $\bar{1}$ 0) surface reveal the formation of multilayers with the molecular plane orientated strictly parallel to the substrate. In the C \equiv N region for the F_6 -TCNNQ monolayer, two sharp vibrational bands are observed, with pronounced red shifts relative to the multilayer. As confirmed by DFT results, these shifts are inconsistent with a neutral adsorbate. Instead, from the good agreement with theoretical results obtained for a molecular anion, we conclude that F_6 -TCNNQ molecules in the monolayer are negatively charged. This information provides the so-far missing evidence of interfacial electron transfer from high ionization energy inorganic semiconductors to molecular acceptors. In this case, the transfer is made possible by n-doping. Consequently, the comprehensive understanding of charge rearrangements at inorganic/organic interfaces is substantially ameliorated and can now be exploited to further tailor such interfaces for advanced applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.9b08768>.

Top and side view of the theoretically found lowest energy local adsorption site of F_6 -TCNNQ on the ZnO surface; MODOS and orbital population analysis of F_6 -TCNNQ on ZnO; most relevant molecular orbitals for charge transfer upon adsorption of F_6 -TCNNQ on ZnO, two most prominent features that appear in gas-phase calculations; depiction of C=C/C-C and C \equiv N frequency shifts of flat-laying F_6 -TCNNQ; theoretical results of C-C/C=C stretching vibrations; theoretical results of C \equiv N stretching vibrations; chemical structure and double bond locations within the molecule; bond lengths of all bonds within the F_6 -TCNNQ molecule; and experimental IRRAS spectra of F_6 -TCNNQ measured with p- and s-polarized light (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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