Reply to “Comment on ‘Insight into Organometallic Intermediate and Its Evolution to Covalent Bonding in Surface-Confinned Ullmann Polymerization’”

Song comments on our recent paper, stating “it is apparent that the conclusion drawn from the XPS measurements and analysis is questionable, and the discussion of the XPS section was not well addressed.” In this reply, we show that while some of Song’s comments are pertinent to certain technical aspects of photoelectron spectroscopy, most of his assumptions are unjustified and the critique as a whole does not alter any of the scientific conclusions of our original work. The combination of scanning tunneling microscopy (STM), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, X-ray photoelectron spectroscopy (XPS) and first-principles calculations fully supports our interpretation of the reported results, that is, the transition from an organometallic to polymeric phase.

Below we respond to the specific criticisms raised by Song. The discussion of these points was not included in the original article to maintain its clarity for a broad audience.

Calibration. Each of the XPS spectra was calibrated by rigidly shifting it to set the Fermi level at a binding energy (BE) equal to zero (to within <5 meV). The Fermi levels were collected while recording each of the experimental spectra, using identical electron analyzer settings and without altering the energy setting of the beamline. After this rigid shift, the positions of the Cu 3p½ core level spectra were consistently found at a BE of 75.0 eV, indicating reliable energy scale calibration. These results are shown in Figure 1, where a series of core levels (Br 3d and 3p, C 1s, and Cu 3p) are collected along with the valence band, which contains the Fermi level. We also point out that the abrupt shift of C 1s from room temperature (RT) to 500 K was observed in real time using fast-XPS measurements, as reported in Figure 7a of our paper.

Moreover, the shifts observed in Br 3d were not accompanied by concomitant shifts of Cu 3p, whose signal remains at a fixed BE (Figure 2). These observations rule out any calibration errors, as alleged in the Comment. Figure 2 also shows that it is possible to clearly resolve the Br 3d peak in proximity to the Cu 3p core level.

Attribution of C 1s Components and Absolute BE Energy Positions. The three C 1s spectra reported in Figure 4 of our paper arise from two types of carbon atoms, C1 and C2 (Scheme 1 in our paper). The C2 contribution is always the most intense since there are twice as many C2 atoms as C1 atoms in each molecular building block. The component from C1 carbon atoms is shifted relative to C2, from a higher BE at LT (when C1 is linked to bromine atoms) to a lower BE at RT (when C1 is linked to the copper substrate) and again to a higher BE after annealing at 500 K (C1 atoms linked to each other in the polymer chain). This is summarized in Figure 1 above and was also theoretically predicted in the work of Björk et al. for the formation of biphenyl starting from bromophenyl on the (111) surfaces of copper, silver, and gold.

Furthermore, the BE value of C2-type carbons (Scheme 1 in our paper) is affected by the different atoms bound to C1 atoms in the three phases (i.e., second nearest-neighbor species). This effect is particularly important in conjugated
systems, in which charge is delocalized throughout the entire molecule. This behavior has been theoretically predicted and experimentally observed by gas phase synchrotron radiation photoelectron spectra of several molecules (e.g., when comparing phenylacylene and para-nitrophenylacetylene\(^4\) and studying methyl-substituted benzenes\(^5\)). The work of Björk \textit{et al.}\(^3\) also describes a BE shift of C2-type carbons of about 0.4 eV when transitioning from an organometallic phase to the biphenyl on Cu(111).

Finally, when considering the absolute BE position of the C 1s signals obtained at different phases (LT, RT, and after annealing at 500 K), one must also take into account surface screening. This is an electrostatic effect observed when a photoelectron is emitted at a certain distance from a metal surface and is unrelated to chemical bonding. A photoelectron’s kinetic energy is reduced (i.e., the apparent BE is increased) with an increase in the distance of its originating photoemitter from the surface. The dependence of surface-state energies with image-plane distance for low Miller index metal surfaces has been described theoretically by Smith \textit{et al.}\(^6\) and has been experimentally observed in several works; for example, Maxwell \textit{et al.}\(^7\) showed a BE shift of the C\(_{60}\) C 1s level as a function of coverage on Au(110), consistent with a surface screening model.

The changes in absolute BEs observed for C 1s in our paper\(^1\) are thus expected, considering both the calculated BEs from Björk \textit{et al.}\(^3\) and surface screening effects. The latter is stronger in the case of the multilayer at LT, where the overlayer is thicker and the photoemitters are further away from the substrate.

\textbf{Fit of C 1s at RT.} Regardless of the particular details of the fit, the conclusions drawn from the C 1s XPS peak remain unaltered: there is an absence of a high-BE Br—C state in the RT spectrum, but there is a new low-BE state corresponding to Cu—C. After annealing, this state vanishes, and the transition temperature can be estimated to be 460 K by visually inspecting the fast-XPS map (Figure 7a in our paper\(^1\)).

Various fitting approaches were tested for the fit of the C 1s peak at RT, and the one reported in our paper was chosen because it better accounts for the spectrum’s line shape, which exhibits a shoulder at about 284.2 eV (very close to the main peak at 283.8 eV). Asymmetric C 1s spectra have been observed for benzene in gas phase\(^8\) and for adsorbed molecules\(^9,10\) on surfaces and attributed to vibrational coupling in the final states. The C 1s spectrum measured at RT is likely affected by this vibrational broadening, due to the high order of the RT organometallic molecular superstructure. Moreover, the RT unit cell comprises 4 phenyl groups, with a total of 16 C2-type carbon atoms that are all in different positions with respect to the substrate atoms. A change of “physical position”\(^2\) implies a change in the chemical bonding since the initial-state wave functions of the photoelectrons depend on the relative positions between the nuclei and thus may give rise to different BEs, such as is observed for graphene on Ru(0001).\(^11\) Component 3 in our Figure 4\(^1\) accounts for vibrational broadening and/ or different positions of the C2 atoms on the surface.

\textbf{Br 3d and Br 3p Levels.} We presented chemical shifts of Br 3d spectra in our paper\(^1\) and referred to the work by Folkesson \textit{et al.}\(^12\) However, that work reports data based on Br 3p spectra. The Comment is correct in that the reference is not appropriate for Br 3d: more suitable references are the work of Vasquez\(^13\), where the correct value for Cu—Br in Br 3d can be found, and the article of Krasnikov \textit{et al.}\(^14\) for the corresponding C—Br value. However, as we also measured Br 3p spectra during our experiments (Figure 3), we note that the BE shifts due to the chemical modifications have identical magnitude and signs for both the core level peaks. The Br 3d peak has a better signal-to-noise ratio (its photoionization cross section is approximately 3 times higher at 390 eV\(^15\)) and was therefore more desirable for presenting in our article. However, it is clear that the same information can be obtained by the analysis of either of these two core levels.

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\textbf{References:}

The presence of the additional Br 3d component observed at higher BE at RT has been confirmed in other experiments performed at the CASSIOPEE beamline of the SOLEIL synchrotron. In our paper, we stated that this component is due to different chemical environments of bromine atoms, with the aim of not over-interpreting the spectra in the absence of further details. In fact, we know from STM experiments that the organometallic structures are present in a large number of separate domains. The domains are always surrounded by Br atoms (clearly apparent in Figure 1a and Figure 2a in our paper), and this increases the ratio of side-Br atoms to top-Br atoms. In addition, we point out that the diminished intensity may also be due to photoelectron diffraction effects, which should be quite strong at the low kinetic energies involved in our experimental conditions. Variations in the polar emission pattern of the photoemission were not examined during this measurement. Without this type of investigation, it is not possible to comment on the absolute magnitude of the intensity ratios.

In conclusion, the Comment on our XPS results has given us the opportunity to add some details that were not included in the original paper for the sake of simplicity. However, we have identified no incorrect statements in our original paper, and neither the comments by Song nor the details provided above give any reason to alter the conclusions originally drawn in our work.

REFERENCES AND NOTES


