

Electronic supplementary information

Theoretical Insights into the Interplay between Metal-Organic and Covalent Bonding in Single-Layer Molecular Networks Formed by Halogen Dissociation

Andrius Ibenskas^{*a}, Mantas Šimėnas^b and Evaldas E. Tornau^a

¹*Center for Physical Sciences and Technology, LT-10257 Vilnius, Lithuania*

²*Faculty of Physics, Vilnius University, Saulėtekio 9, LT-10222 Vilnius, Lithuania*

* To whom corresponding should be addressed.

E-mail: andrius.ibenskas@ftmc.lt

1. DFT calculations and choice of interaction parameters for covalent bonding

The intermolecular interaction energies of the covalent-bonded Br₃Py-Br₃Py dimers were obtained using the DFT and performing geometry optimizations with the ORCA 5.0.3 package [1]. The DFT calculations were carried out in the gas phase using the ω B97X-D4 range-separated hybrid functional [2] with the DFT-D4 dispersion correction [3]. The def2-TZVP basis set was used on all atoms. Integration grid was increased to 'DefGrid3'. Default convergence thresholds ('opt') were applied in the geometry optimizations. Planarity constraint was implemented by starting from a flattened configuration (z=0) and then freezing dihedral angles.

Homolytic bond dissociation energy (BDE) of a covalent dimer, e_d , was calculated as the total energy (E_d) of the cluster minus energies (E_1) of its radical constituents (possessing one unpaired electron for each broken C-Br bond),

$$e_d = E_n - nE_1$$

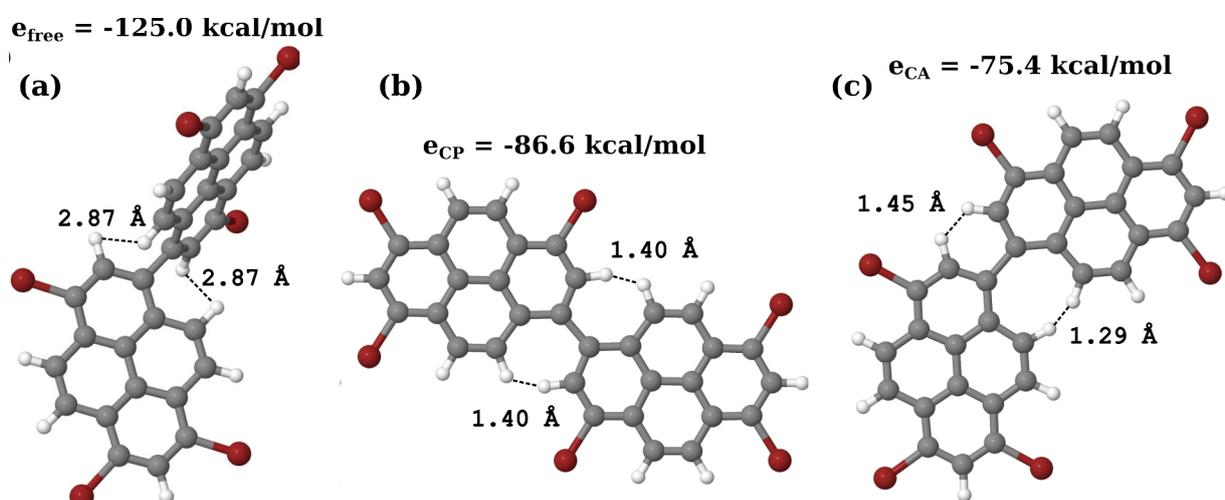


Figure S1 Results of the DFT gas-phase calculations for the covalent-bonded dimer of Br₃Py radicals: (a) molecules are unconstrained; (b) parallel and (c) angular arrangements, where molecules of a dimer are constrained in a plane.

In the absence of binding of Br₃Py-Br₃Py dimer with the underlying surface, the dimer behaves as shown in Fig. S1a. It twists to overcome the strong repulsion between the nearest H atoms of two molecules, but the backbones of both molecules remain rigid. When the dimer is tethered to an imaginary surface, it can have two covalent-bonded configurations: parallel and angular (see Fig. 1b and c). The initial configurations of these two clusters correspond to the arrangement of molecules suggested in Ref. 4.

The energy difference between the free dimer and constrained dimers might give us the idea of the steric hindrance magnitude, which amounts to about 38.5 kcal/mol and 49.6 kcal/mol for the parallel and angular dimers, respectively. Slightly lower BDE of the parallel dimer with respect to that of the angular one leads to the following ratio of the covalent interactions: $e_{\text{ang}}/e_{\text{par}} = 0.87$. We also calculated this ratio for the equivalent configurations of the pyrene dimer and obtained the same value. This confirms that Br atoms are not involved in either attraction or repulsion between molecules of the dimer. Therefore, we assume that the same value of $e_{\text{ang}}/e_{\text{par}}$ is valid for all Br_{*n*}Py ($n=0\dots3$) species.

2. Distribution function for dehalogenated molecules

In ref. 5, the distribution of singly, doubly and fully debrominated radicals of 1,3,5-tris(4-bromophenyl)benzene (TBB) on Au(111) was calculated as a function of temperature, using the thermodynamic description of debromination. The TBB molecule possesses three Br molecules in a normal (non-dissociated) state. Assuming the sustained equilibrium between dehalogenation and (re)halogenation, the probability of the state with n Br atoms removed can be written as

$$P_n = (1/Z)\exp[(-\Delta H/T + \Delta S) n/k_B],$$

where ΔH and ΔS are changes in the energy and entropy, when Br atoms are removed from either intact or partly debrominated TBB molecule; k_B is the Boltzmann constant, and Z is the partition function.

We adapted this model for our study in order to find the appropriate percentages of different Br_nPy species for modeling the Br_4Py debromination and self-assembly on Au(111). A five-level system is necessary to describe Br_nPy , since $n = 0...4$, and the total dehalogenation probability was

$$P_{\text{debrom}} = (1/4)P_1 + (2/4)P_2 + (3/4)P_3 + P_4.$$

We also used the value of ΔH which was obtained by the DFT calculations of TBB molecule on Au(111) [5]. In the latter work, Br atoms were gradually removed from a molecule one by one, and each step yielded a similar enthalpy change, $\Delta H \approx 0.4$ eV.

Using ΔH as a known parameter, we estimated the reaction entropy by the least-square fitting of the constructed debromination probability function to three XPS measurement points (at 300, 473, and 573 K, see Fig. S2). The latter were determined here by integrating the higher- and the lower-binding energy doublet of the Br 3d core level XPS spectra [4], attributed respectively to Br atoms in the intact C-Br bonds and Br atoms dissociated from the Br_4Py molecule on Au(111). Each percentage is roughly equal to the ratio of respective integrated doublet with the total integral of both doublets. At 473 K, they are 7.9% and 92.1%. At 573 K, this procedure gives 96% of dissociated Br, rounded further to 100% assuming the effect of Br desorption. At 300 K, all molecules are still intact.

The resulting entropy difference, $\Delta S = 0.97$ meV/K, is within the estimated theoretical range based on the Sackur-Tetrode equation. We also tested other ΔS values to verify the fitting results.

The obtained probability distribution was employed to calculate the relative concentrations of debrominated radicals Br_nPy as a function of temperature (Fig. S2), which we use in our MC simulations.

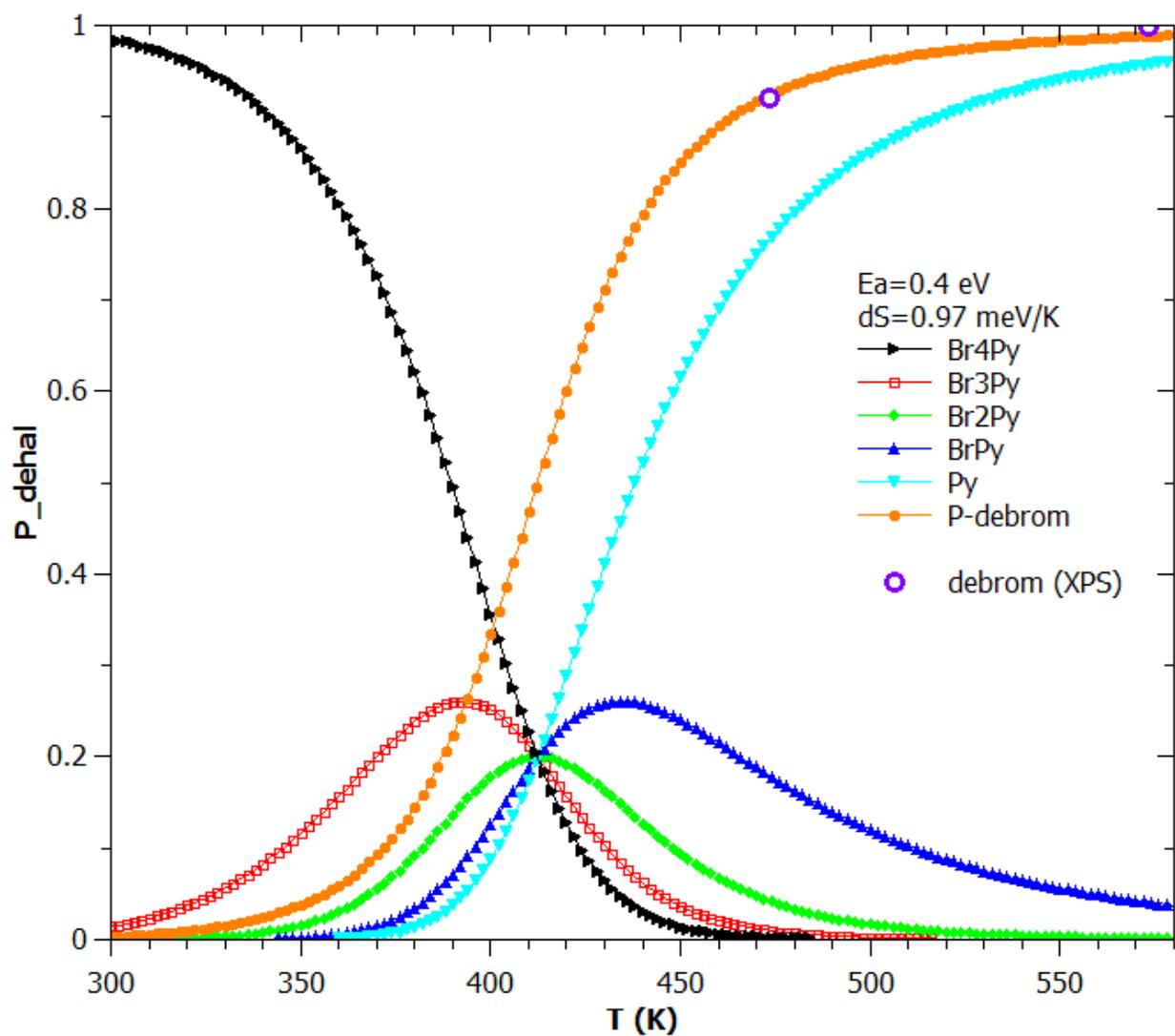


Figure S2 The normalized number of molecules (probability) with different number of Br atoms removed. Three open dots denote the XPS results at 300 K, 473 K, and 573 K taken from ref. 4.

3. Additional results of MC simulations

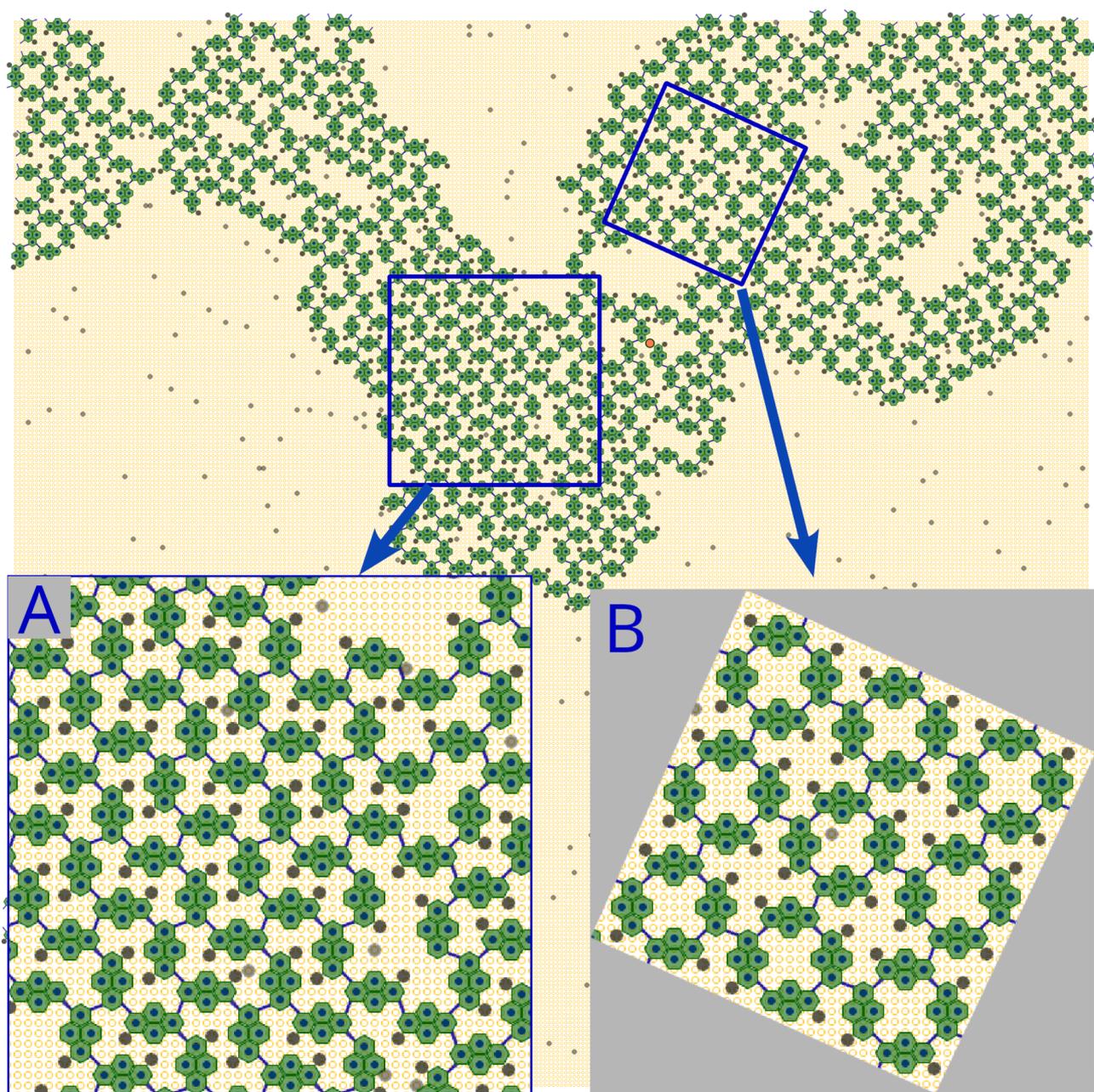


Figure S3 Covalently linked network featuring dense irregular patterns (inset A), as well as ordered fragments of the CO₂ phase (inset B). The system consists of 700 threefold debrominated molecules (Br₁Py). Chemisorbed Br-to-molecule ratio is 0.5. Bonding interactions are $e_{CA}/e_{CP} = 0.87$ and $e_M/e_{CP} = 0.35$.

Literature

1. F. Neese, Software update: the ORCA program system - Version 5.0, WIREs Comput. Mol. Sci. **8**, e1606 (2022).
2. A. Najibi, L. Goerigk, DFT-D4 counterparts of leading meta-generalized-gradient approximation and hybrid density functionals for energetics and geometries, J. Comput. Chem. **41**, 2562-2572 (2020).
3. E. Caldeweyher, C. Bannwarth, S. Grimme, Extension of the D3 dispersion coefficient model, J. Chem. Phys. **147**, 034112 (2017).
4. T. A. Pham, F. Song, M.-T. Nguyen, Z. Li, F. Studener, M. Stöhr, Comparing Ullmann coupling on noble metal surfaces: on-surface polymerization of 1,3,6,8-tetrabromopyrene on Cu(111) and Au(111), Chem. Eur. J. **22**, 5937-5944 (2016).
5. M. Fritton, D. A. Duncan, P. S. Deimel, A. Rastgoo-Lahrood, F. Allegretti, J. V. Barth, W. M. Heckl, J. Björk, M. Lackinger, The Role of Kinetics versus Thermodynamics in Surface-Assisted Ullmann Coupling on Gold and Silver Surfaces, J. Am. Chem. Soc. **141**, 4824–4832 (2019).