

Electronic and Magnetic Properties of a Monolayer of VOTPP Molecules Sublimated on Ag(100)

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Vanadyl(IV) 5,10,15,20-tetraphenylporphyrin (VOTPP) is an $S = 1/2$ molecular system with remarkable spin qubit properties. Its structure offers a higher chemical tunability with respect to archetypal molecular qubits, such as vanadyl(IV)Phthalocyanines (VOPc), and a less rigid organic scaffold where peripheral phenyl rings can promote electron decoupling from the substrate. The properties of a VOTPP monolayer on the Ag(100) surface by photoemission spectroscopies and synchrotron radiation are studied. The results indicate that the electronic and spin features of the massive phase are retained in the monolayer. Moreover, X-ray photoelectron spectroscopy revealed the existence of two distinct species characterized by varying strengths of molecule-surface interactions. Like VOPc, these species can be assigned to molecules with the vanadyl group oriented upward or toward the surface. However, in contrast to VOPc, only subtle screening effects are observed in the oxygen-down configuration, suggesting a more pronounced decoupling effect inherent in the VOTPP structure. This opens broader perspectives for investigations focusing on spin characteristics at the single-molecule level.

their potential use as molecular spin qubits,^[1,2] the fundamental units of quantum computers. In the quest for new molecular systems for quantum technology, transition metal complexes containing macrocyclic ligands (e.g., porphyrins and porphyrazines) are attractive for their room temperature appreciable coherence time,^[3–5] i.e., the lifetime of the superimposition state of the qubit, and the capability to self-assemble in ordered molecular arrays by thermal sublimation.^[6–8] For instance, the vanadyl(IV)phthalocyanine (VOPc) complex represented a prototypal molecular spin qubit candidate.^[9–13] The structural and physical properties of this system have been thoroughly studied on the surface down to the monolayer and single molecule level.^[9–11,14] Surface-molecule interactions were tuned by selecting a proper molecular geometry thanks to the asymmetric structure of the VOPc

complex, bearing the vanadyl group out of the Pc plane. The two possible adsorption configurations induced different surface interaction strengths: exposing the VO outward the surface, “UP,” led to a moderate decoupling, while a more effective interaction

1. Introduction

Paramagnetic $S = 1/2$ transition metal complexes are gaining attention in the field of quantum technologies because of

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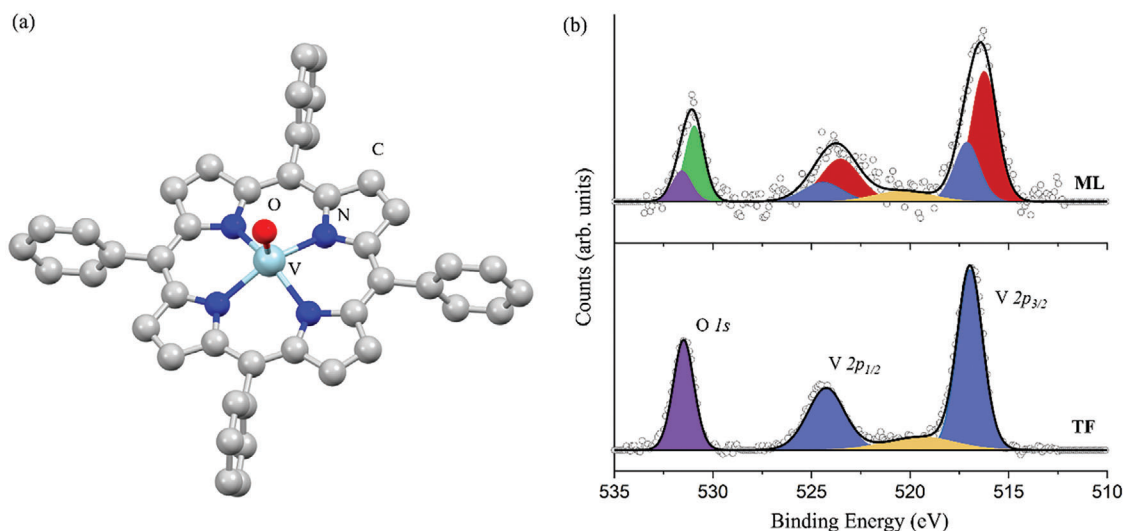


Figure 1. a) Structure of the VOTPP molecule. Atom color code: C, grey; N, blue; V, light blue; O, red; H atoms are omitted for clarity; b) O $1s$ and V $2p$ XPS spectra of the VOTPP complex sublimated on Ag(100) as monolayer (ML, top) and thick film (TF, bottom). A linear background was subtracted from both spectra for clarity. Peak color code: V $2p$, blue; O $1s$, violet; satellite, yellow (bulk-like signals). Additional shifted components in the monolayer (see text) are depicted in red (V $2p$) and green (O $1s$).

was observed in the “DOWN” configuration, i.e., the VO pointing toward the surface.^[12,15]

From the perspective of tuning surface–molecule interaction, metalloporphyrins provide an even more promising framework. The simplest member of this family is the vanadyl(IV) 5,10,15,20-tetraphenylporphyrin (VOTPP) system.^[3,16] VOTPP, **Figure 1a**, contains four phenyl groups at the *meso*-position that, in the crystalline phase, are tilted almost 90° with respect to the porphyrin plane.^[17] Compared to planar phthalocyanine ligands, the phenyl groups could further tune molecule–surface interactions, increasing the decoupling from the substrate. Additionally, the backbone of porphyrin ligands can be modified through well-established organic chemistry approaches.^[18] Concerning magnetism, VOTPP offers quantum coherence properties similar to VOPc molecules^[3] with additional interesting features. When embedded in multi-porphyrin scaffolds, it promotes magnetic exchange interactions of the suitable strength to implement multi-qubit logic quantum gates.^[3,16] It also offers the possibility of exploiting the $I = 7/2$ as a nuclear qubit with the electron spin acting as an ancilla^[19] and the perspective for improving coherence at clock transitions.^[20]

Contrary to VOPc complexes, only little is known about the electronic and magnetic properties of VOTPP on the surface. Recent experiments have demonstrated that, despite their nonplanar geometry, ordered molecular arrays can be obtained on an ultra-thin iron-oxide film.^[21]

In this work, the VOTPP film on Ag(100) was probed by X-ray Photoelectron Spectroscopy (XPS), Ultra-violet Photoelectron Spectroscopy (UPS), and Inverse Photoemission Spectroscopy (IPES) to investigate the surface–molecule interaction strength. The system was then characterized by synchrotron radiation to confirm the retainment of its magnetic properties using the X-ray magnetic circular dichroism (XMCD) technique. These studies indicate that VOTPP molecules, oriented with the vanadyl group upward or toward the surface, do not undergo strong interaction

with the surface suggesting a greater decoupling with respect to the VOPc species.

2. Results and Discussion

A thick film and a monolayer of VOTPP were sublimated on Ag(100) and are referred to as VOTPP-TF and VOTPP-ML, respectively. Both films were studied by XPS and VOTPP-TF was used as a reference for a non-interacting system. **Figure 1b** shows the O $1s$ and V $2p$ XPS signals of the VOTPP-ML (top) and VOTPP-TF samples (bottom). In the VOTPP-TF spectra, the V $2p$ region shows two main peaks at 516.8 and 524.0 eV corresponding to the V $2p_{3/2}$ and V $2p_{1/2}$ spin-orbit components, respectively; a broad satellite contribution of the V $2p$ is observed at 519.3 eV (yellow component in **Figure 1b**).^[10,22]

The O $1s$ signal consists of a single component at 531.3 eV. These features are consistent with literature reports of VOPc thick films on surfaces.^[9–11,15,22] The C $1s$ and N $1s$ spectra are reported in the Supporting Information (**Figure S1**, Supporting Information). The C $1s$ signal (**Figure S1a**, Supporting Information) is composed of two principal components: the main one at 285.1 eV attributed to the C–C aromatic bonds of the TPP ligand, arising from both the phenyl carbon–carbon bonds and the porphyrin macrocycle carbon–carbon bonds, and the second one at 285.9 eV attributed to the C–N bonds of the porphyrin core ring.^[11,22] A shake-up satellite is also present at 288.2 eV, typical of organic molecules with conjugated π systems.^[23,24] The N $1s$ signal (**Figure S1b**, Supporting Information) shows a main component at 399.3 eV and a shake-up component at 400.1 eV.^[9] The V/O and V/N signal intensity ratios extracted from the XPS fit are equal to about 1.0 and 0.3, respectively. These values and the XPS elemental analysis (see **Table S1**, Supporting Information) agree with the stoichiometry of the pristine material, confirming the success of the sublimation procedure.

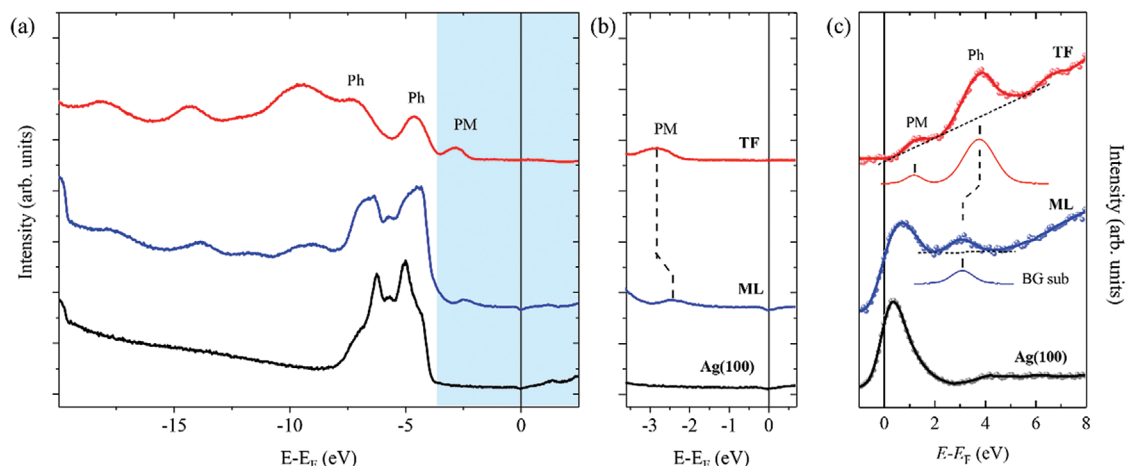


Figure 2. a) UPS spectra of VOTPP-ML and VOTPP-TF on Ag(100). The clean Ag(100) spectrum is also reported as a reference of the surface. b) Magnification of the UPS spectra close to the Fermi energy region (shaded pale blue area in panel a). Dotted lines are superimposed as a guide for the peaks' attribution. c) Inverse photoemission spectra acquired at normal electron incidence on the bare Ag(100) surface and on two VOTPP films with different molecular coverages. All the spectra have been rescaled and vertically offset for clarity. Thick lines are the result of a smoothing operation performed on raw data (dots). The position of the spectroscopic features attributed to VOTPP molecules is highlighted and evaluated after the linear background subtraction (*BG sub*). The feature attributed to inverse photoemission from the porphyrin macrocycl (phenyl groups) is marked with PM (Ph) in the thick film.

A different situation is found in the VOTPP-ML sample; both O *1s*, V *2p*, and C *1s* signals clearly show the presence of an additional intense contribution at lower binding energies (Figure 1b, top; Figure S1a, Supporting Information). The latter lies at 530.9 eV (O *1s*), 516.2 eV, and 523.5 eV (V *2p*_{3/2} and V *2p*_{1/2}, respectively). These new features indicate the presence of different species. The observation of two different components is compatible with two opposite molecular orientations (oxygen UP and oxygen DOWN) interacting differently with the surface. The local interface dipole generated by the molecules induces an electron screening, shifting the XPS components toward lower energies,^[25] presumably, only on the DOWN fraction as observed for TiOPc on Ag(111).^[25] This effect is likely to act only on this fraction due to the opposite orientation of the dipole and/or to a difference in the distance of the system from the Ag surface. From the signal intensity, we can assess that the DOWN configuration is the majority due to the high oxygen affinity to the Ag surface. A similar double XPS component was observed in the V *2p* spectrum of the VOPc compound,^[15,22,26] where the presence of both UP and DOWN configurations was also detected by STM on different surfaces, e.g., Ni, Si,^[22] and Pb.^[11] However, an opposite shift was observed in the O *1s* peak of VOPc, hence highlighting the occurrence of a partial charge transfer from the oxygen of the VO group to the substrate. This charge transfer must be excluded or considered less relevant here.

We remark that the intensity of these two components is also in line with the expected V/O ratio. The minority components, attributed to the UP configuration, coincide within an energy range of 0.2 eV with the TF reference (similar peak shifts are ascribed to a different screening of the final core hole between the monolayer and thick film deposits).^[27] The signature of two different interacting VOTPP species is also found in the C *1s* and N *1s* signals (see Figure S1, Supporting Information). VOTPP-ML spectra are broadened and shifted toward lower binding energies than the TF deposition. However, the low energy resolution and the over-

lap with the Ag *3d* shake-up satellites and plasmons signals^[22,28] do not allow a proper peak fitting.

The low-energy molecular orbitals of the VOTPP-ML and VOTPP-TF samples were investigated by UPS and IPES techniques, probing the filled and empty states of the surface, respectively. The He(II) UPS spectra are shown in Figure 2a in comparison with that of the clean Ag(100) single crystal. The latter features a characteristic structure between -4 and -8 eV attributed to the Ag *4d* bands.^[29] The shape of the UPS spectrum changes when VOTPP molecules are present on the surface. In the VOTPP-TF spectrum, the peak at -2.8 eV can be ascribed to the Highest Occupied Molecular Orbital (HOMO).^[30] A similar peak has been attributed to the porphyrin macrocycle (PM) in VOTPP deposits on Fe(001)-*p*(1 × 1)O^[21] or other porphyrin deposits.^[30–33] The feature of the PM signal is well resolved in the VOTPP-TF spectrum, where the substrate contribution is completely suppressed.

In the VOTPP-ML spectrum, this signal is shifted by 0.3 eV (-2.5 eV). For ZnTPP on Ag, this effect was ascribed to a more efficient screening from the substrate in the multilayer deposit with respect to the monolayer.^[30] Moving to more negative energies in the VOTPP-TF spectrum, the intensity of the Ag *4d* states (region from -4 to -8 eV) decreases, and new components arise. These components are related to phenyl groups (Ph) of the TPP ligand and are visible at -4.6 and -7.3 eV, in good agreement with the literature.^[21,30,32,33] Other peaks related to the molecular complex are also present at lower energies from -9 to -18 eV both in VOTPP-ML and VOTPP-TF spectra. To allow a more accurate comparison of the TF and ML spectra, Figure S2 (Supporting Information) shows the subtraction between the VOTPP-ML and the Ag(100) spectra, evidencing the molecular contribution of the UPS valence band in the monolayer and the energy screening induced by the thickness (energy shift of ca. 0.4 eV).

Figure 2c shows the IPES results acquired on the VOTPP-ML and TF samples (see Experimental Section). The bottom

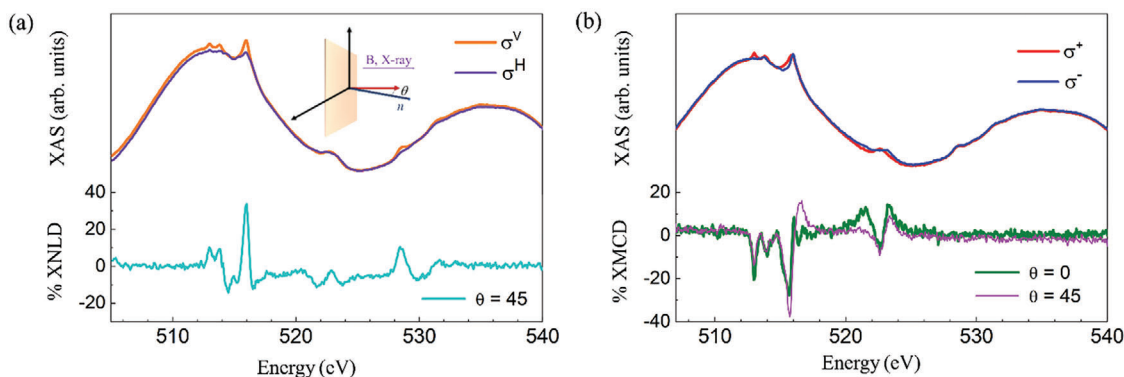


Figure 3. a) XAS and XNLD spectra recorded on the VOTPP-ML sample at $\theta = 45^\circ$, $B = 6\text{ T}$, and $T = 2.0\text{ K}$. Inset: geometry of the experiment; n is the surface normal, θ is the angle between n and the X-ray propagation vector and magnetic field direction. b) XAS (top) and XMCD (bottom) spectra were recorded at $\theta = 0^\circ$ and XMCD at $\theta = 45^\circ$, $B = 6\text{ T}$, and $T = 2.0\text{ K}$.

spectrum, acquired on bare Ag(100), is compatible with other results in the literature.^[34,35] On the thick film, two peaks are visible at 1.2 and 3.8 eV. These molecular features are related to inverse photoemission from orbitals mainly located in the porphyrin macrocycle (PM) and the phenyl groups (Ph), respectively, as reported in the literature for the same molecule.^[21] Passing to VOTPP-ML, the spectrum resembles that of the substrate, but with a new feature peaking at 3.1 eV, highlighted by the background-subtracted curves (BG sub, see supporting information Figure S2). We interpret the IPES line shape of the thin film as the result of the superposition between the spectroscopic features of the substrate and the signal characteristic of VOTPP molecules, shifted toward lower energies, as highlighted with a vertical dotted line in Figure 2c for the phenyls (Ph) feature. The observed shift is attributed to more effective screening of the electron added during the inverse photoemission process, thanks to the proximity of the Ag substrate.^[21–38] The precise energy position of the macrocycle (PM) feature, and therefore of the Lowest Unoccupied Molecular Orbital (LUMO), is difficult to evaluate since this feature overlaps with the Ag peak.

Synchrotron measurements were carried out on the VOTPP-ML sample to evaluate the adsorption geometry and magnetic properties of the molecular layer. X-ray Absorption Spectroscopy (XAS) was used to investigate the vanadium $L_{2,3}$ edges (L_3 at 513–520 eV and L_2 at 522–527 eV) and the oxygen K edge (at 530 eV), see Figure 3; the prominent background comes from the Ag (100) surface.

The information about the molecular orientation on the Ag surface was inferred by the XNLD ($\sigma^V - \sigma^H$) signal obtained by collecting XAS spectra with vertical (σ^V) and horizontal polarized light (σ^H) as reported in Figure 3a.^[10,11,39–42] The XNLD spectrum shows a significant dichroic signal at the $L_{2,3}$ edges of V (more than 30%), suggesting that the PM leans down preferentially toward the Ag(100) surface.^[10,11,43] For the sake of completeness we performed XNLD characterization also at a very low magnetic field (0.02T) to exclude the presence of an X-ray Magnetic Linear Dichroism (XMLD) contribution (see Figure S3, Supporting Information). An XNLD signal of analogous shape and intensities was found for VOPc monolayers on Pb(111).^[11]

Magnetic properties of the monolayer were then addressed by measuring the signals with the right (σ^-) and the left (σ^+) circu-

lar polarization of the X-rays and evaluating the XMCD as ($\sigma^- - \sigma^+$). The XMCD measurements reported in Figure 3b were taken at normal incidence, $\theta = 0^\circ$, and at $\theta = 45^\circ$ (see the Supporting Information and inset of Figure 3a) to determine the variation of the magnetic properties of the complex also as a function of the angle. Both XMCD signals reveal a main dichroic peak at 515.7 eV and have a similar shape, comparably to that of other vanadyl compounds.^[10,11] The percentage of the XMCD signal varies slightly, passing from 0° to 45° , following the trend previously observed and modeled for VOPc deposits.^[43] The shape of the XMCD signal is in line with those obtained on VOPc species on different surfaces such as Ag(111),^[15] Graphene/SiC, and Pb(111).^[10,11] Recent experiments have intriguingly linked the XMCD signals of VOPc monolayer films on Ag(100) to the molecular adsorption configuration. Both experimental and simulated results reveal a variation of the main V $L_{2,3}$ dichroic signal, dependent on the ratio between the two VO-group orientations (UP or DOWN), as well as the degree of molecular interaction with the substrate, which is weakened by a TiOPc interlayer.^[44] Comparing these findings with the dichroic signal detected on the VOTPP layer supports the coexistence of both UP- and DOWN-standing molecules. Moreover, unlike the VOPc layer in direct contact with Ag(100), the narrow dichroic peak of VOTPP aligns closely with those of weakly interacting VOPc molecules on TiOPc^[44] and graphene.^[10] This further supports the hypothesis that the phenyl groups of the ligand exert a decoupling function.

Finally, the field dependence of the dichroism at the L_3 edge of VOTPP-ML on Ag(100) was recorded at 2K and $\theta = 0^\circ$ (see Figure S4, Supporting Information). A paramagnetic behavior is clearly visible from the experimental magnetization curve, which follows the trend of an $S = 1/2$ species expected for the VOTPP compound (see magnetization curve and fit in Figure S4, Supporting Information).

3. Conclusion

We have studied the structural, electronic, and magnetic properties of a VOTPP monolayer on Ag(100) and compared them with those of a thick film where molecules are decoupled from the surface. The spectroscopic techniques used for the study

confirm the integrity of the molecular layer after deposition. The XPS elemental analysis is in line with that expected from the molecular structure. Features attributed to the VOTPP orbitals were observed by UPS and IPES on both the thick film and the monolayer deposits. Additionally, synchrotron XMCD and XNLD measurements confirm the retainment of the molecular magnetic properties in the monolayer, as evidenced by the observed paramagnetic behavior typical of an $S = 1/2$ system. XPS spectra evidence the presence of two different interacting species in the monolayer deposit. In analogy with the previous results on a VOPc layer, this effect can be ascribed to the presence of molecules with the vanadyl group pointing upward or downward, the latter promoting a higher interaction strength with the surface. Noteworthy, here XPS features suggest weak electron screening effects occurring in the VOTPP monolayer, at variance with VOPc where a marked charge transfer toward the surface was observed. The electron screening could arise from the interface dipole generated by the molecules, shifting all the XPS components toward lower energies,^[25] but preserving the electronic features of the massive material. Such reduced, though not negligible, interaction is likely due to the presence of peripheral phenyl rings in the TPP structure moving away the VO group from the surface with respect to its position in the Pc ligand.

This could be interesting for addressing spin coherence properties in ESR-STM experiments, avoiding the use of a decoupling layer *ad hoc* deposited on the Ag(100) surface such as MgO.^[45,46] Additionally, thanks to the versatility of the porphyrin ligand, one could benefit from chemical strategies involving more complex porphyrin-based frameworks.^[47–49]

4. Experimental Section

VOTPP films were prepared using Ultra High Vacuum (UHV) facilities. Before molecular deposition, the Ag(100) single crystal was cleaned by several cycles of Ar⁺ sputtering (1500 eV) and annealing (770 K for 30 min) in UHV. VOTPP was sublimated in a UHV chamber equipped with a home-made Knudsen cell filled with VOTPP powders and heated to ≈ 600 K. Before deposition, the powders were degassed in UHV for several hours to remove solvent contaminants. The sublimation rate was estimated using a quartz microbalance and used to calibrate the surface coverage to produce a monolayer deposition (VOTPP-ML) and a thick film sample (VOTPP-TF) of ca. 10 nm.

XPS data were acquired using monochromatic Al K α radiation ($h\nu = 1486.6$ eV, SPECS mod. XR-MS focus 600) operating at a power of 100 W (13 kV and 7.7 mA) and a SPECS Phoibos 150 1DL electron analyzer mounted at 54.4 to the X-ray source that faced the sample surface (normal emission detection). The XPS spectra were collected at normal emission with the fixed pass energy set to 40 eV. The spectra were analyzed using the CasaXPS software, and all the XPS spectra were calibrated to the Ag 3d_{5/2} signal at 368.3 eV.^[50] The deconvolution of the XPS spectra was carried out by combining Gaussian and Lorentzian functions (70/30). A complete table with all the fitting parameters is reported in Table S3 (Supporting Information).

UPS data were collected using a non-monochromatized gas discharge UV lamp (VG Scientific 22–101) using the He(II) line (40.8 eV). The analyzer pass energy was set to 10 eV, and a fixed bias of -30 V was applied to the sample. UPS spectra were measured at normal emission and calibrated to the Fermi energy of Ag(100). All the spectra were calibrated to the Fermi level of the clean Ag(100) single-crystal spectrum.

IPES was performed using a custom-made UHV spectrometer in the isochromat mode, i.e., by sending low-energy electrons on the sample from a GaAs(001) photocathode and detecting 9.6 eV photons. The over-

all Full Width at Half Maximum (FWHM) resolution of the spectrometer is of the order of 0.7 eV.^[51] Both the silver substrate and the molecular film were prepared in situ in a dedicated organic molecular beam evaporation (OMBE) chamber following the same procedure used for XPS experiments.

X-ray absorption spectroscopy (XAS) experiments were performed at the DEIMOS^[52] beamline (SOLEIL synchrotron, France), employing both linear and circular polarizations and using total electron yield (TEY) detection for surface sensitivity. Samples were transported to the DEIMOS beamline using a UHV suitcase ($P_{\text{base}} = 5 \cdot 10^{-10}$ mbar). Additional details are reported in the Supporting Information.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

absorption configurations, IPES, molecular electronic structure, molecular qubit, molecules/surface interaction, synchrotron radiation, UPS

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