Supporting Information

Title: An unexpected organometallic intermediate in surface-confined Ullmann coupling

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1. Fast-XPS: observed phases

Figure S1 presents the kinetic curves, extracted from the fast-XPS maps of the C 1s core level signal acquired during the annealing of the sample, using the procedure previously reported by Di Giovannantonio et al.[1] Each horizontal profile of the fast-XPS map represents a single C 1s XPS spectrum. The line shape and peak position of the signal is related to the chemical state of the molecules on the surface.[2, 3] At room temperature (and up to 130 °C), the typical shape and position of the spectrum from the organometallic phase is visible (signal f1 in the blue frame, Figure S1), while after the transition, the C 1s signal of the 2D-OM appears (signal f2 in the green frame, Figure S1). After the second transition, the C 1s signal relative to the polymer phase is visible (signal f3 in the red frame, Figure S1). These three model spectra are used as components to fit each of the spectra in the whole dataset, producing a plot with the relative abundance of the three species on the surface (linear-OM, 2D-OM, and polymers) as a function of the temperature (Figure S1c).

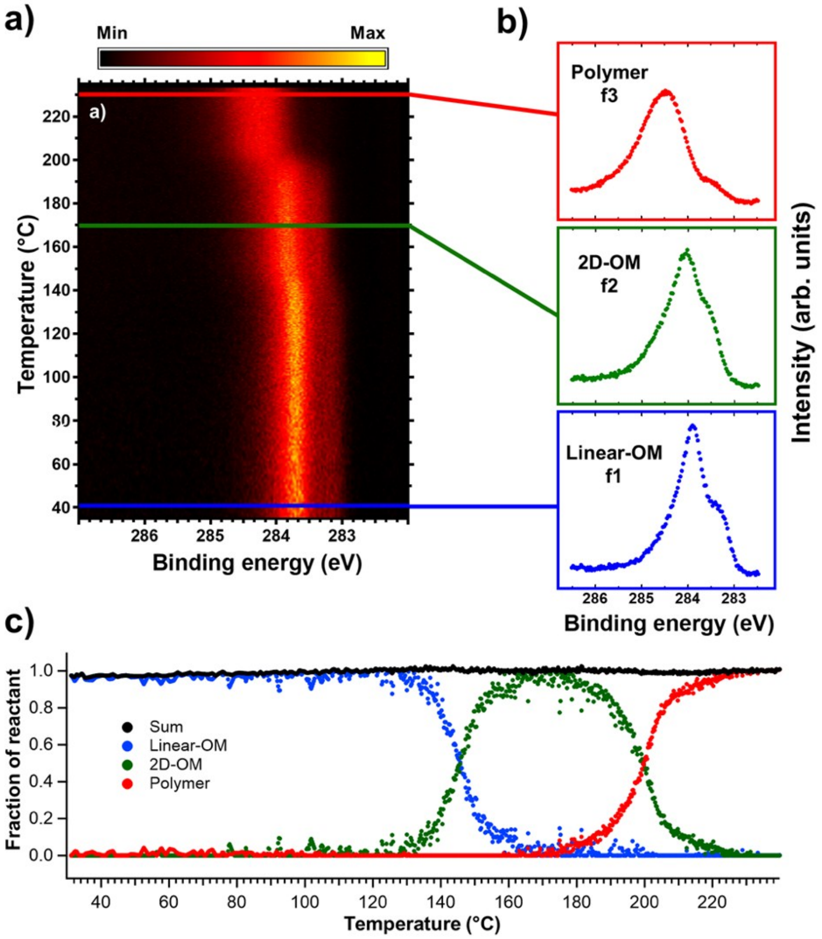

Figure S1. *Fast-XPS map of the C 1s core level signal during annealing (a). The coverage of dBB deposited on Cu(110) at RT was 0.5 ML. Each horizontal profile of the map is one C 1s spectrum at one specific temperature. All the spectra were fitted using f1, f2 and f3, attributed to linear-OM, 2D-OM, and polymer, respectively (b), producing the plot reported in (c).*

2. DFT calculations

Two classes of structures were considered, with building blocks consisting of either biphenyls or single phenyls, and the results are reported in Figure S2. For the biphenyls, we examined two structures. In the first (case a) the four biphenyls form a junction at a Cu adatom and the phenyls are twisted out-of-plane from the surface to prevent overlap of the H atoms. The resulting ring-like structure corresponds to a local minimum of the complex energy landscape but disagrees with the phenyls being almost parallel to the surface, as found by NEXAFS experiments. In the second structure (case b) an attempt was made to keep the dimers in-plane. In order for the H atoms to remain attached to the phenyls near the intersection of the dimers, the H atoms have been forced vertically with respect to the plane of the structure. From a solution chemistry standpoint the sp^3 hybridization is unusual; however, chemistry in 2D can be drastically different due to interaction with the substrate and symmetry breaking imposed by the surface. Despite their relative stability, the biphenyl-based structures are not compatible with the experimental STM results from the boundaries between 2D-OM domains, and the NEXAFS results. This issue can be resolved by considering the second class of structures based on single phenyls, for which four cases have been considered. In the first, Cu atoms are pulled out of the surface to anchor the phenyls (case c). For the other three Cu adatoms in the on-top (case d), short bridge (case e), and hollow (case f) surface positions are bounded to phenyls. The adatoms are not stable in the on-top position and the resulting structure (case d) presents a symmetry which does not match with the experiments.

To further discern between the three remaining models, Br atoms have been added between the phenyl junctions. For cases c and e, the Br atoms are found to be located in the relatively stable hollow and long bridge positions, respectively. For case f, the Br atoms are located in the top position, and stabilized by the surrounding phenyls (an isolated Br atom is however not stable in the top position). The STM images simulated for each case at four different biases (Figure S3) show that a better agreement with the experimental results is obtained for the structure with the Cu adatoms in the short bridge position (case e).

The energetic properties of structure e are computed to evaluate its stability. A suitable figure of merit is:

$$\frac{E_{Total} - \left(E_{Substrate} + 4 * E_{Free\ Phenyl}\right)}{4} = -4.6\ eV/phenyl$$

where E_{Total}, $E_{Substrate}$ and $E_{Free\ Phenyl}$ are total DFT ground state energies for: (i) the 2D-OM on the substrate with Cu adatoms, (ii) the substrate with Cu adatoms and (iii) for an isolated phenyl (with the two end H atoms missing), respectively. A negative figure of merit indicates energetic stability. For sake of completeness the corresponding figures of merit for structures c and f in Figure S2 are -4.3 and -5.0 eV/phenyl, respectively. While the value for structure f is lower than that of the suggested structure e, the endpoint stabilities cannot be directly correlated with the energy barriers that must be traversed to reach the intermediate phase. The sign of the energetic figure of merit is the important aspect in determining the stability of each individual structure.

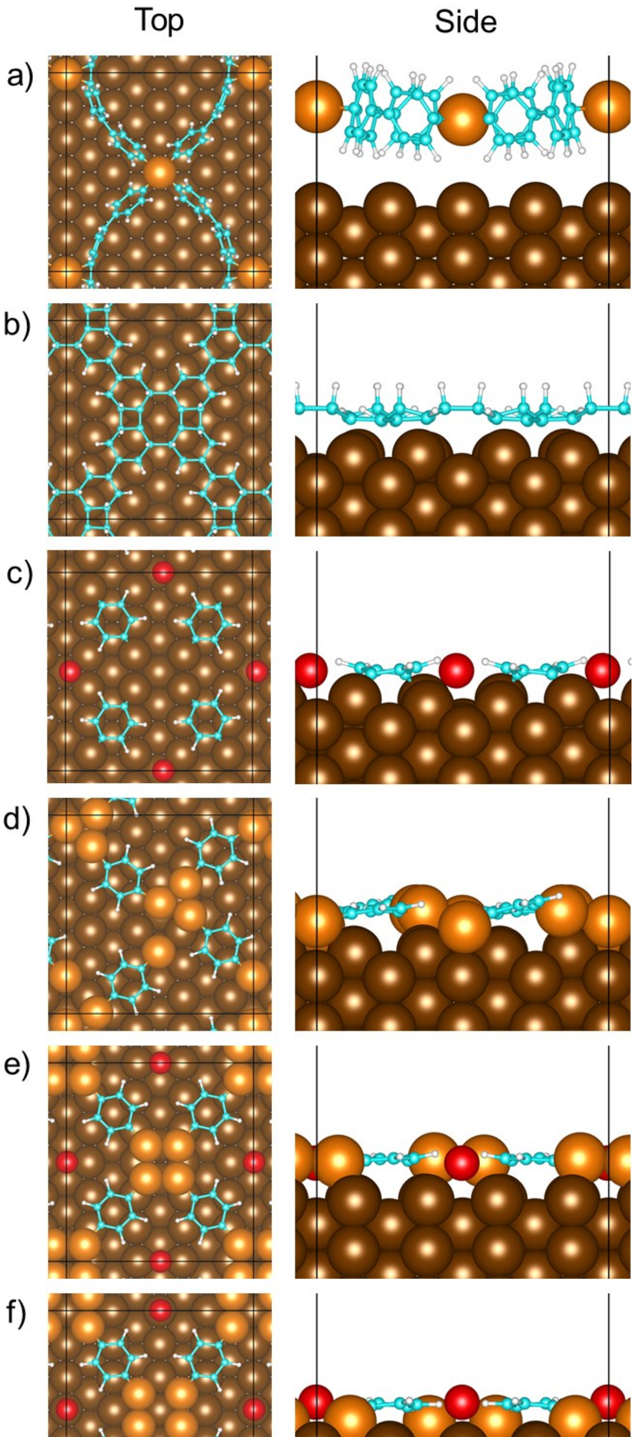

Figure S2. *Top and side views of the considered atomic models for the 2D-OM intermediate phase. (a) Biphenyls distorted out-of-plane. (b) Biphenyls kept in-plane with H atoms forced out-of-plane. (c) Phenyls bounded to surface Cu atoms. (d) Phenyls bounded to on-top Cu adatoms. (e) Phenyls bounded to short bridge Cu adatoms. (f) Phenyls bounded to hollow Cu adatoms.*

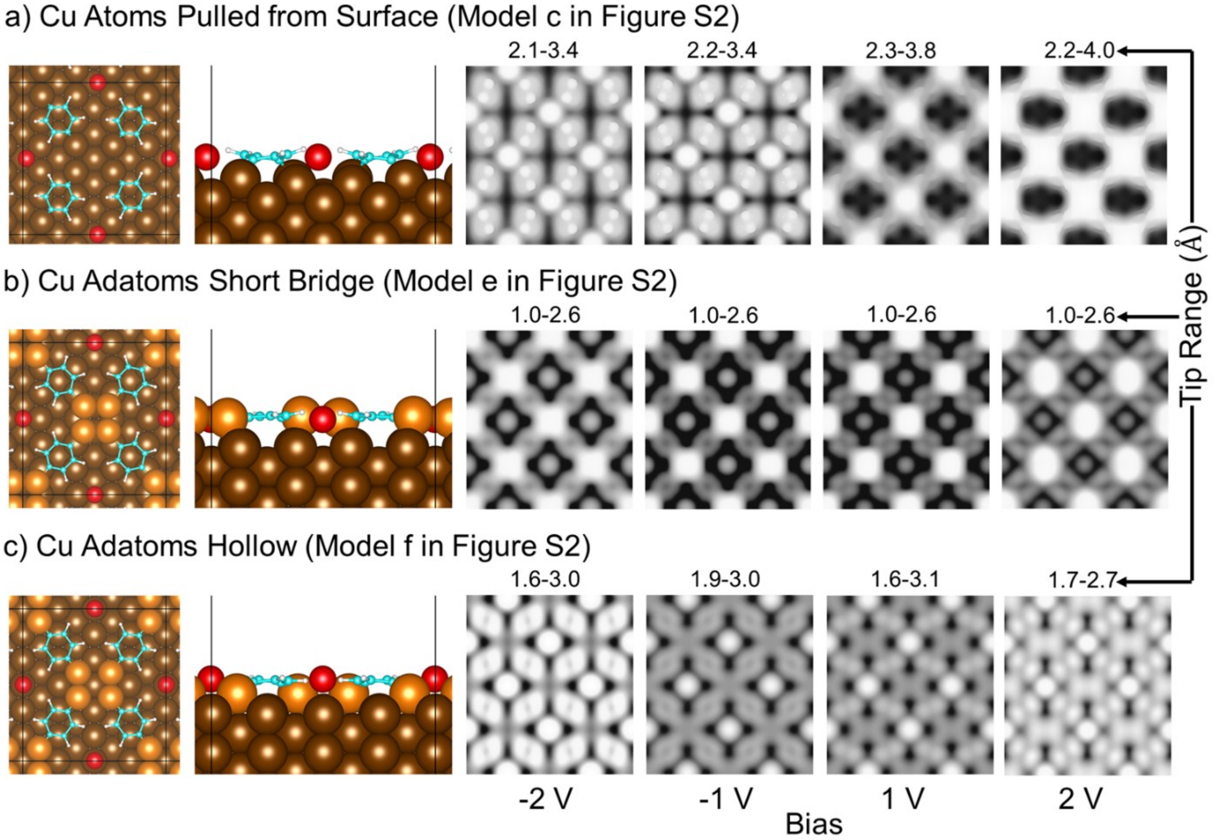

Figure S3. *Simulated STM images (2.8x2.8 nm^2) at different bias voltages (tip radius = 0.9-0.95 Å) for three models reported in Figure S2; the center of each image corresponds to the four Cu atoms cluster. The simulated STM images for model e are in reasonable agreement with the experimental STM images presented in the main text.*

3. Structural models of phases

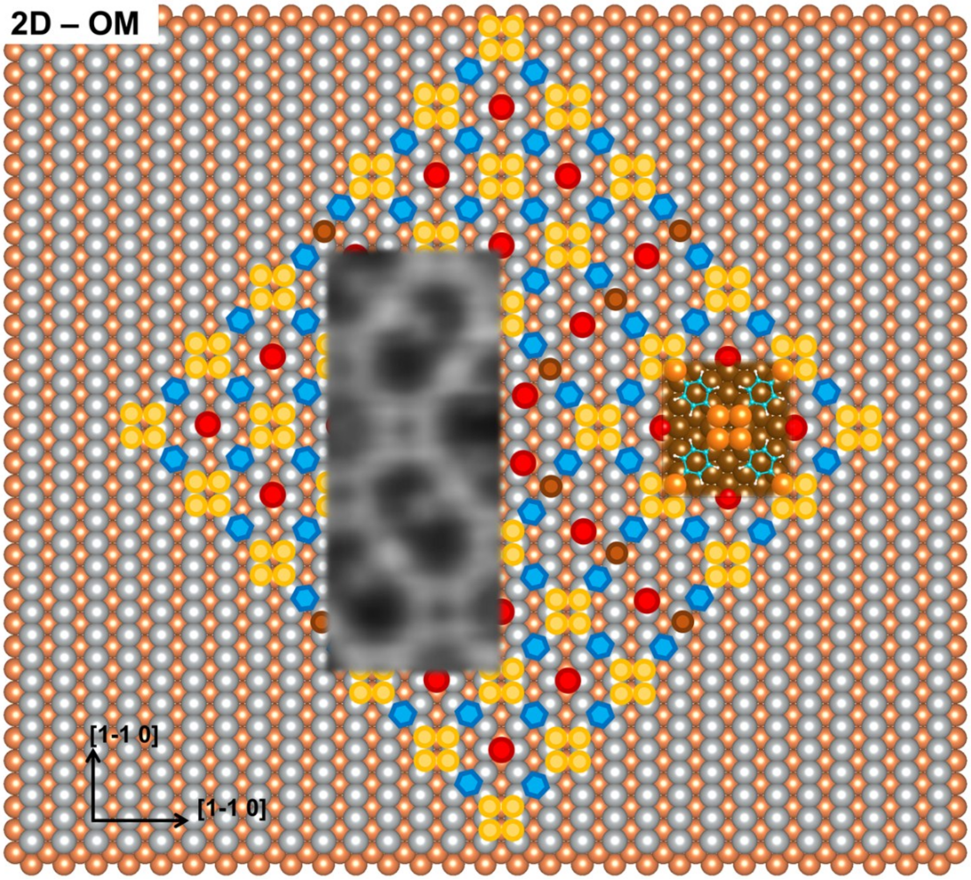

Figure S4. *Model of the 2D-OM phase with superimposed both an STM image and the DFT calculated model.*

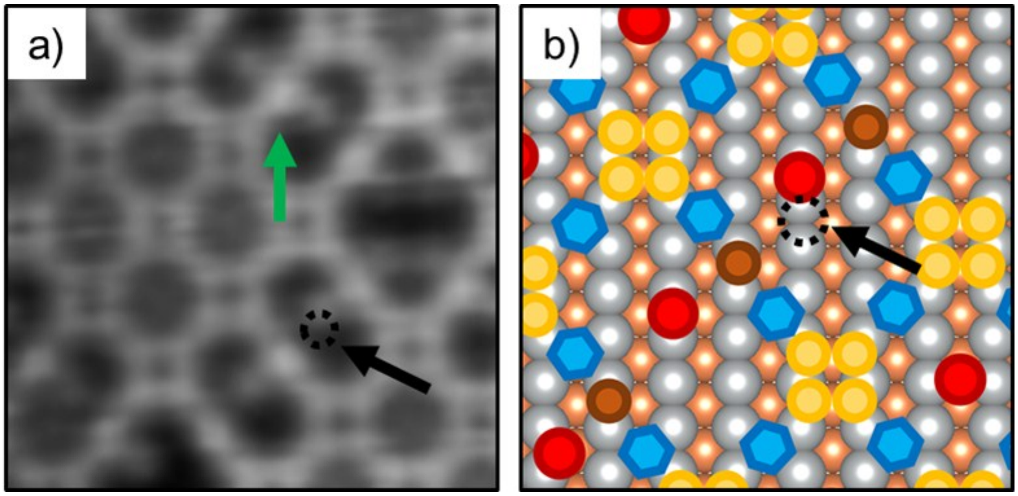

Figure S5. *a) 4×4 nm^2 STM image of the 2D-OM phase and b) atomic model of the same phase, zoomed in the inter-patch region between two chessboard-like domains. The Br atoms in the inter-patch regions are placed in the favourable short-bridge sites. For each Br atom two equivalent* *positions are present. The green arrow indicates a Cu atom with adjacent Br atoms. Black arrows indicate the empty short-bridge positions.*

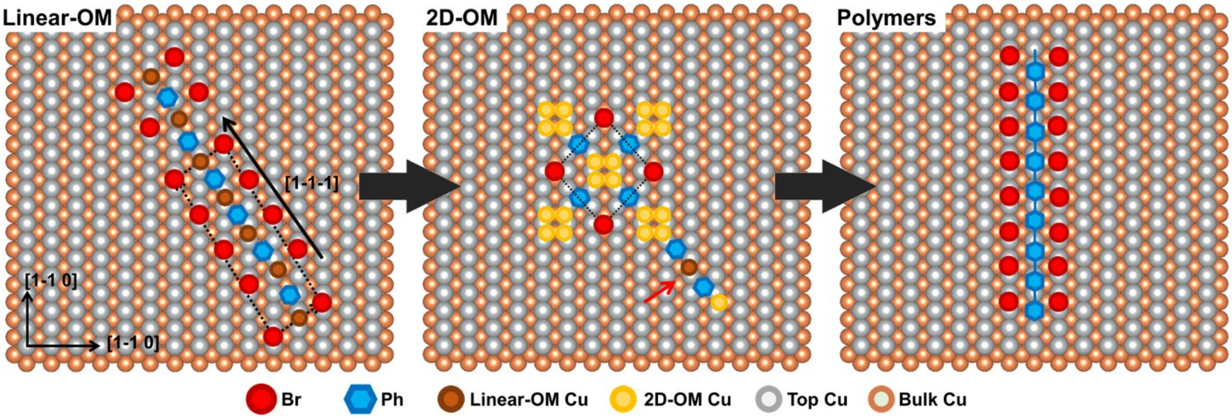

Figure S6. *Models of the three different phases observed at low coverage, linear-OM, 2D-OM and polymers. Different color schemes have been used for Cu atoms to help identification. The red arrow indicates the linear-OM bridge between different chessboard-like domains of the 2D-OM phase.*

4. Details of XPS peak analysis

Table S1. *Binding energy (BE), full width at half maximum (FWHM) and relative peak area (%) of the components used to fit the C 1s spectra shown in Figure 4. The fit has been performed by linear least squares minimization using Voigt line-shapes, using the starting position for the three linear-OM components in the position identified by Di Giovannantonio et al.*[2, 3] *and allowing free variations of parameters without applying any constraints*

Phase	C-C(1)			C-C(2)			C-Cu(1D)			C-Cu(2D)		
	BE (eV)	FWHM (eV)	%	BE (eV)	FWHM (eV)	%	BE (eV)	FWHM (eV)	%	BE (eV)	FWHM (eV)	%
Linear-OM	283.9	0.52	39.3	284.3	0.79	36.7	283.3	0.50	24.0			
2D-OM	284.0	0.60	55.7	284.6	0.85	24.3	283.2	0.46	3.4	283.6	0.49	16.6
Polymer	284.3	0.81	40.3	284.8	1.24	53.7	283.4	0.56	6.0			

5. XPS and STM comparison

The XPS presented in the MS have been performed at the ALOISA beamline of the Elettra synchrotron, where there is no possibility to perform STM measurements. XPS experiments were also performed in-house with a UHV system including both STM and XPS instruments. This permits to identify the correspondence between the 2D-OM phase observed by STM and the C 1s shift measured by XPS, as can be seen in Figure S7. The C 1s spectra in Figure S7a are relative to a submonolayer coverage (0.6 ML) of dBB on Cu(110) at RT (blue) and after annealing at 170 °C (green) and 230 °C (red). The BE trend and peak maxima positions obtained with in-house XPS are in agreement with those obtained with synchrotron radiation, even if the signal-to-noise ratio and energy resolution of the peaks are lower, permitting the structures observed by STM to be correlated with the fast-XPS measurements.

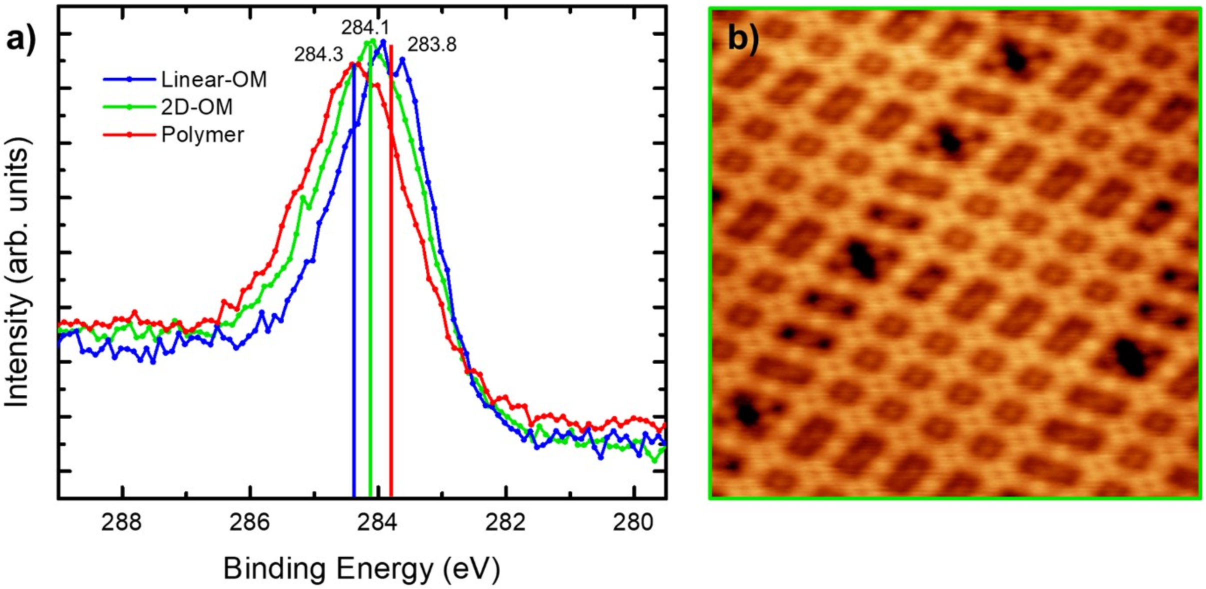

***Figure S7**. a) C 1s XPS spectra (30 eV Pass Energy) measured in our home-laboratory in a UHV system equipped with STM and XPS, confirming that the chemical shift revealed in the C 1s XPS spectrum corresponds to the observed 2D-OM phase. b) 9×9 nm^2 STM image (-1.0 V, -0.64 nA) corresponding to the green XPS spectra.*

6. Bibliography

1. Di Giovannantonio, M.; Tomellini, M.; Lipton-Duffin, J.; Galeotti, G.; Ebrahimi, M.; Cossaro, A.; Verdini, A.; Kharche, N.; Meunier, V.; Vasseur, G.; Fagot-Revurat, Y.; Perepichka, D. F.; Rosei, F.; Contini, G., *J. Am. Chem. Soc.* **2016,** *138* (51).
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3. Di Giovannantonio, M.; El Garah, M.; Lipton-Duffin, J.; Meunier, V.; Cardenas, L.; Fagot-Revurat, Y.; Cossaro, A.; Verdini, A.; Perepichka, D. F.; Rosei, F.; Contini, G., *ACS Nano* **2014,** *8* (3), 1969-1971.