

Supporting Information

Initial Coupling and Reaction Progression of Directly Deposited Biradical Graphene Nanoribbon Monomers on Iodine-Passivated Versus Pristine Ag(111)

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Additional STM data

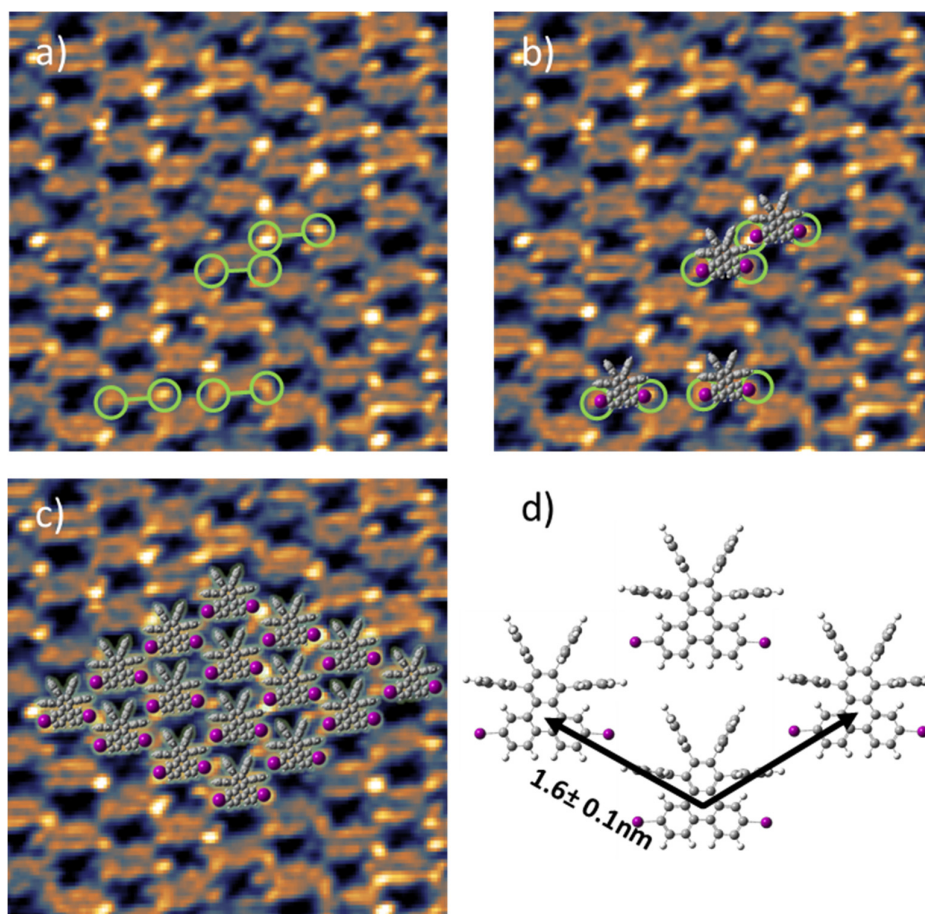


Figure S1. (a)–(c) STM image of the self-assembled monolayer observed after conventional deposition of intact DITTP onto pristine Ag(111). Assigning the observed features to DITTP molecules is not trivial, but pairs of bright spots appear with a similar distance of $1.1 \pm 0.1 \text{ nm}$ (green dumbbells in (a)). This is in perfect agreement with the expected spacing of the para iodine substituents in a single DITTP molecule, and also consistent with the commonly observed bright STM appearance of iodine substituents. This allows us to (b) allocate individual molecules, and, consequently to (c) derive a model of the supramolecular packing. The so obtained structure is shown in more detail in (d). It features one molecule per unit cell. This leads us to exclude halogen-halogen interactions as the commonly expressed binding motif for aryl halides.[50–53] This type of interaction would require at least two non-collinear orientations of the C-I bond axis, which is at odds with the observation of one unique orientation for the DITTP molecules. Instead, we tentatively suggest stabilization by halogen-hydrogen bonds, where the iodine substituents interact with the phenyl substituents of DITTP through its nucleophilic end.[54] Yet, a more definitive assignment of the supramolecular interactions would require appropriate simulations of the packing. (image parameters: a-c: $11 \times 11 \text{ nm}^2$, 93 pA, 1.13 V)

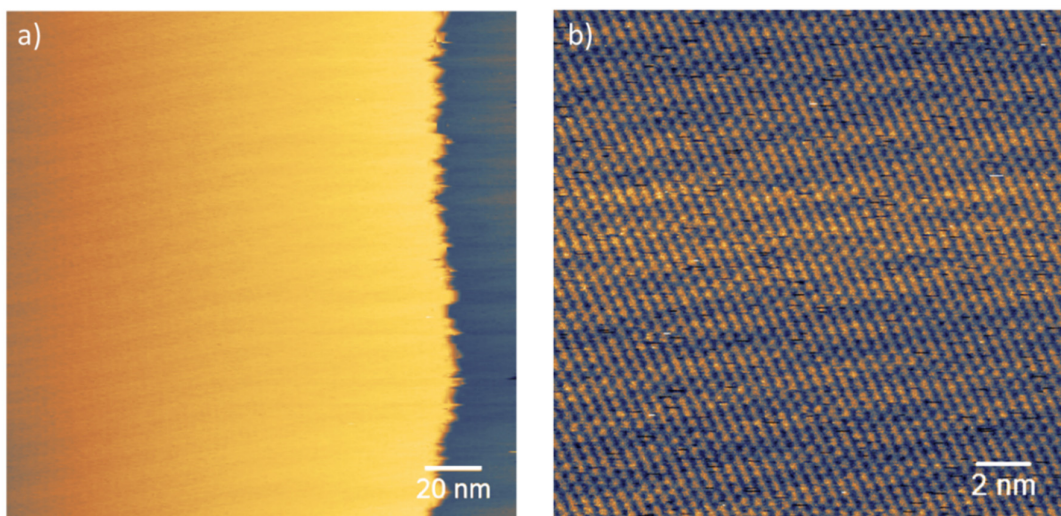


Figure S2. STM images of the empty I-Ag(111) observed after conventional deposition of DITTP and heating to 200 °C. The iodine $\sqrt{3} \times \sqrt{3} R30^\circ$ superstructure is clearly visible, but no traces of the DITTP molecules could be observed anymore, indicating complete desorption. We interpret these experiments as evidence that I-Ag(111) surfaces behave inert with respect to a dehalogenation. Otherwise, larger aggregates would have formed that cannot be desorbed anymore at this relatively low temperature. (image parameters: a: $180 \times 180 \text{ nm}^2$ 140 pA, 1.2 V; b: $19 \times 19 \text{ nm}^2$, 140 pA, 1.2 V)

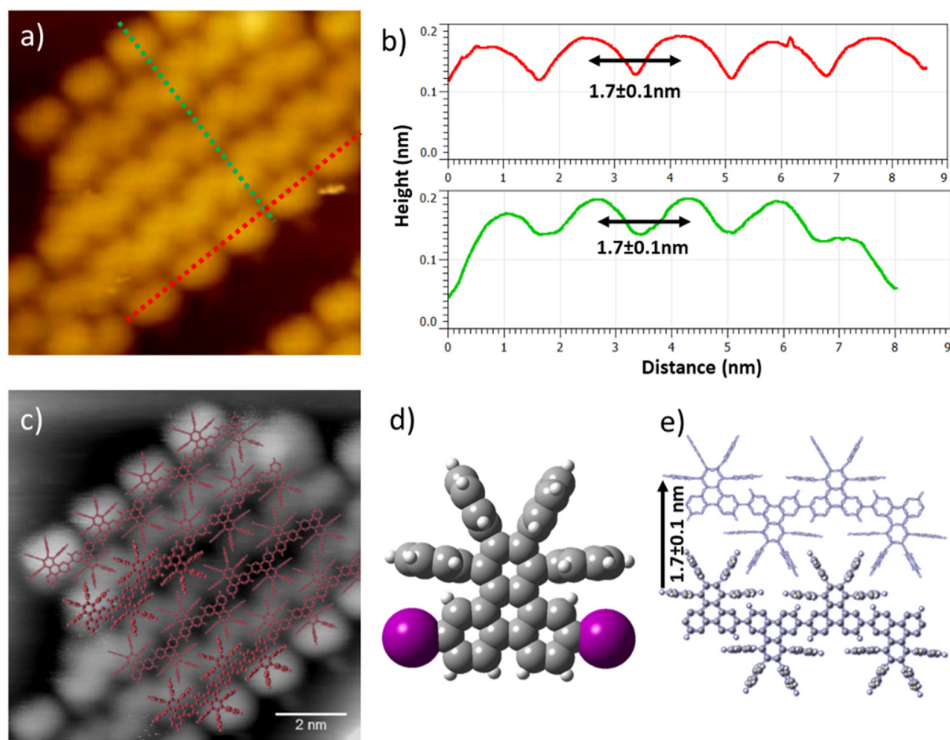


Figure S3. Covalent polymer chains on I-Ag(111). Packing of the covalent polymer chains as observed on I-Ag(111) after deposition via the RaDeS and heating to 200 °C. (a) STM image and (b) corresponding line-profiles as indicated in (a) by the dashed lines; The interchain distance amounts to 1.7 nm (green curve). (c) similar STM image as in (a) with overlaid models of the covalent chains; (d) DFT optimized structure of isolated DITTP; the phenyl substituents are oriented perpendicular to the triphenylene core; (e) Model of the covalent chains to illustrate their self-complementary packing. The spacing was derived from experimental data. The model suggests that π - π interactions between the phenyl substituents of adjacent chains determine and stabilize the packing. (image parameters: $12 \times 12 \text{ nm}^2$, 90 pA, 2.5 V).

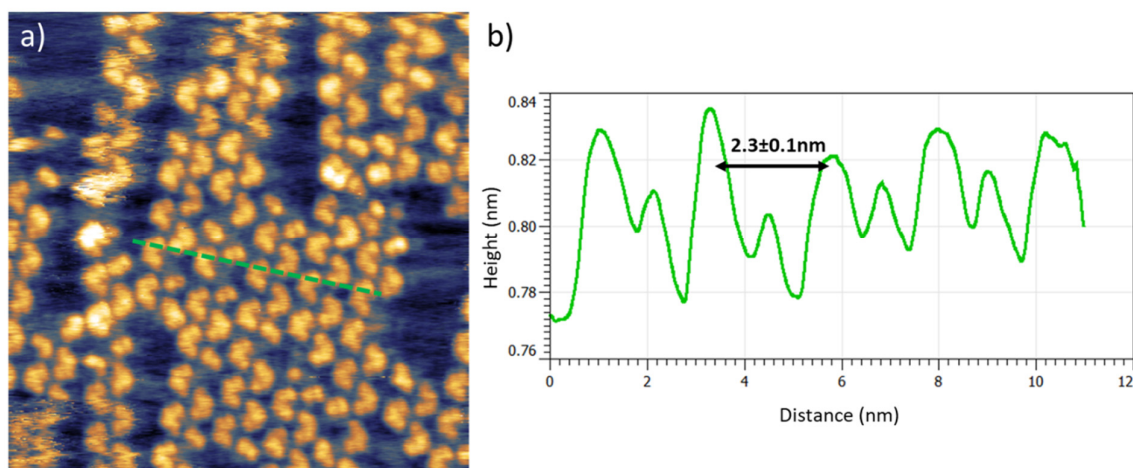


Figure S4. Covalent polymer chains on Ag(111). **(a)** STM image of covalent chains acquired after annealing to 400 °C. Initially, the covalent chains formed on the iodine-passivated surface. But upon heating the iodine monolayer had already been fully desorbed, and the covalent chains became adsorbed directly on the pristine Ag(111) surface. **(b)** Line-profile as indicated in (a). The interchain distance has increased markedly to 2.3 nm on the bare Ag(111) surface as compared to 1.7 nm on I-Ag(111) (cf. Figure S3). A possible explanation is offered by flattening of the chain structure imposed by a stronger interaction of the phenyl-substituents with the Ag(111) surface. Thereby, the packing with almost upright phenyl substituents proposed in Figure S3d would no longer be feasible, and consequently each chain would require more space. (image parameters: $20 \times 20 \text{ nm}^2$, 87 pA, 2.5 V).

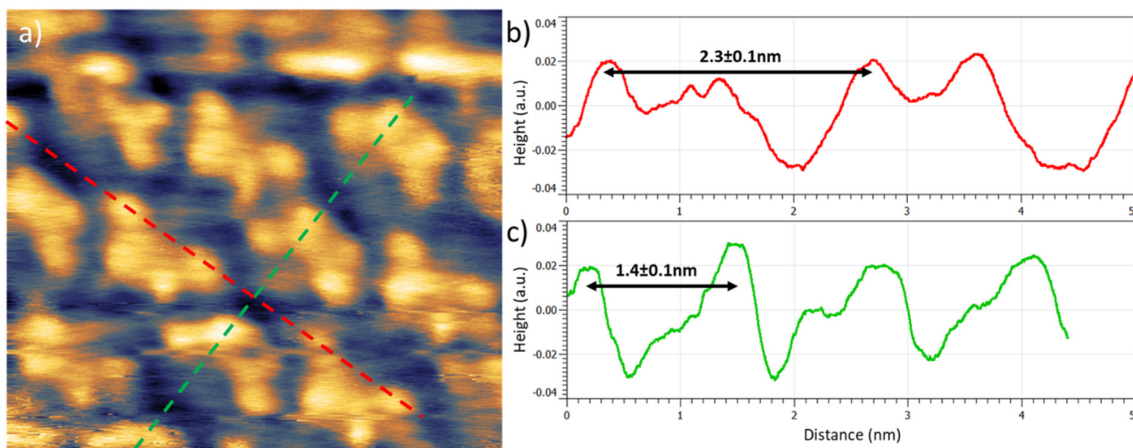


Figure S5. Organometallic structures on Ag(111). **(a)** STM image of organometallic chains obtained by deposition of DIITP with the RaDeS onto pristine Ag(111); **(b)/(c)** Line-profiles along the chains (red curve) and perpendicular to them (green curve) as indicated in (a). The intrachain distance has increased from 1.7 nm found for the covalent chains (Figure S3) to 2.3 nm for the organometallic chains, because each organometallic C-Ag-C bond is $\sim 0.25 \text{ nm}$ longer than a covalent C-C bond. Interestingly, we find a notably reduced interchain distance of the organometallic chains of 1.4 nm as compared to 1.7 nm and 2.3 for the covalent chains on iodine-passivated (Figure S3) and pristine (Figure S4) Ag(111). This can readily be explained by the possibility for a tighter packing facilitated by the increased repeat distance in the organometallic chains. (image parameters: $5.0 \times 4.5 \text{ nm}^2$, 92 pA, 0.3 V).

Wet chemical Scholl reaction and Raman characterization

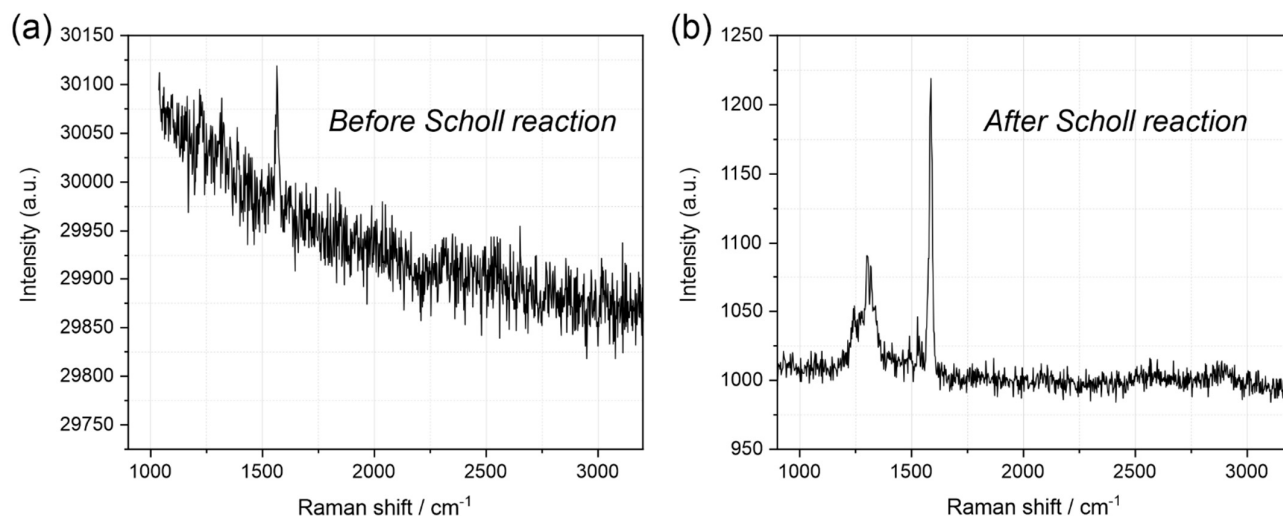


Figure S6. Transformation of the covalent polymers on I-Au(111) into GNR in solution by the Scholl reaction. Raman spectra acquired (a) before and (b) after the Scholl reaction. The direct comparison reveals clear differences that indicate a fundamental chemical transformation. In particular, emergence of a strong and narrow band at 1610 cm^{-1} corresponding to the G mode indicates GNR formation.[55] Under the applied conditions, desorption of the covalent polymers appears exceedingly implausible, insinuating that the CDH has been induced in the adsorbed state. Unfortunately, a complementary STM characterization was not possible after the harsh wet chemical treatment due to persistent contaminations that could not be removed by sample heating at the accessible temperatures.