Dimerization of Tri(4-bromophenyl)benzene by Aryl−Aryl Coupling from Solution on a Gold Surface

James C. Russell,[†] Matthew O. Blunt,[†] Jason M. Garfitt,[†] David J. Scurr,[‡] Morgan Alexander,[‡] Neil R. Champness,[§] and Peter H. Beton*,[†]

[†]School of Physics & Astronomy, [‡]School of Pharmacy, and [§]School of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

S *Supporting Information*

ABSTRACT: Monolayers of monomer 1,3,5-tri(4-bromophenyl)benzene (TBPB) and the dimerized product 3,3‴,5,5‴-tetra(4-bromophenyl)quaterphenyl (TBPQ) on a gold surface have been studied using ambient scanning tunneling microscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Molecular layers are prepared by allowing sessile drops of solution to dry on a gold substrate. For room-temperature deposition we observe ordered arrays of TBPB in three distinct packing arrangements. Deposition on a heated substrate leads to the formation of the dimerized product, TBPQ, through a surface-induced aryl−aryl coupling. Regions of TBPQ coexist with regions of disordered multiply linked molecules. The conversion of monomer TPBP to dimers is confirmed using ToF-SIMS. Our results demonstrate an alternative, solution-phase approach to the formation of large molecules and nanostructures by coupling reactions.

Covalent coupling of molecules on metallic surfaces provides a new route to the formation of large molecules and extended nanostructures.[1−3] There are several approaches to inducing such coupling based commonly on either the Ullmann reaction or other related aryl−aryl coupling reactions,[2,4] in which a carbon−halogen bond of an adsorbed molecule is cleaved, or a condensation reaction between amine and carbonyl groups.[1] Following Grill et al.,[2] covalent coupling of molecules has recently been used to form extended structures such as graphene[5] strips and nanostructured templates,[6] and there is great potential to form a wide range of functional polymeric systems using this approach. However, the work reported to date has been performed under ultra-high-vacuum conditions, often in conjunction with single-crystal metallic surfaces, and it is highly desirable to develop an analogous, but methodologically simpler, technique compatible with solution deposition and surfaces that are stable under ambient conditions.

In this report we show that aryl−aryl coupling can be promoted on a metallic surface under ambient/liquid conditions. In particular we show that the molecule tri(bromophenyl)benzene (TBPB, see Figure 1), which has previously been demonstrated to form covalent networks under vacuum conditions,[6−8] can be dimerized to form 3,3‴,5,5‴-tetra(4-bromophenyl)quaterphenyl (TBPQ) through aryl−aryl coupling

on a gold surface by the drop deposition of an ethanolic or butanolic solution of the parent compound. The conversion of TBPB monomers to TBPQ is confirmed using scanning tunneling microscopy (STM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

Our experiments are undertaken using Au (111) thin films deposited on mica which are supplied commercially[9] and cleaned in an O_2 plasma. A 10 μL droplet of TBPB dissolved in either ethanol or butanol is deposited on the sample surface and allowed to dry. The substrate is either held at room temperature or heated on a hot plate at a temperature up to 200 °C. All deposition is performed under atmospheric conditions. Full details of experimental procedures and substrate preparation are provided in the Supporting Information.

STM images of the surface following droplet deposition at room temperature are shown in Figure 1. It is possible to identify TBPB molecules, which are resolved as trigonal features in the images. Three different packing arrangements are observed for the TBPB monomers, as shown in Figure 1. Phase I (Figure 1a) is essentially equivalent to that observed for sublimed monolayers in vacuum,[6−8] but phase II (Figure 1e) and phase III (Figure 1g) have not been reported previously. Simple schematic models of these molecular phases are shown in Figure 1 c, f, and h, on which the unit cells are overlaid. For phase I we determine the values of a and b to be 16.8 ± 0.4 and 24.1 ± 0.5 Å, respectively, with an angle between them of 58 ± 2°. For phase II the values are determined to be 16.7 ± 0.4 and 19 ± 1 Å, with an angular separation of 90 ± 5°, while for phase III the values are determined to be 17.6 ± 0.2 and 22.1 ± 0.9 Å, with an angular separation of 70 ± 7°. In each case we identify a two-molecule basis (for all schematics the basis is centered on the vertices of the unit cells). The two molecules forming the basis are rotated by 180° with respect to each other and are slightly offset, as illustrated in Figure 1d. For all phases we measure the offset, Δ, to be 2 ± 1 Å. We attribute this offset to the stabilization of this intermolecular junction by halogen bonding,[10] as recently demonstrated for TBPB.[8] The regular arrangement of phase III is often interspersed with domain boundaries across which there is mirror symmetry in the molecular arrangement (further images and discussion are provided in the Supporting Information). No such analogous features are observed for phases I and II.

To promote covalent bonding of TBPB molecules, the solution was deposited onto heated Au substrates (still under
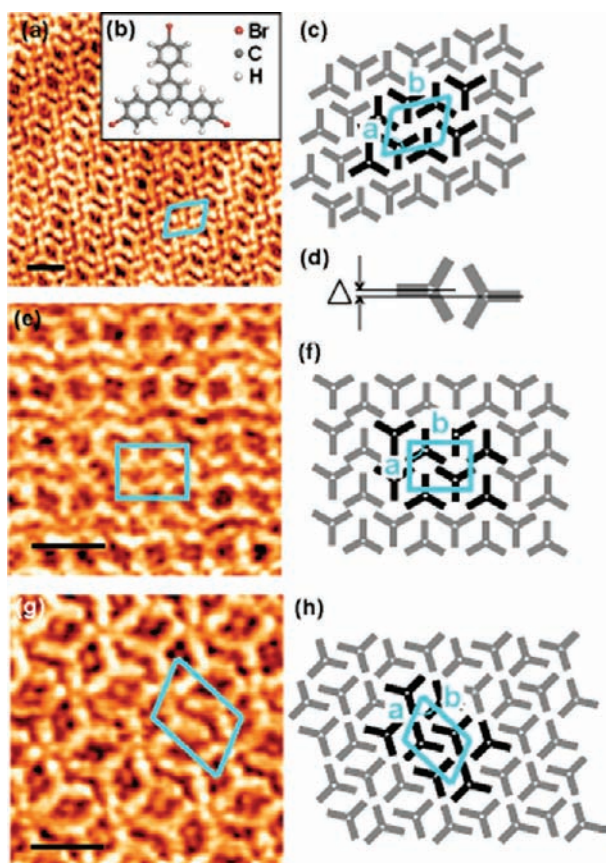
Figure 1. STM images of TBPB (b) adsorbed on the Au (111) surface at room temperature. The molecules have been observed to form three distinct phases: I (a), II (e), and III (g). Diagrams highlighting the molecular packing of the three phases are shown in (c), (f), and (h), respectively. Molecules were deposited from solutions of ethanol ((a) and (e)) and butanol (g). Illustrated in (d) is a schematic diagram of the molecular pair which forms the basis of the regular arrangement for all three phases. The small offset of the two molecules is described by the parameter Δ. Imaging parameters: (a) $I = 0.4$ nA, $V_{tip} = 0.6$ V; (e) $I = 0.5$ nA, $V_{tip} = 0.4$ V; (g) $I = 0.5$ nA, $V_{tip} = 0.4$ V. All scale bars are 2 nm. Unit cells are drawn for each phase.

Figure 2. Aryl–aryl coupling of TPBP by drop deposition on heated substrates. (a) An image showing the TBPB network formed when the substrate was heated to 150 °C prior to deposition from ethanol. The black circles illustrate a few examples of covalently bonded molecules, including a dimer (right) and trimer (left). Imaging parameters: $I = 0.2$ nA; $V_{tip} = 0.3$ V. The scale bar is 5 nm. (b) Schematic diagram of the TBPB dimer. (d) Image showing the network formed at 200 °C from ethanol. On the right-hand side a new phase can be seen due to the formation of TBPB dimers. Imaging parameters: $I = 0.5$ nA; $V_{tip} = 0.5$ V. The scale bar is 5 nm. A zoom of the TBPB dimer phase is shown in (c). The unit cell is drawn highlighting the molecular packing. The scale bar is 1 nm.

ambient conditions). Figure 2 shows examples of the resulting surfaces. Figure 2a shows that heating the substrate to 150 °C leads to the appearance of a number of apparent bonding events at domain boundaries involving isolated groups of molecules (circled; monomer phase II is also present in this image). These features are consistent with the formation of a covalent bond through aryl–aryl coupling, which arises from cleavage of C–Br bonds on neighboring molecules followed by the formation of a C–C, which results in a quaterphenyl backbone to which four bromophenyl groups are attached. The molecular structure of the dimerized TBPB, TBPQ, is shown in Figure 2b. The length of the quaterphenyl backbone is determined to be 13.1 ± 1 Å, consistent with DFT simulations of TBPQ.[6]

It is also possible for the TBPQ molecules to undergo further aryl–aryl coupling reactions to form multiply connected species which are the precursors of extended polymers, and we observe several examples where three TBPB molecules have combined to form a trimer.

Heating the Au sample to 200 °C during deposition resulted in the emergence of an ordered phase of TBPQ, as shown on the
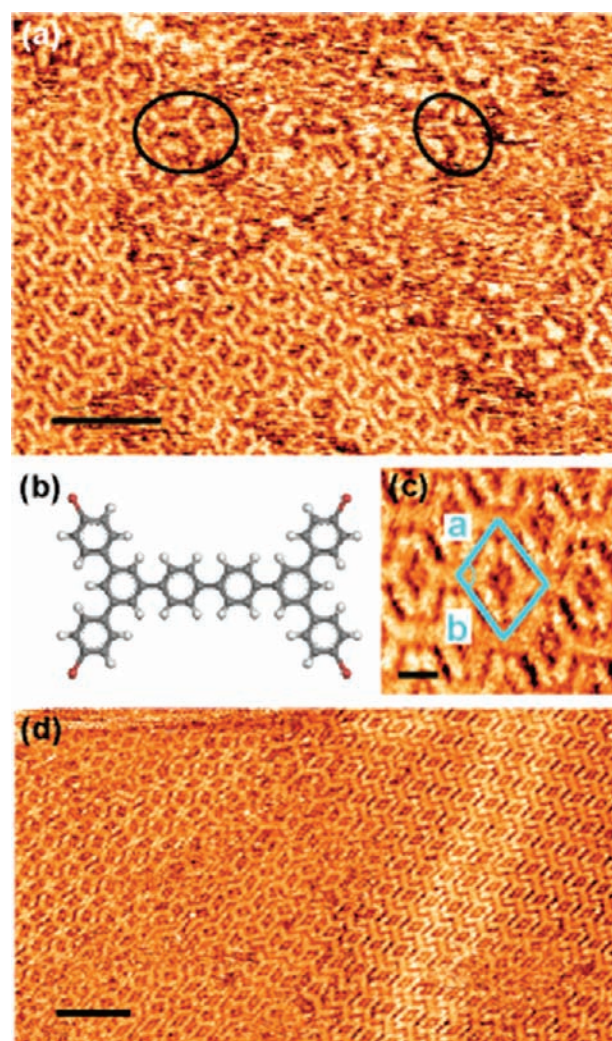
right of Figure 2d (on the left of this image are regions of monomer phases II and III). In this case we find that not only has the TBPB dimerized, but it has also been organized into extended regular structures. It is clear that the appearance of TBPQ in Figure 2d is very similar to those identified in Figure 2a; furthermore, the lengths of the quaterphenyl backbone are identical in both cases, within experimental error. The values for a and b in the unit cell for the bonded phase are determined to be 16 ± 1 and 17 ± 1 Å, respectively, with an angle of $93° \pm 14°$ between them.

While our STM results show very clearly that the adsorbed molecules have undergone some changes as a consequence of annealing, it is difficult to identify the product unambiguously
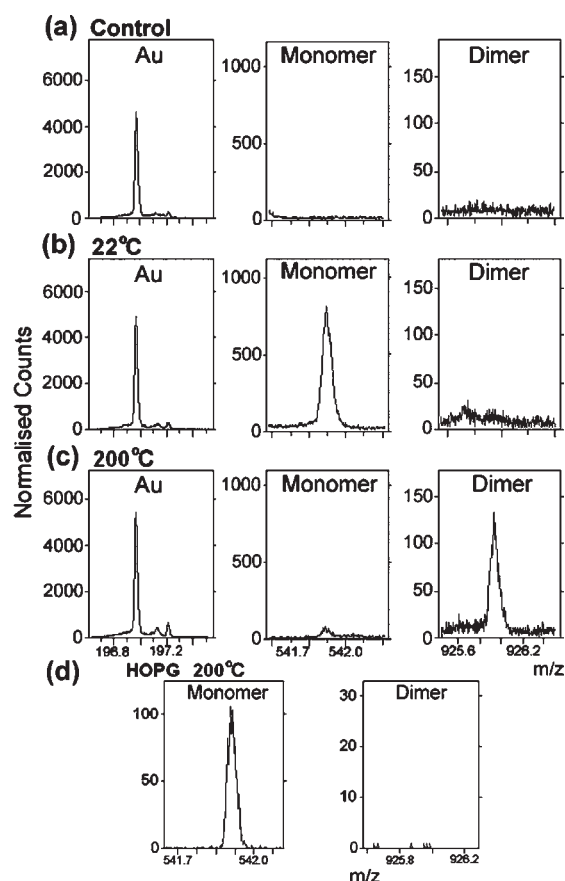
Figure 3. Secondary ion mass spectrometry of surfaces: (a) a control Au sample exposed to ethanol while being heated to 200 °C, (b) a Au sample with TBPB deposited at room temperature, (c) a Au sample with TBPB deposited at 200 °C, and (d) a HOPG sample with TBPB deposited at 200 °C. The columns correspond to spectral data for Au (a–c only), TBPB, and TBPQ. The data confirm that TBPQ formation arises from deposition on a heated Au substrate, as discussed in the text.

from STM images alone. In fact, this is further complicated by the existence of other possible reaction products, such as the partial loss of one or more of the remaining Br atoms attached to the dimer (see structure in Figure 2b) caused by further interaction with the surface. In addition, alternative bonding configurations involving Au atoms providing a connecting link between halogen atoms have been proposed. This type of metal coordination has been reported previously in vacuum studies of TBPB[8] and other halogenated molecules.[11]

To distinguish between the formation of TBPQ and other possible products, we have investigated the films formed at different temperatures using ToF-SIMS. This analytical technique provides a direct measurement of the mass spectra of surface-adsorbed species. The sample is exposed to a rastered primary ion beam under vacuum conditions, and the resulting secondary ions generated are analyzed using their time-of-flight (see Supporting Information for further details).

In Figure 3 we show extracts from the full spectra over the relevant mass ranges for Au atoms, TBPB, and TBPQ. The top row shows the spectra acquired for a control sample which was heated to 200 °C before the deposition of a 10 μL droplet of pure ethanol. In this case we observe the expected peak for Au$^+$ (m/z = 196.96) but no evidence of species with masses close to that of TBPB ($C_{24}H_{15}Br_3^+$, m/z = 541.88) or the TBPQ ($C_{48}H_{30}Br_4^+$,

m/z = 925.92). The second and third rows in Figure 3 show spectra for samples for which the TBPB molecules were deposited at room temperature and 200 °C, respectively. The Au peak is detected for all the samples. For the room-temperature sample a peak corresponding to the TBPB monomer is clearly resolved, but there is no evidence for TBPQ, indicating that dimerization does not occur under these conditions. Finally, the sample heated to 200 °C shows a significant peak for the dimer, confirming that the molecule identified in Figure 2b is present on the surface and that it is formed by heating the Au substrate (the spectrum in Figure 2d shows that the dimer is not formed on a graphite substrate under equivalent conditions, confirming that the role of the Au surface is critical). In Figure 2c we also observe a significant reduction in the monomer peak height to a value ~10% of that observed for room-temperature deposition. This indicates that a substantial fraction of TBPB has been modified through conversion to TBPQ.

We have also inspected the spectral regions that correspond to TBPB and TBPQ with attached gold atoms and/or with missing Br atoms. We have been able to identify small peaks corresponding to TBPB and TBPQ molecules with one Br atom missing. For the monomer the peak height was of the order of 30 counts for both the room-temperature and 200 °C samples. For the dimer the peak height corresponded to 20 counts and was present only in the 200 °C sample. We have been unable to identify any other specific peaks due to larger bonded species such as trimers. Our ToF-SIMS spectra specifically confirm that four Br atoms remain attached to TBPQ for the vast majority of molecules and only a relative small fraction undergo further fragmentation, for example through additional C–Br bond cleavage.

The combination of ToF-SIMS and STM shows conclusively that a surface-induced aryl–aryl coupling may be induced through solution deposition of a brominated molecule on a heated gold surface. For this particular molecule, the reaction proceeds only to the formation of dimers and a small number of trimers, although in principle larger products and extended polymers might be expected. It is likely that the suppression of further coupling reactions is not intrinsic but related to the reduction in surface mobility following dimer formation, similar to recent observations in vacuum experiments.[6] This approach may be viewed as a powerful complementary approach to recent vacuum studies and provides a facile route to the formation of large molecules and nanostructures, with the potential for the coupling of functional units that are difficult to introduce into a vacuum. In addition, our results show that the highly specific approaches to single-molecule chemistry may be realized using simple methodologies.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Details of sample preparation procedures, experimental protocols for the STM and ToF-SIMS measurements, and additional images showing defect structures in monomer phases. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
peter.beton@nottingham.ac.uk

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