Electronic supplementary information (ESI)

Host guest chemistry and supramolecular doping in triphenylamine-based covalent frameworks on Au(111)

Christian Steiner,[†,⊥] Lukas Fromm,[‡,⊥] Julian Gebhardt,[‡,¶,⊥] Yi Liu,[†,⊥] Alexander Heidenreich,[§] Natalie Hammer,[§] Andreas Görling,[*,‡] Milan Kivala,[*,‖] and Sabine Maier[*,†]

†*Department of Physics, Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany*
‡*Chair of Theoretical Chemistry, Department of Chemistry and Pharmacy, Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany*
¶*Fraunhofer Institute for Mechanics of Materials IWM, 79108 Freiburg, Germany*
§*Chair of Organic Chemistry I, Department of Chemistry and Pharmacy, Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany*
‖*Organisch-Chemisches Institut & Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany*
⊥*Contributed equally to this work*

Received April 14, 2021; E-mail: andreas.goerling@fau.de; milan.kivala@oci.uni-heidelberg.de; sabine.maier@fau.de

Reaction pathway of the CTPA on Au(111)

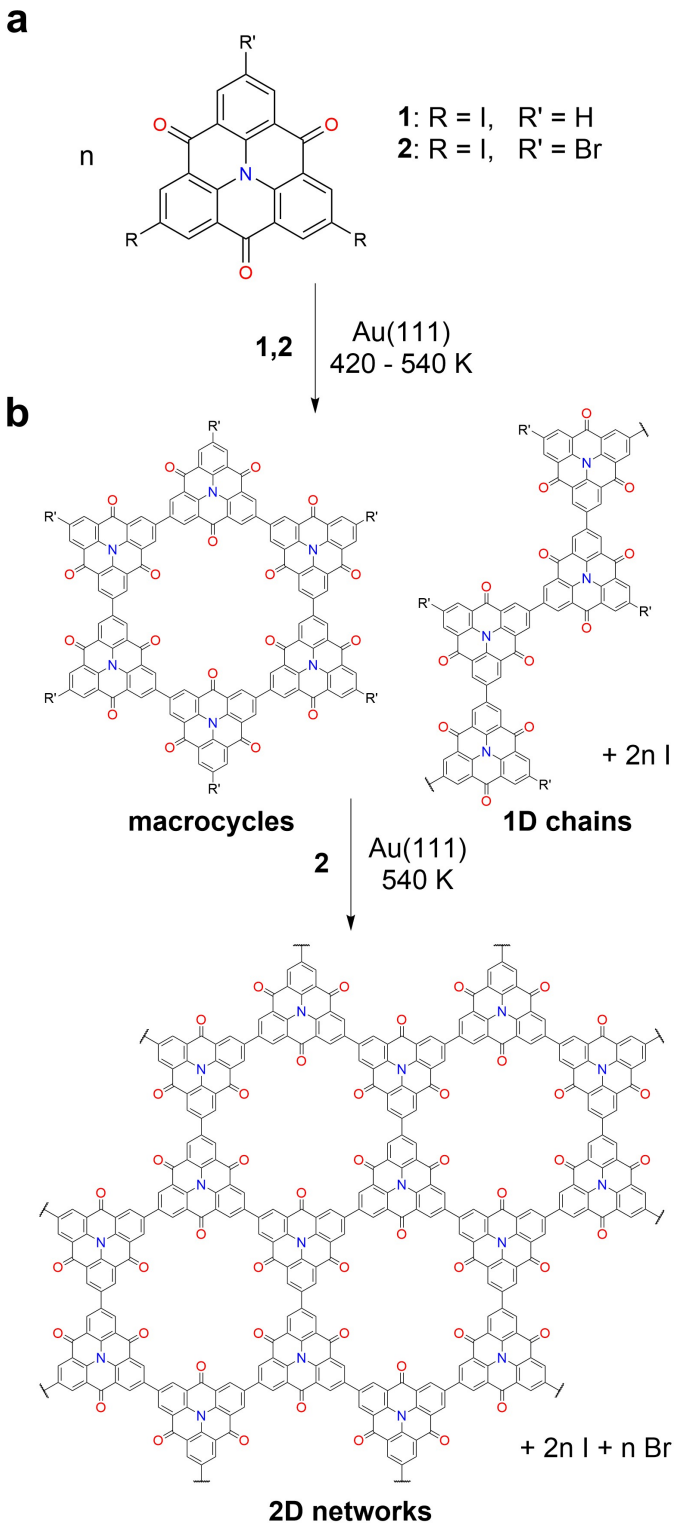

Figure S1. Reaction scheme of the hierarchical on-surface synthesis of triphenylamine-based macrocycles, chains, and two-dimensional polymers on Au(111). (a) Structure of the used carbonyl-bridged triphenylamine (CTPA) precursors CTPA1 and CTPA2. (b) Surface-assisted Ullmann-type reaction of CTPA towards macrocycles and 1D chains in the first step followed by their conversion into 2D networks in the second step. Further details on the preparation of CTPA macrocycles and networks *via* on-surface synthesis as well as the synthesis of the precursors are found in Steiner et al. [1].

Host-guest experiments of TMA adsorbed in CTPA pores

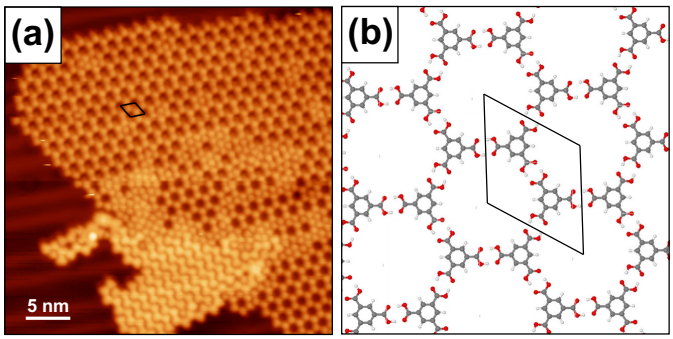

Figure S2. Self-assembly of the trimesic acid (TMA) with polymerized CTPA chains on Au(111). (a) Overview scanning tunneling microscopy (STM) image showing the H-bonded honeycomb network of the TMA along with some polymerized CTPA chains. The unit cell of the TMA network measures (highlighted in black) measures $a = b = 1.62$ nm $\pm$ 0.04 nm and $\gamma = 60° \pm 2°$ consistent with previously reported values.[2] (b) Structural model of the H-bonded TMA honeycomb network. The TMA was adsorbed at 300 K on Au(111).

Table SI1. Additional DFT adsorption energies of TMA in 2D CTPA networks on Au(111). Our results suggest that previously reported adsorption energies of TMA were overestimated.[3]

Structure	E_{ads} / eV	E_{VDW} / eV
TMA with C_{3h} symmetry	-2.31	-1.89
TMA with C_s symmetry	-2.24	-1.88

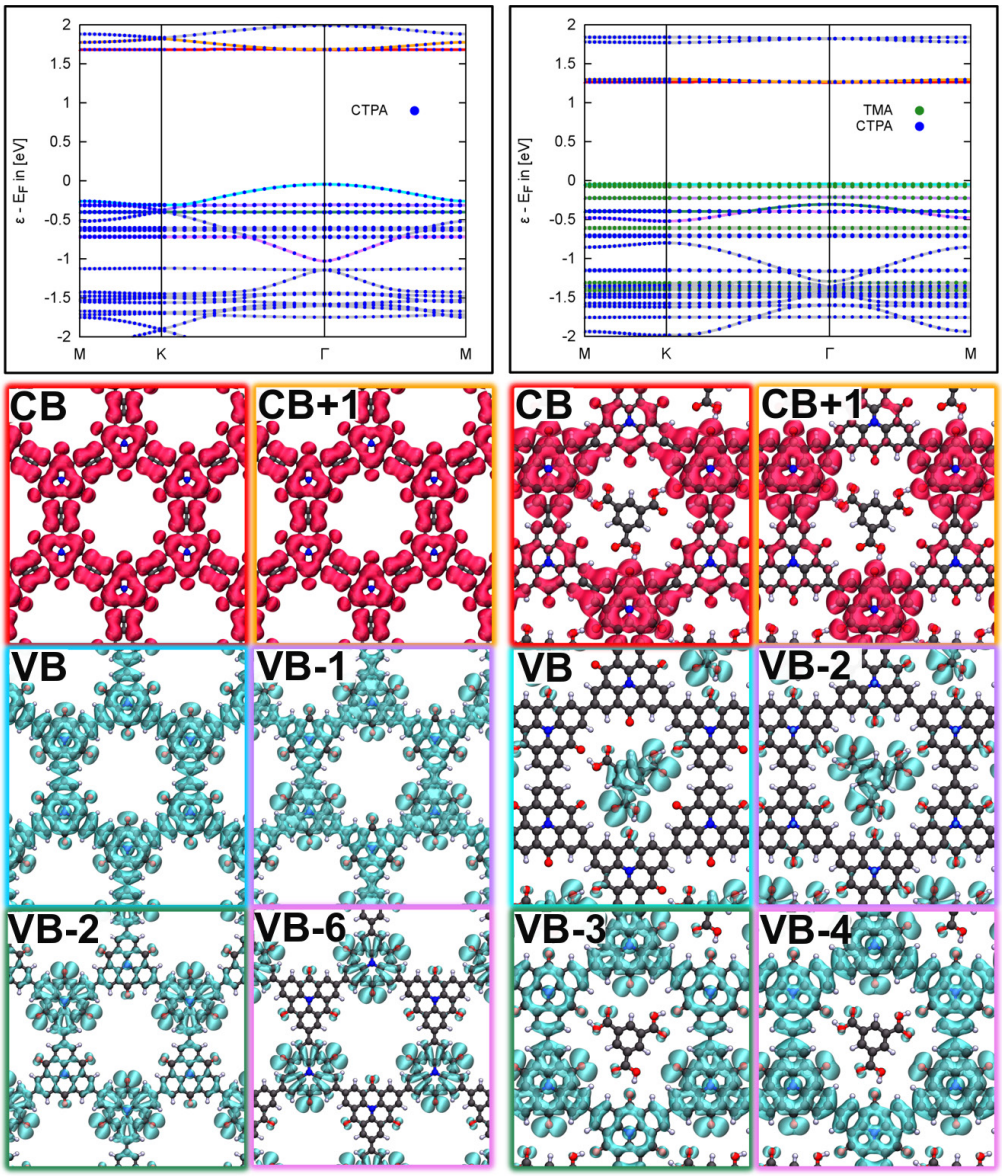

Figure S3. Band structures and corresponding calculated local density of states maps of the CTPA network (left) with and (right) without co-adsorbed TMA.

Interaction of iodines and bromines within the covalently-linked CTPA structures

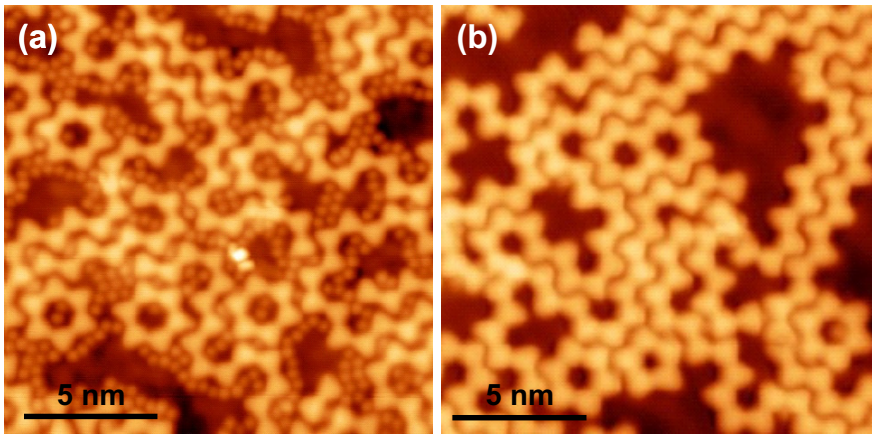

Figure S4. STM images demonstrating the desorption of iodine upon annealing the Au(111) surface above 470 K. CTPA1 on Au(111) after annealing at (a) 470 K and (b) 540 K. We note that at both temperatures the Ullmann-type coupling reactions are completed. STM parameter: (a) I =300 pA, V =−0.1 V and (b) I =400 pA, V =−0.05 V.

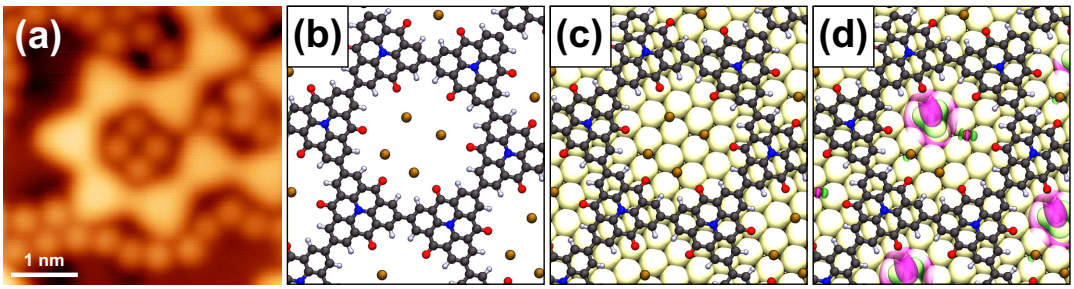

Figure S5. (a) STM image showing an open CTPA macrocycle with four iodines adsorbed inside. Closed CTPA macrocycles with four iodines are experimentally not observed in STM images, which indicates that the stress is too high to accommodate four iodine simultaneously into the pore of a CTPA macrocycle. (b-c) DFT-optimized adsorption configuration on Au(111) (Au substrate is omitted for clarity in (b)) and (d) corresponding CDD plot of four Br adsorbed in a CTPA pore. We note the van der Waals radius of Br is smaller than I, and a stable adsorption geometry could be obtained. STM parameters: I =300 pA, V =−50 mV.

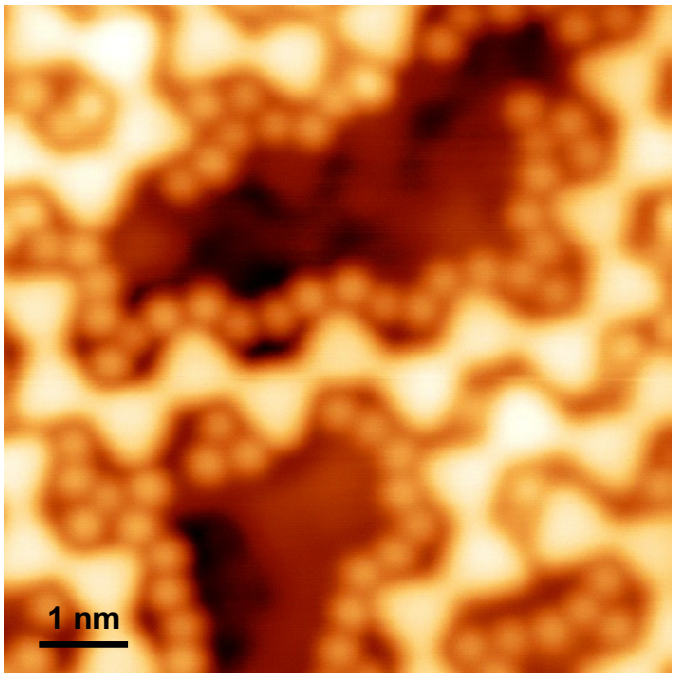

Figure S6. The chemisorbed iodine atoms as byproducts from the Ullmann-type surface reaction experience competing I···CTPA and I···I interactions. The iodine atoms surrounding the CTPA macrocyclyes and chains self-assemble often in form of chains hold together by the I···I interactions. STM parameters: I =300 pA, V =−50 mV.

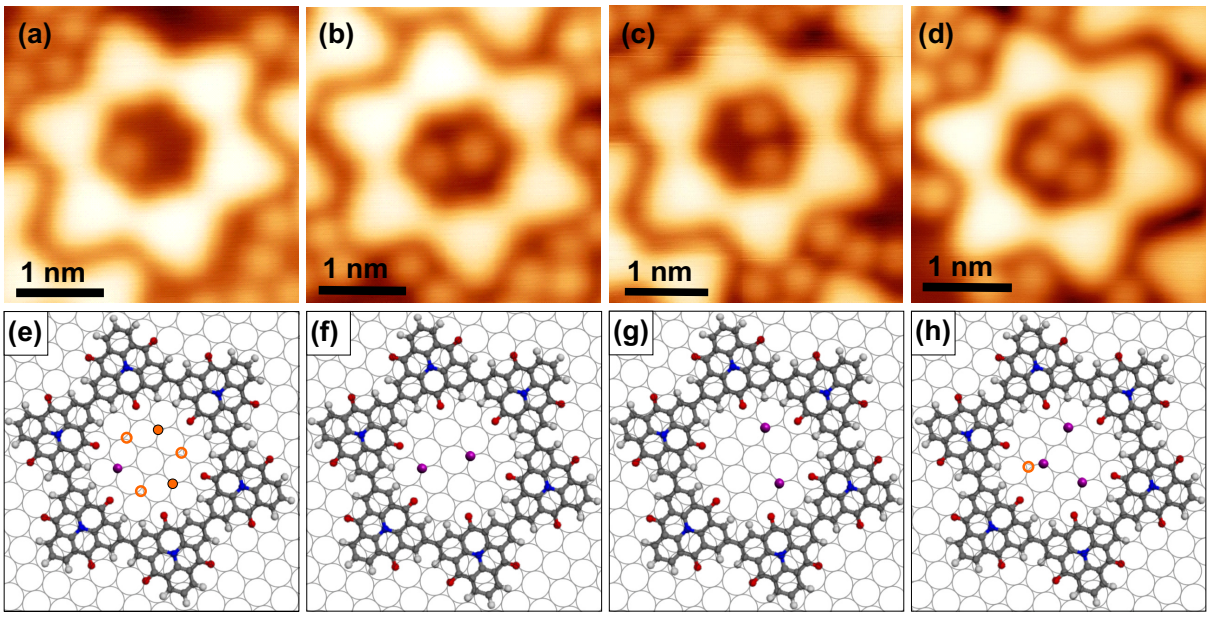

Figure S7. (a-d) STM images of CTPA macrocycles filled with (a) one, (b-c) two, and (d) three iodines, respectively. (e-h) Tentative models for the adsorption sites determined from measured distances in the STM images. In (e) the filled orange circles highlight equivalent sites; the closed circles mark the other sites at the other hollow site, which however are in the experiments however less frequently (about 20%) observed to be filled. In (h) the orange circle shows the shift in the adsorption site from one hollow site to the other. STM parameters: (a-d) I=300 pA, V=−0.05 V.

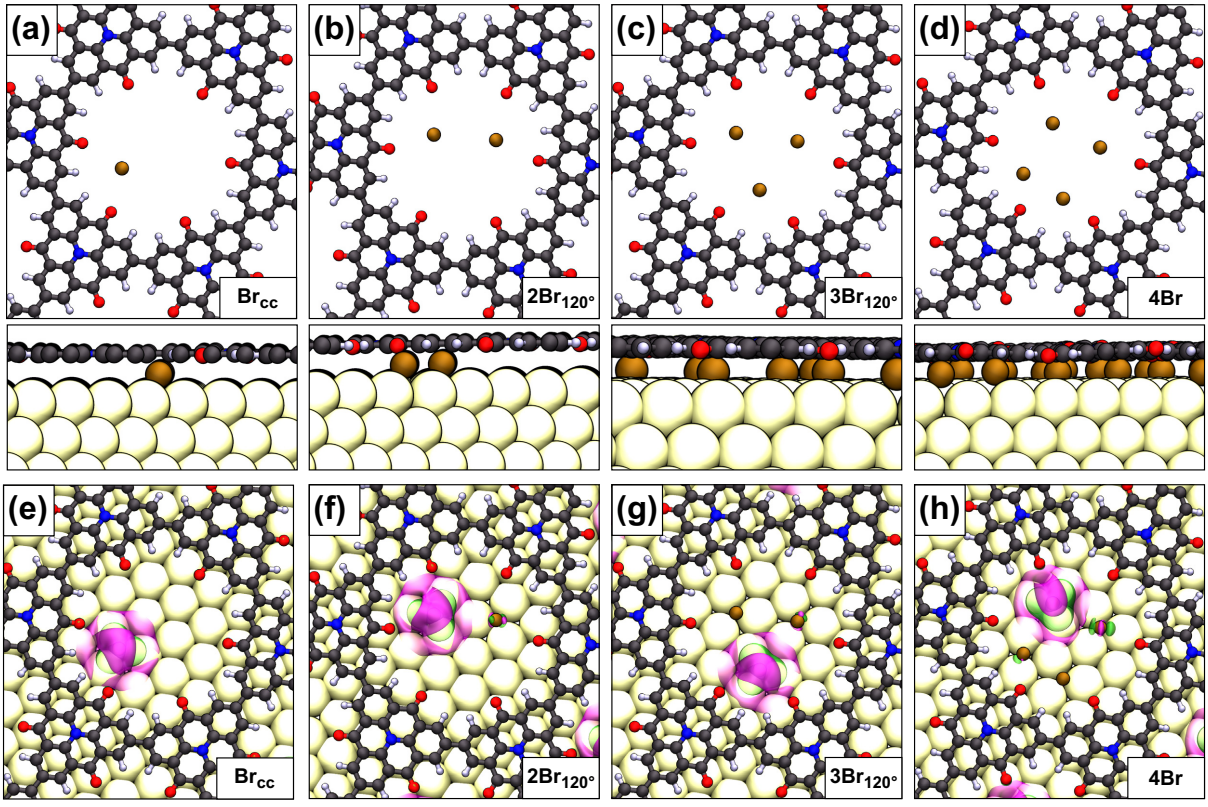

Figure S8. (a-d) DFT-optimized adsorption configurations of (a) one, (b) two, (c) three, and (d) four Br adsorbed in the CTPA network on Au(111). The Au surface is not displayed for clarity in the top view. (e-h) Corresponding calculated charge density difference plots. The corresponding adsorption energies and the bond-lengths are given in Table 1 in the manuscript.

Table SI2. Additional DFT adsorption energies of isolated I and HBr without the CTPA network on Au(111) (positions in braces were fixed).

Structure	(E_{ads}/X) / eV
I_{fccH}-free	-2.75
$2I_{120°}$-free	-2.75
$3I_{120°}$-free	-2.73
Br_{bridge}-H_{top}	-0.38
Br_{fccH}-H_{top}	-0.38
$\{H_{top}\}$	-0.38
$\{H_{fccH}\}$	-0.35
$\{Br_{top}\}$	-0.33
$\{Br_{fccH}\}$	-0.27

References

(1) Steiner, C.; Gebhardt, J.; Ammon, M.; Yang, Z.; Heidenreich, A.; Hammer, N.; Görling, A.; Kivala, M.; Maier, S. *Nat. Commun.* **2017**, *8*, 14765.
(2) Ye, Y.; Sun, W.; Wang, Y.; Shao, X.; Xu, X.; Cheng, F.; Li, J.; Wu, K. *J. Phys. Chem. C* **2007**, *111*, 10138–10141.
(3) Iancu, V.; Braun, K.-F.; Schouteden, K.; Van Haesendonck, C. *Langmuir* **2013**, *29*, 11593–11599.